1970


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THE DETERMINATION OF THE IONIZATION CONSTANTS OF
WEAK ACIDS IN MIXED SOLVENT SYSTEMS:
A STUDY OF MEDIUM EFFECTS

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

Doctor of Philosophy

in

The Department of Chemistry

by

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January, 1970
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENT</td>
<td>ii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF SYMBOLS</td>
<td>viii</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>xi</td>
</tr>
<tr>
<td>CHAPTER</td>
<td></td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. THEORY</td>
<td>10</td>
</tr>
<tr>
<td>III. EXPERIMENTAL WORK</td>
<td>29</td>
</tr>
<tr>
<td>IV. EXPERIMENTAL DATA AND RESULTS</td>
<td>41</td>
</tr>
<tr>
<td>V. DISCUSSION AND CONCLUSIONS.</td>
<td>89</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>111</td>
</tr>
<tr>
<td>VITA</td>
<td>119</td>
</tr>
</tbody>
</table>

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# LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Time Rate of Change of Cell EMF for the Cell, Pt, H₂ (1 atm.)</td>
<td>36</td>
</tr>
<tr>
<td>HOAc (m₁), NaOAc (m₂), NaCl (m₃), THF (9.1%)</td>
<td></td>
</tr>
<tr>
<td>Water (90.9%)</td>
<td></td>
</tr>
<tr>
<td>AgCl-Ag</td>
<td></td>
</tr>
<tr>
<td>II. Standard Electrode Potentials of the Ag-AgCl Electrode in Several Mixed Solvent Systems at Different Temperatures</td>
<td>42</td>
</tr>
<tr>
<td>III. Density Data of Tetrahydrofuran, Ethanol, Acetone, and Water at 25°C</td>
<td>43</td>
</tr>
<tr>
<td>IV. Vapor Pressure Data of Tetrahydrofuran, Ethanol, Acetone, and Water</td>
<td>44</td>
</tr>
<tr>
<td>V. Values of ( E_{\text{obs}} ), ( pK_a^* ), m₁, m₂, m₃, and ( \sqrt{\mu} ) for Acetic Acid in Tetrahydrofuran-Water Mixtures at 25.0°C</td>
<td>46</td>
</tr>
<tr>
<td>VI. Values of ( E_{\text{obs}} ), ( pK_a^* ), m₁, m₂, m₃, and ( \sqrt{\mu} ) for Acetic Acid in Ethanol-Water Mixtures at 25.0°C</td>
<td>47</td>
</tr>
<tr>
<td>VII. Values of ( E_{\text{obs}} ), ( pK_a^* ), m₁, m₂, m₃, and ( \sqrt{\mu} ) for Acetic Acid in Acetone-Water Mixture at 25.0°C</td>
<td>48</td>
</tr>
<tr>
<td>VIII. Values of m₁, m₂, m₃, ( \sqrt{\mu} ), ( E_{\text{obs}} ), and ( pK_a^* ) for 16.26 percent (weight) Ethanol-Water Mixture at Various Temperatures</td>
<td>49</td>
</tr>
<tr>
<td>IX. Values of pH, ( E_{\text{obs}} ), ( pK_a^* ), m₁, m₂, m₃, and ( \sqrt{\mu} ) for Acetic Acid at 25.0°C Using the Cell: Glass Electrode</td>
<td>51</td>
</tr>
<tr>
<td>HOAc (m₁), NaOAc (m₂), NaCl (m₃), Acetone (X), Water (Y)</td>
<td></td>
</tr>
<tr>
<td>AgCl-Ag</td>
<td></td>
</tr>
<tr>
<td>X. Ionization Constants of Acetic Acid in 9.1 and 18.21 weight percent Tetrahydrofuran-Water and in 10.0, 20.0, and 40.0 weight percent Acetone-Water at 25.0°C</td>
<td>56</td>
</tr>
</tbody>
</table>
XI. Values of log $k^*_a$, $t^2$, $pt^2$, and log $k^*_a + pt^2$
for Acetic Acid in 16.26 percent (weight) Ethanol-Water at Various Temperatures ........................................ 57

XII. Ionization Constants of Acetic Acid in 16.26
percent (weight) Ethanol-Water at Various
Temperatures ........................................ 60

XIII. Enthalpy of Ionization for Acetic Acid in
16.26 percent (weight) Ethanol-Water at
Various Temperatures ........................................ 62

XIV. Dielectric Constants of Some Pure Compounds
at 25° C ................................................ 63

XV. Values of pK$^*_a$ for Various Acids in Several
Mixed Solvent Systems and some Dielectric
Constant Functions for those Systems .............. 64

XVI. Values of pK$^*_a$(obs), pK$^*_a$, $b$, $c$, $d$, Goodness of
Fit, and Sum of the Squares for the Equation:
pK$^*_a$ = pK$^*_a$ + b(1/$\varepsilon^* -$ 1/$\varepsilon$) + 10$c^d(1/\varepsilon^* -$ 1/$\varepsilon$) ........ 86

XVII. Values of pK$^*_a$(obs), pK$^*_a$, $\beta$, Goodness of Fit, and
Sum of Squares for the Equation:
pK$^*_a$ = pK$^*_a$ + $\beta$(1/$\varepsilon^* -$ 1/$\varepsilon$) ........... 87

XVIII. Values of pK$^*_a$(obs), pK$^*_a$, $b'$, Goodness of Fit, and
Sum of Squares for the Equation:
pK$^*_a$ = pK$^*_a$ + $b'$(1/$\varepsilon^* -$ 1/$\varepsilon$) ........... 88

XIX. Values of the Slope ($\beta$), The Anionic Contribution
to Minimum Distance of Approach ($r_{A^-}$), and the
Minimum Distance of Approach ($a^o$) for a Number
of Acids at 25° C .................................. 109

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**LIST OF FIGURES**

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Diagram of Experimental Cell.</td>
<td>30</td>
</tr>
<tr>
<td>2.</td>
<td>Time Rate of Change of Cell EMF as a Function of Time.</td>
<td>37</td>
</tr>
<tr>
<td>3.</td>
<td>pK(_a^*) vs. (\sqrt{\mu}) for Acetic Acid in Tetrahydrofuran-Water Mixtures at 25° C</td>
<td>52</td>
</tr>
<tr>
<td>4.</td>
<td>pK(_a^*) vs. (\sqrt{\mu}) for Acetic Acid in Ethanol-Water Mixtures at 25° C</td>
<td>53</td>
</tr>
<tr>
<td>5.</td>
<td>pK(_a^*) vs. (\sqrt{\mu}) for Acetic Acid in 16.26% Ethanol-Water at Various Temperatures</td>
<td>54</td>
</tr>
<tr>
<td>6.</td>
<td>pK(_a^*) vs. (\sqrt{\mu}) for Acetic Acid in Acetone-Water Mixtures at 25° C</td>
<td>55</td>
</tr>
<tr>
<td>7.</td>
<td>log K(_a^*) (\pm pt^2) vs. Temperature for Acetic Acid in 16.26% Ethanol-Water.</td>
<td>59</td>
</tr>
<tr>
<td>8.</td>
<td>Ionization Constants of Acetic Acid vs. Dielectric Constant Functions in Various Mixed Solvents at 25° C</td>
<td>76</td>
</tr>
<tr>
<td>9.</td>
<td>Ionization Constants of Acetic and Benzoic Acids vs. Dielectric Constant Function in Various Mixed Solvent Systems at 25° C</td>
<td>78</td>
</tr>
<tr>
<td>10.</td>
<td>Ionization Constant of Formic Acid and Propanoic Acid vs. Dielectric Constant Function in Various Mixed Solvents at 25° C</td>
<td>79</td>
</tr>
<tr>
<td>11.</td>
<td>Ionization Constants of Butanoic Acid vs. Dielectric Constant Function in Various Mixed Solvents at 25° C</td>
<td>80</td>
</tr>
<tr>
<td>12.</td>
<td>Ionization Constants of Some Acids vs. Dielectric Constant Function in Various Mixed Solvents at 25° C (Linear Portion)</td>
<td>82</td>
</tr>
</tbody>
</table>
FIGURE

13. Ionization Constants of Various Acids vs. Dielectric Constant Function in Ethanol-\(\text{H}_2\text{O}\) at 25° C ............................................ 83

14. Ionization Constants of Some Acids vs. a Dielectric Constant Function in Various Mixed Solvent Systems at 25° C (Linear Portion) .......... 84

15. Ionization Constants of Various Acids vs. Dielectric Constant Function in Ethanol-\(\text{H}_2\text{O}\) at 25° C ....................................................... 85
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>area of condenser plates, polynomial curve-fitting parameter</td>
</tr>
<tr>
<td>$a, a_0$</td>
<td>average minimum distance of approach</td>
</tr>
<tr>
<td>$a_i$</td>
<td>activity of species $i$</td>
</tr>
<tr>
<td>$C$</td>
<td>capacitance</td>
</tr>
<tr>
<td>$C_i$</td>
<td>concentration of species $i$</td>
</tr>
<tr>
<td>$C_0$</td>
<td>capacitance in vacuum</td>
</tr>
<tr>
<td>$c$</td>
<td>molar concentration</td>
</tr>
<tr>
<td>$d$</td>
<td>distance between condenser plates, derivative</td>
</tr>
<tr>
<td>$E$</td>
<td>electrode potential, cell emf, energy</td>
</tr>
<tr>
<td>$E^0$</td>
<td>standard electrode potential</td>
</tr>
<tr>
<td>$E_{obs}$</td>
<td>corrected cell emf</td>
</tr>
<tr>
<td>$e$</td>
<td>electronic charge</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday</td>
</tr>
<tr>
<td>$f$</td>
<td>fugacity, function of (prefix)</td>
</tr>
<tr>
<td>$f_H$</td>
<td>degenerate activity coefficient</td>
</tr>
<tr>
<td>$\Delta G$</td>
<td>Gibbs free energy change</td>
</tr>
<tr>
<td>$\Delta G^0$</td>
<td>standard Gibbs free energy change</td>
</tr>
<tr>
<td>$\Delta G_{nonel}$</td>
<td>nonelectrostatic contribution to free energy change</td>
</tr>
<tr>
<td>$\Delta H$</td>
<td>enthalpy change</td>
</tr>
<tr>
<td>$\Delta H^0$</td>
<td>standard enthalpy change</td>
</tr>
<tr>
<td>$K$</td>
<td>equilibrium constant</td>
</tr>
<tr>
<td>$K_a$</td>
<td>ionization constant of weak acid in water</td>
</tr>
<tr>
<td>$K_a^*$</td>
<td>ionization constant of weak acid in mixed solvent</td>
</tr>
<tr>
<td>$K_\theta$</td>
<td>maximum value of ionization constant</td>
</tr>
</tbody>
</table>
k Boltzmann constant, rate constant
M molar concentration
$m_i$ molality of species $i$
N Avogadro's number
$N_D^{\infty}$ index of refraction at $20^\circ$ C.
n number of moles
p gas pressure, universal constant for electrolytes
$pK_a$ negative log of $K_a$
$pK_a^*$ negative log of $K_a^*$
QY ratio of activity coefficients
q electrical charge
R gas constant
r mean radius, distance, rate of reaction
$r_i$ radius of species $i$
$\Delta S$ entropy change
s subscript denotes measurement (or quantity) relative to infinite dilution in mixed solvent, superscript denotes measurement (or quantity) in mixed solvent
T absolute temperature
t temperature degrees Celsius
V electrical potential
$V_D$ electrical potential in vacuum
W work
w subscript denotes measurement (or quantity) relative to infinite dilution in water, superscript denotes measurement (or quantity) in water
$X$ field strength

$Y$ activity function

$Z_A$ charge on ion A

$\gamma_i$ activity coefficient of species i

$\gamma_0$ activity coefficient when electrolyte concentration is zero

$\gamma_\pm$ mean activity coefficient

$\varepsilon$ dielectric constant of water

$\varepsilon^*$ dielectric constant of mixed solvent

$\varepsilon' = \varepsilon + (\varepsilon_{\text{MeOH}} - \varepsilon_{\text{organic}})$

$\varepsilon'^* = \varepsilon^* + (\varepsilon_{\text{MeOH}} - \varepsilon_{\text{organic}})$

$\varepsilon'' = 2\varepsilon - \varepsilon_{\text{organic}}$

$\varepsilon'^* = \varepsilon^* + (\varepsilon - \varepsilon_{\text{organic}})$

$\theta$ temperature at which ionization constant is maximum

$\phi_w$ volume fraction of water

$\mu$ ionic strength, dipole moment

$\mu_i$ chemical potential of species i

$\mu^0$ standard chemical potential

* measurement made in mixed solvent

\partial partial derivative
ABSTRACT

This Dissertation is part of a program which has had as one of its purposes the determination of an analytical function for converting thermodynamic values computed from experimental data for a reversible process in one solvent to the corresponding values in another solvent -- such as water.

Of the various types of ionic equilibria, that of a weak monoprotic acid is the easiest to study and the most amenable to mathematical treatment. Fourteen weak acids in eleven different solvent systems were studied. Primarily, data from the literature were used, although in a number of cases these values were checked or additional values were determined by the author.

Previous work by Sen, Roy, and Johnson as well as a preliminary literature survey indicated that the relation sought would be a function of the bulk dielectric constant (\( \epsilon \)) of the system. To obtain the relation sought, plots of \( pK^*_a \) against various functions of the dielectric constant were investigated. The * is used to indicate any term measured in the mixed solvent systems. Quantities without the * were measured in pure water.

Plots of \( pK^*_a \) against \( (1/\epsilon^* - 1/\epsilon) \) indicated that in order to place all the points on the same continuous curve a suitable term had to be added to the primary variable. The final plots were of \( pK^*_a \) versus \( (1/\epsilon'^* - 1/\epsilon'') \) in which

\[
\epsilon'^* = \epsilon^* + (\epsilon - \epsilon_{\text{organic}})
\]

and

\[
\epsilon'' = \epsilon + (\epsilon - \epsilon_{\text{organic}}).
\]
The analytical function found for the weak acids has the form

\[ pK_a^* = pK_a + b \left( \frac{1}{\varepsilon^*} - \frac{1}{\varepsilon} \right) + 10^{c+d \left( \frac{1}{\varepsilon^*} - \frac{1}{\varepsilon} \right)} \]

Each set of values of \( b, c, \) and \( d \) for five acids was evaluated using a computer curve-fitting program. The first two terms of the right member represent the linear portion of the curve where the interactions are primarily coulombic. A similar expression can be written for the linear portion of the curve for the plot of \( pK_a^* \) against \( (1/\varepsilon^* - 1/\varepsilon) \). This expression is

\[ pK_a^* = pK_a + \beta \left( \frac{1}{\varepsilon^*} - \frac{1}{\varepsilon} \right). \]

This expression is identical in form with Born's equation relating the ionization constant of an acid in two media:

\[ pK_a^* = pK_a + \frac{Ne^2}{4.60RT} \left( \frac{1}{r_{H^+}} + \frac{1}{r_{A^-}} \right) \left( \frac{1}{\varepsilon^*} - \frac{1}{\varepsilon} \right). \]

For regions of high aqueous concentration, an electrostatic model for estimating medium effects has been shown to be a good first approximation.

In addition, a method was devised for the calculation of the minimum distance of approach of the hydrated proton to the hydrated carboxylate anion. These distances were about 4.0 Å which agrees with values determined for hydrohalide acids. It was also found that these distances increased as the polar character of carboxylate anion increased.
A method was established for the determination of the dielectric constant of a pure organic solvent from data in a single highly aqueous mixed solvent system of this organic solvent. The relative error was within seven percent.
CHAPTER I

INTRODUCTION

For a number of reasons it is important to know the ionization constant (or any equilibrium constant) for a process with reference to an infinitely dilute aqueous solution. Though weak acids present no problems, there are numerous cases where the reversible process cannot be studied in water. Hydrolysis, aqueous insolubility, and other complicating properties of reactants and/or products frequently cause difficulties. This is particularly true of chelates where the aqueous insolubility of many of these compounds necessitates the use of nonaqueous or mixed solvent systems. For example, the work of Calvin and Wilson,\(^1\) of Shuman and Sen,\(^2\) and of van Uitert and Haas\(^3\) in studying chelate stability and determining thermodynamic equilibrium constants by potentiometric methods required such solvents as dioxane-water, acetone-water, and anhydrous ethanol.

There is a fundamental difficulty that arises when such thermodynamic quantities are to be calculated in mixed solvent systems. This difficulty is in the choosing as the basis for the standard reference state the infinitely dilute aqueous solution. Thus, activities measured in a given solvent system have as their reference states "hypothetical one-molal solutions" in that solvent system which obey a dilute solution limiting law. While the relative thermodynamic properties in such a solvent system are of practical importance, these would be of greater value if a means for converting them to the corresponding values in the pure aqueous system were available.
Medium Effects.

This Dissertation is part of a continuing program to determine an analytical function for converting thermodynamic values computed from experimental data obtained for a reversible process in one solvent to the corresponding values in another solvent - such as water. This involves the corrections for the two medium effects.\(^4\)\(^5\) The interaction between a given ion and one solvent will be different from the interaction of the same ion and a different solvent. This interaction involves no ion-ion interactions and therefore is independent of the solute concentration. This is the primary medium effect.\(^5\) It is the difference in solvation energies in the two solvents; i.e., it is a measure of the energy involved in transferring one gram-ion (or mole) of solute from a large volume of solution in one solvent at infinite dilution to a large volume of the solution in another solvent also at infinite dilution. The difference in ion-ion interactions in the two different solvents is called the secondary medium effect,\(^5\) and is, of course, concentration dependent. The transfer of an ion from a solution of finite concentration in one solvent to a solution of finite concentration in another solvent can be broken down into three steps. These steps are:

1. the transfer of the solute from a finite concentration in one solvent to infinite dilution in the same solvent;
2. the transfer of the solute from infinite dilution in the first solvent to infinite dilution in another solvent;
(3) the transfer of the solute from infinite dilution in the second solvent to some finite concentration in that solvent.

The sum of the free energy changes corresponding to these steps is a measure of the total medium effect.⁵

The total, the primary, and the secondary medium effects are related by the following equation:⁴

\[
\ln \frac{\gamma^+_W}{\gamma^+_s} = \ln \frac{\gamma^+_W}{\gamma^+_o} + \ln \frac{\gamma^+_S}{\gamma^+_W} \quad \ldots \quad 1
\]

<table>
<thead>
<tr>
<th>Total</th>
<th>Primary</th>
<th>Secondary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Medium</td>
<td>Medium</td>
<td>Medium</td>
</tr>
<tr>
<td>Effect</td>
<td>Effect</td>
<td>Ion-ion</td>
</tr>
<tr>
<td>Ion-</td>
<td>Solvent</td>
<td></td>
</tr>
</tbody>
</table>

It should be mentioned here that equation 1 was derived for the case of symmetrical electrolytes such as hydrochloric acid. The superscripts w and s denote that measurements are made in water and in mixed solvent, respectively. The subscripts w and s indicate that the mean activity coefficient, \( \gamma^+_w \), is measured relative to unit value at infinite dilution in water or in mixed solvent. The subscript o on the term \( \gamma^+_o \) indicates that the concentration of electrolyte is zero (i.e., \( m = 0 \)).

**Determination of Ionization Constants of Weak Electrolytes.**

One way of studying these medium effects has been the determining of the ionization constants of weak acids in mixed solvent systems. Such determinations have been made conductometrically⁶ or
colorimetrically, but more often the potentiometric method has been used, particularly with cells that have no liquid junctions.

