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AND RESIN PHASE ION DIFFUSIVITIES

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by

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Controlled Exchange
 Ion-exchange is essentially a mass transfer process where one species of ion in a resin phase is exchanged for a different species of ion in the liquid phase. The proper design of ion-exchange unit operation equipment requires a knowledge of the rate of ion-exchange. One piece of information needed is the interdiffusion coefficient that describes the rate of exchange within the ion exchange resin bead. This parameter is determined in the laboratory by obtaining exchange rate data for the particular system desired. This work is a study of this experimentally determined interdiffusion coefficient.

Theoretical considerations have shown that this interdiffusion coefficient is a variable whose magnitude depends upon the concentration of the exchanging ions in the resin phase. Based on this theoretical hint an integral interdiffusion coefficient is defined and hypothesized to exist during the progress of the diffusion-exchange. Employing a recent model for diffusing ions in a charged resin matrix (Nernst-Plank model) this integral interdiffusion coefficient is developed to a point where it is shown to be a complex logarithmic function of the concentration of the resin phase. Consideration is then given to the experimental technique for determining the interdiffusion coefficient. Re-interpretation of an established method of calculating interdiffusion coefficients (Fick's Law) reveals that these experimentally determined coefficients are actually integral interdiffusion coefficients. This earlier Ficks' Law model is used as a means of transforming raw exchange kinetic data into integral interdiffusion coefficients at their various values of resin capacity. The
transformed data is free of the unsteady state-spherical geometry complexities that plaqued the raw data.

Extensive analysis of experimental integral interdiffusion coefficients in the light of the developed integral interdiffusion coefficient model was undertaken. Rate of exchange data from seven authors who employed cations and strong acid exchange resins was taken from published literature. Rate of exchange data produced experimentally in this work is for anions in a weakly basic exchange resin; specifically the Cl - HCO exchange in Amberlite IRA-68.

Analysis of the transformed exchange rate data showed that the proposed integral interdiffusion coefficient concept is correct. Five points in the analysis support this conclusion:

1. During the beginning of the exchange there exist a lower than normal integral interdiffusion coefficient. This is to be expected since during this period a stagnant liquid film that surrounds the resin particle hampers exchange.

2. Experimental integral self diffusion coefficients show no variation in magnitude with resin concentration. Self-diffusion coefficients are constant, resulting in an integral self-diffusion coefficient which is constant.

3. Experimental integral interdiffusion coefficients do change considerably with resin phase concentration.

4. Fitting the experimental integral interdiffusion coefficients with the developed integral interdiffusion coefficient relation allowed precise duplication of the exchange rate data.
5. A unique limiting process was developed to compute ion diffusivities from the regression coefficients of the fitted integral interdiffusion coefficient relation. These predicted ion diffusivities were nearly equal to the ion's self-diffusivities which were available from independent exchange rate data.

Presently exchange rates are interpreted by the Ficks' Law model or the Nernst-Plank model. The Ficks' Law model employs one empirical interdiffusion parameter and the solution to a linear partial differential equation. The Nernst-Plank model employs two empirical interdiffusion parameters, an independent variable (the resin phase concentration) and the solution to a non-linear partial differential equation. The model developed in this work employs two empirical interdiffusion parameters and an independent variable (the resin phase capacity) but retains the linearity and simplicity of the Ficks' Law model and the precision of the Nernst-Plank model.
CHAPTER I.

INTRODUCTION

An ion-exchange operation is a mass transfer process, ions being transferred from a solution (usually aqueous) to an ion-exchanger (usually a solid, and a polymerized organic resin), with an equivalent number of ions of the same charge, but of different species, are transferred in the opposite direction. Ion-exchangers are insoluble materials which carry exchangeable cations or anions that can be exchanged for the stoichiometrically equivalent amount of other ions of the same sign when the exchanger is in contact with an electrolyte solution. Carriers of exchangeable cations are called cation exchangers, and carriers of exchangeable anions are called anion exchangers. Materials capable of exchanging both cations and anions are called amphoteric ion-exchangers. Ion-exchange is a frequently used unit operation in the chemical process industries.

The practical applications of ion-exchange have greatly increased in number and scope in the last twenty-five years because of the ready availability of synthetic ion-exchange resins of reliable properties. Ion-exchange has been commonly used for water softening for many years, but is now used as well in demineralization of boiler feed water, in extraction metallurgy, in the recovery of waste metal, in effluent treatment, in the purification of pharmaceuticals and in the deionization of brackish water.

The design of ion-exchange equipment requires a knowledge of the equilibrium of the resin phase ion concentration with the surrounding liquid
phase ion concentration and also requires kinetic data on the rate of mass transfer. Equilibrium information is obtained by experimentally determining the mass action equilibrium constants for the exchange reaction. The rate of exchange is computed by employing experimentally determined mass transfer coefficients for both the liquid and the resin phase.

The main purpose of this work is to establish the proper mass transfer coefficient for the resin phase. This mass transfer parameter is commonly referred to as the resin phase interdiffusion coefficient. A technique for determining resin phase ion diffusivities must be developed. Experimental rate data are analyzed to show the effect of resin phase ion concentration and liquid phase ion concentration on the resin phase diffusivities.
CHAPTER II.

ION-EXCHANGE MATERIALS

A. Discovery and Development of Ion-Exchange Materials

Two agricultural chemist, J. T. Way and H. S. Thompson (1) reported the first systematic observations on ion exchange with clays in 1850. They observed that the exchange of ions involved equivalent quantities and that certain ions are more readily exchanged than others. Commercial use of reversible ion-exchange reactions did not come about until 1905 when a German chemist, R. Gans, found that "hardness" (calcium and magnesium ions) could be removed from water and replaced with sodium ions.

Ion-exchange became more than a water treatment technique after the synthesis of resinous cation exchangers from phenol and formaldehyde, and weak-base anion exchangers from aromatic amines and formaldehyde by B. A. Adams and E. L. Holmes in 1935. The development of ion-exchange as a process industry unit operation began in the United States with the production of the first commercial resins in 1939.

B. Natural Ion-Exchange Materials

There are many natural occurring substances that have ion exchange properties (2) but only a few are commercially attractive. Water hardness (calcium and magnesium ions) can be removed from water and replaced with sodium by means of natural sodium aluminum silicates. Naturally occurring
greensand zeolites, still mined in southern New Jersey, were the first ion-
exchangers to be used extensively in the United States. Zeolites are low in
capacity but are still fairly widely used in the textile industry for softening
large quantities of relatively low hardness water.

The zeolite minerals (chabazite, neulandite, analcyle, and sodalite),
which are the only natural substances that have been useful commercially as
ion-exchangers, are complex aluminosilicates. They are stable in water only
within the pH range of 6.5 to 8.0 and are therefore useful only in water
softening (3).

C. Synthetic Ion-Exchange Materials

An excellent general review of all aspects of ion-exchange is given by
Helfferich (4) in his book "Ion Exchange". If amplification of any topic, with­
out a specific literature reference, discussed in this dissertation, is required
it can be found in Helfferich.

In recent years, various zeolites with completely regular crystal
structure have been synthesized; most of them by a method which involves
crystallization at an elevated temperature from solutions containing silica,
alumina, and alkali. These synthetic zeolites are exact counterparts of the
natural materials. As commercial ion exchangers, they are of little im­
portance. Inorganic cation exchangers with satisfactory properties have been
prepared by combining group IV oxides with acid oxides of group V and VII,
but are not readily prepared in the form of mechanically stable particles of
convenient size. Only very few synthetic inorganic anion exchangers have been made. The most important class of ion-exchangers are the organic ion-exchange resins.

Organic ion-exchange resins are typical gels. They are crosslinked polyelectrolytes. Their framework, the so called matrix, consists of an irregular, macromolecular, three dimensional network of hydrocarbon chains. An ion-exchange resin particle is practically one single macromolecule. Innumerable types of ion-exchange resins with different properties can be prepared.

Monomeric organic electrolytes can be polymerized in such a way that a crosslinked network is formed. As an alternative, the matrix can be built from nonionic monomers; the fixed ionic groups are then introduced into the completed network. The matrix can be formed by polycondensation or by addition polymerization. The bulk of modern commercial ion exchange material is polymerized organic compounds in the form of spherical beads 0.01 to 2.0 millimeters in diameter.
CHAPTER III.

THE EXCHANGE PROCESS

A. A Qualitative Description of Synthetic Ion-exchange Resin Particles

Organic ion-exchange resins for general application in the chemical process industries are available in the form of spherical particles. Each particle consists of a three dimensional molecular framework of cross-linked hydrocarbon chains. The framework of the resin is a flexible random network whose mesh width is not uniform and is referred to as "hetroporous". The average mesh width of a highly crosslinked resin is of the order of only a few angstrom units. This three dimensional framework carries a positive or a negative electric surplus charge which is compensated by ions of opposite sign called counter ions. Figure 1 is a somewhat simplified representation of a moisture free framework for a cation exchanger in the hydrogen form, the cross-links being indicated by mesh tie-points.

The hydrocarbon matrix of a resin is hydrophobic, however the structurally bound ionic groups incorporated on the matrix usually renders the resin hydrophillic. The resin remains insoluble because of the cross-links which interconnect the various hydrocarbon chains.

Ion-exchange resins are able to absorb solvents in which they are placed. As the solvent (water) molecules enter the pores of the resin framework, the elastic hydrocarbon matrix expands until equilibrium is attained beyond which swelling does not proceed. The degree of crosslinking, which
FIGURE 1. FRAMEWORK OF CATION EXCHANGER IN HYDROGEN FORM (1)
determines the mesh width of the matrix pores, also determines the swelling ability of the resin. As crosslinking increases, swelling ability decreases. This swelling is an attempt by the solvent to dissolve the resin.

The ionic groups embedded in the matrix, as well as the ions which they form, tend to surround themselves with polar solvent molecules. There is a drive for dissolution and the coiled and packed chains of the matrix unfold and make room for the solvent molecules, but the chains cannot separate completely. As a result, the resin swells but does not dissolve. Equilibrium is attained when the elastic forces of the matrix balances the dissolution tendency.

It is important in the following discussions that a distinction be made concerning the nature of water molecules within an exchanger. There is a tendency for solvent molecules to surround fixed and mobile ions forming solvation shells. This solvent is termed "water of hydration". The remainder of the solvent that is sorbed within a resin particle is "free" water. This water attempts to dilute the concentrated solution of ions within the resin particle.

Ion-exchange resins can sorb electrolytes (both counter ions and co-ions) from solutions with which they are in contact. In an ion-exchanger containing counter ions of species A is placed a strong electrolyte solution containing other counter ions of species A along with co-ion Y, it will sorb AY into the matrix. If the counter ion was of species B, ion-exchange occurs, and the exchanger is partially converted to the B form. The counter ion A within the resin prior to contacting the electrolyte solution are indistinguishable from the sorbed counter ions. Strong electrolytes are subject to
electrostatic forces arising from the presence of fixed ionic groups and counter ions in the resin. The result is a Donnan-type sorption equilibrium which is unique for ionic sorbents.

The electrolyte uptake is stoichiometrically equivalent to the co-ion uptake since electroneutrality requires that the co-ions which enter the ion-exchanger be accompanied by an equivalent amount of counter ion. Figure 2 is a schematic diagram of a section of a cation exchange particle in equilibrium with an electrolyte solution.

B. Ion-Exchange Resin Equilibrium

There are two equilibrium phenomena which are important in ion-exchange. Sorption equilibria, which was mentioned above, is an important consideration for exchangers in strong electrolyte solutions. Exchange equilibria occurs when an exchanger contains one species of counter ion and the contacting electrolyte solution contains another. Exchange in aqueous environments is common and all discussion that follows will be with respect to water as the solvent.

1. Donnan Sorption Equilibrium

When an exchanger is placed in a dilute solution of a strong electrolyte there exist considerable concentration differences between the two phases. The counter ion concentration is larger in the exchanger than it is in the external solution phase, whereas the co-ion concentration is larger in the solution
**FIGURE 2. SCHEMATIC - RESIN PHASE ENVIRONMENT**

- Matrix with fixed charges
- Counter ions (charge opposite that of Matrix)
- Co-ions (charge same as that of Matrix)
- Remaining Space occupied by "water of hydration" and "free water" (A)

---

**Matrix with fixed charges**

**Counter ions (charge opposite that of Matrix)**

**Co-ions (charge same as that of Matrix)**

**Remaining Space occupied by "water of hydration" and "free water" (A)**
phase than in the solid phase. If the ions carried no electric charges, all concentration differences would be annihilated by diffusion. Migration does occur to a small extent. Counter ions move into the solution phase and co-ions move into the resin phase resulting in an accumulation of positive charge in the solution and a negative charge in the exchanger. The first few ions which diffuse thus build up an electric potential difference between the two phases. Equilibrium is established when the tendency of the ions to annihilate the existing concentration differences is balanced by the action of the electric field. In the resin phase, the counter ion concentration thus remains much higher and the co-ion concentration much lower than in the external solution.

The Donnan equilibrium (5), which is essentially a special case of the Donnan membrane theory, provides a quantitative description of concentrations in the respective phases. This theory predicts the unequal distribution of a diffusible electrolyte between a solid phase which has one ion non-diffusible and an aqueous solution phase. Consider the electrolyte in the aqueous phase to be AB and let A be the counter ion associated with the non-diffusible ion R (attached to the matrix) of the resin phase. When equilibrium has been established, a certain amount of A and B will have diffused into the resin phase and the chemical potential of the substances on both sides of the membrane must be equal; i.e.,

$$\mu_{\overline{AB}} = \mu_{\overline{AB}}$$

where the bar above refers to the resin phase and no bar is the liquid phase. The chemical potential of an electrolyte can be taken as a sum of the
potentials of the ions,

\[ \mu_A^0 + RT \ln a_A + \mu_B^0 + RT \ln a_B = \mu_A + RT \ln a_A + \mu_B + RT \ln a_B \quad (2) \]

and

\[ a_A^{-} a_B^{-} = a_A a_B \quad (3) \]

where "a" represents the activity of the indicated ions. If it is assumed that the solutions are dilute, and this is the case for ion exchange, activities can be replaced with concentrations,

\[ C_A^{-} C_B^{-} = C_A C_B \quad (4) \]

In order for the principle of electroneutrality to be obeyed

\[ C_A^{-} = C_B^{-} + C_R \quad (5) \]

and

\[ C_A = C_B \quad (6) \]

Substituting these identities for \( C_A^{-} \) and \( C_B^{-} \) into Equation (4)

\[ C_A^{-2} + C_R C_B = C_B^{-2} \quad (7) \]

Equation (7) shows that

\[ C_B^{-} < C_B \quad (8) \]

and this implies that the concentration of the co-ion in the resin phase is less than that in the liquid phase. There is some AB in the resin (i.e. \( \bar{AB} \)) but its concentration is less than in the liquid phase. The high fixed ionic
concentration of a high capacity resin will exclude the diffusion of free electrolytes into the resin phase from solutions having considerably lower ionic concentrations than that found within the resin.

2. The Exchange Equilibria

When an electrolyte solution containing ion A and the exchanger containing counter ion B are contacted, ion exchange will occur. Exchange will occur until all potentials are exhausted and this final state is the state of exchange equilibrium. It is convenient to regard the overall exchange process as a metathetical chemical reaction between the dissolved ion and the ion which the resinous exchanger contains. The above described exchange can be written as follows:

\[
A + B \rightleftharpoons \bar{A} + \bar{B}
\]

The exchange is as a rule reversible and the reactions like chemical reactions, are all governed by mass action.

Ion-exchange equilibrium is developed further in Appendix A. There the equilibrium data for the resin employed in this work is presented and correlated.

C. A Qualitative Description of the Exchange Process

As two different ion species drive toward equilibrium of the phases (the
exchanger will be called the solid phase and the electrolyte solution will be the liquid phase) a particular mechanism for the exchange process seems logical. Resins are gel-like substances whose exchange sites are dispersed randomly through the interior and on the surface of each particle. The exchange is actually an ion transfer and substitution process whose mechanism can be described by seven sequential events.

A counter ion in the liquid phase (1.) diffuses through a stagnant film that surrounds each exchange particle then (2.) diffuses past the interface into (3.) the solid phase and finally (4.) fixes itself on an active site within the resin and simultaneously displaces from this site an equivalent amount (equivalence in electrical charge) of another counter ion. This exchanged counter ion must now (5.) diffuse through the solid phase (6.) past the interface, and (7.) diffuse through the liquid film finally arriving into the bulk agitated liquid phase thus completing the exchange.

Because of the consequences of the electroneutrality requirement (i.e. there can be no net transfer of electric charge at any point in the exchange) all diffusion steps are actually interdiffusion of counter ions and the ion substitution step is made in stoichiometric amounts (i.e. exchange of equivalents of electric charge). The total counter ion content (in equivalents) along the path of diffusion and during substitution must remain constant regardless of ionic composition.

