1986

Development of a New Conductivity Model for Shaly Sand Interpretation.

Pedro L. Silva
Louisiana State University and Agricultural & Mechanical College

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DEVELOPMENT OF A NEW CONDUCTIVITY MODEL FOR SHALY SAND INTERPRETATION

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Petroleum Engineering Department

by

Pedro L. Silva
B.S., Universidad Nacional Autonoma de Mexico, 1976
M.S., Louisiana State University, 1981
May 1986
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In this dissertation, a new theoretical conductivity model for shaly sands is developed. The model is based on dual water concepts. In addition, the equivalent counterion conductivity changes as the diffuse electrical double layer expands and is then a function of temperature, shaliness, and of the conductivity of the far water. The formation resistivity factor used in the model is independent of shaliness. A method to calculate the equivalent counterion conductivity is proposed. This method is based on treating the double layer region as a hypothetical electrolyte, the properties of which are derived from basic electrochemistry theory.

The new model was used to calculate conductivities of specific shaly sand samples @ 25°C. The calculated values display an excellent agreement with published experimental data. The new model is shown to be superior in predicting core conductivities to the two models currently accepted by the industry.

The developed model has been extended to represent hydrocarbon bearing formations as well as to predict membrane potentials in shaly sands. Calculated water saturation and membrane potential values from the new model also show excellent agreement with accurate experimental data obtained at laboratory conditions.

The effect of temperature on the conductive behavior of shaly sands has been revised under the basis of the new model. The representativity of conductivities predicted by the new model for temperatures up to 200°C warrants its application under actual field conditions.
Several new concepts useful in the analysis of shaly sands are introduced in this work. In addition, the new model is used to enhance the interpretation of the SP log in shaly environments. Finally, a new interpretation technique for shaly sands is proposed. This interpretation tool is based on the new conductivity model and makes use of log derived data. It allows the proper evaluation of the potential of a reservoir formation.
INTRODUCTION

The most difficult problem facing the log analyst lies in the identification of potential zones and the proper quantification of the amounts of hydrocarbons they contain. The quantitative evaluation of the commercial potential of a prospective formation is mainly achieved by estimating its water content, $S_w$.

It is recognized that the electrical conductive properties of clean, i.e. clay free, porous rocks depend on the amount and conductive characteristics of the fluids saturating its pore space. Since hydrocarbons are poor electrical conductors, then a formation partially containing either oil or gas should exhibit lower conductive response than that of an otherwise clean rock, of the same porosity, whose pore space is completely filled by the same brine. Both the qualitative and quantitative evaluation of clean formations are easily accomplished. Qualitative interpretation in such formations is based on the existence of sharp resistivity contrasts between water filled and hydrocarbon bearing zones. The evaluation of water saturation follows from the application of simple petrophysical models that relate the water content to the resistivity of formation water $R_w$, the Formation resistivity factor $F$, and the recorded electrical resistivity of the potential zone, $R_e$.

Values of $R_w$ can be obtained from the SP deflection recorded by the Spontaneous Potential (SP) log. The Formation resistivity factor is related to the porosity of the rock. It can also be calculated, in clean water formations, from the magnitudes of $R_w$ and the resistivity of
the water filled rock, $R_0$. The use of these basic concepts forms the basis of log interpretation.

Although these early concepts have been extensively used in Formation evaluation, in the late forties evidence began to accumulate regarding their limitations when applied to the evaluation of certain formations, namely those containing variable amounts of clay. The problems associated with shaly sand interpretation arises from the fact that the presence of clay considerably alters both the electrochemical and conductive behavior of reservoir rocks. These effects are reflected in a reduction of the SP deflection and an increase in the electrical conductivity of these formations. As a result, the application in shaly formations of interpretation techniques based on clean rock models yields erroneous information about the magnitude of $R_w$ and $F$. Consequently, the estimation of the water content of a shaly formation may be considerably affected. In general, the use of "clean models" results in the estimation of higher water saturations in the case of shaly reservoirs. As a result, potential zones may be neglected or even completely overlooked.

The effects of the presence of clay materials in reservoir rocks have been recognized for almost forty years as being perhaps the most complex problem encountered in Formation Evaluation. Attempts to solve the interpretation problems have resulted in the establishment of various empirical techniques. At the same time, numerous attempts have been made to establish a conceptual model to predict the conductive behavior of shaly sands. It must be stated that in general, no practical and accurate technique has been developed (Chapter I).
Moreover not much attention has been focused on improving the practical aspects of SP log interpretation for shaly sands.

The present study represents the continuation of research activity conducted at LSU and directed at obtaining more reliable \( R_w \) values from the SP log. Originally the purpose of the study was to adapt an existing conductivity model into a practical, yet conceptually sound interpretation technique for shaly sand evaluation. An analysis of the existing conductivity models revealed that no existing model could be confidently used in the study (Chapter III). Therefore it was necessary to develop a new theoretical conductivity model for shaly sands.

In this dissertation, the development of the new conductivity model is presented (Chapters II and IV). Its ability to predict water saturation and membrane potentials is evaluated under a variety of conditions (Chapters V, VI and VII). Several new concepts useful in the analysis of the general electrochemical behavior of shaly sands are introduced in this work. In addition, the superiority of the new model over the existing ones is established as a consequence of the analysis.

Finally, the new conductivity model is used in the development of an interpretation algorithm (Chapters VIII and IX). Such interpretation tool makes use of log derived data and allows the proper evaluation of the potential of a reservoir formation.
I.1 Clean Formations Models

The major problem in the exploration and exploitation of commercial hydrocarbon reservoirs lies in the identification of potential zones and the quantification of the volumes of oil and/or gas present in such formations.

The development of the resistivity tool and the spontaneous potential (SP) log opened new avenues for the sizing of hydrocarbon reservoirs and helped the establishment of Formation Evaluation as a specialized and important part of the petroleum technology. It was recognized, there, that the answer to the critical questions of "where" and "how much" could be obtained once the bases for quantitative log interpretation were established. A giant step in that direction, in particular for the evaluation of sandy reservoirs, was taken with the publication of Archie's empirical petrophysical correlations and the theory of the electrochemical component of the SP.

Working with clean formations (i.e. clay free) Archie introduced in 1942 the concept of the Formation Resistivity Factor, $F$, which he defined as:

$$ F = \frac{R_o}{R_w} = \frac{C_w}{C_o} $$

where $R_o$ is the resistivity of the rock when fully saturated by an electrolyte of resistivity $R_w$, and $C_o$ and $C_w$ are the respective...
conductivities. Thus, a plot of $C_0$ vs. $C_w$ for a clean formation should yield a straight line of slope $1/F$ passing through the origin. Furthermore, the Formation Resistivity Factor was found to be related to the porosity $\phi$ of the rock, resulting in a second empirical relationship which, in its generalized form is expressed as:

$$F = \frac{a}{m\phi}$$  \hspace{1cm} (1.2)

where the coefficient $a$ and the cementation factor, $m$, are generally assumed constant for a given formation.

Experimental evidence led Archie to conclude that the resistivity exhibited by a clean formation is not only affected by the resistivity of the saturating brine and its porosity, but also by the amount of electrolyte present in the pore space. This dependency is expressed by the basic saturation equation:

$$C_t = \left( \frac{C_w}{F} \right) S_w^n$$  \hspace{1cm} (1.3)

in which $S_w$ is the water saturation expressed as a fraction of the pore space, $n$ is the saturation exponent, and $C_t$ is the conductivity of the reservoir rock under $S_w$ saturation conditions. Equation (1.3) states that the less water present in the formation, the more resistive it appears to be. Therefore, the saturation equation became important not only for quantitative evaluation, but for qualitative purposes as well. In fact, once permeable zones were identified, prospective zones could be selected on the basis of sharp resistivity contrasts, and their potential evaluated by estimating their water content ($S_w$) from equations (1.1) through (1.3).
For example, if an adjacent water zone of resistivity $R_o$ can be identified, the water saturation of a zone of resistivity $R_t$ could be estimated from:

$$S_w = \left( \frac{R_o}{R_t} \right)^{1/n}$$  \hspace{1cm} (1.4)

provided that both zones exhibit the same porosity, contain the same brine, and the value of $n$ is known. On the other hand, when no adjacent water zones are available, or when the conditions of uniform porosity and salinity are not met, the determination of $S_w$ could be carried out from the knowledge of $F$ and $R_w$, for the formation of interest, from the general model:

$$S_w = \left( \frac{FR_w}{R_t} \right)^{1/n} = \left( \frac{aR_w}{\phi R_t} \right)^{1/n}$$  \hspace{1cm} (1.5)

The latter is frequently the case and the need arose for further research and experimentation directed towards the estimation of formation water resistivity, the determination of saturation exponents, and the correlation between rock porosity and $F$ for different formation types.

After Mounce and Rust\(^{(3)}\) experimentally showed the importance of the role played by shales in the generation of the SP, Wyllie\(^{(4)}\) published in 1949 the basic theory for the interpretation of the SP log. Wyllie established that the electrochemical potential is the major component of the SP deflection recorded opposite of permeable formations, and results from the contributions of a boundary potential at the interface of the mud filtrate and the interstitial water in the porous bed, and an electromotive force between the interstitial water and the borehole mud across adjacent shales.
The boundary potential occurring within a clean formation arises from the migration of electrical charges at the interface of electrolytes of different concentration. For dilute univalent salts, such as NaCl, this potential $E_b$ is given by the thermodynamic relationship:

$$E_b = \frac{RT}{F} \left( \frac{v-u}{v+u} \right) \ln \frac{a_1}{a_2} \quad (1.6)$$

where $v$ and $u$ are the ionic mobilities of cations and anions, $R$ is the gas constant, $F$ is the Faraday constant, $T$ the absolute temperature, and $a_1$ and $a_2$ represent the mean ionic activities of the two electrolytes.

Based on experimental work conducted with NaCl solutions of low to moderate concentration, Wyllie concluded that shales tend to behave as perfect cationic membranes and give potentials which may be calculated from the Nernst equation:

$$E = \frac{RT}{F} \ln \frac{a_1}{a_2} \quad (1.7)$$

so that the total electrochemical potential, $E_T$, is given by the sum of the potentials expressed by eqs. (1.6) and (1.7). At low concentrations, the activity ratio can be approximated by the ratio of the conductivities of the solutions; moreover, by assuming that the principal electrolyte in both formation waters and drilling fluids is NaCl, Wyllie established the basic model:

$$SP = E_T = -K \log \frac{R_{mf}}{R_w}; \quad (mv) \quad (1.8)$$

where $SP$ is the total deflection recorded by the SP log and $R_{mf}$ is the resistivity of the mud filtrate. The parameter $K$ is a constant related to the formation temperature, $t_f$, by the expression:

$$K = 61 + 0.133 t_f \quad (^\circ \text{F}) \quad ; \quad (mv) \quad (1.9)$$
The estimation of formation water resistivity, $R_w$, could then be accomplished by the use of the SP log from the knowledge of $R_{mf}$ and $t_f$.

The publication of Wyllie's basic model for the SP acquired a great deal of importance since it added flexibility to the use of the basic saturation equation given by expression (1.5).

With the problem of determining $R_w$ apparently solved, a great deal of attention was then concentrated on the study of the petrophysical characteristics of reservoir rocks and their influence on the Formation Resistivity Factor. The proper quantification of the parameters $a$ and $m$, needed in eq. (1.2) for specific formation types, was the subject of extensive experimental work. However, by the early 1950's evidence began to accumulate regarding the limitations of the interpretation techniques when applied to certain formations, and the problems associated with shaly sand interpretation were fully recognized and addressed.

### 1.2 Emergence of Interpretative Complexities in Shaly Sands

The recognition of the problems associated with the interpretation of shaly sand reservoirs started in 1949, when Doll\(^{(6)}\) established that the amplitude of the SP deflection recorded in permeable strata is less in front of shaly formations, as compared to that expected in front of a clean formation saturated by a brine of the same salinity. Although the amplitude of the SP does not depend on the type or distribution of the shaly material, concluded Doll, the deflection is a maximum for clean formations and is reduced proportionally to the percentage of shaly material.
The effect of shale on the conductive behavior of reservoir rocks was addressed by Patnode and Wyllie (7) in 1950. While collecting experimental data on the Formation Resistivity Factor they found that for certain samples the ratio \( C_w/C_o \) is not always constant for a given rock as implied from eq. (1.1). In fact, the ratio decreases as the conductivity \( C_w \) of the saturating brine decreases. This effect was found to be more pronounced for shalier samples, as illustrated in Fig. 1.1.

The effect of the shaly material is reflected in an increase of sample conductivity as compared to the conductivity of an otherwise clean rock of the same porosity. This increase of the conductivity of the sample was described by Winsauer and McCardell (8) in terms of an "excess conductivity", as the electrical manifestation of the shale effects.

From these early observations, it was clear that the correct evaluation of shaly formations would suffer by the application of models originally derived for clean rocks. The result being the underestimation of hydrocarbon saturation.

It was a rather customary practice (8) to infer the magnitude of \( F \) from log data by using an alternate form of eq. (1.1) for clean sands. Eq. (1.1) can be written as:

\[
F = \frac{R_{xo}}{R_{mf}}
\]  

(1.10)

where \( R_{xo} \) is the resistivity of the flushed zone, i.e., that portion of the formation immediately behind the mud cake and which is assumed to be fully flushed by mud filtrate of resistivity \( R_{mf} \). However, since mud filtrates in many instances contain low saline concentrations, the use
Fig. 1.1 Variation of apparent formation factor with $C_w$ for shaly sands
(Ref. 15)
of eq. (1.10) as can be inferred from Fig. (1.1), would result in the calculation of a non-representative apparent formation factor value, $f_a^{(7,9)}$.

On the other hand, because of the reduction in the magnitude of the SP deflection in shaly formations, the calculation of water resistivity yields an apparent $R_{wa}$ which exceeds the true $R_w$ for the formation of interest. Moreover, since the true formation resistivity, $R_t$, is also reduced by the presence of clay, it was evident then that the evaluation of water saturation from eq. (1.5) could not be confidently accomplished in shaly reservoirs.

Two types of efforts to solve the problem of shaly sand interpretation emerged:

a) The development of practical, and in most cases empirical, interpretation techniques based on modifications of the existing clean formation models. These techniques attempted to handle the problems associated with shaly sands in an indirect manner. They have originated because of the inevitable necessity faced by the log analysts to perform quantitative evaluations of prospective zones using log-derived data.

b) Research activities directed at acquiring a better understanding of the problem, and the establishment of models describing the behavior of shaly formations from which scientifically sound interpretation methods could be derived.
1.3 Early Interpretation Techniques

a) Qualitative Evaluation

Early attempts to evaluate shaly reservoirs were mainly directed towards the development of qualitative interpretation methods. Because of their interrelation as potential sources of information, the resistivity and SP logs were used extensively in a combined manner to obtain information about the water content of shaly formations.

Wyllie and Southwick\(^{(9)}\) took advantage of the concepts of apparent formation factor and apparent water resistivity to propose a qualitative technique to assess whether or not a shaly sand is water bearing. For shaly sands, reasoned the authors, the apparent formation factor as calculated from eq. (1.10) is lower than the true \( F \) due to the dilute nature of the mud filtrates common of that time. By virtue of the fact that for those formations \( R_{wa} > R_w \), it was suggested that the product:

\[
F R_{wa} = (R_{xo}/R_{mf})R_{wa}
\]

approximates the magnitude of \( R_o \), the resistivity of the water shaly sand. Thus, qualitative interpretation could be carried out in a manner similar to that used for clean formations. It was apparent that if:

\[
R_t > F R_{wa}
\]

then the shaly sand probably contains hydrocarbons. In expression (1.12) \( R_t \) represents the true resistivity of a given shaly formation as read from the log.
Using experimental work conducted on artificial shaly samples, Wyllie and Southwick\(^{(9)}\) verified that a variation of the SP equation for clean water bearing rocks which is given by:

\[
SP = K \log \frac{R_{xo}}{R_o}
\]  

(1.13)

could be also applied for water bearing shaly formations. This can be accomplished by varying the magnitude of the parameter \(K\). Using field data Poupon, Loy, and Tixier\(^{(10)}\) arrived at the same conclusion.

Poupon et al.\(^{(10)}\) extended the applicability of those findings to propose another qualitative technique for the screening of potential zones. This technique is based on describing the SP deflection, \(PSP\), recorded in front of shaly formations as:

\[
PSP = -K' \log \left( \frac{R_{xo}}{R_t} \right) + A
\]  

(1.14)

where the parameter \(A\) is expressed as a function of the logarithm of the quotient of water saturation \(S_{xo}\) in the flushed and uninvaded zone, \(S_w\). The parameter \(K'\) is an empirical value obtained from water bearing shaly sand data.

This technique proposes the plotting of the ratio \(R_{xo}/R_t\) vs. the observed SP deflection for zones of interest. A "water line", calculated from eq. (1.13) using the appropriate \(K'\) value is also included in the plot, as shown in Fig. 1.2. Since for zones containing movable oil:

\[
S_{xo} > S_w \text{ and } A > 0
\]  

(1.15)

then, as illustrated in the figure, points not lying on the "water line" should represent potential hydrocarbon zones, irrespective of the type and distribution of the shaly material\(^{(10)}\).
Fig. 1.2 Qualitative Technique for Potential Zone Identification
(Ref. 10)
b) **Quantitative Evaluation**

Early quantitative interpretation procedures for shaly sands were in general devised for local use and dealt not only with the quantification of water saturation, but also with the calculation of water resistivity.

In 1949 Tixier\(^{(11)}\) showed that more accurate \(R_w\) values determined from the interpretation of the SP log in the Rocky Mountain area could be obtained by estimating the "correct" value of the constant \(K'\). In addition, an algorithm for the estimation of \(S_w\) from SP and resistivity data was prepared specifically for that area.

Poupon et al.\(^{(10)}\) published a more general chart for \(S_w\) determination in formations containing either laminated or dispersed shaly material. The use of this algorithm also required the knowledge of the local \(K'\) value to describe the water line. Although attractive, its widespread application suffered from the fact that, either \(R_w\) or the magnitude of the theoretical SP deflection for an equivalent clean formation had to be known, or at least reasonably estimated, in order to obtain reliable results.

An interesting idea was introduced in 1955 by Varjao de Andrade\(^{(12)}\) who, instead of modifying the value of \(K\), proposed to express the apparent water resistivity \(R_{wa}\) in terms of the true \(R_w\) of the shaly formation as:

\[
\log R_w = a + b \log R_{wa}
\]  

(1.16)

where the constants \(a\) and \(b\) are to be determined regionally. This technique, as well as the previous one dealing with the estimation of \(K'\), are restricted to cases where reliable water...
samples are available. Nevertheless, the use of relationships between $R_{wa}$ and $R_w$ represented an attractive concept.

c) Comments

The empirical nature of these interpretation techniques described in this section gave a great deal of insight into the complexity of the problems associated with the interpretation of shaly sand log data. Their empirical character emphasized the need for a better understanding of how the presence of clay affects the conductive and electrochemical properties of reservoir rocks. From that knowledge, more general and scientifically sound descriptive models could be established and used, along with information collected from logs, to estimate the potential of shaly formations under a variety of conditions in both a practical and reliable manner.

I.4 The Effect of the Presence of Clay on the Conductive Behavior of Rocks

As already mentioned, the conductivity of a water bearing clean rock, $C_o$, varies linearly with the conductivity $C_w$ of the saturating fluid as:

$$C_o = \frac{C_w}{F}$$

(1.17)

Shaly sands on the other hand, exhibit a complex behavior as illustrated in Fig. 1.3. At low concentrations of the saturating electrolyte, the conductivity of a shaly sand rapidly increases at a greater rate that can be accounted for by the increase in $C_w$. With
Fig. 1.3 Typical Conductivity \((C_0 - C_w)\) Plot for Shaly Sands

\[ C_0 = \frac{C_w}{F} \]
further increase in solution conductivity, the sand conductivity increases linearly in a manner analogous to that of clean rocks. However, the magnitude of \( C_0 \) for a shaly sand is generally larger than the conductivity exhibited by an otherwise clean formation of the same porosity. This "excess conductivity" is attributed to the presence of shaly material.

A more general relationship between \( C_0 \) and \( C_w^{(15)} \) incorporates the excess conductivity \( X \) as:

\[
C_0 = \frac{C_w}{F} + X
\]  

(1.18)

For clean rocks, the magnitude of \( X \) is zero and eq. (1.18) reduces to the model given by eq. (1.17). On the other hand, if \( C_w \) is large enough, the shale term exerts little effect on \( C_0 \) and again eq. (1.18) transforms into (1.17). From an electrical viewpoint, shale effects are effectively controlled not only by the absolute magnitude of \( X \), but also by its relative value with respect to the term \( C_w/F^{(15)} \).

Although the absolute value of \( X \) is recognized as an electrical property of clays, its magnitude and dependence on the electrical properties of the saturating solution is still the subject of considerable study. The most accepted fact regarding the effect of shaliness on the conductive behavior of a rock sample is that the absolute magnitude of \( X \) increases with \( C_w \) to some maximum level after which it remains constant for higher salinities. This corresponds respectively to the non-linear and linear portions of the conductivity plot of fig. 1.3.
1.5 Conductivity Models for Shaly Sands

a) Early Concepts

Better understanding of the conductive behavior of shaly sands led to the establishment of various models applicable to these formations. A brief synopsis of the stages of early developments is presented hereafter. The analysis is restricted to water saturated conditions in order to simplify the treatment of what has proven to be a complex problem. The applicability of each of those early conductivity models over the entire range of salinities is also considered.

Based on their experimental work on the Formation factor, Fatnode and Wyllie (7) realized that, for shaly samples, current is carried not only by the saturating solution but also by "conductive solids", namely wet clay components in the form of either shale streaks or disseminated particles. The total conductance of the system appeared to be equal to the sum of the conductance of both mediums. The authors proposed that the total conductivity of the rock can be expressed as:

$$ C_o = \frac{C_w}{F} + C_s $$

(1.19)

where \( C_s \) is the conductivity of the conductive solids. \( C_s \) represents the X term in eq. (1.18). Since \( C_s \) was found to be constant for the range of salinities considered in the experiments, the model of eq. (1.19) is representative of the linear portion of the \( C_o - C_w \) plot.
L. de Witte\(^{(16)}\) stated that the model presented by Patnode and Wyllie is equivalent to two parallel resistances requiring the two elements i.e. conductive solids and pore fluid, to be electrically insulated, while in actuality they are not. De Witte undertook the investigation of the problem hoping to present theories leading to generalized formulas applicable in all cases. In so doing, he concluded that the "conductive solids" occur mostly in small quantities randomly distributed throughout the rocks. De Witte proposed that the fluid contained in the pores of a shaly sand can be considered as a mixture of the electrolyte and the so called conductive solids. Following the work of Patnode and Wyllie\(^{(7)}\) in clay slurries, De Witte established a conceptual two element model given by:

\[
C_o = \frac{1}{F} [(1-X_w)C_s + X_w C_w] \quad (1.20)
\]

where \(X_w\) is the volumetric fraction of water in the slurry occupying the pore space. Since \(C_s\) is assumed constant, the model is then of the form:

\[
C_o = A + BC_w \quad (1.21)
\]

Therefore it only describes the linear portion of the conductivity plot.

De Witte made two important contributions. First, he gave a basic criteria to measure the importance of shale effects; i.e., he proposed that shale effects are controlled not only by the value of the term \((1-X_w)C_s\), but also on its relative magnitude as compared with \(X_w C_w\). Second, he proposed a specific value for the magnitude of the conductivity of the wet clay, \(C_s\).
Winsauer and McCardell\textsuperscript{(8)} introduced a fundamentally different approach. The abnormal conductive behavior of shaly sands was attributed to the presence of a "double layer" with definite conductive properties. The excess conductivity, or double layer conductivity $Z$, was ascribed to adsorption of ions on the clay surface resulting in a high concentration of mobile positive charges gathered at a close distance from the surface. The existence of two types of solutions in the pore space of a shaly sand was implied, namely a "double layer solution" and an equilibrating solution. Based on these concepts, a two-parallel resistor model was proposed:

$$C_o = \frac{1}{F} (C_w + Z)$$  \hspace{1cm} (1.22)

The geometric factor $F$ applies to both elements and is taken as a formation factor independent of shale effects. The model of eq. (1.22) differs from previous ones in that it was experimentally shown that $Z$ varies with the conductivity of the equilibrating solution, and depends on the type of ions present.

Because of the variable character of $Z$, the model describes the non-linear portion of the conductivity plot. Little insight was gained, however, regarding its nature at high salinities\textsuperscript{(15)}. At any rate, the authors' work stated the basis for a solution to the problems associated with shaly sands based on extensive laboratory work and strong theoretical concepts.

Wyllie and Southwick\textsuperscript{(9)} conducted an experimental investigation on the effects of ion-exchange materials on the electrical properties of natural and synthetic porous materials.
They concluded that as the amount of ion exchange material decreases, the intercept of the straight-line portion of the $C_o - C_w$ plot also decreases. This observation suggests that the conductivity of the "conductive solids" also decreases. In addition, it was observed that the slope of the $C_o - C_w$ plot at high salinities varies with the amount of conductive material.

Wyllie and Southwick stated that a two-element model seems inadequate to describe the conductivity of a shaly sand. Not only there are two conductivities in parallel, they concluded, but there is also a conductivity component in series with the two in parallel. This concept resulted in a conductivity model given by:

$$C_o = \frac{C_s}{x} + \frac{C_w}{y} + \frac{C}{z}$$

where $x$ and $y$ are geometric factors describing the arrangement of conductive solids and interstitial water that are effectively in series; $z$ is the dimensionless geometrical factor for the conductive solids, and $F$ is the true formation factor. The term $C_s/z$ is analogous to the quantity $X$ in eq. (1.18).

It was also concluded from their experiments that the Formation factor, $F'$, derived from the straight line portion of the $C_o - C_w$ plot is generally less than the true $F$. Although the model gave good agreement with experimental values, it was not developed further due to the difficulties encountered in defining more precisely the geometrical factors. However, since the interactive term is capable of modeling the curvature exhibited at low salinities, the model could be used to represent both the linear and non-linear zones of the $C_o - C_w$ plot.
Following on the work of Winsauer and McCardell\(^{(8)}\), L. de Witte\(^{(18)}\) introduced the concept of reduced activity of the double layer counterions. This concept is based on electrochemistry theory and statistical considerations for the ionic distribution of the counterions associated with the negative charges fixed at the clay surface. It allowed the double layer solution to be considered as an electrolyte with specific properties. Based on these concepts, de Witte proposed a conductivity model which, for the case of water bearing shaly sands, is given by the expression \(^{(18)}\):

\[
C_o = \frac{C}{F^*} [m_R + 2.15 m_w]  \tag{1.24}
\]

where \(C\) is a constant which depends on the mobility of the positive ions in the internal (double layer) solution and is somewhat analogous in concept to the equivalent conductivity of electrolytes; \(m_R\) and \(m_w\) are the molal concentrations of the fixed charges and external or equilibrating solution respectively. The parameter \(F^*\) was defined as the "cell constant" of the inert rock network and is therefore equivalent to the Formation factor.

Eq. \((1.24)\) can be expressed in a general form as:

\[
C_o = \frac{1}{F^*} (a + bC_w)  \tag{1.25}
\]

in which the constants \(a\) and \(b\) depend on the "shaliness and texture of the rock". As pointed out by de Witte, eq. \((1.25)\) and consequently \((1.24)\) are analogous to the previous models suggested by Patnode and Wyllie, and by de Witte himself. Eq. \((1.24)\) is of linear form and therefore applies only to the straight line portion of the \(C_o - C_w\) relationship. However, the theoretical approach
followed by de Witte led also to the establishment of a general equation for the SP. His work, along with the work of Winsauer and McCardell, is at the origin of contemporary concepts and models capable of describing equally well both the conductive and electrochemical behavior of shaly sands.

Most of the experimental work performed to this date regarding the effect of clay on both the electrochemical potentials and conductivity of shaly sands is attributed to Hill and Milburn. The large amount of experimental work, as well as the wide variety of samples analyzed enabled the authors to arrive at important conclusions and to present interesting concepts, two of which set the bases for recent developments.

Without doubt, the single most important result from Hill and Milburn's work is the fact that both the electrochemical and conductive behavior of shaly sands are strongly related to the cation exchange capacity (CEC) per pore volume of the rock. This physical property is expressed by means of the parameter "b". The parameter "b" reflects the "effective clay content" of the sample. It renders unnecessary the knowledge of clay fraction, type, and distribution.

The second important concept introduced by these latter authors is the establishment of a conductivity model in which the formation factor varies with both shaliness and $C_w$. Analogous to Archie's equation for clean sands, the Hill and Milburn's model is given by:

$$C_o = \frac{C_w}{F_a}$$ (1.26)
where the apparent formation factor $F_a$ is expressed as:

$$F_a = F_{100} \left( \frac{100}{C_w} \right)$$

where $b$ is the shaliness parameter empirically related to CEC by:

$$b = -0.0055 - 0.135 \frac{CEC}{PV}$$

where CEC/PV is expressed as milliequivalents exchange capacity per cubic centimeter of pore volume.

The term $F_{100}$ in eq. (1.27) represents an idealized formation factor determined at a hypothetical water conductivity of 100 mho/m at room temperature. Following from the work of Winsauer and McCardell\(^8\), the hypothetical $F_{100}$ is taken at a $C_w$ high enough to minimize clay effects. $F_{100}$ is then analogous to the classical definition of Archie's formation factor for clean rocks.

The conductivity model given by eqs. (1.26) through (1.28) is capable of representing both the linear and non-linear regions of the $C_o - C_w$ plot. Although the proposed model describes satisfactorily the author's experimental data, its practical application is limited and has not been further explored. The model predicts that core conductivities reach a minimum as the conductivity of the equilibrating solution decreases down to a critical point, after which core conductivities increase sharply with further decrease in $C_w$. The conductivity value at which the minimum occurs is related to the effective clay content "b".
b) **Modern Concepts**

The models discussed in the preceding section were used to relate the conductivity $C_t$ to the hydrocarbon saturation. Their practical application, however, was limited in most cases by their inability to accurately predict the complex behavior of shaly sands over a wide range of conditions. In addition, readily available log data could not be used to directly quantify the model's shale related parameters.

At the beginning of the 1960's, attention was focused on the search for a model which did not suffer of as many shortcomings. The evolution of contemporary shaly sand concepts\(^{(15)}\) has produced two well defined types of models.

The so called $V_{sh}$ models correspond to the first category. They are empirical models developed for practical application using log-derived data. The cation-exchange or "Double layer" models represent the second type. The latter models evolved from stronger theoretical bases. They represent more complete models, developed to explain and predict to a better degree the effects of clay on the general electrochemical behavior of reservoir rocks. A review of the $V_{sh}$ models will follow. Because of their influence on the current status of shaly sand interpretation, the analysis shall be extended to include hydrocarbon bearing formations. The Double layer models are reviewed in Chapter III.

The shale volume fraction, $V_{sh}$, is defined\(^{(15)}\) as the volume of wet shale per unit volume of reservoir rock. This definition takes into account the volume of water associated with the shale. $V_{sh}$ models originated from early evidence of the relationship
between the amount of "conductive solids" and the conductivity of the system \(^{(7),(16)}\). Although the \(V_{sh}\) models are considered to be scientifically inexact \(^{(16)}\), they are suited for the application of log derived data. These models have hence been used extensively in practical application.

An excellent review of the \(V_{sh}\) models have been recently presented by Worthington \(^{(15)}\) and an in-depth treatment of the subject will not be presented here. The discussion will only be restricted to the relevant points and the limitations of these concepts.

Several "\(V_{sh}\)" relationships describing the conductivity of water saturated shaly sands have appeared in the literature. These basic models are presented in chronological order in Table I.a. taken from reference \(\text{(15)}\).

<table>
<thead>
<tr>
<th>TABLE I.a.</th>
</tr>
</thead>
</table>

**\(V_{sh}\) Models - Water Bearing Shaly Sands**

(After Ref. 15)

\[
\begin{align*}
C_o &= \frac{C_w}{F} + V_{sh}^2 C_{sh} \quad \text{Hossin (1960)} \\
C_o &= \frac{C_w}{F} + V_{sh} C_{sh} \quad \text{Simandoux (1963)} \\
\sqrt{C_o} &= \sqrt{\frac{C_w}{F}} + V_{sh} \sqrt{C_{sh}} \quad \text{Doll (Unpublished)} \\
\sqrt{C_o} &= \sqrt{\frac{C_w}{F}} + V_{sh}^{(1-V_{sh}/2)} \sqrt{C_{sh}} \quad \text{Poupon and Leveaux (1971)}
\end{align*}
\]

The parameter \(C_{sh}\) appearing in the models presented in Table I.a. represents the conductivity of the wet shale. An analysis of
the table readily reveals that those models proposed by Hossin and Simandoux are of linear form and therefore describe only the linear region of the $C_q-C_w$ plot. Doll's model can be obtained by separately taken the square root of each term in the Hossin equation. As pointed out by Worthington\(^{(15)}\), the expanded version of Doll's equation takes on the form of the three resistor model proposed earlier by Wyllie and Southwick\(^{(9)}\), and neither equation considers the variation of the shale related term with $C_w$. The relationship proposed by Poupon and Leveaux falls also into the same category.

Although the three element models accommodate the non-linear zone of the $C_q-C_w$ relationship, this is done at the expense of a poor representation of the linear zone\(^{(15)}\). Therefore, the models of Table I.a do not allow a continuous representation of the conductive behavior of water bearing shaly sands over the entire range of possible $C_w$.

$V_{sh}$ models have been extensively used for practical interpretation purposes. The modifications of these models to describe hydrocarbon zones resulted in the saturation models listed in Table I.b.

From the saturation models presented in Table I.b the Simandoux equation has received more attention\(^{(13)}\). In its practical form, the "Total Shale" or Simandoux equation is written as (13):

$$
S_w = \frac{0.4 R_w}{\phi_e} \left[ - \frac{V_{sh}}{R_{sh}} + \left( \frac{V_{sh}}{R_{sh}} \right)^2 + \frac{5 \phi_e^2}{K_t} \right]
$$  \(1.29\)
TABLE I.b

<table>
<thead>
<tr>
<th>V&lt;sub&gt;sh&lt;/sub&gt; Models - Hydrocarbon Zone (Ref. 15)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_t = \frac{C_w}{F} S_w^n + V_{sh} C_{sh} )</td>
</tr>
<tr>
<td>Simandoux (1963)</td>
</tr>
<tr>
<td>( C_t = \frac{C_w}{F} S_w^n + V_{sh} C_{wh} S_w )</td>
</tr>
<tr>
<td>Modified Simandoux Eq.</td>
</tr>
<tr>
<td>Bardon and Pied (1969)</td>
</tr>
<tr>
<td>( \sqrt{C_t} = \sqrt{\frac{C_w}{F} S_w^{n/2} + V_{sh} \sqrt{C_{sh}}} )</td>
</tr>
<tr>
<td>Doll (Unpublished)</td>
</tr>
<tr>
<td>( \sqrt{C_t} = \sqrt{\frac{C_w}{F} S_w^{n/2} + V_{sh} (1-V_{sh}/2)^{n/2} \sqrt{C_{sh}} S_w^{n/2}} )</td>
</tr>
<tr>
<td>Poupon and Leveaux (1971)</td>
</tr>
</tbody>
</table>

where \( \phi_e \) is the effective porosity which, contrary to the total porosity \( \phi \), excludes the pore space within the shale itself. Eq. (1.29) has been employed in the earliest computer supported well evaluation work(20).

Aside from the limitations in reproducing the conductive behavior of shaly water sands, the derivation and application of eq. (1.29) is marred by several additional shortcomings(13):

1. The basic experimental work performed by Simandoux consisted in measurements on only four synthetic samples using one type of clay (montmorillonite) and apparently at constant porosity. In addition, the clay used in the experiments was not in the fully wet state(15). Therefore, the \( V_{sh} \) term in eq. (1.29) does not strictly conform to its definition.
2. The use of the correction term \( \frac{V_{\text{sh}}}{R_{\text{sh}}} \) does not apply to disseminated clay conditions \(^{(21)}\).

3. \( V_{\text{sh}} \) is determined from tool (shale indicators) responses that do not fully separate clay minerals and other shale materials. They also do not distinguish between clays with high CEC (e.g. montmorillonites) and those with low CEC (e.g. kaolinite).

4. \( R_{\text{sh}} \) is taken equal to the resistivity of adjacent shales which usually tend to present different mineralogical characteristics.

5. The formation factor is not included in the shale correction term \( \frac{V_{\text{sh}}}{R_{\text{sh}}} \).

Fertl and Hammack \(^{(22)}\) made a comparative study of the various \( V_{\text{sh}} \) models using actual field examples for various degrees of shaliness. Based on their study, the authors recommended the Simandoux equation \((1.29)\) as being the most representative. They also proposed their own empirical equation which was found to be of equal statistical representativity.

The recommended model by Fertl and Hammack can be written in the form:

\[
S_w = \left( \frac{F R_w}{R_t} \right)^{\frac{1}{2}} - \frac{V_{\text{sh}} R_w}{0.4 \phi_e R_{\text{sh}}} \quad (1.30)
\]

in which \( F \) reflects the effective porosity \( \phi_e \).

Equation \((1.30)\) is a \( V_{\text{sh}} \) saturation model that includes most of the previously mentioned shortcomings. It represents, however, few advantages. In addition of being a simpler expression, it treats the shale effect as a correction term \( \Delta S_w \).
\[ \Delta S_w = \frac{V_{sh} R_w}{0.4 \phi e_{sh}} \]  

(1.31)

taken out from the clean sand model:

\[ S_{w_c} = (\frac{F R_w}{R_e})^{\frac{1}{2}} \]  

(1.32)

In general, eq. (1.32) takes the form:

\[ S_{w'} = S_{w_c} - \Delta S_w \]  

(1.33)

where \( S_{w'} \) and \( S_{w_c} \) represent the water saturation of the shaly sand and the equivalent clean formation respectively.

The equation readily points out the practical aspect of the shale effect and its magnitude as a correction term. First, treating a shaly sand as a clean one will result in the underestimation of potential zones as high \( S_w \) values will be obtained. On the other hand, the use of an inflated \( V_{sh} \) will produce the opposite effect. Finally, the net effect of the presence of clay in a potential zone will ultimately depend on the absolute magnitude of the shale term \( \Delta S_w \), as compared to that of \( S_{w_c} \).