It can be shown that the thermodynamic ionization constants of a weak acid HA in pure water ($K_a$) and in the mixed solvent ($K_a^*$) are related by the expression:

$$K_a = \frac{\gamma_{OH^+} \gamma_{A^-}}{\gamma_{HA}} K_a^* = QV^* K_a^*$$

The * will be used hereafter to refer to terms in a mixed solvent system. It is quite obvious that the activity coefficient term represents the primary medium effect. The experimental determinations of $K_a$ and $K_a^*$ are relatively simple. These terms are computed from the emf data of the cell:

$$\text{Pt, } \text{H}_2 (1 \text{ atm.}) | \text{HA (}m_1\text{)}, \text{NaA (}m_2\text{)}, \text{NaCl (}m_3\text{)}, \text{Organic (}X\text{)}, \text{Water (}Y\text{)} | \text{AgCl-Ag}$$

where $m_1$, $m_2$, and $m_3$ represent the molalities of the weak acid, its sodium salt, and sodium chloride respectively, $X$ is the weight percent of the organic solvent and $Y$ is the weight percent of water.

The electromotive force of this cell is given by the equation

$$E_{obs} = \frac{E^O_m}{F} - \frac{RT}{F} \ln \gamma_{H^+} \gamma_{Cl^-} \cdot m_{H^+} m_{Cl^-}$$

The ionization constant of the weak acid is given by:

$$K_a^* = \frac{\gamma_{H^+} \gamma_{A^-}}{\gamma_{HA}} \cdot \frac{m_{H^+} m_{A^-}}{m_{HA}}$$
Solving this expression for $m_{H^+}$ and substituting into equation 3, one obtains:

$$E_{obs} = E^0_m - \frac{RT}{F} \ln \frac{\gamma_{H^+} \gamma_{Cl^-} \gamma_{HA}}{\gamma_{H^+} \gamma_{A^-}} - \frac{RT}{F} \ln \frac{m_{HA} \gamma_{Cl^-}}{m_{A^-}} - \frac{RT}{F} \ln K_a a$$ .... 5

Rearrangement gives:

$$E_{obs} = E^0_m + \frac{RT}{F} \ln \frac{m_{HA} \gamma_{Cl^-}}{m_{A^-}} = -\frac{RT}{F} \ln \frac{\gamma_{H^+} \gamma_{Cl^-} \gamma_{HA}}{\gamma_{H^+} \gamma_{A^-}} - \frac{RT}{F} \ln K_a a$$ .... 6

The first term on the right-hand side of equation 6 contains a ratio of activity coefficients which becomes unity at infinite dilution and is nearly that at low ionic strength.

If we replace the right-hand side of equation 6 with $-\frac{RT}{F} \ln K_a a$, we obtain:

$$E_{obs} = E^0_m + \frac{RT}{F} \ln \frac{m_{HA} \gamma_{Cl^-}}{m_{A^-}} = -\frac{RT}{F} \ln K_a a$$ .... 7

The log $K_a a$ can be plotted against the ionic strength, $\mu$ (or some function of $\mu$), and the intercept at $\mu = 0$ will be $\log K_a^* a$.

The left-hand side of equation 7 can be readily evaluated since $m_{Cl^-} = m_3$, $m_{HA} = m_1 - m_{H^+} \approx m_1$, and $m_{A^-} = m_2 + m_{H^+} \approx m_2$. It has been shown that $m_{H^+}$ is negligible even in the most dilute solution of weak acid used. $E^0_m$ is the standard molal potential of the cell

Pt, H\textsubscript{2} (1 atm.) | HCl (m), Organic (X), Water (Y) | AgCl-Ag

and is determined in a manner described in the following section.
Thus, the ionization constant of the weak acid, HA, in mixed solvent systems can be obtained from the observed emf measurements of cell I.

When $X$, the weight percent of organic solvent, is equal to zero, the value of the ionization constant is $K_a$ - that for the pure aqueous solution.

**Determination of $E^\circ_m$.**

The electromotive force of cell II, Pt, $H_2$ (1 atm.) | $HCl$ (m), Organic ($X$), Water ($Y$) | AgCl-Ag is expressed by equation 3 which may be written as

$$E_{obs} + \frac{2RT}{F} \ln m = E^\circ_m - \frac{2RT}{F} \ln \gamma_+$$

and it has been shown\textsuperscript{4,20} that the natural logarithm of the stoichiometric mean activity coefficient for the symmetrical valence type electrolyte is given by the equation

$$\ln f_+ = \frac{-e^2 z^2}{2kTca} \cdot \frac{x}{1+x} + \sum_{m=1}^{\infty} \frac{e^2 z^2}{kTca} \cdot \frac{X_{2m+1}(x) - 2mY_{2m+1}(x)}{2m+1}$$

in which $\varepsilon$ is the dielectric constant of the solvent, $T$ is the absolute temperature, $x = \kappa a$ and $\kappa^2 = \frac{8TNc^2e^2c}{10^9kTc^2}$, $c$ is the molar concentration, $N$ is Avogadro's number, $k$ is the Boltzmann constant, $ez$ is the charge on the ions and $a$ is the average minimum distance of approach of the ions. The terms $X_{2m+1}(x)$ and $Y_{2m+1}(x)$ have been obtained by Gronwall, LaMer, and Sandved\textsuperscript{10} up to the fifth order. Sen, Johnson, and Roy\textsuperscript{11} have shown that the above expression can be simplified and
written in the form:

\[ \ln \gamma_+ = A_1 \gamma_m^{1/2} + A_2 \gamma_m + A_3 \gamma_m^{3/2} + \ldots \]  \quad \ldots \text{10}

Substitution of equation 10 into equation 8 yields

\[ E_{\text{obs}} + \frac{2RT}{F} \ln \gamma_m = E^0_m + A_1 \gamma_m^{1/2} + A_2 \gamma_m + A_3 \gamma_m^{3/2} + \ldots \]  \quad \ldots \text{11}

The coefficients in equation 11 are not arbitrary, adjustable parameters, but are composed of a number of constants, the temperature, the dielectric constant of the system, and only one adjustable parameter - the ion-size parameter. Johnson has demonstrated explicitly the composition of these constants and, hence, the dependence of the cell potential on the factors comprising the coefficients. If one assumes that the ion-size parameter is practically constant within the range of validity of the Debye-Hückel theory, then the standard potential of the galvanic cell in a particular system and at a particular temperature will be determined primarily by the bulk dielectric constant.

The \( E^0_m \) values may be calculated from the experimental emf and molalities using an appropriate polynomial curve-fitting program.\(^{11}\)

Relation Between \( K_a \) and \( K_a^* \).

The relation between the ionization constant \( (K_a) \) of the weak acid, HA, in pure water and the ionization constant \( (K_a^*) \) in a mixed solvent is given by equation 2

\[ K_a = \frac{S^w \gamma_{OH^+} + S^w \gamma_{OA^-}}{S^w \gamma_{OH^A}} \quad K_a^* = QV \cdot K_a^* \]  \quad \ldots \text{2}
Thus, one should be able to calculate the thermodynamic ionization constant of a weak acid in one solvent if the value is known in another solvent, provided the ratio of the activity coefficients is also known. Difficulty arises in computing single ion activity coefficients, however, since one cannot use mean activity coefficients as was done in the case of the hydrochloric acid cell. In fact, there is no way of determining single ion activity coefficients. Thus, the best way of converting any thermodynamic equilibrium constant measured in one medium to its value in another medium seems to be to assume some reasonable and extrapolatable function relating $K_a$ and $K_a^*$. From equation 2 it can be seen that $K_a^*$ approaches $K_a$ as the ratio of the activity terms approaches unity. Rearrangement of equation 11 gives

$$E_{\text{obs}} = E^0_m + \frac{2RT}{F} \ln \frac{m}{m_a} = A_1 m^{1/2} + A_2 m + A_3 m^{3/2} + \ldots \quad 11a$$

By comparison of equations 2, 6, 10, and 11a, one can assume further that the function sought is a function of the bulk dielectric constant of the system at a given temperature. These conclusions can be summarized by the following expression:

$$K_a = K_a^* f_QY(\varepsilon) \quad 12$$

where $\varepsilon$ is the bulk dielectric constant of the system.

One may find this function by plotting the ionization constants (or some function thereof) of the weak acid in solvents of varying composition against some function of the bulk dielectric constants of these mixed solvents. An acceptable plot should have the following characteristics:
(1) it should be continuous;
(2) it should contain values from as many mixed solvent systems as possible;
(3) it should have no maximum nor minimum;
(4) it should preferably be linear;
(5) it should be capable of being interpreted in terms of the physical process of ionization if it is assumed that the interactions are coulombic in nature.
CHAPTER II
THEORY

Chemical Potential and Chemical Equilibrium

A general equation for a reversible chemical reaction can be given by

\[ aA + bB \rightleftharpoons cC + dD \]  \( \ldots 13 \)

where \( a, b, c, \) and \( d \) represent the number of moles of \( A, B, C, \) and \( D \) respectively.

If the reaction in equation 13 occurs spontaneously from left to right at constant temperature and pressure, there will always be a decrease in a function of the state of the system known as the chemical potential (\( \mu \)). For such a reaction under these conditions, the change in chemical potential may be considered to be a change in chemical potential energy (or a change of free energy). Since the less energy a system has, the more stable the system is, the above spontaneous reaction will be accompanied by a decrease in the chemical potential energy of the system.

The chemical potential of a substance (e.g., A) is given by the equation

\[ \mu_A = \mu_A^0 + RT \ln a_A \]  \( \ldots 14 \)

where \( \mu_A^0 \) is a constant representing the standard molal chemical potential of A when its activity \( (a_A) \) is unity, \( R \) is the gas constant, and \( T \) is the absolute temperature.
When applied to solutes in ideal solutions, the activity is the ratio of the fugacity \( f \) in any given state to the fugacity \( f^\circ \) some standard state, generally taken at the same temperature.

\[ a_A = \frac{f_A}{f_A^\circ} \quad \ldots \ldots 15 \]

For a solute, the standard state (the state of unit activity) is arbitrarily chosen as the state which has the fugacity that a one molal solution would have if it obeyed the limiting law.

\[ \lim_{m \to 0} \left( \frac{\mu_m}{m} \right) = \lim_{m \to 0} \left( \frac{f}{f_m^\circ} \right) = 1 \quad \ldots \ldots 16 \]

The standard state for a solute is defined in such a way that the value of the activity approaches the molal concentration in the limit of infinite dilution. Since most real solutions deviate from ideality (except at very low concentrations), the activity of a solute is related to its molal concentration in any real solution by the equation

\[ a_A = \gamma_A m_A \quad \ldots \ldots 17 \]

in which \( \gamma_A \) is the activity coefficient of A.

For any spontaneous chemical reaction in which the reactants in their standard states react to form the products in their standard states, the change in Gibbs free energy for the reaction is \( \Delta G^\circ \). The standard free energy change for the general reaction (13) is given by

\[ \Delta G^\circ = (c \mu_c^\circ + d \mu_d^\circ) - (a \mu_A^\circ + b \mu_B^\circ) \quad \ldots \ldots 18 \]
If the substances are not in their standard states, then

\[
\Delta G = (c\mu_C^0 + d\mu_D^0) - (a\mu_A^0 + b\mu_B^0) + \\
RT(c \ln a_C + d \ln a_D - a \ln a_A - b \ln a_B)
\] ....19

or

\[
\Delta G = \Delta G^0 + RT \ln \frac{a_C a_D}{a_A a_B}
\] ....20

at equilibrium \( \Delta G = 0 \), therefore

\[
\Delta G^0 = -RT \ln \frac{a_C a_D}{a_A a_B} = -RT \ln K
\] ....21

At a given temperature and pressure, the left hand side of equation 21 is a constant. This fact is used to define the equilibrium constant \( K \) for the reaction, giving the familiar result

\[
K = \frac{a_C a_D}{a_A a_B}
\] ....22

For real solutions in which ideal behavior is not observed, equation 22 becomes

\[
K = \frac{a_C a_D}{a_A a_B} \frac{\gamma_C \gamma_D}{\gamma_A \gamma_B} \frac{m_C m_D}{m_A m_B}
\] ....23

For the reversible ionization reaction of a weak acid \( (HA) \)-

\[
HA \rightleftharpoons H^+ + A^-
\] ....24
equation 23 becomes

\[ K_a = \frac{\gamma_{H^+} \gamma_{A^-}}{\gamma_{HA}} \cdot \frac{m_{H^+} m_{A^-}}{m_{HA}} \]  

**The Nernst Equation**

The change in Gibbs free energy (\( \Delta G \)) can be defined as the maximum possible useful work a system can do when a chemical reaction occurs under reversible conditions. When the reaction is allowed to occur in a galvanic cell under conditions where the maximum possible electrical work is done, the change in free energy is given by

\[ \Delta G = -nF \varepsilon \]  

\[ \Delta G^0 = -nF \varepsilon^0 \]

where \( n \) is the number of electrons transferred in the reaction, \( F \) is the Faraday (96,487 absolute coulombs of electrical charge), and \( \varepsilon \) is the electromotive force of the galvanic cell. If the activities of the products and reactants are unity, the electromotive force of the cell is \( \varepsilon^0 \). The sign convention used in writing equations 25 and 26 is the Stockholm (Lewis) convention adopted by the International Union of Pure and Applied Chemistry in 1953. A positive value of \( \varepsilon \) corresponds to a free energy decrease.

Combining equations 25 and 26 with equation 20 gives

\[ E = E^0 - \frac{RT}{nF} \ln \frac{\gamma_A^{c^a d^b}}{\beta_a^{a^b} A_B^{a^b}} \]

This is the Nernst equation.

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the corresponding values in another solvent, one must consider the medium effect corrections. These are the primary medium effects involving ion-solvent interactions and the secondary medium effects involving ion-ion interactions. These two effects are related by equation 1:

\[
\frac{S_{\gamma}^+}{S_{\gamma^-}} \ln \frac{w_{\gamma^+}}{w_{\gamma^-}} = \ln \frac{w_{\gamma^+}}{w_{\gamma^-}} + \ln \frac{w_{\gamma^+}}{w_{\gamma^-}}
\]

Total Primary Secondary
Medium Medium Medium
Effect Effect Effect

To obtain the thermodynamic treatment of the medium effects, consider again the special case of cell II -

Pt, H₂ (1 atm.) | HCl (m), Organic (Y), Water (Y) | AgCl-Ag

Where the weight percent of the organic solvent is zero, one has the aqueous cell:

Pt, H₂ (1 atm.) | HCl (m) | AgCl-Ag

The electromotive force of this cell can be given by the following form of equation 8:

\[
E_{\text{obs}} = E^0 - \frac{2RT}{F} \ln \frac{w_{\gamma^+}}{w_{\gamma^-}}
\]

Using a more convenient symbolism, we can write

\[
w_{E} = w_{E}^0 - \frac{2RT}{F} \ln \frac{w_{\gamma^+}}{w_{\gamma^-}}
\]
When all the activities in equation 27 are equal to unity (i.e., the substances are in their standard states), \( E \) becomes equal to \( E^\circ \). Standard states are specified as follows:

1. The standard state of a pure gas is the state at any fixed temperature in which the fugacity of the gas is equal to one atmosphere. For an ideal gas, the activity and the fugacity of a gas are numerically identical. Hence the activity of a gas and its pressure are numerically identical. For a real gas, the fugacity equals the pressure as the pressure goes to zero.

\[
\lim_{p \to 0} \frac{f}{p} = 1
\]

2. The standard state of a pure solid or liquid is taken as the state of the solid or liquid at one atmosphere pressure at each temperature. Since the free energies of solids and liquids are not very dependent on pressure, the activity \( a \) is approximately equal to unity at all temperatures and for wide ranges of pressure.

3. The standard state for the components of a solution is normally selected in such a way that the molality is equal to the activity. It is the state which has the fugacity that a one molal solution would have if it obeyed a dilute solution limiting law.

**Thermodynamic Representation of the Medium Effect.**

As mentioned in the Introduction, in order to convert experimental data obtained for a reversible process in one solvent to
the corresponding values in another solvent, one must consider the medium effect corrections. These are the primary medium effect involving ion-solvent interactions and the secondary medium effect involving ion-ion interactions. These two effects are related by equation 1:

\[
\frac{S^+}{w^+} = \ln \frac{S^+}{w^+} + \ln \frac{S^+}{w^+} \quad \ldots1
\]

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To obtain the thermodynamic treatment of the medium effects, consider again the special case of cell II -

Pt, \( H_2 (1 \text{ atm.}) \) | HCl (m), Organic (X),
Water (Y) | AgCl-Ag

Where the weight percent of the organic solvent is zero, one has the aqueous cell:

Pt, \( H_2 (1 \text{ atm.}) \) | HCl (m) | AgCl-Ag

The electromotive force of this cell can be given by the following form of equation 8:

\[
E_{\text{obs}} = E^0 - \frac{RT}{F} \ln \frac{S^+}{w^+} m \quad \ldots29
\]

Using a more convenient symbolism, we can write

\[
w = w^0_m - \frac{RT}{F} \ln \frac{S^+}{w^+} m \quad \ldots30
\]
Again, the superscript \((w)\) denotes water as the solvent and the subscript \((w)\) that \(\gamma^+\) is measured relative to unit value in an infinite dilute solution.

When mixed solvent is used rather than water (Cell II), the standard reference state may be defined in terms of the infinitely dilute solution in the mixed solvent or in terms of the infinitely dilute solution in water. Thus, equation 30 can be written

\[
\begin{align*}
\frac{s^E}{m} &= \frac{s^{E^o}}{m} - \frac{2RT}{F} \ln \frac{\gamma^+}{m} \\
\end{align*}
\]

in which

\[
\frac{s^{E^o}}{m} = \lim \left[ \frac{s^E}{m} + \frac{2RT}{F} \ln m \right] \\
\]

The term \(\ln \frac{\gamma^+}{m}\) is zero as \(m \to 0\) since \(\frac{\gamma^+}{m}\) becomes unity.

Equation 31 may also be written

\[
\begin{align*}
\frac{s^E}{m} &= \frac{w^{E^o}}{m} - \frac{2RT}{F} \ln \frac{\gamma^+}{m} \\
\end{align*}
\]

Since the activity coefficient \(\gamma^+_\|\) is measured relative to unity in the infinitely dilute aqueous medium, it no longer approaches unity as \((m)\) approaches zero in the mixed solvent. Thus,

\[
\frac{w^{E^o}}{m} = \lim \left( \frac{s^E}{m} + \frac{2RT}{F} \ln m + \frac{2RT}{F} \ln \gamma^+_\| \right) \\
\]

Subtracting equation 32 from equation 34 gives
This is the thermodynamic representation of the primary medium effect and is a measure of the free energy change when a pair of ions is transferred from infinite dilution in one solvent to infinite dilution in another solvent under conditions involving only coulombic ion-solvent interactions.

The secondary medium effect can be determined by calculating the total medium effect and subtracting the primary medium effect from it. The thermodynamic representation of the total medium effect can be obtained by coupling cells II and III:

\[
\begin{align*}
\text{Ag-AgCl} & \mid \text{HCl (m)} \mid \text{H}_2 \mid \text{HCl (m)}, \text{Organic (X)}, \\
\text{Water (Y)} & \mid \text{AgCl-Ag} \\
\end{align*}
\]

The overall cell reaction consists of transferring hydrochloric acid from the aqueous to the mixed solvent solution, and the cell potential is given by

\[
E_{\text{cell}} = \delta E - \delta E = (\delta E_{\text{m}} - \delta E_{\text{m}}) - \frac{2RT}{F} (\delta n s_\text{Y} - \delta n s_\text{Y}) \]

Since the molality of hydrochloric acid is the same in each half cell, any energy changes due to changes in concentration have been eliminated. Thus, only the energy changes which depend on departures from solution ideality are considered.