It is now generally conceded that the actual exchange of ions at sites in the resin phase (step 4.) is instantaneous or nonexistent for ordinary ion-exchange (6, 7) but, a recent finding (8) has shown that the chemical
exchange reaction can occur in resins with chelating groups which form sluggish reacting complexes. The interface between the phases contributes no resistance to the diffusing ions (9) possibly because of the intimate contact of the aqueous phase with the "free" water filled pores of the resin phase (step 2, and 6.). This implies that ion-exchange, as a rule, is purely a diffusion phenomena and is governed by diffusion laws.

There remain four steps (steps 1., 3., 5. and 7.) in the exchange mechanism which do present resistances to the movement of counter ions do occur in all ion-exchange processes. These four steps are combined into two rate-determining steps called film resistance and particle resistance respectively. Boyd et al (6) have shown that the rate determining steps of exchange are inter-diffusion of the counter ions through the film and within the particle.
CHAPTER IV.

PARTICLE DIFFUSION CONTROLLED EXCHANGE

A. Laboratory Conditions for Particle Diffusion Controlled Exchange

An ion-exchange resin in B form (i.e., ion B is the exchangeable counter-ion in the resin phase) is contacted with an aqueous solution containing counter-ion A initiates the exchange process. Particle-diffusion-controlled exchange occurs when the rate of exchange is restrained only by the inter-diffusion of the exchanging counter-ions in the resin phase. This condition is met experimentally by rendering negligible the resistance to interdiffusion of ions in the laminar liquid film that surrounds each particle. Laboratory operations which make the film resistance small compared to the particle resistance are of two general types: a) shallow-bed technique and b) limited-bath technique.

1. Shallow-Bed Technique

This technique was first used by deDomain, Swain, and Hougen (10) and later modified by Boyd et. al. (6) and Tatenbaum and Gregor (7). This technique has been modified still further by Kuo (13) and Gopala Rao (14) to include flow past a single resin particle. The shallow-bed technique employs a thin bed of resin through which the liquid phase flows. The rate of liquid flow is such that the stagnant layer is made very thin and provides little resistance to ion diffusion. This condition of flow is found by increasing the liquid flow
rate increment-wise until there is no further change in the exchange rate with increased flow.

The shallow-bed technique maintains the surface of the exchanger at a constant concentration of the entering ion, A, and removes the exiting ion, B, at such a rate that it exerts no "back pressure" on the exchanger surface. Interdiffusion of the counter-ions occurs until the equilibrium concentration of A is attained in the resin phase. Figure No. 3 shows the effect of inter-diffusion on the concentration of ion A in the resin and liquid phases during a shallow-bed run.

The shallow-bed technique is preferred from a chemical engineering design point of view because it will also provide data for the film resistance (under the proper operating conditions) (11, 12) and more nearly simulates the actual flow in a unit operation of ion-exchange.

2. **Limited-Bath Technique**

The particle-diffusion-controlled exchange condition is effected in the limited-bath technique by vigorously agitation a quantity of the liquid phase and a quantity of the resin phase together with a stirrer-like device. This technique was the first used to study kinetics of exchange and recently modified by Hering and Bliss (15). The stirrer or agitator speed is increased until there is no further change in the exchange rate with increased speed. Figure No. 3 applies also to the limited bath if the counter ion capacity of the exchanger is much less than the quantity of A in the liquid phase. If this restriction does not apply,
FIGURE 3. Effect of Interdiffusion on Resin Concentration
the ion concentration in the liquid phase will decrease during exchange.

B. Ion Diffusion Inside the Resin Phase

Synthetic ion exchange resins have been described as gel-like particles, swelling in electrolytic solutions, permeable to ions and water molecules, and possess exchange groups randomly distributed throughout the particles. This view of ion-exchange resins is obtained chiefly from the work of Boyd et al (6, 16) and Myers (17). The view of the resin phase environment suggest that the ion-exchanger is quasi-homogeneous, i.e. that the diffusion phenomena in the ion-exchanger can be described by relations which hold for homogeneous phases. The resin phase may be viewed as a "microreticular" gel type of porous media with molecular flexible hydrocarbon chains as the framework. The pore structure is "open", i.e. the interstices are interconnected and provide uninterrupted diffusion paths across the medium; a necessary condition for mass transfer.

Diffusion in ion-exchange resins is assumed to be no different from that in solutions of analogous organic electrolytes (benzyltrimethylammonium chloride has been used as a model electrolyte for Dowex - 1 anion exchangers in the Cl- form (18)). Early comparisons of the diffusion mechanism of ions inside the resin phase and in an aqueous medium were based on the studies of Gregor et al (19, 20) and Kressman and Kitchener (21). In such systems, the diffusion of the counter ions is retarded essentially due to the "excluded-volume" effect (occupancy of volume and cross section by the organic matrix).
All the exchange sites in the resin are considered to be fully accessible for occupation by moderately sized ions. Self-diffusion coefficients inside the resin are of the order of 1/10th to 1/500th of the corresponding values in free solution. For cations smaller in size than the pores of the resin, the mechanism of diffusion inside the resin is basically the same as in water. The conclusion was reached because the energy of activation for such cases is approximately 5K cal/mole, about the same as for the diffusion of ions in water.

1. Self-Diffusion

The simplest case of resin phase diffusion where no other simultaneous processes interfere is self-diffusion. Here, the flux is proportional to the concentration gradient, and the diffusion coefficient thus is constant. Isotopic diffusion is an example of self-diffusion where a system is in equilibrium except for isotopic distribution. The diffusion coefficient of the isotopes in such systems is called the self-diffusion coefficient (individual diffusion coefficient, or tracer diffusion coefficient) of the species. Its value is constant throughout any single phase of the system but, of course, depends on the nature and composition of the particular phase and on the temperature.

The first use of isotopic redistribution for the study of particle diffusion controlled exchange was by Boyd and co-workers (22, 23, 24) in a series of papers published in 1953. They (22) studied the self-diffusion of nine cations in Dowex - 50 resins of different crosslinkages, and noted that the self-diffusion rates were lowered by increased crosslinkage of the resin. Boyd and Soldano (23)
noted that the diffusing species in the exchanger were hydrated ions. They postulated a method to distinguish free and bound water and inferred that the transport of mobile hydrated ions contributed negligibly to the rate of diffusion of water molecules into the exchanger. In another article (24) the authors studied self-diffusion of cations in heteroionic exchangers. They observed that in general, the diffusion rate of the mobile cation was lowered and that of the less mobile ion was increased.

Gregor and Tatenbaum (7) investigated self-diffusion of the K$^+$ ion using a shallow-bed technique. They noted a five fold increase in the self-diffusion coefficient when the solution concentration increased from 0.1M to 4.0M.

Boyd, Soldano and Bonner (25) investigated self-diffusion rates of cations in desulfonated ion exchangers. The authors found that the diffusion coefficients increased initially with decreasing exchange capacity but at still lower capacities, the coefficient decreased, indicating interaction between the diffusing ion and the environment. The initial increase in the diffusion coefficients also coincided with the increase in equivalent moisture content.

Self diffusion data is also given by Kuo (13), Rao (14), and Hering (15).

2. Interdiffusion

Early research workers in the field of ion exchange kinetics assumed the model of constant interdiffusion coefficient (mutual diffusion coefficient). The rate of exchange is described by the differential equation governed by Fick's second law. Barrer (26), and Boyd et al. (6) presented an exact infinite series
solution of the rate equation by assuming constant resin surface concentration. Tien and Thodas (27) discussed analytical methods and give approximate solutions for the treatment of the rate equation for variable resin surface concentrations for linear equilibrium between the resin surface and the liquid film interface. These equations are approximations of the differential equation for the rate of exchange in the resin phase described by Ficks' second law and are more readily solvable for variable boundary conditions.

Values for the interdiffusion coefficient in the resin phase for a number of alkali metal ion pairs in Amberlite IR-1 were given by Boyd et al. (6) and by Selke et al. (28) for the system Cu$^{++}$-H$^{+}$ - Amberlite IR-120. In view of the simple physical picture of the rate mechanism and other assumptions involved, one should not expect great accuracy in these values.

Unlike interdiffusion in electrolytic solutions, interdiffusion rates of cations in an ion exchanger are coupled with each other because of the fixed ionic groups in the exchanger. The fluxes and the concentration gradients of the interdiffusing cations are equal and opposite. However because of the differences in mobilities of counter-diffusing ions, a diffusion potential will be set up which slows down the faster ion and speeds up the slower ion. The mathematical expressions for interdiffusion of charged particles was derived quite some time ago by Nernst and Plank. These mathematical expressions applied to ion exchange resins appears in Section D-1 of Chapter IV.

Recently Helfferich (29) employed a disc made of ion exchange material which gave experimental verification to the Nernst-Plank model. Turner and co-workers (30) verified the model again with an ion exchange resin. Ion
exchange rate data have been interpreted employing the Nernst–Plank model by Hering and Bliss (15), Gopola Rao and David (14), Morig and Rao (31), and Kuo and David (13) with limited success.
C. Resin Phase Interdiffusion Coefficients

Experimental data and theoretical considerations have shown that the resin phase interdiffusion coefficient is dependent on many variables. For a given exchange process some variables are set by the nature of the system and some are controllable by the designer while others are not controllable but are present and do influence the interdiffusion coefficient. Table No. 2 lists and categorizes all the variables known to influence the resin phase interdiffusion coefficient. Note that because of variable 11 the interdiffusion coefficient varies from point to point throughout the exchanger.

This list of twelve variables is not as formidable as it seems. Variables 1, 2, 3 and 4 are set by the particular choice of system upon which exchange of some ion is desired. Usually some design criteria other than the magnitude of the interdiffusion coefficient dictates the choice of the resin to be employed and also dictates the temperature of operation, thus removing variables 5, 6, 7, 8 and 12. Variables 9, 10, and 11 are not controllable by the designer or are they set by the particular system. These three variables influence the magnitude of the interdiffusion coefficient and must be analyzed to ensure proper kinetic design.

1. The Intrinsic Resin Phase Interdiffusion Coefficient

During exchange the concentrations of the exchanging ion species changes (variable 11). This changes the environment of the resin phase and allows solvent and solute to be absorbed or desorbed. This implies that there exist
TABLE NO. 1

Variables that affect the Interdiffusion Coefficient

1. The solvent that contains the ion species
   The species of the ions being exchanged
   2. Size of the ion species
   3. Valence of the ion species
   4. Chemical nature of the ion species

The exchange matrix
   5. Chemical nature of the matrix
   6. Degree of cross-linking of the matrix
   7. Mesh width of the pores of the matrix
   8. Charge density of the matrix

The composition of the pore liquid in the resin
   9. Solvent concentration in the resin
   10. Solute concentration in the resin

11. The Counter-ion concentration of the resin

12. The temperature of the exchange
only one truly independent variable; the counter ion concentration of the resin phase. Therefore, the most important, but uncontrollable, variable influencing the interdiffusion coefficient is the resin phase concentration of the entering and exiting ions. Knowing the relationship of the interdiffusion coefficient with ion concentration will allow better approximation of the interdiffusion coefficient and will result in more accurate prediction of exchange rates.

At a certain point during the exchange process there exist an intrinsic interdiffusion coefficient, \( D' \), which is a function of variable \( u_1 \). The intrinsic interdiffusion coefficient is a function of the resin phase exchangeable counter ion concentration.

\[
\bar{D}_{i} = \phi_{i} (\bar{X}_{A}),
\]

where \( \bar{X}_{A} \) is the fractional resin phase concentration of the entering ion.

2. The Integral Resin Phase Interdiffusion Coefficient

As exchange occurs \( \bar{X}_{A} \) increases and the intrinsic interdiffusion coefficient changes. The interdiffusion rate at any time is set by the present magnitude of the intrinsic interdiffusion coefficient, but the current concentration of ion A, \( \bar{X}_{A} \), is a cumulative function of the resins' intrinsic-interdiffusion coefficient history from the start of the exchange. This implies that there exists an integral interdiffusion coefficient, \( \bar{D}_{e} \), which is defined as a concentration integrated average of the individual intrinsic interdiffusion coefficients:
A similar defined expression for diffusion in liquids is given by Tyrrell (32).

By this definition the integral interdiffusion coefficient is also a function of the concentration of ion A in the resin:

$$\bar{D}_I = \frac{\int_{X_{A,0}}^{X_A} \phi_i(X_A) \, dx_A}{\int \frac{\phi_i(X_A) \, dx_A}{X_A - X_{A,0}}}$$

(11)

3. The Experimental Resin Phase Interdiffusion Coefficient

By employing either of the two experimental techniques described above, for particle diffusion controlled exchange, diffusion in the resin phase may be studied. Although one technique is carried out in a flow device and the other in a batch device, the actual diffusion phenomena is quantitatively very similar.

The experimental data obtained from particle diffusion controlled exchange studies are the resin phase concentration of the entering ion (or exiting ion) and the time of phase contact. The resin phase contains a fixed exchange capacity, $\Omega$. During all stages of exchange, the number of exchange sites occupied by the entering and exiting ions must equal the exchange capacity (in equivalents). This is the electroneutrality condition (33) and quantitatively it is

$$\varepsilon A \, \Omega_A + \varepsilon B \, \Omega_B = -\omega \Omega,$$

(13)

where $\omega$ is the sign of the fixed ionic charges in the resin phase (-1 for cation
exchangers and +1 for anion exchangers) and \( z_A \) and \( z_B \) are the signed valences of the exchanging counterions. The fractional capacity of counter ion A in the resin phase is defined as

\[
\bar{X}_A = \frac{z_A Q_A}{C - \omega Q}
\]

and varies from 0 to 1 as exchanges proceed. Experimental data usually appears as a table of \( \bar{X}_A \) vs. \( t \) or as a plot like Figure 4.

Resin phase diffusion for the exchange of two counter ions A and B will now be considered quantitatively. Ion B is initially in the resin phase (the exiting ion) and ion A (the entering ion) is entering the resin phase and displacing an equivalent amount of ion B. There is a flux of ion A inward and an equivalent flux of ion B outward. The flux of ion B in the resin phase is given by

\[
\mathbf{J}_B = - D_i \nabla \bar{C}_B
\]

where \( D_i \) is the intrinsic resin phase interdiffusion coefficient. This flux expression appears identical to the Ficks' law flux employed by Boyd (6) where the interdiffusion coefficient was assumed constant, but it has been argued above that the interdiffusion coefficient is a function of resin phase concentration, \( \bar{X}_A \). For the purposes of this derivation \( D_i \) is a "floating variable" dependent on \( \bar{X}_A \), but will be treated as a constant in the following mathematical development.