\( V_{sh} \) models have been steadily displaced by concepts based on the existence of an electrical double layer generated when clays come in contact with saline solutions. Although the Double Layer Theory is not a contemporary concept, its application in log interpretation has been lately emphasized by the conductivity models currently in use.
CHAPTER II
THE ELECTRICAL DOUBLE LAYER IN SHALY SANDS

II.1 General Aspects of Clay Mineralogy

Clays are sediments with grains less than 1/256 mm. in diameter. They are composed almost exclusively of hydrous aluminum silicates and alumina (Al₂O₃). These components are referred to as clay minerals.

The clay minerals have a sheet structure similar to that of micas in which the principal building elements are: (i) sheet of silicon (Si) and oxygen (O) atoms in a tetrahedral arrangement; and (ii) sheet of aluminum (Al), oxygen and hydroxyle (OH) arranged in octahedral arrangement. A schematic representation of the two building elements is presented in Fig. 2.1. These sheets of tetrahedra and octahedra are superimposed in different manners giving as a result different groups of clay minerals. The principal groups of clay minerals are the Kaolinite group, the Montmorillonite group, the Illite group, and the sedimentary chlorites.

A montmorillonite crystal is composed of two unit layers as illustrated in Fig. 2.2. Each unit is characterized by a three-sheet lattice in which there are two tetrahedral sheets and an octahedral one sandwiched in between. The unit layers are held together rather loosely in the C-direction, with water occupying the interlayer spaces. The amount of the water present varies so that the C-dimension ranges between 9.7 to 17.2 Å (angstrom) units.

In the tetrahedral sheet, tetravalent silica (Si⁴⁺) is sometimes partially replaced by trivalent aluminum (Al³⁺). In the octahedral sheet, there may be replacement of Al³⁺ by divalent magnesium (Mg²⁺).
Fig. 2.1 Clay Structure Elements

a) Tetrahedral Sheet

b) Octahedral Sheet
Fig. 2.2 Schematic of Different Clay Minerals Crystal Structure
without complete filling of the vacant positions. The aluminum atoms may also be replaced by iron, chromium, zinc, lithium, and other atoms. When an atom of lower positive valence (cation) replaces one of higher valence a deficit of positive charge, or in other words, an excess of negative charge results. In the presence of an electrolyte, this excess of negative charge is compensated by the absorption of cations on the layer surfaces, ions which are otherwise too large to be accommodated in the interior of the crystal. In the case of montmorillonite, the compensating cations, or counterions, are also present between the layers as illustrated in Fig. 2.2.

In the presence of a saline solution, the counterions such as $\text{Mg}^{++}$, $\text{Na}^+$, and $\text{Ca}^{++}$ on the layer surfaces may be readily exchanged by other cations; hence they are also referred to as exchangeable cations. The total amount of these cations can be determined analytically and is called cation exchange capacity (CEC) of clay, expressed as milliequivalents per gram (meq/gm) of dry clay.

The exchangeable cations can be displaced only by other cations. The replacing power of different cations is variable; however, there is a definite order of replaceability, namely, $\text{Na} < \text{K} < \text{Mg} < \text{Ca} < \text{H}$; this is that hydrogen will replace calcium, calcium will replace magnesium, etc.

Montmorillonite is a swelling clay which takes in variable amounts of water. When contacted with water, the water molecules penetrate between layers and the interlayer cations become hydrated. The large hydration energy involved is able to overcome the attractive forces between the layers, resulting in interlayer swelling that in some cases could double the volume of dry clay.
An illite crystal, also shown in Fig. 2.2, is basically the same as the montmorillonite; however, illites are distinguished from the latter primarily by the absence of interlayer swelling. Also, the negative charges are usually compensated by potassium ions. Only the K\(^+\) ions on the external surface can be exchanged; those between the layers are fixed and provide a layer-linking force that is responsible for the non-swelling character of illites.

Fig. 2.2 also illustrates the kaolinite and chlorite crystals. Because of the absence of interlayer cations, these minerals are characterized by being of a non-expandable nature. Unlike other clays, kaolinite and chlorite show little variation in their chemical composition. In their natural state, they show little exchange capacity, which results from broken bonds around the edges of the crystals giving rise to unsatisfied negative charges. These negative charges are balanced by cations which undergo limited substitution.

Montmorillonite and illite have generally high CEC values, while kaolinite and illite show little to zero CEC values. Table II.a lists the formula, density, percent hydrogen, and average CEC value for the different clay groups. Clays with high cation exchange capacity play an important role in electric conduction of shales and shaly sands.

<table>
<thead>
<tr>
<th>Clay Name</th>
<th>Density gm/cc</th>
<th>% Hydrogen</th>
<th>Average CEC meq/gm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>2.69</td>
<td>1.5</td>
<td>0.03</td>
</tr>
<tr>
<td>Illite</td>
<td>2.76</td>
<td>0.5</td>
<td>0.20</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>2.33</td>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Chlorite</td>
<td>2.77</td>
<td>1.2</td>
<td>0.0</td>
</tr>
</tbody>
</table>
II.2 Distribution of Clays in Sandstones

Clays are often found in sands, siltstones, and conglomerates. Core analysis, petrographic thin section examination and most recently scanning electron microscopy (SEM) revealed that clay material, often referred to as "shale", may be distributed in sand formations in three different forms: laminated, structural, and dispersed. These distribution modes are pictorially shown in Fig. 2.3.

Within a sand body, thin laminae of clay and other fine-grained material may occur. They are of detrital origin; i.e. they are formed outside the sandstone framework and are usually referred to as laminated clays or laminated shale. The laminae do not affect the porosity or permeability of the sand streaks themselves; however, these laminae are more or less continuous and act as vertical permeability barriers.

Clays can be of diagenetic origin, i.e., they were formed within the sand framework. A source of diagenetic clay is the in-situ alteration of non-quartz particles due to reaction with interstitial waters. Of these alterations, the most common are those of feldespar to kaolinite and of hornblende to chlorite. This alteration leads to structural clays. Also considered as structural clays are those originated when pellets or clasts of clays are deposited as an integral part of a matrix predominated by sand.

"Dispersed" clay is the main mode of occurrence of diagenetic clays. Dispersed clays develop by precipititation of clay crystals from pore fluids, in response to changes in pore water chemistry as a result of changes in temperature, and pressure during burial and compaction of sediments. Subsequently, dispersed clays develop within the pore system and are generally attached to rock mineral surfaces.
Fig. 2.3 Clay (Shale) Distribution Modes

a) Dispersed

b) Laminated

c) Structural

- Clay
- Sand
Dispersed clays can occur in pores as (i) discrete particles, (ii) intergrown crystals lining on the pore walls forming a relatively thin and continuous coating, and (iii) crystals extending far into, or completely across, a pore or pore throat creating a bridging effect. Dispersed clay markedly reduces the porosity and permeability of the formation (14).

II.3 Double Layer Concepts in Clay Systems

a) Electrical Double Layer (EDL) Structure (23)

The negative charge carried by the clay lattice is compensated by cations concentrated on the unit-layer surfaces of the clay minerals. When brought in contact with an electrolyte, the compensating cations have the tendency to move away towards the bulk of the solution where their concentration is lower. At the same time, however, these compensating ions are retained close to the surface by electrostatic forces. As a result, an electrical double layer is generated on the exterior surface of the clay. The electrical double layer is formed then by the particle charge and the charge of the associated compensating ions. These compensating cations, or counterions, can be exchanged by other ions in solution. The generation of an EDL is schematically illustrated in Fig. 2.4.

b) Character of the EDL (23)

Double layers are generated both in the flat unit-layer surfaces and at the edge of clay plateletes. As previously discussed, the negative charge of the clay lattice results from
Figure 2.4 Generation of a Double Layer in Clay Systems (Ref. 35)
substitution of certain positive elements by others of lower valence. Cations accumulated on the unit layer surfaces compensate the excess of negative charge, resulting in the generation of a EDL.

The unit-layer surfaces exhibit a constant charge which is determined by the lattice substitutions. The associated EDL is then one of fixed charge. The double layer charge depends also on the type and degree of lattice substitutions.

Platelete-like clay particles also expose an edge surface composed mainly of broken bonds. Their structure differs from that in the flat unit-layers and is a consequence of disruptions of the tetrahedral silica sheets and the octahedral alumina sheets. The different structure results in a different character of the EDL at the edges than that at the layer surfaces. The EDL at the edge surfaces is generated by the adsorption of specific ions, called Peptizing or Potential determining ions.

Despite the existence of an EDL at the edge surfaces, the double layer associated with the large flat surface of the unit-layers predominates in the case of clay materials.

c) The Guoy Model of the EDL

A relatively large negative potential exists at the surface of the clay particles due to the ionic concentration differences between the surface and the solution far away. As the diffuse counterion atmosphere is traversed, the potential becomes less negative, reaching a value of zero at a distance $X_d$ where no electrical forces are exerted on the ions by the surface. The
distance $X_d$ is then the distance up to which the EDL is operative.

Under equilibrium conditions the counterions are concentrated in the liquid surrounding the charged particle forming a ionic atmosphere. As illustrated in Fig. 2.5, the counterion concentration decreases with increased distance from the surface. The diffuse nature of the ionic atmosphere in the double layer was first explained in the Guoy Theory of the double layer. For that reason, the counterion atmosphere is often described as the Guoy layer, or diffuse layer.

The Guoy theory establishes, as shown in Fig. 2.5, that the diffuse double layer exhibits an excess of cations in the proximity of the surface. The ionic deficiency of anions near the surface arises from repulsion forces. The Guoy theory allows the calculation of the distribution of both positive an negative ions in the diffuse double layer. In addition, the average electric potential at any point, as a function of the distance from the surface, may also be evaluated. The charge distribution in the EDL depends on the character of the surface charge, the nature of the surface potential, and the concentration of the equilibrating electrolyte.

Typical distributions for ionic concentration and electric potential, as predicted by the Guoy theory, are schematically presented in Figs. 2.6(a) and 2.6(b). Fig. 2.6(a) indicates that the cation concentration attains a maximum value at the surface and then decreases as the distance from the surface increases. The opposite is true for anions. It can also be noticed that the concentrations of both positive and negative ions are equal and
Fig. 2.5 Guoy Model of the Diffuse Double Layer
Fig. 2.6.(a) Charge Distribution in the EDL (Guoy Theory)
Fig. 2.6.(b) Electric Potential Distribution in the EDL (Guoy Theory)
reach the concentration of the bulk solution at a distance $X_d$ from the surface. The distance $X_d$ up to which the EDL is operative is referred to as the "thickness" of the diffuse double layer.

Fig. 2.6.(b) reveals that the electrical potential reaches a maximum value $\Phi_0$ at the particle surface and then decreases with increased distance, becoming zero at a point where the reference concentration exists.

The type of mechanism responsible for the generation of the EDL affects both the surface potential and the surface charge; therefore, it bears an effect on the charge distribution. For the case of constant surface charge prevailing in clay systems, the electrical potential $\Phi_0$ at the surface varies with the concentration (or activity) of the bulk solution, its magnitude decreasing as the concentration increases.

The Guoy theory predicts that the thickness of the diffuse atmosphere is reduced as the concentration of the bulk solution increases. In addition to the concentration, the compaction effect also depends on the valence of the counterions. In general, the higher the valence, the thinner the double layer.

d) The Stern Model of the EDL

Certain assumptions implicit in the Guoy theory do not fully apply in real situations. Ion size effects are neglected as the ions are considered point charges. Also, interactions between the counterions, the charged surface and the medium are not considered. The Stern theory of the EDL eliminates some of these idealistic concepts.
The Stern theory establishes that, at the closest, the counterions approach the charged surface at a distance limited by the size of these ions. Fig. 2.7 shows, schematically, the basics of the Stern's model of the EDL. According to the diagram, a "Stern layer" of thickness $\delta$ is formed between the surface and a plane passing through the centers of the closest counterions. The Stern Layer carries a fraction $\sigma_1$ of the total charge $\sigma$. $\sigma_1$ is assumed concentrated at the distance $\delta$ corresponding to the plane of centers.

The remainder of the counterions beyond the plane of centers are distributed in an outside layer identical to the Guoy atmosphere. The potential in the inner layer decreases linearly from its surface value $\phi_0$ to a value $\phi_{\delta}$ at a distance $\delta$. $\phi_{\delta}$ is known as the Stern Potential. Beyond $\delta$, the potential distribution follows pretty much the Guoy theory.

The net surface charge is given by the Stern model as the sum of the charges in the Guoy atmosphere and in the inner layer. As with the Guoy theory, the Stern model predicts that the outer diffuse atmosphere is compressed as the electrolyte concentration increases. Moreover, this theory predicts that an increase in concentration forces counterions in the outer layer towards the inner layer.

In real systems such as clay suspensions or shaly sands, the distance of closest approach for the counterions depends on the presence of adsorbed water molecules at the surface of the particle, as well as on hydration water surrounding the counterions.
\( \sigma_1 = \text{Net counterion charge of Stern layer} \)

\( \sigma_2 = \text{Net counterion charge of diffuse layer} \)

\( \sigma = \text{Total charge} = \sigma_1 + \sigma_2 \)

Fig. 2.7 Stern Model of the EDL
II.4 Double Layer Concepts in Compacted Shales and Shaly Sands\(^{(8),(24)}\)

So far in the analysis only the structure of the EDL associated with discrete particles has been considered. When clay particles are brought close together, the presence of repulsive forces influence the individual ionic layers. Although the ionic distribution is altered, the essential structure and character of the EDL persists.

Shales are composed of conglomerates of clay particles forming a complex network of large numbers of interconnecting pores. When the shale is saturated with an electrolyte solution, the total concentration of mobil positive ions exceeds that of negative ones, due to anion immobilization at the surface. If the pores are small, or the thickness of the resulting double layer is large, then the pore solution, at equilibrium conditions, will have an effective excess of positive ions. On the other hand, if the double layer is thin or the pores are large enough, then the solution in the center of the pores will have a composition of equal number of positive and negative ions. This "far" solution, or "centermost" solution is the same as the equilibrating solution outside the pores. The "far" solution can then be defined as that portion of the solution in the pore space which is not under the influence of the double layer.

The existence of the EDL in shales results in the ionic distribution shown schematically in Fig. 2.8. As illustrated in the figure, at the boundary between the pore network and the equilibrating solution there exists an abrupt concentration change. This concentration difference gives rise to an electrical potential difference at the interface of shales and electrolytes. These potential differences are known as Boundary potentials.
Fig. 2.8 Schematic of Clay-Solution Boundary. Concentration Change
The excess in mobil positive ions in the pore solution is believed to be responsible for the conductive properties of the EDL.

The above discussion for shales is also applicable for the case of shaly sands. The ionic distribution in the solution saturating the pores of these formations is illustrated in Fig. 2.9.

II.5 Applications of the Theories of the Electrical Double Layer

The ionic distribution and the electrical potential distribution in the EDL can be computed, in the simplest form, from the Guoy theory. As evidenced by the early work of Winsauer and McCardell(8,24), this simple theory appears to be adequate for establishing the theoretical bases underlying the interpretation of the boundary potentials and the conductivity of the double layer.

a) Single Flat Double Layer Computations. Guoy Theory

a.1) Potential Distribution

Under equilibrium conditions, the average ionic concentrations in the EDL at any distance from the surface can be calculated. Assuming the ions as point charges, the local concentrations are expressed from the Boltzman's theorem as a function of the average electric potential $\phi$ at a distance $x$ from the surface as (23):

$$n_-=n^*_\exp (\frac{v_e \phi}{kT})$$

$$n_+=n^*_\exp (-\frac{v_e \phi}{kT})$$  (2.1)

in which:

$$n_-, n_+ = \text{local ionic concentrations; (no. of ions/cm}^3\text{)}$$

$$n^-, n^* = \text{ionic concentrations in the equilibrium solution; (no. of ions/cm}^3\text{)}$$
Figure 2.9 Charge Distribution in Shaly Sands
\( v_- , v_+ = \text{valences of ions} \)

\( e = \text{elementary charge} \)

\( k : \text{Boltzman's constant} \)

\( T : \text{Absolute temperature} \)

The local density of charge is given by the excess of positive ions:

\[
\rho = v_+ e n_+ - v_- e n_- \quad (2.2)
\]

The local electric potential and the density of charge are related by Poisson's equation:

\[
\frac{d^2 \phi}{dx^2} = -\left( \frac{4\pi}{D} \right) \rho \quad (2.3)
\]

where:

\( D = \text{dielectric constant of the medium} \)

\( \frac{d^2 \phi}{dx^2} = \text{variation of the field strength } \frac{-d\phi}{dx} \)

For the case of univalent electrolytes such as NaCl:

\( v_+ = v_- \)

and:

\( n^*_+ = n^*_- = n \quad (2.4) \)

The fundamental equation for the EDL is obtained by combining eqs. (2.1) through (2.4) such as:

\[
\frac{d^2 \phi}{dx^2} = \left( \frac{8\pi n e v e}{D} \right) \sinh \left( \frac{ve\phi}{kT} \right) \quad (2.5)
\]

A solution of eq. (2.5), attributed\(^{(8)}\) to Verwey and Overbeck, can be obtained by utilizing the dimensionless variables \( y, z \) and \( \xi \) defined by\(^{(23)}\):

\[
y = \frac{ve\phi}{kT}
\]
\[ z = \frac{ve^0}{kT} \]  
\[ \xi = \kappa x \]

where:
\[ \kappa^2 = \frac{8\pi ne^2v^2}{DKT} \text{ cm}^{-2} \]

Substituting variables results in:
\[ \frac{d^2\psi}{d\xi^2} = \left( \frac{ve}{kT} \right) \frac{d^2\phi}{d\xi^2} \]  \hspace{1cm} (2.8)

and,
\[ \frac{d^2\phi}{dx^2} = \kappa^2 \left( \frac{kT}{ve} \right) \frac{d^2\psi}{d\xi^2} = \left( \frac{8\pi nev}{D} \right) \frac{d^2\psi}{d\xi^2} \]  \hspace{1cm} (2.9)

Therefore, the basic equation (2.5) transforms into:
\[ \frac{d^2\psi}{d\xi^2} = \sinh (y) \]  \hspace{1cm} (2.10)

The sinh function exhibits the property:
\[ \sinh (x) = x \text{ if } x \ll 1 \]

For small potentials \( z \ll 1 \), the fundamental equation becomes:
\[ \frac{d^2\psi}{dx^2} = \left( \frac{8\pi ne^2v^2}{DKT} \right) \phi = \kappa^2 \phi \]  \hspace{1cm} (2.11)

which has as solution:
\[ \phi = \phi_0 \exp (-\kappa x) \]  \hspace{1cm} (2.12)

Expression (2.12) indicates that for small distances from the surface, the potential decreases in an exponential fashion.

a.2) Thickness of the Diffuse Double Layer

Eq. (2.12) gives the potential distribution for small surface potentials \( z \ll 1 \). The center of gravity of the
space charge coincides with the plane \( \kappa x = 1 \). The thickness of the EDL is given by \( \kappa \):

\[
X_d = \frac{1}{\kappa} \tag{2.13}
\]

The quantity \( (1/\kappa) \) is equal to the "characteristic length" in the Debye-Hückel theory for strong electrolytes. Replacing the magnitude of \( \kappa \) given by eq. (2.7) results in:

\[
X_d = \frac{DkT}{8\pi e^2 \nu^2} \frac{1}{\sqrt{n}} \tag{2.14.a}
\]

If the concentration \( n \) is expressed in normality units, the thickness of the EDL given by eq. (2.14.a) becomes:

\[
X_d = \frac{1}{B_0} \sqrt{n} \tag{2.14.b}
\]

in which \( B_0 \) is known as the ion-size coefficient in the Debye-Hückel theory \( \text{\cite{25}} \).

As can be inferred from eq. (2.14.a) the EDL is compressed towards the surface as the concentration increases.

a.3) **Double Layer Charge**

The total charge of the EDL can be calculated from eq. (2.3) as:

\[
\sigma = - \int_0^\infty \rho dx = \frac{D}{4\pi} \int_0^\infty \frac{d^2 \phi}{dx^2} dx = -\frac{D}{4\pi} \left[ \frac{d\phi}{dx} \right]_{x=0} \tag{2.15}
\]

Therefore, the surface charge is determined by the initial slope of the potential distribution function. In terms of the dimensionless variables, the initial slope is given by:

\[
\left[ \frac{d\phi}{dx} \right]_{x=0} = \kappa \left( \frac{kT}{ve} \right) \left[ \frac{dy}{d\xi} \right]_{\xi=0} \tag{2.16}
\]
Integrating (2.10) once with the boundary condition $y = z$
for $\xi = 0$ yields:
\[
\left[ \frac{dy}{d\xi} \right]_{\xi=0} = -2 \sinh \left( \frac{z}{2} \right)
\]  
(2.17)

- Substituting (2.17) in (2.16) and (2.15), and expressing
the result in terms of the original variables:
\[
\sigma = \left( \frac{D}{4\pi} \right) \left( \frac{8\pi n k T}{D} \right)^{\frac{1}{2}} \sinh \left( \frac{\nu e \phi}{kT} \right)
\]  
(2.18)

For small potentials ($z \ll 1$) the total charge becomes
\[
\sigma \approx \left( \frac{D}{4\pi} \right) \left( \frac{8\pi n v^2 e^2}{D k T} \right)^{\frac{1}{2}} \phi_0
\]
or
\[
\sigma \approx \left( \frac{\kappa D}{4\pi} \right) \phi_0
\]  
(2.19)

The term $C = \kappa D/4\pi$ represents the capacity of the EDL.

For a constant surface potential, eq. (2.19) indicates
that the surface charge varies with the square root of $n$. It
should increase as the concentration of the equilibrating
solution increases. For the case of constant surface charge,
the surface potential decreases as $n$ increases.

b) Potential and Charge Distribution for the Stern Model of the
Electrical Double Layer

As discussed in a preceding section, the Stern theory
modifies the Guoy concepts by limiting the distance of closest
approach. In the Stern model, no charge exists between the plane
at which the surface of the charge is located and the plane of
centers of the Stern counterions. This inner layer represents then
a molecular condenser in which the potential decreases linearly. The Stern model also includes a reduction of the dielectric constant of the medium.

The total charge in the Stern theory is given by\(^{(23)}\):

\[
\sigma_1 = \left( \frac{D^*}{4\pi\varepsilon} \right) (\phi_0 - \phi_\delta)
\]

in which \(D^*\) is the dielectric constant in the zone of the molecular condenser.

The charge of the outer diffuse layer is given\(^{(23)}\) as a function of the Stern potential \(\phi_\delta\) by:

\[
\sigma_2 = \left( \frac{Dn_kT}{2\pi} \right) \frac{\nu e\phi_\delta}{2kT} \sinh \left( \frac{\nu e\phi_\delta}{2kT} \right)
\]

II.6 Double Layer Conductivity

Winsauer and McCardell\(^{(8)}\) proposed that the relatively high conductivities observed in shaly sands originates as a result of a high concentration of mobil cations in the double layer. These authors concluded that the excess conductivity in shaly sands must therefore be a reflection of the conductivity of the EDL.

The character of the conductivity of the EDL was explained by Winsauer and McCardell\(^{(8)}\) from basic Double layer theory. Although these authors made valid conclusions on the subject, their analysis was based on assumptions that are not strictly applicable in clay systems. The analysis was based on the existence of a constant surface potential on the clay surface. As it has been previously discussed, the predominant double layer phenomena in clays arises from a condition of constant surface charge\(^{(23)}\). Under those conditions, the surface potential varies with the concentration of the electrolyte.
The analysis performed by Winsauer and McCardell was conducted by applying the Guoy theory of the EDL. There are indications that specific counterion adsorption often takes place in clay systems\((23)\). For these situations, the Stern theory of the EDL should be applied. The conductivity of the double layer was predicted to vary with electrolyte concentration at low salinities; however, little evidence was given about its apparent constant magnitude at higher salinities, a behavior that is currently accepted\((15)\).

In this section, an attempt to review and explain the theoretical bases of the conductive nature of the EDL will be made. As in clay suspensions, it is assumed that the Stern model of the EDL applies for the case of shaly sands. Moreover, it is considered that the condition of constant surface charge also predominates in these formations.

In general terms, the Stern model considers the EDL as a system composed of the charged particle surface, a Stern or inner layer, and a diffuse outer layer. In addition, the charge of the Stern layer is assumed concentrated at the plane of centers of the Stern counterions. The plane of centers is located at a distance \(\delta\) from the surface. At that plane, a Stern potential \(\Phi_\delta\) also exists with respect to a point far away. The Stern layer then could be visualized as a "charged surface" which generates a Guoy-type diffuse double layer. The charge \(\sigma_2\) of this diffuse layer is given by eq. (2.21) as a function of both \(\Phi_\delta\) and the concentration \(n\) of the equilibrating, or bulk solution.

For a clay particle carrying a constant surface charge, it follows that the number of counterions present in the system is a constant quantity \(S^+\) that depends only on the magnitude of the surface charge and the valence of the counterions. Some of the counterions will be located
on the Stern plane, the remainder are concentrated in the diffuse layer. Their concentration $n^+_* \, (# \text{ ions/unit volume})$ is therefore controlled by the thickness of the double layer.

At low salinities, i.e. low $n$, the diffuse outer layer predominates. Under these conditions, the effect of increasing $n$ on the thickness of the double layer can be reasonably predicted from the Guoy theory. Moreover, it has been suggested that, for practical purposes, the Stern potential can be assumed constant. The work by Winsauer and McCardell tends to support these assumptions.

As suggested by these authors, the excess of mobil cations in the system, as compared with their concentration in the equilibrating solution, can be approximately estimated from the net difference of positive and negative charges in the diffuse layer. This procedure should yield reasonable results since the double layer theories predict that anions occur roughly in the same amounts in both the EDL and the bulk solution. The difference between mobil positive and negative ions is then obtained from:

$$n^+_* = (n^+ - n^-) = \frac{\sigma_2}{(\text{ve})}$$  \hspace{1cm} (2.22)

as deduced from eq. (2.2).

By applying the condition of constant $\Phi_5$, then it follows from eq. (2.21) that the magnitude $\sigma_2$ at the "Stern charged surface" will increase with increasing salinity. Consequently, the excess of mobil counterions will also increase.

As with the Guoy theory, the Stern theory also predicts that the thickness of the diffuse layer decreases as the salinity increases. Moreover, the outer counterions are progressively transferred towards
the inner layer. This process continues until all the counterions are concentrated in the Stern layer. According to the Gouy theory, this condition is reached when the thickness of the double layer is equal to \( \delta \), when the salinity of the bulk solution attains a limiting value \( n_0 \).

When \( n_0 \) is reached, the diffuse layer disappears and the double layer system is reduced to one of constant surface charge \( \sigma \), that of the particle surface. Under these conditions, the excess of mobil cations attains a maximum concentration given by:

\[
(y_+^*) = \frac{S^+}{V_\delta}
\]  

where \( V_\delta \) is the volume of the Stern layer. This maximum possible concentration remains constant with further increase in bulk solution concentration.

The conductivity of the EDL at any salinity can be expressed as the product of the concentration and mobility of the excess cations. In analogy with electrolyte solutions, the double layer conductivity is represented as:

\[
C_{DL} = \lambda^+ n_+^*
\]

where \( \lambda^+ \) is the equivalent conductivity of the counterions. \( \lambda^+ \) is a measure of the effective mobility, as it takes into account ionic interaction effects. From basic electrochemistry theories for electrolytes, it would be reasonable to expect \( \lambda^+ \) to be a function of the type and concentration of the mobil counterions. However, the magnitude of \( C_{DL} \) must be ultimately controlled by the magnitude of \( n_+^* \). Because of the dependence of \( n_+^* \) on \( n \), the foregoing discussion suggests that a dependence of \( \lambda^+ \) on \( C_w \) might be expected.
In summary, the conductivity of the EDL should exhibit the following behavior:

1) For concentrations \( n < n_\delta \), \( C_{DL} \) should gradually increase as the concentration and thus the conductivity of the equilibrating solution, \( C_w \), increases.

2) For \( n \geq n_\delta \), \( C_{DL} \) should reach a maximum value which remains constant with further increase in \( C_w \).

It is evident, as pointed out by Winsauer and McCardell\(^{(8)}\), that any shaly sand conductivity model based on constant \( C_{DL} \), independent of \( C_w \), will provide erroneous representations of the conductive behavior of these formations.

In a porous material such as a shaly sand, the actual magnitude of the double layer conductivity may be affected by many other factors. One of them, for example, would be the existence of different tortuosity paths at the interface of the EDL and the bulk solution as proposed by Rink and Schopper\(^{(26)}\).

Both the equivalent counterion conductivity, and the quantification of other factors affecting the magnitude of \( C_{DL} \) may not be the subject of easy theoretical calculations. However, they could be determined through empirical correlations using accurate experimental data. Regardless, the theoretical predictions of the conductive nature of the EDL proposed in this section can be used as an aid to explain, and quantify, the effects of the presence of clay on the abnormal conductive behavior of shaly sands.
CHAPTER III
DOUBLE LAYER MODELS CURRENTLY IN USE

III.1 The Waxman-Smits Model

The limitations, discussed in Section I.5.a, of the model presented by Hill and Milburn\(^{(19)}\) led Waxman and Smits\(^{(27)}\) to propose a new conductivity model. According with the new model, a shaly sand behaves just as a clean one of the same porosity and tortuosity but saturated with a solution appearing to be more conductive than expected from its bulk concentration. The excess in conductivity is attributed to compensating cations concentrated in a diffuse layer around the clay particles. In that sense, the W-S model is analogous to that proposed by Winsauer and McCardell\(^{(8)}\). The W-S model consists of two resistance elements in parallel in which one of the elements is given by the conductance contribution of the exchange cations associated with the clay, the other being the contribution of the electrolyte saturating the pore space. In analogy with the work by Hill and Milburn\(^{(19)}\), the concentration of exchange cations (counterions) is expressed in terms of the parameter \(Q_v\) which represents the amount of fixed charges. As the parameter "b" in the early work, the counterion concentration per pore volume \(Q_v\) is also related to the cation exchange capacity of the rock. This dependency is given by:

\[
Q_v = \frac{\rho_c(1-\phi)CEC}{100\phi} \quad \text{(meq/cc)}
\]

where:

\(\rho_c\) = Average density of the dry clay-mineral mixture present in the formation, (gm/cc.)

\(\phi\) = Total rock porosity
CEC = Cation exchange capacity of th rock; (meq/100 gm. dry clay)

The conductance of a water saturated shaly sand is expressed as:

$$C_o = x C_C + y C_w$$

(3.2)

in which $C_C$ is the conductance associated with the exchange cations, and $x$ and $y$ are geometrical factors. Those geometrical factors are assumed equal and given by the Formation resistivity factor for shaly sands $F^*$. Therefore, eq. (3.2) results in:

$$C_o = \frac{1}{F^*} (C_C + C_w)$$

(3.3)

with the assumption that the tortuous path followed by the electric current is the same for both contributions. It is also assumed that $F^*$ is related to the total porosity by $m^*$, the cementation exponent for shaly sands.

Equation (3.3) is almost identical with the expression used by Winsauer and McCardell\(^{(8)}\) to show the change in double layer conductivity. It differs only in the definition of the formation factor. While refs. (8) and (19) used a formation factor for which clay effects are supposed at a minimum at high $C_w$, the term $F^*$ proposed by Waxman and Smits is taken as the inverse of the slope of the straight line portion of a $C_o - C_w$ plot; i.e., where clay effects are essentially constant.

a) **Counterion Conductance**

Perhaps the most important aspect of the W-S model is that the conductance contribution of the clay counterions can be evaluated if the concentration of fixed charges, $Q_v$, is known or can be estimated for a particular rock. The volume conductance of the
counterions is given in this model as the product of the volume counterion concentration \( Q_v \) times the equivalent counterion conductance \( B \). Thus, the general conductance model for shaly sands is written as:

\[
C_o = \frac{1}{F_A} (BQ_v + C_w) \text{ (mho/cm)}
\]  

(3.4)

where \( B \) is assumed a function of the counterion mobility and is expected to vary with the temperature. By applying eq. (3.4) on experimental data measured in samples exhibiting a wide range of \( Q_v \) values, the authors found that the equivalent conductance \( B \) changes with the conductivity of the equilibrating solution. An expression relating the averages of observed \( B \) to \( C_w \) was obtained at 25°C and is given by:

\[
B_{25} = 0.046[1-0.6 \exp (-C_w/0.013)] \text{ (mho-cm}^2\text{-meq}^{-1})
\]  

(3.5)

The constants in this equation were determined from data obtained by the authors. Eq. (3.5) reveals that the equivalent counterion conductance increases exponentially as \( C_w \) increases, eventually approaching a maximum constant value equal to:

\[
B_{\text{max}} = 0.046 \text{ (mho-cm}^2\text{-meq}^{-1})
\]  

(3.6)

at 25°C for the case of NaCl solutions used by the authors as the equilibrating brine.

It is interesting to notice that eq. (3.5) predicts that for different shaly rocks saturated with NaCl solutions of the same concentration, the equivalent conductance is the same for all rocks, independent of the counterion concentration \( Q_v \). General electorchemistry theory (25),(28) establishes that the equivalent conductance of an electrolyte solution depends on its
concentration. By assuming $B$ independent of $Q_v$, the W-S model treats the increase in bulk solution conductivity as a result of a mere increase in its effective ionic concentration.

The dependence of $B$ on $C_w$ found by the authors appears to be justified from the nature of the double layer conductivity, as proposed in the previous chapter. However, as already discussed, this dependence of $B$ on $C_w$ alone would be expected if there exists a solution of specific properties under the influence of the double layer. This solution could then be considered separately from the bulk solution.

b) Experimental Data

The validity of the results and conclusions drawn by Waxman and Smits are supported by the large amount and quality of the data used in the study. Besides including data previously utilized by Hill and Milburn (19), the study presents detailed conductance data obtained in 27 shaly sand cores saturated with NaCl brines of diverse concentration. These data, designated as Group II samples have become extremely valuable for further studies not only because of their quality, but because of the diversity in $Q_v$, porosity, type and distribution of clay, and range of $C_w$ used in the conductance measurements as well. Particular attention was paid to collect data at low salinities of equilibrating solution.

The conductance data available for Group II samples is reproduced in Table III.a. The table also includes pertinent information regarding measured values of $Q_v$ and porosity for each core.
<table>
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<th>Core No.</th>
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<th>Porosity (%)</th>
<th>Water Conductivity (m mho/cm)</th>
<th>Ref.</th>
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<td>3.88</td>
<td>2.97</td>
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</tr>
</tbody>
</table>
Cores exhibiting moderate to high $Q_v$ values contained fairly pure montmorillonite mainly surrounding the grains and interstitial. Cores with low to intermediate $Q_v$ contained kaolinite and illite occurring around the grains mainly in laminae. These different characteristics of the cores make eq. (3.6) even more important since it is apparent that the equivalent counterion conductance is independent of the type and distribution of clay in the pore space, which corroborates some previous observations made by Hill and Milburn(19).

c) **Relation Between the Resistivity Index and Hydrocarbon Saturation**

The W-S conductivity model was extended by Waxman and Thomas(29) to include the effect of variations in water saturation upon the conductivity of shaly sands. The application of the model for hydrocarbon bearing formations introduced two additional considerations. First, it is assumed that the counterion concentration increases in the pore water as $S_w$ decreases:

$$Q'_v = \frac{Q_v}{S_w}$$

(3.7)

$Q'_v$ is then the effective concentration of compensating cations at $S_w$ conditions. Secondly, it is considered that a reduction in $S_w$ does not exert any effect on the mobility of the counterions.

The saturation equation, as derived from eqs. (3.4) and (3.7) is then:

$$C_t = \frac{1}{G} \left( \frac{BQ_v}{S_w} + C_w \right)$$

(3.8)

where the parameter $G$ is related to $S_w$ and $F*$ by:
\[ \frac{1}{G} = \frac{S_w^{n^*}}{F^*} \] (3.9)

according to the relation established by Archie for clean rocks. The parameter \( n^* \) in eq. (3.9) is the saturation exponent for shaly sands in the W-S model.

The water content of a formation is commonly expressed as a function of the Resistivity index, \( I \), by:

\[ S_w^{-n} = \frac{R}{R_0} = I \]

The Resistivity index expressed through the W-S model, in practical units, is given by:

\[ I = S_w^{-n^*} = \frac{1 + R_w B_{Q_w}}{1 + R_w B_{Q_w} / S_w} \] (3.10)

Conductance measurements on twelve samples under different conditions of water saturation were performed by the authors\(^{(29)}\). \( S_w \) values between 40% and 100% of the pore space were attained. The measurements were conducted at room temperature under 1000 psig of effective stress.

The \( Q_v \) value for each core was determined from an analytical procedure previously proposed\(^{(27)}\). The intercept \( C_y \) of the straight-line portion of the \( C_o - C_w \) plot, for a water bearing shaly sand, is given by:

\[ C_y = \frac{B_{Q_v}}{F^*} \] (3.11)

from which \( Q_v \) can be easily evaluated.

For the analysis of the Resistivity index, Waxman and Thomas\(^{(29)}\) proposed a new expression for \( B \). Expressed in practical
units, \( B \) is given as the equivalent counterion conductivity at 25°C as:

\[
B_{25} = 3.83[1-0.83 \exp (-0.5/R_w)]; \text{ (lt-equiv}^{-1}\text{-ohm}^{-1}\text{-m}^{-1})
\]  

(3.12)

This new expression for \( B \) originated from a statistical comparison between \( Q_v \) values measured independently and the observed conductivity associated with the counterions, for the set of cores utilized by Hill and Milburn. Waxman and Thomas found that the \( Q_v \) values calculated from eq. (3.11) by the use of \( B_{max} = 3.83 \) from expression (3.12) agree, within experimental error, with those values determined from independent measurements for the samples used in their study.

The application for the \( W-S \) model under conditions of reduced water saturation confirmed the validity of eq. (3.7) and the assumption regarding the counterion mobility. It was also observed that the Resistivity Index is definitely affected by the presence of clay material and by the conductivity of the formation waters. The \( W-S \) model predicts greater hydrocarbon saturation values than those otherwise calculated from clean formation models. In general, \( I \) is more affected in formations of moderate to high \( Q_v \), containing brines of low concentration.

d) The Effect of Temperature on the Conductivity of Shaly Sands

The effect of temperature was analyzed by Waxman and Thomas (29) from conductance measurements carried out on 9 core samples. These measurements were conducted by saturating the cores with \( \text{NaCl} \) solutions of five different concentrations. The range of
temperatures selected varied from 22°C up to 200°C. In addition, the variation of equilibrating solution conductance with temperature was also experimentally determined by the authors.