The first term on the right hand side of equation 36 is the negative of the primary medium effect, so that substitution gives:
By subtracting equation 30 from equation 33, one obtains

\[ s_E - w_E = \frac{-2RT}{F} \ln w_{+} - \frac{2RT}{F} \left( \ln s_{Y+} - \ln w_{+} \right) \]  

Equating equations 37 and 38 gives the relation between the total, the primary, and the secondary effects:

\[ \frac{\ln s_{Y+}}{w_{+}} = \frac{\ln s_{Y+}}{w_{+}} + \frac{\ln s_{Y+}}{w_{+}} \]

The primary medium effect is determined by the difference between the ion-solvent interactions at infinite dilution in the two solvents. The secondary medium effect is composed of two parts. The term measures the difference in the "non-ideal" part of the chemical potential of the electrolyte at a finite concentration and at infinite dilution in the mixed solvent system. It will be given by some form of the Debye-Hückel equation and will be dependent on the dielectric constant of the medium. The term measures a difference in the "non-ideal" part of the chemical potential of the electrolyte at the same finite concentration and at infinite dilution in pure water. This term will also be dependent on the dielectric constant.

**The Ionization Constants of Weak Monoprotic Acids and the Medium Effects**

Again consider cell I:

\[ \text{Pt, H}_2 (1 \text{ atm.}) | \text{HA (m}_1\text{), NaA (m}_2\text{) NaCl (m}_3\text{),} \]

\[ \text{Organic (X), Water (Y) | AgCl-Ag} \]
where \( X \) is equal to zero, i.e., the pure aqueous cell. The ionization constant of the weak monoprotic acid (HA) is given by the equation

\[
K_a = \frac{\gamma_{H^+} \gamma_{A^-}}{\gamma_{HA}} \cdot \frac{m_{H^+} m_{A^-}}{m_{HA}}
\]

When \( X \) is not equal to zero, the ionization constant is represented by

\[
K_a^* = \frac{\gamma_{H^+} \gamma_{A^-}}{\gamma_{HA}^*} \cdot \frac{m_{H^+} m_{A^-}}{m_{HA}}
\]

To find the relation between \( K_a \) and \( K_a^* \), first consider the activity coefficient of a symmetrical valence type electrolyte such as HCl

\[
\ln \frac{\gamma_{\text{w}}} = \ln \frac{\gamma_{\text{w}}} + \ln \frac{\gamma_{\text{w}}}{\gamma_{\text{w}}}
\]

\( \gamma_{\text{w}} \) is the mean activity coefficient of the electrolyte at a finite concentration in a mixed solvent relative to unity at infinite dilution in pure water. \( \gamma_{\text{w}}^* \) is the mean activity coefficient of the electrolyte at zero concentration in a mixed solvent relative to unity at infinite dilution in pure water. \( \gamma_{\text{w}}^* \) is the mean activity coefficient of the electrolyte at a finite concentration in a mixed solvent relative to unity at infinite dilution in the mixed solvent.

The validity of equation 41 is shown by adding the term 

\[-\ln \frac{\gamma_{\text{w}}}{\gamma_{\text{w}}^*} \]

to both sides. The result is equation 1:

\[
\ln \frac{\gamma_{\text{w}}}{\gamma_{\text{w}}} = \ln \frac{\gamma_{\text{w}}}{\gamma_{\text{w}}} + \ln \frac{\gamma_{\text{w}}}{\gamma_{\text{w}}^*}
\]
Equation 41 can be given as

$$wY_j = (wY_j^+) ^{-1} (wY_+^-)$$

Equation 42

K_a is related to K* by the following definitional equation

$$K_a = \frac{wY^2 a}{wY^2 a} K^*$$

Equation 43

where

$$wY^2 a = \frac{wY^2 H^+ + wY^2 A^-}{wY^2 HA}, \frac{wY^2 a}{wY^2 oH A} = \frac{wYO^2 H^+ + wYO^2 A^-}{wYO_H^2 A}, \frac{wY^2 a}{wY^2 HA},$$

and

$$k_a = \frac{m_{H^+} m_{A^-}}{m_{HA}}.$$

By appropriate substitution for the $wY^2 oA$ term in equation 43, one obtains equation 2:

$$K_a = \frac{wYO^2 H^+ + wYO^2 A^-}{wYO_H^2 A}. K^*$$

Equation 2

The determination of $K_a$ and $K^*$ has been described earlier (pages 3-6).

It is evident from equation 2 that one needs to know the primary medium effect upon each of the species involved in the equation.

The Born Equation

Using the Born-Haber approach, it is possible to calculate the amount of energy necessary to transfer a mole of uni-univalent electrolyte with hydrated cation radius ($r_1$) and hydrated anion...
radius ($r_2$) from one solvent of dielectric constant ($\varepsilon_1$) to another solvent of dielectric constant ($\varepsilon_2$). This energy is given by

$$W_t = \frac{Ne^2}{2} \left(\frac{1}{\varepsilon_1} - \frac{1}{\varepsilon_2}\right) \left(\frac{1}{r_1} + \frac{1}{r_2}\right) = \Delta G \quad \ldots \ldots 44$$

By substitution of this expression for the primary medium effect into equation 35

$$W_m^0 - S_m^0 - \frac{2RT}{F} \ln \frac{W_m^0}{W_m^0^+} \quad \ldots \ldots 35$$

and using the relationship given by equation 26

$$\Delta G^0 = -nF\varepsilon^0 \quad \ldots \ldots 26$$

one obtains

$$W_m^0 - S_m^0 - \frac{Ne^2}{2F} \left(\frac{1}{\varepsilon^*} - \frac{1}{\varepsilon}\right) \left(\frac{1}{r_1} + \frac{1}{r_2}\right) \quad \ldots \ldots 45$$

Since

$$\Delta G^0 = -nF\varepsilon^0 \quad \ldots \ldots 26$$

and

$$\Delta G^0 = -RT \ln K \quad \ldots \ldots 21$$

substitution and rearrangement of equation 45 produces

$$\ln K - \ln K^* = \frac{Ne^2}{2RT} \left(\frac{1}{\varepsilon^*} - \frac{1}{\varepsilon}\right) \left(\frac{1}{r_1} + \frac{1}{r_2}\right) \quad \ldots \ldots 46$$

which can be written as

$$pK^*_a - pK_a = \frac{Ne^2}{4.606RT} \left(\frac{1}{\varepsilon^*} - \frac{1}{\varepsilon}\right) \left(\frac{1}{r_1} + \frac{1}{r_2}\right) \quad \ldots \ldots 47$$
We can now consider the effect of the solvent on the ionization constant of the weak acid (HA). The standard free energy change on ionization is \(-RT \ln K_a\). It is the energy change when a mole of unionized acid in its standard state is replaced by an equivalent amount of its ions each in its standard state. Then \(RT \ln K^*_a/K_a\) measures the change in free energy when a mole of unionized acid is transferred from the mixed solvent to pure water and the ions are transferred in the opposite direction. Since these transfers occur between states where the activity coefficients are unity, one does not need to introduce a term for interionic effects. Robinson and Stokes\(^{15}\) plotted \(\log K^*_a/K_a\) against \(1/\varepsilon\) for a number of weak acids. The points clustered around a single straight line. Using the slope of this line, the Born equation, and an assumed value of 3.73 Å for the radius of the hydrated hydrogen ion, Robinson and Stokes calculated a value of 1.2 Å for radius of the carboxylic anions. This is a "small but not impossible value". The authors concluded that the Born equation was a first approximation of the properties of weak acids in different solvents, but that some other highly specific effects should be considered to completely study the weak acids.

From equation 47 it is obvious that a plot of \(pK^*_a\) against \(1/\varepsilon\) should be linear. Harned made such a plot for the \(pK^*_a\) values of water, formic acid, acetic acid, and propanoic acid in dioxane-water mixtures. The plots he obtained were not linear and, therefore, he concluded\(^{17}\) that Born's equation was not valid. He noted a similar result when the standard potentials of the hydrogen, silver-
silver chloride were plotted against $1/\varepsilon$. The same result occurred at all temperatures between $0^\circ$ and $50^\circ$ C.

Day and Selbin\textsuperscript{18} proposed that the lack of linearity of such plots might be due to inaccuracies in $E^0$ values, to the inconstancy of ionic radii in different solvents, and to questionable reasonableness of the Born model. Actually, these plots are linear for high values of the dielectric constant ($\varepsilon > 33$).

Gurney\textsuperscript{18} and Baughan\textsuperscript{18} developed a theory for the temperature variation of ionization constants. Using the Born equation, they derived an expression for standard free energy change involved in a reaction of the type

\[ \text{RCOOH} + \text{H}_2\text{O} \rightleftharpoons \text{RCOO}^- + \text{H}_3\text{O}^+ \]

\[ \text{...48} \]

This reaction involves both the shifting of a proton and the creation of a new field.

The total free energy for this process can be separated into a chemical part ($\Delta G^0(\varepsilon = \infty)$) and an electrical part ($\Delta G^0(\text{elec})$), which is calculated from the Born equation.

\[ \Delta G^0(\text{elec}) = \frac{Ne^2}{2\varepsilon} \left( \frac{1}{r^+} + \frac{1}{r^-} \right) \]

\[ \text{...49} \]

\[ \Delta G^0(\text{total}) = \Delta G^0(\varepsilon = \infty) + \Delta G^0(\text{elec}) \]

\[ \text{...50} \]

Equation 50 can be written:

\[ -\ln K = -\ln K(\varepsilon = \infty) + \frac{Ne^2}{2eRT} \left( \frac{1}{r^+} + \frac{1}{r^-} \right) \]

\[ \text{...51} \]

Substituting equation 51 into the following equation
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favor of a relationship between the standard potential on the molar
scale ($E^\circ$) and the volume fraction of water ($\bar{w}$) in the mixed solvent:

$$E^\circ_c = w^\circ_c - 2.5 k \log \bar{w}$$

The 2.5 denotes the supposition that 2.5 moles of water accompany the
transfer of a hydrogen ion from one solvent to another. They applied
this relationship with some success to eleven solvent mixtures, but
it did not hold true for glucose-water, glycol-water, and dioxane-
water mixtures.

The ionization constants of many weak acids have been
determined in a large number of mixed solvent systems. Extensive
work has been done in dioxane-water mixtures by Harned and his co­
workers. Harned and Done determined the ionization constants of
formic acid in dioxane-water mixtures from 20 to 82 percent by weight,
while Harned and Kazanjian, Harned and Fallon, and Harned deter­
mined $K_a$ for acetic acid in the same mixtures. The $K_a$ values for
propanoic acid were determined in these mixtures by Harned and Dedell. All the values in 82% dioxane-water mixture were later revised by
Danyluk, Taniguchi, and Janz. Dunsmore and Speakman determined
the ionization constants of benzoic acid in 20 to 50 percent (weight)
dioxane-water.

Work on formic, acetic, propanoic, benzoic, butanoic, iso­
valeric, chloroacetic, cyanoacetic, glycolic, lactic, malonic, suc­
cinic, glutaric, and salicylic acids in ethanol-water mixtures from
20 to 80 percent (weight) has been done or summarized by Grundwald

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and Berkowitz.\textsuperscript{26} This author has determined values for acetic acid in 8.04 and 16.26 percent (weight) ethanol-water.

Glover\textsuperscript{27} has summarized data for formic, acetic, propanoic, and benzoic acids in methanol-water mixtures ranging from 10 to 76 weight percent and for acetic and benzoic acids to 100 percent. The work is that of Shedlovsky and Kay\textsuperscript{6} and Bacarella, Grundwald, Marshall, and Purlee.\textsuperscript{28} Glover has summarized data for weak acids in a number of other mixed solvent systems - acetone-water, dioxane-water and several others. Additional values for $K_a^*$ for benzoic acid in methanol-water mixtures have been determined by Patterson and Felsing\textsuperscript{29} and $K_a^*$ values for butanoic acid for 16 to 76 weight percent methanol-water mixtures have been determined by Parton and Rogers.\textsuperscript{30}

Acetone-water mixtures have been investigated by Morel,\textsuperscript{31} Dippy, Hughes, and Rozanski,\textsuperscript{32} Reynaud,\textsuperscript{33} and this author. Dippy, Hughes, and Rozanski measured the ionization constants of acetic, propanoic, benzoic, and several other acids in 10 and 25 percent acetone-water mixtures conductometrically. A glass electrode was used with a potentiometric cell without a liquid junction by Morel to determine $pK_a^*$ values for acetic acid, and by Reynaud to determine $pK_a^*$ values for acetic and benzoic acids and a number of organic bases. This author has determined $pK_a^*$ values for acetic acid using the unplatinized hydrogen electrode of Feakins and French\textsuperscript{34} for 10 percent weight acetone-water mixtures and a Corning glass electrode for 20 and 40 weight percent acetone-water mixtures.

In utilizing the glass electrode for measurements of cell emf, the following cells are used:
\[ \text{Pt, } H_2 (1 \text{ atm.}) \mid \text{HCl (m), Organic (X), Water (Y)} \mid \text{AgCl-Ag}^\oplus \ldots \text{Is} \]

\[ \text{Glass electrode} \mid \text{HCl (m), Organic (X), Water (Y)} \mid \text{AgCl-Ag}^\oplus \ldots \text{IIs} \]

\[ \text{Glass electrode} \mid \text{HCl (m = 0.01)} \mid \text{AgCl-Ag}^\oplus \ldots \text{IIw} \]

\[ \text{Pt, } H_2 (1 \text{ atm.}) \mid \text{HCl (m = 0.01)} \mid \text{AgCl-Ag}^\oplus \ldots \text{Iw} \]

The electromotive forces of cells Is and IIs are

\[ E_{\text{Is}} = E_{\text{AgCl-Ag}}^{\text{glass}} - E_{\text{H}_2}^{\text{glass}} - 2k \log a_{\text{HCl}} \ldots 57 \]

\[ -E_{\text{IIs}} = E_{\text{AgCl-Ag}}^{\text{glass}} - E_{\text{glass}}^{\text{glass}} - 2k \log a_{\text{HCl}} \ldots 58 \]

Subtracting equation 58 from equation 57 gives

\[ E_{\text{Is}} = E_{\text{glass}}^{\text{glass}} - E_{\text{IIs}} \ldots 59 \]

\( E_{\text{H}_2}^{\text{glass}} \) is assumed to be zero in all the mixtures).

Similarly, in water, one obtains

\[ E_{\text{Iw}} = E_{\text{glass}}^{\text{glass}} - E_{\text{IIw}} \ldots 60 \]

If \( E_{\text{glass}}^{\text{glass}} \) does not depend on the composition of the mixture, one can obtain

\[ E_{\text{Is}} = E_{\text{Iw}} + E_{\text{IIw}} - E_{\text{IIs}} \ldots 61 \]

A plot of \( E_{\text{Is}} \) against \( E_{\text{Iw}} - E_{\text{IIs}} \) gives a straight line with a slope of unity, demonstrating that \( E_{\text{glass}}^{\text{glass}} \) is independent of solvent composition.
Knowing $E_{lw}$ and $E_{IIw}$ and measuring $E_{IIIs}$, $E_{Is}$ can be calculated. $E_{Is}$ corresponds to $E_{observed}$.

Work in two propanol-water mixtures has been done by Moore and Felsing\textsuperscript{35} for propanoic acid, and Felsing and May\textsuperscript{36} for butanoic acid. The $pK_a^\star$ values were determined potentiometrically in 5, 10, and 20 weight percent solutions.

Reynaud\textsuperscript{33,37} also used the glass electrode to determine $pK_a^\star$ values of acetic and benzoic acids in 20, 30, 40, and 50 volume percent organic solvent-water mixtures for 2-methoxyethanol, 1,2-dimethoxyethane, and tetrahydrofuran. Morel\textsuperscript{38} applied the glass electrode to the determination of $pK_a^\star$ values for acetic acid in 10 to 80 weight percent dimethyl sulfoxide-water solutions.

The name Akerl"of is synonymous with the determination of dielectric constants in various mixed solvent systems. $e$ values in ethanol-water, methanol-water, acetone-water, 2-propanol-water, and several other mixed solvents have been determined by Akerl"of,\textsuperscript{39} while Akerl"of and Short\textsuperscript{40} determined $e$ in dioxane-water systems. Values of $e$ in 2-methoxyethanol-water, acetone-water, 1,2-dimethoxyethane-water, tetrahydrofuran-water, 2-ethoxyethanol-water mixtures were determined by Reynaud.\textsuperscript{33,37} Lindberg and Kentt"amaa\textsuperscript{41} have obtained $e$ values for dimethyl sulfoxide-water systems which seem to be too high.
CHAPTER III

EXPERIMENTAL WORK

The following cell was used in all experiments except those involving 20 and 40 percent acetone-water mixtures in which cases glass electrode was substituted for the H₂ electrode:

\[ \text{Pt, } H_2 (1 \text{ atm.}) \mid HOOAc \,(m_1), \, \text{NaOAc} \,(m_2), \, \text{NaCl} \,(m_3), \]

\[ \text{Organic} \,(X), \, \text{Water} \,(Y) \mid \text{AgCl}-\text{Ag} \]

The basic cell design is given in Figure 1. Two hydrogen electrodes and two silver-silver chloride electrodes were used in each cell. Thus, it was possible to take a total of four readings for each solution by interchanging electrode pairs; two readings were made in the higher acetone-water concentrations where a single glass electrode was used. The electromotive force of each cell was measured by a Leeds and Northrup K-3 Universal potentiometer calibrated against an Eppley unsaturated-type standard cell. Null readings were obtained using a sensitive (0.004 \( \mu \) a/mm) Rubicon or (0.001 \( \mu \) a/mm) Leeds and Northrup galvanometer. For readings in higher acetone-water concentrations, a Leeds and Northrup Model 7405 expanded scale pH meter was used with a Corning No. 476022 glass electrode. The meter was standardized against Leeds and Northrup or Corning standard buffer solutions using a Corning No. 476002 calomel reference electrode.

The hydrogen electrodes were prepared from Sargent No. 5-30505 platinum electrodes which had been cleaned by brief immersion in 50% aqua regia (3 volumes of 12 M hydrochloric acid, 1 volume of
FIGURE 1

DIAGRAM OF EXPERIMENTAL CELL
FIGURE 1

Ag-AgCl Electrode

Teflon

Hydrogen electrode

fritted

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16 M nitric acid, and 4 volumes of distilled water). After thorough rinsing with double-distilled water, the electrodes were plated in a solution of chloroplatinic acid which had been prepared as follows:

One and one-half grams of scrap platinum were cleaned in hot, concentrated nitric acid, rinsed with distilled water, and ignited in a Bunsen flame. The metal was then cut into small fragments which were dissolved by digesting for several days in warm aqua regia. The solution was then evaporated to dryness over a steam bath and the residue dissolved in 20 ml. of concentrated hydrochloric acid. The evaporation to dryness and subsequent addition of the concentrated hydrochloric acid was repeated twice. A fourth evaporation to dryness produced a residue of chloroplatinic acid hexahydrate, $\text{H}_2\text{PtCl}_6\cdot6\text{H}_2\text{O}$. The platinizing solution (1-3% chloroplatinic acid) was prepared by dissolving a weighed amount of chloroplatinic acid and 80 mg. of lead acetate trihydrate in 100 ml. of double-distilled water, and it was stored in a glass-stoppered bottle.