For a system with spherical geometry (radius \( a \)) the flux of ion B at
Figure 4: Plot of Typical Experimental Data (6)

Exchange $\text{Na}^+$ from 0.1M KCl Solution

Resin: Amberlite IR-1
some point in the interior, \( r \), is

\[
J_B = -D_i \frac{\partial C_A}{\partial r}.
\] (16)

Applying a component balance on ion B across an arbitrary differential shell within the resin particle results in the equation

\[
\frac{\partial \overline{C_B}}{\partial t} = D_i \left( \frac{\partial^2 \overline{C_B}}{\partial r^2} + \frac{2}{r} \frac{\partial \overline{C_B}}{\partial r} \right).
\] (17)

This linear partial differential equation must be solved under the appropriate initial and boundary conditions that apply to the two experimental techniques. The initial conditions for both techniques are the same. All ions B are in the ion exchanger at a uniform concentration \( \overline{C_B} \) and no ion B is in the liquid phase, quantitatively

\[
\begin{align*}
  r > a, & \quad t = 0 \quad \overline{C_B}(r) = 0 \\
  0 \leq r \leq a, & \quad t = 0 \quad \overline{C_B} = \overline{C_B} = \text{constant}
\end{align*}
\] (18)

Two boundary conditions will be considered; one for each contacting technique. The "infinite solution volume" boundary condition applies to the shallow bed technique, it is

\[
\begin{align*}
  r = a, & \quad t > 0 \quad \overline{C_B}(t) = 0
\end{align*}
\] (19)

Under shallow bed operating conditions, the concentration of ion B at the bead surface is the same as in the bulk solution (i.e. \( \overline{C_B} = 0 \)). This boundary condition will also apply to the limited bath technique if the liquid phase
concentration of ion B remains negligible throughout the process. This condition is met in a limited bath technique when the solution volume is so large that

$$\bar{C} \bar{V} \ll CV$$

(20)

where C is the total concentration of counter ions and \( V \) is the total volume of the liquid phase. If this second boundary condition is not met, a second boundary condition called the "finite solution volume" condition must be applied.

a. Infinite Solution Volume Condition

The solution of Equation (7) under Conditions (18) and (19) is

$$\frac{\bar{C}_B(t, r)}{C_0} = \frac{2}{\pi(\pi a)} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin n \pi \left( \frac{r}{a} \right) \exp(-n^2 \pi^2 \bar{Z}_i)$$

(21)

where \( \bar{C}_B(t, r) \) is the concentration of ion B in the ion exchanger at time t and position r from the center (34), and

$$\bar{Z}_i = D_i t \sqrt{\frac{2}{V/a^2}}$$

(22)

Integration of Equation (11) throughout the bead

$$\int_0^a \int_0^{2\pi} r^2 \frac{\bar{C}_B(t, r)}{C_0} \, dr \, d\theta = \int_0^{2\pi} \int_0^{\infty} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin n \pi \left( \frac{r}{a} \right) \exp(-n^2 \pi^2 \bar{Z}_i) \, dr \, d\theta$$

(23)
leads to

\[ \frac{Q_B(t)}{Q_B^0} = \frac{6}{n^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 \pi^2 \bar{z}_X) \]  \hspace{1cm} (24)

where \( Q_B(t) \) is the amount of B in the ion exchanger at time \( t \), and \( Q_B^0 \) is the initial amount of B in the ion exchanger. Expression (24) gives the average resin phase concentration of ion B with time. This average concentration is due to the cumulative effect of the intrinsic resin phase–interdiffusion coefficients encountered to this point. The interdiffusion coefficient employed in Expression (24) which predicts the average resin phase concentration must be the integral resin phase interdiffusion coefficient

\[ \bar{z}_X = D_x t / \pi^2 \]  \hspace{1cm} (25)

If the exchanger contains initial all ion B then by Equation (13)

\[ \bar{z}_B \overline{Q}_B^0 = -\omega \overline{Q} \]  \hspace{1cm} (26)

Substituting (26) plus the electroneutrality condition into Equation (24) and applying the identity Expression (14) results in

\[ \overline{X}_A(\overline{z}_X) = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 \pi^2 \overline{z}_X) \]  \hspace{1cm} (27)

The fractional attainment of the exchange capacity \( \overline{X}_A(\overline{z}_X) \) is seen to be dependant only on the magnitude of the dimensionless parameter \( D_x t / \pi^2 \). The function is plotted in Figure 5 and tabulated in Appendix B.
FIGURE 5. INFINITE SOLUTION VOLUME CONDITION FOR PARTICLE DIFFUSION CONTROLLED EXCHANGE
Equation (27) does not converge rapidly for small values of $\bar{t}_x$ and the following approximation is more useful (35)

$$\bar{x}_A(\bar{t}_x) \equiv 3 \left[ 2 \left( \frac{\bar{t}_x}{t_0} \right)^{1/2} \right] \bar{x}_A(\bar{t}_x) < 0.5. \tag{28}$$

For large values of $\bar{x}_A(\bar{t}_x)$ the terms higher than first order in Equation (27) can be disregarded resulting in

$$\bar{x}_A(\bar{t}_x) = 1 - \frac{6}{n^2} \exp(-n^2 \bar{t}_x), \bar{x}_A(\bar{t}_x) > 0.8. \tag{29}$$

The fractional capacity of the exchanger to entering ion A is a function of a dimensionless parameter $\bar{t}_x$ which contains the integral resin phase-interdiffusion coefficient, the resin particle radius and the time of phase contact. This equation applies to any particle diffusion controlled ion exchange phenomena. Experimental data consist of $\bar{x}_A(\bar{t}_x)$ vs. t. Employing $\bar{x}_A(\bar{t}_x)$ from this rate data and the solution to Equation (27) allows determination of $\bar{t}_x$. The phase contacting time needed to bring about this average fractional capacity is also known, as is the particle diameter. Solution of Equation (25) for an effective interdiffusion coefficient necessary to yield this $\bar{x}_A(\bar{t}_x)$ vs. t data is possible. This effective interdiffusion coefficient must be the cumulative effect of the individual intrinsic interdiffusion coefficients necessary to attain this experimentally determined fractional capacity, i.e. this effective interdiffusion coefficient is the integral resin phase interdiffusion coefficient, $\overline{D}_x$. 
It is necessary to solve Equation (27) in reverse to obtain $\overline{t}_I$. This was done by employing a Newton's interpolating polynomial of the third degree (36)

$$
\overline{t}_I = \overline{t}_{I,o} + (X_A - X_{A,o})\overline{t}_{I,o}' + (X_A - X_{A,o})(X_A - X_{A,1})\overline{t}_{I,o}''
+ (X_A - X_{A,o})(X_A - X_{A,1})(X_A - X_{A,2})\overline{t}_{I,o}''' + R(X_A).
$$

Solution of Equation (27) was obtained for thirty points ranging from $X_A=0.0034$ to $X_A=0.9857$ with corresponding $\overline{t}_I$ of 0.000001 and 0.38. These thirty points and the divided differences for the interpolating polynomial are shown in Appendix B.

b. Finite Solution Volume Condition

If in the limited bath technique the concentration of ion B in the liquid phase becomes appreciable solution of Equation (17) becomes more complex. This complexity is brought about by the boundary condition for the "finite solution volume" condition. The more general "finite solution volume" condition is obtained from the material balance $-dQ = dQ$. The condition is (equilibrium at the interface is assumed)

$$
\mathbf{r} = a, \tau > 0 \quad \overline{C}_A(\tau) = \frac{3Vc}{aVC} \int_0^\tau J_A(\zeta) d\zeta.
$$

The solution of Equation (31) under initial Condition (18) and Boundary Condition (31) is given by Paterson (37) for the corresponding heat-transfer problem. Tabulated results are also given in Helfferich (4). For the condition of
Inequality (20) Boundary Condition (31) reduces to Boundary Condition (19) for the "infinite solution volume" condition. At this condition, the solutions of Equation (31) are equivalent.

Interpretation of resin phase diffusion was performed with the simpler "infinite solution volume" expression. The "finite solution volume" solution has been included for completeness.

D. The Nernst - Plank Interdiffusion Coefficient

In the exchange of two different ionic species, the fluxes of the species are coupled with one another. Such processes cannot be adequately described in terms of a constant diffusion coefficient. A most important feature of ion-exchange of different species is the electric coupling of the ionic fluxes. Helfferich and Plesset (38) considered the effect of electric coupling for diffusing ions within the resin phase.

It has already been pointed out that conservation of electroneutrality requires stoichiometric exchange, i.e. the fluxes (in equivalents) of the exchanging ions must be equal in magnitude since otherwise a net transfer of electric charge would result. The regulating mechanism which enforces the equality of the fluxes is the electric field set up by the diffusion process. The faster counter ion, of course, tends to diffuse at the higher rate. However, any excess charge transfer by the faster ion would build up a space charge which slows down the faster ion and accelerates the slower ion. The slightest deviation from electroneutrality results in a very strong electric field which prevents
accumulation of net charge. Thus electroneutrality is preserved. In other words the electric field generated by the diffusion process produces an electric transference of both counter ions in the direction of diffusion of the slower counter ion; this electric transference is superimposed on the chemical potential diffusion. The resulting net fluxes of the counter ions are equivalent to one another, while the purely diffusional fluxes are usually not. This discussion implies that the action of the electric forces is an essential feature of the resin phase diffusion phenomena and must be taken into account in any quantitative approach.

1. Derivation of the Nernst–Plank Interdiffusion Coefficient

This derivation follows that presented by Helfferich (4) but with some modifications to maintain continuity of this presentation.

An electric field in an electrolyte solution produces transference of ions (i.e. diffusion of ions from an area of high charge density to an area of lower charge density). In a solution of uniform composition, the transference \((J_A)_{el}\) of species \(A\) in the direction of the current is proportional to the gradient of the electric potential \(\phi\) and to the concentration \(\bar{C}_A\) and electrochemical valence \(z_A\) of the species:

\[
(J_A)_{el} = -U_A z_A \bar{C}_A \nabla \phi
\]

The proportionality factor \(U_A\) is defined as the electrochemical mobility of the species and is related to the individual ion diffusivity, \(D_A\), of the species by
the Nernst–Einstein Equation

$$U_A = \frac{\bar{D}_A \bar{\mathcal{J}}}{RT}$$

(33)

where $F$ is the Faraday constant, $R$ is the gas constant, and $T$ is the absolute temperature. Relation (33) is derived for ideal solutions but experience has shown that it can be used as a good approximation even in ion exchangers.

Deformation of ionic clouds by the electric field is known to contribute to the deviations of Equation (33) in nonideal systems but the smallness of the pores in an ion-exchange material may prevent the formation of ionic clouds.

Inside the resin phase concentration gradients exist to provide the chemical potential for the purely statistical diffusion given by Equation (15). The electric transference is superimposed on the purely statistical diffusion and the resulting net flux of species $A$ is

$$\mathcal{J}_A = (\mathcal{J}_A)_{\text{diffusion}} + (\mathcal{J})_{\text{electric}}$$

(34)

Substituting Expressions (15) and (32) results in:

$$\mathcal{J}_A = -\bar{D}_A \left( \nabla \bar{C}_A + \bar{z}_A \bar{C}_A \frac{\nabla \Phi}{RT} \right)$$

(35)

This relation is known as the Nernst–Plank Equation and holds, in ideal systems, for all mobile species present. This equation is derived under the simplifying assumptions that there is no convection transfer and that the gradients of pressure and activity coefficients are not included.

The Nernst–Plank Equations have been solved for particle–diffusion controlled exchange with the following additional assumptions. The presence
of co-ions in the ion exchanger is neglected, and the molarity of the fixed ionic
groups and the individual diffusion coefficients is assumed to remain constant.
The first assumption is a justified approximation if Donnan exclusion of the co-
ions is strong. This is the case unless the concentration of the solution is high
and the ion exchanger is weakly dissociated. The other assumptions are reason-
able approximations if swelling changes and specific interactions are not sig-
nificant.

Under these assumptions, the system is subject to the electroneutrality
condition (Equation (13) ) in concentration units

\[ z_A \bar{C}_A + z_B \bar{C}_B = -\omega \bar{C} \]  \hspace{1cm} (36)

It has been mentioned before that if the electroneutrality condition applies then
the inward and outward fluxs in equivalents must be identical, quantitatively

\[ z_A \bar{J}_A + z_B \bar{J}_B = 0 \]  \hspace{1cm} (37)

The Nernst Plank Equations for both ion species

\[ \bar{J}_A = -D_A (\nabla \bar{C}_A + z_A \bar{C}_A \frac{Z}{RT} \nabla \phi) \]  \hspace{1cm} (35a)

\[ \bar{J}_B = -D_B (\nabla \bar{C}_B + z_B \bar{C}_B \frac{Z}{RT} \nabla \phi) \]  \hspace{1cm} (35b)

These two equations for the two counter ions A and B can be combined, elimina-
ting the electric potential group of terms by using Equations (36) and (37) re-
sulting in a flux expression for \( \bar{J}_A \) of the form
\[ J_A = -\left[ \frac{D_A D_B (z_A^2 C_A + z_B^2 C_B)}{z_A^2 C_A D_A + z_B^2 C_B D_B} \right] \nabla C_A \]  \hspace{1cm} (38)

This equation may be considered as a special form of Fick's first law. It describes the coupled interdiffusion of the ion species in terms of one interdiffusion coefficient (the Nernst-Plank interdiffusion coefficient)

\[ \overline{D}_{AB} = \frac{D_A D_B (z_A^2 C_A + z_B^2 C_B)}{z_A^2 C_A D_A + z_B^2 C_B D_B} \]  \hspace{1cm} (39)

The Nernst-Plank interdiffusion coefficient for resin phase diffusion depends on the relative concentrations of A and B, i.e. on the fractional exchange capacity of a species in the exchanger which changes in the course of ion exchange. For \( C_A \ll C_B \) (i.e. \( X_A \ll 0 \)), the interdiffusion coefficient assumes the value \( \overline{D}_A \), and for \( C_B \ll C_A \) the value \( \overline{D}_B \). This implies that the ion in the smaller concentration has the stronger effect on the rate of interdiffusion.

Applying a component balance across an arbitrary differential shell results in an expression similar to Equation (17) but of non-linear form

\[ \frac{\partial \overline{C}_B}{\partial \xi} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \overline{D}_{AB} \frac{\partial \overline{C}_B}{\partial r} \right) \]  \hspace{1cm} (40)

where \( \overline{D}_{AB} \) is given by Equation (39). \( \overline{D}_{AB} \) cannot be assumed constant under the operation \( \partial / \partial r \) because it contains the dependent variable \( \overline{C}_A \). This partial differential equation has not been solved analytically. Numerical solutions
have been calculated by Helfferich and Plesset (38) and Plesset, Helfferich and Franklin (39) for different values of the ratio $\overline{D}_A/\overline{D}_B$ and for complete conversion from B form to A form (Conditions (18) and (19)) by the use of electronic computers. The results are presented in tabulated and graphical form. Recently additional numerical solutions have been produced by Hering and Bliss (15)

2. Experimental Resin Phase Ion Diffusivities

The interdiffusion coefficient defined by Equation (39) contains the ion diffusivities of the entering an exciting ions $\overline{D}_A$ and $\overline{D}_B$ respectively. The name "ion diffusivity" is chosen to distinguish this coefficient from the ions self diffusion coefficient. This distinction needs to be made because the self diffusion coefficient is obtained under equilibrium conditions (resin phase contains only one ion species) whereas the ion diffusivities are operative under conditions of changing resin phase concentration (the two species of ions and their relative concentration are continuously changing). The Nernst-Plank interdiffusion coefficient depends not only on the individual ion diffusivities $\overline{D}_A$ and $\overline{D}_B$; it is also a function of the concentration ratio $\overline{c}_A/\overline{c}$ and therefore a function of the time and space coordinates. Figure 6 shows the dependence of the interdiffusion coefficient $\overline{D}_{AB}$ on the ionic concentration of the exchanger, calculated from Equation (39), for the interdiffusion of ions of equal valence. The different curves correspond to different ratios $\overline{D}_A/\overline{D}_B$.

Numerical calculations produced by Helfferich and Plesset (38, 39)
Figure 6: Interdiffusion Coefficient in the Ion Exchanger as a Function of Composition

Interdiffusion Coefficient, $\bar{D}_{AB}$

Ionic Fraction of B

$\bar{D}_B/\bar{D}_A = 10/1$

$\bar{D}_B/\bar{D}_A = 5/1$

$\bar{D}_B/\bar{D}_A = 2/1$

$\bar{D}_B/\bar{D}_A = 1/1$

$Z_A = Z_B$
showing the variation of resin phase concentration with radius for various
values of $X_A$ appear in Figures 7, 8, and 9. The three plots represent
various ratios of $D_A/D_B$ and $X_A/X_B$. These plots show the dramatic effect
of the space coordinate ($r$-radius) on the ionic composition, and seems to
cloak any hope of determining ion diffusivities from Equation (39) and $X_A$ vs. $t$
data. These results are brought into better perspective if the following trans-
formations are performed:

$$
\frac{Z_B \overline{Q_B} (V/V_0)}{(-\omega Q)} = 3 \int_0^1 \left( \frac{r}{a} \right)^2 \frac{Z_B \overline{Q_B} (r/a)}{(-\omega C)} d(r/a) \quad (41)
$$

and

$$
V/V_0 = (r/a)^3. \quad (42)
$$

Plots of $Z_B \overline{Q_B}/(-\omega Q)$ vs. $(V/V_0)$ appear in Figures 10, 11, and 12. The plots
show that for a particular value of $X_A$ the bulk volume of the resin phase is
experiencing an approximate average concentration of $X_A$:

$$
\overline{X_A} \approx 1 - \frac{Z_B \overline{Q_B}}{(-\omega \overline{Q})} \quad (43)
$$

In the limit as $X_A$ approaches 1.0 this result is exact. This implies that $X_A$
influences the magnitude of the interdiffusion coefficient more strongly than the
spacial concentrations in determining bulk fractional resin capacity. This is
a very fortunate result and allows the concentration terms in Equation (39) to
be replaced with capacity terms with good approximation:
Figure 7  Radial Concentration Profile (4)

Ion A Entering Exchanger
Ion B Exiting Exchanger
$\frac{D_B}{D_A} = 10, \ z_A = z_B$

Concentration, $\frac{C_B}{C}$

Radial Coordinate, $r/a$
Figure 8 Radial Concentration Profile (34)
Ion A Entering Exchanger
Ion B Exiting Exchanger
$D_B/D_A = 1, \Xi_A = \Xi_B$

![Radial Concentration Profile](image_url)

- Concentration, $C_B/C$
- Radial Coordinate, $r/a$
- Curves for different $\bar{X}_A$: 0.22, 0.49, 0.77, 0.92
Figure 9: Radial Concentration Profile
Ion A Entering Exchanger $\frac{D}{D_0} = 0.1$, $\bar{z}_A = \bar{z}$

