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Further relationships in the grunwald treatment of acid-base equilibria in hydroxylic solvents

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UNITED STATES ATOMIC ENERGY COMMISSION

FURTHER RELATIONSHIPS IN THE GRUNWALD TREATMENT OF ACID-BASE EQUILIBRIA IN HYDROXYLIC SOLVENTS

By
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December 1957

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FURTHER RELATIONSHIPS IN THE GRUNWALD TREATMENT OF ACID-BASE EQUILIBRIA IN HYDROXYLIC SOLVENTS*

Wilfred George Borduin and G. S. Hammond

ABSTRACT

It was observed by Grunwald that acid-base equilibria in several pure and mixed hydroxylic solvents could be treated by the relation

$$\log \frac{f_A}{f_{AH}} = m_A Y$$

wherein $f_A$ and $f_{AH}$ are degenerate activity coefficients of a base and its conjugate acid, respectively, $m_A$ is a parameter depending only upon the base, and $Y$ is a parameter depending only on the solvent and charge type of the base.

It is shown in this work that the proton donating ability of a solvent can be related to a suitable function of appropriate $m_A$ values. Utilizing Grunwald's data for mixtures of water and ethanol, values of $m_A$ are derived for the solvent components.

In addition, a relationship is derived between the proton donating ability of a solvent and the Hammett acidity function. This relationship is shown to correlate data already available in the literature on the Hammett acidity function in water-ethanol mixtures.

*This report is based on Part II of a Ph. D. thesis by Wilfred G. Borduin submitted December, 1957, to Iowa State College, Ames, Iowa. This work was done under contract with the Atomic Energy Commission.
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FURTHER RELATIONSHIPS IN THE GRUNWALD
TREATMENT OF ACID-BASE EQUILIBRIA IN HYDROXYLIC
SOLVENTS

Introduction

The problem under consideration is an attempt to establish a quantitative relationship among the basicities of a series of compounds. Such a problem is trivial in the case in which all of the compounds of interest can be observed in the same medium. However, it frequently occurs that considerations of solubility and leveling effect of a solvent make it difficult or impossible to carry out suitable experiments. In these cases the experimenter's only recourse generally has been to find a more suitable solvent. In this manner one can only hope at best to find qualitative relationships among the basicities of a series of compounds if it be impossible to measure the basicities of all the compounds in the same solvent. In general, one can not even be sure that the order of relative basicities will not be changed on changing solvents. It would be very desirable, therefore, if in some way it were found possible to relate the basicities of compounds to some common reference state, together with the relationships which would make it possible to calculate the basicities in various other solvents. Two attempts at establishing such a relationship for at least a limited series
of solvents will be mentioned here; that of Hammett (1) for
strong acid solutions and that of Gutebezahl and Grunwald
(2) for hydroxylic and mixed hydroxylic solvents.

In 1932 Hammett and Deyrup (3) and Hammett and Paul (4)
carried out a spectrometric study of the ratio of concentra-
tions of neutral indicator bases to the concentrations of
their conjugate acids when the bases were dissolved in a
mixture of water and a strong acid, chiefly sulfuric. On
the basis of these studies they concluded that the ratio of
activity coefficients of the base and its conjugate acid is
independent of the base, and it was tacitly assumed also
independent of the solvent components. This extended the
range of possibilities of measuring the basicities of com-
pounds too weakly basic to be measured in water because of
the leveling effect of that solvent. If it is assumed that
the ratio is a constant then it is possible to define for a
solvent an acidity function, which they denote by $H^0$, which
is in a sense a measure of the proton donating ability of
that solvent with respect to the pH scale in water.

Grunwald and Winstein (5) observed for certain solvents
a property of solvents reminiscent of that for which we seek.
They found that the rates of solvolysis of a number of com-
pounds could be correlated by the relationship;

$$\log \frac{k}{k_0} = mY$$
wherein $k_0$ is the rate of some standard reaction under some standard conditions of temperature and solvent, $m$ is a constant depending only on the compound undergoing reaction and $Y$ is a constant which is a function of the solvent related to the solvating power of the solvent. This observation suggested a possible similar treatment for equilibrium reactions. Gutebezahl and Grunwald (2) indeed found that acid-base equilibria in a number of pure and mixed hydroxylic solvents could be treated by similar relationship. Grunwald's treatment, together with the Debye-Hückel limiting law, allows one to calculate concentration ionization constants of numerous acids and bases in these media. A quantity denoted by $\log f_H$ is also obtained by Grunwald which is a function of the solvent medium and is again in a sense a measure of the solvents' acidic properties. Since $\log f_H$ and $H^0$ purport to be measures of the same property, we have attempted to develop the relationship between these two parameters.

Discussion of the Significance of the Grunwald Activity Postulate

Grunwald's treatment of acid-base equilibria in mixed hydroxylic solvents involves the use of an extra-thermodynamic assumption, namely:

$$\log \frac{f_B}{f_{BH}} = m_B Y_S$$  \hspace{1cm} (1)
where $f_B$ and $f_{BH}$ are the degenerate activity coefficients of a base and its conjugate acid, respectively. The $f$'s are called degenerate because they are concentration independent. They are related to the free energy difference between different possible reference states. In this case they represent the difference in molar free energy between the reference state of an infinitely dilute solution in any solvent, $S$, and infinitely dilute solution of the same solute in water. Thus they are a function of solvent composition. The constant $Y_S$ in Equation 1 is also a function of solvent composition. It is called the solvent power of solvent $S$. Ideally $Y_S$ should be independent of the choice of base $B$ and depend only on the solvent. However, it is found that $Y$ is also dependent on the charge type of the base. Since we will be interested in only two types of base here, namely, neutral and singly negatively charged bases, no great loss of generality is involved. The constant $m_B$ is as its subscript implies a function of the base $B$ only. That is, it is a measure of the sensitivity of base $B$ to changes in solvent power $Y_S$.