A current of 200 to 400 milliamperes was passed for one to three minutes in such a direction that the electrode being coated was the cathode. A similar platinum electrode served as the anode. Since repeated use of a given platinizing solution will decrease current efficiency, close current control does not necessarily insure the production of satisfactory electrodes. The best guide seems to be the appearance of the electrodes which should be very black, uniform, and free from streaking. The addition of lead to the plating solution is essential if the deposits are to be smooth and adherent.
The finished electrodes were intercompared, and electrodes which did not agree within ± 0.01 millivolts of the others were discarded. The electrodes were stored in doubly-distilled water and lasted for several months.

Unplatinized hydrogen electrodes\textsuperscript{42} for use in acetone-water where solvent reduction is a problem were prepared by polishing a platinum foil with the rounded end of a glass rod on a glass plate sheet. The electrodes were warmed in 50\% aqua regia until the polish was just destroyed, and were then placed in warm concentrated nitric acid to remove absorbed chlorine, and were washed successively with tap water, doubly-distilled water, and the acetone-water solution to be used in the cell. The electrodes were inserted immediately into the cells which had been flushed clean of dissolved air by passage of the hydrogen gas.

Silver-silver chloride electrodes were prepared by a thermal-electrolytic method adapted from Bates.\textsuperscript{43} A helix of number 26 platinum wire about 7 mm. in length and 2 mm. in diameter was sealed in a flint glass tube. The platinum bases were cleaned in a warm 6 M nitric acid and thoroughly rinsed with doubly-distilled water. A thick paste of well-washed silver oxide (prepared by the method of Bates\textsuperscript{45}) and water was applied to each helix. The electrodes were placed in a crucible furnace at 500\textdegree~C. and allowed to remain until they were completely white. This usually took about 4 to 5 minutes. Three additional layers were added to each electrode using successively thinner paste followed by heating in the furnace.
The electrodes were electrolyzed in a 1 M solution of twice-distilled hydrochloric acid for 45 minutes at a current of 10 milliamperes, using a platinum wire as the cathode. The finished electrodes were placed in a 0.05 M hydrochloric acid overnight and then stored in double-distilled water. Their potentials were intercompared in dilute hydrochloric acid and individual electrodes that differed from the average of the group by more than 0.1 millivolt were rejected.

A Sargent Thermonitor regulated water bath together with a Sargent water bath cooler provided temperatures of 16°, 20°, 25°, 30°, 35°, and 40° with a precision of ± 0.01° C.

The double-distilled water was obtained by distilling distilled water from a solution of reagent grade potassium permanganate through an all-glass still containing a column 18 inches high and 2.5 inches in diameter filled with glass beads. The conductivity of this water was 3 x 10^-7 reciprocal ohms as determined with a Serfass Conductance Bridge. Where the term "distilled water" occurs in this Dissertation, it will refer to water prepared in the above manner.

The acetic acid was prepared following the method used by Harned and Kazanjian. Glacial acetic acid was distilled three times in an all-glass still. The first two distillations were from an initial 2% chromic trioxide solution. The middle fraction of the third distillation, \( N_D^{o} = 1.3715 \), lit. \( N_D^{o} = 1.37152 \)), was diluted with distilled water to form a 2.5 M solution. The exact concentration of this solution was determined by titration with a 2.5 M sodium hydroxide solution standardized with potassium hydrogen phthalate.
Commercially available tetrahydrofuran (Fisher Scientific) was found to be sufficiently pure by chromatographic method for use without further purification. Baker's Analyzed Reagent grade acetone was purified by the method of Feakins and French. Both the purified acetone and the commercial product were run through an ethyl hexyl phthalate column at 105° C. on a Cenco Vapor Phase Gas Chromatograph and showed only an acetone peak. Another run of commercial acetone through a Silicon 550 column at 30 to 200° C. programmed temperature using the F and M Research Chromatograph showed only the acetone peak. The commercial product was used in the present work. "Extra-dry" ethanol was obtained by distillation of commercial absolute ethanol following the method of Manske. Ethyl phthalate was added to a reacted mixture of absolute ethanol and metallic sodium. The entire mixture was refluxed for an hour, and then was distilled in an all-glass still ($N_D^{20} = 1.3618$, lit. $N_D^{19.5} = 1.36175$).

The purified acetic acid together with Fisher Reagent sodium acetate and sodium chloride were used to prepare stock solutions which were approximately 2.5 M in each component. The densities of these solutions were determined with pycnometers.

All the solutions used in potentiometric determinations of $pK_a$ were made up volumetrically from the acetic acid-salt stock solutions, solvents, and distilled water. The volume of each solution or solvent was determined individually by buret or pipet. Concentrations were converted to the weight scale using the appropriate density data.
The hydrogen gas used in these measurements was Matheson ultra-pure hydrogen which was further purified by passing it through a Deoxo catalytic purifier. The hydrogen was saturated with the cell solution by passage through a bubbler before entering the cell.

The procedure generally followed was to rinse the cell, the bubbler, and the electrodes with the solution under investigation, to fill the cell and the bubbler with the solution, to insert the electrodes, and to commence bubbling hydrogen through the solution. Readings were taken at approximately thirty-minute intervals until subsequent values of $E$ agreed with 0.1 millivolt, it was then assumed that equilibrium had been attained.

About five to six hours were usually required for equilibrium to be reached, although often less time was needed. Figure 2 is a graph of the time-rate of change of cell voltage as a function of time for a $10\%$ tetrahydrofuran-water solution. There is a very sharp decrease in cell voltage during the first hour and a more gradual decrease thereafter. After five to six hours elapse, a steady decrease in cell voltage is noted on the order of 0.001 mv. per minute. It was assumed that the system remained in equilibrium once the steady state had been reached and that evaporation of the solvent caused the gradual drop in cell emf. Other systems gave similar results.

When utilizing the unplatinized electrodes in $10\%$ acetone-water solutions, Feakins and French found that equilibrium was reached by these electrodes within one to two hours and that prolonged exposure to hydrogen caused electrode failure. After initial erratic
TABLE I
TIME RATE OF CHANGE OF CELL EMF FOR THE CELL,

\[ \text{Pt, } \text{H}_2 (1 \text{ atm.}) | \text{HOAc (m}_1\text{), NaOAc (m}_2\text{); NaCl (m}_3\text{), THF (9.1%), Water (90.9%)} | \text{AgCl-Ag} \]

<table>
<thead>
<tr>
<th>At 25.0° C</th>
<th>Time in Minutes</th>
<th>(\Delta E/\Delta t) in 10 microvolts/minute</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time</td>
<td>Time</td>
<td>(\Delta E/\Delta t )</td>
</tr>
<tr>
<td>67</td>
<td>6.37</td>
<td>-0.25</td>
</tr>
<tr>
<td>101</td>
<td>0.97</td>
<td>0</td>
</tr>
<tr>
<td>120</td>
<td>0.58</td>
<td>0.03</td>
</tr>
<tr>
<td>191</td>
<td>0.65</td>
<td>-0.14</td>
</tr>
<tr>
<td>219</td>
<td>0.54</td>
<td>-0.06</td>
</tr>
<tr>
<td>268</td>
<td>-0.27</td>
<td>-0.30</td>
</tr>
<tr>
<td>300</td>
<td>0.78</td>
<td>-0.09</td>
</tr>
</tbody>
</table>

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FIGURE 2

TIME RATE OF CHANGE OF CELL EMF AS A FUNCTION OF TIME
results in 10% acetone-water, it was decided to allow the silver-
silver chloride electrodes to remain in the solution with hydrogen
bubbling through the solution for at least four hours before insert­
ing the hydrogen electrodes. Readings were made usually one and a
half hours after insertion of the hydrogen electrodes and agreement
to the nearest 0.1 millivolt was obtained.

With the glass electrode, the silver-silver chloride elec­
trodes were allowed to equilibrate in the acetone-water solution for
five hours. Then the glass electrode was inserted and allowed to remain
for fifteen minutes to attain temperature equilibrium, and then the
readings were obtained.

The glass electrode was calibrated against the hydrogen
electrode using the following cells:

Glass electrode | HCl (m = 0.01) | AgCl-Ag ....IIw
Pt, H₂ | HCl (m = 0.01) | AgCl-Ag ....Iw

The hydrogen and glass electrodes were calibrated against
the same AgCl-Ag electrodes in the same hydrochloric acid solution.

In using the cell:
Pt, H₂ (1 atm.) | HA (m₁), NaA (m₂), NaCl (m₃),
Organic (X), Water (Y) | AgCl-Ag ....I
to find Kₐ and Kₐ⁺, the half reactions for this cell are given by

\[ \text{H}^+ + e \rightleftharpoons \frac{1}{2} \text{H}_2 (g) \] ....62

\[ \text{AgCl} (s) + e \rightleftharpoons \text{Ag} (s) + \text{Cl}^- \] ....62a
Combining these gives the over-all reaction

\[ \text{AgCl} + \frac{1}{2} \text{H}_2 \text{(g)} \rightleftharpoons \text{Ag} \text{(s)} + \text{Cl}^- + \text{H}^+ \] ....62b

The electromotive force of the cell is written as

\[ E = E^\circ - \frac{RT}{F} \ln \frac{a_{\text{Ag}^+}a_{\text{Cl}^-}}{a_{\text{AgCl}}^{\frac{1}{2}}a_{\text{H}_2}^{\frac{1}{2}}} \] ....63

Using the conventions regarding standard states, the activities of solid silver and solid silver chloride are unity and the activity of the hydrogen can be replaced by its partial pressure.

Equation 63 then becomes

\[ E = E^\circ - \frac{RT}{F} \ln \frac{a_{\text{H}^+}a_{\text{Cl}^-}}{(p_{\text{H}_2})^{\frac{1}{2}}} \] ....64

\( E(p) \), the electromotive force of the cell measured at a partial pressure \((p)\) of hydrogen gas is given by

\[ E(p) = E^\circ - \frac{RT}{F} \ln a_{\text{H}^+}a_{\text{Cl}^-} + \frac{RT}{2F} \ln p_{\text{H}_2} \] ....65

The electromotive force of the same cell, measured at a partial pressure of hydrogen of exactly one atmosphere, is given by

\[ E(1) = E^\circ - \frac{RT}{F} \ln a_{\text{H}^+}a_{\text{Cl}^-} + \frac{RT}{2F} \ln 1 \text{ atm.} \] ....65a

\( E(1) \) is the \( E \) observed of equation 3.

By converting \( E(p) \) to \( E_{\text{obs}} \), it is unnecessary to measure the partial pressure of the hydrogen gas. The difference between \( E_{\text{obs}} \) and \( E(1) \) is due to the difference in the partial pressure of hydrogen and
is given by

\[ \Delta E = E_{\text{obs}} - E(p) = \frac{RT}{2F} \ln \frac{760}{p_{H_2}} = \frac{RT}{2F} \ln \frac{760}{p_{\text{atm}} - p_s} \]

where \( \Delta E \) is the quantity which must be added to the measured electromotive force of the cell to get the \( E_{\text{obs}} \) values, \( p_{\text{atm}} \) is the barometric pressure, and \( p_s \) represents the partial pressure of the solvent as calculated by Raoult's Law.
CHAPTER IV

EXPERIMENTAL DATA AND RESULTS

Either the IBM 1620 or the IBM 360 computer was used to calculate the values of $pK_*^a$, $E_{\text{observed}}$, $m_1$, $m_2$, $m_3$, and $\sqrt{\mu}$ for all mixed solvent systems studied. Each individual program was checked by performing several long-hand calculations. The standard electrode potentials for the silver silver-chloride electrodes, $E_0$, are given in Table II. The molalities of the acetic acid ($m_1$), sodium acetate ($m_2$), and sodium chloride ($m_3$) were calculated from the appropriate density data of tetrahydrofuran, 47 of ethanol, 48, of acetone*, and of water 48 given in Table III.

In order to calculate $E_{\text{observed}}$, it was necessary to add $\Delta E$, given by equation 66, to the measured electromotive force

$$\Delta E = \frac{RT}{2F} \ln \frac{760}{P_{\text{atm}} - P_s}$$

in which $P_{\text{atm}}$ equals the barometric pressure and $P_s$, the partial vapor pressure of the solvent. Vapor pressure data for water were taken from the Handbook of Chemistry and Physics. 48 These values together with vapor pressure data for tetrahydrofuran 50 and for ethanol 51 at various temperatures, and for acetone 52 are given in Table IV. Other corrections due to the depth of the hydrogen jet and due to the effect of dissolved acids and salts on the solvent vapor pressure were neglected because their contribution is beyond the limit of sensitivity of our measurement (0.1 millivolt).

The average values for the density of acetone 49 at 25° C. was used.
TABLE II
STANDARD ELECTRODE POTENTIALS OF THE Ag-AgCl ELECTRODE
IN SEVERAL MIXED SOLVENT SYSTEMS AT DIFFERENT TEMPERATURES

<table>
<thead>
<tr>
<th>Wt. %</th>
<th>T, °C</th>
<th>E°, Volts</th>
<th>Wt. %</th>
<th>T, °C</th>
<th>E°, Volts</th>
<th>Wt. %</th>
<th>T, °C</th>
<th>E°, Volts</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.1</td>
<td>25.0</td>
<td>0.21368</td>
<td>8.04</td>
<td>25.0</td>
<td>0.2182</td>
<td>10.0</td>
<td>25.0</td>
<td>0.2156542</td>
</tr>
<tr>
<td>18.21</td>
<td>25.0</td>
<td>0.20375</td>
<td>16.26</td>
<td>16.0</td>
<td>0.2151</td>
<td>20.0</td>
<td>25.0</td>
<td>0.2079542</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>16.26</td>
<td>20.0</td>
<td>0.2134</td>
<td>20.0</td>
<td>25.0</td>
<td>0.2075 46</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>16.26</td>
<td>25.0</td>
<td>0.2109</td>
<td>40.0</td>
<td>25.0</td>
<td>0.1879542</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>16.26</td>
<td>30.0</td>
<td>0.2089</td>
<td>40.0</td>
<td>25.0</td>
<td>0.1865 48</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>16.26</td>
<td>35.0</td>
<td>0.2058</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>16.26</td>
<td>40.0</td>
<td>0.2027</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Interpolated values.*

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TABLE III
DENSITY DATA OF TETRAHYDROFURAN, ETHANOL, ACETONE, AND WATER AT 25° C

<table>
<thead>
<tr>
<th>Tetrahydrofuran (g/ml)</th>
<th>Ethanol (g/ml)</th>
<th>Acetone (g/ml)</th>
<th>Water (g/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.885</td>
<td>0.785</td>
<td>0.786</td>
<td>0.9971</td>
</tr>
<tr>
<td>t, °C</td>
<td>Tetrahydrofuran</td>
<td>Ethanol</td>
<td>Acetone</td>
</tr>
<tr>
<td>------</td>
<td>-----------------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>16</td>
<td></td>
<td>35.4 * mm</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>44.4 mm</td>
<td>183.6 mm</td>
</tr>
<tr>
<td>25</td>
<td>176.0 mm</td>
<td>59.7 mm</td>
<td>228.0 mm</td>
</tr>
<tr>
<td>30</td>
<td></td>
<td>79.3 mm</td>
<td>282.3 mm</td>
</tr>
<tr>
<td>35</td>
<td>263.0 mm</td>
<td>103.1 mm</td>
<td>345.7 mm</td>
</tr>
<tr>
<td>40</td>
<td></td>
<td>134.6 mm</td>
<td></td>
</tr>
</tbody>
</table>

*Interpolated.*
The ionization constants for acetic acid in the various mixed solvent systems are obtained by plotting $pK_a^*$ against the $\sqrt{\mu}$, as shown in Figures 3, 4, 5, and 6.

The quantity $pK_a^*$ is calculated from the following form of equation 7:

$$ pK_a^* = \frac{(E_{obs} - E_\text{m})F}{2.303 RT} + \log \frac{m_2m_3}{m_2} \quad \ldots 67 $$

Values for $E_{obs}$, $pK_a^*$, $m_1$, $m_2$, $m_3$, and $\sqrt{\mu}$ ($\mu = m_2 + m_3$) are given in Table V for the 9.1 and 18.21 weight percent tetrahydrofuran-water system; in Table VI for the 8.14 and 16.26 weight percent ethanol-water system; and in Table VII for the 10.0 weight percent acetone-water system. Table VIII contains the values for these quantities in the 16.26 weight percent ethanol-water system at 16.0°, 20.0°, 30.0°, 35.0°, and 40.0° C.

Values for $E_{obs}$ for 20.0 and 40.0 percent acetone-water systems are calculated from the following expression:

$$ E_{obs} = E_{Iw} + 0.05916 (pK_a^* - pH_{H_2O}) \quad \ldots 68 $$

and the $pK_a^*$ values are then calculated from equation 67 above. The values of $pH$, $E_{obs}$, $pK_a^*$, $m_1$, $m_2$, $m_3$, and $\sqrt{\mu}$ are given in Table IX. The value of the ionization constants are given in Tables X and XI.