Concentration, $\bar{C}_A / \bar{C}$

Radial Coordinate, $r/a$

$\bar{z}_A = 0.90$

$\bar{z}_A = 0.75$

$\bar{z}_A = 0.50$

$\bar{z}_A = 0.25$
Figure 10 Resin Phase Saturation of Ion B with Volume
Ion A Entering Exchanger,
Ion B Exiting Exchanger,
$D_B/D_A = 10$, $Z_A = Z_B$
Figure 11  Resin Phase Saturation of Ion B with Volume
Ion A Entering Exchanger
Ion B Exiting Exchanger
$D_B / D_A = 1$, $Z_A = Z_B$
Figure 12  Resin Phase Saturation of Ion B with Volume
Ion A Entering Exchanger
Ion B Exiting Exchanger
$\overline{D}_B / \overline{D}_A = 1/10$, $\overline{\zeta}_A = \overline{\zeta}_B$
The interdiffusion coefficient defined by Equation (44) is the intrinsic interdiffusion coefficient, \( \overline{D_i} \), discussed in section C, and postulated to be a function of resin phase capacity as shown by Equation (10). The interdiffusion coefficients calculated from \( \overline{X_A} \) vs. t data and discussed in section C3 are actually experimental values of the integral interdiffusion coefficient defined by Equation (11). An integrated average of Equation (44) with respect to \( \overline{X_A} \) should yield an analytical expression for the integral interdiffusion coefficient. The following integration and algebraic manipulations are made simpler if the inverse of Equation (44) is employed:

\[
\frac{1}{\overline{D_{AB}}} = \frac{D_A D_G (Z_A^2 \overline{Q_A} + Z_B^2 \overline{Q_B})}{Z_A^2 \overline{Q_A} D_A + Z_B^2 \overline{Q_B} D_B}
\]  

This transformation entails nothing more than interpreting the reciprocal interdiffusion coefficient as a resistance coefficient. Applying the electroneutrality condition with capacity terms, Equation (13) results in:

\[
\frac{1}{\overline{D_{AB}}} = \left[ \frac{1}{\overline{D_G}} \right] \left( \frac{Z_A^2 \overline{Q_A}}{\overline{Q_A} [Z_A^2 - Z_A Z_B - \omega Z_B Q]} \right) \left[ \frac{1}{\overline{D_A}} \right] \left( \frac{Z_A Z_B \overline{Q_A} + \omega Z_B Q}{\overline{Q_A} [Z_A^2 - Z_A Z_B - \omega Z_B Q]} \right)
\]

From Equation (13) the following follows:

\[
\overline{X_A} + \overline{X_B} = 1
\]
where $\overline{X}_B$ is the fractional resin capacity occupied by ion B and is defined by

$$\overline{X}_B \equiv \frac{\omega_{AB} Q}{\omega Q} \quad (48)$$

After substitution of Equation (47), Equation (46) reduces to

$$\frac{1}{D_{AB}} = \left[ \frac{\omega_A}{D_A} - \frac{\omega_B}{D_B} \right] \left[ \frac{\overline{X}_A}{[\omega_A - \omega_B] X_A + \omega_B} \right] + \left[ \frac{\omega_B}{D_A} \right] \left[ \frac{1}{[\omega_A - \omega_B] X_A + \omega_B} \right] \quad (49)$$

A concentration averaged reciprocal interdiffusion coefficient is now defined by:

$$\left[ \frac{1}{D_{AB}} \right] \equiv \frac{\int \overline{X}_A d\overline{X}_A}{\overline{X}_A} \quad (50)$$

This integrated form of the reciprocal intrinsic interdiffusion coefficient will be the reciprocal integral interdiffusion coefficient,

$$\left[ \frac{1}{D_{AB}} \right] = \left[ \frac{\omega_A}{D_A} - \frac{\omega_B}{D_B} \right] \left[ \frac{\overline{X}_A}{[\omega_A - \omega_B] X_A + \omega_B} \right] + \left[ \frac{\omega_B}{D_A} \right] \left[ \frac{1}{[\omega_A - \omega_B] X_A + \omega_B} \right] \quad (51)$$

The indicated integrals may be found in any elementary calculus text (30).

Performing the indicated operations yields:

$$\left[ \frac{1}{D_{AB}} \right] = \left[ \frac{1}{D_A} \right] \left[ \frac{\omega_A}{D_A} - \frac{\omega_B}{D_B} \right] \left[ \frac{\omega_B Z_B}{[\omega_A - \omega_B] X_A + \omega_B} \right] + \left[ \frac{1}{D_B} \right] \left[ \frac{1}{D_A} \right] \left[ \frac{1}{\omega_A Z_B} \right] \quad (52)$$
This form of the reciprocal integral interdiffusion coefficient is unsuited for the case \( \Xi_A = \Xi_B \) since
\[
\frac{1}{\Xi_A - \Xi_B} \quad \text{and} \quad \frac{\Xi_A \Xi_B}{(\Xi_A - \Xi_B)^2}
\] are undefined.

Setting \( \Xi_A = \Xi_B \) in Equation (47) and integrating results in
\[
\left[ \frac{1}{D_{AB}} \right] = \frac{1}{D_A} + \frac{1}{2} \left[ \frac{1}{D_B} - \frac{1}{D_A} \right] \Xi_A. \tag{53}
\]

A check for the limit of \( (1/D_{AB})^\ast \) at \( \Xi_A = 0 \) shows
\[
\lim_{\Xi_A \to 0} \left[ \frac{1}{D_{AB}} \right] = \left[ \frac{1}{D_A} \right]. \tag{54}
\]

The following equality is used in the limiting process:
\[
\lim_{\Xi_A \to 0} \left( \ln \left( \frac{\Xi_B}{(\Xi_A - \Xi_B)\Xi_A + \Xi_B} \right) \right) = -\frac{\Xi_A - \Xi_B}{\Xi_B}. \tag{55}
\]

This limit check shows that the entering ion has the stronger influence of the magnitude of the interdiffusion coefficient. The limit at \( \Xi_A = 1 \) has no meaning because of the integration process.

Numerical results for Equations (52) and (53) appear in Figures 13, 14, 15, and 16. These results are for \( D_A / D_B \) ratios of 0.1 and 10.0 and Table 2 shows the valences which apply to the various combinations of valences for the entering and exiting ions. It should be noted in these figures that the valence has a strong influence on the reciprocal interdiffusion coefficient.
TABLE NO. 2

Valence Combinations - Entering and Exiting Ions

<table>
<thead>
<tr>
<th>Case</th>
<th>Valence ion A $Z_A$</th>
<th>Valence ion B $Z_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>II</td>
<td>-1</td>
<td>-2</td>
</tr>
<tr>
<td>III</td>
<td>-1</td>
<td>-3</td>
</tr>
<tr>
<td>IV</td>
<td>-1</td>
<td>-4</td>
</tr>
<tr>
<td>V</td>
<td>-2</td>
<td>-1</td>
</tr>
<tr>
<td>VI</td>
<td>-2</td>
<td>-2</td>
</tr>
<tr>
<td>VII</td>
<td>-2</td>
<td>-3</td>
</tr>
<tr>
<td>VIII</td>
<td>-2</td>
<td>-4</td>
</tr>
<tr>
<td>IX</td>
<td>-3</td>
<td>-1</td>
</tr>
<tr>
<td>X</td>
<td>-3</td>
<td>-2</td>
</tr>
<tr>
<td>XI</td>
<td>-3</td>
<td>-3</td>
</tr>
<tr>
<td>XII</td>
<td>-3</td>
<td>-4</td>
</tr>
<tr>
<td>XIII</td>
<td>-4</td>
<td>-1</td>
</tr>
<tr>
<td>XIV</td>
<td>-4</td>
<td>-2</td>
</tr>
<tr>
<td>XV</td>
<td>-4</td>
<td>-3</td>
</tr>
<tr>
<td>XVI</td>
<td>-4</td>
<td>-4</td>
</tr>
</tbody>
</table>
Figure 13 Reciprocal Integral Interdiffusion Coefficient with Resin Capacity

\[
\frac{1}{D_A} = 10 \\
\frac{1}{D_B} = 1
\]

\( \bar{X}_A \), Fractional Resin Capacity
Figure 14: Reciprocal Integral Interdiffusion Coefficient with Resin Capacity

Reciprocal Integral Interdiffusion Coefficient, $\left[1/D_{AB}\right]^2$

$1/D_A = 10$
$1/D_B = 1$

$x_A$, Fractional Resin Capacity
Figure 15: Reciprocal Integral Inter-diffusion Coefficient with Resin Capacity

Reciprocal Integral Inter-diffusion Coefficient \( \left[ \frac{1}{1 + D_{AB}} \right] \)

- \( \frac{1}{D_A} = 1 \)
- \( \frac{1}{D_B} = 10 \)

\( X_A \), Fractional Resin Capacity

Graph showing the relationship between \( X_A \) and the reciprocal integral inter-diffusion coefficient for different values of \( \frac{1}{D_A} \) and \( \frac{1}{D_B} \).
Figure 16 Reciprocal Integral Interdiffusion Coefficient with Resin Capacity

Reciprocal Integral Interdiffusion Coefficient $\left[ \frac{1}{D_A} \right]^2$

$1/D_A = 1$
$1/D_B = 10$

$\chi_{AI}$, Fractional Resin Capacity
CHAPTER V

EXPERIMENTAL TECHNIQUE

A. Shallow Bed Reactor

A shallow bed reactor consists of a thin bed of resin held in a circular section of glassware supported above and below by screen. The liquid containing an exchangeable counter ion is forced through the bed either upflow or downflow at a high, constant rate. The change in effluent composition with time is measured. This can be done by collecting and analyzing samples. The measurement gives the exchange flux as a function of time. The fractional attainment of equilibrium as a function of time can be obtained from the flux by graphical integration. This technique is applicable to ion exchange and isotopic exchange.

Boyd (6) was the first to employ this device for particle diffusion control studies. duDomain and co-workers (10) were first to use a shallow bed made of ion exchange material. This method of contacting resin and liquid has been developed (7) until the bed has been replaced by a single particle (13, 14). The device employed in this study is constructed in a manner similar to that employed by Tien (11).

The device consists of a Buchner funnel (with frit removed) fitted with two removable screens. Diameter of the funnel is 1.65 inches. The bottom screen is supported below by glass shot. The upper screen rests upon the resin. The funnel is attached to the reactor entrance section with a specially adopted 1 1/2 inch union and associated O-ring seal. The reactor entrance section consists
of a 1/2" X 1 1/2" swedge. Construction details are shown in Figure 17. The reactor is proceeded by a three-way stopcock which can be opened instantaneously to send feed to the reactor. The completed apparatus contains service lines to set the flow rate and prepare the reactor for operation. Figure 18 shows the reactor and accessory apparatus. The resin is not regenerated in the reactor but is prepared within standard laboratory glassware and slurried into the reactor with distilled water.

B. Chloride Analysis Techniques

1. Silver Electrode

Chloride ion concentrations were measured using a Beckman Silver Electrode (40) with associated Standard Calomel Reference Electrode and a Leeds and Northrup Expanded Range pH Meter (41). The electrode was calibrated with solutions of known chloride concentrations. A calibration curve was prepared. A straight line was obtained on a semi-log plot of chloride concentration with millivolt potential (\( \Delta \text{pH} \) units). The millivolt potential was obtained for each unknown sample and the calibration curve was used to obtain the corresponding chloride concentration. The electrode was recalibrated anew prior to each batch of samples. This technique gave satisfactory results and was employed for all equilibrium runs and several of the shallow bed reactor runs. The remaining shallow bed reactor runs were analyzed by tracer techniques anticipating a self-diffusion run.
Figure 17, Essential Features of Shallow Bed Reactor

- Swedge ½" x 1½"
- Teflon Seat
- "O"-ring
- 1½" Union
- Resin Bed
- Glass Shot
- Screen
- Buchner Funnel

Direction of Flow

Scale 1 inch
2. Liquid Scintillation Counter

Chloride analysis was improved by employing chlorine - 36 as a tracer. Each batch of 0.1N NaCl was tagged with a quantity of Cl-36 available as 0.32 N HCl. Table 3 gives technical data on the isotope. The amount of Cl-36 added to each batch was equivalent to approximately 5,000 disintegrations per minute. A Tri-Carb Liquid Scintillation Spectrometer System (42) was used to measure the activity of the samples.

Problems were encountered while trying to incorporate 1 ml. of aqueous NaCl sample into the naphthalene - paradoxane scintillation solvent suggested by Peng (43). The suggested solvent incorporated the aqueous phase but "salted out" the dissolved NaCl which settled to the bottom of the vial as a white perci-citate and in turn drastically lowered the measurable counts. This problem was overcome by employing a thixotropic gel (44) which suspended the insoluble matter and stopped settling almost completely. The final liquid scintillator developed was 4 grams PPO, 0.1 grams POPOP, 625 ml. Toluene, 375 ml. ethyl alcohol and 50 grams of Thixcin. Settling over a three day period showed no reduction in counts. Measurement was made with 1 ml. of sample in 20 ml. of scintillator liquid.

Tests were made to determine any chemical quenching exerted by the presence of HCO$_3^-$ in shallow bed run samples. It is conceivable that HCO$_3^-$ could adsorb some energy associated with the $\beta$-particle and degrade it to a form not capable of exciting the fluor. No quenching was detected and the main source of error was found to be due to variation in delivery of 1 ml. of the
**TABLE 3**

Technical Data Cl - 36 Radioisotope Solution

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isotope</td>
<td>Cl - 36</td>
</tr>
<tr>
<td>Mode of Decay</td>
<td>( \beta )</td>
</tr>
<tr>
<td>Half Life</td>
<td>( 3 \times 10^5 ) yr.</td>
</tr>
<tr>
<td>Energy</td>
<td>0.71 Mev.</td>
</tr>
<tr>
<td>Assay Date</td>
<td>10/20/67</td>
</tr>
<tr>
<td>Chemical Form</td>
<td>.32 N. HCl</td>
</tr>
<tr>
<td>Specific Activity</td>
<td>1.04 ( \mu ) curies/gr.</td>
</tr>
<tr>
<td>Concentration</td>
<td>11.84 ( \mu ) C/ml.</td>
</tr>
<tr>
<td>Radiometric Purity</td>
<td>99%</td>
</tr>
<tr>
<td>Principal Radioactive Contaminants</td>
<td>none</td>
</tr>
<tr>
<td>Total Solids</td>
<td>0.1 mg./ml.</td>
</tr>
<tr>
<td>Method of Preparation</td>
<td>Cl - 35 (n,( \gamma )) Cl - 36.</td>
</tr>
</tbody>
</table>
sample. After obtaining the correct pipet and perfecting a technique very satisfactory results were obtained.

C. Resin Preparation

Five pounds of virgin IRA-68 was obtained from the Rohm and Haas Company, Philadelphia, Pennsylvania. The following steps were performed to prepare the resin prior to and after shallow bed reactor runs.

1. Screening

The virgin resin (received in free base form) was washed with tap water. The resin was then slurried onto a U.S. Standard 20 mesh screen with tap water. Only those beads which became entrapped in the screen openings were used in the shallow bed. Particles of diameter of 0.0841 cm. were used in all runs. The remainder of the resin was set aside for equilibrium studies.

2. Chemical Treatment of Resin

The resin was treated through two cycles of HCl-NH₄OH additions to leach out any unpolymerized organics and other foreign materials. One reactor charge of resin (4 - 5 grams) was placed in a fritted Buckner funnel and treated with a 4% NH₄ solution for a period of not less than twenty four hours. The resin was then washed with distilled water for twenty four hours. A day prior to entering the shallow bed reactor the resin was carbonated for a period of not less than twenty four hours with the carbonation apparatus shown in Figure 19.
Figure 19, Resin Carbonation Apparatus

1" Glass Carbonation Column

CO₂
The reaction representing the carbonation treatment is

$$[R-N] + H_2O + CO_2 \rightleftharpoons [R-NH]HCO_3.$$ (56)

The resin is now in the bicarbonate form. Prior to entering the reactor, the resin was again flushed with distilled water. Reactor feed was NaCl and the chloride ion replaced the $\text{HCO}_3^-$ ion on the resin by the reaction

$$[R-NH]HCO_3 + \text{NaCl} \rightleftharpoons [R-NH]Cl + \text{NaHCO}_3.$$ (57)

After completion of a shallow bed run the resin was removed from the reactor leached with NaCl to replace any remaining $\text{HCO}_3^-$ ions and treated with 4% NH solution, rinsed and dried at 60°C. Drying was for ten days, the time required for the resin to approach a constant weight. After weighing the resin was discarded.