The effect of temperature on the conductivity of shaly sands was treated by Waxman and Thomas in terms of the temperature coefficient of electrical conductivity, \( \alpha \), defined as \(^{29}\):

\[
\frac{C_T}{C_{22}} = (1 + \alpha)^{T-22}
\]

where \( C_T \) and \( C_{22} \) are the specific conductances of the system at temperature \( T \) and at a reference one of 22°C. The parameter \( \alpha \) represents the rate of increase in conductivity with increase in temperature \(^{29}\).

It was found for the analyzed samples that the magnitude of \( \alpha \) increases with \( Q_w \) for temperatures up to 120°C. The values of \( \alpha \) in shaly sands are within upper and lower values dictated by its magnitude in shales and electrolyte solutions respectively.

It was also observed that the apparent formation factor \( (F_a = C_w / C_o) \) decreases with increasing \( Q_w \) and temperature for a given \( C_w \). Such a behavior agrees with the variations of \( F_a \) at low salinities observed at room conditions. In addition, \( C_o - C_w \) plots for different temperatures are similar to those obtained at reference conditions (22°C-25°C). At low \( C_w \) values, sample conductivities increase sharply as the concentration of the equilibrating solution increases. For concentrations higher than 0.5m NaCl, \( C_o \) varies linearly with \( C_w \) at all the temperatures considered in the study. However, it was found that \( C_o \) measured at \( m = 0.26 \) NaCl fall near or at the limits of the curved portion of the conductivity plot.
F* values for individual cores were found essentially temperature independent.

The conductivity $C_o(T)$ of a water bearing shaly sand is expressed by the W-S model as a function of temperature as:

$$C_o(T) = \frac{1}{F^*} [B(T)Q_v + C_w(T)] \quad (3.14)$$

This expression predicts that the effect of temperature in shaly sands is accounted for by only the two temperature dependent parameters $B$ and $C_w$.

Experimental data was used by Waxman and Thomas to estimate the variation of the equivalent counterion conductivity $B(T)$ from the intercept $C_y$ for a given temperature. The appropriate $Q_v$ value for each core was also calculated from this method by using the data obtained at 22°C. The $Q_v$ thus determined was assumed independent of temperature.

Average $B(T)$ values were presented by the authors in a graphical form. For low concentrations, the average $B(T)$ values vary with $C_w$ analogously to their variation at room conditions.

An empirical expression relating $B(T)$ to $R_w$ and the temperature in °C has been credited to Juhász (30), (60) as:

$$B(T) = 1.28 + 0.225 T - 0.0004059 T^2$$

$$\quad \frac{1}{1 + (0.045T - 0.27)R_w^{1.23}} \quad (3.15)$$

The temperature dependence of the Resistivity Index is inferred from the W-S model by assuming that the saturation exponent $n^*$ is a temperature independent parameter. Although a small decrease of apparent saturation exponents was observed (29) for temperatures between 25°C and 80°C, the I vs. $S_w$ relation was
found to be practically independent of temperature, irrespective of the values of $Q_v$, $R_w$, and $n^*$. 

III.2 The Dual-Water Model

The Dual-Water model was first proposed by Clavier, Coates, and Dumanoir in 1977\(^{(33)}\). Since the paper was first presented in an SPE meeting, it has been considered one of the most controversial in recent well logging literature\(^{(34)}\). At the time this research work was initiated, many questions raised about the model had not been yet resolved. Also, the information about the D-W model was only available in pre-print form. A revised version of the concepts was finally approved for publication in 1984\(^{(35)}\). The exposé of the D-W model that follows includes material taken mainly from the final paper, ref. (35).

a) Theoretical Bases

Because of its simplicity and the amount of supporting experimental work, the W-S model has been widely accepted. However, there appeared to be some effects related to the adsorptive properties of the clays that had not been taken into account, namely the exclusion of salt from some fraction of the pore space, arising as a consequence of the presence of the double layer associated with the clay.

As the double layer is assumed to contain mainly the positive cations required to balance the negative charge on the clay surface, this diffuse layer can be considered as being a salt-free zone\(^{(33)}\),\(^{(35)}\) whose effects extend up to some distance from the clay surface. So, the pore space of a shaly sand is assumed to be filled with two kinds of waters: the "clay water" or solution
closely associated with the clay which is salt free but contains all the necessary counterions, and the solution beyond the influence of the double layer. This "far" water is assumed identical with the equilibrating solution. Each one of these two waters occupy a fraction of the available pore space designated as "clay water porosity" and "far water porosity" respectively. These fractional volumes depend on the counterion concentration $Q_v$ and the salinity of the equilibrating solution.

The D-W model, as with the W-S model, considers that the conductivity of the saturating fluid is complemented by the conductivity of the clay counterions. However, a basic step in the development of the model is taken when assigning both the far water and the clay water with specific conductive properties.

According to the D-W model, a shaly formation is characterized by its total porosity, $f_T$; its formation factor, $F_o$; its shaliness parameter, $Q_v$; and its bulk conductivity $C_T$ observed at total $S_w T$ conditions. The D-W model also considers that the formation behaves as a clean rock of the same porosity, tortuosity, and water saturation, but containing a water of effective conductivity, $C_{we}$.

In analogy with the Archie's relationship for clean rocks, the conductivity of a shaly sand is expressed as:

$$C_T = \left( \frac{C_{we}}{F_o} \right) S_{wT}^{n_o} \tag{3.16}$$

where $n_o$ is the saturation exponent in the D-W model.

The equivalent water conductivity $C_{we}$ saturating a shaly sand is taken as the contributions of the "clay" and "far" waters:

$$C_{we} = C_{cw} V_{cw} + C_{fw} V_{fw} \tag{3.17}$$
where \( C_{cw} \) and \( V_{cw} \) are the conductivity and volumetric fraction of the clay water. Likewise, \( C_w \) and \( V_{fw} \) represent the conductivity and volumetric fraction for the far water.

The model purports that the conductivity \( C_{cw} \) of the clay water surrounding the clay particles is independent of the type and amount of clay. \( C_{cw} \) is given only by the conductivity of the clay counterions. The fractional volume \( V_{cw} \) is proportional to the counterion concentration in terms of the total pore volume, \( Q_v \):

\[
V_{cw} = v_Q Q_v \phi_T
\]

where \( v_Q \) is the amount of clay water associated with 1 unit of clay counterions.

The conductivity \( C_w \) of the far water is assumed identical to that of the bulk-formation water. It occupies the remaining of the pore space:

\[
V_{fw} = V_w - V_{cw} = \phi_T (S_{WT} - v_Q Q_v)
\]

where \( V_w \) is the total water content.

The conductivity \( C_{we} \) is given by the combined volumetric averages expressed in terms of the total water content as:

\[
C_{we} = \frac{1}{S_{WT}} [v_Q Q_v C_{cw} + (S_{WT} - v_Q Q_v) C_w]
\]  

From eqs. (3.20) an (3.16), the basic expression for the D-W model results:

\[
C_t = \frac{S_{WT}}{F_0} \left[ C_w + \frac{v_Q Q_v}{S_{WT}} (C_{cw} - C_w) \right]
\]

which for the case of water saturated shaly sands is customarily written as:

\[
C_o = \frac{1}{F_0} \left[ (v_Q Q_v) C_{cw} + (1-v_Q Q_v) C_w \right]
\]  

(3.22)
The clay water is assumed to be that portion of the pore fluid under the influence of an electrical double layer. Such a double layer contains mainly all the positive ions (counterions) necessary to balance the internal negative charge of the clay particle. The distance up to which the diffuse layer is operative, i.e., the "thickness" of the EDL was given in the first publication of the D-W model in terms of the basic Guoy layer theory. In the final version, the expression for the "thickness" at 25°C is given by:

\[ X_d = 3.06 \sqrt{\frac{1}{n \gamma}} \text{ Å} \]  

(3.23)

where \( n \) is the molar concentration of the bulk water, and \( \gamma \) is the NaCl activity coefficient for the type of electrolyte solutions considered in the analysis. Eq. (3.23) differs from (2.14.b) only by the inclusion of the activity coefficients. It is proposed that a zone of salt exclusion exists up to \( X_d \), while for distances greater than \( X_d \), a zone of constant salt concentration is found. In addition, it is considered that, at the closest, the counterions are kept at some distance from the surface by adsorbed water molecules and hydration water surrounding the counterions. This situation is illustrated in Fig. (3.1). At the closest, the Na\(^+\) counterions are located with their centers lying in a plane called the Outer Helmoltz plane. The OHP is analogous in concept to the Stern plane in the Stern theory of the EDL. The OHP is located at a distance \( X_H \) from the surface. Assuming one layer of adsorbed water, and one layer of hydration water, Clavier et al. determined that the distance of closest approach \( X_H \) equals 6.18 Å for Na\(^+\) counterions at 25°C.
Figure 3.1 Distance of Closest Approach (Ref. 33)
Knowing \( X_H \), the concentration \( n_1 \) at which \( X_d \) equals \( X_H \) can also be determined from eq. (3.23). The limiting \( n_1 \) value was calculated by the authors to be equal to 0.35 mole NaCl/lt, also at 25°C. Therefore, for bulk concentration in excess of \( n_1 \), the zone of salt exclusion occupies a volume proportional to \( X_H \). For concentrations lower than \( n_1 \), the zone of salt exclusion expands up to \( X_d \) and its volume becomes salinity dependent. Clavier et al. proposed that in general:

\[
X_d = \alpha X_H
\]  

(3.24)

where the parameter \( \alpha \) represents the expansion of the diffuse double layer and is derived from the expression for \( X_d \) as:

\[
\alpha = \sqrt{\frac{n_1}{n}} ; \quad n < n_1
\]  

(3.25.a)

in the first paper. In the final version, \( \alpha \) takes the form:

\[
\alpha = [\frac{\gamma_1 n_1}{\gamma n}]^{\frac{1}{2}}
\]  

(3.25.b)

where \( n \) and \( \gamma \) are the bulk concentration and NaCl activity coefficient, respectively. The magnitude of \( \alpha \) is constant and equal to 1 for concentrations exceeding the limiting value \( n_1 \).

Clavier et al. calculated that the minimum amount of associated clay water is equal to:

\[
v_H^Q = 0.28 \text{ lt/equiv.}
\]  

(3.26)

for Na\(^+\) ions and the conditions assumed in the estimation of the distance of closest approach. In general, the volume of associated clay water is proposed by the authors as:

\[
V_{cw} = \alpha v_H^Q \phi_T = v_\Omega v_T
\]  

(3.27)

for any concentration \( n \) of the bulk solution.
The counterions are concentrated in the clay water in an amount equal to:

\[ Q_{cw} = \frac{Q \cdot \phi}{V_{cw}} \]  

(3.28)

If \( \beta \) is the equivalent counterion conductivity, the conductivity \( C_{cw} \) of the clay water is given from eqs. (3.28) and (3.27) as:

\[ C_{cw} = \frac{\beta}{\nu_{Q}} \]  

(3.29)

As evidenced from eq. (3.29), the conductivity of the clay water is independent of \( Q_{v} \) and type of clay (33), (35).

An important assumption in the D-W model is introduced in the analysis by assuming the equivalent counterion conductivity \( \beta \) as a constant. It is claimed by the authors that for the case of NaCl solutions, "\( \beta \) and \( C_{cw} \) are universal parameters that depend only on temperature" (Ref. 33), "and somewhat on salt concentration" (final version, Ref. 35).

Replacing the magnitude of \( C_{cw} \) in eq. (3.22), the conductivity of a water bearing shaly sand is given by the D-W model as:

\[ C_{o} = \frac{1}{F_{o}} \left[ \beta Q_{v} + (1 - \nu_{Q} Q_{v}) C_{w} \right] \]  

(3.30)

b) Comparison with the W-S Model

For the straight line portion of the \( C_{o} - C_{w} \) plot, the expansion factor is equal to 1 and \( \nu_{Q} = \nu_{Q}^{H} \). A comparison with the Formation factor \( F^{*} \) in the W-S model and the slope of the \( C_{o} - C_{w} \) plot as given by eq. (3.30) reveals that:

\[ F^{*} = \frac{F_{o}}{1 - \nu_{Q}^{H} Q_{v}} \]  

(3.31)
According to the D-W model, then, the slope of the conductivity plot is not independent of shaliness, but decreases as \( Q_v \) increases. Based on this, the authors concluded that \( F_0 \), instead of \( F^* \), is the parameter related to \( \phi_T \) where:

\[
F_0 = \phi_T^{-m_0}
\] (3.32)

The relationship in eq. (3.32) was supported by experimental data in two ways. A reduction in scattering was observed for a plot of formation factor vs. porosity, when compared with the same plot for \( F^* \) vs. \( \phi_T \). In addition, an apparent dependence of \( m^* \) on \( Q_v \) was minimized by the use of the cementation factor, \( m_o \).

Experimental data (Group I, Ref. 27) was used to estimate from the \( x \)-intercept of the conductivity plot:

\[
-C_x = \frac{\beta Q_v}{1 - v^H Q_v^H}
\] (3.33)

the approximate magnitudes of both \( \beta \) and \( v^H Q_v^H \). The estimates obtained from regression analysis at 25°C were:

\[
\beta = 2.05 \times (\frac{\text{mho}}{\text{m}})(\frac{\text{lt}}{\text{equiv.}})
\]

and

\[
v^H_Q = 0.30 \times (\text{lt/equiv.})
\]

c) Curvature of the \( C_o - C_w \) Plot

The curvature of the \( C_o \) line observed at low salinities is explained by the authors as a result of the expansion of the EDL\(^{(33)}\). Although the model follows the curvature down to \( C_w = 1 \) mho/m with reasonable accuracy, Clavier et al. recognized in their second publication\(^{(35)}\) that the equivalent counterion conductivity
might be affected by changes in the counterion mobility. A new expression for \( \beta \), valid for \( C_w < 1 \text{ mho/m} \) was proposed as:

\[
\beta_{\text{dil}} = \beta[1 - 0.4 \exp(-2 C_w)]
\]  

(3.34)

where \( \beta = 2.05 \) as determined from the previous regression analysis.

d) The Concept of the "Perfect Shale"

The parameter \( \nu^H_Q \) imposes a limit on the \( Q_v \) values to be expected in shaly sands:

\[
Q_v \leq \frac{1}{\nu^H_Q}
\]  

(3.35)

Clavier et al. stressed the fact that the counterion concentration \( Q_v \) in (3.35) refers to the effective concentration of mobil (conductive) counterions.

In their first publication, the authors defined the concept of the "Perfect Shale" as a formation for which the clay water occupy the entire pore space. The "perfect" shale should exhibit the maximum attainable \( Q_v \), given by:

\[
(Q_v)_{\text{SH}} = \frac{1}{\nu^H_Q} \quad \text{(equiv/lt)}
\]

This "perfect" shale must be therefore completely saturated by a fluid of conductivity \( C_{cw} = \beta/\nu^H_Q \).

e) The Effect of Temperature

Clavier et al. predicted the effect of temperature on the associated water fraction \( \nu_Q \). For salinities greater than \( n_1 \), it is assumed that temperature decreases the average residence time of the adsorbed water molecules, thus decreasing the thickness of the
water layer. It is therefore expected that $v_Q^H$ should decrease with temperature.

For salinities less than $n_1$, the variation of the double layer thickness is derived from the basic Guoy theory as:

$$\left( v_Q^H \right)_T = \left( v_Q^H \right)_{T_0} \left[ \frac{T}{T_0} \right]^{1/2} \quad (3.36)$$

Accordingly, the diffuse layer expands as temperature increases.

The same set of experimental data obtained by Waxman and Thomas for their study of the effect of temperature\(^{(29)}\) was used by Clavier and co-workers to establish the variation of $v_Q^H$ and $\beta$.

The expected reduction in $v_Q^H$ was qualitatively inferred from the available conductivity data. It was found that the slope of the $C_w - C_w$ plot changes with temperature. Moreover, it was determined that these changes increase with salinity. These observations agree with what could be expected from eq. (3.31) if both $F_Q$ and $Q_v$ are assumed temperature independent parameters.

Average $v_Q^H$ values were determined at each temperature. A relationship between both parameters is presented\(^{(35)}\) as:

$$v_Q^H(T) = 0.30 \left( \frac{295+25}{T_K+25} \right) = \frac{96}{T_K+25} \quad (3.37)$$

where $T_K$ is the absolute temperature in °K.

The variation of $\beta$ with temperature was obtained from the $X$-intercept values calculated for each core and each temperature. Values of $v_Q^H$ utilized in the calculations were determined from eq. (3.37). The average $\beta$ values are approximated\(^{(35)}\) by:

$$\beta(T) = 2.05 \left( \frac{T+8.5}{22+8.5} \right) = 0.067 (T+8.5) \quad (3.38)$$

where $T$ is given in °C.
The variation of the clay water conductivity with temperature is obtained by combining eqs. (3.38), (3.37), and (3.29) as:

\[ C_{cw} = 7.1 \times 10^{-4} (T+8.5)(T+298) \]  

(3.39)

The magnitude of \( v^H_Q \) at 22°C was calculated from conductivity data to be 0.27 (lt/equiv) which agrees very closely with the values obtained from chemistry and regression analysis.\(^{(33),(35)}\)

Values of \( v^H_Q \) and \( \beta \) were used to estimate the conductivity of selected cores at 200°C. The results were compared to experimental data and to those obtained from the W-S model. It was concluded that the D-W model yields better results than the W-S model.

Additional comparisons between the models were performed by Clavier et al.\(^{(35)}\) on the samples used by Waxman and Thomas in their saturation studies.\(^{(29)}\) It was again concluded that the D-W model exhibits lower variability and better fit than the W-S model.

f) The Saturation Exponents\(^{(35)}\)

The analysis of the saturation data\(^{(29)}\) was apparently restricted to the estimation of saturation exponents. It was determined that average \( \bar{n}_o \) values exhibit a lower variability than average saturation exponents derived from the W-S model.

The study on the saturation exponent led Clavier and co-workers to make an interesting observation. It was found that a definite correlation exists between \( \bar{n}_o \) and the cementation exponent \( \bar{m}_o \). However, there was no significant advantage in using \( \bar{n}_o = f(\bar{m}_o) \) instead of \( \bar{n}_o \).

Clavier et al. proposed\(^{(35)}\) that a better estimation of the productive nature of a shaly sand can be obtained from the
calculation of the fraction of the porosity filled by far water:

\[ S_w = \frac{S_{WT} - v_Q Q_V}{1 - v_Q Q_V} \quad (3.40) \]

where \( S_{WT} \) is the total water saturation, as determined from eq. (3.21) and which includes the volume of clay water.

III.3 Discussion

Once the fundamentals of each model have been presented it is apparent that both models are equivalent. They seem to differ mainly in the treatment given to the formation factor and the equivalent counterion conductivity. It is appropriate now to attempt a more detailed discussion of these parameters in order to identify whether either model offers a clear advantage, either practical or conceptual, over the other one.

When referring to the D-W model, special attention will be given to the concepts as proposed in the first publication (Ref. 33) which, as previously mentioned, was the only source of information available in 1982 at the time the present research work was initiated.

a) Equivalent Counterion Conductivity

The conductivity contribution due to the clay counterions is expressed in both models, according to general electrochemistry principles (25), (28), as the product of the counterion concentration times an equivalent conductivity:

\[ C_c = B Q_V \quad ; \quad \text{W-S model} \quad (3.41) \]

\[ C_c = \frac{B Q_V}{V_{cw}} = B \left( \frac{1}{\alpha v_Q H} \right) \quad ; \quad \text{D-W model} \quad (3.42) \]
Expression (3.42) follows directly from eq. (3.29). The term \( \frac{1}{\alpha v Q} \) represents the counterion concentration within the EDL as first proposed\(^{(33)}\).

The equivalent conductivity \( B \) in the W-S model is related to the counterion mobility and was found to be independent of \( Q_v \); its magnitude given by the concentration of the equilibrating solution and temperature. This dependence appears to be justified from the effect of the concentration, or conductivity, of that solution on the excess of positive ions in the double layer as proposed by Winsauer and McCardell\(^{(8)}\) and reiterated in Chapter III. Moreover, this dependency clearly implies the effect of a double layer, and suggests that a portion of the pore fluid may be analyzed as a specific entity with definite conductive properties.

The D-W model, as first published\(^{(33)}\), considers the equivalent counterion conductivity as a constant for a given temperature. In other words, \( \beta \) is assumed independent of both \( Q_v \) and \( C_w \).

The "dual water" concept allows the estimation of the actual concentration of counterions in the double layer \( \frac{1}{\alpha v Q} \) for any salinity of the equilibrating solution. This aspect constitutes a salient feature of the D-W model that apparently has been neglected. Basic electrochemistry theories\(^{(25),(28)}\) established that the equivalent conductivity of an electrolyte solution, or ionic species in an electrolyte, is related among other parameters to the ionic concentration. It seems somewhat logic to expect \( \beta \) to vary with the double layer concentration \( \frac{1}{\alpha v Q} \); in general, a dependency on \( C_w \) could be suspected due to the relationship between
the expansion factor $\alpha$ and the concentration of the equilibrating solution.

By $\beta$ being a constant, the work of Clavier et al. seems to imply that the clay water is not analogous to an electrolyte solution; however, there is evidence of the opposite. For example, Kern et al. (36) found that the variation of the clay conductivity term in the W-S model shows a dependence on temperature given by:

$$\frac{(C_c)_T}{T+22} = \text{constant} \quad (3.43)$$

which is of the form of relationship commonly used for NaCl solutions (5), (37):

$$\frac{(C_w)_T}{T+22} = \text{constant} = \frac{(C_w)_T}{T_r+22} \quad (3.44)$$

where $T_r$ is a reference temperature. The same analogy is obtained from the work of Clavier and co-workers by noticing that eq. (3.38), which gives the variation of $\beta$ with temperature, is surprisingly of the same form as (3.44).

Winsauer and McCardell (8) observed that the conductivity contribution of the clay was systematically higher for a core saturated with a NaCl solution than that obtained when a CaCl$_2$ solution was used. Conductivities of solutions of both salts follow the same trend for concentrations higher than about 5% by weight (38).

The variation in the double layer concentration, and the apparent analogy between the behavior of the clay water and that of an electrolyte solution suggests that assuming a constant equivalent counterion conductivity introduces a conceptual limitation in the theory of the D-W model.
b) **Formation Factor**

Waxman and Smits\(^{(33)}\) first defined \(F^*\), the formation factor of a shaly sand, as the inverse of the slope of the straight-line portion of the \(C_o - C_w\) plot. The W-S model uses a formation factor for which clay effects are constant. On the other hand, the D-W model proposed that the slope of the conductivity plot depends on \(Q_v\) and an idealized formation factor \(F_o\) as:

\[
\text{Slope} = \frac{1}{F^*} = \frac{1 - v}{F_o} \frac{H_Q}{Q_v} \tag{3.45}
\]

According to eq. (3.45), the slope of the \(C_o - C_w\) plot decreases with shaliness. An analogous effect was reported by Wyllie and Southwick\(^{(9)}\) while working with artificial cores made up of glass spheres and spheres of a cation-exchanger resin. These authors observed that the slope of a \(C_o - C_w\) for these artificial dirty sands decreased as the percentage of exchanger resin in the core increases.

Evidence of the possible dependence of \(F^*\) on \(Q_v\) can be inferred from the work of Kern\(^{(36)}\) and co-workers on the effect of temperature on the conductivity of shaly sands through the application of the W-S model.

As explained by these authors, when the conductivity of a saline solution is plotted as a function of temperature, a straight line is obtained whose slope depends on the concentration of the solution. The \(x\)-intercept, i.e., the temperature at which the conductivity is zero becomes an isoconductivity point since it is the same for apparently all concentrations. The authors found that the conductivity of a clean formation follows the same exact
behavior; the slopes of the lines in a $C_0$ vs. $T$ plot are given by the conductivity of the saturating solution. Moreover, the isoconductivity point (at zero rock conductivity) occurs for the analyzed concentrations at the same temperature than for the saline solutions (-22°C for NaCl). On the other hand, when the procedure is applied in a shaly core, the isoconductivity point deviates from that for the clean sample by an amount $\Delta_t$ defined as the Temperature shift. From their experimental data, the authors found a strong correlation between the clay conductivity at room temperature and this temperature shift. The obtained relationship is given by:

$$\Delta_t = 3.0 \ C_c @ 23^\circ C$$ (3.46)

The salinities of the NaCl solutions used in the study correspond to the range at which the straight line portion of the Co-Cw plot is normally observed, so that the term $C_c$ can be safely assumed to reach a maximum and constant value. From the maximum B value determined for Group II samples, the value of the temperature shift can be expressed from eq. (4.46) as a function of $Q_v$:

$$\Delta_t = 13.2 \ Q_v @ 23^\circ C$$ (3.47)

As in the work of Waxman and Thomas, the variation of the conductivity of the clay, like for the equilibrating solution, was found to be independent of $Q_v$ as temperature was increased.

The magnitude of $F^*$ was observed to vary with temperature. The temperature dependence increases with increasing $\Delta_t$, i.e., with increasing shaliness. This effect is in contradiction with the conclusions reached by Waxman and Thomas about $F^*$. 
Kern and co-workers concluded that:

\[ F* \left( \frac{T+22-A_t}{T+22} \right) = \text{constant} \quad (3.48) \]

Replacing eq. (3.47) in (3.48) results in:

\[ F* = \frac{A}{(1-0.293Q_v)} \quad (3.49) \]

Waxman and Smits proposed that for \( Q_v = 0 \) then \( F* \) equals the Formation factor of an equivalent clean sand. Using the definition of \( F_o \) in the D-W model as equal to the constant \( A \), eq. (3.49) becomes:

\[ F* = \frac{F_o}{(1-0.293Q_v)} @ 23^\circ C \quad (3.50) \]

which is essentially identical to the expression derived by Clavier et al. (33), (35), eq. (3.31), with \( v_Q^H = 0.30 \) (lt/eqiv) at 25°C.

From the preceding discussion it is apparent that the D-W model allows for a more comprehensive definition of the Formation factor. However, \( F_o \) in this model is presented as an "idealized" parameter whose magnitude can not be determined without the previous knowledge of \( Q_v \).

c) Properties of the "Perfect Shale"

The D-W model allows for the definition of a "perfect shale", as discussed in Section III.2.d, which according to the model (33) exhibits a maximum \( (Q_v)_{sh} \) equal to \( 1/(v_Q^H)^T \) at a temperature \( T \).

It is assumed that this perfect shale contains no far water, therefore \( (1-v_Q^H)_{Q_v} = 0 \). From the D-W model, the conductivity of such a formation is deduced from eq. (3.30):
\( (C_0)_{sh} = \frac{\beta Q_v}{F} \)  \( (3.51) \)

is a constant for a given temperature.

From the W-S model, on the other hand, Smits\(^{(39)}\) deduced that the theoretical \(Q_v\) for the perfect shale should approach infinity. From a practical standpoint, Smits proposed that shales exhibiting \(Q_v \geq 10\) equiv/lt should behave as perfect ones. This limit for \(Q_v\) has been questioned by Clavier et al.\(^{(33)}\)

The application of the W-S model to predict the conductivity of the perfect shale produces an interesting result, if one applies the relationship between \(F^*\) and the slope of the \(C_o-C_w\) plot as proposed in the D-W model. Since \(\nu^H(Q_v)_{sh} = 1\) for the perfect shale, then its conductivity would be zero for any temperature. This is, of course, physically impossible.

d) Curvature of the \(C_o-C_w\) Plot

The curvature of the conductivity plot is explained\(^{(33)}\) in the D-W model solely on the basis of the expansion of the EDL. Under those circumstances, the conductivity of a water bearing shaly sand at low salinities, as calculated from eq. (3.30), is expected to approach a minimum value. If an unlimited expansion of the EDL layer is allowed, then:

\[
\lim_{Q_v \rightarrow 1} C_o = \frac{\beta Q_v}{F} = C_y
\]

\( (3.52) \)

Predicted conductivities will therefore "level-off" at a value proportional to \(Q_v\). In some cases, the calculated \(C_o\) values will not follow the experimental data. This situation is easily
observed from Figs. 15 and 16 in Ref. 33. It is reasonable to expect this condition at high $Q_v$ values. At any rate, Clavier and co-workers must undoubtedly have realized this situation and in their final version of the D-W model\(^{(35)}\) introduced a variable $\beta$ for $C_w < 1$ mho/m as given in eq. (3.34).

Because eqs. (3.5) and (3.12) were obtained from numerous data pertaining to the curved portion of the conductivity plot, the W-S model is expected to provide with an adequate representation of both the linear and non-linear zones of the $C_o-C_w$ plot.
CHAPTER IV

ESTABLISHMENT OF A NEW SHALY SAND CONDUCTIVITY MODEL BASED ON VARIABLE EQUIVALENT COUNTERION CONDUCTIVITY AND DUAL WATER CONCEPTS

From the preceding discussion in Section III.3 it is apparent that the two theoretical conductivity models currently used for shaly sand interpretation are marred with shortcomings. On the other hand, they also have made important contributions to advance the state of understanding of the shaly sand problem. In this regard, it is evident that there is still plenty of room for improvement.

The problems associated with the establishment of a model for shaly sands are certainly too many. The model itself must be based on theoretical argumentation of phenomena and mechanisms still not fully understood; moreover, corroboration of the theory may be seriously handicapped by the uncertainties introduced by some of the parameters. Up to this date, only $Q_v$ and $C_w$ can be measured independently; however, the conductivity of the equilibrating solution is the only variable that can be accurately determined.

A model should be conceptually sound as to be applied under a variety of conditions; yet it must be simple enough to insure its practical use. Although the use of few variables should be advisable, simplicity may not be traded for accuracy, especially when the resulting model may not agree with the physical reality(17). Finally, the model should yield better accuracy than the existing ones.

A new theoretical model for shaly sand conductivity has been developed. The model meets the above mentioned criteria.
The new model is based on the far and bound waters concept but differs fundamentally from the Dual water model. In this model, contrary to the Dual water model, the equivalent counter-ion conductivity changes as the diffuse double layer expands and is therefore a function of temperature and the conductivity of the far water. This concept of variable equivalent counter-ion conductivity is a fundamental premise of the Waxman and Smits Model. The formation resistivity factor included in this model is independent of $Q_v$.

A method to calculate the equivalent counter-ion conductivity was devised. The method is based on treating the double layer region as an equivalent electrolyte, the properties of which are derived from basic electrochemical theory.

As with the work of Waxman et al., and Clavier et al., this study considers only NaCl solutions as the equilibrating electrolyte.

IV.1 The New Conductivity Model. Water Bearing Shaly Sands

It is assumed that the conductive behavior of a shaly sand can be equated to that of a clean sand of the same porosity containing a water of effective conductivity $C_{we}$ \(^{(33),(35)}\). $C_{we}$ is the sum of the effective contributions of the solution under the influence of the diffuse double layer ($C_{wDL}^\epsilon$) and the free equilibrating solution \(^{(33),(35)}\), ($C_{wES}^\epsilon$):

$$C_{we} = (C_{wDL}^\epsilon) + (C_{wES}^\epsilon)$$

(4.1)

Each of the terms on the right is given by the conductivity of the solution corrected by the fraction of the volume it occupies. $C_{we}$ can then be expressed as:

$$C_{we} = (\lambda n^+)_{DL} \cdot f_{DL} + (\lambda n)_{ES} \cdot f_{ES}$$

(4.2)
where:

\( \lambda^+ \) = Equivalent conductivity for the counter-ions in the double layer solution

\( n^+ \) = Counterion concentration within the double layer

\( \Lambda \) = Equivalent conductivity of the equilibrating solution

\( n \) = Ionic concentration in the equilibrating solution

\( f_{DL}, f_{ES} \) = Fractional volumes being occupied by the double layer solution and equilibrating solution, expressed as fractions of the total porosity such as:

\[ f_{DL} + f_{ES} = 1.0 \]  \hspace{1cm} (4.3)

The counter-ion concentration required to balance the excess of charge on the clay surface is a function of the cation exchange capacity of the rock, and it is customarily expressed in terms of the total pore volume by the quantity \( Q_v \). The fractional volume occupied by the two solutions in the pore space is controlled by the expansion of the double layer which in turn depends on the salinity of the equilibrating solution.

The ionic concentration of the solution within the influence of the double layer can be expressed as:

\[ n^+ = \frac{Q_v}{f_{DL}} \]  \hspace{1cm} (4.4)

for any stage of expansion of the double layer. The electrical properties of the equilibrating solution are assumed equal to those in the bulk solution utilized to saturate the rock. Therefore:

\[ (An)_{ES} = C_w \]  \hspace{1cm} (4.5)

Substituting values from equations (4.3), (4.4), and (4.5) in (4.2) results in:
The shaly sand conductivity is proposed in analogy with the equivalent expression for clean formation as:

\[ C_0 = \frac{1}{F_e} \left[ \lambda^+ n^+_{DL} + (1-f_{DL})C_w \right] \]  \hspace{1cm} (4.7)

Where \( F_e \) is the formation factor of an equivalent clean formation of the same total porosity, \( \phi_T \), that can be expressed as:

\[ F_e = \phi_T^{-m_e} \]  \hspace{1cm} (4.8)

where \( m_e \) is an appropriate cementation exponent.

It should be emphasized that \( f_{DL} \) varies with the salinity of the equilibrating solution. Variations in \( f_{DL} \) result in variations of \( n^+ \) and \( \lambda^+ \).

The model given by equation (4.7) describes the typical \( C_0 \) vs. \( C_w \) curve shown by figure 4.1. Since \( F_e \) and \( Q_v \) are independent of salinity, it can be safely assumed that the remaining parameters of expression (4.7) are essentially constants over the linear portion of the \( C_0 - C_w \) plot. At high salinity, it is then expected for the apparent equivalent counter-ion conductivity to reach a limiting maximum value, \( \lambda^+_{\text{max}} \), and for the double layer fractional volume to reach a limiting minimum value \( f_{\text{min}} \).

The equation of the straight line segment is:

\[ C_0 = \frac{1}{F_e} \left[ \lambda^+_{\text{max}} n^+_{\text{min}} + (1-f_{\text{min}})C_w \right] \]  \hspace{1cm} (4.9)

and exhibits a slope \( S* \) and y and x intercepts defined by:

\[ S* = \frac{1-f_{\text{min}}}{F_e} \]  \hspace{1cm} (4.10)

\[ C_y = \frac{1}{F_e} \left( \lambda^+_{\text{max}} n^+_{\text{min}} \right) \]  \hspace{1cm} (4.11)
Fig. 4.1 Typical $C_o - C_w$ curve for shaly sand showing the concept of "Neutral Point".
\[-C_x = \lambda^+_{\text{max}} n^+ \left( \frac{f_{\text{min}}}{1-f_{\text{min}}} \right) \quad (4.12)\]

a) **Nature of the Formation Factor, \( F_e \)**

One of the premises of the proposed model is that the shaly sand behavior mimics that of a clean sand. Then \( F_e \) can be expressed as in the case of clean sand as:

\[
F_e = \frac{C_{\text{we}}}{C_0} \quad (4.13)
\]

For the parameter \( F_e \) to be equal to \( F \) in an equivalent clean formation it is necessary for the shaly sand to behave as a clean one for a particular \( C_w \). In other words, \( F_e = F \) if and only if there exists a \( C_w \) value such that \( C_w = C_{\text{we}} \).

The formation water conductivity \( C_{\text{WN}} \) of the equivalent clean sand having a formation factor \( F \) equal to \( F_e \) can be derived from equation (4.9). \( C_{\text{WN}} \) which is referred to as the "Neutral point" is given by:

\[
C_{\text{WN}} = \lambda^+_{\text{max}} n^+ = \lambda^+_{\text{max}} \frac{Q_v}{f_{\text{min}}} \quad (4.14)
\]

When the apparent equivalent counter-ion conductivity is at a maximum and the double layer fractional volume is at a minimum. Replacing (4.14) in (4.9) yields:

\[
C_{\text{ON}} = \frac{1}{F_e} (C_{\text{WN}}) \quad (4.15)
\]

So independently of the fractional volumes occupied by the double layer and free solutions, the shaly sand behaves as a clean one, of the same porosity and tortuosity, whose pores are saturated by only one homogeneous solution of conductivity \( C_{\text{WN}} \). This Neutral point given by \( C_{\text{WN}} \) is analogous to the equiconductance point in the
theory of ion exchangers \(^{(40)}\), and can be determined from equation (4.14) if the limiting values \(\lambda^+_{\text{max}}\) and \(f_{\text{min}}\) are known or can be estimated. \(F_e\) is then defined as the apparent formation factor observed when \(C_w = C_{wN}\) and can be easily calculated from the equation (4.9) of the straight line portion of the \(C_o - C_w\) curve.

It follows that the slope of the straight line given by equation (4.10) varies with shaliness. For clean sand of the same porosity and tortuosity the slope reaches a maximum value equal to \(1/F_e\). As shown on figure 4.1 the clean sand line intercepts the shaly sand curve at the neutral point where \(C_w = C_{we} = C_{wN}\).

The concept of the neutral point makes it possible to relate the shaly formation conductivity to that of a clean sand by a mere selection of the conductivity of the fluid saturating the clean rock. Figure 4.1 shows that a shaly sand saturated with a solution of conductivity \(C_{w1}\) exhibit the same conductivity as a clean sand of the same porosity and tortuosity containing a fluid of conductivity \(C_{w2}\). Likewise, for an equilibrating solution conductivity \(C_{w3}\), the shaly sand is analogous, conductivity wise, to the clean sand when saturated with a solution of conductivity \(C_{w4}\). Since \(C_w\) and \(C_{we}\) are related by equation (4.6), if \(F_e\) is known the conductivity profile for the shaly sand can be entirely defined.

b) **Volumetric Fraction Under the Influence of the Double Layer**

The use of the model presented in equation (4.7) requires the estimation of the fractional volume under the influence of the double layer. This fractional volume is related to the distance
from the clay surface up to which the double layer is operative, which is referred to as the "thickness" of the double layer.