Earned and Embree\textsuperscript{53} noted that the ionization constants of a number of weak electrolytes exhibit maxima between 0° and 60° C., and suggested that this is a property of all weak electrolytes. As a first approximation, the temperature dependence of the ionization
TABLE V
VALUES OF $E_{obs}$, $pK^*_{aq}$, $m_1$, $m_2$, $m_3$, and $\sqrt{\mu}$ FOR ACETIC ACID IN TETRAHYDROFURAN-WATER MIXTURES AT 25.0°C

$X = \text{wt. \% of tetrahydrofuran}$

<table>
<thead>
<tr>
<th>$E_{obs}$</th>
<th>$pK^*_{aq}$</th>
<th>$m_1$</th>
<th>$m_2$</th>
<th>$m_3$</th>
<th>$\sqrt{\mu}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$X = 9.1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.56458</td>
<td>4.955</td>
<td>0.10500</td>
<td>0.105740</td>
<td>0.106560</td>
<td>0.4605</td>
</tr>
<tr>
<td>0.58296</td>
<td>4.962</td>
<td>0.052175</td>
<td>0.052543</td>
<td>0.052849</td>
<td>0.3247</td>
</tr>
<tr>
<td>0.60059</td>
<td>4.958</td>
<td>0.026007</td>
<td>0.026190</td>
<td>0.026343</td>
<td>0.2292</td>
</tr>
<tr>
<td>0.60612</td>
<td>4.954</td>
<td>0.020793</td>
<td>0.020959</td>
<td>0.021061</td>
<td>0.2049</td>
</tr>
<tr>
<td>0.61307</td>
<td>4.947</td>
<td>0.015585</td>
<td>0.015695</td>
<td>0.015786</td>
<td>0.1774</td>
</tr>
<tr>
<td>0.62281</td>
<td>4.935</td>
<td>0.010383</td>
<td>0.010457</td>
<td>0.010517</td>
<td>0.1448</td>
</tr>
<tr>
<td>0.64188</td>
<td>4.956</td>
<td>0.005189</td>
<td>0.005225</td>
<td>0.005255</td>
<td>0.1024</td>
</tr>
<tr>
<td>$X = 18.21$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.56745</td>
<td>5.163</td>
<td>0.104350</td>
<td>0.103720</td>
<td>0.103720</td>
<td>0.4555</td>
</tr>
<tr>
<td>0.58676</td>
<td>5.189</td>
<td>0.051880</td>
<td>0.051567</td>
<td>0.051567</td>
<td>0.3211</td>
</tr>
<tr>
<td>0.60327</td>
<td>5.166</td>
<td>0.025868</td>
<td>0.025711</td>
<td>0.025711</td>
<td>0.2268</td>
</tr>
<tr>
<td>0.60880</td>
<td>5.162</td>
<td>0.020849</td>
<td>0.020559</td>
<td>0.020559</td>
<td>0.2029</td>
</tr>
<tr>
<td>0.61569</td>
<td>5.154</td>
<td>0.015504</td>
<td>0.015410</td>
<td>0.015410</td>
<td>0.1756</td>
</tr>
<tr>
<td>0.62598</td>
<td>5.150</td>
<td>0.010330</td>
<td>0.010267</td>
<td>0.010267</td>
<td>0.1433</td>
</tr>
</tbody>
</table>
TABLE VI
VALUES OF $E_{obs}$, $pK^*_{a'}$, $m_1$, $m_2$, $m_3$, AND $\sqrt{\mu}$ FOR ACETIC ACID IN ETHANOL-WATER MIXTURES AT 25.0°C

$X$ = wt. % of ethanol

<table>
<thead>
<tr>
<th>$E_{obs}$</th>
<th>$pK^*_{a'}$</th>
<th>$m_1$</th>
<th>$m_2$</th>
<th>$m_3$</th>
<th>$\sqrt{\mu}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$X$ = 8.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.56086</td>
<td>4.841</td>
<td>0.11606</td>
<td>0.10614</td>
<td>0.10232</td>
<td>0.4566</td>
</tr>
<tr>
<td>0.57881</td>
<td>4.850</td>
<td>0.05769</td>
<td>0.05155</td>
<td>0.05085</td>
<td>0.3200</td>
</tr>
<tr>
<td>0.59796</td>
<td>4.873</td>
<td>0.02876</td>
<td>0.02570</td>
<td>0.02535</td>
<td>0.2258</td>
</tr>
<tr>
<td>0.60284</td>
<td>4.857</td>
<td>0.02299</td>
<td>0.02055</td>
<td>0.02027</td>
<td>0.2020</td>
</tr>
<tr>
<td>0.61363</td>
<td>4.849</td>
<td>0.01483</td>
<td>0.01026</td>
<td>0.01012</td>
<td>0.1498</td>
</tr>
<tr>
<td>0.63745</td>
<td>4.838</td>
<td>0.005734</td>
<td>0.005128</td>
<td>0.005058</td>
<td>0.1009</td>
</tr>
<tr>
<td>$X$ = 16.26</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.56291</td>
<td>5.022</td>
<td>0.11867</td>
<td>0.10607</td>
<td>0.10462</td>
<td>0.4590</td>
</tr>
<tr>
<td>0.56267</td>
<td>5.018</td>
<td>0.11867</td>
<td>0.10607</td>
<td>0.10462</td>
<td>0.4590</td>
</tr>
<tr>
<td>0.58088</td>
<td>5.023</td>
<td>0.058973</td>
<td>0.052711</td>
<td>0.051994</td>
<td>0.3236</td>
</tr>
<tr>
<td>0.59877</td>
<td>5.023</td>
<td>0.029397</td>
<td>0.026276</td>
<td>0.025918</td>
<td>0.2284</td>
</tr>
<tr>
<td>0.59747</td>
<td>5.001</td>
<td>0.029397</td>
<td>0.026276</td>
<td>0.025918</td>
<td>0.2284</td>
</tr>
<tr>
<td>0.60146</td>
<td>4.971</td>
<td>0.025504</td>
<td>0.021008</td>
<td>0.021008</td>
<td>0.2043</td>
</tr>
<tr>
<td>0.61064</td>
<td>5.001</td>
<td>0.017617</td>
<td>0.015746</td>
<td>0.015532</td>
<td>0.1769</td>
</tr>
<tr>
<td>0.62208</td>
<td>5.019</td>
<td>0.011738</td>
<td>0.010491</td>
<td>0.010349</td>
<td>0.1444</td>
</tr>
<tr>
<td>0.62007</td>
<td>4.985</td>
<td>0.011738</td>
<td>0.010491</td>
<td>0.010349</td>
<td>0.1444</td>
</tr>
<tr>
<td>0.63734</td>
<td>4.975</td>
<td>0.005586</td>
<td>0.005524</td>
<td>0.005517</td>
<td>0.1020</td>
</tr>
</tbody>
</table>
### TABLE VII

VALUES OF $E_{\text{obs}}$, $pK_a^*$, $m_1$, $m_2$, $m_3$, AND $\sqrt{\mu}$ FOR ACETIC ACID IN ACETONE-WATER MIXTURE AT 25.0°C

$X = \text{wt. \% of acetone} - 10.0$

<table>
<thead>
<tr>
<th>$E_{\text{obs}}$</th>
<th>$pK_a^*$</th>
<th>$m_1$</th>
<th>$m_2$</th>
<th>$m_3$</th>
<th>$\sqrt{\mu}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.56748</td>
<td>4.987</td>
<td>0.10870</td>
<td>0.11442</td>
<td>0.11438</td>
<td>0.4783</td>
</tr>
<tr>
<td>0.57510</td>
<td>4.990</td>
<td>0.081255</td>
<td>0.085530</td>
<td>0.085496</td>
<td>0.4136</td>
</tr>
<tr>
<td>0.58579</td>
<td>4.993</td>
<td>0.053988</td>
<td>0.056828</td>
<td>0.056806</td>
<td>0.3371</td>
</tr>
<tr>
<td>0.60847</td>
<td>4.977</td>
<td>0.021510</td>
<td>0.022642</td>
<td>0.022633</td>
<td>0.2128</td>
</tr>
<tr>
<td>0.62490</td>
<td>4.953</td>
<td>0.010741</td>
<td>0.011306</td>
<td>0.011301</td>
<td>0.1504</td>
</tr>
<tr>
<td>0.64133</td>
<td>4.930</td>
<td>0.005367</td>
<td>0.005649</td>
<td>0.005647</td>
<td>0.1063</td>
</tr>
</tbody>
</table>
TABLE VIII
VALUES OF $m_1$, $m_2$, $m_3$, $\sqrt{\mu}$, $E_{\text{obs}}$, and $pK_{a}$' FOR 16.26 PERCENT (WEIGHT) ETHANOL-WATER MIXTURE AT VARIOUS TEMPERATURES

<table>
<thead>
<tr>
<th>$T = 16.0^\circ$</th>
<th>$T = 20^\circ$</th>
<th>$T = 30^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sqrt{\mu}$</td>
<td>$E_{\text{obs}}$</td>
<td>$pK_{a}$'</td>
</tr>
<tr>
<td>0.4590</td>
<td>0.55719</td>
<td>5.035</td>
</tr>
<tr>
<td>0.4590</td>
<td>0.56011</td>
<td>5.033</td>
</tr>
<tr>
<td>0.3235</td>
<td>0.57750</td>
<td>5.028</td>
</tr>
<tr>
<td>0.2284</td>
<td>0.59041</td>
<td>5.003</td>
</tr>
<tr>
<td>0.2284</td>
<td>0.59562</td>
<td>5.003</td>
</tr>
<tr>
<td>0.2043</td>
<td>0.59719</td>
<td>4.968</td>
</tr>
<tr>
<td>0.1769</td>
<td>0.60321</td>
<td>5.009</td>
</tr>
<tr>
<td>0.1444</td>
<td>0.61189</td>
<td>4.984</td>
</tr>
<tr>
<td>0.1444</td>
<td>0.61570</td>
<td>4.984</td>
</tr>
<tr>
<td>0.1020</td>
<td>0.63258</td>
<td>4.972</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>$\sqrt{\mu}$</th>
<th>$E_{obs}$</th>
<th>$pK_a^*$</th>
<th>$E_{obs}$</th>
<th>$pK_a^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4590</td>
<td>0.56820</td>
<td>4.999</td>
<td>0.57111</td>
<td>5.001</td>
</tr>
<tr>
<td>0.5255</td>
<td></td>
<td></td>
<td>0.58999</td>
<td>5.002</td>
</tr>
<tr>
<td>0.2284</td>
<td>0.60450</td>
<td>4.987</td>
<td>0.60890</td>
<td>5.004</td>
</tr>
<tr>
<td>0.2043</td>
<td></td>
<td></td>
<td>0.61418</td>
<td>4.992</td>
</tr>
<tr>
<td>0.1769</td>
<td>0.61849</td>
<td>4.994</td>
<td>0.62208</td>
<td>4.995</td>
</tr>
<tr>
<td>0.1444</td>
<td>0.62853</td>
<td>4.982</td>
<td>0.63309</td>
<td>4.995</td>
</tr>
</tbody>
</table>

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TABLE IX

VALUES OF pH, $E_{\text{obs}}$, $pK_a^*$, $m_1$, $m_2$, $m_3$, and $\sqrt{\mu}$ FOR ACETIC ACID AT 25.0°C USING THE CELL:

GLASS ELECTRODE | HOAc ($m_1$), NaOAc ($m_2$), NaCl ($m_3$), ACETONE ($X$), WATER ($Y$) | AgCl-Ag

$X = \text{wt. \% of acetone}$

<table>
<thead>
<tr>
<th>pH</th>
<th>$E_{\text{obs}}$</th>
<th>$pK_a^*$</th>
<th>$m_1$</th>
<th>$m_2$</th>
<th>$m_3$</th>
<th>$\sqrt{\mu}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X = 20.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.710</td>
<td>0.5751</td>
<td>5.196</td>
<td>0.096818</td>
<td>0.10191</td>
<td>0.10187</td>
<td>0.4514</td>
</tr>
<tr>
<td>5.846</td>
<td>0.5832</td>
<td>5.206</td>
<td>0.072378</td>
<td>0.076166</td>
<td>0.076156</td>
<td>0.3903</td>
</tr>
<tr>
<td>6.010</td>
<td>0.5928</td>
<td>5.192</td>
<td>0.048035</td>
<td>0.050562</td>
<td>0.050542</td>
<td>0.3180</td>
</tr>
<tr>
<td>6.424</td>
<td>0.6173</td>
<td>5.206</td>
<td>0.019138</td>
<td>0.020145</td>
<td>0.020157</td>
<td>0.2007</td>
</tr>
<tr>
<td>6.701</td>
<td>0.6337</td>
<td>5.182</td>
<td>0.009566</td>
<td>0.010069</td>
<td>0.010065</td>
<td>0.1449</td>
</tr>
</tbody>
</table>

| X = 40.0 |
| 6.040 | 0.5946 | 5.900 | 0.097158 | 0.10227 | 0.10223 | 0.4522 |
| 6.143 | 0.6007 | 5.876 | 0.072638 | 0.076459 | 0.076429 | 0.3910 |
| 6.344 | 0.6132 | 5.909 | 0.048138 | 0.050722 | 0.050702 | 0.3185 |
| 6.730 | 0.6554 | 5.886 | 0.019194 | 0.020204 | 0.021960 | 0.2010 |
| 7.340 | 0.6715 | 5.893 | 0.004786 | 0.005038 | 0.005036 | 0.1004 |
FIGURE 3

$pK_a^* \text{ vs } \sqrt{\mu}$ FOR ACETIC ACID IN TETRAHYDROFURAN-WATER MIXTURES AT 25°C.
FIGURE 3

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FIGURE 4

$pK_a^*$ vs $\sqrt{\mu}$ FOR ACETIC ACID IN ETHANOL-WATER MIXTURES AT 25°C.
FIGURE 5

$\text{pK}_{a}^{*} \text{ vs } \sqrt{\gamma}$ FOR ACETIC ACID IN 16.26% ETHANOL-WATER AT VARIOUS TEMPERATURES
FIGURE 6

$pK_a^\infty$ vs $\sqrt{\mu}$ FOR ACETIC ACID IN ACETONE-WATER MIXTURES AT 25°C.
FIGURE 6

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TABLE X
IONIZATION CONSTANTS OF ACETIC ACID IN 9.1 AND 18.21 WEIGHT PERCENT
TETRAHYDROFURAN-WATER AND IN 10.0, 20.0, AND 40.0
WEIGHT PERCENT ACETONE-WATER AT 25.0° C

<table>
<thead>
<tr>
<th></th>
<th>Tetrahydrofuran</th>
<th>Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>9.1%</td>
<td>18.21%</td>
</tr>
<tr>
<td>$pK_a$</td>
<td>4.89</td>
<td>5.14</td>
</tr>
<tr>
<td>$K_{a1}$</td>
<td>$1.29 \times 10^{-5}$</td>
<td>$7.24 \times 10^{-6}$</td>
</tr>
</tbody>
</table>
TABLE XI

VALUES OF \( \log K_a^x \), \( t^2 \), \( pt^2 \), and \( \log K_a^x + pt^2 \) FOR ACETIC ACID IN 16.26 PERCENT (WEIGHT) ETHANOL-WATER AT VARIOUS TEMPERATURES

<table>
<thead>
<tr>
<th>( \log K_a^x )</th>
<th>( t^0 \text{C} )</th>
<th>( t^2 )</th>
<th>( pt^2 )</th>
<th>( \log K_a^x + pt^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>-4.906</td>
<td>16.0</td>
<td>256</td>
<td>0.0128</td>
<td>-4.893</td>
</tr>
<tr>
<td>-4.904</td>
<td>20.0</td>
<td>400</td>
<td>0.0200</td>
<td>-4.884</td>
</tr>
<tr>
<td>-4.904</td>
<td>25.0</td>
<td>625</td>
<td>0.03125</td>
<td>-4.873</td>
</tr>
<tr>
<td>-4.908</td>
<td>30.0</td>
<td>900</td>
<td>0.0450</td>
<td>-4.863</td>
</tr>
<tr>
<td>-4.914</td>
<td>35.0</td>
<td>1225</td>
<td>0.06125</td>
<td>-4.853</td>
</tr>
<tr>
<td>-4.920</td>
<td>40.0</td>
<td>1600</td>
<td>0.0800</td>
<td>-4.840</td>
</tr>
</tbody>
</table>
The equation is applicable in the vicinity of the temperature \( \theta \) at which the ionization constant has its maximum value \( K_\theta \). The term \( p \) is a universal constant for all weak electrolytes, and has the value of \( 5 \times 10^{-5} \) deg.\(^{-2} \). Thus if \( \log K + pt^2 \) is plotted against \( t \), a straight line should result whose slope is \( 2p\theta \) and whose intercept at \( t \) equals \( 0^\circ \) is \( \log K_\theta - p\theta^2 \).

Table XI contains the values of \( \log K^* \), \( t^2 \), \( pt^2 \), and \( \log K_a^* + pt^2 \) for acetic acid in 16.26 weight percent ethanol-water at various temperatures. Figure 7 shows the straight line that results from the plot of \( \log K_a^* + pt^2 \) versus \( t \). The temperature \( \theta \) at which \( K_a^* \) is a maximum was found to be \( 21.8^\circ \) C., and the value of the ionization constant at this temperature \( K_\theta \) was \( 1.235 \times 10^{-5} \).

Harned and Embree obtained values of \( \theta = 22.6^\circ \) C. and \( K_\theta = 1.760 \times 10^{-5} \) for acetic acid in pure aqueous solution.

Table XII contains the observed values of \( K_a^* \) for acetic acid at \( 16^\circ, 20^\circ, 25^\circ, 30^\circ, 35^\circ, \) and \( 40^\circ \) C. and the values calculated from equation 69. The maximum deviation is \( 0.3\% \) at \( 35^\circ \) C.

By using the equation
\[
\log K - \log K_\theta = p(t-\theta)^2
\]
and since
\[
\frac{\partial \ln K}{\partial T} = \frac{\Delta H}{RT^2} = 2.3 \frac{\Delta E(t-\theta)}{\Delta T}
\]
FIGURE 7

$\log K^* + pt^2$ vs TEMPERATURE FOR ACETIC ACID

IN 16.26% ETHANOL-WATER

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\[ \log K_a + \text{Pl}^2 \]

vs

\[ t \, ^\circ C \]

**Figure 7**

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TABLE XII

IONIZATION CONSTANTS OF ACETIC ACID IN 16.26 PERCENT (WEIGHT) ETHANOL-WATER AT VARIOUS TEMPERATURES

Density 20% (volume) ethanol in water = 0.97608

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>16.0</th>
<th>20.0</th>
<th>25.0</th>
<th>30.0</th>
<th>35.0</th>
<th>40.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$pK_a^*$</td>
<td>4.906</td>
<td>4.904</td>
<td>4.904</td>
<td>4.908</td>
<td>4.914</td>
<td>4.920</td>
</tr>
<tr>
<td>$K_a^*$ (m scale) (obs)</td>
<td>1.242</td>
<td>1.248</td>
<td>1.247</td>
<td>1.256</td>
<td>1.219</td>
<td>1.202</td>
</tr>
<tr>
<td>$K_a^*$ (m scale) (calc)</td>
<td>1.241</td>
<td>1.248</td>
<td>1.247</td>
<td>1.239</td>
<td>1.223</td>
<td>1.201</td>
</tr>
<tr>
<td>$K_a^*$ (c scale) (obs)</td>
<td>1.212</td>
<td>1.218</td>
<td>1.218</td>
<td>1.207</td>
<td>1.190</td>
<td>1.174</td>
</tr>
</tbody>
</table>

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Harned and Embree found that

$$\Delta H = -2.3 \times 10^{-4} RT^2(t-\theta)$$

Values of $\Delta H$ were calculated and are listed in Table XIII, along with the $\Delta H$ values given by Harned and Embree for acetic acid in aqueous solution.

Equation 12,

$$K_a = K_a^{*} f_Q Y(\varepsilon)$$

shows that the function necessary to correlate $K_a$ and $K_a^{*}$ is dependent on the dielectric constant of the solvent. Table XIV contains the bulk dielectric constants of the pure organic solvents used in preparing the mixed organic-water systems studied.