D. Data Processing

1. Rough Reactor Data
   a. An Interdiffusion Run

With the resin in the bicarbonate form the reactor is ready for an interdiffusion run (i.e. exchange of $\text{HCO}_3^-$ for Cl$^-$). The feed solution contains 0.100N NaCl tagged with Cl-36. Flow rate through the reactor is adjusted (approximately) with distilled water by the rate control valve. After adjusting the desired rate the valve remains at the set opening and the run is initiated by switching the three-way stopclock to the feed position. Samples are obtained
at the reactor outlet at predetermined intervals of time. Sample interval was 15 to 30 seconds for a duration of 8 to 10 minutes. All liquid through the reactor including sample volume was collected to obtain a precise flow rate. Analysis of the samples were performed with the Silver Electrode or the Liquid Scintillation Counter. Figure 20 is an example of the rough data obtained from an interdiffusion run. Note that the outlet concentration approaches the inlet concentration as run time increases.

b. A Self-diffusion Run

The self-diffusion run was performed differently than the interdiffusion run. A reactor charge of resin in the bicarbonate form was treated for a period of twenty-four hours with a 0.100 N. NaCl solution tagged with Cl-36. This placed tagged Cl-36 on the resin. The feed solution to the reactor contained un-tagged 0.100 N. NaCl. Figure 21 is an example of the rough data obtained from a self-diffusion run. Note that the outlet concentration of Cl-36 approaches zero as run proceeds.

2. Final Experimental Data

a. Interdiffusion Data

Graphical integrating the rough reactor data of the exchange flux allows determination of the resin concentration of the entering ion, $C_{Cl}$, with time. As was pointed out in Section A of Chapter IV, the rate of flow past the resin beads must be increased until the condition of particle diffusion is controlling.
Figure 20, Liquid Concentration Reactor Outlet with Run Time

Run 9
Feed: 0.100 N. NaCl.
Feed tagged Cl\textsuperscript{36}.
HCO\textsubscript{3} on Resin.
Resin: IRA-68
Temperature: 29\textdegree C.
Figure 21, Liquid Concentration at Reactor Outlet with Run Time

Run 105
Feed: 0.1 N NaCl
Resin Tagged Cl\textsuperscript{36}
Resin: IRA-68
Cl\textsuperscript{-} on Resin
Temperature: 29\degree C.
Figure 22 shows average resin phase concentration of the entering chloride ion, $\overline{C_{Cl}}$, as a function of contact time for various linear flow rates. Linear rates in cm/min are calculated as being four times the volumetric flow rate divided by the bed area. The bed area for all runs was 13.85 cm$^2$. The factor of four is used because for a bed of closely packed spheres of uniform size, the bed voids are about 25% of the bed volume.

In order to determine fractional capacity of the entering ion, $\overline{X_{Cl}}$, the effective capacity of the resin for each run must be known. Inspection of Figure 22 shows that there is no consistent trend of chloride uptake with linear flow rate. Note that Run 68-9 falls below Run No. 3 although its rate is nearly twice that of No. 3. The effective resin capacity of a weakly basic resin is a strong function of the pH as indicated in Appendix A. pH values of the feed varied from 6.48 to 6.83 which is a significant variation. These inlet pH values were below the range used for equilibrium study and effective capacity data was obtained by other means.

It is possible to fit each curve with the relation

$$\log \overline{C_{Cl}} = a + \frac{b}{t}$$

Setting $t = \infty$ (i.e. extrapolating to large times) allowed procurement of the capacity at large times which should be the effective capacity for the particular run conditions:

$$\overline{C_{Cl}}^e = \text{antilog } a$$

After effective capacities are obtained fractional capacity with contact time is
Figure 22 Resin Phase Chloride Concentration with Contact Time
Interdiffusion: Cl\(^-\) Entering - HCO\(_3\)\(^-\) Exiting
Resin: IRA-68, Liquid Phase: 0.100 M NaCl

- Run 68-4, 79.7 cm/min
- Run 68-9, 87.5 cm/min.

- Run 68-3, 50.5 cm/min.
- Run 68-2b, 48.5 cm/min.

Resin Phase Concentration, mg Cl/ltr

Contact Time, seconds
immediate, Figure 23. This plot reveals that a linear flow rate of 79.7 to 87.5 cm/min. is within the region of particle diffusion control. Even the data at 50.5 cm./sec. is approaching this condition. These particle diffusion linear flow rates are in agreement with those reported by Boyd (6) and much higher than those of Kuo (13) and Rao (14).

b. Self-diffusion Data

Once the linear rate for the particle diffusion controlling condition was established, a self diffusion run was performed. This data was obtained at a flow rate of 84.2 cm/sec. This data was handled similar to that of the interdiffusion data. Figure 24 shows the chloride self-diffusion data along with the \( \text{Cl}^- - \text{HCO}_3^- \) interdiffusion data. Note that the self-diffusion data approached equilibrium more rapid than the interdiffusion data indicating the \( \text{HCO}_3^- \) ion diffuses at a slower rate than the \( \text{Cl}^- \) ion. Data for all runs appears in Appendix C.
Figure 23, Fractional Resin Concentration Chloride with Contact Time
Interdiffusion: Cl⁻ Entering - HCO₃⁻ Exiting
Resin: IRA-68, Liquid Phase: 0.100 N NaCl

- □ Run 68-4, 79.7 cm/sec.
- ○ Run 68-9, 87.5 cm/sec.
- △ Run 68-3, 50.5 cm/sec.
- ○ Run 68-2b, 48.5 cm/sec.
Figure 24, Fractional Resin Concentration Chloride with Contact Time
Resin: IRA-68
Liquid Phase: 0.100 N NaCl

Cl⁻ Self-diffusion, ○ Run 68-105, 84.2 cm./sec.
Cl⁻-HCO₃⁻ Interdiffusion, + Run 68-9, 87.5 cm./sec.
CHAPTER VI

ANALYSIS OF PARTICLE DIFFUSION CONTROLLED EXCHANGE

The most desirable method of obtaining ion exchange kinetic data is through an experimental technique which approaches the idealized "infinite solution volume" condition. The only changing variable is the concentrations of ions in the exchange resin. In chapter four is presented a model for the diffusion process occurring in a spherical resin particle. This model defines a diffusion coefficient which is dependent on the ion concentrations of the resin phase and is developed to the point of an integral interdiffusion coefficient. This integral interdiffusion coefficient is the same coefficient obtainable from kinetic data.

All interdiffusion and self-diffusion data may be presented as a plot of $X_A$ vs. $t$; where $X_A$ is the fractional capacity of the exchanger occupied by the entering ion and $t$ is the time of phase contact. This information along with the solution to the partial differential equation for spherical geometry and the "infinite solution volume" condition may be transformed to the corresponding values of $D_x$ vs. $X_A; D_x$ being the integral interdiffusion coefficient. This transformation is exact since there exist and is available an analytical solution. This solution transforms the original kinetic data with its associated un-steady state-spherical geometry conditions to a set of linear variables. This transformation was performed with an interpolating polynomial as shown in Appendix B. All numerical calculations were performed by electronic computer. The discussions to follow are all based on the transformed data.
This study provides basic kinetic data for the interdiffusion of \( \text{Cl}^- \) and \( \text{HCO}_3^- \) ions in Amberlite IRA-68. Extensive literature data by six authors is also employed to amplify and give support to the ideas presented. This body of published data is under the conditions of particle diffusion controlled kinetics with the added infinite solution volume restriction. For the purpose of analysis it is convenient that these data be presented in plot form. Figures 25 through 39 present fifteen individual kinetic studies representing three types of resin and six ions. The fractional resin capacity, \( \bar{X}_A \), is the independent variable and the reciprocal integral interdiffusion coefficient, \( 1/\bar{D}_z \), is the dependent variable. Table 4 contains a summary of the data presented in the figures.
Table 4

Summary of Integral Interdiffusion Coefficient Data

<table>
<thead>
<tr>
<th>Figure No.</th>
<th>Resin</th>
<th>Electrolyte Solution</th>
<th>Entering Ion</th>
<th>Exiting Ion</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>Amberlite IRA-68</td>
<td>0.1 N. NaCl</td>
<td>Cl⁻</td>
<td>Cl⁻</td>
<td>Thibodeaux</td>
</tr>
<tr>
<td>26</td>
<td>Dowex 50W-X8</td>
<td>2N. BaCl₂</td>
<td>Ba⁺⁺</td>
<td>Ba⁺⁺</td>
<td>Kuo, David (13)</td>
</tr>
<tr>
<td>27</td>
<td>Dowex 50W-X8</td>
<td>0.1N. Cl⁻</td>
<td>Na⁺</td>
<td>Na⁺</td>
<td>Morig, Rao (31)</td>
</tr>
<tr>
<td>28</td>
<td>Dowex 50W-X8</td>
<td>0.1NCl⁻</td>
<td>Sr⁺⁺</td>
<td>Sr⁺⁺</td>
<td>Morig, Rao (31)</td>
</tr>
<tr>
<td>29</td>
<td>Dowex 50W-X8</td>
<td>1.0N. NaCl</td>
<td>Na⁺</td>
<td>Na⁺</td>
<td>Rao, David (14)</td>
</tr>
<tr>
<td>30</td>
<td>Polysulfonic Acid</td>
<td>0.1N. KCl</td>
<td>K⁺</td>
<td>K⁺</td>
<td>Tetenbaum (7)</td>
</tr>
<tr>
<td>31</td>
<td>Amberlite IRA-68</td>
<td>0.1N. NaCl</td>
<td>Cl⁻</td>
<td>HCO⁻</td>
<td>Thibodeaux</td>
</tr>
<tr>
<td>32</td>
<td>Dowex 50W-X8</td>
<td>2N. BaCl₂</td>
<td>B⁺⁺</td>
<td>Na⁺</td>
<td>Kuo, David (13)</td>
</tr>
<tr>
<td>33</td>
<td>Dowex 50W-X8</td>
<td>2N. NaCl</td>
<td>Na⁺</td>
<td>Ba⁺⁺</td>
<td>Kuo, David (13)</td>
</tr>
<tr>
<td>34</td>
<td>Dowex 50W-X8</td>
<td>0.5N. NaCl</td>
<td>Sr⁺⁺</td>
<td>Na⁺</td>
<td>Morig, Rao (31)</td>
</tr>
<tr>
<td>35</td>
<td>Dowex 50W-X8</td>
<td>0.5N. NaCl</td>
<td>Na⁺</td>
<td>Sr⁺⁺</td>
<td>Morig, Rao (31)</td>
</tr>
<tr>
<td>36</td>
<td>Dowex 50W-X8</td>
<td>0.1N. CuCl₂</td>
<td>Cu⁺⁺</td>
<td>Na⁺</td>
<td>Rao, David (14)</td>
</tr>
<tr>
<td>37</td>
<td>Dowex 50W-X8</td>
<td>1.0N. CuCl₂</td>
<td>Cu⁺⁺</td>
<td>Na⁺</td>
<td>Rao, David (14)</td>
</tr>
<tr>
<td>38</td>
<td>Dowex 50W-X8</td>
<td>2.0N. CuCl₂</td>
<td>Cu⁺⁺</td>
<td>Na⁺</td>
<td>Rao, David (14)</td>
</tr>
<tr>
<td>39</td>
<td>Dowex 50W-X8</td>
<td>4.0N. CuCl₂</td>
<td>Cu⁺⁺</td>
<td>Na⁺</td>
<td>Rao, David (14)</td>
</tr>
</tbody>
</table>
Figure 25 Self-Diffusion Coefficient
Exchange: Cl⁻ Entering - Cl⁻ Exiting
Resin: Amberlite IRA-6B
Electrolyte Solution: 0.1 M NaCl
Figure 26
Self-Diffusion Coefficient Exchange: Ba⁺ Exchanging -Ba⁺ Exiting
Electrolyte Solution: 2.0M BaCl₂
Data Source: Pico (15)
Figure 27 Self-Diffusion Coefficient
Exchange: Na+ Entering - Na+ Exiting
Resin: Dowex 50W-X8
Electrolyte Solution: 0.5 M NaCl
Data Source: Merig and Gopala Rao (31)

Reciprocal Integral Interdiffusion Coefficient, $1/D_s \times 10^{-6}$

$X_n$ - Fractional Resin Capacity

0.0  0.2  0.4  0.6  0.8  1.0
Figure 28  Self-Diffusion Coefficient
Exchange: Sr$^{++}$ Entering - Sr$^{++}$ Exiting
Resin: Dowex 50W-X8
Electrolyte Solution: 0.6N SrCl$_2$
Data Source: Norig and Gopala Rao (31)
Figure 29 Self-Diffusion Coefficient
Exchange: Na⁺ Entering - Na⁺ Exiting
Resin: Dowex 50W-X8
Electrolyte Solution: 1.0N NaCl
Data Source: Rao and David (14)
Figure 30 Self-Diffusion Coefficient  
Exchange: Potassium Self-Diffusion  
Resin: Polystyrenesulfonic Acid - 12% DVB  
Electrolyte: Solution: 0.1 M KCl  
Data Source: Tetenbaum and Gregor (7)
Figure 31 Reciprocal Integral Interdiffusion Coefficient
Exchange: Cl<sup>-</sup> Entering - HCO<sub>3</sub><sup>-</sup> Exiting
Resin: Amberlite IRA-68
Electrolyte Solution: 0.1 N NaCl
Figure 9.2 Reciprocal Integral Interdiffusion Coefficient
Exchange: Ba\(^{+4}\) Entering - Na\(^{+}\) Exiting
Resin: Dowex 50W-X8
Electrolyte Solution: 2.0 N. BaCl\(_2\)
Data Source: Kuo (13)
Figure 33  Reciprocal Integral Interdiffusion Coefficient
Exchange: Na⁺ Entering - Ba⁺⁺ Exiting
Resin: Dowex 50 W-X8
Electrolyte Solution: 2.0N NaCl
Data Source: Kuo (13)
Figure 34  Reciprocal Integral Interdiffusion Coefficient
Exchange: Sr$^{++}$ Entering - Na$^+$ Exiting
Resin: Dowex 50W-X8
Electrolyte Solution: 0.5N NaCl
Data Source: Morig and Gopala Rao (31)
Figure 35 Reciprocal Integral Interdiffusion Coefficient
Exchange: Na\(^+\) Entering - Sr\(^{2+}\) Exiting
Resin: Dowex 50H-8X
Electrolyte Solution: 0.5 N SrCl\(_2\)
Data Source: Morig and Gopala Rao (31)
Figure 36: Reciprocal Integral Interdiffusion Coefficient
Exchange: Cu** Entering - Na+ Exiting
Resin: Dowex 50W - X
Electrolyte Solution: 0.1 N CaCl₂
Data Source: Rao and David (140)
Figure 37  Reciprocal Integral Interdiffusion Coefficient
Exchange: Cu$^{2+}$ Entering - Na$^+$ Exiting
Resin: Dowex 50W-8X
Electrolyte Solution: 1.0 M CuCl$_2$
Data Source: Rao and David (197)
Figure 3B: Reciprocal Integral Interdiffusion Coefficient, $1/D_t \times 10^{-6}$

- Xa: Fractional Resin Capacity
- Exchange: Dowex 50W-8X
- Electrolyte Solution: 2M CuCl₂
- Data Source: Rao and David (19)
Figure 39  Reciprocal Integral Interdiffusion Coefficient
Exchange: Cu$^{2+}$ Entering - Na$^+$ Exiting
Resin: Dowex 50W-8X
Electrolyte Solution: 1.0 N CuCl$_2$
Data Source: Rao and David (14)
A. Experimental Integral Resin Phase Interdiffusion Coefficient

The diffusion coefficients presented above are experimental reciprocal integral interdiffusion and self-diffusion coefficients. Most plots show that for low values of $X_A$ (near zero) a high reciprocal coefficient is measured. Figure 26 does not show this but it should be noted that they contain no data for low values of $X_A$ (0.12 is the lowest value of $X_A$ for this plot). This particular behavior is entirely in accord with the exchange at early contact times and gives support to the hypothesized integral interdiffusion coefficient.

Prior to contacting the two phases, the resin contains all of one ion and the liquid phase contains all of another. Upon contact there is an infinite concentration gradient presented to the entering ion because the resin contains none of its species. If the interdiffusion process is described by a relation of the form

$$J_A = - D_1 \nabla C_A$$

(60)

it is obvious that a infinite rate of exchange is demanded. An infinite transfer rate is impossible but must always be finite. Finite rates are measured. The mathematics of particle diffusion controlled exchange as a consequence produce very small values of $D_1$ in an attempt to satisfy the equality of Equation (60). Small values of $D_1$ result in large reciprocal coefficients. A reason for not achieving infinite fluxes is given by Helfferich and Plesset (38). For a very short initial period (small $X_A$) film diffusion must be the rate controlling step.
Also during these first few minutes of contact, there is a sudden change in
environment for the resin particle. The particle upon contact with the exchang­
ing ion's phase is simultaneously plunged into an electrolyte solution. Kuo (13)
and Morig (31) show that the resin particle decreases in size when placed in an
electrolyte environment. A reduction in size results after the expulsion of
"free" water. This water expulsion and resin matrix contraction may also
contribute to the initial high resistance (reciprocal coefficient).