The thickness, $X_d$, of a flat double layer has been derived from the Guoy theory and is given by eq. (2.12):

$$X_d = \frac{1}{\kappa}; \quad X_d \geq X_H$$

where $X_H$ is the distance of closest approach (33),(35).

The "characteristic length", as given by eq. (2.14.a) requires (23) the electrolyte concentration to be given in units of # ions/cm$^3$.

The local ion concentration $n$ can be expressed as:

$$n = N \times 10^{-3} \times \text{Avogadro's Number}$$

$$n = N \times 6.02 \times 10^{20}; \text{(ions/cm}^3) \quad (4.16)$$

Where $N$ is the electrolyte concentration of the equilibrating solution in normality units.

Replacing (4.16) in (2.7):

$$\kappa = \left[ \frac{8\pi e^2 V^2 (6.02 \times 10^{20})}{Dk T} \right]^{\frac{1}{2}} \sqrt{N} \quad (4.17)$$

For 1-1 electrolytes such as NaCl solutions, the normality of the solution equals its molarity and $v=1$.

If the magnitudes of both the elementary charge and Boltzmann's constant (23):

$$e = 4.8 \times 10^{10} \text{ (esu)}, \text{ and}$$

$$k = 1.3803 \times 10^{16} \text{ (erg}^{-1}\text{-deg}^{-1})$$

are replaced in (4.17):

$$\kappa = \frac{50.29}{(eT)^2} \sqrt{n} = Bo \sqrt{n} \quad (4.18)$$
Where \( n \) is the concentration of the electrolyte in molar units and \( B_0 \) is known as the coefficient of ion-size term in the Debye-Hückel theory\(^{25},(28)\). Using published data\(^{25}\), \( B_0 \) is empirically related to temperature by the following polynomial:

\[
B_0 = 0.3248 + 1.5108 \times 10^{-4} \ (T) + 8.9354 \times 10^{-7} \ (T^2) \\
15 \leq T \leq 100^\circ C \quad (4.19)
\]

Finally from (2.14.b) and (4.18), the thickness of a single flat double layer can be calculated from:

\[
\frac{1}{B_0 \sqrt{n}} \ ; \ X_d = X_H' \\
(4.20)
\]

The minimum concentration \( n_{\text{lim}} \) at which \( X_d = X_H \) is:

\[
n_{\text{lim}} = \left(\frac{1}{X_H B_0}\right)^2 \\
(4.21)
\]

So that for any concentration \( n > n_{\text{lim}} \), the thickness of the double layer remains at a minimum and constant value \( X_H \). At any concentration \( n < n_{\text{lim}} \), the thickness of the double layer can be expressed relative to the thickness \( X_H \) as:

\[
\alpha = \frac{X_d}{X_H} = \sqrt{n_{\text{lim}}/n} \\
(4.22)
\]

where \( \alpha \) is known as the double layer expansion factor\(^{33}\).

Based on experimental work by Hill, Shirley, and Klein, Juhász\(^{41}\) expressed the effective porosity occupied by free water, \( \phi_e \), as:

\[
\phi_e = \phi_T \ [1-(\frac{0.084}{C_w} + 0.22)O_v] \\
(4.23)
\]

The fractional volume, or fractional porosity, under the influence of the double layer can in turn be expressed from (4.23) as:
\[ f_{DL} = 1 - \frac{\phi_e}{\phi_T} = (\frac{0.084}{C_W} + 0.22)Q_v \] (4.24)

At 25°C, equation (4.19) yields \( B_0 = 0.3291 \) which when substituted in eq. (4.20) gives:
\[ X_d = 3.039n^{-\frac{1}{2}} \] (4.25)

The thickness \( X_H \) when assuming one layer of absorbed water and one layer of hydration water around \( \text{Na}^+ \) cations was determined by Clavier et al. \(^{(33),(35)}\) to be 6.18Å. Using this value in equation (4.21) results in:
\[ n_{lim} = 0.242 \text{ mole}/\text{lt} @ 25°C \] (4.26)
which corresponds approximately to 14 gm/lt NaCl.

Equation (4.24) predicts that the value of \( f_{DL} \) changes with salinity even for \( n>n_{lim} \). In a range of salinity of .242 to 5.416 molar NaCl for which \( \alpha \) is assumed equal to one \( f_{DL} \) varies between .274\( Q_v \) and .24\( Q_v \). Since the change is minimal and since conductivity data exhibit essentially perfect linearity, \( f_{\text{min}} \) will be considered constant expressed by the relationship derived theoretically by Clavier et al. \(^{(33),(35)}\):
\[ f_{\text{min}} = 0.28Q_v \] (4.25)
In general:
\[ f_{DL} = 0.28\alpha Q_v @ 25°C \] (4.26)

c) Determination of Equivalent Counter-ion Conductivities

The basic principle underlying the calculation of apparent counter-ion conductivities is the premise that hydrated ion exchangers can be considered electrolyte solutions for which the negative ions are fixed \(^{(40)}\). Presumably, the conductive properties
of these ion exchangers can be related to the properties of an equivalent electrolyte.

Clays in the water saturated pores of a shaly sand can be considered as ion exchangers. Moreover, it is assumed that the "solution" within the double layer contains equal number of positive counter-ions and negative fixed charges. For the case of a NaCl equilibrating solution, the fluid within the double layer can be considered a 1-1 electrolyte for which the negative ions are immobile, or more specifically, as a 1-0 electrolyte whose conductive properties may be related to those of a regular 1-1 electrolyte similar in nature to the equilibrating solution, i.e. same solute.

From electrochemistry theory for 1-1 electrolytes, the equivalent conductivity $\Lambda$ which is proportional to the total current in the system can be expressed as (25):

$$\Lambda = \Lambda^0 - \frac{B_2 \sqrt{n}}{1 + B_0 \tilde{a} \sqrt{n}}$$  \hspace{1cm} (4.27)

where:

$\Lambda^0$ = Eq. conductivity at infinite dilution

$B_0$ = Coefficient of ion-size in the Debye-Huckel theory of strong electrolytes

$B_2$ = Coefficient of the electrophoretic term in the theory of conductivity

$n$ = molar concentration

$\tilde{a}$ = equivalent ion size
Likewise, the current carried by the $i$-ionic species in an electrolyte solution is proportional to (25):

$$\lambda = t_A$$  \hspace{1cm} (4.28)

where $\lambda$ and $t_A$ are the equivalent conductivity and transference number of the $i$-ionic species.

Let the fluid within the double layer be a hypothetical 1-1 electrolyte of molar concentration $n = n_1$. Since the counter-ions are the only ions responsible for transporting current, the cation transference number is unity and:

$$\lambda^+ = \Lambda$$  \hspace{1cm} (4.29)

Using expression (4.27):

$$\lambda^+ = \Lambda^o - \frac{B_2 \sqrt{n_1}}{1 + B_2 \frac{\Lambda^o}{\Lambda}}$$  \hspace{1cm} (4.30)

This expression should provide with an approximation of the actual equivalent counter-ion conductivity for an effective concentration $n_1$; unfortunately, both the equivalent conductivity at infinite dilution, $\Lambda^o$, and the equivalent ion size $\Lambda_1$ are unknowns for the hypothetical solution. The equivalent conductivity should be corrected for viscosity effects which are also unknown for the double layer fluid. The concept of an equivalent electrolyte is introduced to overcome this problem. Let an equivalent NaCl solution of concentration $n_{eq}$, whose equivalent conductivity is proportional to the total current in the system and is given by:

$$\Lambda_{NaCl} = \Lambda_{NaCl} - \frac{B_2 \sqrt{n_{eq}}}{1 + B_2 \frac{\Lambda_{NaCl}}{\Lambda}}$$  \hspace{1cm} (4.31)

where $\Lambda_2 = 5.2$ Å is the equivalent ion size for a NaCl solution as used in the transport equation (25). It follows that:
From (4.30) and (4.31):

\[
\Lambda^0 - \frac{B_{2}^{0}\gamma_{1}}{1+B_{0}^{2}\gamma_{1}\gamma_{2}^0\gamma_{1}^0} = \Lambda^0 \text{NaCl} \quad \frac{B_{2}^{0}\gamma_{1}}{1+B_{0}^{2}\gamma_{1}\gamma_{2}^0\gamma_{1}^0} (4.33)
\]

At infinite dilution conditions for which \( n_{1} \to 0 \) it is considered that:

\[
\lim_{n_{1} \to 0} \Lambda = \Lambda^0 = \lim_{n_{eq} \to 0} \Lambda^0 \text{NaCl} = \Lambda^0 \text{NaCl} (4.34)
\]

Then eq. (4.33) reduces to:

\[
n_{eq} = \frac{n_{1}}{[1-B_{0}^{2}(8_{2}^{0}-8_{1}^{0})\gamma_{n_{1}}]^{2}} (4.35)
\]

From eqs. (4.4) and (4.26), the ionic concentration \( n_{1} \) is given by:

\[
n_{1} = n_{=} = \frac{Q_{v}}{F_{DL} \alpha} = \frac{3.571}{\alpha} \text{ mole/lt} (4.36)
\]

The concentration of the equivalent electrolyte is then a function of the equilibrating solution concentration and temperature, and is independent of the counter-ion concentration \( Q_{v} \). When the double layer reaches its minimum thickness, the counter-ions are assumed concentrated in the inner layer under crowded conditions analogous to those experienced by the ions in a saturated solution. The maximum counter-ion concentration at \( \alpha = 1 \) is given by eq. (4.36) for any \( Q_{v} \) as 3.571 mole/lt. Likewise, the maximum concentration for a NaCl solution under saturating conditions is equal to 5.416 mole/lt. Replacing these two values in (4.35) and rearranging:

\[
B_{0}^{2}(8_{2}^{0}-8_{1}^{0}) = 9.95 \times 10^{-2}; \text{ (lt/mole)}^{\frac{1}{2}} (4.37)
\]

The equivalent conductivity \( \Lambda^{+} \text{NaCl} \) as a function of the equivalent concentration \( n_{eq} \) can be obtained at 25°C from:

\[
\lambda^{+} = \Lambda^{0} \text{NaCl} (4.32)
\]
\[ \Lambda'_{\text{NaCl}} = \Lambda/F(n_{eq}); \text{(mho/m) (lt/mole)} \]  \hspace{1cm} (4.38)

where:
\[ \Lambda = \frac{12.645 + 7.6725/n_{eq}}{1 + 1.3164/n_{eq}} \]  \hspace{1cm} (4.39)

and
\[ F(n_{eq}) = \begin{cases} 1.0 & ; n_{eq} \leq 0.5 \text{ mole/lt} \\ 1 + 3.83 \times 10^{-2}(n_{eq} - 0.5) + 1.761 \times 10^{-2}(n_{eq} - 0.5)^2 & ; n_{eq} > 0.5 \text{ mole/lt} \end{cases} \]  \hspace{1cm} (4.40)

where \( F(n_{eq}) \) is a correction factor that was empirically determined from experimental data. It corrects (4.39) for effects associated with high salinities such as the increase in electrolyte viscosity. At \( \alpha = 1 \), using eqs. (4.32), (4.36), and (4.35), and (4.37) through (4.40) for the equivalent NaCl solution results in:
\[ \lambda^+_{\text{max}} = 4.65 \text{ (mho/m)(lt/mole)} \]  \hspace{1cm} (4.41)

This value closely agrees with the maximum \( B \) value obtained by Waxman and Smits from their Group II samples. It will be retained in this study.

The above discussion is valid for \( \alpha = 1 \) where the concentration \( n_1 \) remains constant and the solution within the double layer occupies a minimum reference volume proportional to \( f_{\text{min}} \). As the double layer expands \( n_1 \) decreases and the volume increases. The result should be a net decrease in equivalent conductivity. Eq. (4.30) fails to predict that behavior because it does not take into account the geometry of the system. For a changing geometry which is the case for \( \alpha > 1 \), equation (4.32) should be modified to include
a geometrical correction factor \( f_g \). Consequently it should be written as:

\[
\lambda^+ = \frac{A}{f_g F(n_{eq})} = \frac{A_{NaCl}}{f_g} \tag{4.42}
\]

The correction factor \( f_g \) is to be derived empirically. It should assume a value of 1 at \( \alpha=1 \) and should be expressed in terms of geometric parameters controlling the double layer. Since \( f_g \) is to be determined from actual conductivity measurements, it is expected to include several effects such as the increased concentration of mobil anions in the diffuse layer as it expands as well as actual conditions affecting the ionic mobility. In that sense, the effect of \( f_g \) is analogous to that of the tortuosity term \( (1/\lambda^2) \) found by Rink and Schopper to be an integral part of the conductance associated with clay.

IV.2 Application of the New Model

a) Calculation of Basic Parameters

The test of the model requires detailed conductivity measurements in shaly sands. The data presented by Waxman and Smits for their Group II samples are specially suited for this purpose since detailed information regarding the conductive behavior of shaly sands for a wide range of \( Q_v \) values and salinities is available. This data is listed in Table III.a.

The proper use of the model for the estimation of apparent counter-ion conductivities requires the determination of the formation factor, \( F_e \), and the effective \( Q_v \) for each core. After
having determined the magnitude of $\lambda_{\text{max}}^+$, it is now possible to specify the neutral point $C_{\text{wN}}$. From equations (4.14) and (4.25):

$$C_{\text{wN}} = \frac{4.65 Q_v}{0.28Q_v} = 16.61 \text{ mho/m}$$  \hspace{1cm} (4.43)

Least squares was applied on the conductivity data. A linear equation for $C_o$ as a function of $C_w$ was obtained from each one of the 27 cores, considering $C_w$ values equal or greater than 2.82 mho/m. The correlation coefficient in each case was essentially a perfect 1.0.

The core conductivity at $C_{\text{wN}}$ was evaluated for each core from the appropriate regression line. The values for the formation factors were calculated using eq. (4.15). From the calculated formation factors and the porosity data, the cementation exponent for each core, $m_e$, was calculated. The calculated values of $F_e$ and $m_e$ are presented in Table XV.a.

The proper estimation of apparent equivalent counter-ion conductivities requires the use of the most representative value of $Q_v$. The $Q_v$ data presented in Ref. 27 for Group II samples were not used in this study for two reasons. First, the value assigned for each sample was not actually measured in the particular core. The data from Table 6 in ref. 27 shows that there is considerable variation in the $Q_v$ values measured on samples taken from adjacent pieces of the same rock. Second, it is recognized that the method utilized for CEC determinations influences considerably the results. Moreover, the effect of grinding on the CEC values depends also on the type of clay present in the sample.
For this study, it was judged that the most representative value of $Q_v$ for each core is the value calculated from $F_e$ and the slope of the regression line. From eqs. (4.10) and (4.25):

$$f_{\text{min}} = 1 - S \cdot F_e$$

Therefore:

$$Q_v = \frac{1 - S \cdot F_e}{0.28}$$  \tag{4.45}

The $Q_v$ values calculated from (4.45) are compared with the ones assigned by Waxman and Smits\(^\text{(27)}\) in Table IV.b.

The model of equation (4.7), together with the previously determined values for $F_e$ and $Q_v$ was applied on conductivity data at low salinities to estimate the apparent equivalent counter-ion conductivities. Five cores exhibiting a wide range of $Q_v$ were selected from Group II samples in order to investigate the possible effect of this parameter. The results of the calculations are shown in fig. 4.2 in which the apparent $\lambda^+$ values are plotted against the expansion factor $\alpha$ as a function of $Q_v$ for each core. It is evident that a well defined correlation exists between $\lambda^+$ and $\alpha$ for each value of $Q_v$, suggesting a strong dependency on the stage of expansion of the double layer. Furthermore, fig. 4.2 reveals that, as proposed by Waxman and Smits\(^\text{(27)}\), the equivalent counter-ion conductivities show some sort of exponential decline as the conductivity of the equilibrating solution decreases.
<table>
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<th>$m_e$</th>
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TABLE IV.b. COMPARISON BETWEEN EXPERIMENTAL AND CALCULATED $Q_v$
VALUES GROUP II SAMPLES

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Fig. 4.2 Effect of $Q_v$ and $\alpha$ on the equivalent counter-ion conductivity $\lambda^+$. 
b) **Model for the Geometric Correction Factor** $f_g$

The magnitude of the equivalent counter-ion conductivity for low salinity conditions can be calculated from eq. (4.42) if a general model for the geometrical correction factor can be established. From the $\lambda^+$ data obtained for the five selected cores, values for $f_g$ were calculated from (4.42) and were found to follow an exponential-type equation of the form:

$$f_g = a^{1/\eta}$$  \hspace{1cm} (4.46)

Where the exponent $\eta$ is a function of $f_{DL}$ and thus of $\alpha$ and $Q_v$. From regression analysis, an expression for $\eta$ was empirically found as:

$$\eta = 0.6696 + 0.3303(aQ_v) - 1.13 \times 10^{-2}(aQ_v)^2$$  \hspace{1cm} (4.47)

Expressing eq. (4.47) as a function of $f_{DL}$ as given by eq. (4.26) results:

$$\eta = 0.6696 + 1.796 f_{DL} - 1.4426 \times f_{DL}^2$$  \hspace{1cm} (4.48)

It is interesting to notice the similitude between the tortuosity term $2(26)\lambda^2$ and the form of eq. (4.46) for $f_g$.

c) **Prediction of Core Conductivities**

Using the appropriate petrophysical parameters, the model was used to predict core conductivities as a function of the conductivity of the equilibrating solution for each one of the cores in Group II samples. The model predicts conductivities which agree very closely with experimental data, as evidenced by sample of the results presented in figs. 4.3 through 4.5. A complete set of results obtained for all cores are included in Appendix A.
Figure 4.3 Conductivities Predicted by the New Model for a Low $Q_v$ Core Sample
Figure 4.4 Conductivities Predicted by the New Model for an Intermediate \(Q_v\) Core Sample
Figure 4.5 Conductivities Predicted by the New Model for a Relatively High $Q_v$ Core Sample
In some cases, at very low salinities, the calculated $C_q$ deviates from the measured values e.g. core #22. It is believed that this is due to the limited expansion aspect of the double layer. It has been implied so far that the double layer can expand indefinitely to occupy the total pore space, so displacing completely the free electrolyte. Actually, this may not be the case. Expansion of the double layer with decreasing $C_w$ should reach a point for which two or more layers come close together and interference, in form of repulsive forces, is exerted between layers. A stage is reached where any decrease in the concentration of the equilibrating solution does not produce any more changes in the thickness of the double layers. The conductivity of the rock should exhibit then a linear decreasing behavior, similar to that observed at high salinities. The slope of this line should be much smaller than the slope at high $C_w$, so that core conductivities should appear to "level off" at very low salinities. The point at which this interference occurs may depend on the distribution of the clay and $Q_v$. It would be reasonable to expect it to appear sooner as $Q_v$ increases.

IV.3 Statistical Evaluation of the New Models

The performance of the new model in predicting core conductivities at low salinities is presented in this section. The basis of the evaluation is a comparison between calculated conductivities and accurate laboratory data available for water saturated rocks. The model's performance is also compared to that of the W-S and D-W models.
The W-S and D-W models have experienced modifications throughout the years. Although both models have been published under what could be considered their final form, it is judged interesting to evaluate their performance at the various stages of development. Subsequently, two versions of the W-S model have been studied while three variations of the D-W model are considered. A description of the different versions is summarized in Table IV.c and is given hereafter. Details of each model and the required variables have been already documented in Chapter III.

a) Versions of the existing models

The Waxman-Smits Model

Two variations of this model W-S I and W-S II were defined according to the expression used to estimate the equivalent counterion conductivity, B, as follows:

i) W-S I - The expression for B as it was first derived for Group II samples as given from eq. (3.5):

\[ B = 4.6 \left[ 1 - 0.6 \exp \left( -C_w/1.3 \right) \right]; \frac{\text{mho/m}}{\text{meq/cc}} \]

ii) W-S II - In a later publication, Waxman and Thomas modified eqn. (3.5) into what is accepted as the final form. The new expression for B is given by eq. (3.12):

\[ B = 3.83 \left[ 1 - 0.83 \exp \left( -C_w/2.0 \right) \right]; \frac{\text{mho/m}}{\text{meq/cc}} \]

The Dual Water Model

Three versions of this model were considered. D-W I, D-W II and D-W III differ in the way the parameter \( \alpha \) and/or \( \beta \) are defined.
TABLE IV.c
MODELS CONSIDERED IN THE STATISTICAL COMPARISON

<table>
<thead>
<tr>
<th>MODEL</th>
<th>GENERAL EXPRESSION</th>
<th>FEATURES</th>
</tr>
</thead>
</table>
| W - S I | \( C_o = \frac{1}{\beta} (BQ_v + C_u) \) | \( B = 4.6 \ (1 - 0.6 \ exp(-C_u/1.3)) \)  
\( B_{max} = 4.6 \ (\text{mho/m})/(\text{meq/cc}) \) |
| W - S II| \( B = 3.83 \ (1 - 0.83 \ exp(-C_u/2.0)) \)  
\( B_{max} = 3.83 \) |
| D - W I | \( B = 2.05 \ (\text{mho/m}) = \text{constant} \)  
(\text{mho/m})/(\text{meq/cc}) |
| D - W II| \( C_o = \frac{1}{\beta} (BQ_v + (1-0.3Q_v)C_u) \) | \( B = 2.05 \)  
Activity coefficients considered |
| D - W III| \( C_o = \frac{1}{\beta} (1 + C_u) \)  
\( \beta = 2.05 \)  
\( \beta = C_v > 1.0 \ \text{mho/m} \)  
\( \beta = C_v < 1.0 \ \text{mho/m} \)  
Activity coefficients considered |
| New Model| \( C_o = \frac{1}{\beta} \left[ \lambda^+ Q_v + (1-f_{DL})C_u \right] \)  
\( \lambda^+_{max} = 4.65 \ (\text{mho/m})/(\text{meq/cc}) \) |
1) **D-W I** - This version represents the model as it first appeared in the literature. The parameters $\alpha$ and $\beta$ are defined as follows:

$$\beta = 2.05 \frac{\text{mho/m}}{\text{meq/cc}} = \text{constant},$$

and

$$\alpha = \frac{n_1}{n} \quad \text{for } n < n_1$$

ii) **D-W II** - This second version of the D-W model is characterized by:

$$\beta = 2.05 \frac{\text{mho/m}}{\text{meq/cc}} = \text{constant}, \quad \alpha = \sqrt[\gamma \pm ]{n_1/(\gamma \pm )} n$$

iii) **D-W III** - The D-W model, in what can be considered its final version exhibits the following characteristics:

$$\alpha = \sqrt[\gamma \pm ]{n_1/(\gamma \pm )} n$$

$$\beta = 2.05 \frac{\text{mho/m}}{\text{meq/cc}} = \text{constant}; \quad C_w > 1.0 \frac{\text{mho/m}}{\text{meq/cc}}$$

$$\beta = 2.05 \left(1.0 - 0.4 \exp(-2.0 C_w]\right); \quad C_w < 1.0 \frac{\text{mho/m}}{\text{meq/cc}}$$

b) **Laboratory Data**

The objective when developing a conductivity model for shaly sands is to explain and predict the abnormal conductive behavior exhibited by these formations, this being particularly true when low salinity solutions saturate the pore space. In order to make proper performance comparisons, it is then necessary to use as a reference accurate data obtained for a wide range of water conductivities and various degrees of shaliness. The conductivity data presented by Waxman and Smits for their Group II samples is specially suited for the purposes of this study. These
conductivity measurements are regarded as being perhaps the most complete and accurate set of data available. Furthermore, these conductivity measurements were used in some manner in the basic work for the development of the three models under consideration.

As it will be shown later, the proper values of $Q_v$ and formation factor required for the use of each model were estimated from data pertaining to the straight-line portion of the $C_o - C_w$ relationship observed for each core. Therefore, it was expected and later confirmed that the evaluation of the models at high salinities was unnecessary and that the real test lies in the model's ability to reproduce the data at low salinities, i.e., to reproduce the curvilinear portion of the $C_o - C_w$ plot. Therefore, the data of Table III.a was used as follows:

-The data at high salinities ($C_w > 2.82$ mho/m) were used to obtain, for each one of the 27 cores in Group II, an equation of the form:

$$C_o = a_0 + a_1 C_w$$  \hspace{1cm} (4.49)

The individual correlation coefficients were essentially unity in each case. The coefficients $a_0$ and $a_1$ are used to estimate $Q_v$ and the formation factor.

-The data at low salinities ($C_w < 2.82$ mho/m) were used for the actual comparison. A total of 102 data points are available in this conductivity range.

c) Calculation of Petrophysical Parameters

The appropriate values for $Q_v$ and formation factor needed for use in the models, were calculated from the straight line portion
of the conductivity data by using the appropriate regression equation for each core as follows:

For the W-S models:

\[ F^* = \frac{1}{a_1} \]  (4.50)

\[ Q_v = (a_o/a_1) \left( \frac{1}{B_{\max}} \right) \]  (4.51)

For the D-W models:

\[ Q_v = \frac{(a_o/a_1)}{2.05 + 0.3 (a_o/a_1)} \]  (4.52)

\[ F_o = (1 - 0.3 Q_v) \frac{1}{a_1} \]  (4.53)

And for the new model:

\[ C_{wN} = 16.61 \text{ mho/m} \]  (4.54)

\[ F_e = \frac{C_{wN}}{a_o + a_1 (C_{wN})} \]  (4.55)

\[ Q_v = 3.571 (1 - a_1 F_e) \]  (4.56)

A summary of the petrophysical data is presented in tables IV.d and IV.e.

The petrophysical data were used along with the appropriate equations to estimate shaly sand conductivities for each core in Group II samples at \( C_w \) values of 1.492, 0.7802, 0.4049, and 0.2085 mho/m.

Because in their present form both the D-W model and the new model assume infinite expansion of the double layer, the computer program used for the study was designed to stop the calculations whenever the double layer theoretically occupies the entire pore space; i.e., whenever the term \( 0.3 a_1 Q_v \) or \( f_{DL} \) exceeds the value of 1.0 for a given \( C_w \).
TABLE IV.d
SUMMARY OF $Q_v$ DATA

<table>
<thead>
<tr>
<th>Core #</th>
<th>$Q_v$ (Ref.29) (meq/cc)</th>
<th>W - S I</th>
<th>W - S II</th>
<th>D - W</th>
<th>S - B*</th>
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<tbody>
<tr>
<td>1</td>
<td>0.017</td>
<td>0.045</td>
<td>0.054</td>
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<td>0.053</td>
<td>0.063</td>
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<tr>
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<td>0.050</td>
<td>0.060</td>
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<td>0.316</td>
<td>0.501</td>
<td>0.242</td>
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<tr>
<td>13</td>
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<td>1.636</td>
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<tr>
<td>27</td>
<td>1.480</td>
<td>1.709</td>
<td>2.052</td>
<td>1.783</td>
<td>1.148</td>
</tr>
</tbody>
</table>

*Model proposed in this study*
**TABLE IV.e**

SUMMARY OF FORMATION FACTOR DATA

<table>
<thead>
<tr>
<th>Core #</th>
<th>W - S (F*)</th>
<th>D - W (F_o)</th>
<th>S - B* (F_e)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>12.32</td>
<td>11.96</td>
<td>12.17</td>
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<td>2</td>
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<td>3</td>
<td>11.30</td>
<td>10.93</td>
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<tr>
<td>4</td>
<td>48.46</td>
<td>46.51</td>
<td>47.78</td>
</tr>
<tr>
<td>5</td>
<td>14.90</td>
<td>14.07</td>
<td>14.55</td>
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<tr>
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<td>17.68</td>
<td>18.27</td>
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<td>26.13</td>
</tr>
<tr>
<td>8</td>
<td>25.81</td>
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</tr>
<tr>
<td>9</td>
<td>18.17</td>
<td>17.08</td>
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<td>160.94</td>
<td>136.71</td>
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<tr>
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<td>55.90</td>
<td>27.33</td>
<td>39.09</td>
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<tr>
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<td>41.18</td>
<td>19.60</td>
<td>28.34</td>
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<tr>
<td>27</td>
<td>44.41</td>
<td>20.65</td>
<td>30.14</td>
</tr>
</tbody>
</table>

*Model proposed in this study*
d) \textbf{Statistical Parameters}

The performance of the models was evaluated by calculating two statistical parameters:

i) The average error, $E$, defined as:

$$E = \frac{\sum d_i}{N}; \quad (%) \quad (4.57)$$

Where $d_i$ is the percent error calculated as:

$$d_i = \frac{C_M^M - C_C^C}{C_C^0} \times 100 \quad ; \quad (%) \quad (4.58)$$

in which:

- $C_M^N = \text{Measured core conductivity}; \quad \text{(mho/m)}$
- $C_C^C = \text{Calculated core conductivity}, \quad \text{(mho/m)}$

and $N$ is the appropriate number of comparison points.

ii) The standard error, $S$, defined as $(61)$:

$$S = \sqrt{\frac{\sum (C_M^M - C_C^C)^2}{N}} \quad ; \quad \text{(mho/m)} \quad (4.59)$$

These two statistics have proven valuable and are considered adequate tools for the purpose of the study.

e) \textbf{Statistical Results}

The results of the comparisons between measured and calculated conductivities are summarized in Table IV, and are presented individually for each model in figs. 4.6 thru 4.11. Several points of interest deserve further discussion.

i) \textbf{W-S Model} - The use of eqn. (3.5) in the calculation of equivalent counterion conductivities and $Q_v$ values result in low average error and standard error of 4.6\% and $\pm 0.014 \text{ mho/m}$ respectively. This was somewhat expected
### TABLE IV.f

RESULTS OF STATISTICAL ANALYSIS

**GROUP II SAMPLES**

LOW SALINITIES ($C < 2,82 \text{ mho/m}$) @ $25^\circ C$

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>M O D E L S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>W-S I</td>
</tr>
<tr>
<td># Points, $N$</td>
<td>102</td>
</tr>
<tr>
<td>Std. Error, $S$ (mho/m)</td>
<td>$\pm0.014$</td>
</tr>
</tbody>
</table>
since eq. (3.5) was derived using the same group of conductivity data considered in this study. When the $Q_v$ and $B$ values calculated using expression (4.12) are utilized, the average error for this group of samples increases drastically to 23.9% and the variability of the predicted values is essentially doubled as evidenced by the resulting standard error of ±0.030 mho/m. It is not the purpose of this study to question the reasons behind the modification of eq. (3.5); nevertheless, it is clear that the W-S model in its final form does not yield the best results for this group of samples at low $Q_w$ values. It is interesting to notice that the results are contributed to a large extent by the value of $B$ rather than the value $Q_v$.

ii) **D-W Model** - The first observation regarding the performance of this model as first published is that nine useful comparison points have been lost for the analysis as a result of the model's unlimited expansion of the double layer. The magnitude of the average error (-22.2%) compares to that for the W-S II model; however, the conductivities calculated from the D-W I model are essentially larger than the experimental ones as indicated by the negative sign of $E$. On the other hand, it is interesting to notice that the low standard error (±0.011 mho/m) compares very favorably with that obtained for the W-S I model.
The inclusion of activity coefficients does not produce any significant changes in the statistical parameters, except for the fact that an additional comparison point is lost for the analysis. In fact, since the activity coefficients are less than 1.0 for concentrations above infinite dilution, their use in the model increases slightly the magnitude of the expansion factor \( \alpha \), thus causing the term \( (0.3\alpha Q_v) \) to approach the critical unity value at a lower \( Q_v \) value.

On the other hand, the last version of the D-W model produces interesting results. The inclusion of a variable equivalent counterion conductivity for \( C_w < 1.0 \) mho/m drastically reduces the average error to \(-8.6\%\). Although the predicted conductivities are still larger, on the average, than the experimental ones, the average error now reaches a value that may be considered by many as acceptable. More importantly, the standard error reaches its minimum value as table IV.e reveals.

iii) New Model - So far in the analysis, it is evident that a pattern has emerged. It appears that a model using \( Q_v \) and equivalent counterion conductivities based on expression (3.5) yields a low average error, and that the use of dual water concepts and variable equivalent counterion conductivities as in the D-W III model results in the lowest variability for the predictions. It should come as no surprise then that the new model, which
combines those features, scores very highly in the statistical test. This model yields average error of 3.2% which is the smallest of all the models. The standard error of ±0.005 mho/m is essentially equal to the lowest value. Compared to the D-W model, this new model results in the loss of only one comparison point due basically to the lower \( Q_v \) values required. The modification of the model to limit the expansion of the double layer has been already discussed in another section and could be attempted. Such modification should be required for cases of very low \( C_w \) and/or \( Q_v \) values higher than those normally expected in shaly sands \(^{31}\) and may not be of real practical utility.

f) Conclusions

Based in the results obtained for Group II samples at laboratory conditions, the following conclusions have been reached:

1. The new model, the earlier version of the W-S model and the final version of the D-W model perform equally well in predicting shaly sand conductivities when the samples are saturated with fluids whose resistivities are lower than 0.354 ohm/m, provided the proper petrophysical data are used in the calculations.

2. The use of a maximum equivalent counterion conductivity defined as in the new model results in lower values of average error for this group of samples at low salinities.
Figure 4.6 Comparison of Measured Conductivity Values of Shaly Sands to Values Calculated Using the New Model
Figure 4.7 Comparison of Measured Conductivity Values of Shaly Sands to Values Calculated Using W-S I Model
Figure 4.8 Comparison of Measured Conductivity Values of Shaly Sands to Values Calculated Using W-S II Model
Figure 4.9 Comparison of Measured Conductivity Values of Shaly Sands to Values Calculated Using D-W I Model
Figure 4.10 Comparison of Measured Conductivity Values of Shaly Sands to Values Calculated Using D-W II Model

N = 92 POINTS
E = -20.8 PERCENT
S = 0.010 MHO/M
Figure 4.11 Comparison of Measured Conductivity Values of Shaly Sands to Values Calculated Using D-W III Model
3. The use of dual water concepts and variable equivalent counterion conductivity produces conductivity predictions exhibiting the lowest variability for \( C_w < 2.8 \text{ mho/m} \).

4. These three features mentioned above seem to compliment each other. When used combined, they allow for conductivity predictions that agree more closely with experimental data and exhibit the lowest variability.

5. The new model appears to be the best compromise for predicting shaly sand conductivities in the range of shaliness and water conductivities expected in shaly sand interpretation.

IV.4 Practical Aspects

a) Laboratory Analysis. The Estimation of \( Q_v \) and \( F_e \)

Laboratory analysis on reservoir rocks are routinely performed to obtain petrophysical data in formations of interest. Accurate laboratory-determined values of \( Q_v \), formation factor, and cementation exponents for shaly sands play an important role in the evaluation of these formations.

Wet chemistry methods\(^{(45)}\) were extensively used in the estimation of \( Q_v \). These methods have the disadvantage of requiring the destruction of the core sample. In addition, it has been observed\(^{(43),(46)}\) that the \( Q_v \) so derived is affected by the method used in the preparation of the sample and the type of rock.

Wet chemistry methods have been steadily displaced by the use of non-destructive techniques for the estimation of \( Q_v \). The most practical of those techniques are the Multiple salinity
method\((27),(29),(31),(33)\) and the one based on membrane potentials\((30),(47)\).

The multiple salinity method appears to be preferable since information about the formation factor is simultaneously obtained. The method consists in measuring core conductivities at two or more salinities of the equilibrating solution. The data is treated using a conductivity model and the magnitudes of \(Q_v\) and the formation factor are calculated.

Although not explicitly mentioned, this very procedure was applied to obtain the required petrophysical data used for the evaluation of the new conductivity model proposed in this study. The accuracy obtained in the statistical comparisons make the new model the best choice for the determination of petrophysical parameters in shaly sands. It is recommended that conductivity data be collected at \(C_w \geq 2.4\) mho/m (linear portion of the \(C_o-C_w\) plot) as the determination of \(F_e\) and \(Q_v\) for a given shaly sand core is straightforward from this range of conductivities.

For NaCl solutions, it is apparent from the analysis that the calculation procedure would be simplified if one conductivity measurement is performed at the conditions of the Neutral point, \(C_{\text{WN}}\) i.e. 16.61 mho/m, as \(F_e\) can be estimated readily from eq. (4.15). The magnitude of \(Q_v\) may then be estimated from a second data point by using an expression derived from eqs. (4.7), (4.25), and (4.41) as:

\[
Q_v = \frac{C_o F_e - C_w}{(4.65-0.28C_w)} \tag{4.60}
\]
If data is available at \( C_w \) values other than \( C_{WN} \), then the determination of \( Q_v \) and \( F_g \) is accomplished by first obtaining the equation of the straight line. The petrophysical parameters are then estimated from eqs. (4.55) and (4.56).

The magnitude of the cementation exponent, \( m_e \), is evaluated from \( F_g \) and porosity data using eq. (4.8).

b) Calculation of \( \lambda^+ \)

Aside from determining the appropriate \( Q_v \) and \( F_g \) values for a particular rock sample, the need may rise for the log analyst to predict the conductivity of the core at a specific salinity. The knowledge of \( \lambda^+ \) is required if the salinity of interest is less than 0.242 mole NaCl/lt (i.e. \( C_w < 2.4 \) mho/m @ 25°C).

Figs. (4.12) and (4.13) have been prepared to facilitate the calculations when water conductivities are available. The magnitude of the expansion factor is determined from fig. (4.12). This value, along with \( Q_v \), is used in the calculation of the geometric factor \( f_g \) from eqs. (4.46) and (4.47). The value of \( \lambda'(NaCl) \) is read from fig. (4.13) at the appropriate \( C_w \) value and is used along with \( f_g \) to calculate the equivalent counterion conductivity from eq. (4.42).

If only NaCl salinities are available figs. (4.12) and (4.13) can be used by first calculating the conductivity of the solution. This can be done using charts (5), (37), (38) or using theoretical equations such as (4.38) through (4.40):

\[
C_w = \Lambda' NaCl \cdot n \tag{4.61}
\]
Figure 4.12 Variation of the Double Layer Expansion Factor with the Conductivity of the Far Water at 25°C.
Figure 4.13 Variation of the Corrected Equivalent Conductivity $\Lambda'(\text{NaCl})$ with the Conductivity of the Far Water at 25°C
The calculation of $\lambda^+$ in automated calculations can be carried out from the knowledge of $Q_v$ and $n$, the concentration in molar units, by following a simple procedure. The equations used in the calculations are a simple form of those given in section IV.1.

The estimation of $\lambda^+$ at 25°C is done as follows.