In Table XV are the values of $pK_a^{*}$, $pK_a$, and the functions of bulk dielectric constants used in finding the appropriate relationship between $pK_a^{*}$ and $pK_a$. The $pK_a^{*}$ values for the following acids were studied:

(1) Formic acid - fifteen values in three mixed solvent systems over a dielectric constant range of 10 to 74;

(2) Acetic acid - sixty-nine values in ten mixed solvent systems over a dielectric constant range of 10 to 78;

(3) Propanoic acid - twenty values in five mixed solvent systems over a dielectric constant range of 10 to 75;

(4) Butanoic acid - twelve values in three mixed solvent systems over a dielectric constant range of 24 to 71;
TABLE XIII

ENTHALPY OF IONIZATION FOR ACETIC ACID

IN 16.26 PERCENT (WEIGHT) ETHANOL-WATER AT VARIOUS TEMPERATURES

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>10</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔH (Cal)</td>
<td>435</td>
<td>71</td>
<td>-130</td>
<td>-345</td>
<td>-816</td>
</tr>
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(a) For aqueous solutions.²²
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(a) Extrapolated value.$^{48c}$
TABLE XV
VALUES OF pK\textsubscript{a} FOR VARIOUS ACIDS IN SEVERAL MIXED SOLVENT SYSTEMS
AND SOME DIELECTRIC CONSTANT FUNCTIONS FOR THOSE SYSTEMS

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(a) Determined by the author
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TABLE XV (Continued)

Methanol-Water

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<th>$(\frac{1}{e^2} - \frac{1}{e}) \times 10^3$</th>
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<th>$\text{Acetic}^{27}$</th>
<th>$\text{Propanoic}$</th>
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TABLE XV (Continued)

Dioxane-Water

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<th>$\frac{1}{e^{*x+n}} - \frac{1}{e^2}$</th>
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TABLE XV (Continued)

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(a) Determined by the author.
### TABLE XV (Continued)

#### Acetone-Water

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<th>(\frac{1}{\varepsilon - \frac{1}{\varepsilon}} \times 10^3)</th>
<th>(\frac{1}{\varepsilon - \frac{1}{\varepsilon}} \times 10^3)</th>
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#### 2-Propanol-Water

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<th>(\text{pk}^*_{A})</th>
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TABLE XV (Continued)

Dimethyl sulfoxide-Water

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<td>68.90$^{s3}$</td>
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<td>0.527</td>
<td>5.07</td>
<td>4.60</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>63.93$^{s3}$</td>
<td>2.910</td>
<td>0.834</td>
<td>5.27</td>
<td>4.86</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>58.49$^{s3}$</td>
<td>4.365</td>
<td>1.19h</td>
<td>5.19</td>
<td>5.16</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>52.81$^{s3}$</td>
<td>6.204</td>
<td>1.613</td>
<td>5.81</td>
<td>5.52</td>
<td></td>
</tr>
</tbody>
</table>

1,2-Dimethoxyethane-Water

<table>
<thead>
<tr>
<th>Volume %</th>
<th>$e^*$</th>
<th>$(\frac{1}{e^*} - \frac{1}{e}) \times 10^3$</th>
<th>$pK_{a}^{X_{22}}$</th>
<th>Acetic</th>
<th>Benzoic</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>78.54</td>
<td>0</td>
<td>4.76</td>
<td>4.20</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>66.87$^{s3}$</td>
<td>2.223</td>
<td>5.13</td>
<td>4.71</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>60.90$^{s3}$</td>
<td>3.678</td>
<td>5.37</td>
<td>5.04</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>54.47$^{s3}$</td>
<td>5.627</td>
<td>5.65</td>
<td>5.41</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>47.38$^{s3}$</td>
<td>8.374</td>
<td>6.05</td>
<td>5.88</td>
<td></td>
</tr>
</tbody>
</table>
### TABLE XV (Continued)

2-Ethoxyethanol-Water

<table>
<thead>
<tr>
<th>Volume %</th>
<th>$e^x$</th>
<th>$(\frac{1}{e^x} - \frac{1}{e}) \times 10^6$</th>
<th>$\text{pK}^a$ Acetic</th>
<th>$\text{pK}^a$ Benzoic</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>78.54</td>
<td>0</td>
<td>4.76</td>
<td>4.20</td>
</tr>
<tr>
<td>20</td>
<td>68.37</td>
<td>1.884</td>
<td>4.93</td>
<td>4.49</td>
</tr>
<tr>
<td>30</td>
<td>62.69</td>
<td>3.220</td>
<td>5.09</td>
<td>4.78</td>
</tr>
<tr>
<td>40</td>
<td>56.63</td>
<td>4.926</td>
<td>5.29</td>
<td>5.07</td>
</tr>
<tr>
<td>50</td>
<td>49.83</td>
<td>7.336</td>
<td>5.42</td>
<td>5.34</td>
</tr>
</tbody>
</table>
TABLE XV (Continued)

Tetrahydrofuran-Water

<table>
<thead>
<tr>
<th>Volume %</th>
<th>$e^x$</th>
<th>$(\frac{1}{e^x} - \frac{1}{e}) \times 10^3$</th>
<th>$pK^a_{\text{Acetic}}$</th>
<th>$pK^a_{\text{Benzoic}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>78.54</td>
<td>0</td>
<td>4.76</td>
<td>4.20</td>
</tr>
<tr>
<td>10</td>
<td>73.4034</td>
<td>0.892</td>
<td>4.89b</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>65.7034</td>
<td>2.182</td>
<td>5.1434</td>
<td>4.87</td>
</tr>
<tr>
<td>30</td>
<td>58.8334</td>
<td>4.268</td>
<td>5.1434</td>
<td>5.33</td>
</tr>
<tr>
<td>40</td>
<td>59.8234</td>
<td>6.928</td>
<td>5.7034</td>
<td>5.78</td>
</tr>
<tr>
<td>50</td>
<td>42.5834</td>
<td>10.734</td>
<td>6.0834</td>
<td>6.23</td>
</tr>
</tbody>
</table>

Glycerol-Water

<table>
<thead>
<tr>
<th>Weight %</th>
<th>$e^x$</th>
<th>$(\frac{1}{e^x} - \frac{1}{e}) \times 10^3$</th>
<th>$(\frac{1}{e^{x7}} - \frac{1}{e^{7}}) \times 10^3$</th>
<th>$(\frac{1}{e^{x77}} - \frac{1}{e^{77}}) \times 10^3$</th>
<th>$pK^a_{\text{Acetic}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>78.54</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4.76</td>
</tr>
<tr>
<td>50</td>
<td>64.0</td>
<td>2.89</td>
<td>3.74</td>
<td>1.202</td>
<td>5.27</td>
</tr>
</tbody>
</table>

(a) Extrapolated Value  (b) Determined by the author
(5) Benzoic acid - forty values in eight mixed solvent systems over a dielectric constant range of 10 to 74;

(6) Isovaleric, cyanoacetic, glycolic, lactic, chloroacetic, malonic, succinic, glutaric, and salicylic acids - five values each in the ethanol-water system over a dielectric constant range of 33 to 67.

Some of the values of $pK_a^*$ for acetic acid in different systems were obtained by plotting $pK_a^*$ against $\sqrt{\mu}$. These included original values and checks on values in the literature. The values of $pK_a^*$ for other acids in different solvent systems were obtained from the literature.

The primary goal of this study was to obtain a function correlating $K_a^*$ (the value of the ionization constant in a mixed solvent system at infinite dilution) to $K_a$ (the value of the ionization constant in aqueous solution at infinite dilution). To achieve this goal, plots were made of $pK_a^*$ against various functions of the bulk dielectric constant. As mentioned previously, the criteria for an acceptable plot are:

(1) it should be continuous;
(2) it should have no maximum nor minimum;
(3) it should contain values from as many mixed solvent systems as possible;
(4) it should preferably be linear;
(5) it should be capable of being interpreted in terms of the physical process of ionization, if it is assumed that the interactions are coulombic in nature.

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Though a preliminary literature investigation showed the Born equation to contain the most likely function, numerous functions of the dielectric constants were plotted against $pK_a^*$ (or some function of $pK_a^*$). Some of these plots were: $K_a/K_a^*$ versus $\varepsilon^*$; $pK_a^*$ versus $\varepsilon^*$; $\Delta pK_a^*$ versus $\varepsilon^*$; $\Delta pK_a^*$ versus $\varepsilon^* \varepsilon$; $K_a/K_a^*$ versus $\log \varepsilon^*$; $\Delta pK_a^*$ versus $\log \varepsilon^*$; $\Delta pK_a^*$ versus $\sqrt{\varepsilon^*}$; and $K_a/K_a^*$ versus $\log \varepsilon/\varepsilon^*$. The plot which gave promise of fulfilling most of the criteria proposed for an acceptable curve was that of $pK_a^*$ against $(1/E^* - 1/\varepsilon)$ - the plot for the expression derived from the Born equation. In Figure 8a, one sees that the curves for ethanol-water, methanol-water, dioxane-water, and acetone-water systems are linear in regions of high dielectric constant ($\varepsilon > 40$). The curve is for acetic acid, but similar plots were obtained for formic, propanoic, and benzoic acids.

It can be seen from Figure 8a that in order for all the data to fit a single curve, a suitable term must be added to the primary variable. The close similarity of the ethanol-water and the methanol-water curves suggested that these two curves could be made to coincide by adding the term $(\varepsilon_{\text{MeOH}} - \varepsilon_{\text{organic}})$ to both $\varepsilon^*$ and $\varepsilon$. The addition of this term gives the following expressions:

$$\varepsilon^* = \varepsilon^* + (\varepsilon_{\text{MeOH}} - \varepsilon_{\text{organic}})$$  \hspace{1cm} \text{....72}

and

$$\varepsilon' = \varepsilon + (\varepsilon_{\text{MeOH}} - \varepsilon_{\text{organic}})$$  \hspace{1cm} \text{....73}

$\varepsilon$ = dielectric constant of pure water.
FIGURE 8

IONIZATION CONSTANTS OF ACETIC ACID VS.

DIELECTRIC CONSTANT FUNCTIONS IN VARIOUS MIXED SOLVENTS AT 25° C.

○ ETHANOL-H₂O
△ METHANOL-H₂O
□ DIOXANE-H₂O
○ ACETONE-H₂O
Data for $pK^*_a$ and $(1/e^* - 1/e')$ are found in Table XV for formic, acetic, propanoic, butanoic, and benzoic acids in ethanol-water, dioxane-water, and acetone-water systems. Figure 8b is a plot of this data for acetic acid. Similar plots were obtained for the other acids. The acetone and dioxane curves coincided but were somewhat displaced from the methanol-ethanol composite curve. The shapes of both these composite curves were the same, however. This indicated that, by using some other appropriate term, all the curves might be brought together. This term was found to be $(\varepsilon_{\text{water}} - \varepsilon_{\text{organic}})$.

When this factor was added to both $\varepsilon^*$ and $\varepsilon$, the following expressions were obtained:

$$
\varepsilon'' = \varepsilon^* + (\varepsilon - \varepsilon_{\text{organic}})
$$

and

$$
\varepsilon'' = \varepsilon + (\varepsilon - \varepsilon_{\text{organic}}) = (2\varepsilon - \varepsilon_{\text{organic}})
$$

Plots of $pK^*_a$ against $(1/e'' - 1/e)$ indicate that this is the function sought. See Figures 9, 10, and 11.

The equation that fits these curves has the general form

$$
pK^*_a = pK_a + b \left( \frac{1}{e''} - \frac{1}{e'} \right) + 10^{c+d} \left( \frac{1}{e''} - \frac{1}{e} \right)
$$

The first two terms of the right member of this equation represent the linear portion of the curve, where the interactions are primarily coulombic. A similar expression can be written for the linear portion of the curves like that for acetic acid in Figure 8a.

$$
pK^*_a = pK_a + \beta \left( \frac{1}{e''} - \frac{1}{e} \right)
$$
FIGURE 9
IONIZATION CONSTANTS OF ACETIC AND BENZOIC ACIDS VS.
DIELECTRIC CONSTANT FUNCTION IN VARIOUS MIXED SOLVENT SYSTEMS AT 25° C.

○ ETHANOL-H$_2$O
△ METHANOL-H$_2$O
□ DIOXANE-H$_2$O
◆ ACETONE-H$_2$O
▼ GLYCOL-H$_2$O
▼ 2-METHOXYETHANOL-H$_2$O
◆ DIMETHYL SULFOXIDE-H$_2$O
FIGURE 10

IONIZATION CONSTANT OF FORMIC ACID AND PROPAANOIC ACID VS.
DIELECTRIC CONSTANT FUNCTION IN VARIOUS MIXED SOLVENTS AT 25°C.

○ ETHANOL-H₂O
△ METHANOL-H₂O
□ DIOXANE-H₂O
▽ 2-PROPAANOI-H₂O
○ ACETONE-H₂O

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FIGURE 11

IONIZATION CONSTANTS OF BUTANOIC ACID VS.
DIELECTRIC CONSTANT FUNCTION IN VARIOUS MIXED SOLVENTS AT 25° C.

○ ETHANOL-H₂O
△ METHANOL-H₂O
▽ 2-PROPAHOL-H₂O

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Equation 77 is identical with Born's equation\(^1\) (equation 47) relating the ionization constant of an acid in two different media:

\[
pK_a^* - pK_a = \frac{Ne^2}{4.606RT} \left( \frac{1}{e^*} - \frac{1}{e} \right) \left( \frac{1}{r_1} + \frac{1}{r_2} \right)
\]

Born's equation may be derived from Born's thermodynamic cycle assuming an electrostatic model. It is quite obvious that equation 76 is a modification of Born's equation with an additional term to account for the noncoulombic interactions. In the limiting case, when \((1/e^* - 1/e) = 0\) -- i.e., in pure water -- the exponential term becomes vanishingly small, making \(pK_a^* = pK_a\).

Figures 12 to 15 are plots of the linear portions of the equations 76 and 77 for all the acids and all the mixed solvent systems studied.

The constants \(b, c, d, \) and \(\beta\) for equations 76 and 77 have been evaluated using the IBM 360 computer and a curve-fitting program developed at the Louisiana State University Computer Research Center. The curve-fitting program is based on a damped Taylor's series method for minimizing a sum of squares. Values of these constants are given in Tables XVI and XVII, along with the values of goodness of fit and sum of the squares.

Table XVIII contains the values of \(b\) one obtains by considering only the linear portion of equation 76.

\[
pK_a^* = pK_a + b \left( \frac{1}{e^*} - \frac{1}{e} \right) + 10^{c+d} \left( \frac{1}{e^{*n}} - \frac{1}{e^n} \right)
\]
FIGURE 12

IONIZATION CONSTANTS OF SOME ACIDS VS. DIELECTRIC CONSTANT FUNCTION IN VARIOUS MIXED SOLVENTS AT 25°C. (LINEAR PORTION)

\[
\begin{align*}
\text{\textbullet} & \quad 2\text{-METHOXYETHANOL-H}_2\text{O} \\
\text{\textcircled{}} & \quad \text{ETHANOL-H}_2\text{O} \\
\text{\triangle} & \quad \text{METHANOL-H}_2\text{O} \\
\text{\square} & \quad \text{DIOXANE-H}_2\text{O} \\
\text{\textcircled{}} & \quad \text{ACETONE-H}_2\text{O} \\
\text{\textcircled{}} & \quad 2\text{-PROPANOL-H}_2\text{O} \\
\text{\textcircled{}} & \quad \text{GLYCEROL-H}_2\text{O} \\
\text{\textcircled{}} & \quad 2\text{-ETHOXYETHANOL-H}_2\text{O} \\
\text{\textcircled{}} & \quad 1,2\text{-DIMETHOXYETHANE-H}_2\text{O} \\
\text{\textcircled{}} & \quad \text{TETRAHYDROFURAN-H}_2\text{O}
\end{align*}
\]
Figure 12

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FIGURE 13

IONIZATION CONSTANTS OF VARIOUS ACIDS VS. DIELECTRIC CONSTANT FUNCTION IN ETHANOL-H$_2$O AT 25° C.

- ○ MALONIC ACID
- △ LACTIC ACID
- □ SUCCINIC ACID
- ○ CYANOACETIC ACID
- △ SALICYLIC ACID
- □ GLUTARIC ACID
- ○ CHLOROACETIC ACID
- △ GLYCOLIC ACID
- □ ISOVALERIC ACID
Figure 15

\[
\left( \frac{1}{\varepsilon^*} - \frac{1}{\varepsilon} \right) \times 10^3
\]

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FIGURE 14

IONIZATION CONSTANTS OF SOME ACIDS VS. A DIELECTRIC CONSTANT
FUNCTION IN VARIOUS MIXED SOLVENT SYSTEMS AT 25°C. (LINEAR PORTION)

○ ETHANOL-H₂O
△ METHANOL-H₂O
□ DIOXANE-H₂O
□ ACETONE-H₂O
\(\checkmark\) 2-PROPA NOL-H₂O
\(\checkmark\) GLYCEROL-H₂O
\(\checkmark\) 2-METH OXYETHANOL-H₂O

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FIGURE 14

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FIGURE 15

IONIZATION CONSTANTS OF VARIOUS ACIDS VS. DIELECTRIC CONSTANT FUNCTION IN ETHANOL-H₂O AT 25°C.

- ○ MALONIC ACID
- △ LACTIC ACID
- □ SUCCINIC ACID
- ○ CYANOACETIC ACID
- △ SALICYLIC ACID
- □ GLUTARIC ACID
- ○ CHLOROACETIC ACID
- △ GLYCOLIC ACID
- □ ISOVALERIC ACID
Figure 15

\[
\left( \frac{1}{\varepsilon''} - \frac{1}{\varepsilon'''} \right)
\]

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TABLE XVI

VALUES OF $pK_a^{\text{obs}}$, $pK_a$, b, c, d, GOODNESS OF FIT, AND
SUM OF THE SQUARES FOR THE EQUATION:

$$pK_a^* = pK_a + b\left(\frac{1}{e^{x_a}} - \frac{1}{e^y}\right) + 10^c+d\left(\frac{1}{e^{y_a}} - \frac{1}{e^y}\right)$$

<table>
<thead>
<tr>
<th>Acid</th>
<th>$pK_a^{\text{obs}}$</th>
<th>$pK_a$</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>Goodness of Fit</th>
<th>Sum of Squares</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formic</td>
<td>3.75</td>
<td>3.75</td>
<td>321</td>
<td>-1.80</td>
<td>463</td>
<td>0.9967</td>
<td>0.20</td>
</tr>
<tr>
<td>Acetic</td>
<td>4.76</td>
<td>4.76</td>
<td>530</td>
<td>-1.70</td>
<td>423</td>
<td>0.9959</td>
<td>0.23</td>
</tr>
<tr>
<td>Propanoic</td>
<td>4.87</td>
<td>4.88</td>
<td>508</td>
<td>-2.00</td>
<td>484</td>
<td>0.9972</td>
<td>0.16</td>
</tr>
<tr>
<td>Butanoic a</td>
<td>4.82</td>
<td>4.85</td>
<td>482</td>
<td>-2.08</td>
<td>500</td>
<td>0.9992</td>
<td>0.05</td>
</tr>
<tr>
<td>Benzoic</td>
<td>4.20</td>
<td>4.27</td>
<td>631</td>
<td>-2.80</td>
<td>620</td>
<td>0.9996</td>
<td>0.26</td>
</tr>
</tbody>
</table>

(a) Extrapolated curve was used.
TABLE XVII
VALUES OF $pK_a^{(obs)}$, $pK_a$, $\beta$, GOODNESS OF FIT, AND SUM OF SQUARES FOR THE EQUATION:

$$pK_a^* = pK_a + \beta \left( \frac{1}{e^{pK_a^*}} - \frac{1}{e} \right)$$

<table>
<thead>
<tr>
<th>Acid</th>
<th>$pK_a^{(obs)}$</th>
<th>$pK_a$</th>
<th>$\beta$</th>
<th>Goodness of Fit</th>
<th>Sum of Squares</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formic</td>
<td>3.75</td>
<td>3.78</td>
<td>110</td>
<td>0.9809</td>
<td>0.06</td>
</tr>
<tr>
<td>Acetic</td>
<td>4.76</td>
<td>4.87</td>
<td>125</td>
<td>0.9024</td>
<td>0.56</td>
</tr>
<tr>
<td>Propanoic</td>
<td>4.87</td>
<td>4.98</td>
<td>128</td>
<td>0.9471</td>
<td>0.14</td>
</tr>
<tr>
<td>Butanoic</td>
<td>4.82</td>
<td>5.00</td>
<td>140</td>
<td>0.9592</td>
<td>0.29</td>
</tr>
<tr>
<td>Benzoic</td>
<td>4.20</td>
<td>4.45</td>
<td>152</td>
<td>0.8925</td>
<td>0.14</td>
</tr>
<tr>
<td>Isovaleric</td>
<td>4.78</td>
<td>4.98</td>
<td>141</td>
<td>0.9750</td>
<td>0.11</td>
</tr>
<tr>
<td>Glycolic</td>
<td>3.83</td>
<td>3.96</td>
<td>106</td>
<td>0.9849</td>
<td>0.04</td>
</tr>
<tr>
<td>Lactic</td>
<td>3.86</td>
<td>3.86</td>
<td>122</td>
<td>0.9709</td>
<td>0.07</td>
</tr>
<tr>
<td>Cyanoacetic</td>
<td>2.47</td>
<td>2.47</td>
<td>113</td>
<td>0.9900</td>
<td>0.02</td>
</tr>
<tr>
<td>Salicylic</td>
<td>3.00</td>
<td>3.04</td>
<td>115</td>
<td>0.9951</td>
<td>0.02</td>
</tr>
<tr>
<td>Malonic</td>
<td>2.75</td>
<td>2.90</td>
<td>88</td>
<td>0.9762</td>
<td>0.04</td>
</tr>
<tr>
<td>Glutaric</td>
<td>4.34</td>
<td>4.40</td>
<td>114</td>
<td>0.9596</td>
<td>0.12</td>
</tr>
<tr>
<td>Succinic</td>
<td>4.13</td>
<td>4.28</td>
<td>111</td>
<td>0.9832</td>
<td>0.05</td>
</tr>
<tr>
<td>Chloroacetic</td>
<td>2.86</td>
<td>2.98</td>
<td>116</td>
<td>0.9893</td>
<td>0.03</td>
</tr>
</tbody>
</table>