1. **Self-Diffusion Coefficients**

The self-diffusion process is characterized by a constant diffusion coeffi­
cient as discussed in section B1 of Chapter 4. Figures 25 through 30 contain
data for the self-diffusion kinetics. Figures 26, 28 and 29 show dramatically
the effect of a constant intrinsic interdiffusion coefficient on the reciprocal
integral interdiffusion coefficient. In these figures the coefficient maintains a
near constant value throughout the remainder of the exchange after the charac­
teristic high at the start. The remaining curves show a decreasing coefficient
well into the exchange and then a leveling off. This gradual approach to a
constant value may be due to the film resistance. The condition of particle
diffusion controlling is not attained for early stages of the exchange.

2. **Interdiffusion Coefficients**

The interdiffusion of two counter ion species should produce a reciprocal
integral interdiffusion coefficient that varies with resin capacity. A constant
Coefficient should result only if each species diffuses at the same rate (i.e. equivalent self-diffusivities). Figures 31 through 39 show transformed results for interdiffusion kinetics. After the initial high the reciprocal integral interdiffusion coefficient continues to vary with $X_A$. Several curves reveal a tendency toward slope reversal for large values of $X_A$, particularly Figures 34, 35, 37, 38 and 39. No explanation can be given for this behavior.

These plots show, uniformly, a varying reciprocal integral interdiffusion coefficient unlike those for self-diffusion. This continued variation is due to different self-diffusivities of the exchanging ion species. Chapter 4, Section D2 contains theoretical curves for interdiffusing species of typical valence combinations for the case of $D_A = 10D_B$ and $D_B = 10D_A$. Ion A is entering and ion B is exiting the exchanger. For the case $D_D = 10D_A$ the theoretical curves predict a reciprocal integral interdiffusion coefficient that should increase with resin capacity. This means that when the exchanger contains the faster ion there should be an increase in the resistance coefficient with $X_A$. None of the plots show this trend. Morig and Rao (31) have shown from self-diffusion studies that $Na^+$ diffuses faster than $Sv^{++}$ but inspection of Figure No. 34 shows no reversal trend. This same case is evident in Figure 32 where Barium is the slower ion entering to replace a faster Sodium ion (13). The theoretical curves do not contain any concentration effects that may be occurring from point to point through out the resin bead. The curves were made possible only after fractional capacity was substituted for average resin concentration (see Chapter 4, section D2 for details).
B. Experimental Resin Phase Ion Diffusion Coefficients

Current methods of predicting particle diffusion controlled exchange are the Ficks' law model and the Nernst-Plank model. The Ficks' law model consists of averaging the experimental integral interdiffusion coefficients and employing it as a constant diffusion coefficient. The Nernst-Plank model goes a step further. This method defines the above averaged integral interdiffusion coefficient as the mutual diffusion coefficient of the ion initially present in the exchanger. This definition is used because all the numerical results produced by Helfferich and Plesset (38) are calculated with this condition. Using this mutual diffusion coefficient, \( t \) and \( a \), a corresponding \( \mathcal{C} \) may be obtained for each data point. Superimposing the data of \( \bar{X}_A \) vs. \( \mathcal{C} \) upon the numerical solutions allow graphical procurement of the mutual diffusion coefficient of the entering ion. These mutual diffusion coefficients are employed in Equation (39).

Solution of the non-linear partial differential Equation (40) will nearly duplicate the experimental data. This second model has been employed by Hering and Bliss (15), Kuo and David (13), and Rao and David (14).

Both of the above models suffer because of gross simplifications. The Nernst-Plank model produces better results because it consists of two empirical mutual diffusion coefficients and an independent variable while the Ficks' law model contains only one empirical constant. The Nernst-Plank has the added computation difficulties because of its non-linear nature while the Ficks' law has no such difficulty. It is possible to retain the good attributes of each model by employing the integral interdiffusion coefficient developed in this work.
Equations (52) and (53) are the expressions for the reciprocal integral interdiffusion coefficient as a function of individual ion diffusivities and the fractional resin capacity. It is possible to fit these equations to the transformed data of $1/D_I$ vs. $\bar{x}_A$ and determine the necessary constants. The equations are:

\[ \frac{1}{D_I} = A + B \ln \left( \frac{\bar{x}_B}{(\bar{x}_A - \bar{x}_B)\bar{x}_A + \bar{x}_B} \right) / \bar{x}_A \quad (60) \]

for $\bar{x}_A \neq \bar{x}_B$ and

\[ \frac{1}{D_I} = A' + B' \bar{x}_A \quad (61) \]

for $\bar{x}_A = \bar{x}_B$. A multiple regression computer program (45) evaluates the complex natural log function and performs a simple regression to yield values of $A$ and $B$. Values of $A'$ and $B'$ are obtained similarly.

This regression was performed on the data shown in Figures 38 and 39. Average Ficks' law diffusion coefficients were also obtained from this data. Figures 40 and 41 show a comparison of models in repredicting the particle diffusion controlled exchange. The integral interdiffusion coefficient model does a considerably better job of prediction. An iterative technique was employed with this model since a value of $\bar{x}_A$ is needed before an interdiffusion coefficient can be computed. The iterative technique was initiated by employing the Ficks' law coefficient for the first try and switching to Expression (60) for the remainder of the computation. The program converged within a differential
Figure 40 Prediction of Particle Diffusion Controlled Exchange

\[ \frac{D}{D_t} = \frac{9.64 \times 10^{-7}}{1.529 \times 10^{-6} \ln \left( \frac{X_A + 1}{X_A} \right)} \]

- Experimental Data
- Fick's Law Model
- Integral Interdiffusion Model

O. 0.5 0.7 0.6 0.8 0.9 1.0
X_A, Fractional Capacity

0 100 200 300 400 500 600 700 800
Contact time, seconds
Figure 4.1 Prediction of Particle Diffusion Controlled Exchange

\[ \chi_A, \text{Fractional Capacity} \]

- Experimental Data
- Fick's Law Model
  \[ D = 6.912 \times 10^{-7} \]
- Integral Interdiffusion Model
  \[ \frac{1}{D} = -1.386 \times 10^6 \left( -3.649 \times 10^6 \frac{1}{k_A} - \frac{1}{k_A+1} \right)^{1/2} \]

\( t, \text{contact time, seconds} \)
in $X_A$ of 0.01% with six or less iterations.
C. Experimental Resin Phase Ion Diffusivities

1. Determination of Ion Diffusivities

Inspection of equation (6.9) and (5.2) reveals that once the regression coefficients A and B are obtained, 1/D_A and 1/D_B are also available.

Simultaneous solution of

\[
A = \left[ \frac{1}{z_A - z_B} \right] \left[ \frac{z_A}{D_B} - \frac{z_B}{D_A} \right]
\]  

(62)

and

\[
B = \frac{z_A z_B}{(z_A - z_B)^2} \left[ \frac{1}{D_B} - \frac{1}{D_A} \right]
\]  

(63)

results in

\[
\frac{1}{D_A} = A - B \left[ \frac{z_A - z_B}{z_B} \right]
\]  

(64)

and

\[
\frac{1}{D_B} = A - B \left[ \frac{z_A - z_B}{z_A} \right]
\]  

(65)

The corresponding results for the case of z_A = z_B is

\[
\frac{1}{D_A} = A'
\]  

(66)
and

\[ \frac{1}{D_B} = A' + 2B'. \] 

This technique allows experimental determination of the effective ion diffusivities for all or part of the experimental data.

The ion diffusivities computed in the above fashion are not the ion diffusivities employed in the Nernst-Plank model. Regression Equations (52) and (53) were obtained after concentrations were replaced with capacity terms. These equations are only valid for $X_A = 1$ as discussed in section D2 of Chapter 4. Very few of the experimental curves of $1/D_I$ vs. $X_A$ extend to values of $X_A = 1$ however fluctuation in the data would void the results of such available data. The following technique was developed to obtain the limit of $1/D_I$ at $X_A = 1$.

It is possible to fit various sets of the experimental reciprocal integral inter line, $X_A$. The sections are called bands. Bands are defined by variable line, $X_A$. The sections are called bands. Bands are defined by

\[ B = 1 - \overline{X_A^o} \] 

(68)

where $\overline{X_A^o}$ is the value of the smallest $X_A$ in the section. Regression coefficients are determined for each band starting with all the data points and reducing the band width until it includes the four last points. The corresponding ion diffusivities are computed for each set of regression coefficients $A$ and $B$. Ion diffusivities are plotted for the corresponding band width. Extrapolation of the plotted data to $B = 0$ should yield the limiting values of $1/D_A$ and $1/D_B$, the
individual ion diffusivities.

2. Comparison of Ion Diffusivities to Self-Diffusivities

The above described technique of determining ion diffusivities was performed on the data shown in Figures 31, 32, 33, 34, and 35. Table 5 shows typical regression data, band width, and computed ion diffusivities for a particular set of data. Four of the five above Figures were chosen because of the available self-diffusion data. Figures 42, 43, 44, 45 and 46 show the corresponding B vs. $1/D_A$ and $1/D_B$ for the experimental data. Extrapolation of B to zero yields the ion diffusivities. Table 6 shows the ion diffusivities along with statistical information of the extrapolation process. Also shown are values of the self-diffusivities of the ions in the resin phase.

1. Correctness of the Integral Interdiffusion Coefficient Model

The above analysis of the transformed exchange rate data showed that the proposed integral interdiffusion coefficient concept is correct. Five points in the analysis support this conclusion:

--During the beginning of the exchange there exist a lower than normal integral interdiffusion coefficient. This is to be expected since during this period a laminar liquid film that surrounds the resin particle hampers exchange.

--Experimental integral self-diffusion coefficients show no variation in magnitude with resin concentration. Self-diffusion coefficients are constant,
resulting in an integral self-diffusion coefficient which is constant.

--Experimental integral interdiffusion coefficients do change considerably with resin phase concentration.

--Fitting the experimental integral interdiffusion coefficients with the developed integral interdiffusion coefficient relation allowed precise duplication of the exchange rate data.

--A unique limiting process was developed to compute ion diffusivities from the regression coefficients of the fitted integral interdiffusion coefficient relation. These predicted ion diffusivities were nearly equal to the ion's self-diffusivities which were available from independent exchange rate data.

2. Suggestions for Future Research

The effect of adsorbed co-ions on the integral interdiffusion coefficient can be studied by performing duplicate exchanges with the "infinite solution volume" condition and the "finite solution volume" condition. During a limited bath run the concentration of the liquid phase varies and hence the adsorbed co-ion concentration, while this does not occur for a shallow bed run. Comparison of the experimental integral interdiffusion coefficients should show any effect of sorbed co-ion concentration.

Exchange rate predictions when both film and particle exert significant resistances are not reliable. Slower than actual rates are usually predicted. This may be due the inclusion of the initial high resistance, noted above
for all particle diffusion experiments, in evaluation of the empirical inter-
diffusion constants. In other words the film resistance is erroneously accounted
for twice producing a higher than actual resistance and in turn a slower exchange
rate.
Figure 43 Ion Diffusivity with Band Width
Ba\textsuperscript{++} Entering - Na\textsuperscript{+} Exiting
Computed from data in Figure 32
Figure 44: Ion Diffusivity with Band Width
Na⁺ Entering - Ba⁺⁺ Exiting
Computed From Data in Figure 33
Figure 45 Ion Diffusivity with Band Width
Sr$^{++}$ Entering - Na$^{+}$ Exiting
Computed from data in Figure 34
Figure 46 Ion Diffusivity with Band Width
Na⁺ Entering - Sr⁺⁺ Exiting
Computed from data in Figure 35
Figure 47 Ion Diffusivity with Band Width
Cl⁻ Entering - HCO₃⁻ Exiting
Computed from data in Figure 31
TABLE 5

STATISTICAL PARAMETERS, $\text{Cl}^- - \text{HCO}_3^-$ ION DIFFUSIVITY DETERMINATIONS

<table>
<thead>
<tr>
<th>No. Data</th>
<th>B</th>
<th>$S_E$</th>
<th>$R^2$</th>
<th>$A \times 10^{-7}$</th>
<th>$B \times 10^{-7}$</th>
<th>$t$</th>
<th>$1/D \times 10^{-7}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.872</td>
<td>0.11</td>
<td>0.62</td>
<td>0.6872</td>
<td>-0.6778</td>
<td>-6.8</td>
<td>-0.6685</td>
</tr>
<tr>
<td>25</td>
<td>0.620</td>
<td>0.01</td>
<td>0.88</td>
<td>0.3841</td>
<td>-0.2365</td>
<td>-12.8</td>
<td>-0.0881</td>
</tr>
<tr>
<td>22</td>
<td>0.517</td>
<td>0.008</td>
<td>0.85</td>
<td>0.3399</td>
<td>-0.1757</td>
<td>-10.8</td>
<td>-0.0115</td>
</tr>
<tr>
<td>18</td>
<td>0.408</td>
<td>0.007</td>
<td>0.69</td>
<td>0.3076</td>
<td>-0.1320</td>
<td>-5.9</td>
<td>0.0395</td>
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<tr>
<td>13</td>
<td>0.304</td>
<td>0.006</td>
<td>0.11</td>
<td>0.2412</td>
<td>-0.0471</td>
<td>-1.2</td>
<td>0.1470</td>
</tr>
<tr>
<td>4</td>
<td>0.208</td>
<td>0.008</td>
<td>0.36</td>
<td>0.4254</td>
<td>-0.2754</td>
<td>-1.0</td>
<td>-0.1264</td>
</tr>
<tr>
<td>Exchange</td>
<td>Data Figure</td>
<td>Reciprocal Diffusivity</td>
<td>Diffusivity</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>-------------</td>
<td>------------------------</td>
<td>-------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr(^{++}) Entering - Na(^+) Exiting</td>
<td>34</td>
<td>0.34 X 10(^7)</td>
<td>0.03 X 10(^7)</td>
<td>0.026 - 0.021</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na(^+) Entering - Sr(^+) Exiting</td>
<td>35</td>
<td>0.48 X 10(^7)</td>
<td>0.29 X 10(^7)</td>
<td>0.090 - 0.025</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr(^{++}) Self-Diffusion</td>
<td>28</td>
<td>0.78 X 10(^7)</td>
<td>----</td>
<td>----</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na(^+) Self-Diffusion</td>
<td>27</td>
<td>----</td>
<td>0.044 X 10(^7)</td>
<td>----</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba(^{++}) Entering - Na(^+) Exiting</td>
<td>32</td>
<td>0.19 X 10(^7)</td>
<td>0.18 X 10(^7)</td>
<td>0.019 - 0.024</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na(^+) Entering - Ba(^{++}) Exiting</td>
<td>33</td>
<td>4.85 X 10(^7)</td>
<td>0.033 X 10(^7)</td>
<td>0.730 - 0.430</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba(^{++}) Self-Diffusion</td>
<td>26</td>
<td>1.13 X 10(^7)</td>
<td>----</td>
<td>----</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na(^+) Self-Diffusion</td>
<td>29</td>
<td>----</td>
<td>0.063 X 10(^7)</td>
<td>----</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl(^-) Entering - HCO(^3)(^-) Exiting</td>
<td>31</td>
<td>0.20 X 10(^7)</td>
<td>0.23 X 10(^7)</td>
<td>0.087 - 0.148</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl(^-) Self-Diffusion</td>
<td>25</td>
<td>0.10 X 10(^7)</td>
<td>----</td>
<td>----</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
SELECTED BIBLIOGRAPHY


20. Ibid., p. 304
23. Ibid., p. 6105.
24. Ibid., p. 6107.


The exchange of ions within the resinous phase can be regarded as a
metathetical chemical reaction between the dissolved compound and the com-
 pound comprised of the resinous exchanger and the ion which it contains. The
The organic resin matrix and the co-ion is effectively an insoluble ion of the
opposite polarity from that which it exchanges. The stoichiometric equation
for exchange is written in the same way as that for a typical chemical reaction,
usually with R representing the insoluble resinous matrix and the co-ion en-
closed in brackets. The exchange reaction for IRA-68 (bicarbonate form) in
a sodium chloride solution is represented:
\[
[R-NH]HCO_3^- + NaCl \rightleftharpoons [R-NH]Cl^- + NaHCO_3
\]  \hspace{1cm} (A-1)

In simplified notation this reaction appears:
\[
\overline{HCO_3^-} + \overline{Cl^-} \rightleftharpoons \overline{HCO_3^-} + \overline{Cl^-}
\]  \hspace{1cm} (A-2)

where the bar indicates the ion in the resin phase.