1 - Determine the expansion factor $\alpha$ from:

$$\alpha = \sqrt[3]{0.242/n} \quad (4.62)$$

2 - Estimate the concentration $n_{eq}$ of the equivalent NaCl solution by:

$$n_{eq} = \frac{3.571}{[\sqrt[3]{\alpha - 0.188}]^2} \quad \text{mole/lit} \quad (4.63)$$

3 - Calculate $\Lambda$ and $F(n_{eq})$ from eqs. (4.39) and (4.40).

4 - Determine the value of the exponent $n$ from eq. (4.47) or from eq. (4.48) if the volumetric fraction $f_{DL}$ has been calculated from eq. (4.26).

5 - Obtain $f$ from eq. (4.46).

6 - Determine the magnitude of $\lambda^+$ from eq. (4.42) and the values obtained in steps 3 and 5.

c) Limitations

The calculation procedure for $\lambda^+$ has been presented on the basis that, for a given $C_w$, the volumetric fraction under the influence of the double layer has not yet expanded to occupy the entire pore space. For cases of high $Q_v$ and/or very low salinities, the procedure must be applied with caution.

The applicability of the model is then theoretically limited by the condition:
Likewise, the estimation of $\lambda^+$ is limited by the condition:

$$n \geq n_{min}$$

(4.65)

where the minimum concentration can be determined for a given $Q_v$ as:

$$\alpha_{max} = \frac{3.571}{Q_v} = \frac{0.242}{n_{min}}$$

(4.66)

Therefore, $\lambda^+$ can be calculated if:

$$n \geq 1.897 \times 10^{-2} \frac{Q_v^2}{Q_v}$$

(4.67)
CHAPTER V
EXTENSION OF THE NEW MODEL TO HYDROCARBON BEARING FORMATIONS AT LABORATORY CONDITIONS

The new model contributes two major ideas towards the understanding of the conductive behavior of shaly sands. These ideas can be summarized as follows:

i) The equivalent counterion conductivity, $\lambda^+$, is related to that of an equivalent electrolyte.

ii) By introducing the concept of the Neutral Point, it has been proven that a shaly sand behaves just as a clean formation saturated with a fluid of conductivity $C^\text{we}$; the magnitude of which depends on the shaliness and the conductivity $C^\text{w}$ of the saturating electrolyte. Under these conditions, the conductivity of a shaly sand can be expressed in terms of the general Archie's relationship.

The model is now extended to predict water saturation and membrane potentials.

V.1. The Saturation Equation in Shaly Sands

Following the same line of thought, the new conductivity model can be extended for hydrocarbon bearing formations. Three assumptions are made:

1) The counterion concentration increases in the pore water as $S_w$ decreases. This assumption has been experimentally supported\(^{(19),(29),(32)}\). Then for $S_w < 1$ the formation
appears to be shalier. Its effective counterion concentration is given by eq. (4.7) as:

\[ Q_v' = \frac{Q_v}{S_w} \]  

(5.1)

ii) An oil bearing shaly sand behaves as an equivalent clean one whose formation factor, according to Archie's relationship, can be expressed from eq. (3.9) as:

\[ \frac{1}{\frac{1}{G_e}} = \frac{s_{we}^{n_e}}{F_e} \]  

(5.2)

in which \( n_e \) represents the saturation exponent of an equivalent clean rock, and \( F_e \) is the formation factor of that clean formation when fully saturated with water.

iii) It is also assumed, as with the D-W model\(^{(35)}\), that the hydrocarbons displace preferentially the far water.

In analogy with the expression for water saturated formations, the conductivity of a hydrocarbon bearing shaly sand can be expressed in general as:

\[ C_t = \frac{s_{we}^{n_e}}{F_e} (C_{we}') \]  

(5.3)

The equivalent water conductivity \( C_{we}' \) can be written using eq. (4.6) as:

\[ C_{we}' = \lambda f'_{DL} + (1-f'_{DL})C_w \]  

(5.4)

From eqs. (4.26) and (5.1) the volumetric fraction \( f'_{DL} \) can be expressed as:

\[ f'_{DL} = 0.28 \frac{Q_v}{S_w} \]  

(5.5)
and the local counterion concentration within the double layer is inferred from eq. (4.4) as:

$$n^+ = \frac{Q_Y}{f_{DL}}$$  \hspace{1cm} (5.6)

Replacing (5.1), (5.5), and (5.6) in (5.4) results:

$$C'_{sw} = \lambda' \frac{Q_Y}{S_w} + \left( \frac{S_w - 0.28aQ_Y}{S_w} \right) C_w$$  \hspace{1cm} (5.7)

Substituting (5.7) in (5.3) and rearranging:

$$C_t = \frac{S_w}{F_e} (C_w) + \frac{S_w}{F_e} (Q_Y) (\lambda'_+ - 0.28aC_w)$$  \hspace{1cm} (5.8)

Eq. (5.8) is the basic saturation equation for shaly sands, as derived from the new conductivity model. The equivalent counterion conductivity is given in eq. (5.8) as $\lambda'_+$ as a reminder that its magnitude depends on $n^+_+$ and $Q_Y$.

Expressing (5.8) in practical units, the total water saturation of a shaly sand is:

$$S_w = \left[ \frac{F_{e\, SW}}{R_t} - \frac{n_e}{n_e - 1} \frac{1}{(\lambda'_+ R_w - 0.28a)^{1/n_e}} \right]$$  \hspace{1cm} (5.9)

or as:

$$S_w = \left[ \frac{F_{e\, SW}}{R_t} - \Delta S_w \right]$$  \hspace{1cm} (5.10)

where:

$$\Delta S_w = S_w \frac{n_e}{n_e - 1} Q_Y (\lambda'_+ R_w - 0.28a)$$  \hspace{1cm} (5.11)

As in the case of Fertl's equation (22), expression (5.9) treats the effects of shaliness as a compound correction factor $\Delta S_w$ taken out from the clean sand term $F_{e\, SW}/R_t$.

The sign of $\Delta S_w$ depends only on the conductivity of the equilibrating solution. For $C_w > C_{w\, R}$, the correction factor becomes
positive and the shaly sand contains less water than it would be otherwise estimated from an expression applicable to clean rocks. The inverse is true for $C_w > C_{wN}$.

For $C_w = C_{wN}$ shale effects vanish from the equation and both eqs. (5.8) and (5.9) transform into the models for clean rocks. As in the case of $F_e$ and $m_e$ in water bearing formations, the concept of the Neutral point becomes an important part of the analysis. It is evident that the appropriate saturation exponent $n_e$ is equal to the apparent one that would be determined from $S_w$ and $C_t$ data obtained at $C_{wN}$.

In the $V_{SH}$ models, specially Fertl's, the shale effect results always in higher $S_w$ values if the clean sand model is used. Eq. (5.9) disputes this fact and shows that the sign of the correction term depends on the salinity of the formation water.

a) The Effect of the Presence of Hydrocarbons on the Equivalent Counterion Conductivity

Both the W-S and D-W models assume that changes in the water content of a shaly sand do not exert any effect on the mobility of the counterions. In other words, the magnitudes of $B$ and $\beta$ remain unaffected by the presence of hydrocarbons.

The new model makes use of an equivalent counterion conductivity whose magnitude at low salinities depends on $Q_w$. The magnitude of $\lambda_+^i$ at low salinities, as used in the saturation equation, is expected to vary with $S_w$ according to the assumed apparent increase in shaliness. The effect of hydrocarbons on $\lambda_+^i$
can be readily predicted by analyzing such effects on the parameters required for the calculation of $\lambda_+^i$.

From eqs. (5.1), (5.5), and (5.6), the local ionic concentration in the double layer for a hydrocarbon bearing formation is:

$$n_+^i = \frac{1}{0.28\alpha} \frac{3.571}{\alpha} = n_1; \quad \text{mole/lt}$$

just as in the case of a water saturated formations. The concentration $n_{eq}$ of the equivalent NaCl is therefore not affected. This concentration $n_{eq}$ can be obtained from eq. (4.63):

$$n_{eq} = \frac{3.571}{[\sqrt{\alpha - 0.188}]^2}; \quad \text{mole/lt}$$

It is used to determine the corrected equivalent conductivity $\lambda_{NaCl}^i$ for the equivalent electrolyte.

In analogy with eq. (4.42), the magnitude of $\lambda_+^i$ is given by:

$$\lambda_+^i = \frac{\lambda_{NaCl}^i}{f^i_g}$$

where $f^i_g$ is derived from (4.46) and (4.48) as:

$$f^i_g = \alpha^{1/\eta^i}$$

where:

$$\eta^i = 0.6696 + 1.1796 f_{DL}^i - 1.4426 \times 10^{-1}(f_{DL}^i)^2$$

Since the volumetric fraction $f_{DL}^i$ increases as $S_w$ decreases then for conditions such that $\alpha > 1$, the magnitude of the equivalent counterion conductivity also increases. Its magnitude is not affected at higher salinities ($\alpha=1$) and is given at 25°C by eq. (4.41). In the presence of hydrocarbons, the double layer occupies a larger fraction of the conductive medium. Therefore its effect on $C_t$ will be larger; i.e., the formation really behaves as it were shalier.
V.2 Test of the Saturation Equation

The validity of eq. (5.8) and thus (5.9) can be established by comparing calculated $S_w$ values against accurate experimental data. In so doing, the application of the concept of the neutral point in the estimation of saturation exponents can also be established.

a) Description of the Data

The test of the saturation equation will be carried out by utilizing the conductivity data obtained by Waxman and Thomas (29) at room temperature, which is published by Clavier, et al. (35). The data is composed of detailed information on $C_w$, $S_w$, and resistivity index $I$ for 12 cores. Information on core porosities is also available so that estimation of cementation exponents is feasible. Two out of the 12 available cores do not include enough information for the estimation of $Q_v$ and $F_e$ from the procedures described in section IV.3.c (multiple salinity method) and were left out of the analysis. Conductivities $C_r$ were calculated at each $C_w$ value from the value of $I$ and the conductivity $C_o$ observed at 100% water saturation. The data, as used in this study, is presented in Table V.a. As inferred from the table, the available data includes information pertaining to the curved portion of the $C_o-C_w$ plot ($C_w = 1.015$ mho/m). Therefore, the validity of the saturation equation can be adequately evaluated for a wide range of salinities.

From the data obtained at $S_w = 100\%$ for $C_w > 3.058$ mhom, the individual values of $F_e$ and $Q_v$ for the 10 remaining cores were
obtained following the procedures outlined in section IV.3.c. The porosity data and the appropriate formation factor were used to estimate cementation exponents, \( n_e \). Table V.b. summarizes the basic petrophysical data used in this study.

The new model, along with appropriate values of \( F_e \) and \( Q_v \) were used to reproduce core conductivities at \( S_w = 100\% \) and \( C_w = 1.015 \) m\( \text{mho/m} \) (curved portion of the \( C_o-C_w \) plot). The calculated values are compared with the experimental data in Fig. 5.1. The very low average error (-1.5\%) and standard error (±0.007 m\( \text{ho/m} \)) attest for the good quality of the data.

b) **Methods for the Estimation of Saturation Exponents in Shaly Sands**

One of the basic premises of this study is that the saturation exponent for a shaly sand is that of an equivalent clean formation. In other words, the magnitude of \( n_e \) is independent of shaliness and can be calculated by utilizing the concept of the neutral point.

From eq. (5.8) for conditions such that \( C_w = C_{WN} \):

\[
C_t = \frac{C_{WN} S_w}{F_e} \quad n_e
\]

Therefore, the appropriate saturation exponent is easily determined for a shaly sand if experimental data is available at \( C_w = C_{WN} \). When such data is not available, as it is the case in this study, saturation exponents can be estimated from either two of the methods described hereafter.
### TABLE V.a

**DATA USED IN THE TEST OF THE SATURATION EQUATION.**

**INFORMATION DERIVED FROM REF. 35**

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*Core conductivities expressed in (mho/m)*
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<td>0.0120</td>
</tr>
<tr>
<td></td>
<td>0.539</td>
<td>0.0176</td>
<td>0.535</td>
<td>0.0185</td>
</tr>
<tr>
<td></td>
<td>0.671</td>
<td>0.0221</td>
<td>0.800</td>
<td>0.0364</td>
</tr>
<tr>
<td></td>
<td>0.960</td>
<td>0.0355</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE V.a (Continued)

| WATER CONDUCTIVITY,  
<table>
<thead>
<tr>
<th>$C_w$ (mho/m)</th>
<th>CORE #7</th>
<th>CORE #8</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$S_w$</td>
<td>$C_t$</td>
</tr>
<tr>
<td>12.407</td>
<td>0.541</td>
<td>0.2318</td>
</tr>
<tr>
<td></td>
<td>0.589</td>
<td>0.2746</td>
</tr>
<tr>
<td></td>
<td>0.652</td>
<td>0.3321</td>
</tr>
<tr>
<td></td>
<td>0.725</td>
<td>0.3923</td>
</tr>
<tr>
<td></td>
<td>0.821</td>
<td>0.5064</td>
</tr>
<tr>
<td>10.132</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.061</td>
<td>0.528</td>
<td>0.0781</td>
</tr>
<tr>
<td></td>
<td>0.652</td>
<td>0.1105</td>
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<tr>
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<td>0.794</td>
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<tr>
<td>3.058</td>
<td>0.510</td>
<td>0.0374</td>
</tr>
<tr>
<td></td>
<td>0.589</td>
<td>0.0442</td>
</tr>
<tr>
<td></td>
<td>0.693</td>
<td>0.0550</td>
</tr>
<tr>
<td></td>
<td>0.837</td>
<td>0.0698</td>
</tr>
<tr>
<td>WATER CONDUCTIVITY, $C_w$ (mho/m)</td>
<td>CORE #9</td>
<td>CORE #10</td>
</tr>
<tr>
<td>---------------------------------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td></td>
<td>$S_w$</td>
<td>$C_e$</td>
</tr>
<tr>
<td>12.407</td>
<td>0.427</td>
<td>0.0434</td>
</tr>
<tr>
<td>10.132</td>
<td>0.558</td>
<td>0.0717</td>
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<tr>
<td>8.00</td>
<td>0.588</td>
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<td>6.061</td>
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</tr>
<tr>
<td>0.519</td>
<td>0.0274</td>
<td>0.478</td>
</tr>
<tr>
<td>0.594</td>
<td>0.0345</td>
<td>0.562</td>
</tr>
<tr>
<td>0.692</td>
<td>0.0449</td>
<td>0.662</td>
</tr>
</tbody>
</table>
### TABLE V.b

**BASIC PETROPHYSICAL DATA**

<table>
<thead>
<tr>
<th>Core Number</th>
<th>Sample Ref. (29)</th>
<th>$\phi$</th>
<th>$F_e$</th>
<th>$Q_v$</th>
<th>$m_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3218C</td>
<td>0.130</td>
<td>46.28</td>
<td>0.328</td>
<td>1.880</td>
</tr>
<tr>
<td>2</td>
<td>3279B</td>
<td>0.264</td>
<td>14.98</td>
<td>0.240</td>
<td>2.032</td>
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<tr>
<td>3</td>
<td>3281</td>
<td>0.194</td>
<td>29.49</td>
<td>0.260</td>
<td>2.063</td>
</tr>
<tr>
<td>4</td>
<td>499C</td>
<td>0.123</td>
<td>42.17</td>
<td>0.199</td>
<td>1.786</td>
</tr>
<tr>
<td>5</td>
<td>521C</td>
<td>0.115</td>
<td>41.53</td>
<td>0.188</td>
<td>1.723</td>
</tr>
<tr>
<td>6</td>
<td>3280B</td>
<td>0.192</td>
<td>30.68</td>
<td>0.196</td>
<td>2.075</td>
</tr>
<tr>
<td>7</td>
<td>3282C</td>
<td>0.237</td>
<td>17.67</td>
<td>0.177</td>
<td>1.995</td>
</tr>
<tr>
<td>8</td>
<td>512C</td>
<td>0.114</td>
<td>46.08</td>
<td>0.187</td>
<td>1.764</td>
</tr>
<tr>
<td>9</td>
<td>3227A</td>
<td>0.232</td>
<td>15.19</td>
<td>0.098</td>
<td>1.862</td>
</tr>
<tr>
<td>10</td>
<td>3228B</td>
<td>0.296</td>
<td>9.72</td>
<td>0.121</td>
<td>1.868</td>
</tr>
</tbody>
</table>
Fig. 5.1. Comparison between calculated and measured conductivities for the cores used in the test of the saturation equation.
b.1) Constant $S_w$ Method

As its name implies, this procedure applies when $C_t$ measurements are obtained at several $C_w$ levels while maintaining a constant water saturation. From eqs. (5.1), (5.3), and (5.7), the conductivity $C_t$ for conditions such as $\alpha=1$ can be expressed as:

$$
C_t = \frac{n_{w}}{F_{e}} + \frac{n_{e}}{F_{e}} (1-0.28Q'_v) C_w ; S_w = \text{constant} \quad (5.16)
$$

Eq. (5.16) represents the straight line portion of the conductivity plot, as exhibited by an equivalent water saturated shaly sand of shaliness $Q'_v$ and whose formation factor is $1/G_e = S_w^{n_e}/F_e$. It follows that the saturation exponent can be evaluated using the same procedure utilized for the estimation of $F_e$ in a water shaly sand.

Eq. (5.16) can be written as:

$$
C_t = a_0 + a_1 C_w
$$

where $a_0$ and $a_1$ are the regression coefficients for the straight line.

The formation factor of the equivalent sand is obtained at the neutral point from eq. (4.55) as:

$$
G_e = \frac{C_{wN}}{a_0 + a_1 C_{wN}} \quad (5.18)
$$

from which $n_e$ is calculated from:

$$
n_e = \frac{\log(F_e/C_e)}{\log(S_w)} \quad (5.19)
$$

The estimation of $n_e$ using this procedure then requires the previous knowledge of $F_e$. In other words, data at $S_w =$
100% must be available. On the other hand, the previous knowledge of \( Q_y \) is unnecessary, as the theory predicts that \( n_e \) is independent of shaliness.

b.2) Apparent \( n_a \) Method

When the available data does not meet the condition of constant \( S_w \), the saturation exponent for a shaly sand can be estimated from an alternate procedure. This method is based on the evaluation of apparent exponents, \( n_a \), at particular water conductivities by assuming a clean model.

Eq. (5.8) can be written, in terms of the clean sand model as:

\[
C_t = \frac{n_e C_w}{F_e}
\]  

(5.20)

For regression purposes, eq. (5.20) is assumed of the form:

\[
\log (C_t) = \beta_0 + \beta_1 \log (S_w) + \varepsilon
\]  

(5.21)

where \( \varepsilon \) is the error introduced by neglecting the shale effect.

By assuming a clean model, applying regression analysis on \( C_t \) and \( S_w \) data obtained at a fixed water conductivity allows the estimation of the coefficients \( \beta_0 \) and \( \beta_1 \). The slope \( \beta_1 \) then represents an apparent saturation exponent, \( n_a \), corresponding to that specific \( C_w \) value. If the regression process is repeated, a different \( n_a \) value is anticipated. It is therefore assumed that a relationship of the form:
155

\[ \beta_1 = f(C_w) = n_a \]  
(5.22)

can be established, from which the magnitude of \( n_e \) can be obtained from its definition as:

\[ n_e = \frac{f(C_w)}{C_{wN}} \]  
(5.23)

The application of this method does not require the previous knowledge of either \( F_e \) or \( Q_v \).

c) Prediction of \( S_w \) Using the New Conductivity Model

The validity of the theory can be tested by predicting \( S_w \) values for the available data. In so doing, saturation exponents for the samples under study are determined from the two methods previously discussed.

c.1) Constant \( S_w \) Method

The available experimental data for cores 1 through 8 contain information for at least two \( C_w \) levels in which \( C_t \) was measured at constant, or essentially constant water saturation. The appropriate \( n_e \) values for each core were calculated from the procedures outlined in section b.1. and are presented in Table V.c. The values of \( n_e \) were calculated from data pertaining to the straight line portion of the conductivity plot, \( C_w \geq 3.058 \text{ mho/m} \).

The obtained values of \( n_e \), along with those for \( F_e \) and \( Q_v \) for each core were used to test the validity of the saturation
### TABLE V.c

VALUES OF THE SATURATION AND CEMENTATION EXPONENTS FOR THE CORES USED IN THIS STUDY

| Core | $n_e$ \(^{(1)*}\) | $n_e$ \(^{(2)**}\) | $m_e$  
|------|------------------|------------------|--------
| 1    | 1.923            | 1.894            | 1.880  
| 2    | 1.919            | 1.857            | 2.032  
| 3    | 1.826            | 1.839            | 2.063  
| 4    | 1.727            | 1.713            | 1.786  
| 5    | 1.685            | 1.668            | 1.723  
| 6    | 2.083            | 2.040            | 2.075  
| 7    | 1.887            | 1.819            | 1.995  
| 8    | 1.646            | 1.690            | 1.764  
| 9    | 1.979***         | -                | 1.862  
| 10   | 1.823***         | -                | 1.868  

(1)* Calculated from apparent $n_a$ method  
(2)** Calculated from constant $S_w$ method  
(3)***Estimated from data pertaining to cores 1 through 7
equation. The solution of eq. (5.8) requires a trial and error procedure. The calculation procedure was conducted by assuming an $S_w$ value and comparing the calculated $C_t$ to the experimental value. This process was continued until the resulting conductivity agreed with the measured one usually within four decimal places. An average of four iterations were required for each conductivity point.

The overall result of the calculations is presented in fig. 5.2. The result of individual cores are presented in Appendix B. It is evident from fig. 5.2 that eq. (5.8), along with the appropriate saturation exponent results in accurate estimations of water saturation for the shaly sands used in the study. The average error and standard error are respectively, $0.33$ and $\pm 0.013\%$.

The performance of the model given by eq. (5.8) at low salinities is also satisfactory, as evidenced by the results presented in fig. 5.3 for $C_w = 1.015$ mho/m. Consequently, the effect of $S_w$ on $\lambda'_\tau$ follows the established theory. In addition, the increase of the shaliness effect as $S_w$ decreases has been corroborated.

c.2) Apparent $n_a$ Method

Saturation exponents using the apparent $n_a$ method were calculated for cores 1 through 8 from the procedures outlined in section b.2.

The regression process suggested by eq. (5.21) was applied only to data taken at $C_w > 3.06$ mho/m for which $\alpha = 1$. 
Fig. 5.2. Comparison Between Calculated and Experimental $S_w$ Values.

$n_e$ Values Calculated from Constant $S_w$ Method
Figure 5.3 Comparison Between Calculated and Experimental $S_w$ Values at a Low Salinity. $n_e$ Values Calculated from Constant $S_w$ Method.
This was done in order to make more appropriate evaluations of the theoretical dependency of $\lambda^1$ on $S_w$ at low salinities.

For each core, values of the apparent saturation exponents $n_a$ were obtained, and correlations of the form:

$$n_a = \delta_0 (C_w)^{\delta_1} \quad (5.24)$$

were used to represent the data. Values for the correlation coefficients were higher than 0.95, except in the case of core #5 which exhibited a value of 0.90. Saturation exponents $n_e$ for cores 1 through 8 were evaluated from eq. (5.23) at $C_w = C_{wN}$ by using the respective values of the regression coefficients $\delta_0$ and $\delta_1$. These values are also included in Table V.c. The table also shows, for comparison, the cementation exponents for each core. It is interesting to notice from the table that, for practical purposes, the magnitudes of both $n_e$ and $m_e$ can be assumed equal. Moreover, these magnitudes remain close to the value of 2.0 customarily assumed in Well Log interpretation.

Table V.c also reveals that, practically speaking, the magnitudes of the saturation exponents obtained from the two methods are equal. It is therefore expected that the use of $n_e$ values obtained from the apparent $n_a$ method should allow the estimation of accurate $S_w$ values. The result of the calculations using these $n_e$ values is presented in figs. 5.4 and 5.5. Individual results are also included in Appendix B. It is evident from these figures that the expectations are fully met.
Figure 5.4 Statistical Comparison Between Calculated and Measured $S_w$ Values. $n_e$ Values Calculated from Apparent $n_a$ Method.
Figure 5.5 Comparison Between Calculated and Experimental $S_w$ values at a Low Salinity. $n_e$ Values Calculated from Apparent $n_a$ Method.
It is important to realize that the concept of the Neutral point has played an important role as an aid for the appropriate determination of both the saturation and cementation exponents for shaly sand. Regarding the determination of $n$, this concept also adds flexibility in handling specific data.

d) Estimation of $n$ from Limited Data

Within the salinity range considered in the calculations, cores 9 and 10 exhibit information obtained only at water conductivities of 3.06 mho/m and 1.015 mho/m. Under these conditions, neither of the proposed models can be used for the estimation of $n$ in such cores.

The evaluation of $n$ in cores 9 and 10 was carried out following an alternate procedure, based on the observed similarities between the saturation and cementation exponents. It was observed that for cores 1 through 7, a strong correlation exists between $m$ and the apparent saturation exponent evaluated at $C_w = 3.058$ mho/m; and the appropriate $n$ value for each of these cores. The relationship is shown in fig. 5.6 and is given by:

$$n = 1.05 (m \cdot n)^{0.51}$$  \hspace{1cm} (5.25)

the correlation coefficient $R^2$ was found equal to 0.95.

Values of $n$ for cores 9 and 10 were then estimated from eq. (5.25) and the appropriate values of $m$ and $n$ at $C_w = 3.06$ mho/m. These values, included in Table V.b., were used to predict $S_w$ values for these cores. The result of the calculations is
Figure 5.6 Relationship Between Saturation and Cementation exponents.

Apparent Saturation Exponent $n_a$ Calculated at $C_w = 3.058$ mho/m
presented in figs. 5.7 and 5.8. As it may be expected, the variability and average error for cores 9 and 10 are larger than those for the rest of the data set, mainly because of the uncertainties associated with the estimation of $n_e$. However, the average error for these two cores lies well within experimental limits, thus reinforcing the validity of the dependence of $n_e$ on the cementation exponent $n_e$. This dependency has also been suggested elsewhere (48).

Conclusions

It can be concluded from the analysis that the saturation equation derived from the new conductivity model is valid and accurate. It is applicable for the range of salinity (35) and $Q_v$ (31) values encountered in shaly sand interpretation.
Figure 5.7 Individual Results. $n_e$ Calculated from Relationship Between $n_e$ and $(m_e \cdot n_a) \Theta C_w = 3.06$ mho/m
Figure 5.8 Individual Results. $n_e$ Calculated from Relationship Between $n_e$ and $(m_e \cdot n_a)$ @ $C_w = 3.06$ mho/m
CHAPTER VI
MEMBRANE POTENTIALS IN SHALES AND SHALY SANDS

The determination of membrane potentials in shales and shaly sands constitutes an important aspect of shaly sand interpretation. Membrane potentials generated across sands and adjacent shales form the electrochemical component of the SP (23),(31). This electrochemical component is believed to be the main origin of the SP deflection recorded in front of permeable formations (3),(4),(5). Therefore, SP log interpretation should benefit from the proper estimation of the membrane potentials occurring in the wellbore; this being particularly true for SP recorded in shaly environments.

Because of the non-destructive nature of the procedures used in their measurement, membrane potentials determined in the laboratory could be used to estimate the Q_v parameter in shaly sands (40),(47). Finally, the accurate prediction of membrane potentials in shaly sands constitutes an independent test for the validity and applicability of a conductivity model such as the one proposed in this work.

VI.1. Definition of Membrane Potentials and Membrane Efficiency

Diffusion potentials originate from difference in the mobilities of the cations and anions, when two electrolyte solutions are brought in contact and are allowed to diffuse freely into each other (31). These diffusion potentials are referred to as liquid-liquid junction potentials, or simply liquid-junction potentials.

Junction potentials are also generated when an inert porous medium separates the two solutions. Membrane potentials, on the other hand,
are generated when the pore walls of the material separating the two solutions carry an electrical double layer\(^{(23)}\).

The definitions given above are quite precise in terms of the characteristics of the separating membrane. For that reason they describe completely the type of diffusion potentials generated across clean sands and shaly sands, as well as shales. Just as a clean sand could be described as a particular case of shaly sands, the diffusion potential across a clean sand can also be treated as a particular case of membrane potentials. Therefore, for the purposes of this work, a membrane potential will be considered as one in which two solutions of different salinity are separated by a porous medium, regardless of the charge on its pore walls. This concept is useful, as will be discussed in the next section, to establish the limiting magnitudes of membrane potentials expected in well logging.

Charged membranes block, either partially or totally, the passage of one kind of ion. Such membranes are referred to as ion-selective membranes. A perfectly selective membrane; i.e., one which is completely impermeable to one kind of ion is called 100% efficient\(^{(23)}\), or simply perfect membrane. The selective properties of a membrane are determined by the nature of the charge on its pore walls. Shales and shaly sands which possess a negative charge are more permeable to the passage of cations and consequently fall into the classification of cationic membranes.

A 100% efficient shale is referred to as perfect shale\(^{(4),(5),(31),(33),(49)}\). Theoretically\(^{(4),(23),(31)}\), these formations should generate the largest and maximum attainable membrane potentials. In general shales and shaly sands are not 100% efficient;
their membrane potentials being less than the theoretical maximum\(^{(4)}\). The lowest possible membrane potential is given by that generated across a clean sand which, as previously discussed, equals in magnitude the liquid-junction potential\(^{(4),(31)}\). A clean sand, then, exhibits the lowest possible electrochemical efficiency.

VI.2. Transport Numbers in Shaly Sands

The electrochemical efficiency of a shale or shaly sand acting as a cationic membrane can be expressed in terms of their electrical cation transport number\(^{(31),(35)}\). In electrochemistry, transport numbers provide with an indication of the relative mobility of ions\(^{(25),(31)}\).

Electrical transport numbers \(t_i\) of a specific ionic species in an electrolyte solution, or a membrane, are defined as the fraction of the current carried by the species \(i\) relative to the total current in the system, when an electric potential is applied under conditions of zero pressure and concentration gradients\(^{(31)}\):

\[
t_i = \frac{J_i}{J} = \frac{Q_i n_i v_i}{\mathcal{J}}
\]

where:

- \(Q_i\) = Charge of the species \(i\); coulombs/mol
- \(n_i\) = Molar concentration of the species \(i\); mol\(^{-1}\)\(\cdot\)l\(^{-3}\)
- \(v_i\) = Velocity of species \(i\); l\(^{-}\)t\(^{-1}\)
- \(J_i\) = Current density due to species \(i\); charge\(^{-1}\)\(\cdot\)t\(^{-1}\)
- \(J\) = Total current density; charge\(^{-1}\)\(\cdot\)t\(^{-1}\)

Besides the transport of charge, an effective transport of water occurs across the diffusion boundary\(^{(31)}\) or across a charged membrane\(^{(23),(31)}\). Although water carries no charge, the transport of water is an integral part of the phenomena. When the ionic velocities
\( v_1 \) in eq. (6.1) are measured with respect to the velocity of the water, the transport numbers then are referred to as Hittorf transport numbers.\(^{(25),(31)}\)

For the case of NaCl saturating solutions, the cation transport number \( T_{Na}^+ \) in shales or shaly sands is defined in terms of the fraction of the current carried by the clay counterions, \( J_{Na}^C \), and the fractional current carried by the \( Na^+ \) ions in the bulk phase, \( J_{Na}^b \), as

\[
T_{Na}^+ = \frac{J_{Na}^C + J_{Na}^b}{J} \tag{6.2}
\]

For a clean sand, its transport number, as inferred from eqs. (6.1) and (6.2) is equal to:

\[
(T_{Na}^+)_{\text{clean}} = \frac{J_{Na}^b}{J} = \frac{t_{Na}^{hf}}{J} \tag{6.3}
\]

where \( t_{Na}^{hf} \) is the Hittorf transport number of the sodium ions in an electrolyte solution equal to that saturating the pore space.

When a shale or shaly sand behaves as a perfect cationic membrane, all the transport of current is attributed to the \( Na^+ \) ions\(^{(23),(31)}\) and consequently its transport number is unity. In general, the magnitude of transport numbers in shales and shaly sands will be limited by:

\[
t_{Na}^{hf} \leq T_{Na}^+ \leq 1 \tag{6.4}
\]

Expression (6.4) implies that the presence of a double layer on the pore walls of a permeable formation affects the ionic relative mobility. The exact nature of these effects is not clearly understood\(^{(28)}\). Smits\(^{(31)}\) has shown that for the analysis of membrane potentials, it is convenient to assume that the relative transport of positive and negative ions changes only by the presence of a higher concentration of mobil positive ions. The excess in concentration is consequently
attributed to the amount of counterions associated with the clay in shales and shaly sands.

VI.3. Smits' Model for the Membrane Potential in Shaly Sands

Hill and Milburn\(^{(19)}\) found from experimental data that the effect of clay on the membrane potentials is related to the cation exchange capacity per pore volume, \(Q_v\). This dependency was found to hold true regardless of the type and distribution of the clay. Despite this important finding, Hill and Milburn did not attempt to develop a model for the membrane potential. It was only after Waxman and Smits\(^{(27)}\) had proposed their conductivity model that Smits developed a model to quantitatively predict shaly sand membrane potentials as a function of \(Q_v\) and the salinity of the saturating water\(^{(31)}\). This model is based on the W-S conductivity model; however, it has been proposed\(^{(33)}\) that the Smits' theory can also be used to obtain similar theoretical expressions.

In deriving his theoretical expression, Smits made the following assumptions:

i) The current carried by the counterions is parallel to that carried by the solution saturating the pore space.

ii) Mobil species are considered to be the EDL counterions, water, and positive as well as negative ions contained in the bulk solution in the pore space.

iii) Counterions associated with the clay are \(\text{Na}^+\) ions and NaCl solutions saturate the pore space.

iv) The conductivity of the bulk phase is equal to that in the equilibrating solution.
v) Concentrations and relative velocities of the ions in the bulk phase are also considered equal to those in the equilibrating solution.

The basic expression for the membrane potential, \( E^* \), in shaly sands obtained by Smits is:

\[
E^*_m = - \int_{m_1}^{m_2} \frac{Q_{Na}^+}{Q_{Na}} \frac{d\mu_{NaCl}}{dm} \, dm
\]

(6.5)

where \( m_1 \) and \( m_2 \) are the molal concentrations of the two solutions separated by the membrane, and \( d\mu_{NaCl}/dm \) is the variation of the chemical potential of NaCl with concentration. \( Q_{Na}^+ \) is the charge of the Na\(^+\) ions.

The chemical potential is related to the liquid junction potential \( E^*_t \) by (31):

\[
E^*_t = - \int_{m_1}^{m_2} \frac{Q_{Na}^{hf}}{Q_{Na}} \frac{d\mu_{NaCl}}{dm} \, dm
\]

(6.6)

The effect of clay on the membrane potential of a shaly sand is observed by substituting (6.5) in (6.6). The result is:

\[
E^*_m = - \int_{m_1}^{m_2} \frac{Q_{Na}^{hf}}{Q_{Na}} \frac{dE^*_t}{dm} \, dm
\]

(6.7)

It follows that the membrane potentials in shaly sands can be represented as increased liquid-junction potentials. The shalier the formation, the larger the potential as compared to that in a clean rock.

The chemical potential of NaCl is related to the activity \( a_{NaCl} \) by:

\[
\mu_{NaCl} = RT \ln a_{NaCl}
\]

(6.8)
where \( R \) is the gas constant and \( T \) is the absolute temperature. The activity \( a_{NaCl} \) of the solute is expressed in terms of the mean activity \( a_\pm \) by:

\[
a_\pm = \gamma_\pm a_{NaCl}
\]

(6.9)
in which \( \gamma_\pm \) is the mean molal activity coefficient and \( m \) the molality of the solution.

Differentiating (6.6) and using (6.8) and (6.9) to express \( a_{NaCl} \) and \( \gamma_{NaCl} \):

\[
dE^* = \frac{-2RT}{F} \left( \frac{h \gamma_{Na}}{m_1 T_{Na}} \right) d \ln(m \gamma_{Na})
\]

(6.10)

where the charge \( Q_Na \) is replaced by the Faraday constant.

Replacing (6.10) in (6.7), the equation for the membrane potential becomes:

\[
E^* = \frac{-2RT}{F} \left( \frac{m_2}{m_1} \right) \ln(m \gamma_{Na})
\]

(6.11)

An expression for \( T_{Na}^+ \) can be obtained through eq. (6.2) from a conductivity model. Using the W-S conductivity model, \( T_{Na}^+ \) is given by:

\[
T_{Na}^+ = \frac{BQ_v + \gamma_{Na}^h C_w}{BQ_v + C_w}
\]

(6.12)

And eq. (6.11) becomes:

\[
E^* = \frac{-2RT}{F} \left( \frac{m_2}{m_1} \right) \ln(m \gamma_{Na})
\]

(6.13)

Besides \( C_w \) and \( B \) (at low salinities), \( \gamma_{Na}^h \) and \( \gamma_\pm \) are also functions of the concentration \( m \). If these relationships are known or can be estimated then (6.13) can be solved by a numerical procedure, as proposed by Thomas.
In order to test the model given by eq. (6.13) Smits performed membrane potential measurements on the cores pertaining to Group II samples. In addition, measurements were carried out also on five shale core samples. All the experimental work was conducted at 25°C. NaCl solutions ranging in concentration between 0.012 m NaCl (0.7 gm/lt NaCl) up to 6.144 m NaCl (saturation) were used. The concentration of the solutions at one end of the core was twice that at the other end. The experimental data is presented in Tables VI.a and VI.b. Transport numbers were calculated using equivalent counterion conductivities given by the original expression derived by Waxman and Smits, eq. (3.5).

For Group II samples a good agreement was observed between calculated and experimental membrane potentials for NaCl concentrations up to 3.072 mole/Kg H₂O. Deviations from the theory were observed for concentrations between 3.072 m and saturation conditions. The measured potentials were found to be lower than those predicted from eq. (6.13); the deviations being more evident for high \( Q_v \) values at these high salinities. These deviations from the theory are shown in fig. 6.1.

To study such deviations more closely, experiments were carried out on three shaly sand cores exhibiting relatively high \( Q_v \). Membrane potentials were measured with the brine at one side constant at 1.536 m NaCl; the other varying from 2 m NaCl up to saturation. The measurements revealed that deviations from the theory gradually increase for concentrations higher than 4 m, with the largest deviation occurring at concentrations between 5.831 m and 6.144 m NaCl, a shown in fig. 6.2.