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TABLE XVIII
VALUES OF $pK_{a(\text{obs})}$, $pK_a$, $b'$, GOODNESS OF FIT, AND
SUM OF SQUARES FOR EQUATION:

$$pK^*_a = pK_a + b'(\frac{1}{e^x} - \frac{1}{e^y})$$

<table>
<thead>
<tr>
<th>Acid</th>
<th>$pK_{a(\text{obs})}$</th>
<th>$pK_a$</th>
<th>$b'$</th>
<th>Goodness of Fit</th>
<th>Sum of Squares</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formic</td>
<td>3.75</td>
<td>3.70</td>
<td>4.77</td>
<td>0.9080</td>
<td>0.38</td>
</tr>
<tr>
<td>Acetic</td>
<td>4.76</td>
<td>4.76</td>
<td>5.50</td>
<td>0.9071</td>
<td>0.99</td>
</tr>
<tr>
<td>Propanoic</td>
<td>4.87</td>
<td>4.83</td>
<td>4.76</td>
<td>0.9614</td>
<td>0.10</td>
</tr>
<tr>
<td>Butanoic</td>
<td>4.82</td>
<td>4.82</td>
<td>4.82</td>
<td>0.8874</td>
<td>0.81</td>
</tr>
<tr>
<td>Benzoic</td>
<td>4.20</td>
<td>4.38</td>
<td>6.27</td>
<td>0.9033</td>
<td>0.97</td>
</tr>
<tr>
<td>Malonic</td>
<td>2.75</td>
<td>2.75</td>
<td>4.20</td>
<td>0.9361</td>
<td>0.02</td>
</tr>
<tr>
<td>Cyanacetic</td>
<td>2.47</td>
<td>2.42</td>
<td>4.71</td>
<td>0.9870</td>
<td>0.03</td>
</tr>
<tr>
<td>Lactic</td>
<td>3.86</td>
<td>3.80</td>
<td>4.80</td>
<td>0.9911</td>
<td>0.02</td>
</tr>
<tr>
<td>Glycolic</td>
<td>3.83</td>
<td>3.85</td>
<td>4.80</td>
<td>0.9954</td>
<td>0.01</td>
</tr>
<tr>
<td>Succinic</td>
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<td>4.13</td>
<td>5.00</td>
<td>0.9945</td>
<td>0.01</td>
</tr>
<tr>
<td>Salicylic</td>
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<td>2.91</td>
<td>5.14</td>
<td>0.9889</td>
<td>0.03</td>
</tr>
<tr>
<td>Chloroacetic</td>
<td>2.86</td>
<td>2.86</td>
<td>5.30</td>
<td>0.9916</td>
<td>0.02</td>
</tr>
<tr>
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<td>4.26</td>
<td>5.52</td>
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<td>6.40</td>
<td>0.9954</td>
<td>0.01</td>
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CHAPTER 5
DISCUSSION AND CONCLUSIONS

Experimental Values of the Ionization Constant of Acetic Acid

The values of the ionization constant of acetic acid in mixed solvent systems determined by the author agree, for the most part, very well with those determined by other investigators. The pK\textsubscript{a} values in 8.0\% and 16.26 weight percent ethanol-water mixtures are in line with those given by Grunwald and Berkowitz\textsuperscript{28} for higher ethanol concentrations. The pK\textsubscript{a} values in 10 and 20 percent by volume of tetrahydrofuran-water and in 10 percent by weight acetone-water are also in agreement with those reported by Reynaud\textsuperscript{37} and by Dippy, Hughes and Rozanski\textsuperscript{32} respectively. The pK\textsubscript{a} values reported by Morel\textsuperscript{31} for acetone-water systems were somewhat higher compared with those determined by the author and others.\textsuperscript{32} E\textsuperscript{0} values reported by Feakins and French,\textsuperscript{42} which are different from those reported by Morel in acetone-water systems, were used in our calculations. This explains the disagreement of the pK\textsubscript{a} values reported by the author and those reported by Morel.

Plots of pK\textsubscript{a} Against (1/e\textsuperscript{*} - 1/e) and (1/e\textsuperscript{*} - 1/e)

The pK\textsubscript{a} values corresponding to 10 and 20 percent by weight determined by the author, the values corresponding to 10 and 25 percent reported by Dippey et. al.,\textsuperscript{32} and those for 20, 30, 40, and 50 percent reported by Reynaud\textsuperscript{33} fit the curve well. The pK\textsubscript{a} values reported by Morel lie consistently above the curve. The reason for this discrepancy has been explained in the previous paragraph.
The values for $pK^*_a$ for the dimethyl sulfoxide-water system determined by Morel do not fit the curve at all. The dielectric constant data of Lindberg and Kenttämaa also show the unusual behavior of this system. A change from 0 to 50 weight percent organic solvent produces a change of approximately 2 in the system's dielectric constant for methanol, 29.6 for ethanol, and 30 for acetone. A change of only 2.1 is observed for dimethyl sulfoxide. This suggests the possibility of some strong interaction between the dimethyl sulfoxide and water. Thus, even in solutions of high water content the reaction may not be between the weak acid and water to produce hydronium ions and the carboxylate anion, but rather a reaction of the acid and some dimethyl sulfoxide-water specie. This may greatly reduce the ionization of the acid.

The $pK^*_a$ values for benzoic acid plotted against $(1/e^* - 1/e^s)$ for five different solvent systems are given in Figure 9. All the points fall on a smooth continuous curve. The same result (Figure 10) is found for formic acid (3 systems) and propanoic acid (5 systems). For butanoic acid (3 systems) there are not enough points to definitely establish the complete curvature of the plot, but the beginnings of this curvature can be seen (Figure 11).

Plots of $pK^*_a$ values against $(1/e^* - 1/e^s)$ for the nine other acids (Figure 15) are all linear since there are no values in the region where curvature would occur. The linear segment of the plots for formic, acetic, propanoic, butanoic, and benzoic acids are reproduced in Figure 14. Again, all the points except those determined by Morel fit the curves.
Figure 12 shows graphs of $pK^*_a$ plotted against $(1/e^*_a - 1/e)$ for the linear portion of the weak acid curves. These plots demonstrate that when the water content of the system is high (mole fraction of water usually greater than 0.5), the ionization of the weak acid is independent of the nature of the organic solvent component of the mixed system. Data for ten different mixed solvent systems are given in these plots.

It is in this linear portion that the coulombic interactions are of much greater importance than the non-coulombic interactions. Therefore, it is in this region that theoretical treatments based on an electrostatic approach are most applicable.

In an earlier section we have seen that the equation

$$pK^*_a = pK_a + b\left(\frac{1}{e^*_a} - \frac{1}{e^*_w}\right) + 10^{c+d\left(\frac{1}{e^*_w} - \frac{1}{e^*_w}\right)} \quad \ldots 76$$

describes the plots in Figure 14 covering the entire range of dielectric constant from that of pure water to that of pure organic component. The linear segment of these plots is represented by the equation

$$pK^*_a = pK_a + b'\left(\frac{1}{e^*_w} - \frac{1}{e^*_w}\right) \quad \ldots 78$$

The discrepancy between the computed values of $b$ and $b'$ is due to the fact that in the former case the linear part of the equation is somewhat weighted by the exponential part, and the program does not attach any special importance to the linear portion of the plot in evaluating the constant $b$. In computing $b''s$, only points from graphically selected linear segments of the plots were used.
The linear plots $pK_a^*$ versus $(1/e^* - 1/e)$ given in Figure 12 are represented by the equation

$$pK_a^* = pK_a + \beta \left( \frac{1}{e^*} - \frac{1}{e} \right)$$

In the following section are presented two different theoretical approaches for correlating $pK_a^*$ and $pK_a$. Both the treatments yield a final function similar to that obtained by us using a curve-fitting technique. Most importantly, a primary variable, which is some linear combination of only the reciprocals of the bulk dielectric constants of the solvents, yields the analytical function which satisfies the experimental plots. In our subsequent discussion we do not pretend to explain any microscopic phenomenon involved in the ionization process, nor is it relevant to the purpose of the present investigation.

**Condenser Model for Effect of the Medium on Ions**

The following discussion is based on Wiberg's work. Consider a condenser with plates of area ($A$) separated by a distance ($d$). The capacitance ($C$) of the condenser is given by the ratio of the charge on the plates ($q$) to the potential ($V$) required to produce that charge. For the case where the area of the plates is large compared to the distance between them, the capacitance of the condenser is

$$C = \frac{q}{V} = \frac{A}{4\pi d}$$

The field strength ($X$) between these plates is given by

$$X = \frac{V}{d}$$
The electrical work required to charge the condenser to the potential \( V \) is

\[ W = \frac{1}{2} q V \] ....81

In terms of the capacitance and the field strength, this work is given by

\[ W = \frac{1}{2} CV^2 = \frac{1}{2} (Xd)^2 \frac{A}{4\pi d} = \frac{X^2}{8\pi} Ad \] ....82

Since \( Ad \) is the volume of the condenser, the work per unit volume is given by \( (X^2/8\pi) \). This work is equal to the change in free energy:

\[ W = \Delta G = \int_{X^2/8\pi}^{X_0^2} dV \] ....83

If a dielectric material is inserted between the plates of the condenser, the dielectric material is attracted into the space between the plates and work is done on the material. This results in a decrease in the free energy of the condenser. The dielectric constant of the material between the condenser plates is the ratio of the potential on the plates in a vacuum to the potential on the plates when the dielectric material is between the plates, provided that the charge on the plates is constant.

\[ e = \frac{V_0}{V} \] ....84

From equation 79

\[ CV = q = C_0 V_0 \] ....85
and by combination with equation 84.

\[ C = C_0 \varepsilon \]  

\[ \Delta G = W = \frac{1}{2} CV^2 \]  

From equations 82 and 83

\[ \Delta G = \frac{1}{2} C_0 \varepsilon (\frac{V_0}{\varepsilon})^2 = \frac{1}{2} C_0 V_0^2 \varepsilon \]  

Substitution from equations 84 and 86 gives

The free energy required to charge the condenser in the presence of the dielectric is \( 1/\varepsilon \) times as great as it would be when there is a vacuum between the plates.

\[ \varepsilon_{\text{vac}} = 1 \]  

The entropy change for this charging process is given by

\[ -\Delta S = \left( \frac{\partial \Delta G}{\partial T} \right)_p \]  

When the dielectric material is between the plates, the change in entropy per unit volume is given by a combination of equation 90 with equation 83. The result is:

\[ \Delta S = -\frac{x^2}{3N_0} \frac{d}{dT} \left( \frac{1}{\varepsilon} \right) \]  

Since for most compounds the temperature coefficient of \( \varepsilon \) is negative, \( d/dT(1/\varepsilon) \) is positive and entropy is lost when a dielectric material is subjected to an electrical field.
For a sphere in a vacuum

\[ \Delta G = \int_{r_1}^{\infty} \left( \frac{\chi^2}{2\mu} \right) \, dv \]

...92

where the integration is taken over all space outside the sphere. The volume of a spherical shell of thickness (dr) is

\[ dv = 4\pi r^2 \, dr \]

...93

and the field strength

\[ \chi = \frac{q}{r^2} \]

...94

where \( r \) is the distance from the center of the sphere. Therefore,

\[ \Delta G = \frac{\sigma^2}{8} \int_{r_1}^{\infty} \frac{4\pi r^2}{r^4} \, dr = \frac{\sigma^2}{2r} \]

...95

The free energy change can be considered as the work done in producing an ion in a vacuum.

In a medium of dielectric constant (\( \varepsilon \)), this free energy change is \( 1/\varepsilon \) of the value in a vacuum.

Now consider the charged sphere in a medium of dielectric constant (\( \varepsilon \)), where \( r_1 \) is the radius of the sphere and \( r_2 = 2r_1 \).

Since from

\[ \Delta G = \frac{\sigma^2}{2r} \]

...95

\( \Delta G \) outside \( r_2 \) is one-half \( \Delta G \) inside \( r_1 \). As a result, half of the net free energy change is in the region between \( r_1 \) and \( r_2 \).

Thus, for an ion of small radius, a very large field is imposed on a very small volume element. As a result, one can postulate
two types of solvation:

1. In the co-sphere between $r_1$ and $r_2$, the solvent molecules are strongly polarized and the specific solvent effects are probably fairly strong.

2. Outside the co-sphere the effects are much weaker and the bulk dielectric constant would be expected to apply.

Using the ideas brought out above on the equilibrium given by:

$$
\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-
$$

$$
\Delta G = -RT \ln K_a = \Delta G_{\text{nonel}} + \frac{Ne^2}{2\varepsilon} \left( \frac{1}{r_{H^+}} + \frac{1}{r_{A^-}} \right) - \frac{1}{r_{H^+}} - \frac{1}{r_{A^-}} 
$$

or

$$
\Delta G = -RT \ln K_a = \Delta G_{\text{nonel}} + \frac{Ne^2}{2\varepsilon} \left( \frac{1}{r_{H^+}} + \frac{1}{r_{A^-}} \right)
$$

where $\Delta G_{\text{nonel}}$ is the nonelectrostatic contribution to the free energy change, and

$$
\frac{Ne^2}{2\varepsilon} \left( \frac{1}{r_{H^+}} + \frac{1}{r_{A^-}} \right)
$$

is the Born representation of the coulombic work done in ionizing HA in a medium of dielectric constant ($\varepsilon$). The terms $r_{H^+}$ and $r_{A^-}$ represent the radii of the solvated $H^+$ and $A^-$ ions.

If equation 98 is allowed to represent the free energy change for the ionization of HA in pure water, then for a mixed solvent this equation becomes

$$
\Delta G^* = -RT \ln K_a^* = \Delta G_{\text{nonel}}^* + \frac{Ne^2}{2\varepsilon^*} \left( \frac{1}{r_{H^+}^*} + \frac{1}{r_{A^-}^*} \right)
$$
Equations 98 and 99 can be written

\[ p_{K_a} = \frac{\Delta G_{\text{nonel}}^{\text{nonel}}}{2.303RT} + \frac{Ne^2}{4.606RTe^*} \left( \frac{1}{r_{H^+}^{*}} + \frac{1}{r_{A^-}^{*}} \right) \]  

\[ \ldots 100 \]

and

\[ p_{K_a}^{*} = \frac{\Delta G_{\text{nonel}}^{*}}{2.303RT} + \frac{Ne^2}{4.606RTe^*} \left( \frac{1}{r_{H^+}^{*}} + \frac{1}{r_{A^-}^{*}} \right) \]  

\[ \ldots 101 \]

Subtracting equation 100 from equation 101, one obtains

\[ p_{K_a}^{*} = p_{K_a} + \frac{\Delta G_{\text{nonel}}^{*} - \Delta G_{\text{nonel}}^{\text{nonel}}}{2.303RT} \]

\[ + \frac{Ne^2}{4.606RT} \left[ \frac{1}{e^*} \left( \frac{1}{r_{H^+}^{*}} + \frac{1}{r_{A^-}^{*}} \right) - \frac{1}{e} \left( \frac{1}{r_{H^+}} + \frac{1}{r_{A^-}} \right) \right] \]  

\[ \ldots 102 \]

One can assume that in the region where the concentration of water is fairly high (\( e^* \) is also fairly high), that \( \Delta G_{\text{nonel}}^{*} \) will be equal to \( \Delta G_{\text{nonel}}^{\text{nonel}} \) and also that \( r_{H^+}^{*} = r_{H^+} \) and \( r_{A^-}^{*} = r_{A^-} \). Thus,

\[ p_{K_a}^{*} = p_{K_a} + \frac{Ne^2}{4.606RT} \left( \frac{1}{e^*} - \frac{1}{e} \right) \left( \frac{1}{r_{H^+}} + \frac{1}{r_{A^-}} \right) \]  

\[ \ldots 47 \]

The ionization constants of weak acids go through maxima at about room temperature -

\[ \log K_a - \log K_{\theta} = -p(t-\theta)^2 \]  

\[ \ldots 69 \]

Since for a number of common solvents

\[ \epsilon = \epsilon_0 e^{-T/\theta} \]  

\[ \ldots 103 \]

and since

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\[-RT \ln K_a = \Delta G_{\text{nonel}} + \frac{Ne^2}{2\epsilon} \left(\frac{1}{r_{H^+}} + \frac{1}{r_{A^-}}\right) \]

if we let

\[\frac{Ne^2}{2} \left(\frac{1}{r_{H^+}} + \frac{1}{r_{A^-}}\right) = A\]

then the

\[-RT \ln K_a = \Delta G_{\text{nonel}} + \frac{A}{\epsilon_0} e^{T/\theta} \]

Now if we consider conditions under which \(\Delta G_{\text{nonel}} = 0\), then \(K_\theta\) can be obtained by differentiation with respect to \(T\) and setting the derivative equal to zero:

\[0 = \frac{e^{T/\theta}}{T^2} - \frac{e^{T/\theta}}{\theta T} \]

The ionization constant is a maximum at \(T = \theta\).

Work on the temperature dependence of the medium effects in mixed solvent systems is being investigated in this laboratory.

**Kinetic Approach to the Medium Effects**

Bradley and Lewis\(^57\) proposed that the rate of ionization of \(HA\) to form \(H^+\) and \(A^-\) could be given by

\[
\text{rate of ionization} = k_1 e^{-E/RT} C_{HA} \]

where \(k_1\) is the rate constant and \(E\) is the energy needed to separate \(H\) and \(A\).

In a medium of dielectric constant \((\epsilon)\) equal to unity, the energy required for this separation is \(E_0\). Therefore
\[ E = \frac{E_0}{e} \quad \text{...109} \]

and

\[ \text{rate of ionization} = k_1 e^{-\frac{E_0}{eRT}} C_{HA} \quad \text{...110} \]

The rate of association of \( H^+ \) and \( A^- \) is given by

\[ \text{rate of association} = k_2 e^{-\frac{E_0'}{eRT}} C_{H^+} C_{A^-} \quad \text{...111} \]

In aqueous medium

\[ K_a = \frac{C_{H^+} C_{A^-}}{C_{HA}} f_{H^+} f_{A^-} = \frac{k_1}{k_2} e^{\frac{(E_0' - E)}{eRT}} \quad \text{...112} \]

and in mixed solvent

\[ K_a^* = \frac{k_1}{k_2} e^{\frac{(E_0' - E)}{e^*RT}} \quad \text{...113} \]

Dividing equation 113 by equation 112 and taking the negative logarithm, one obtains:

\[ \text{pK}^*_a = \text{pK}_a + \frac{(E_0 - E_0')}{2.303 \text{ RT}} \left( \frac{1}{e^*} - \frac{1}{e} \right) \quad \text{...114} \]

Equation 114 is a form of equation 47.