Ion exchange resin IRA-68 is a weakly basic crosslinked-acrylic anion
exchanger (46). IRA-68 is produced by the Rohm and Haas Company, Phil-
adelphia, Pennsylvania. This resin is employed in deacidification, deion-
ization, and desalination of water where only the removal of strong acids is
desired and deionization of process liquors. A recently developed process
(47) employs IRA-68 and IRA-84 (weakly acid) is a dual bed exchange unit.
This process has promise for desalination of brackish water and renovation of industrial waste water (47). Table A-1 contains the manufacturer's data on IRA-68.

Ion exchange reactions like chemical reactions are all governed by mass action. The feasibility of ion exchange rests on the very fact that these exchanges can be reversed. Considering Equation A-1 the mass action equilibrium constant can be written in terms of activities as follows:

\[ K = \frac{[a_{\text{HCO}_3}] [a_{\text{Cl}}]}{[a_{\text{HCO}_3}] [a_{\text{Cl}}]} \]  

(A-3)

Substituting the product of the concentration and the activity coefficients for activities

\[ K' = \left\{ \frac{[c_{\text{HCO}_3}] [c_{\text{Cl}}]}{[c_{\text{HCO}_3}] [c_{\text{Cl}}]} \right\} \]  

(A-4)

where

\[ K' = K \left( \frac{\gamma_{\text{HCO}_3}}{\gamma_{\text{Cl}}} \right) \left( \frac{\gamma_{\text{HCO}_3}}{\gamma_{\text{Cl}}} \right) \]  

(A-5)

Since normality of the resin phase and the liquid phase remains constant

\[ c_{\text{HCO}_3} + c_{\text{Cl}} = C \]  

(A-6)

and

\[ \overline{c}_{\text{HCO}_3} + \overline{c}_{\text{Cl}} = \overline{C} \]  

(A-7)

If X is defined as the fractional normality of an ion in a phase (i.e. \( \overline{x}_{\text{Cl}} = \overline{c}_{\text{Cl}}/\overline{C} \)) a convenient relation for the selectivity coefficient results:
**TABLE A-1**

Manufacturers Data IRA - 68 (46, 47)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functional Group</td>
<td>$-\text{N}(\text{R})_2$</td>
</tr>
<tr>
<td>Ionic Form Available</td>
<td>Free Base</td>
</tr>
<tr>
<td>Density, gr./cc.</td>
<td>1.06</td>
</tr>
<tr>
<td>Shipping Weight, lbs/ft$^3$</td>
<td>46</td>
</tr>
<tr>
<td>Effective size, mesh</td>
<td>20 - 50</td>
</tr>
<tr>
<td>Moisture content, %</td>
<td>60</td>
</tr>
<tr>
<td>Total Exchange Capacity, meg/gr.</td>
<td>5.6</td>
</tr>
</tbody>
</table>
Experimental values of \( K' \), the selectivity coefficient, are obtained by determining the concentration of chloride remaining in the liquid phase after equilibrium has been attained. This treatment allows finding \( K' \) for strong acid and strong base exchangers, but a modification is needed in the case of weak acid and weak base exchangers (48).

If the resin is in the bicarbonate form, exchange reaction A-1 occurs when the resin is placed in a chloride solution (NaCl). Chloride ions now occupy some exchange sites within the resin and bicarbonate ions are released to the liquid phase.

The equilibration process for a weak base anion exchanger in an aqueous solution is a complex phenomena as compared to a strong base anion exchange equilibrium. Helfferich (49) points out that weak base exchange groups such as \( \text{R-NR}_2^+ \) lose a proton, forming uncharged \( \text{R-NR}_2 \) when the pH is high resulting in an operative capacity which is pH dependent. Kunin (50) draws an analogy between weakly basic amine exchange resins in the "free base" form and soluble amines. Soluble amines ionize in aqueous solutions according to the equilibrium:

\[
\text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_3^+ + \text{OH}^- \tag{A-9}
\]
and polymeric amines behave quite similarly:

\[ R-NR_2' + H_2O \rightarrow R-NR_2'H^+ + OH^- \]  \hspace{1cm} (A-10)

When the resin is in an acidic environment

\[ HCl + H_2O \rightarrow H_3O^+ + Cl^- \]  \hspace{1cm} (A-11)

the hydroxide ions may be replaced by the anion of the acid,

\[ R-NR_2'H^+ + OH^- + H_2O^+ + Cl^- \rightarrow R-NR_2' + Cl^- + 2H_2O \]  \hspace{1cm} (A-12)

the hydroxide ions combining with the hydronium ion of the acid. The neutralization of the hydroxide ion shifts the equilibrium of reaction A-10 to the right. A shift to the right results in a higher ionized resin and, in turn, to a higher exchange capacity for the resin (i.e. more ionized sites provide more sites for exchange). Selke (48) suggest altering the normal treatment by allowing for exchange groups which are unavailable at a given pH. This consists of using an effective total capacity, \( C \), which is a function of pH. In the normal treatment a fixed capacity is assumed, but this assumption is only valid for strong base resins which are completely ionized in acidic or basic environments.

Using the above concepts the following explanation is presented for IRA-68 equilibrium in a NaCl solution. The 0.1N NaCl solution is neutral (pH \( \approx \) 7.0). At this pH there is moderate ionization of the bicarbonate form of IRA-68
HCO$_3^-$ is the ion available for exchange. Placing this resin in a 0.1N.NaCl solution results in the reaction

$$R-NR_2^+H_2CO_3 \rightleftharpoons R-NR_2^+H^+ + HCO_3^- \quad (A-13)$$

Sodium bicarbonate is now in the liquid phase. Hydrolysis occurs with this salt of a strong base (NaOH) and weak acid (H$_2$CO$_3$) resulting in an excess of hydroxide ions thus giving the solution a high pH. This higher pH drives the equilibrium in reaction A-13 to the left resulting in decreased ionization of the resin and, in turn, reduced capacity. Quantitatively this mechanism implies that an increased pH should reduce the exchange capacity of IRA-68.

Equilibrium data were obtained by contacting a known amount of resin with a known amount of 0.1N.NaCl solution. Contact was maintained for a time of not less than 24 hours. The phases were then separated. Chloride analysis was performed on the liquid phase with a Beckman Silver electrode designed specifically for chloride determination. The equilibration apparatus designed, by Fuchs (51), which combines temperature control and constant agitation, was employed. Solid phase composition was obtained by difference.

Thirty data points (five sets of six runs) were obtained for the chloride-bicarbonate exchange equilibrium. For all runs the resin was initially in the bicarbonate form. Table A-2 contains the equilibrium data.
TABLE A-2

Summary of Equilibrium Data, Resin IRA-68

<table>
<thead>
<tr>
<th>Temperature 21°C</th>
<th>Temperature 24°C</th>
<th>Temperature 27°C</th>
<th>Temperature 28°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{Cl}$</td>
<td>$\overline{C}_{Cl}$</td>
<td>$pH$</td>
<td>$C_{Cl}$</td>
</tr>
<tr>
<td>0.07531</td>
<td>5.462</td>
<td>8.23</td>
<td>0.07476</td>
</tr>
<tr>
<td>0.05956</td>
<td>3.427</td>
<td>8.23</td>
<td>0.05581</td>
</tr>
<tr>
<td>0.05110</td>
<td>2.998</td>
<td>8.25</td>
<td>0.05679</td>
</tr>
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<td>0.04333</td>
<td>2.553</td>
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<td>0.06634</td>
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<tr>
<td>0.03808</td>
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<td>8.63</td>
<td>0.07647</td>
</tr>
<tr>
<td>0.03454</td>
<td>1.056</td>
<td>8.82</td>
<td>0.08457</td>
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|                  |                  |                  |                  |
|                  |                  |                  |                  |
|                  |                  |                  |                  |
|                  |                  |                  |                  |

continued ---
<table>
<thead>
<tr>
<th>Temperature 31°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{C1} )</td>
</tr>
<tr>
<td>0.07584</td>
</tr>
<tr>
<td>0.05906</td>
</tr>
<tr>
<td>0.04540</td>
</tr>
<tr>
<td>0.02484</td>
</tr>
<tr>
<td>0.00940</td>
</tr>
<tr>
<td>0.00594</td>
</tr>
</tbody>
</table>
A plot of resin phase concentration with equilibrium liquid phase concentration appears in Figure A-1. This plot is unlike the equivalent plot for a strong resin (48) when plotted in the normal adsorption-exchange fashion (52). The resin concentration should approach a constant value with increasing liquid phase concentration. This value is the resin capacity.

Extensive data analysis was undertaken to show quantitatively the effect of pH on IRA-68 equilibrium. Table A-3 shows the conditions of temperature and pH of the runs. Even though A pH within each run was less than one pH unit the effect of pH was highly significant on the solid phase-liquid phase equilibrium. A very satisfactory correlating equation was developed which predicts resin phase concentration as a function of liquid phase concentration and liquid phase pH. This equation is

\[
\log \frac{C_{ei}}{C_{ei}} = a + b_1 \frac{C_{ei}}{C_{ei}} + b_2 \rho H
\]  

(A-15)

where \( C_{ei} \) is resin phase concentration,
\( C_{ei} \) is liquid phase concentration,
\( a \), \( b_1 \), and \( b_2 \) are regression coefficients.

A typical plot of this equation for a fixed pH appears in Figure A-1 superimposed on the data. This curve behaves much like a normal absorption-exchange equilibrium except in the neighborhood of the origin. By employing this equation it was possible to obtain values of the selectivity coefficient for the chloride-bicarbonate exchange and to study the effect of temperature on the selectivity coefficient.
FIGURE A-1  RESIN IRA-68 EQUILIBRIUM

○ 21°C  HCO₃⁻ initially on Resin
△ 24°C  Cl⁻ in Liquid
▲ 27°C
○ 28°C
+- 31°C

Equation A-15

Ca₁, Resin Concentration, meq Cl⁻/gram

Cₐ₁, Liquid Phase Concentration, meq Cl⁻/ml.
TABLE A-3

Conditions of the Equilibrium Runs

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temperature, °C</th>
<th>pH Range</th>
<th>$\Delta$ pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24</td>
<td>8.81 - 9.21</td>
<td>0.40</td>
</tr>
<tr>
<td>2</td>
<td>28</td>
<td>9.24 - 9.31</td>
<td>0.07</td>
</tr>
<tr>
<td>3</td>
<td>31</td>
<td>8.98 - 9.31</td>
<td>0.33</td>
</tr>
<tr>
<td>4</td>
<td>27</td>
<td>9.20 - 9.48</td>
<td>0.28</td>
</tr>
<tr>
<td>5</td>
<td>31</td>
<td>8.23 - 8.82</td>
<td>0.59</td>
</tr>
</tbody>
</table>
Multiple regression techniques allow determination of the constants of Equation A-15. Table A-4 shows the regression coefficients along with other statistical information. This statistical analysis shows that $b_1$ and $b_2$ are significant, indicating that liquid phase concentration and pH are important when determining the equilibrium concentration of the resin phase. Both $b_1$ and $b_2$ are negative which agrees with theory; as liquid phase concentration increases resin phase concentration increases, and pH increases resin phase concentration decreases. Statistical parameters of the pooled data for all temperatures and for individual runs appear in Table A-4.

An important aspect of Equation A-15 is that it approaches an asymptotic value for large values of $C$. Taking the limit of Equation A-15 for large $C$ and defining it as

$$\lim_{C \to \infty} \left[ \log C_{cl} \right] = \log C$$

(A-16)

results in

$$\log C = a + b_2 \, pH$$

(A-17)

where $C$ is the resin phase capacity. This expression gives a resin phase capacity as a function of pH as suggested by Selke (48).

Employing Equation A-17 a value of $C$ for each value of pH was obtained. The fractional resin capacity for chloride, $X_{cl}$, was then obtained. Values of $X_{cl}$ and $X_{el}$ were plotted on a normalized equilibrium diagram, Figure A-2 (Data appear in Table A-5). This diagram is like that obtained with strong
### TABLE A-4

**Statistical Parameters for Regression Equation (A-15)**

<table>
<thead>
<tr>
<th>Run Temp. °C</th>
<th>$S_p$</th>
<th>$r^2$</th>
<th>$a_0$</th>
<th>$b_1$</th>
<th>$b_2$</th>
<th>$z_1$</th>
<th>$z_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>0.0939</td>
<td>0.906</td>
<td>3.010</td>
<td>-0.0292</td>
<td>-0.2337</td>
<td>-1.74</td>
<td>-0.59</td>
</tr>
<tr>
<td>24</td>
<td>0.0390</td>
<td>0.970</td>
<td>5.440</td>
<td>-0.0280</td>
<td>-0.480</td>
<td>-2.43</td>
<td>-1.85</td>
</tr>
<tr>
<td>27</td>
<td>0.0130</td>
<td>0.996</td>
<td>14.770</td>
<td>-0.00145</td>
<td>-1.520</td>
<td>-5.52</td>
<td>-0.23</td>
</tr>
<tr>
<td>28</td>
<td>0.0130</td>
<td>0.990</td>
<td>2.370</td>
<td>-0.0100</td>
<td>-0.181</td>
<td>-15.9</td>
<td>-0.83</td>
</tr>
<tr>
<td>31</td>
<td>0.120</td>
<td>0.970</td>
<td>16.50</td>
<td>-0.0058</td>
<td>-1.702</td>
<td>-5.24</td>
<td>-3.12</td>
</tr>
<tr>
<td>pooled</td>
<td>0.192</td>
<td>0.562</td>
<td>0.821</td>
<td>-0.00658</td>
<td>-0.1647</td>
<td>-5.66</td>
<td>-0.16</td>
</tr>
</tbody>
</table>
**FIGURE A-2 RESIN IRA-68 EQUILIBRIUM-NORMALIZED DIAGRAM**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>○</td>
<td>21</td>
</tr>
<tr>
<td>Δ</td>
<td>24</td>
</tr>
<tr>
<td>△</td>
<td>27</td>
</tr>
<tr>
<td>○</td>
<td>28</td>
</tr>
<tr>
<td>†</td>
<td>31</td>
</tr>
</tbody>
</table>

![Graph showing the relationship between fractional Cl⁻ in the resin phase and fractional Cl⁻ in the liquid phase with different symbols representing different temperatures.]
TABLE A-5

Normalized Resin Concentration $\overline{X_{Cl}}$ with Normalized Liquid

Concentration $X_{Cl}$

<table>
<thead>
<tr>
<th>Temperature 21°C</th>
<th>Temperature 24°C</th>
<th>Temperature 27°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_{Cl}$</td>
<td>$\overline{X_{Cl}}$</td>
<td>$X_{Cl}$</td>
</tr>
<tr>
<td>0.7531</td>
<td>0.7531</td>
<td>0.4747</td>
</tr>
<tr>
<td>0.5956</td>
<td>0.5956</td>
<td>0.5581</td>
</tr>
<tr>
<td>0.5110</td>
<td>0.5110</td>
<td>0.5679</td>
</tr>
<tr>
<td>0.4333</td>
<td>0.4343</td>
<td>0.6634</td>
</tr>
<tr>
<td>0.3808</td>
<td>0.3808</td>
<td>0.7647</td>
</tr>
<tr>
<td>0.3454</td>
<td>0.3454</td>
<td>0.8457</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature 28°C</th>
<th>Temperature 31°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_{Cl}$</td>
<td>$\overline{X_{Cl}}$</td>
</tr>
<tr>
<td>0.4028</td>
<td>0.5744</td>
</tr>
<tr>
<td>0.3525</td>
<td>0.5238</td>
</tr>
<tr>
<td>0.3352</td>
<td>0.4776</td>
</tr>
<tr>
<td>0.2902</td>
<td>0.4428</td>
</tr>
<tr>
<td>0.2568</td>
<td>0.4172</td>
</tr>
<tr>
<td>0.1953</td>
<td>0.3061</td>
</tr>
</tbody>
</table>
acid and basic resins and is also known as an exchange isotherm. This diagram allows determination of resin phase concentration in equilibrium with a liquid phase. Expression A-17 is valid only if the liquid phase pH is within the interval over which the regression analysis for $a$ and $b_2$ were obtained. pH intervals appear in Table A-3.