Smits reasoned that such deviations might have been probably the result of not considering extra water molecules as hydration water to the counterions. The author proposed that eq. (6.5) should be modified
TABLE VI.a

MEMBRANE POTENTIALS FOR GROUP II SAMPLES AT 25°C.

ELECTRODE POTENTIALS INCLUDED. (REF. 31)

<table>
<thead>
<tr>
<th>Core Number</th>
<th>mol/ kg H₂O</th>
<th>-E* at 25°C (mV) for NaCl Solutions m₁ and m₂ at Each Side of Core</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m₂</td>
<td>m₁</td>
</tr>
<tr>
<td>1</td>
<td>19.9</td>
<td>14.79</td>
</tr>
<tr>
<td>2</td>
<td>20.0</td>
<td>14.90</td>
</tr>
<tr>
<td>3</td>
<td>19.9</td>
<td>14.97</td>
</tr>
<tr>
<td>4</td>
<td>19.8</td>
<td>15.5</td>
</tr>
<tr>
<td>5</td>
<td>20.0</td>
<td>15.3</td>
</tr>
<tr>
<td>6</td>
<td>20.2</td>
<td>15.35</td>
</tr>
<tr>
<td>7</td>
<td>20.2</td>
<td>15.6</td>
</tr>
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<td>8</td>
<td>20.1</td>
<td>15.7</td>
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<td>9</td>
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<td>15.3</td>
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<td>10</td>
<td>20.4</td>
<td>16.1</td>
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<td>20.6</td>
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<td>15</td>
<td>21.4</td>
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<td>18.6</td>
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<td>18.2</td>
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<td>20.7</td>
<td>16.9</td>
</tr>
<tr>
<td>21</td>
<td>20.6</td>
<td>17.2</td>
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<tr>
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<td>20.3</td>
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<tr>
<td>23</td>
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<td>26</td>
<td>24.7</td>
<td>22.95</td>
</tr>
<tr>
<td>27</td>
<td>24.6</td>
<td>22.90</td>
</tr>
</tbody>
</table>
Table VI.b

Membrane potentials for shale cores at 25°C.

Electrode potentials included (Ref. 31)

<table>
<thead>
<tr>
<th>Core Number</th>
<th>( m_2 )</th>
<th>6.144**</th>
<th>3.077</th>
<th>1.536</th>
<th>0.768</th>
<th>0.384</th>
<th>0.192</th>
<th>0.096</th>
<th>0.048</th>
<th>0.24</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>23.5</td>
<td>20.9</td>
<td>21.4</td>
<td>22.6</td>
<td>24.9</td>
<td>26.7</td>
<td>29.0</td>
<td>29.3</td>
<td>29.8</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>24.8</td>
<td>22.0</td>
<td>22.65</td>
<td>25.5</td>
<td>26.6</td>
<td>28.8</td>
<td>31.0</td>
<td>31.5</td>
<td>32.2</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>25.3</td>
<td>23.4</td>
<td>24.9</td>
<td>26.6</td>
<td>28.4</td>
<td>29.9</td>
<td>30.7</td>
<td>31.7</td>
<td>32.9</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>25.5</td>
<td>23.7</td>
<td>24.9</td>
<td>26.7</td>
<td>27.6</td>
<td>29.6</td>
<td>30.3</td>
<td>30.5</td>
<td>29.4</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>33.5</td>
<td>30.6</td>
<td>29.9</td>
<td>31.15</td>
<td>31.5</td>
<td>32.0</td>
<td>32.2</td>
<td>32.6</td>
<td>33.3</td>
<td></td>
</tr>
</tbody>
</table>
Figure 6.1 Deviations Between Measured and Calculated Membrane Potentials. W-S Model (Ref. 31)
Figure 6.2 Deviation of Membrane-Potentials as a Function of Concentration NaCl Solution. (Ref. 31)
to include this hydration water. The modification of eq. (6.5) requires the introduction of a reduced transport number for the counterion water. Unfortunately, this parameter cannot be measured independently (31).

An important finding was obtained by Smits when, from the experimental work, he observed that eq. (6.13) is applicable to predict membrane potentials in shales. As for shaly sand samples, measurements also differed from the theory at high salinities as shown in fig. 6.1 which includes shale cores.

It was observed that there is a continuous transition in membrane potentials from clean sand to shaly sands and to shales. Therefore it was concluded that, electrochemically speaking, shales are not very different than shaly sands. The only difference is mainly due to the relatively higher $Q_v$ measured in shales.

Smits also concluded that the theory predicts the maximum attainable membrane potential. From (6.12), $T_{Na}^+$ reaches the limiting upper limit if:

$$\lim_{Q_v \to \infty} T_{Na}^+ = \lim_{Q_v \to \infty} \left( \frac{BQ_v + t_{Na}C_w}{BQ_v + C_w} \right) = 1$$

According to the W-S model, a perfect membrane should exhibit an infinitely high $Q_v$. Smits found that the theoretically calculated membrane potentials become essentially constant for $Q_v \geq 10$ meq/cc. The author established then that the range of $Q_v$ values applicable to shales lies between 1 and 10 meq/cc.

A similar analysis of eq. (6.12) at low salinities reveals another interesting point:
Therefore, any shaly sand at low salinities behaves as a perfect cationic membrane. This perfect membrane behavior is not controlled by the magnitude of $Q_v$.

VI.4 Prediction of Membrane Potentials in Shales and Shaly Sands Using the New Conductivity Model

Although Clavier et al. did not extend the D-W model to the estimation of membrane potentials, they presented\textsuperscript{(33)} comparison between calculated and experimental $T_{Na}^+$ values. From these comparisons they concluded that the D-W model provides better estimates of $T_{Na}^+$ as compared with those calculated from the W-S model, eq. (6.12).

As with the W-S and D-W models, the conductivity model proposed in this work may be extended to provide with an expression for the transport number in shaly sands.

In previous sections it has been inferred that the use of dual water concepts improves the modeling of the conductive behavior of shaly sands. The new model, which is also based on those concepts, is initially expected to perform satisfactorily when applied to the estimation of membrane potentials in shaly sands. From Smits' findings, the calculation of membrane potentials in shales seems also feasible.

The successful application of the model to the prediction of the electrochemical behavior of shaly formations should contribute towards making a more comprehensive use of the SP and resistivity logs for interpretation purposes.
a) The Membrane Potential Equation

The same assumptions used by Smits will be initially considered for the development of the expression for $T_{Na}^+$. In addition, it is considered that the bulk phase in the Smits' theory corresponds, under the new model, to the solution beyond the influence of the double layer.

The current density $J^b$ due to the bulk or "far" phase can be expressed as:

$$ J^b = \frac{(1-f_{DL})C_w}{F_e} \quad (6.14) $$

Likewise, the current density due to the clay counterions $J_{Na}^c$ is expressed as:

$$ J_{Na}^c = \frac{\lambda^+ Q_v}{F_e} \quad (6.15) $$

The fraction of the total current transported by $Na$ is then:

$$ \frac{J_{Na}^c}{J} = \frac{\lambda^+ Q_v}{\lambda^+ Q_v + (1-f_{DL})C_w} \quad (6.16) $$

Assuming equal composition and ionic mobility, the transport number in the bulk phase equals the Hittorf transport number in the solution outside the core:

$$ t_{Na}^b = t_{Na}^{hf} \quad (6.17) $$

and the transport number in shaly sands, as derived from the new model is given by:

$$ T_{Na}^+ = \frac{\lambda^+ Q_v + t_{Na}^{hf}(1-f_{DL})C_w}{\lambda^+ Q_v + (1-f_{DL})C_w} \quad (6.18) $$
The perfect membrane behavior is controlled by the volumetric fraction of the double layer, $f_{DL}$:

$$\lim_{f_{DL} \to 1} \frac{\nu^{+}}{\nu^{+} + \nu^{-}} = 1$$  \hspace{1cm} (6.19)

The condition $f_{DL} = 1$ is approached either at low salinities for which $\alpha > 1$, or when the formation exhibits a $Q_v$ value high enough for the double layer to occupy the entire pore space. Such a limiting $Q_v$ is inferred from the definition of $f_{DL}$. At high salinities ($\alpha = 1$) and 25°C:

$$Q_v^P = \frac{1}{0.28} = 3.571 \text{ meq/cc}$$  \hspace{1cm} (6.20)

$Q_v^P$ corresponds to the maximum attainable $Q_v$ derived by Clavier, et al. (33)

Replacing (6.18) in (6.11), the membrane potential equation becomes:

$$E^* = \frac{2RT}{F} \int_{m_1}^{m_2} \left[ \frac{\lambda^+ Q_v + t_{Na}^f (1-f_{DL}) C_w}{\lambda^+ Q_v + (1-f_{DL}) C_w} \right] d\ln \left( m \gamma_\pm \right)$$  \hspace{1cm} (6.21)

b) Calculation of Membrane Potentials

Eq. (6.21) can be used to compare calculated values of membrane potentials to those experimentally determined by Smits (31). In so doing, it is necessary to know the variation of $\lambda^+$, $t_{Na}^f$, and $\gamma_\pm$ with concentration.

The calculation of $\lambda^+$ and $f_{DL}$ has been covered in a preceding section. However, it should be mentioned that the previously determined $Q_v$ values for Group II samples (Table IV.c) will be used for the calculations.
b.1) Calculation of Hittorf Transport Numbers, $t_{Na}^{hf}$.

Based on measurements on liquid-junction potentials, Smits (49) calculated Hittorf transport numbers for NaCl solutions at 25°C. The variation of $t_{Na}^{hf}$ with concentration was derived by Smits as:

$$t_{Na}^{hf} = 0.372 - 1.179 \times 10^{-2} \log(my_{+}); \quad 0.024 \leq m \leq 6.144$$

(6.22)

The experimental data (31) for the membrane potentials covers a lower salinity range than that of eq. (6.22). For the lower salinity range, transport numbers can be derived theoretically as explained hereafter.

Based on the Fuoss-Onsager theory of conductance, Stokes derived a theoretical expression that can be used to approximate the Hittorf transport numbers. For 1-1 electrolytes, the Stokes equation is given by (25):

$$t_{+} = \frac{\lambda_{+}^{\infty} - \frac{1}{2} B_{2} \sqrt{n/(1 + B_{2} \sqrt{n})}}{\lambda^{\infty} - B_{2} \sqrt{n/(1 + B_{2} \sqrt{n})}}$$

(6.23)

where:

- $\lambda_{+}^{\infty}$, $\lambda^{\infty}$ = limiting equivalent conductivities of the cation and electrolyte, respectively,
- $B_{2}$ = coefficient of the electrophoretic term in the theory of conductivity,
- $B$ = coefficient of ion-size term in the Debye-Hückel theory,
- $\bar{\theta}$ = mean ionic diameter
n = electrolyte concentration in molar units
    (moles solute/lt. solution).

For NaCl solutions at 25°C(25),(50):
\[ A° = 126.45 \]
\[ A° = 126.45 \]
\[ B = 0.3291 \]
\[ B = 0.3291 \]
\[ \lambda_+^0 = 50.1 \]
\[ \lambda_+^0 = 50.1 \]
\[ \lambda_+^0 = 50.1 + 55.402 \sqrt{n} \]
\[ \lambda_+^0 = 50.1 + 55.402 \sqrt{n} \]
\[ B_2 = 60.668 \]
\[ B_2 = 60.668 \]

and eq. (6.23) becomes:
\[ t_{Na} = \frac{50.1 + 55.402 \sqrt{n}}{126.45 + 155.726 \sqrt{n}} \]

Transport numbers obtained from eq. (6.24) are compared in fig. 6.3 with some of the experimental data obtained by Smits(49) and presented by Thomas(47). Although Smits(31) has recommended the use of eq. (6.24) to estimate approximated \( t_{Na}^{hf} \) values at salinities lower than 0.024 m NaCl, it is evident from the figure that eq. (6.24) could be used throughout a wider concentration range. Transport numbers appear in fig. 6.3 as a function of molality, rather than molarity, as used in eq. (6.24). This was done just to be consistent with the molal concentration scale used in the membrane potential equation.

The conversion of electrolyte concentration from molarity (mole/lt. of solution) to molality units (mole/kg. H\(_2\)O) is accomplished from the general expression(25),(52):
\[ m = \frac{n}{d_o - (\frac{\lambda_{MA}}{1000})n} \]

where:
\[ m = \text{Molal concentration of electrolyte} \]
Figure 6.3 Comparison Between Hittorf Transport Number Values
Approximated by Eqn. (6.24) and Those Measured by Smits (31)
\[ n = \text{Molar concentration of electrolyte} \]
\[ d^0 = \text{Density of the solution} \]
\[ W_{MA} = \text{Molecular weight of the solute} \]

From published data\(^{(51)}\), an empirical relationship between density and molar concentration for NaCl solutions at 25°C was obtained\(^{(50)}\) by restricting the regression process to meet saturation conditions as:

\[ d^0 = 9.8986 \times 10^{-1} + 4.1839 \times 10^{-2} (n)^{0.95} \quad (6.26) \]

Combining eqs. (6.25) and (6.26), the molal concentration of a NaCl solution at 25°C can be calculated\(^{(50)}\) from:

\[ m = \frac{n \times 10^3}{9.8986 \times 10^2 + 41.839 (n)^{0.95} - 58.448 (n)} \quad (6.27) \]

b.2) Calculation of Mean Activity Coefficient; \( \gamma^0 \)

Mean activity coefficients for NaCl solutions at 25°C may be estimated from a theoretical expression. The Debye-Hückel expression for the mean activity coefficient in its general form is\(^{(25)}\):

\[ \log \gamma^0 = \frac{-A|z_1z_2|^{1/2}n}{a + B n^{1/2}} - \left( \frac{h}{\nu} \right) \log a_A \]

\[ - \log[1 - \frac{W_A}{1000} (\nu-n)m] \quad (6.28) \]

where:
\[ h = \text{Hydration number}, \]
\[ |z_1z_2| = \text{Absolute valence product of anion and cation}, \]
\( \nu = \) Number of moles of ions formed from one mole of electrolyte,

\( a_A = \) Activity of the solvent

\( n,m = \) Electrolyte concentration in molar and molal units, respectively,

\( W_A = \) Molecular weight of solvent,

\( A = \) Constant of Debye-Hückel equation for the activity coefficient, and

\( \delta_1 = \) Equivalent ion size for the activity coefficient.

For aqueous solutions at 25°C, \( A = 0.5115 \) (Ref. 28) and \( B = 0.3291 \) (Ref. 50) if \( \delta_1 \) is expressed in Å. For NaCl solutions:

\[ \left| z_1 z_2 \right| = 1.0 \]

\( \nu = 2 \)

\( h = 3.5 \) (Ref. 25)

\( \delta_1 = 3.97 \) (Ref. 25)

\( W_A = 18.0 \)

Replacing these values in eq. (6.28):

\[ \log \gamma_\pm = -0.5115/n \frac{1}{1+1.3065/n} - 1.75 \log a_A - \log (1-0.027 m) \]

(6.29)

From published data (25) for NaCl solutions ranging in concentration from 0.1 to 6 molal, an empirical expression for the activity of the solvent was obtained (50) as:
Values of $\gamma_+^q$ for NaCl concentrations from 0.01 up to 6.144 molal (saturation) were calculated from eqs. (6.29) and (6.30) and are presented in fig. 6.4. For comparison purposes, experimentally derived data given in ref. 52 are also plotted. It is evident from this figure that reliable values of $\gamma_+^q$ can be obtained over a wide range of concentration.

b.3) Solution of the Membrane Potential Equation

Using the relationship between the main variables and electrolyte concentration, eq. (6.21) was solved for each $Q_v$ following a numerical procedure suggested by Thomas (47).

First, the concentration interval $[m_1, m_2]$ was divided into 100 concentration points $m(i)$. For each molality $m(i)$, the corresponding molarity $n(i)$ was calculated by a trial and error procedure by using eq. (6.27). The magnitudes of $\lambda^+$, $\tilde{f}_{DL}$, $\tilde{h}_{Na}$, $\gamma_+$, and $C_w$ were evaluated for each concentration point, and the transport number $T_{Na}^+(i)$ was computed. One hundred differentials were evaluated and summed. The result was then multiplied by 51.38, the value of the constant $2RT/F$ at 25°C. The final result was then taken as the magnitude of the membrane potential. This procedure was repeated for each core and for each concentration interval.

c) Analysis of the Results. Group II Samples

The results of the calculations for all 9 salinity intervals are shown in figs. 6.5 through 6.13. These plots provide with the
Fig. 6.4 Mean Activity Coefficients for NaCl Solutions at 25°C and Atmospheric Pressure
comparison between theoretical membrane potentials, calculated from eq. (6.21) as a function of $Q_v$, and the experimental data obtained by Smits. Those experimental values are plotted in the figures at the corresponding $Q_v$ previously determined from conductivity data for each core.

The agreement between theory and experiments at salinities from 0.012 m NaCl up to 3.072 m is quite satisfactory. The average and standard errors range between $-4.03\%$ and $2.23\%$, and 0.332 mV and 2.29 mV respectively. Deviations from the theory observed for certain cores at low salinities may be explained by the inherent difficulties generally encountered when handling shaly sands equilibrated with diluted solutions\(^{(31)}\). Lower measured potentials may result from the introduction of cracks within the sample at low salinities. This condition should facilitate the passage of ions from one solution to the other, resulting in a situation for which a liquid-junction potential is more easily established.

Each figure also contains statistical information about the calculations for Group II samples. From this information it is apparent that the average error, $E$, fluctuates as the concentrations of the external solutions vary. In general, there seems to be a tendency for $E$ to decrease as salinity increases. Not much information can be derived from this statistic. It should be noted, however, that its magnitude remains low, well within experimental limits ($-4.0 < E < 1.27\%$).

On the other hand, the standard error $S$ reveals a significant trend. Its magnitude definitely depends on the salinity of the
Figure 6.5 Comparison Between Measured and Calculated (New Model) Membrane Potentials in Shaly Sands. (Group II Samples)
Figure 6.6 Comparison Between Measured and Calculated (New Model) Membrane Potentials in Shaly Sands. (Group II Samples)
Figure 6.7 Comparison Between Measured and Calculated (New Model).

Membrane Potentials in Shaly Sands. (Group II Samples)
Figure 6.8 Comparison Between Measured and Calculated (New Model)
Membrane Potentials in Shaly Sands. (Group II Samples)
Figure 6.9 Comparison Between Measured and Calculated (New Model)
Membrane Potentials in Shaly Sands. (Group II Samples)
Figure 6.10 Comparison Between Measured and Calculated (New Model) Membrane Potentials in Shaly Sands. (Group II Samples)
Figure 6.11 Comparison Between Measured and Calculated (New Model)
Membrane Potentials in Shaly Sands. (Group II Samples)
Figure 6.12 Comparison Between Measured and Calculated (New Model) Membrane Potentials in Shaly Sands. (Group II Samples)
Figure 6.13 Comparison Between Measured and Calculated (New Model) Membrane Potentials in Shaly Sands. (Group II Samples)
external solutions, reaching a minimum when $m_1 = 1.536$ and $m_2 = 3.072$. From the visual inspection of fig. 6.12 and the magnitudes of both $S$ and $E$, it is evident that the theory essentially reaches a perfect fit of the data. It is interesting to notice that the average salinity $m_{\text{avg}} = 2.304$ for this concentration range compares well with the salinity $m_{N} = 2.43$ at the Neutral Point.

At salinities from 3.072 m NaCl up to saturation, substantial deviations from the theory are observed, fig. 6.13. These deviations are of the same nature as those reported by Smits\(^{(31)}\).

### VI.5 Modification of the Membrane Potential Equation

The observed deviations at high salinities follow a well defined pattern. They are present for conductivities higher than $C_{WN}$; in addition, these deviations seem to be proportional to $Q_v$.

As it was discussed earlier, Smits attributed the deviations from the theory to neglecting hydration water for the counterions. It is proposed in this study that the observed deviations may be mainly due to assuming equal ionic mobilities in the core and outside solutions at all salinities. As a point of interest, Winsauer and McCardell\(^{(24)}\) predicted, based on theoretical considerations, that diffusion potentials of the liquid-junction type in shaly sands should be lower than those observed in clean rocks. Such a reduction in diffusion potential should be mainly controlled by the concentration of fixed charges $n_o$. The quantity $n_o$ is somewhat analogous to $Q_v$. Winsauer and McCardell concluded that diffusion should be reduced for increased $n_o$, this effect becoming more evident at high salinities.
a) **Introduction of the Transport Factor, τ**

By introducing the concept of the Neutral point, the conductive behavior of a shaly sand can be divided into two well-defined regions. For $C_w < C_{wN}$, the conductivity $C_{we}$ of the equivalent electrolyte saturating the pore space is always higher than $C_w$. In this region, the new model is analogous in concept to the W-S model. Applying this philosophy to membrane potential theory it is inferred then that, for conditions such that $C_w < C_{wN}$, the equivalent solution in the pore space of a shaly sand is able to transport as much current than the solution outside the core. In this region the ionic mobility can be assumed equal for both bulk and outside solution. The increase in $\tau_{Na}^+$ can be attributed to the excess of counterions in the pore space, as assumed by Smits.

For conditions such that $C_w > C_{wN}$, the new model predicts that $C_{we} < C_w$. The decrease in $C_{we}$ relative to $C_w$ depends on both $Q_v$ and $C_w$. Again, relating these concepts to the theory of membrane potentials, it is apparent that there should be an effective decrease in ionic mobilities. Such a decrease might be the result of interactions between the double layer and the free solution.

The basic theory of the EDL predicts that a boundary potential should exist at the interface of the charged double layer and the free solution\(^{(24)}\). The magnitude of that potential depends on the difference in concentration, or rather activity, of positive charges in the EDL and the free solution. It was previously shown that the concentration of positive charges in the EDL should reach a constant value at high salinities. As the concentration of the
free solution increases, the magnitude of the boundary potential gradually diminishes since the concentration difference also decreases. Such a process should continue until the ionic activity everywhere in the pore space is the same and the boundary potential becomes zero.Apparently this condition corresponds to the situation when $C_w = C_{wN}$.

At higher salinities, the boundary potential increases, but its sign is reversed. The theoretical treatment of this phenomena on the ionic mobilities at high concentrations is beyond the scope of this study. However, the experimental evidence indicates that the ions are slowed down in their passage through the charged membrane.

In order to take this effect into account, it is proposed that the membrane potential model, eq. (6.11) be modified by introducing a correction factor $\tau$. This correction term, defined here as a transport factor, is in a sense analogous to the concept of transport number. It takes into account the differences between the actual transport properties of the system, and these of the outside solution.

Intuitively, $\tau$ is proposed as:

$$\tau = \frac{C_{we}}{C_w} ; \quad C_w > C_{wN}$$

$$\tau = 1 ; \quad C_w \leq C_{wN}$$

(6.31)

Expressing $C_{we}$ in terms of $C_{wN}$ and $Q_w$, the transport factor at 25°C becomes:
\[ \tau = 1 \frac{0.28Q_V}{C_w} (C_w - C_{wN}) ; \quad C_w > C_{wN} \]

\[ \tau = 1 ; \quad C_w < C_{wN} \] (6.32)

Consequently, the model for the membrane potential is given by:

\[ E^* = \frac{-2RT}{F} \int \tau^+_{Na} d\ln(m\gamma^*_+) \] (6.33)

The correction factor was tested by repeating the calculations for Group II samples at the highest concentration interval. Membrane potentials were also evaluated for the five shale samples. The magnitude of \( Q_V \) for each shale core was estimated at the contrast [1.536, 3.072] from an enlarged version of fig. 6.12. Although the theoretical line in this figure represents uncorrected membrane potentials, fig. 6.12 was chosen on the basis of the statistical results obtained at this salinity contrast. Table VI.c presents the estimated \( Q_V \) for the shale cores. Experimentally determined values, as reported by Smits are also included for comparison.

Table VI.c reveals that the estimated \( Q_V \) values are all lower than those derived from wet chemistry analysis. Moreover, the values for samples I and II fall well within the range assumed for shaly sands \(^{31}\), rather than for shales.

The result of the membrane potential calculations for all 32 samples is shown in fig. 6.14. Experimental data for the shale cores are presented as shaded symbols. It is evident that the inclusion of the transport factor \( \tau \) has improved considerably the results. The analysis of the figure reveals the validity of the
**TABLE VI.c**

ESTIMATED $Q_v$ FOR SHALES FROM MEMBRANE POTENTIAL DATA

<table>
<thead>
<tr>
<th>SHALE CORE</th>
<th>$Q_v$ (Calc.) (meq/cc)</th>
<th>$Q_v$ (Exp.)* (meq/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.81</td>
<td>1.16</td>
</tr>
<tr>
<td>II</td>
<td>0.98</td>
<td>1.88</td>
</tr>
<tr>
<td>III</td>
<td>1.17</td>
<td>1.57</td>
</tr>
<tr>
<td>IV</td>
<td>1.22</td>
<td>2.32</td>
</tr>
<tr>
<td>V</td>
<td>2.22</td>
<td>4.20</td>
</tr>
</tbody>
</table>

*Ref. 31
Fig. 6.14 Corrected Membrane Potentials for Group II Samples and Five Shales Cores.
concept and its applicability for both shaly sands and shales. The continuous variation in membrane potentials from clean sand to shales, as found by Smits, is also well illustrated in the figure.

The result of the calculations for shales at all the salinity intervals is presented in fig. 6.15 and summarized in Table VI.d. Included within parenthesis are the experimental data. The analysis of the results reveals that the modified equation predicts membrane potentials in shales that compare favorably with the experimental data.

As suggested by Smits, the correction of the membrane potential equation for the estimation of the electrochemical component of the SP\(^{(31)}\) may be of little practical importance. However, such a correction through the inclusion of \(\tau\) should be taken into account if membrane potentials measured at high salinities are to be used as a source of reliable \(Q_v\) values for both shaly sands and shales.

Based on all the analysis, there is little doubt now about the validity and utility of the concept of the Neutral point in the analysis of shaly sands. In addition, the use of dual water concepts has helped to simplify and improve the treatment of the problem. The validity of the new model has now been reaffirmed.
Figure 6.15 Comparison Between Experimental and Calculated Membrane Potentials for Five Shale Cores. Transport Factor Included.


<table>
<thead>
<tr>
<th>SALINITY $(m_1, m_2)$</th>
<th>SHALE CORES</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
</tr>
<tr>
<td>(0.012, 0.024)</td>
<td>33.47</td>
</tr>
<tr>
<td></td>
<td>(29.8)*</td>
</tr>
<tr>
<td>(0.024, 0.048)</td>
<td>32.15</td>
</tr>
<tr>
<td></td>
<td>(29.3)</td>
</tr>
<tr>
<td>(0.048, 0.096)</td>
<td>30.45</td>
</tr>
<tr>
<td></td>
<td>(29.0)</td>
</tr>
<tr>
<td>(0.096, 0.192)</td>
<td>28.20</td>
</tr>
<tr>
<td></td>
<td>(26.7)</td>
</tr>
<tr>
<td>(0.192, 0.384)</td>
<td>25.48</td>
</tr>
<tr>
<td></td>
<td>(24.9)</td>
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<tr>
<td>(0.384, 0.768)</td>
<td>22.87</td>
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<td></td>
<td>(22.6)</td>
</tr>
<tr>
<td>(0.768, 1.536)</td>
<td>21.01</td>
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<tr>
<td></td>
<td>(21.4)</td>
</tr>
<tr>
<td>(1.536, 3.072)</td>
<td>20.83</td>
</tr>
<tr>
<td></td>
<td>(20.9)</td>
</tr>
<tr>
<td>(3.072, 6.144)</td>
<td>23.65</td>
</tr>
<tr>
<td></td>
<td>(23.5)</td>
</tr>
</tbody>
</table>

( ) Experimental values, Ref. 31.
The effect of temperature on the conductive properties of shaly sands has been experimentally studied by Waxman and Thomas (29) and by Kern et al. (36). The experimental data obtained by Waxman and Thomas enabled the authors to estimate the effect of temperature on the temperature coefficient of shaly sands. In addition, the variation of the equivalent counterion conductivity $B$ with temperature was determined, as discussed in Chapter III. The same experimental data was used by Clavier et al. (35) to analyze the effect of temperature on parameters appearing in the D-W model.

The practical application of the conductivity model developed in this study requires the analysis of the effect of temperature on the parameters of interest. For that purpose, Dr. M.H. Waxman made available the original experimental data used in refs. (29) and (35). The analysis that follows is based only on this information.

VII.1. Description of the Available Experimental Data

The data provided by Dr. Waxman consists of detailed conductance information for 9 shaly sand cores obtained at seven temperatures and five salinities. The temperatures considered in the experiments were 22, 50, 80, 110, 140, 170, and 200°C. Conductance measurements for each temperature were obtained at concentrations of 0.09, 0.26, 0.858, 1.76, and 4.74 m NaCl. These concentration levels were chosen to provide good definition of the linear portion of the $C_o - C_w$ plot. From that
information, values for $Q_v$ and Formation factor can be obtained for each core.

In addition to core conductivities, Waxman and Thomas also measured the variation with temperature of the brine conductivities. All conductance measurements were obtained with the samples subjected to an effective stress of 1000 psig. Only NaCl solutions were utilized to saturate the cores.

In this study, the provided data at 22°C was used to estimate $Q_v$ and $F_e$ values for each sample by following the procedures outlined in Section IV.3.c. The calculation of these parameters requires the evaluation of the conductivity of the neutral point $C_wN$ at 22°C. It was assumed that this value can be expressed in terms of the known $\lambda_{max}^{25}$ from eq. (4.43) as:

$$C_{wN}^{22} = \frac{a \lambda_{max}^{25}}{0.28} = a \text{ (7.1); (mho/m)}$$

where $a$ is a correction factor estimated in the manner discussed hereafter.

Brine conductivities were calculated for each of the five salinities at 25°C and compared to those measured at 22°C. It was found that the ratio $C_w^{22}/C_w^{25}$ is, for the range considered, essentially independent of salinity and equal to 0.953. Therefore, the conductivity $C_wN$ at 22°C is estimated as:

$$C_{wN}^{22} = 15.83 \text{ (mho/m)}$$

From the knowledge of $C_{wN}^{22}$, reference values of $Q_v$ and $F_e$ were calculated and are presented in Table VII.a. for the samples used in the study.
<table>
<thead>
<tr>
<th>CORE NUM.</th>
<th>POROSITY (Z%)</th>
<th>Fe (meq/cc)</th>
<th>Qv (meq/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>29.3</td>
<td>8.12</td>
<td>0.098</td>
</tr>
<tr>
<td>2</td>
<td>25.6</td>
<td>12.43</td>
<td>0.101</td>
</tr>
<tr>
<td>3</td>
<td>17.7</td>
<td>23.20</td>
<td>0.145</td>
</tr>
<tr>
<td>4</td>
<td>15.4</td>
<td>33.86</td>
<td>0.256</td>
</tr>
<tr>
<td>5</td>
<td>23.5</td>
<td>22.36</td>
<td>0.358</td>
</tr>
<tr>
<td>6</td>
<td>17.9</td>
<td>49.66</td>
<td>0.508</td>
</tr>
<tr>
<td>7</td>
<td>19.5</td>
<td>29.31</td>
<td>0.739</td>
</tr>
<tr>
<td>8</td>
<td>25.6</td>
<td>18.24</td>
<td>0.690</td>
</tr>
<tr>
<td>9</td>
<td>17.9</td>
<td>54.98</td>
<td>0.718</td>
</tr>
</tbody>
</table>
VII.2. **Effect of Temperature on the Parameters Required by the New Model**

The practical use of the new conductivity model can be extended to temperatures higher than 25°C if the effect of temperature on the basic parameters can be predicted.

a) **Variation of Brine Conductivity, \( C_w \)**

From all the parameters required by the new model, \( C_w \) is the obvious one expected to vary with temperature. The effect of temperature on \( C_w \) was empirically determined from the experimental data. This effect is expressed as:

\[
\frac{C_w^T}{C_w^{25}} = \left( \frac{T}{25} \right)^b \quad T \geq 25°C
\]  

(7.3)

where \( C_w^T \) is the brine conductivity at a temperature \( T \). \( T \) is expressed in °C. Eq. (7.3) is of practical utility since accurate values of \( C_w \) at 25°C for NaCl solutions can be calculated or are available from accurate experimental data (42).

The exponent \( b \) in eq. (7.3) was found to be related to the NaCl concentration in molarity units, \( n \), by:

\[
\ln \left( \frac{b}{\sqrt{n}} \right) = -0.388 - 4.96 \times 10^{-1} \ln(n) +
\]

\[+ 8.39 \times 10^{-3} \ln^2(n) \]  

(7.4)

It must be stated that when temperature condition exceed that of room condition it is more convenient to express concentrations in the molal scale, rather than in molar units. However, to facilitate automated calculations, the molar scale is
retained throughout this Chapter. It is therefore implied that the pressure conditions in the system must be such that changes in solution density are negligible.

b) The Effect of Temperature on the Limiting Concentration $n_{lim}$ and the Unit Fractional Volume $\psi$

Clavier et al. (35), as well as Kern et al. (36) observed small variations in the slope of the $C_0 - C_w$ plots for temperatures higher than 25°C. Since $F_0$ and $Q_v$ are assumed independent of temperature in the D-W model, Clavier et al. concluded from both theoretical reasoning and from manipulations of the experimental data that the unit volume $v^H_Q$ assigned to the bound water decreases as temperature increases. This behavior is attributed to a reduction of the thickness hence the volume of the double layer.

Under the new model, the fractional volume occupied by the double layer can be expressed in general terms as:

$$ f_{DL} = \alpha \psi Q_v $$

(7.5)

where, as with the D-W model, $\psi$ is defined as the fractional double layer volume per unit $Q_v$; (cc/meq). The parameter $\psi$ is conceptually identical to $v^H_Q$ in the D-W model (35) and is related to the distance of closest approach by:

$$ \psi = \frac{A_v}{B_{o,n_{lim}}} $$

(7.6)

where $1/B_{o,n_{lim}}$ equals the distance $x_H$ as inferred from eq. (4.20) and $A_v$ is a constant that relates the specific area of clays to the specific cation exchange capacity (35).

The magnitude of the coefficient $B_{o}$ increases with temperature, according to eq. (4.19). However, the change in $B_{o}$
from 22°C to 200°C, as predicted by eq. (4.19) does not explain by itself the decrease in $v^H_Q$ determined by Clavier et al. (29) if $n_{lim}$ remains constant. Although eq. (4.19) is being used beyond its apparent limits of applicability, it is also reasonable to suspect that at temperatures higher than 25°C, the concentration $n_{lim}$ at which the linear conductive behavior first appears is shifted towards a higher salinity.

In order to test this assumption, conductivity plots for each core at each temperature were prepared. For each plot, the best straight line connecting the three highest salinity points was obtained and plotted. Then, a smooth curve was drawn connecting the two lowest salinity points, and the conductivity $C_{w1}$ at which both lines intersect was recorded. The concentration at this intersection point was calculated for each core and average values for each temperature were obtained. Despite some dispersion probably caused by the relatively simplistic approach used in the analysis, a definite increase in the limiting concentration $n_{lim}$ was observed for increasing temperature.

A relationship between both parameters was obtained as:

$$n_{lim}^T = 0.242 + 4.95 \times 10^{-2} \ln (T/25) \quad (7.7)$$

The regression analysis procedure was restricted so that eq. (7.7) yields the proper value previously determined at 25°C (Sec. IV.1.b).

From eqs. (7.7), (7.6), and (4.19), values of $\psi^T$ were calculated and used to establish a practical relationship given by:

$$\psi^T = 0.28 - 3.44 \times 10^{-2} \ln (T/25) \quad (7.8)$$
Again the regression process was restricted as to obtain the value assumed correct at 25°C. Eq. (7.8) indicates that the minimum thickness of the double layer is compressed as temperature increases.

c) Variation of the Expansion Factor $\alpha$ with Temperature

In analogy with its definition at room conditions, the double layer expansion factor can be expressed for a temperature $T$ as:

$$\alpha_T = \sqrt{n_{\text{lim}}^T / n}$$  \hspace{1cm} (7.9)

An interesting result of the increase of $n_{\text{lim}}^T$ with temperature can be inferred from eqs. (7.7) and (7.9). At 25°C, a salinity $m=0.26$ NaCl (0.258 molar) corresponds to the linear portion of the $C_o - C_w$ plot. However, as temperature increases beyond 35°C, the same data point will fall, according to the theory, on the curved portion of the conductivity plot. Therefore, the theory can be tested to predict core conductivities in the curved portion at this salinity in addition to 0.09 m NaCl for $T > 25°C$.

In general, for concentrations less than 0.242 molar, it can be inferred that:

$$\alpha_T > \alpha_{25}$$ \hspace{1cm} (7.10)

and therefore the double layer expands faster as temperature increases. This effect suggests that the double layer solution experiences thermal expansion.
d) The Effect of Temperature on $\lambda_{\text{max}}^+$ and $C_{wN}$

The variation of $\lambda_{\text{max}}^+$ with temperature is identical to that determined for $C_w$, as a result of considering the properties of the double layer solution identical to those of an equivalent NaCl solution. Recalling that $\lambda_{\text{max}}^+$ at 25°C is defined by an equivalent concentration $n_{eq} = 5.416$ NaCl (saturation) from (7.3) and (7.4), the maximum equivalent counterion conductivity at any temperature $25 < T < 200^\circ C$ is proposed as:

$$\lambda_{\text{max}}^+ = \lambda_{\text{max}}^+ \left( \frac{T}{25} \right)^{0.7}$$

or

$$\lambda_{\text{max}}^+ = 4.65 \left( \frac{T}{25} \right)^{0.7} \quad (7.11)$$

0.7 is the value of the exponent $b$ at saturation condition.

For comparison purposes, $\lambda_{\text{max}}^+$ calculated from eq. (7.11) are compared in Table VII.b with $B_{\text{max}}^+$ values derived by Waxman and Thomas (29) for the W-S model and $g$ values derived by Clavier et al. (35) for the D-W model.