A slightly different kinetic approach is given below. Consider the reaction

\[ H^+_A + H_2O^- \xrightarrow{r_F} H_3O^+ + A^- \quad \text{...115} \]

Dipole Dipole Ion Ion

The rate of the forward (dipole-dipole) reaction is given by

\[ r_F = k_F [HA][H_2O] \quad \text{...116} \]
\[ \ln k'_e = \ln k'_{e=\infty} - \frac{2\mu_1\mu_2N}{RT^3e^2} = \ln k_F \] ....117

where \( k'_e \) is the rate constant at any dielectric constant; \( k'_{e=\infty} \) is the rate constant at the infinite value of \( \varepsilon \); \( N/R \) is the Boltzmann gas constant; \( \mu_1 \) and \( \mu_2 \) are the dipole moments of the respective dipolar reactants; and \( r \) is the distance of closest approach.

\[ r_F = k'_{e=\infty}e^{2\mu_1\mu_2N/RT^3} [HA][H_2O] \] ....118

Let

\[ A = 2\mu_1\mu_2N/RT \] ....119

The rate of the reverse (ion-ion) reaction is given by

\[ r_R = k_R[H_2O^+][A^-] \] ....120

The reaction rate constant for a reaction involving ionic reactants is given by an equation derived by Christiansen:

\[ \ln k' = \ln k'' - \frac{Z_A Z_B Ne^2}{eRT} + 2.3 Z_A Z_B \sqrt{\mu} \] ....121

At infinite dilution this equation becomes

\[ \ln k'_{x=0} = \ln k''_o - \frac{Z_A Z_B Ne^2}{eRT} \] ....122

If we let

\[ \frac{Z_A Z_B Ne^2}{RT} = B \] ....123

then

\[ k'_{x=0} = k''_o e^{-B/\varepsilon r} = k_R \] ....124

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At equilibrium
\[ r_F = r_R \]  

or
\[ k'_o e^{-A/\varepsilon R^3} [HA][H_2O] = k''_o e^{-B/\varepsilon R} [H_3O^+][A^-] \]

Rearrangement of equation 124 gives
\[ \frac{[H_3O^+][A^-]}{[HA][H_2O]} = K_A = \frac{k'_o e^{-A/\varepsilon R^3}}{k''_o e^{-B/\varepsilon R}} \]

In aqueous solution
\[ K_A = \frac{k'_o}{k''_o} e^{-A+Br^2/\varepsilon R^3} \]

In mixed solvent solution
\[ K_A^* = \frac{k'_o}{k''_o} e^{-A+Br^2/\varepsilon^* R^3} \]

Dividing equation 128 by 129 and taking the negative logarithm, one obtains
\[ pK_A^* - pK_A = \frac{Br^2-A}{2.303 R^3} \left( \frac{1}{\varepsilon^*} - \frac{1}{\varepsilon} \right) \]

Substitution from equations 119 and 123 gives
\[ pK_A^* - pK_A = \frac{Z_A Z_B Ne^2}{2.303 R^3} \left( \frac{1}{\varepsilon^*} - \frac{1}{\varepsilon} \right) - \frac{2^+H^+N}{2.303 R^3} \left( \frac{1}{\varepsilon^*} - \frac{1}{\varepsilon} \right) \]

Equation 131 is a variation of equation 47.
Test of the Validity of $\text{pK}^*_a = \text{pK}_a + b\left(\frac{1}{\varepsilon^*_a} - \frac{1}{\varepsilon^*_o}\right) + 10^{c+d}\left(\frac{1}{\varepsilon^*_a} - \frac{1}{\varepsilon^*_o}\right)$

From the foregoing resume of various theoretical treatments, we may conclude that our analytical functions (equations 76, 77 and 78) are of correct form. If this is so, there are a number of ways of testing the validity of these functions once the constants of the equations have been determined from experimental results.

For example, one should be able to compute the value of the dielectric constant of the pure organic component of the mixed solvent provided the $\text{pK}^*_a$, the $\text{pK}^*_a'$, and the dielectric constant of the corresponding mixed solvent are known. A few illustrative calculations are given below.

The $\text{pK}^*_a$ of acetic acid in 20 weight percent tetrahydrofuran-water mixture is 5.39. The dielectric constant of this mixture is 58.83 and the dielectric constant of pure water is 78.54. From the acetic acid graph (Figure 9), the value of $\left(1/\varepsilon^*_o - 1/\varepsilon^*\right)$ is $9.2 \times 10^{-4}$.

Since by equations

\[ \varepsilon^{**} = \varepsilon^* + (\varepsilon - \varepsilon_{\text{organic}}) \] ....74

and

\[ \varepsilon^" = 2\varepsilon - \varepsilon_{\text{organic}} \] ....75

the following equation holds:

\[ \frac{1}{\varepsilon^{**}} - \frac{1}{\varepsilon^"} = \frac{1}{\varepsilon^* + \varepsilon - \varepsilon_{\text{organic}}} - \frac{1}{2\varepsilon - \varepsilon_{\text{organic}}} \] ....132

Substitution of the known dielectric constants into equation 132 gives
\[ 9.2 \times 10^{-4} = \frac{1}{58.35 + 78.54 - \varepsilon_{\text{organic}}} - \frac{1}{2(78.54) - \varepsilon_{\text{organic}}} \] ....133

Solving the resulting quadratic equation one obtains 
\( \varepsilon_{\text{THF}} = 6.9 \). Table XIV gives a value of 7.4. The calculated result is only 7 percent off from the experimental value. Alternatively, one could have used the equation for the function

\[ pK^* = pK_a + b \left( \frac{1}{e^{x''}} - \frac{1}{e''} \right) + 10^{c+d} \left( \frac{1}{e^{x''}} - \frac{1}{e''} \right) \] ....134

where for propanoic acid (\( pK_a = 4.88 \)) \( b = 508; c = -2.00; \) and \( d = 484. \) in 20 weight percent 2-propanol-water (\( pK_a = 5.33 \)), \( \varepsilon \) equals 64.1.

Substitution of values into equation 134 gives

\[ pK^* - pK_a = 0.45 = 508\varepsilon + 10^{-2.00+484\varepsilon} \] ....135

where

\[ F = \frac{1}{e^{x''}} - \frac{1}{e''} \] ....136

Solving equation 135 by the method of successive approximations gives \( F = 0.83 \times 10^{-3} \). Appropriate substitution into equation 132 gives

\[ 0.83 \times 10^{-3} = \frac{1}{142.6 - \varepsilon_{\text{org.}}} - \frac{1}{157.1 - \varepsilon_{\text{org.}}} \] ....137

Rearrangement gives

\[ \varepsilon_{\text{org.}}^2 - 299.7 \varepsilon_{\text{org.}} + 2.240 \times 10^4 = 1.750 \times 10^4 \] ....138
Solving the quadratic equation, one obtains: $\varepsilon_{\text{organic}} = 18.0$. Table IV gives a value of 18.0.

On the other hand, if the value of the $pK^*_{a}$ for the mixed solvent lies in the linear portion of the curve for $pK^*_{a}$ versus $(1/\varepsilon^* - 1/\varepsilon''$), the equation for this linear portion only can be used

$$pK^*_{a} = pK^*_{a} + b\left(\frac{1}{\varepsilon^*} - \frac{1}{\varepsilon''}\right)$$

...139

Consider benzoic acid in 20 weight percent 2-methoxyethanol-water where $pK^*_{a} = 5.07$ and $\varepsilon = 68.9$. Table XVI gives $pK^*_{a} = 4.27$ and $b = 631$. Substitution into equation 139 gives

$$\Delta pK^*_{a} = 0.33 = 5.3 \times 10^{2} \left(\frac{1}{147.4 - \frac{1}{\varepsilon_{\text{organic}}}} - \frac{1}{157.1 - \frac{1}{\varepsilon_{\text{organic}}}}\right)$$

...140

Rearrangement gives

$$5.24 \times 10^{-4} = \frac{9.7}{\varepsilon_{\text{org}} - 304.5 \varepsilon_{\text{org}} + 2.316 \times 10^{4}}$$

...141

and

$$\varepsilon_{\text{org}} - 304.5 \varepsilon_{\text{org}} + 2.316 \times 10^{4} = 1.852 \times 10^{4}$$

...142

Solving the quadratic equation, one obtains: $\varepsilon_{\text{organic}} = 16$. Table XIV gives a value of 17.2 -- again within a 7% error.

While 2-propanol-water system was used in deriving equation 76, only three points of the twenty used were from this system and four other mixed solvent systems were also used. In the case of the tetrahydrofuran-water system and in the case of the 2-methoxyethanol-water system, no values from these systems were used in deriving the equation.
The above calculations substantiate the validity of equation 76.

Calculation of Interionic Distances

Equating the coefficients of equation 47 and equation 77, one obtains

\[
\beta = \frac{\text{Ne}^2}{4.606RT} \left( \frac{1}{r_{H^+}} + \frac{1}{r_{A^-}} \right)
\]

The right hand side of this equation cannot be computed unless the value of the radius of the hydrated proton \(r_{H^+}\) and the radius of the hydrated anion \(r_{A^-}\) are precisely known. Even if these radii were precisely known, the experimental \(\beta\) would almost certainly have been different from the computed value of the right member of equation 143; because Born's equation, as well as the other theoretical equations discussed, totally neglects the noncoulombic interactions (at high dielectric constant) which have finite contributions in all real solutions of electrolytes even in solvents of high dielectric constant. The contribution due to these noncoulombic interactions is very small yet significant even at high values of dielectric constant, and it increases rapidly when the bulk dielectric constant is less than a certain critical value (~40). Again this critical value of the bulk dielectric constant will be different for different solvents as it will depend on such factors as the dipole moment of the solvent molecule, its structure, Lewis basicity, polarizability, etc., to mention a few; however, this difference may not be very large. In my opinion, attempts at the theoretical calculation of \(\beta\), regardless of the sophistication of the
model, are at best a good exercise. Further, all these models tacitly assume the equivalent of a spherical monatomic anion. Nevertheless, several investigators have calculated hydrate anionic radii assuming a reasonable value for $r_{\text{H}^+}$.

Thus, the use of the term anionic radius is unfortunate since it implies that the radius considered is that of the entire anion of the weak acid. Such a radius would include a considerable amount of carbon chain "tail" (which is weakly hydrated) as well as the carboxylate "head" which is most certainly strongly hydrated.

It would seem, then, that what is really measured by the term $r_A$ is the anionic contribution to the minimum distance of approach, i.e., the thickness of the solvent (water) sheath between the negative end of the anion and the outer periphery of the solvated (hydrated) proton.

Kielland used a value of 9 Å as the effective diameter of the hydrated proton, while Robinson and Stokes used 3.83 Å of the hydrate proton radius. Earned and Owen give an ionic radius for $\text{H}^+$ of 0.945 Å based on conductivity data. Kielland also listed the ionic diameter of the acetate ion (4.5 Å) and of the benzoate ion (6 Å). Using the corresponding radii and making the appropriate substitutions in equation 143, one gets a calculated $\beta$ value for acetic acid of 57 (measured value = 130) and for benzoic acid of 56 (measured value = 152). Substitution of the values of Robinson and Stokes into equation 143 gives 129 as the slope of most carboxylic acids -- an approximately correct value.
Thus, there is some disagreement as to the size of the hydrated proton parameter. In order to obtain a reasonable value for the radius of the hydrated proton, one should first consider how many water molecules are attached to the proton. Tuck and Diamond$^{60}$ found that when strong acids were extracted from water by organic solvents, they frequently take with them four molecules of water per proton. Glueckauf$^{61}$ obtained a hydration number of the proton of 3.9. These results indicate that there are four molecules of water associated with each proton. One water molecule is involved in covalent bond formation and the other three water molecules are bound by hydrogen bonds to the H$_3$O$^+$. Conway, Bockris, and Linton$^{62}$ give as the linear distance for O-H$^+$-O, 2.45 Å. If one adds to this value the distance (0.59 Å) from the oxygen on one water molecule to a point midway between the two hydrogens on that molecule, one gets a value of 3.0 Å as the "radius" of the hydrated proton. Supporting evidence$^{63}$ comes from the X-ray analyses of liquids which reveal the existence of preferred spacing distances which show up as maxima in a radial distribution curve. The plot of the probability function ($\frac{4\pi r^2 pr}{3}$) for water against r shows a pronounced maximum at about 3.0 Å and two less pronounced maxima at approximately 5 Å and 7 Å. Integration of the area under the sharp maximum at about 3.0 Å corresponds to 4.5 nearest neighbors. Conductivity experiments in conjunction with observations on the acidity function substantiate the H$_3$O$^+$ structure.$^{63}$

Wicke, Eigen, and Ackermann$^{64}$ have also proposed H$_3$O$^+$ as the dominant specie for the hydrated proton.
Using a value of $3.0 \, \text{Å}$ for the hydrated proton radius ($r_{H^+}$), the contribution ($r_{A^-}$) of the hydrated anions to the minimum distance of approach were calculated. These values are given in Table XIX together with values for the minimum distance of approach ($r_{H^+} + r_{A^-}$) for various weak acids. The values of the minimum distance of approach for HCl, HBr, and HI obtained by Harned$^4$ are included for comparison. The values obtained for the weak acids are of the right order of magnitude.

**Relation of $\beta$ to the Polar Character of the Acid Radicals**

An increase in slope ($\beta$) and a corresponding decrease in the anionic contribution to the minimum distance of approach ($r_{A^-}$) is noted for the series formic, acetic, propanoic, butanoic, and isovaleric; for the series malonic, succinic, and glutaric; and for the series glycolic, cyanoacetic, chloroacetic, and acetic. Grundwald and Berkowitz$^{26}$ noticed a similar trend for the parameter $m_A$ in the equation

$$\Delta pK_a = \log f_H + m_A Y^-$$

where $f_H$ is a degenerate activity coefficient referred to the infinitely dilute aqueous state, and $Y^-$ is called the activity function. An increase in the polar character of the acid anion is attended by a decrease in $m_A$. This increase in polar character should correspond to a more strongly held aqueous layer around the carboxylate group and, therefore, to an increase in the anionic contribution to the distance of approach. The present treatment offers a somewhat more satisfactory interpretation of this observation than the use of the parameter $m_A$. 

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TABLE XIX
VALUES OF THE SLOPE ($\beta$), THE ANIONIC CONTRIBUTION TO MINIMUM DISTANCE OF APPROACH ($r_{A^-}$), AND THE MINIMUM DISTANCE OF APPROACH ($a^o$) FOR A NUMBER OF ACIDS AT 25$^\circ$ C.

<table>
<thead>
<tr>
<th>Acid</th>
<th>$\beta$</th>
<th>$r_{A^-}$(Å)</th>
<th>$a^o$(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formic</td>
<td>110</td>
<td>1.3</td>
<td>4.3</td>
</tr>
<tr>
<td>Acetic</td>
<td>125</td>
<td>1.1</td>
<td>4.1</td>
</tr>
<tr>
<td>Propanoic</td>
<td>128</td>
<td>1.1</td>
<td>4.1</td>
</tr>
<tr>
<td>Butanoic</td>
<td>140</td>
<td>1.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Benzoic</td>
<td>152</td>
<td>0.9</td>
<td>3.9</td>
</tr>
<tr>
<td>Malonic</td>
<td>88</td>
<td>1.7</td>
<td>4.7</td>
</tr>
<tr>
<td>Glycolic</td>
<td>106</td>
<td>1.3</td>
<td>4.3</td>
</tr>
<tr>
<td>Succinic</td>
<td>111</td>
<td>1.2</td>
<td>4.2</td>
</tr>
<tr>
<td>Cyanoacetic</td>
<td>113</td>
<td>1.2</td>
<td>4.2</td>
</tr>
<tr>
<td>Glutaric</td>
<td>114</td>
<td>1.2</td>
<td>4.2</td>
</tr>
<tr>
<td>Salicylic</td>
<td>115</td>
<td>1.2</td>
<td>4.2</td>
</tr>
<tr>
<td>Chloroacetic</td>
<td>116</td>
<td>1.2</td>
<td>4.2</td>
</tr>
<tr>
<td>Lactic</td>
<td>122</td>
<td>1.1</td>
<td>4.1</td>
</tr>
<tr>
<td>Isovaleric</td>
<td>141</td>
<td>1.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Hydrochloric</td>
<td></td>
<td></td>
<td>4.3</td>
</tr>
<tr>
<td>Hydrobromic</td>
<td></td>
<td></td>
<td>4.4</td>
</tr>
<tr>
<td>Hydriodic</td>
<td></td>
<td></td>
<td>5.0</td>
</tr>
</tbody>
</table>
Conclusions

One of the purposes of the program, of which this Dissertation is a part, has been to find an analytical function for converting experimental data obtained for a reversible process in one solvent to the corresponding values in another solvent. Such a function for the ionization of weak acids has been developed and is given by the equation

\[ pK^*_{a} = pK_{a} + b\left(\frac{1}{\varepsilon'_{w}} - \frac{1}{\varepsilon'}\right) + 10^{c+d\left(\frac{1}{\varepsilon'_{w}} - \frac{1}{\varepsilon'}\right)} \]

This equation correlates data for fourteen weak acids in ten different solvent systems.

For regions of high aqueous concentration, an electrostatic model for estimating the medium effects has been shown to be a good first approximation. In addition, a method has been devised for the calculation of the minimum distance of approach for the hydrated proton and the hydrated carboxylate radical. These distances have also been correlated to the polar character of weak acids.

A method has also been established for the determination of the dielectric constant of a pure organic solvent from data in a highly aqueous, mixed solvent system of this organic solvent.


29. Patterson, A. and Felsing, W. A. "The Ionization Constants of Propionic Acid in Methyl and Ethyl-Alcohol-Water Mixtures from 0 through 40°", *Journal of the American Chemical Society*, 64, 1480 (1942).


VITA

Louis Henry Adcock was born in Durham, North Carolina, on March 28, 1929. After attending the Durham public schools, he enrolled in Duke University where he received the B.S. degree in Chemistry in 1951, and the M.A. degree in Analytical Chemistry in March, 1953. After working for a year as a chemist with the International Minerals and Chemical Corporation, Mr. Adcock served two years in the U. S. Army Chemical Corps in the Scientific and Professional Personnel Program at Dugway Proving Grounds at Dugway, Utah. Upon completion of his military service, he began his teaching career at the University of North Carolina at Wilmington, where he has taught for thirteen years. During this time he has been very active in the affairs of the Eastern North Carolina Section of the American Chemical Society and in the North Carolina Academy of Science, serving as the Director of the Academy's Southeastern North Carolina Science Fair Program for twelve years.

In 1964, he entered the Louisiana State University National Science Foundation Summer Institute for College Chemistry Teachers and, in 1966, the Louisiana State University National Science Foundation Research Participation Program. He was the recipient of a National Science Foundation Academic Year Extension Grant in 1967, and is presently a candidate for the degree of Doctor of Philosophy at Louisiana State University with a major in Analytical Chemistry and a minor in Inorganic Chemistry.
Mr. Adcock is a member of the American Chemical Society, the American Association for the Advancement of Science, Phi Lambda Upsilon, the North Carolina Academy of Science, and the American Association of University Professors. In addition, he is a Fellow of the American Institute of Chemists.
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Candidate: Louis Henry Adcock

Major Field: Chemistry


Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination:

August 5, 1969