Each run was performed at a specified temperature and therefore each isotherm provides a value of the selectivity coefficient defined by Equation A-8. Average values of $K'$ were obtained for each temperature (Table A-6) and these results appear in Figure A-3. This indicates that the selectivity coefficient increases with temperature. The variation of the selectivity coefficient with temperature has been reported previously by (53).
<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>$K_{\text{Cl}^{-}/\text{HCO}_3^-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>0.277</td>
</tr>
<tr>
<td>24</td>
<td>0.348</td>
</tr>
<tr>
<td>27</td>
<td>1.609</td>
</tr>
<tr>
<td>28</td>
<td>1.930</td>
</tr>
<tr>
<td>31</td>
<td>2.514</td>
</tr>
</tbody>
</table>
FIGURE A-3  Cl⁻-HCO₃⁻ Selectivity Coefficient and Temperature

Resin: IRA-68
HCO₃⁻ initially on resin
Cl⁻ in liquid
APPENDIX B

INFINITE SOLUTION VOLUME CONDITION INTERPOLATION POLYNOMIAL

It is necessary to solve Equation (27) in reverse. Experimental data furnishes values of $\overline{X}_A$; the fractional resin capacity of the exchanger occupied by the entering ion. The corresponding $\overline{Z}_I$ required to yield this fractional capacity must be obtained. An explicit expression of $\overline{Z}_I$ as a function of $X_A$ cannot be obtained from Equation (27). An alternate procedure was chosen to obtain a reverse solution to Equation (27). This procedure consists of obtaining values of $X_A$ for chosen values of $\overline{Z}_I$ then fitting these points with a Newton's Interpolating Polynomial of the third order for successive intervals consisting of four points. The dependent variable in the interpolating polynomial is $\overline{Z}_I$.

Newton's Interpolating Polynomial of the third order is:

$$\overline{Z}_I = \overline{Z}_{I,0} + (X_A - X_{A,0}) \overline{Z}'_{I,0} + (X_A - X_{A,0})(X_A - X_{A,1}) \overline{Z}''_{I,0}$$

(B-1)

$$= (X_A - X_{A,0})(X_A - X_{A,1})(X_A - X_{A,2}) \overline{Z}'''_{I,0} + R(X_A)$$

where $X_A$ is the independent variable whose corresponding $\overline{Z}_I$ is desired, $X_{A,0}$, $X_{A,1}$, and $X_{A,2}$ are values of $X_A$ corresponding to $\overline{Z}_{I,0}$, $\overline{Z}_{I,1}$, and $\overline{Z}_{I,2}$.

$$\overline{Z}_{I,0}' = \frac{(\overline{Z}_{I,0} - \overline{Z}_{I,0})}{(X_{A,1} - X_{A,0})}, \text{ first order finite difference}$$

$$\overline{Z}_{I,0}'' = \frac{\overline{Z}_{I,0}' - \overline{Z}_{I,0}'}{(X_{A,2} - X_{A,1})}, \text{ second order finite difference}$$

$$\overline{Z}_{I,0}''' = \frac{\overline{Z}_{I,0}'' - \overline{Z}_{I,0}''}{(X_{A,3} - X_{A,2})}, \text{ third order finite difference}$$
and \( R(X_A) \) is the error term necessary for obtaining equality.

By employing successive intervals of four points it is possible to obtain the divided differences required by Equation (B-1). A divided difference table constructed for four arbitrary points is:

<table>
<thead>
<tr>
<th>( X )</th>
<th>( \bar{Z} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( X_{A,0} )</td>
<td>( \bar{Z}_{I,0} )</td>
</tr>
<tr>
<td>( X_{A,1} )</td>
<td>( \bar{Z}_{I,1} )</td>
</tr>
<tr>
<td>( X_{A,2} )</td>
<td>( \bar{Z}_{I,2} )</td>
</tr>
<tr>
<td>( X_{A,3} )</td>
<td>( \bar{Z}_{I,3} )</td>
</tr>
</tbody>
</table>

Table B-1 gives the 1st, 2nd, and 3rd order divided differences for use in Equation (B-1). The magnitude of the error term, \( R(X_A) \), was analyzed at various intervals and was found to be within the experimental error so that a very good approximation is obtained by neglecting it, thus obtaining Equation (30). This interpolating polynomial is very accurate but must be employed for values of \( X_A \) between \( X_{A,0} \leq X_A \leq X_{A,3} \).
<table>
<thead>
<tr>
<th>$X_A$</th>
<th>$\overline{Z}'$</th>
<th>$\overline{Z}''$</th>
<th>$\overline{Z}'''$</th>
<th>$\overline{Z}^{(4)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0034</td>
<td>$1 \times 10^{-6}$</td>
<td>$8.000 \times 10^{-6}$</td>
<td>.09017</td>
<td>.063333</td>
</tr>
<tr>
<td>0.0059</td>
<td>$3 \times 10^{-6}$</td>
<td>$1.4583 \times 10^{-3}$</td>
<td>.091128</td>
<td>-.12412</td>
</tr>
<tr>
<td>0.0107</td>
<td>$1 \times 10^{-5}$</td>
<td>$2.5974 \times 10^{-3}$</td>
<td>.087690</td>
<td>.15104</td>
</tr>
<tr>
<td>0.0184</td>
<td>$3 \times 10^{-5}$</td>
<td>$4.6053 \times 10^{-3}$</td>
<td>.093218</td>
<td>-.072882</td>
</tr>
<tr>
<td>0.0336</td>
<td>0.0001</td>
<td>$7.2993 \times 10^{-3}$</td>
<td>.096104</td>
<td>.073435</td>
</tr>
<tr>
<td>0.0473</td>
<td>0.0002</td>
<td>$9.6154 \times 10^{-3}$</td>
<td>.093145</td>
<td>-.13148</td>
</tr>
<tr>
<td>0.0577</td>
<td>0.0003</td>
<td>$1.2121 \times 10^{-2}$</td>
<td>.10060</td>
<td>.034208</td>
</tr>
<tr>
<td>0.0742</td>
<td>0.0005</td>
<td>$1.6779 \times 10^{-2}$</td>
<td>.10360</td>
<td>.081409</td>
</tr>
<tr>
<td>0.1040</td>
<td>0.001</td>
<td>$2.4155 \times 10^{-2}$</td>
<td>.11192</td>
<td>.059635</td>
</tr>
<tr>
<td>0.1454</td>
<td>0.002</td>
<td></td>
<td>.11910</td>
<td>102226</td>
</tr>
<tr>
<td>0.1764</td>
<td>0.003</td>
<td>.032258</td>
<td>.11910</td>
<td>.12658</td>
</tr>
<tr>
<td>0.2244</td>
<td>0.005</td>
<td>.041667</td>
<td>.13104</td>
<td>.077896</td>
</tr>
<tr>
<td>0.2622</td>
<td>0.007</td>
<td>.052910</td>
<td>.14133</td>
<td>.12658</td>
</tr>
<tr>
<td>0.3085</td>
<td>0.01</td>
<td>.064795</td>
<td>.16581</td>
<td>.49843</td>
</tr>
<tr>
<td>0.4187</td>
<td>0.02</td>
<td>.090744</td>
<td>.25709</td>
<td>-.20978</td>
</tr>
<tr>
<td>0.4913</td>
<td>0.03</td>
<td>.13774</td>
<td>.19466</td>
<td>.76223</td>
</tr>
<tr>
<td>0.6061</td>
<td>0.05</td>
<td>.17422</td>
<td>.39810</td>
<td>.79198</td>
</tr>
<tr>
<td>0.6856</td>
<td>0.07</td>
<td>.25157</td>
<td>.61922</td>
<td></td>
</tr>
</tbody>
</table>

continued ---
<table>
<thead>
<tr>
<th>$\bar{x}$</th>
<th>$\bar{z}$</th>
<th>$\bar{z}'$</th>
<th>$\bar{z}''$</th>
<th>$\bar{z}'''$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7705</td>
<td>0.1</td>
<td>0.35337</td>
<td>0.90644</td>
<td>1.5392</td>
</tr>
<tr>
<td>0.7927</td>
<td>0.11</td>
<td>0.45045</td>
<td>1.1742</td>
<td>2.1067</td>
</tr>
<tr>
<td>0.8127</td>
<td>0.12</td>
<td>0.50000</td>
<td>1.6341</td>
<td>6.0354</td>
</tr>
<tr>
<td>0.8467</td>
<td>0.14</td>
<td>0.58824</td>
<td>2.6073</td>
<td>8.5368</td>
</tr>
<tr>
<td>0.9067</td>
<td>0.19</td>
<td>0.83333</td>
<td>4.6504</td>
<td>18.4395</td>
</tr>
<tr>
<td>0.9235</td>
<td>0.21</td>
<td>1.19048</td>
<td>8.8328</td>
<td>46.2144</td>
</tr>
<tr>
<td>0.9372</td>
<td>0.23</td>
<td>1.45990</td>
<td>13.5403</td>
<td>101.0193</td>
</tr>
<tr>
<td>0.9533</td>
<td>0.26</td>
<td>1.86340</td>
<td>22.6548</td>
<td>218.055</td>
</tr>
<tr>
<td>0.9653</td>
<td>0.29</td>
<td>2.5000</td>
<td>41.6651</td>
<td>513.79</td>
</tr>
<tr>
<td>0.9742</td>
<td>0.32</td>
<td>3.3708</td>
<td>75.7871</td>
<td>1240.8</td>
</tr>
<tr>
<td>0.9808</td>
<td>0.35</td>
<td>4.5455</td>
<td>142.706</td>
<td>3280.3</td>
</tr>
<tr>
<td>0.9857</td>
<td>0.38</td>
<td>6.1224</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX C

Resin IRA-68 Particle Diffusion Data

1. Interdiffusion Data:

HCO₃⁻ Exiting - Cl⁻ Entering

a. Run 68 - 2b:

<table>
<thead>
<tr>
<th>time, sec.</th>
<th>( \overline{C}_{Cl} )</th>
<th>( \overline{X}_{Cl} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>34.8</td>
<td>0.0732</td>
<td>0.016</td>
</tr>
<tr>
<td>64.8</td>
<td>0.527</td>
<td>0.117</td>
</tr>
<tr>
<td>125</td>
<td>1.192</td>
<td>0.265</td>
</tr>
<tr>
<td>185</td>
<td>1.620</td>
<td>0.360</td>
</tr>
<tr>
<td>245</td>
<td>1.790</td>
<td>0.438</td>
</tr>
</tbody>
</table>
b. Run 68-3

linear rate: 50.5 cm./min.

temp: 25°C

$C = 5.50$ meq./gram.

<table>
<thead>
<tr>
<th>time, sec.</th>
<th>$\bar{C}_{Cl}$</th>
<th>$X_{Cl}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>35.2</td>
<td>0.594</td>
<td>0.108</td>
</tr>
<tr>
<td>65.2</td>
<td>1.203</td>
<td>0.219</td>
</tr>
<tr>
<td>125</td>
<td>1.978</td>
<td>0.360</td>
</tr>
<tr>
<td>185</td>
<td>2.870</td>
<td>0.522</td>
</tr>
<tr>
<td>245</td>
<td>3.465</td>
<td>0.627</td>
</tr>
</tbody>
</table>
c. **Run 68 - 4**

linear rate: 79.7 cm./min.

temp: 27°C

$\bar{C} = 7.518$ meq./gram.

<table>
<thead>
<tr>
<th>time, sec.</th>
<th>$\bar{C}$</th>
<th>$\bar{X}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.5</td>
<td>0.964</td>
<td>0.128</td>
</tr>
<tr>
<td>46.5</td>
<td>1.79</td>
<td>0.238</td>
</tr>
<tr>
<td>76.5</td>
<td>2.51</td>
<td>0.334</td>
</tr>
<tr>
<td>107</td>
<td>3.14</td>
<td>0.418</td>
</tr>
<tr>
<td>137</td>
<td>3.63</td>
<td>0.438</td>
</tr>
<tr>
<td>167</td>
<td>4.06</td>
<td>0.540</td>
</tr>
<tr>
<td>197</td>
<td>4.45</td>
<td>0.592</td>
</tr>
<tr>
<td>227</td>
<td>4.78</td>
<td>0.636</td>
</tr>
<tr>
<td>257</td>
<td>4.99</td>
<td>0.664</td>
</tr>
<tr>
<td>287</td>
<td>5.37</td>
<td>0.715</td>
</tr>
<tr>
<td>317</td>
<td>5.57</td>
<td>0.742</td>
</tr>
<tr>
<td>347</td>
<td>5.70</td>
<td>0.758</td>
</tr>
<tr>
<td>377</td>
<td>5.80</td>
<td>0.772</td>
</tr>
<tr>
<td>407</td>
<td>5.94</td>
<td>0.791</td>
</tr>
<tr>
<td>437</td>
<td>6.06</td>
<td>0.806</td>
</tr>
</tbody>
</table>
d. Run 68 - 9

linear rate: 87.5 cm./min.

.temp: 29°C

$\bar{C} = 4.110$ meq./gram.

<table>
<thead>
<tr>
<th>time, sec.</th>
<th>$\bar{C}_t$</th>
<th>$\bar{X}_t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.6</td>
<td>0.535</td>
<td>0.130</td>
</tr>
<tr>
<td>60.6</td>
<td>1.144</td>
<td>0.279</td>
</tr>
<tr>
<td>90.6</td>
<td>1.560</td>
<td>0.380</td>
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<tr>
<td>121</td>
<td>1.884</td>
<td>0.459</td>
</tr>
<tr>
<td>151</td>
<td>2.143</td>
<td>0.523</td>
</tr>
<tr>
<td>181</td>
<td>2.361</td>
<td>0.576</td>
</tr>
<tr>
<td>211</td>
<td>2.557</td>
<td>0.624</td>
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<tr>
<td>241</td>
<td>2.719</td>
<td>0.663</td>
</tr>
<tr>
<td>271</td>
<td>2.855</td>
<td>0.696</td>
</tr>
<tr>
<td>301</td>
<td>2.992</td>
<td>0.730</td>
</tr>
<tr>
<td>331</td>
<td>3.076</td>
<td>0.750</td>
</tr>
<tr>
<td>361</td>
<td>3.165</td>
<td>0.772</td>
</tr>
<tr>
<td>391</td>
<td>3.250</td>
<td>0.792</td>
</tr>
<tr>
<td>421</td>
<td>3.332</td>
<td>0.813</td>
</tr>
<tr>
<td>451</td>
<td>3.419</td>
<td>0.834</td>
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</tbody>
</table>
2. **Self-diffusion**

Cl Exiting - Cl Entering

linear rate: 84.2 cm./min.

temp: 29°C

\[ \bar{C} = 1.51 \text{ meq./gram.} \]

<table>
<thead>
<tr>
<th>time, sec.</th>
<th>( \bar{C}_{\text{Cl}} )</th>
<th>( \bar{X}_{\text{Cl}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.160</td>
<td>0.106</td>
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<tr>
<td>60</td>
<td>0.440</td>
<td>0.292</td>
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<tr>
<td>90</td>
<td>0.659</td>
<td>0.435</td>
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<tr>
<td>120</td>
<td>0.822</td>
<td>0.544</td>
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<tr>
<td>150</td>
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<tr>
<td>180</td>
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<td>210</td>
<td>1.14</td>
<td>0.753</td>
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<tr>
<td>240</td>
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<td>0.798</td>
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<tr>
<td>270</td>
<td>1.26</td>
<td>0.835</td>
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<tr>
<td>300</td>
<td>1.31</td>
<td>0.867</td>
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<td>330</td>
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<td>360</td>
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<tr>
<td>390</td>
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<tr>
<td>420</td>
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<td>450</td>
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<td>0.959</td>
</tr>
<tr>
<td>480</td>
<td>1.47</td>
<td>0.971</td>
</tr>
</tbody>
</table>
Louis Joseph Thibodeaux was born November 13, 1939, in Church Point, Louisiana. His father was Clovis Jackob Thibodeaux of Branch, Louisiana and his mother was Lottie Stakes of Crowley, Louisiana. He was the first of three sons. He attended elementary school in Branch, Louisiana and was graduated from Rayne High School in 1957. He entered Louisiana State University in September of 1957 and was graduated with a Bachelor of Science degree in petroleum-chemical engineering in 1962. While a undergraduate, he married Elwana Joyce Lasiter on December 19, 1959 and was blessed with the birth of a son, Jason Scott, on August 8, 1961.

After graduation, he accepted employment with E. I. duPont de Nemours and Co, Inc., Aiken, South Carolina. In February of 1964 he returned to Louisiana State University as a full time graduate student. A daughter, Michele Renee, was born April 21, 1964. He received the Master of Science degree in Chemical Engineering in 1966, and is presently a candidate for the degree of Doctor of Philosophy in the department of Chemical Engineering at Louisiana State University. Upon fulfilling all requirements for this degree, he will join the Chemical Engineering Department Faculty at the University of Arkansas as an Assistant Professor.
Candidate: Louis Joseph Thibodeaux

Major Field: Chemical Engineering

Title of Thesis: Ion-Exchange Resin Diffusion Coefficients and Resin Phase Ion Diffusivities

Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination: January 19, 1968