The variation of $C_{wN}$ with temperature can now be predicted. By definition:

$$C_{wN}^T = \frac{\lambda_{\text{max}}^T}{\psi_T} \quad (7.12)$$

From (7.11) and (7.8):

$$C_{wN}^T = \frac{4.65(T/25)^{0.7}}{0.28 - 3.44 \times 10^{-2} \ln(T/25)} \quad (7.13)$$
<table>
<thead>
<tr>
<th>Parameter (mho/m)(eq/cc)</th>
<th>25</th>
<th>50</th>
<th>80</th>
<th>110</th>
<th>140</th>
<th>170</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_T^{max}$</td>
<td>3.83</td>
<td>9.40</td>
<td>14.0</td>
<td>17.7</td>
<td>21.0</td>
<td>25.0</td>
<td>28.0</td>
</tr>
<tr>
<td>(Ref. 29)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta_T$</td>
<td>2.25</td>
<td>3.93</td>
<td>5.95</td>
<td>7.96</td>
<td>9.98</td>
<td>12.0</td>
<td>14.0</td>
</tr>
<tr>
<td>(Ref. 35)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda_T^{max}$</td>
<td>4.65</td>
<td>7.55</td>
<td>10.50</td>
<td>13.12</td>
<td>15.53</td>
<td>17.79</td>
<td>19.93</td>
</tr>
</tbody>
</table>
e) Expected Variation of $\lambda^+$ with Temperature at Low Salinities

The possible effect of temperature on the equivalent counterion conductivities at low salinities of the equilibrating brine can be analyzed in terms of the variation of the parameters required for its calculation.

The concentration $n_{eq}$ of the equivalent NaCl solution used to represent the electrical properties of the double layer fluid can be expressed, in general, from eq. (4.58) as:

$$n_{eq} = \frac{1}{\psi^T \left[ \alpha^+ - \delta^T \right]^2} \quad (7.14)$$

The constant $\delta^T$ in eq. (7.14) is introduced in order to meet the basic assumption that $n_{eq} = 5.416$ molar NaCl when $\alpha$ equals unity. The variation of $\delta^T$ with temperature can be inferred from the variation of $\psi^T$ as:

$$\delta^T = 1 - 0.4297 \sqrt{1/\psi^T} \quad (7.15)$$

The constant $\delta^T$ takes into account changes in the ion size term $B_o (\bar{a}_1 - \bar{a}_2)$ of eq. (4.35). The decrease of the magnitude of $\delta^T$ given by eq. (7.15) also suggest the thermal expansion of the double layer.

From (7.14), (7.15), and (7.8) the concentration $n_{eq}$ is predicted to increase with temperature. This slight increase in $n_{eq}$ results in a decrease of the equivalent conductivity $\Lambda'_\text{NaCl}$.

From eq. (4.42), the general behavior of $\lambda'$ with temperature is given as:

$$\lambda'^+ = \frac{\Lambda'_\text{NaCl}}{\frac{T}{g}} \quad (7.15)$$
where:

\[ f^T_g = (\alpha^T)^{1/n^T} \quad (7.16) \]

For a given salinity, equivalent counterion conductivities are expected to decrease at a faster rate than it would be predicted at 25°C.

The magnitude of the exponent \( n \) was found in Chapter IV to be related to both \( \alpha \) and \( Q_v \). This relationship was observed to hold true in Chapter V when the presence of hydrocarbons was introduced in the analysis. Under these conditions and according to the model, the formation just appears shallier than it really is. A similar behavior should be encountered for \( T > 25°C \) when the increase in the expansion factor is considered in the term \( (\alpha Q_v) \) in eq. (4.47) and probably the same model for \( n \) should apply at all temperatures.

As an initial assumption, it is considered that eq. (4.47) holds true for \( T > 25°C \), provided that the appropriate \( \alpha^T \) value is used in the calculations. This aspect of the theory can be evaluated later when predicting core conductivities at low salinities.

Expressing \( n \) as a function of \( f_{DL} \), a general model for the exponent is proposed as:

\[ n^T = h_0^T + h_1^T f_{DL}^T + h_2^T (f_{DL}^T)^2 \quad (7.17) \]

in analogy with eq. (4.48)

The magnitudes of the coefficients are given from (4.47) and (4.48) as:

\[ h_0^T = 0.6696 = \text{constant} \quad (7.18a) \]
\[ h_1^T = \frac{3.303 \times 10^{-1}}{\psi^T} \]  
\[ h_2^T = -\frac{1.13 \times 10^{-2}}{(\psi^T)^2} \]  

VII.3 Calculation of Petrophysical Parameters

The variation of both \( C_{WN} \) and the minimum \( f_{DL} \) with temperature suggests the possibility that both the formation factor, \( F_e \), and the effective counterion concentration \( Q_v \) may also vary as temperature increases. In addition, thermal expansion of the rock matrix and clay minerals may result in a slight reduction of the porosity of the core causing changes in \( F_e \) an \( Q_v \).

The estimation of \( F_e \) was carried for each core at each temperature, from the knowledge of \( C_{WN} \), following the procedure discussed in section IV.3.c. The calculated \( F_e \) values are shown in Table VII.c.

\( Q_v \) values were also calculated at each temperature for each core from the slope of the observed straight line and the appropriate \( F_e \) and \( \psi^T \) values. The calculated \( Q_v \) values are presented in Table VII.d.

A review of table VII.c reveals that, for practical purposes, the magnitude of \( F_e \) remains constant and independent of \( Q_v \). The independent nature of \( F_e \) is a requirement of the theory. On the other hand, Table VII.d. reveals that the calculated \( Q_v \) values increase in general as temperature increases. This effect suggests the possible reduction in the porosity of the core. The apparent decrease in porosity, however, is not reflected on \( F_e \). This suggests that the presence of a highly conductive double layer effectively facilitates the travel of the ions by allowing for easier tortuosity paths\(^{(62)}\). This situation appears to be more evident for core \#9.
TABLE VII.c
VARIATION OF $F_e$ WITH TEMPERATURE

<table>
<thead>
<tr>
<th>CORE NUM.</th>
<th>22</th>
<th>50</th>
<th>80</th>
<th>100</th>
<th>140</th>
<th>170</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.12</td>
<td>8.36</td>
<td>8.31</td>
<td>8.32</td>
<td>8.35</td>
<td>8.34</td>
<td>8.42</td>
</tr>
<tr>
<td>2</td>
<td>12.43</td>
<td>12.99</td>
<td>12.74</td>
<td>12.75</td>
<td>12.85</td>
<td>12.81</td>
<td>12.72</td>
</tr>
<tr>
<td>3</td>
<td>23.2</td>
<td>23.46</td>
<td>22.99</td>
<td>23.32</td>
<td>23.60</td>
<td>23.73</td>
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</tr>
<tr>
<td>4</td>
<td>33.86</td>
<td>33.88</td>
<td>33.29</td>
<td>32.58</td>
<td>32.54</td>
<td>33.74</td>
<td>32.91</td>
</tr>
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<td>49.66</td>
<td>50.14</td>
<td>49.14</td>
<td>46.82</td>
<td>46.24</td>
<td>45.32</td>
<td>44.93</td>
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<td>29.31</td>
<td>29.25</td>
<td>28.09</td>
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<td>26.98</td>
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<td>8</td>
<td>18.24</td>
<td>18.29</td>
<td>17.66</td>
<td>17.55</td>
<td>17.04</td>
<td>17.11</td>
<td>17.00</td>
</tr>
<tr>
<td>9</td>
<td>54.98</td>
<td>53.39</td>
<td>50.13</td>
<td>47.88</td>
<td>46.86</td>
<td>46.6</td>
<td>46.28</td>
</tr>
</tbody>
</table>
**TABLE VII.d**

VARIATION OF $Q_V$ WITH TEMPERATURE

<table>
<thead>
<tr>
<th>CORE NUM.</th>
<th>TEMPERATURE, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>22</td>
</tr>
<tr>
<td>1</td>
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<tr>
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<td>0.101</td>
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<tr>
<td>3</td>
<td>0.145</td>
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<tr>
<td>4</td>
<td>0.256</td>
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<tr>
<td>5</td>
<td>0.358</td>
</tr>
<tr>
<td>6</td>
<td>0.508</td>
</tr>
<tr>
<td>7</td>
<td>0.739</td>
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<tr>
<td>8</td>
<td>0.690</td>
</tr>
<tr>
<td>9</td>
<td>0.718</td>
</tr>
</tbody>
</table>
In order to make appropriate tests of the theory, the actual values of \( F_e \) and specially \( Q_v \) will be used in the prediction of core conductivities.

VII.4 Test of the Theory

As in the case of room temperature conditions, the proposed theory can be tested by predicting core conductivities at salinity conditions for which the curved portion of the \( C_o - C_w \) plot is observed for the temperatures of interest.

a) Calculation of Core Conductivities at \( m = 0.26 \text{ NaCl} \)

As already discussed, the theory predicts that conductivities at \( m = 0.26 \) fall in the curved portion of the plot for temperatures higher than 35°C. Conductivities were calculated for all 9 cores in the range \( 50 \leq T \leq 200^\circ\text{C} \). The overall result of the calculations is shown in Fig. 7.1. It is evident from this figure that the proposed theory allows the calculation of accurate core conductivities. The overall average error (-2.95%) and the standard error (±0.062 mho/m) can be considered highly acceptable. It is also implied that the assumptions made regarding the magnitude of the exponent \( \eta \) are valid, for practical purposes throughout the wide temperature range considered.

b) Prediction of Core Conductivities at \( m = 0.09 \text{ NaCl} \)

The theory allows the calculation of core conductivities for all cores from temperatures ranging from 22°C up to 200°C at this particular salinity. The result of the calculations is presented in fig. (7.2) for \( 50 \leq T \leq 200^\circ\text{C} \). Individual results for each
Figure 7.1 Comparison Between Measured and Calculated Core Conductivities at m = 0.26 NaCl

N = 54 POINTS
E = -2.95 PERCENT
S = 0.062 MHO/M

MOALITY=0.26 NaCL
TEMP. = 50-200 (C)
Figure 7.2 Comparison Between Measured and Calculated Core Conductivities at m = 0.09 NaCl

N = 51 POINTS
E = -19.78 PERCENT
S = 0.077 MHO/M

MOLALITY = 0.09 NaCl
TEMP. = 50-200 (C)
core, are presented in figs. (7.3) through (7.11). It is evident from these figures that for certain cores (core # 1, 8) large discrepancies exist between theory and measurements at this particular salinity. However, it can be appreciated from these figures that the new model produces consistent results, as the calculated magnitudes all lie in line parallel to the equal value line, suggesting a consistent error.

Moreover, it is evident that for certain cores, such as 4 and 6, the agreement between theory and experimental is particularly good at all temperatures. Therefore, observed discrepancies on other cores can not be attributed to the theory. As a consequence, it is inferred that there exists a measurement error. As already discussed in Chapter VI, obtaining reliable experimental data on shaly sands at low salinities is difficult. Sample cracking due to clay swelling may occur. To prove that the discrepancy is due to measurement errors in the provided data, a correction factor was introduced. The correction factor $\omega$ is expressed as:

$$\omega = \frac{C_{o,m}}{C_{o,c}} \text{ at } 22^\circ C$$  \hspace{1cm} (7.20)

where $(C_{o,m})$ is the measured conductivity, and $(C_{o,c})$ is the calculated one from the new model. This correction factor was applied to the calculated conductivities for $T \geq 50^\circ C$. Corrected calculated values are compared to the experimental data in fig. 7.12. The improvement in the results is visually obvious, and is supported by the low statistical values obtained.

In conclusion, the proposed theory for the new conductivity model has been satisfactorily tested for temperatures commonly
encountered in Well Logging. Its incorporation in shaly sand interpretation is warranted. Such possibilities are explored in Chapters VIII and IX.
Figure 7.3 Comparison Between Measured and Calculated Core Conductivities, Core #1
Figure 7.4 Comparison Between Measured and Calculated Core Conductivities, Core #2
Figure 7.5 Comparison Between Measured and Calculated Core Conductivities, Core #3

N = 7 POINTS
E = -20.79 PERCENT
S = 0.030 Ω/M

MOlALITY=0.09 NACl
CORE NUM. 3
POROSITY = 0.177
Figure 7.6 Comparison Between Measured and Calculated Core Conductivities, Core #4

N = 7 POINTS
E = -3.10 PERCENT
S = 0.010 MHØ/M

MOLALITY = 0.09 NaCl
CORE NUM. 4
POROSITY = 0.154
Figure 7.7 Comparison Between Measured and Calculated Core Conductivities, Core #5

N = 7 POINTS
E = -24.79 PERCENT
S = 0.063 MHO/M

MOLALITY = 0.09 NaCl
CORE NUM. 5
POROSITY = 0.235
Figure 7.8 Comparison Between Measured and Calculated Core Conductivities, Core #6
Figure 7.9 Comparison Between Measured and Calculated Core Conductivities, Core #7
Figure 7.10 Comparison Between Measured and Calculated Core Conductivities, Core #8
Figure 7.11 Comparison Between Measured and Calculated Core Conductivities, Core #9

- \( N = 7 \) POINTS
- \( E = -22.89 \) PERCENT
- \( S = 0.045 \) MHO/M

MOLALITY = 0.09 NAACL
CORE NUM. 9
POROSITY = 0.179
Figure 7.12 Comparison Between Experimental and Calculated Core Conductivities. Correction Factor $\omega$ Included.

- **N = 51** POINTS
- **E = 0.22** PERCENT
- **S = 0.027** MHO/M

**MOLALITY = 0.09** NAACL
TEMP. = 50-200 (C)
CHAPTER VIII

USE OF THE NEW MODEL TO ENHANCE THE INTERPRETATION OF THE SP LOG

The SP log constitutes an important source of information about the salinity and thus resistivity of formation waters, $R_w$. Unfortunately, its use has suffered from the fact that the most common model for SP log interpretation results in $R_w$ values that usually differ from those obtained from reliable water samples.

VIII.1 The Origin of the SP

The SP deflection recorded in front of a permeable formation arises from current flow in the borehole, as a result of electromotive forces generated in the formations. These electromotive forces, illustrated in fig. 8.1, are electrochemical and electrokinetic in nature.

In fig. 8.1, $E_1$ and $E_4$ represent the electrokinetic component of the SP. $E_1$ and $E_4$, also known as streaming potentials, are generated by the flow of mud filtrate through mud cakes and through shales. On the other hand, the electrochemical component of the SP is the result of diffusion membrane potentials generated across the adjacent shale, $E_3$, and in the permeable sand at the diffusion boundary between formation water and mud filtrate, $E_2$.

There are indications that under actual field conditions the electrochemical component of the SP far exceeds the electrokinetic component. As a consequence, the SP phenomena observed in wells has been usually treated as one of electrochemical nature.
Fig. 8.1 Components of the SP Deflection (After Smits, Ref. 31)
Under these assumptions, the magnitude of the SP deflection will be largely determined by the magnitudes of the membrane potentials across the adjacent shales ($\mathbf{E}_3$) and in the permeable sand ($\mathbf{E}_2$). More specifically, the recorded SP deflection is given by the difference between $\mathbf{E}_3$ and $\mathbf{E}_2$:

$$\text{SP} = \mathbf{E}_3 - \mathbf{E}_2 \quad (8.1)$$

VIII.2 Effect of Shaliness on the SP Deflection

Mounce and Rust$^{(3)}$ experimentally showed that the potential generated across a shale, separating two saline solutions of different concentration, is much larger than that observed for the case of a clean formation. Wyllie$^{(4)}$ took into account this fact when deriving the basic SP model given by eq. (1.8). This author concluded that $\mathbf{E}_3$ might represent between 80 to 90% of the electrochemical component of the SP when the permeable formation is clean. However, it has long been recognized that the SP deflection observed opposite a shaly sand is lower than that otherwise recorded in front of a clean rock$^{(6)}$. It follows then that the magnitude of the diffusion process in shaly formations is considerably altered. It is apparent from eq. (8.1) that, other factors being equal, the magnitude of $\mathbf{E}_2$ increases for a shaly sand as compared to a clean formation. It has been determined that the shalier the sand, the greater the magnitude of the membrane potential$^{(19),(31),(32)}$, $\mathbf{E}_2$.

It is clear then that the use of eq. (1.8) for estimating the magnitude of $\mathbf{E}_2$ in shaly formations will yield erroneous results, even if the adjacent shales can be considered perfect membranes. From the evidence presented in Chapter VI the perfect membrane behavior is reached when relatively dilute solutions are involved in the generation
of the membrane potential and/or when the $Q_v$ of the porous medium is high. From the experimental data obtained by Smits (31) it is apparent that shales may not always behave as perfect cationic membranes.

VIII.3 Corrections to the Basic SP Model

It may not be surprising that the indiscriminated application of eq. (1.8) for SP log interpretation purposes has traditionally resulted, more often than not, in unreliable $R_w$ values (53).

As with the conductivity models for shaly sands, the basic SP model has been the subject of modifications, most of them empirical and of local application. Among such modifications, those involving the determination of the appropriate $K'$ values, as discussed in Chapter I, have been successfully used in local application. However, these methods require the use of reliable water samples which are not always available.

Aside from those empirical corrections, the assumptions implicit in the basic SP model (4):

$$SP = -K \log \frac{a_w}{a_{mf}}$$

have been suspected as potential sources of error (53,54). The basic model was derived by assuming (4):

1) Shales are perfect cationic membranes.
2) The formation is clean
3) Transport numbers do not vary with temperature.

A fourth potential source of error was introduced when Wyllie replaced the activity ratio $a_w/a_{mf}$ by the resistivity ratio $R_{mf}/R_w$, an assumption valid only for dilute solutions.
Gondouin, Tixier, and Simard\(^{(54)}\) conducted experimental work to check the validity of the first and fourth assumptions. Regarding the role of adjacent shales, the authors' main concern was to evaluate the ideality of the shale behavior in tests designed to simulate more accurately the conditions present in the well. The tests were conducted on only one type of shale varying three important parameters which are the confining pressure, temperature and solution concentration. Their results show that apparently the ideal shale behavior trend is more likely to be reached for high confining pressures and higher temperatures. From the reported tests, the ratio of the measured $K$ to the theoretical $K$ revealed that (for the studied shale sample) reaches an apparent maximum value of 0.7. This behavior was not considered, evidently, as fully ideal but based on the fact that high salinity solutions were used and on the observed trend, it was concluded that the shales will behave more as perfect membranes under field conditions, a conclusion that was reinforced in the paper by mentioning the "remarkable consistency of the shale line over wide depth intervals in sand - shale series".

Gondouin et al.\(^{(54)}\), working in the same study on the activity - resistivity relationship, introduced the concept of "equivalent" or "effective" water resistivity, $(R_w)_{e}$. They showed that, as illustrated in Figure 8.2, when the activity of the $Na^+$ ion and the resistivity of a pure NaCl solution are plotted on log-log paper, a linear relation exists for resistivity values greater than 0.1 ohm-meters. For lower resistivities, the relationship loses its linearity.
Figure 8.2 Relationship Between $a_{Na}$ and Resistivity of NaCl Solutions

(After Gondouin, et al. 54)
Equivalent resistivity was defined as the extrapolation of the straight portion of the curve. So, \((R_w)_e\) is therefore proportional to the reciprocal of the activity:

\[
(R_w)_e = \frac{A}{a_w}
\]  (8.3)

where \(A\) is the proportionality factor chosen such that \((R_w)_e = R_w\) for pure NaCl solutions of resistivities higher than about 0.3 ohm-meters. By this definition, Equation (8.3) becomes:

\[
SP = -K \log \left( \frac{(R_{mf})_e}{(R_w)_e} \right)
\]  (8.4)

In order to account for the differences between \(R_w\) and \((R_w)_e\) at \(R_w\) values lower than 0.1 ohm-meters the authors presented the experimental plot shown of Figure 8.3. This figure shows the relationship between effective and true resistivities (for either mud filtrate or formation water) as a function of formation temperature.

Equation (8.4) constitutes the basis of the extensively used method, called the "Schlumberger Method" to estimate \(R_w\) from the SP log(5).

The revision of the assumptions in the basic SP model was recently approached by Silva and Bassiouni\(^{(53, 55)}\). Working with reliable water samples obtained from the Gulf Coast area\(^{(56)}\), the authors found that the use of eq. (1.8) results in the same \(R_w\) values than those obtained from eq. (8.4) for the area under study. Therefore, discrepancies between calculated and measured \(R_w\) values are due exclusively to the idealistic conception of the measurement environment. Silva and Bassiouni decided to explore the possibility of relating the reduction in the SP deflection to some electrical property of the shale. It was found that a strong correlation exists between the observed SP, the
Figure 8.3 Relationship Between $R_w$ and $(R_w)_e$ (After Gondouin, et al.\textsuperscript{54})
ratio $R_{mf}/R_w$ and the parameter $R_{sh}/R_{mf}$. The correlation, presented in fig. 8.4, has been successfully applied in the Gulf Coast area\(^{55,57}\) as a means to obtain more accurate $R_w$ values. The correlation was also found useful to derive accurate values of the constant $K'$.

VIII.4 Establishment of a General SP Model

The new conductivity model can be used to establish a theoretical model for the SP. When electrokinetic effects are negligible, the SP deflection recorded in front of a permeable formation corresponds to the electrochemical potential given by the difference of the membrane potentials of shales and adjacent sands\(^{31}\). From eq. (8.1):

$$SP = E^*_{m_{sh}} - E^*_{m_{ss}}$$

(8.5)

where $E^*_{m_{sh}}$ and $E^*_{m_{ss}}$ are the membrane potentials across adjacent shale and shaly sand respectively. From the expression for the membrane potentials, eq. (6.33):

$$E^*_{m_{sh}} = \int \frac{m_2 - \tau_{Na}^* \frac{dE^*}{dm}}{m_1 - \frac{\tau_{Na}^*}{h_f}} \, dm$$

(8.6)

and:

$$E^*_{m_{ss}} = \int \frac{m_2 - \tau_{Na}^* \frac{dE^*}{dm}}{m_1 - \frac{\tau_{Na}^*}{h_f}} \, dm$$

(8.7)

Replacing the magnitude of the junction potential $E_t^*$, (8.7), and (8.6) in (8.5):

$$SP = -\frac{2RT}{F} \int m_1 \frac{m_2}{m_1} (\tau_{Na}^* \tau_{SH}^* - \tau_{SS}^* \tau_{Na}^*) \, dln (\eta \gamma)$$

(8.8)
Figure 8.4  Empirical Chart for SP Log Interpretation Based on Adjacent Shale Resistivity (Ref. 55).
Eq. (8.8) represents the model for the SP in which shaliness and salinity effects are considered. The magnitudes of $\tau$ and $T^+_{Na}$ are given by eqs. (6.32) and (6.18) using the appropriate $Q_v$ values.

Based on a similar expression, Smits (31) obtained SP (31) log interpretation charts at 25°C. These charts show the magnitude of the SP as a function of salinity, and the $Q_v$ values for shale and shaly sand. In order to make a more rigorous analysis, the effect of temperature is considered in this work.

VIII.5 Effect of Temperature on the SP Model

Temperature affects the magnitude of the SP by affecting $\tau$, $T^+_{Na}$, and $\gamma\tau$. The effect on $\tau$ and $T^+_{Na}$ is controlled by the variation of $t^h_{Na}$, $\lambda^+$, $\psi$, $C_w$, and $C_{wN}$. Only the effect of temperature on $\gamma\tau$, $t^h_{Na}$, and $\tau$ will be discussed in this section, as the variation of the remaining parameters has already been covered in Chapter VII.

a) Variation of Transport Numbers for NaCl Solutions with Temperature

Accurate Hittorf transport number data is available only at 25°C (49). However, it has been shown (31), (50) that the Stokes equation (25) for the transport number:

$$\tau_1 = \frac{\lambda^0 - \frac{1}{2} B_2 \sqrt{n/(1+B^2/n)}}{\lambda^0 - B_2 \sqrt{n/(1+B^2/n)}}$$

(6.23)

can be used as a reasonable approximation. In addition, the effect of temperature can be considered since the parameters $\lambda^0$, $\lambda^+$, $B$, and $B_2$ are all temperature dependent.
The variation of the parameters $B_1$, $B_2$, $\lambda^0$ and $\Lambda^0$ with temperature was obtained from regression analysis on published data as:

$$B = 0.3248 + 1.5108 \times 10^{-4} (T) + 8.9354 \times 10^{-7} (T^2) - 8.5878 \times 10^{-11} (T^3); \ (25 \leq T \leq 100°C) \quad (8.9)$$

$$B_2 = 29.5318 + 1.0657 (T) + 7.3838 \times 10^{-3} (T^2) - 7.7368 \times 10^{-6} (T^3); \ (25 \leq T \leq 100°C) \quad (8.10)$$

$$\lambda^0_{NaCl} = 126.45 + 3.3895 (T-25) - 5.298 \times 10^{-3} (T-25)^2; \quad (25 \leq T \leq 200°C) \quad (8.11)$$

$$\lambda^0_{Na} = 50.1 + 1.13716 (T-25) - 1.4169 \times 10^{-3} (T-25)^2; \quad (25 \leq T \leq 100°C) \quad (8.12)$$

Eqs. (8.9) through (8.12) were used in eq. (6.23) to prepare the plot shown in fig. 8.5 which illustrates the variation of the $Na^+$ transport numbers with temperature as a function of the square root of the concentration in molality units.

b) Variation of Activity Coefficients

Besides being concentration-dependent, mean activity coefficients are also affected by both temperature and pressure.

b.1) The Effect of Pressure on the Activity Coefficient

The basic equations describing the effect of pressure on $\gamma^\pm$ are:

$$\left( \frac{\partial \ln \gamma^\pm}{\partial P} \right)_T = \frac{\left( \bar{V} - \bar{V}^0 \right)_P}{\nu RT} \quad (8.13)$$
Figure 8.5 Theoretical Variation of Na Transport Numbers with Both Temperature and NaCl Concentration
\[
\frac{\partial (\bar{V} - \bar{V}_0)}{\partial P} = - (\bar{K} - \bar{K}_0) \tag{8.14}
\]

where:

\(\bar{V}, \bar{V}_0\) = Partial molal volumes of the electrolyte at the concentration of the solution and infinite dilution, respectively,

\(\bar{K}, \bar{K}_0\) = Partial molal compressibility of the electrolyte at the concentration of the solution and infinite dilution, respectively,

\(P\) = Applied or gauge pressure (at \(P = 0\), the absolute pressure is 1 atm. or 1.01325 bars),

\(T\) = Absolute temperature, and

\(1/\nu RT\) = Thermodynamic constant = \(2.017 \times 10^{-5}\) for 1-1 electrolytes at 25°C \(^{(50)}\)

From eqs. (8.13) and (8.14), Millero \(^{(50)}\) has developed the expression:

\[
\ln \left( \frac{\gamma^P}{\gamma^0} \right) = 2.017 \times 10^{-5} \left[ (\bar{V} - \bar{V}_0)P - (\bar{K} - \bar{K}_0) \frac{P^2}{2} \right] \tag{8.15}
\]

where:

\(\gamma^P\) = Mean activity coefficient at 25°C and pressure \(P\),

and

\(\gamma^0\) = Mean activity coefficient at 25°C and zero gauge pressure as defined by eqns. (6.29) and (6.30).

The terms \((\bar{V} - \bar{V}_0)\) and \((\bar{K} - \bar{K}_0)\) are taken at zero gauge pressure and are empirically related to the NaCl molal concentration by the expressions \(^{(50)}\):

\[
(\bar{V} - \bar{V}_0) = 2.623 m^3 + 0.305 m - 0.07 m^{3/2} \tag{8.16}
\]

\[
10^6 (\bar{K} - \bar{K}_0) = 8.09 m^2 + 6.66 m - 1.63 m^{3/2} \tag{8.17}
\]
Values of the activity coefficient ratio were calculated from eqs. (6.29), (6.30), and (8.15) through (8.17) for NaCl concentrations ranging from 0.01 molal up to saturation at several pressures and are shown in fig. 8.6.

Fig. 8.6 reveals two interesting features. First, the ratio \( \frac{\gamma_f^P}{\gamma_f^0} \) is nearly a linear function of \( \sqrt{m} \) for any pressure. Also, it can be noticed that at 25°C, the change in values is relatively small, even for high salinities and moderately high pressures.

b.2) The Effect of Temperature on the Activity Coefficient

The variation of \( \gamma_f \) with temperature is given by the thermodynamic relationships (50):

\[
\left( \frac{\partial \ln \gamma_f}{\partial T} \right)_P = \frac{(H - H_o)}{vRT^2} = -\frac{L}{vRT^2} \tag{8.18}
\]

\[
\frac{\partial L}{\partial T} = (\tilde{C}_p - \tilde{C}_{po}) = \tilde{J} \tag{8.19}
\]

where:

\( \tilde{H}, \tilde{H}_o \) = Partial molal enthalpy of the electrolyte, at the concentration of the solution and infinite dilution, respectively,

\( \tilde{C}_p, \tilde{C}_{po} \) = Partial molal heat capacities of the electrolyte, respectively, at the concentration of the solution and at infinite dilution,

\( \tilde{L} \) = Relative partial molal enthalpy,

\( \tilde{J} \) = Relative partial molal enthalpy of the electrolyte, and
Figure 8.6 Effect of Pressure on the Activity Coefficient Ratio for NaCl Solutions at 25°C.
$T$ = Absolute temperature.

For a reference temperature of 298.15°C, Millero\(^{(50)}\) has developed the expression:

$$\log \gamma^{\pm}_T = \log \gamma^{298\pm} + \frac{Y}{\nu} \bar{L}_{298} - \frac{Z}{\nu} \bar{J}_{298}$$ \hspace{1cm} (8.20)

where:

$$Y = \frac{(298.15 - T)}{(8.3147)(298.15)(2.3026)T}; T(K)$$ \hspace{1cm} (8.21)

$$Z = 298.15 \ Y + \frac{1}{(8.3147)} \ \log \left( \frac{T}{298.15} \right); T(K)$$ \hspace{1cm} (8.22)

$\gamma^{298\pm}$ is the activity coefficient at 25°C as calculated from eqs. (6.29) and (6.30).

The relationship between $\bar{L}_{298}$ and concentration was empirically determined as\(^{(50)}\):

$$\bar{L}_{298} = \frac{2878.6 \ m^2}{1 + m^2} - 3182.8 \ m + 986.5 \ m^{3/2}$$ \hspace{1cm} (8.23)

Likewise, for $\bar{J}_{298}$:

$$\bar{J}_{298} = \frac{43.5 \ m^2}{1 + m^2} + 72.0 \ m - 20.36 \ m^{3/2}$$ \hspace{1cm} (8.24)

Values of $\gamma^{\pm}_T$ were calculated from eqs. (6.29), (6.30), and (8.20) through (8.24) for temperatures ranging from 50 to 200°C and are shown in figure 8.7 as a function of concentration in molal units.

It can be seen from this figure that the effect of temperature on the activity coefficient is quite large for intermediate to high salinities. Neglecting this effect in the evaluation of electrochemical potentials may well result in significant errors.
Figure 8.7 Effect of Temperature on the Mean Activity Coefficient for NaCl Solutions at Atmospheric Pressure
b.3) Combined Effect of Pressure and Temperature on the Activity Coefficient

The isolated effects of both pressure and temperature have been presented without considering their combined effect on the magnitude of $\gamma^\pm$. Because of the complexity of the problem, not enough data is yet available on the subject. Preliminary investigations indicate that the effect of temperatures between 100°C and 200°C on $\gamma^P$ at high pressures may be quite large; however, the reliability of these conclusions cannot be evaluated due to the mentioned lack of data. Therefore, for the purposes of this study and based on the previous analysis, the calculation of the electrochemical potentials will be carried on by taking into account the effect of temperature alone on both the $Na^+$ transport numbers and the activity coefficients.

VIII.6 Effect of Temperature on the Transport Factor, $\tau$

It was suggested in Chapter VI that the transport factor, although important for the calculation of membrane potentials, might have a negligible effect on the evaluation of the SP. The effect of temperature on $\tau$ can be calculated from eq. (6.32) for $C_w > C_{wN}$ from the variation of $C_w$, $C_{wN}$, and $\psi$ with temperature. The result of these calculations is presented in Table VIII.a. for several $Q_v$ and temperatures ranging between 50 and 200°C for a 6.144 m NaCl solution. Table VIII.a also presents pertinent information used in the evaluation of $\tau$. 
**TABLE VIII.a**

Effect of Temperature on the Transport Factor

\[ \tau = 1 - \frac{\psi Q_v}{C_w} (C_w - C_{WN}) \]

<table>
<thead>
<tr>
<th>TEMPERATURE, °C</th>
<th>50</th>
<th>100</th>
<th>150</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \psi ) (cc/meq)</td>
<td>0.256</td>
<td>0.232</td>
<td>0.218</td>
<td>0.208</td>
</tr>
<tr>
<td>( C_{WN} ) (mho/m)</td>
<td>29.51</td>
<td>52.89</td>
<td>74.77</td>
<td>95.84</td>
</tr>
<tr>
<td>( C_w ) (mho/m)</td>
<td>40.91</td>
<td>66.46</td>
<td>88.27</td>
<td>107.97</td>
</tr>
<tr>
<td>( Q_v ) (meq/cc)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>0.986</td>
<td>0.991</td>
<td>0.993</td>
<td>0.995</td>
</tr>
<tr>
<td>0.5</td>
<td>0.964</td>
<td>0.976</td>
<td>0.983</td>
<td>0.988</td>
</tr>
<tr>
<td>1.0</td>
<td>0.929</td>
<td>0.953</td>
<td>0.967</td>
<td>0.977</td>
</tr>
<tr>
<td>2.0</td>
<td>0.857</td>
<td>0.905</td>
<td>0.933</td>
<td>0.953</td>
</tr>
<tr>
<td>2.5</td>
<td>0.822</td>
<td>0.822</td>
<td>0.917</td>
<td>0.942</td>
</tr>
<tr>
<td>3.906*</td>
<td>0.721</td>
<td>0.815</td>
<td>0.870</td>
<td>0.909</td>
</tr>
<tr>
<td>4.310*</td>
<td></td>
<td>0.796</td>
<td>0.856</td>
<td>0.899</td>
</tr>
<tr>
<td>4.587*</td>
<td></td>
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<td>0.893</td>
<td></td>
</tr>
<tr>
<td>4.808*</td>
<td></td>
<td></td>
<td>0.888</td>
<td></td>
</tr>
</tbody>
</table>

* Theoretical maximum \( Q_v \) corresponding to that in a perfect shale.
VIII.7  Generation of a Theoretical Chart for the SSP

SP log interpretation has been long based on the SP model given by eq. (8.4). Because of the ideal assumptions regarding the characteristics of both shale and permeable formation, eq. (8.4) provides then with a representation of the maximum attainable SP deflection, SSP. Eq. (8.4) can then be written as:

\[ \text{SSP} = -K \log \left( \frac{R_{mf}}{R_e} \right) \]  

(8.25)

The determination of \( R_w \) is accomplished in two steps. First, \( R_{we} \) is calculated from eqn. (8.25). Then, \( R_{we} \) is converted to \( R_w \) using an empirical chart (5). In an effort to speed up the calculation procedures, a one-step chart (59) has been also developed. However, this chart covers only formation temperatures ranging from 125 to 250°F.

As part of the present research work, a practical improvement in the area of SP log interpretation is offered in this section by pursuing the following goals:

1. To establish a mathematical model for the SSP in which the parameters of interest are obtained from basic electrochemistry theory in a more rigorous approach.

2. To generate a one-step chart relating the variation of the static SP directly to the formation temperature and the resistivities of both the mud filtrate and the formation water.

3. To provide the analyst with the necessary information to implement software for computerized interpretation.
a) **SSP Model**

The model for the SSP follows easily from eq. (8.8) and the magnitudes of $T_{Na}^+$. For a perfect membrane, the transport number equals 1. The magnitude of $T_{Na}^+$ for a clean formation is equal to the Hittorf transport number. Therefore, the SSP model is written as:

$$SSP = - \frac{2RT}{F} \int_{m_1}^{m_2} (\tau_{sp} - \tau_{fNa}) \, d\ln (m\gamma^+)$$

(8.26)

for any pair of NaCl solutions of concentration $m_1$ and $m_2$, since $\tau_{SS} = 1$ for a clean rock. The transport factor for a perfect membrane is given from eq. (6.32) as:

$$\tau_{sp} = \frac{C_{wN}}{C_w}; \quad C_w > C_{wN}$$

$$\tau_{sp} = 1; \quad C_w < C_{wN}$$

(8.27)

b) **Solution of the SSP Equation**

Eq. (8.26) can be solved by a numerical method for any salinity range and for a given temperature. Electrochemical potentials were calculated for temperatures ranging from 100 to 400°F selecting a concentration range from 0.03 molar up to saturation. The basic expression for the SSP, eq. (8.26) was solved using a numerical approximation similar to that described by Thomas (47), and selecting a presentation format analogous to that used by Smits (31). The computation procedure was initiated by transforming the concentrations from the molar to the molal scale. Next, the concentration range was divided into 150 concentration points $m_2(i)$ from which as many concentration i-intervals $[m_1, m_2(i)]$ were defined. The magnitude of $m_1$ was always taken as the
saturation concentration at 25°C. The main intervals were then divided into $k$ subintervals. In order to maintain reasonable accuracy in the final results, the number of $k$ subintervals was chosen according to the size of the $i$-interval ($k = 100 + i$). With the appropriate values for $l_{Na}^{hf}$, $m$, and $y^T$, $k$ differentials were evaluated and summed, then the resulting potential was assigned to the concentration $m^2(i)$. The procedure was repeated for all the temperatures and concentrations of interest.

To provide a more useful chart, it was decided to make the final presentation in terms of solution resistivity, rather than concentration. The result of the calculations is presented in Fig. 8.8 which relates the variation of the SSP to fluid resistivities for several temperatures of interest in well logging interpretation.

The determination of $R_w$ from the new chart is easily accomplished, as illustrated in Fig. 8.9, by taking the following steps:

1. Obtain from the log the magnitude of the SSP (correct for thickness and/or invasion effects\(^{(5)}\) if necessary).
2. Calculate $R_{mf}$ at formation temperature.
3. Enter the chart with the value of $R_{mf}$ and proceed vertically to intercept the appropriate temperature line, point A. Then proceed horizontally to define the magnitude $E_{c}$. 

Figure 8.8 New One-Step Chart for SP Log Interpretation (Ref. 50)
Figure 8.9 Determination of $R_w$ from the New Chart
4. Define the magnitude $E_{c_2}$ by subtracting the SSP value from $E_{c_1}$. From $E_{c_2}$, proceed horizontally to intercept the line for the temperature of interest, point B.

5. Determine the value of $R_w$ at $t_f$ by following a vertical line from B down to the resistivity axis.

c) Discussion of the Results

The new chart offers several important advantages over the previous work. Besides the solid theoretical treatment underlying its development, the new chart improves SP log interpretation by offering a better accuracy, easier use, ability to be incorporated in automated calculations, as well as including a wider range of temperatures. With regard to the last point, it must be stated that the temperature range given in the chart exceeds that for which the empirical expressions for the parameters $\lambda_{Na}^0$, $B_1$ and $B_2$ were derived. However, given that these parameters are used in the calculation of $Na^+$ transport numbers, a variable that apparently is little affected by temperature (25), it is unlikely that extending the temperature range may result in significant errors.

As it is, the developed chart may be the most accurate means available to date for the interpretation of the SP log when perfect shale membrane behavior and clean sands are assumed.

VIII.8 SP Log Interpretation in Water-Bearing Shaly Sands

All the information that has been presented so far could be used, along with the general model for the SP given by eq. (8.8) to generate interpretation charts for the determination of $R_w$. However, such charts
must be prepared for specific conditions of shaliness and membrane efficiency. Their use, as with those previously prepared by Smits (31), would be then seriously limited by the fact that $Q_v$ data for a formation of interest is not generally available. Moreover, the proper use of these charts would require the knowledge of $Q_v$ in adjacent shales. This information is definitely inexistent.

To derive information about $Q_v$ and $R_w$ from the SP log alone is not possible. The only information available for the solution of the SP model is the mud filtrate conductivity, the formation temperature, and the magnitude of the SP deflection of course. $Q_v$ in both adjacent shales and formation, as well as $R_w$, are the system unknowns. The reader must undoubtedly infer that there are an infinite number of combinations of $Q_{v_{SH}}$, $Q_{v_{SS}}$, and $R_w$ that satisfy eq. (8.8) for a given temperature and SP deflection. It is therefore necessary to make use of information regarding the general electrochemical behavior of shaly sands. The SP deflection, $R_{xo}$, and $R_t$ values derived from resistivity logs will be used to solve simultaneously for $R_w$, $Q_v$ as shown in a later section.

Previous conductivity models have been handicapped by (15):

i) Their inability to accurately model both the conductive and electrochemical behavior of shaly sands.

ii) Their limited ability to be applied to log-derived data.

iii) Their requiring of the previous knowledge of $Q_v$ for the formation of interest, thus becoming a restricted source of information.

It has been shown in the previous chapters that the conductivity model proposed in this study meets with high marks the description of
the general behavior of shaly sands. In this section it will be shown that, at least in theory, the new model can be used to simulate the measurement environment using log derived data. In addition, it will be shown that valuable information can be obtained, if the required data is available.

a) Concept of Specific Efficiency, $\xi^+$

Specific efficiency is defined in this work as the membrane transport number evaluated at the neutral point:

$$\xi^+ = \frac{T_{Na}^+}{C_{wN}}$$ (8.28)

and applies to either shales or shaly sands. The expression for $T_{Na}^+$, eq. (6.18) can be written as:

$$T_{Na}^+ = \frac{1}{C_{we}} \left[ \lambda^+ Q_v \frac{f_{DL}}{f_{DL}} + (1-f_{DL}) t_{Na}^{hf} C_w \right]$$ (8.29)

At $C_w = C_{wN}$:

$$f_{DL} = \psi Q_v$$

$$C_{we} = C_{wN}$$

$$\lambda^+ Q_v / f_{DL} = C_{wN}$$

Therefore, eq. (8.28) results in:

$$\xi^+ = t_{Na}^{hf} + \psi Q_v (1-t_{Na}^{hf})$$ (8.31)

in which $t_{Na}^{hf}$ is the Hittorf transport number @ $C_{wN}$.

The magnitude of the specific efficiency $\xi^+$ does not depend on $C_w$ and represents a characterizing parameter of the electrochemical properties of a formation. The parameter $\xi^+$ reflects the selectivity of the membrane.
For perfect shale membranes $\psi$ is unity. For clean sand $Q_v$ is zero and:

$$\xi = t_{Na}$$

(8.32)

b) **Optimization of the SP Model. Water Formations**

The proper evaluation of the SP log in shaly formations requires the reduction of the possible number of combinations of $Q_v$ and $R_w$ that satisfies eq. (8.8). Besides the basic data consisting of $R_{mf}$, $t_f$, and SP deflection, additional information is required. Such information, reflecting both $R_w$ and $Q_v$ in the formation can be obtained from resistivity logs. Log values of both $R_o$ and $R_{xo}$ are necessary. In addition, the optimization process requires the knowledge of the porosity of the zone of interest.

A computer program was designed to conduct the optimization procedure. The variables $R_o$ and $R_{xo}/R_o$ are used as converging criteria. The major steps in the calculations are as follows.

1. $Q_v$ values for both shale and sand are assumed, $Q_{vsh}(i)$ and $Q_{vss}(i)$.

2. A value for the salinity of the formation is assumed and used along with the salinity of the mud filtrate and the assumed $Q_v$ values to calculate an $SP_c$ value from eq. (8.8).

3. $SP_c$ is compared to the observed SP deflection. If both values agree within specific limits, then the process continues to step 5.

4. If $SP_c \neq SP_{obs}$, then another salinity is assumed and the process is repeated starting from step 2 until convergence is achieved at salinity $m(i)$. 

5. The new conductivity model is used to predict \( R_o(i) \) by using \( m(i) \), the assumed \( Q_{v,SS} \) (i) and porosity data.

6. \( R_o(i) \) is compared to \( R_o \) from the log. If both values agree within a tolerance, then the process continues to step 8.

7. If \( R_o(i) \neq R_o \), then the assumed \( Q_v \) value for the sand is modified to \( Q_{v,SS} (i+1) \) and the process is repeated from step 2 until convergence.

8. At this point we have determined one possible combination of \( Q_{v,SS} \) and \( R_w \) that satisfies both the SP and the conductivity models for a particular shale. From \( Q_{v,SS} \), \( R_w \), and \( R_{mf} \), the ratio \( (R_{xo}/R_o)^c \) is calculated from the conductivity model and all final values are stored for future plotting and/or printing.

9. New value of \( Q_{v,SH} \) (i) is assumed and the whole process is repeated for several typical \( Q_{v,SH} \) values.

10. Calculated \( R_{xo}/R_o \), \( Q_{v,SS} \) and \( R_w \) values representing the different possible solutions that satisfy the SP and \( R_o \) log values are plotted as a function of shale efficiency.

11. The plot is entered with a log derived \( R_{xo}/R_o \) value which define the unique solution which furnishes \( R_w \), \( Q_v \) and \( \xi^+ \) values.

Two examples have been prepared to illustrate the procedure.

b.1) Example Number 1

The input data which represents typical log derived data is:
The results of the optimization procedure are presented in fig. 8.10. The unique solution is determined, as illustrated in the figure, by the ratio $R_{xo}/R_o$. The obtained information is:

$$\xi^{+}_{SH} = 80\%$$
$$Q^+_{SS} = 0.48$$

$R_{wSS} = 0.031 \text{ ohm-m}$

The $R_{w}$ value that would be obtained by assuming perfect shale and clean is inferred from the SSP chart, fig. (8.8) as:

$$R_{wCS} = 0.10 \text{ ohm-m}$$

which represents more than 300% error.

b.2) Example Number 2

The input data is:

$$R_o = 1.74 \text{ ohm-m} \quad \text{SP} = -20 \text{ mV}$$
$$R_{xo}/R_o = 2.64 \quad t_f = 175^\circ \text{F}$$
$$R_{mf} = 0.76 \quad F = 30.0$$

Fig. 8.11 shows the results of the calculations. From the $R_{xo}/R_o$ data:

$$\xi^{+}_{SH} = 0.67$$
$$Q^+_{SS} = 0.72 \text{ meq/cc}$$
$$R_{wSS} = 0.084 \text{ ohm-m}$$
Figure 8.10 Results of the Optimization Procedure for Example #1
For comparison purposes, the $R_w$ value obtained from the SSP chart is:

$$R_{w_{CS}} = 0.42 \text{ ohm-m}$$

The $R_w$ value derived assuming ideal environmental conditions is five times larger than the actual value.
Figure 8.11 Results for the Optimization Procedure for the Data of Example #2
CHAPTER IX

THE USE OF THE NEW MODEL TO ENHANCE THE ESTIMATION OF WATER SATURATION

The qualitative evaluation of the economic potential of a formation is accomplished by estimating its water content, $S_w$. It can be said that the most important task faced by the log analyst is the proper evaluation of the water saturation of a zone of interest. When the formation is clean the task is relatively simple. However, the determination of $S_w$ in a shaly sand becomes a complex problem.

IX.1 Basics of $S_w$ Determination

When a formation is clean, its electrical conductive properties are readily related to the amount and conductivity of the fluids saturating the pore space. For a given porosity, a clean formation containing hydrocarbons exhibits a conductivity $C_t$ lower than the conductivity $C_o$ that would be otherwise observed if the whole pore space is saturated only by a conductive brine. This conductivity contrast forms the basis for the method used to calculate $S_w$. In clean formations the water content is obtained from the model given by eq. (1.4)

$$S_w = \left( \frac{C_t}{C_o} \right)^{1/n} = \left( \frac{R_o}{R_t} \right)^{1/n}$$

(1.4)

where $R_t$ is the true resistivity of the rock as recorded from an electrical log, and $R_o$ is the equivalent resistivity, had the formation been a water bearing rock.

The magnitude $R_o$ in the "clean sand" model can be inferred from the resistivity of an adjacent water formation provided that both strata contain the same brine and exhibit the same porosity. However, it is
common not to have an adjacent water zone, or the constant porosity and/or salinity condition is not met. In these situations, the magnitude of $R_o$ is estimated from the knowledge of formation porosity and the salinity and thus resistivity of its interstitial water. From eq. (1.5):

$$R_o = FR_w = \frac{aR_w}{\phi_m}$$

(9.1)

The formation water resistivity $R_w$ is determined from the SP log.

The evaluation of clean formations is therefore straightforward. Unfortunately, when the above procedure is employed in the evaluation of shaly sands, erroneous estimations of $S_w$ are obtained.

As it has been discussed in previous chapters, the presence of clay in a formation considerably alters its electrochemical and conductive behavior. As a result, the formation exhibits a higher conductivity and the magnitude of the SP deflection is reduced. Under these conditions, an apparent water resistivity $R_{wa}$ is obtained from the SP log. $R_{wa}$ exceeds the true $R_w$ of the formation water. The calculated resistivity of the equivalent water formation becomes also an apparent one, $R_{oa}$, whose magnitude is higher than the true value so that $R_{oa} = FR_{wa} > R_o$.

The use of this inflated magnitude in the clean sand model results in the estimation of high $S_w$ values. The net result is that potential hydrocarbon zones may be neglected, or in some cases, totally overlooked.

The need for establishing a reliable technique has existed, as inferred from Chapter I, ever since the problems associated with shaly sands were first recognized. Various interpretation techniques have been proposed the most recent ones emphasizing computerized evaluations. One of these techniques is presented in Section IX.2. It must be stated, however, that a reliable and conceptually sound interpretation
technique has not yet been developed. However, this is not entirely due to the number of unknowns in the system, but also due to the lack of an accurate model to describe the abnormal behavior of shaly formations.

IX.2. The "CYBERLOOK" Water Saturation Model

Using the concepts of the Dual-Water model to define a water-bearing shaly formation resistivity $R_o$, Best et al.\(^{(59)}\) introduced the "CYBERLOOK" water saturation model which is the basis of the "CYBERLOOK" wellsite computer processing. The "wet" resistivity $R_o$ is compared to log measured resistivity $R_t$ to detect the presence of hydrocarbons and estimate their content. The model used to define $R_o$ is illustrated in Fig. 9.1. It considers a shaly formation to behave as a clean formation containing two types of water: "Bound Water" and "Free Water".

**Bound Water** is the water associated with shales. It occupies a bulk-volume fraction $\phi_{wB}$ and has a conductivity $C_{wB}$. Free water is the water that is not bound to shale. It occupies a fraction of the bulk volume equals to $\phi_{wF}$, and has a conductivity $C_{wF}$. The total porosity, $\phi_T$, which represent the bulk volume fraction of the formation occupied by all fluids i.e. free water and bound water is:

$$\phi_T = \phi_{wB} + \phi_{wF} \quad (9.2)$$

The free and bound water saturation can then be defined as:

$$S_{wF} = \frac{\phi_{wF}}{\phi_T} \quad (9.3)$$

$$S_{wB} = \frac{\phi_{wB}}{\phi_T}, \text{ and}$$

$$S_{wF} + S_{wB} = 1 \quad (9.5)$$
Figure 9.1 The "Dual Water" Model of Water Bearing Shaly Formation
In the "CYBERLOOK" model the formation factor is defined as

\[ F = \frac{1}{\phi_T^2} \]  

(9.6)

The conductivity \( C_0 \) of the water bearing shaly formation is then

\[ C_0 = \phi_T^2 C_{WM} \]  

(9.7)

Where \( C_{WM} \) is the conductivity of the free and bound water mixture. \( C_{WM} \) is a weighted average conductivity expressed as

\[ \phi_T C_{WM} = \phi_{WB} C_{WB} + \phi_{WF} C_{WF} \]  

(9.8)

or considering equations (9.3), (9.4) and (9.5):

\[ C_{WM} = S_{WB} C_{WB} + (1 - S_{WB}) C_{WF} \]  

(9.10)

Then

\[ C_0 = \phi_T^2 [S_{WB} C_{WB} + (1 - S_{WB}) C_{WF}] \]  

(9.11)

and in resistivity terms

\[ R_0 = \frac{R_{WM}}{\phi_T^2} \]  

(9.12)

where \( R_{WM} \) is the water mix resistivity given by

\[ R_{WM} = \frac{R_{WF} R_{WB}}{S_{WB} R_{WF} + (1 - S_{WB}) R_{WB}} \]  

(9.13)

\( R_{WF} \) and \( R_{WB} \) are respectively the free and bound water resistivity.

The "CYBERLOOK" water saturation is calculated using Archie's model for clean formation, i.e.

\[ S_w = (R_0/R_c)^{1/s} \]  

(9.14)

The estimation of \( S_w \) using eqns. (9.13), (9.15) and (9.14) requires the knowledge of \( S_{WB}, R_{WB} \) and \( R_{WF} \). The bound water saturation is usually assumed equal to the shale content. The shale content is estimated from shale indicators such as the gamma-ray log.
a) **Determination of** \( R_{WF} \) **and** \( R_{WB} \)

\( R_{WF} \) and \( R_{WB} \) are estimated using the apparent water resistivity approach, in clean water bearing formation and in 100-percent shale respectively. Apparent water resistivity, \( R_{wa} \), is defined from clean sand models as the ratio of the rock resistivity divided by the formation factor derived from porosity log

\[
R_{WF} = \frac{R_0}{\phi^2}
\]  
(9.18)

and

\[
R_{WB} = \frac{R_{sh}}{(\phi_T)^2_{sh}}
\]  
(9.19)

The total shale porosity \((\phi_T)_{sh}\) is calculated using eq. (9.17) as:

\[
(\phi_T)_{sh} = \frac{(\phi_N)_{sh} + (\phi_D)_{sh}}{2}
\]  
(9.20)

\( R_{WF} \) and \( R_{WB} \) can be taken from the \( R_{wa} \) curve if available.

b) **Comments**

A quick review of the concepts just presented readily reveals several weak aspects of the Cyberlook \( S_w \) interpretation technique that are open for discussion.

The number of unknowns is reduced to only three, namely \( V_{sh} \), \( R_{wf} \), and \( R_{wb} \). However, this is done at the expense of making questionable assumptions such as that the magnitude of \( R_{WB} \) can be determined from adjacent shales using clean sand models. This implies that the shaly material contained in the formation is identical to that forming the surrounding shales, or at least exhibits the same electrochemical properties.
Although the technique is based on Dual water concepts, the method does not attempt to benefit from the Dual Water model itself, undoubtedly to avoid the inclusion of $Q_v$ in the analysis. In so doing, an alternate model is established that turns out to be a modified $V_{SH}$ model. In fact, expressing eq. (9.11) in terms of (9.16) results in:

$$C_o = \phi^2_T \left[ V_{SH} C_{WB} + (1-V_{SH}) C_{WF} \right]$$

(9.22)

The inclusion of the term $V_{SH}$ introduces some conceptual difficulties, as discussed in the analysis of the $V_{SH}$ models, section (I.5.b).

**IX.3 Ultimate Evaluation of Oil Bearing Shaly Sands**

The availability of a reliable model capable of describing equally well both the conductive and electrochemical behavior of shaly sands should greatly facilitate the development of a reliable interpretation technique. This fact has been proven in Chapter VIII where the new conductivity model has been used in the creation of an algorithm for the simultaneous determination of $R_w$ and $Q_v$ in water bearing shaly sands.

The development of such interpretation technique was also possible due to the fact that, for water formations, there are only three unknowns in the system namely $R_w$, $Q_v$, and the shale efficiency $\xi_{SH}^{+}$ which are entirely defined by three independent equations.

However, in the case of hydrocarbon bearing formations, two additional unknowns appear in the picture. They are the water saturation $S_w$, and the saturation of the flushed zone, $S_{xo}$. The unique solution for the algorithm presented in Chapter VIII is ultimately
defined by the ratio $R_{x0}/R_{o}$ derived from log data. The same criteria
can not be applied in cases where $S_w < 1$ since the ratio $R_{x0}/R_t$ contains
the two new unknowns $S_w$ and $S_{x0}$.

Regardless, the algorithm definitely represents an important step
towards the solution of evaluating $S_w$ in shaly formations. In order to
reduce the number of unknowns it would be advisable to establish
functional relationships or even local correlations that allow the
independent estimation of one or more of the required parameters such as
$R_w$ and shale efficiency.

In fact, local correlations for the determination of $R_w$ such as the
empirical one obtained for the Gulf Coast could be used. Moreover, the relationship between $R_w$, SP, and shale resistivity
inferred from that chart suggests that a correlation between $R_{sh}$ and
adjacent shale efficiency $\xi_{sh}^+$ could be derived. The development of such
an involved technique is beyond the scope of this study. It is
recommended, however, that such possibilities be explored. In the
meantime, a practical interpretation technique using the new model is
presented in this study. An effort to reduce the number of unknowns is
made by allowing reasonable assumptions.

IX.4 New Practical Technique for the Evaluation of $S_w$ in Shaly Sands

A new technique for the evaluation of hydrocarbon bearing shaly
sands is proposed in this study. This technique makes use of the newly
developed conductivity model. In addition, it considers the conductive
response of the formation, $R_f$, and the electrochemical information
available from the SP.
As in the Cyberlook case, the technique is based on the contrast between the conductivity of an oil bearing shaly sand and that of an equivalent water bearing formation exhibiting the same shaliness and porosity. The new technique represents, however, several advantages over the Cyberlook.

From the concepts discussed in Chapter V, the conductivity of an oil bearing shaly sand can be expressed as:

\[ C_t = \frac{S_w^2}{F_e} \left[ \lambda_+ Q^* + (1-f^*_{DL}) C_w^* \right] \]  \hspace{1cm} (9.23)

where

\[ F_e = \frac{1}{\phi_t^2} \]  \hspace{1cm} (9.24)

The conductivity \( C_w^* \) of an equivalent water formation is defined now as:

\[ C_w^* = \frac{1}{F_e} \left[ \lambda_+ Q^* + (1-f^*_{DL}) C_w^* \right] \]  \hspace{1cm} (9.25)

The magnitude of \( S_w \) for the zone of interest is determined from eqs. (9.23) and (9.25) as:

\[ S_w = \left( \frac{C_t}{C_w^*} \right)^{-\frac{1}{2}} = \left( \frac{R^*_w}{R_t} \right)^{\frac{1}{2}} \]  \hspace{1cm} (9.26)

The solution of eq. (9.26) requires the knowledge of \( C_w^* \), \( \phi_t \), \( Q^* \), and \( \lambda^*_t \).

a) Determination of \( C_w^* \)

The conductivity \( C_w^* \) of the formation water is estimated independently from water catalogs, local correlations, empirical charts, or from the \( R_{wa} \) curve if available. In certain areas, such
as the Gulf Coast, $C^*_w$ can be inferred from the empirical chart shown in fig. (8.4). This chart has proven to yield reliable $R_w$ values in the area.

b) **Determination of $\phi_T$**

An estimation of the total porosity of the formation is required for the calculation of $F_i$. $\phi_T$ is customarily determined as the average of the neutron and density porosities:

$$\phi_T = \frac{\phi_N + \phi_D}{2}$$

c) **Estimation of $Q_v^*$**

The shaliness parameter $Q_v^*$ is estimated from the SP deflection recorded in front of the zone of interest. In so doing, the adjacent shales are assumed to behave as perfect cationic membranes. Under this conditions, the parameter $Q_v^*$ is obtained by solving the SP model:

$$SP^* = \frac{-2RT}{F} \int_{m_w^*}^{m_f} (\tau_{SH} - \tau_{SS} T_{SS}^*) d\ln (m_T)$$

where:

$\tau_{SH}, \tau_{SS}$ = Transport factors for the perfect shale and shaly sand.

$m_f, m_w^*$ = Molal concentrations of the mud filtrate of resistivity $R_{mf}$ and that of the formation water of resistivity $R_w^*$.

The transport number $T_{SS}^*$ is defined from the general expression, eq. (6.18) as:
\[ T_{NaSS}^{*} = \frac{\lambda^{+}Q_{v}^{*} + t^{h_{f}}_{Na} (1-f_{DL}^{*}) C_{w}}{\lambda^{+}Q_{v}^{*} + (1-f_{DL}^{*}) C_{w}} ; C_{mf} < C_{w} < C_{w}^{*} \]  

(9.28)

where:

\[ f_{DL}^{*} = a_{*} Q_{v}^{*} \]  

(9.29)

Eq. (9.27) can be solved following the procedures outlined in the description of the algorithm presented in Chapter VIII. Knowing the magnitudes \( m_{f} \) and \( m_{w}^{*} \), assumed \( Q_{v}^{*} \) values are used in eqs. (9.28) and (9.29) to solve for \( SP^{*} \) in eq. (9.27). The proper \( Q_{v}^{*} \) value will be then determined when the calculated \( SP^{*} \) equals, within limits, the recorded SP deflection.

In order to insure the practical application of the technique, a set of interpretation charts such as the one shown in fig. (9.2) have been prepared (see Appendix C). These charts show the variation of SP with solution resistivity for several \( Q_{v} \) of interest. The estimation of \( Q_{v}^{*} \) from these charts is as follows:

1. Select from Appendix C the appropriate chart for the temperature of interest.
2. Draw two vertical lines at the appropriate values of \( R_{mf} \) and \( R_{w}^{*} \).
3. For each \( Q_{v} \) line in the plot, obtain the magnitude \( SP_{1}^{*} \) as the difference in SP values read at the intersections of the vertical lines and the \( Q_{v} \) line. Tabulate the results.
Figure 9.2 Example of SP Chart for Use in $S_w$ Evaluation
4. From the tabulated data, the proper $Q_v^*$ that satisfies the SP equation is determined from interpolation, or from a graph constructed by plotting $SP^*$ vs. $Q_v^*$.

d) **Calculation of $\lambda_+^*$**

The equivalent counterion conductivity $\lambda_+^*$ depends on the magnitudes of $C_w^*$ and $Q_v^*$. It can be calculated from the general expression, eq. (4.42) as:

$$\lambda_+^* = \frac{\Lambda' \text{NaCl}}{f^*_g}$$

(9.30)

where the geometrical factor $f^*_g$ is given by:

$$f^*_g = \frac{1}{n^*_g}$$

(9.31)

The expansion factor $\alpha^*_s$ is calculated from $n^*_w$ and the limiting concentration $n_{lim}^*$ for the temperature of interest. The exponent $n^*_s$ is determined from eq. (4.45) from the knowledge of $\alpha^*_s$ and $Q_v^*$.

To facilitate the practical calculation procedure for $\lambda_+^*$, the interpretation charts shown in figs. (9.3) and (9.4) have been prepared. Fig. (9.3) shows the variation of the parameter $\Lambda' \text{NaCl}$ with temperature as a function of $C_w^*$. Fig. (9.4) illustrates the variation of $\alpha^*_s$ with both temperature and $C_w^*$. The parameters of interest in eqs. (9.30) and (9.31) are estimated from these figures as the magnitude read at the appropriate $R_w^*$ value.

e) **Determination of $S_w^*$**

Once the parameters of interest have been determined, the conductivity $C_o^*$ is calculated from eq. (9.25). The water content of the shaly sand is evaluated from eq. (9.26). For illustration
Fig. 9.3 Variation of the Corrected Eq. Conductivity $A'(NaCl)$ with Temperature and $C_w$
Figure 9.4 Variation of the Expansion Factor $\alpha$ with Temperature and $C_w$
purposes, a typical example has been prepared and discussed in the next section.

f) **Interpretation Example**

The available log information is as follows:

\[
\begin{align*}
t_f &= 150^\circ F \\
R_{sh} &= 1.0 \text{ ohm-m} \\
SP &= -40 \text{ mV} \\
R_t &= 4.0 \text{ ohm-m} \\
R_{mf} &= 0.4 \text{ ohm-m} \\
\phi_T &= 23\% \\
R_{*w} &= \text{ inferred from empirical chart (fig. 8.8)} \\
SP &= -40 \text{ mV}
\end{align*}
\]

In addition, no adjacent water zone is available.

Information regarding \(R_{*w}\) is inferred from the empirical chart (fig. 8.8) as illustrated in fig. 9.5:

\[R_{sh}/R_{mf} = 2.5 \quad \frac{R_{mf}}{R_{*w}} = 7\]

\[SP = -40 \text{ mV}\]

Therefore \(R_{*w} = 0.057 \text{ ohm-m} @ t_f\) \hspace{1cm} (a)

The shaliness parameter \(Q_{*v}\) is estimated from the appropriate SP chart, as illustrated in figs. 9.6 and 9.7, using \(R_{*w}\) and \(R_{mf}\).

From fig. 9.7:

\[Q_{*v} = 0.56 \text{ meq/cc} \hspace{1cm} (b)\]

From fig. 9.4, \(a_* = 1\) for \(C_{*w} = 1/0.057\). Therefore, the equivalent conductivity \(\lambda_{*w}\) is given by:

\[
\lambda_{*w} = 4.65 \left( \frac{T(^\circ C)}{25} \right)^{0.7} = 9.14 \left( \frac{\text{mho}}{\text{m}} \right)(\frac{\text{cc}}{\text{meq}}) \hspace{1cm} (c)
\]

The unit fractional volume \(\psi\) is calculated from eq. (7.8) at \(150^\circ F\) as:

\[\psi = 0.247 \text{ (cc/meq)} \hspace{1cm} (d)\]

From (a), (b), (c), and (d), the conductivity \(C_{*o}\) of the equivalent water formation is calculated as:
Figure 9.5 Determination of $R^*$ for the Example Case
Figure 9.6 Estimation of \( SP(i) \) Values for the Evaluation of \( Q^* \).

*Interpretation Example*
Figure 9.7 Estimation of $Q^*_v$ for the Interpretation Example
The water saturation for the zone of interest is determined as:

\[ S_w = \sqrt{\frac{1}{4(1.07)}} = 0.48 \]

The result of the calculations indicate that the zone of interest may well be a potential hydrocarbon bearing zone.

For comparison purposes, the water saturation that would have been indicated from using clean sand models is calculated. Using the SSP chart to estimate \( R_w \) results:

\[ R_w = 0.118 \text{ ohm-m} \]

\[ S_w = \sqrt{\frac{0.118}{(0.23)^2 \left( \frac{1}{4} \right)}} = 0.75 \]

The \( S_w \) value is quite high for the formation to be considered as potential pay zone. As a result, the zone might have been neglected.
CONCLUSIONS

The research work presented in this dissertation has resulted in several important accomplishments regarding the understanding and prediction of the general electrochemical behavior of shaly reservoir rocks. These achievements can be summarized as follows:

1 - A new conductivity model for shaly sands has been developed. This model is based on variable equivalent counterion conductivity and dual water concepts. The philosophy underlying the new model allows the treatment of a shaly formation as if it were clean, but saturated with an equivalent water of conductivity $C_{we}$. The conductivity $C_{we}$ is determined by the conductivity and volumetric fraction occupied by the bulk solution and the solution under the influence of the double layer.

2 - The solution under the influence of the double layer is treated as a hypothetical electrolyte, the properties of which are related to those of an equivalent NaCl solution. This approach allows the application of basic electrochemistry theory. The application of the theory results in the estimation of equivalent counterion conductivities which are of variable nature and depend on the shaliness of the rock. This is an original contribution to the theory of shaly formation conductivities.

3 - A new important concept has been introduced for the analysis of shaly sands. This concept, referred to in
this study as the neutral point, facilitates the estimation of formation resistivity factor and the shaliness parameter $Q_v$ for a given rock. The neutral point is a new concept.

The ability of the new model to accurately reproduce the conductive behaviour of shaly sands has been tested at 25°C from comparison with reliable experimental data. From those comparisons it is concluded that the new model is superior to the ones currently accepted by the log analysts.

The new model has been extended to the calculation of hydrocarbon saturation under laboratory conditions. The concept of the neutral point has again been proven valuable for the estimation of appropriate saturation exponents. The accuracy of the model in predicting hydrocarbon saturation has been tested. The model reproduces experimental data in an excellent fashion throughout a wide range of salinities. In addition, it was found that saturation exponents in shaly sands can be considered, for practical purposes, equal to the magnitude of the cementation exponent of the rocks.

Membrane potentials in shaly sands and shales can be accurately determined from transport numbers derived from the new model. Excellent agreement between calculated and experimental data was obtained for NaCl solutions ranging in concentration between 0.012 m NaCl and 3.058 m NaCl. Deviations from the theory were observed at higher
salinities. These deviations were explained as arising from different transport properties between the fluid contained in the pore space and those of the solution outside the core. These transport properties conform to the philosophy underlying the new model.

The new model has been extended to include the effect of temperature on the conductivity of shaly sands. The variation of the parameters affecting the volumetric fraction occupied by the double layer solution was empirically determined from available experimental data. The effect of temperature on the equivalent counterion conductivity was conceptually evaluated following the theoretical fundamentals established for room conditions.

Although limited experimental data was available, the basic theory underlying the new model was found valid for temperatures up to 200°C and salinities as low as 0.09 m NaCl.

A one-step chart for the static SP (SSP) was developed for basic SP log interpretation for clean sands and perfect shales. The chart was prepared by taking into account the effect of temperature on NaCl solution conductivity, transport numbers, and mean activity coefficients. The developed chart offers several advantages over existing ones. Being based on a sound theoretical basis is its main advantage.

The new conductivity model has been applied in the development of an algorithm for enhanced interpretation
of shaly sands. The algorithm combines information derived from resistivity, porosity, and SP logs. Using appropriate data, the algorithm provides information regarding $R_w$, the shaliness parameter $Q_v$, as well as information about the electrochemical efficiency of the surrounding shales.

A new practical technique for the evaluation of $S_w$ in shaly sands is defined. This technique offers several improvements over a currently used one. Using typical log data, the use of this interpretation technique considerably improves the estimation of formation potential.
RECOMMENDATIONS

At the conclusion of this study several possible investigations are recommended:

1 - The effect of temperature on the conductivity of shaly formations and the ability of the model to predict the same was tested at only two concentration values in the dilute range. The quality of the data at the lower of the two concentrations was questioned. It might be beneficial to obtain experimental data for concentrations less than 0.26 m NaCl at various temperatures. This data might be useful in fine tuning the model.

2 - The estimation of $Q_v$ and $R_w$ in water bearing shaly sands can be done at the present time using an elaborate computer program. The development of a graphical solution i.e. interpretation charts might be necessary for a wide use of the proposed technique.

3 - As the model gains acceptance by the log analysts, its performance under field conditions should be monitored. Field applications might indicate necessary modifications to adapt the model to specific measurements and/or geologic environments.


APPENDIX A

PREDICTION OF CORE CONDUCTIVITIES FROM THE NEW MODEL.

INDIVIDUAL RESULTS FOR GROUP II SAMPLES
CORE NUM. 1
QV = 0.043
F = 12.17
CORE NUM. 2
QV = 0.050
F = 14.01

-THIS STUDY

□ W-S DATA
CORE NUM. 3
QV = 0.047
F = 11.15

C̄₀ (MHØ/M)

0.00  1.00  1.50  2.00  2.50

CW (MHØ/M)

0.00  4.00  8.00  12.00  16.00  20.00  24.00  28.00

-THIS STUDY
☐ W-S DATA
CORE NUM. 4
QV = 0.079
F = 47.78

Graph:
- THIS STUDY
- W-S DATA
Core Num. 5

$QV = 0.084$

$F = 14.55$

- This Study

W-S Data
CORE NUM. 6
QV = 0.084
F = 18.27

--- THIS STUDY
□ W-S DATA
CORE NUM. 7
QV = 0.107
F = 26.13

---This Study

W-S Data
CORE NUM. 8
QV = 0.105
F = 25.05

THIS STUDY
W-S DATA
CORE NUM. 9
QV = 0.090
F = 17.71

- THIS STUDY
 W-S DATA
CORE NUM. 10
QV = 0.242
F = 150.04

- THIS STUDY
□ W-S DATA
CORE NUM. 11
QV = 0.175
F = 165.75

This study
W-S DATA
CORE NUM. 12
QV = 0.242
F = 41.50

This study
W-S data
CORE NUM. 13

QV = 0.296
F = 42.17

---

THIS STUDY

W-S DATA
CORE NUM. 14
QV = 0.259
F = 30.34

THIS STUDY
W-S DATA
CORE NUM. 15
QV = 0.426
F = 138.62

THIS STUDY
□ W-S DATA
CORE NUM. 16
QV = 0.517
F = 53.46

THIS STUDY
W-S DATA
CORE NUM. 17
QV = 0.524
F = 38.42

-THIS STUDY
□ W-S DATA
CORE NUM. 18
QV = 0.431
F = 16.23

-THIS STUDY
□ W-S DATA
CORE NUM. 19
QV = 0.340
F = 15.42

-THIS STUDY
□ W-S DATA
CORE NUM. 20

QV = 0.279
F = 12.14

-THIS STUDY

W-S DATA
CORE NUM. 21
QV = 0.188
F = 14.07

THIS STUDY
W-S DATA
CORE NUM: 22
QV = 0.642
F = 29.18

---

THIS STUDY

□ W-S DATA
CORE NUM. 23
QV = 0.737
F = 21.15

- THIS STUDY
□ W-S DATA
CORE NUM. 24
QV = 0.847
F = 34.14

- THIS STUDY
□ W-S DATA
CORE NUM. 25
QV = 1.074
F = 39.09

-THIS STUDY
□ W-S DATA
CORE NUM. 26
QV = 1.114
F = 28.34

-THIS STUDY
☐ W-S DATA
CORE NUM. 27
QV = 1.148
F = 30.14

-THIS STUDY
□ W-S DATA
APPENDIX B.a

B.1. PREDICTION OF $S_w$ VALUES FROM THE NEW MODEL FOR INDIVIDUAL CORES.

SATURATION EXPONENTS CALCULATED FROM THE CONSTANT $S_w$ METHOD
N = 17 POINTS
E = 0.59 PERCENT
S = 0.011 PERCENT

CORE 1
N = 12 POINTS
E = -0.55 PERCENT
S = 0.007 PERCENT.
\[ N = 15 \quad \text{POINTS} \]
\[ E = -0.27 \quad \text{PERCENT} \]
\[ S = 0.004 \quad \text{PERCENT} \]
$N = 16$ POINTS
$E = 0.62$ PERCENT
$S = 0.009$ PERCENT.

CORE 4
N = 17  POINTS
E = 1.95  PERCENT
S = 0.019  PERCENT

CORE 5
N = 10 POINTS
E = 3.01 PERCENT
S = 0.023 PERCENT

CORE 6
N = 12 POINTS
E = -1.25 PERCENT
S = 0.013 PERCENT.

CORE 7
N = 13 POINTS
E = -1.59 PERCENT
S = 0.016 PERCENT

CORE 8
APPENDIX B.b

B.2. PREDICTION OF $S_w$ VALUES FROM THE NEW MODEL FOR INDIVIDUAL CORES.

SATURATION EXPONENTS CALCULATED FROM THE APPARENT $n_a$ METHOD
N = 17 POINTS
E = -0.29 PERCENT
S = 0.010 PERCENT.
N = 12 POINTS
E = -1.82 PERCENT
S = 0.014 PERCENT
N = 15 POINTS
E = 0.03 PERCENT
S = 0.004 PERCENT.

CORE 3
N = 16 POINTS
E = 0.09 PERCENT
S = 0.007 PERCENT

CORE 4
N = 17 POINTS
E = 1.37 PERCENT
S = 0.016 PERCENT.
N = 10  POINTS
E = 1.87  PERCENT
S = 0.017  PERCENT

CORE 6
N = 12  POINTS
E = -2.97  PERCENT
S = 0.021  PERCENT.
N = 13 POINTS
E = 0.15 PERCENT
S = 0.014 PERCENT

CORE 8
APPENDIX C

SP LOG CHARTS

SHALY SAND INTERPRETATION
Pedro L. Silva, the son of Pedro E. Silva and Ana M. L. Lopez, was born in Mexico City on August 12, 1953. He attended Universidad Nacional Autonoma de Mexico, receiving a Bachelor of Science degree in Petroleum Engineering in 1976. Pedro joined the Petroleum Engineering Department at Louisiana State University where he received a Master of Science degree in Petroleum Engineering in August, 1981. Upon graduation, Pedro continued working towards the Doctor of Philosophy degree also in Petroleum Engineering. He is married to the former Guadalupe V. Flores and has a daughter, Gabriela, and a son Rafael. Pedro is a member of the Society of Professional Well Log Analysts, of the Society of Petroleum Engineers, and of the Sociedad de Ingenieros Petroleros de Mexico.
DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Pedro L. Silva

Major Field: Petroleum Engineering

Title of Dissertation: Development of a New Conductivity Model for Shaly and Interpretation

Approved:

Major Professor and Chairman

Dean of the Graduate School

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Date of Examination:

April 29, 1986