By utilization of this "activity postulate" Grunwald has derived further functions of the solvent which might be considered a measured part of its relative basicity, namely

\[
\log f_H = \Delta pK_B + m_B Y_S. \tag{2}
\]

The term $\Delta pK_B$ is given by
\[ \Delta pK_B = pK_B^S - pK_B^W \]  

where \( pK_B^S \) and \( pK_B^W \) are the thermodynamic pK's for the acid dissociation of BH as measured in solvent S and water, respectively. Thus \( \log f_H \) can also be written

\[ \log f_H = \log a_H - \log a_H^\infty \]  

where \( a_H \) is the proton activity relative to infinite dilution in water and \( a_H^\infty \) is the proton activity with respect to solvent S.

Once given \( \log f_H \) one can define a further function to the solvent, \( \log f_{OH} \), which represents the relative acidity of the solvent from the relation

\[ pK^S - pK^W = \log f_H - \log f_{OH} \]  

where the pK's now represent the autoprotolysis constants of solvent S and water, respectively. The term \( \log f_{OH} \) can not be as conveniently expressed as \( \log f_H \) is in Equation 4. However, the expression

\[ \log f_{OH} = \log a_{OH}^\infty - \log a_{S-}^\infty \]  

can be satisfactory if it is remembered that \( S^- \) ions may be partly composed of \( OH^- \) ions in a mixed solvent. A similar restriction applies to Equation 4 when one recognizes that the proton is not free but attached to some other species,
thus Equation 4 becomes

\[ \log f_H = \log a_{H2O^+} - \log a_{SH^+} \]  

(7)

Grunwald has tabulated experimental values of both log \( f_H \) and log \( f_{OH} \) derived from measured values of the parameters \( m \) and \( Y \) for a large number of neutral and negatively charged bases in various water-ethanol mixtures. The question arises as to whether or not these data can be represented by \( m \) values for water and ethanol together with the already measured \( Y \) values. To illustrate the problem further, consider that the ionization constants of bases in some solvent define proton levels for that solvent in terms of free energy. The capacity of a level for protons is of course a function of a concentration of the base. This treatment is quite similar to that of Gurney (6). Solvents, therefore, have associated with them basicity scales which are generally treated as being independent of each other. However, adoption of Grunwald's activity postulate allows one to relate in a definite manner basicity scales of different solvents. Illustrated schematically in Figure 1 are the basicity scales of water and ethanol for different bases \( A \) and \( B^- \) which are represented by the vertical lines at each side of the diagram. The activity postulate allows one to determine the levels of bases \( A \) and \( B^- \) in water-ethanol mixtures as a function of composition of the solvent and is illustrated by the dotted lines connecting the two scales. Since the \( Y \) values are a monotonic function
Figure 1. Proton levels versus mole fraction ethanol.
of the composition, the mole fraction abscissa can be replaced
by one of an appropriate Y scale in which case the dotted
curves would become straight lines, the slope of which is
equal to appropriate m values. It will be shown that it is
possible to obtain m values for the solvent molecules as
well as for other bases, as is illustrated by the levels
indicated for H₂O, OH⁻, EtOH, and EtO⁻. This will be ac-
complished by observing what relationship these m values have
to Grunwald's log f₄⁻ and log f₂OH functions. In order to do
this a somewhat different notation will be introduced. In
particular, this notation should be such that it centers
attention on the free energy changes involved in the various
equilbria under consideration.

Consider a reaction

\[ \text{QH} + \text{R} = \text{Q} \cdot \text{RH} \quad (8) \]

for the transfer of proton between bases Q and R of an un-
specified charge type. Associated with such a reaction is a
standard free energy change given by

\[ u_{SH}(Q,R) = 2.3 \text{RT} \ pK = -2.3 \text{RT} \ \log \frac{aQ^aRH}{aQ^aR} \quad (9) \]

where pK is the negative log of the thermodynamic equilibrium
constant for Reaction 8 as measured in some solvent S.

The subscript of u, therefore, indicates the solvent with
which we are concerned. The order of the terms within the
brackets associated with U denotes the direction of the re-
action, i.e., the transfer of one mole of protons from one
mole of QH to one mole of R. It will be convenient to split
the left side of Equation 9 into two terms as follows:

\[ u_{SH}(Q, R) = u_{SH}(Q) - u_{SH}(R) = -2.3 \text{ RT} \left( \log \frac{a_Q}{a_{QH}} - \log \frac{a_R}{a_{RH}} \right) \]

This corresponds to splitting the expression for the pK of
Reaction 8 into the two terms

\[ pK = -\log \frac{a_Q}{a_{QH}} + \log \frac{a_R}{a_{RH}} \]

We now define a function \( u_s^\ast(Q) \) such that for any base Q

\[ u_{SH}^\ast(Q) = u_{SH}(Q) - u_w(Q) \]

where subscript 's again refers to some solvent S and w denotes
water as reference solvent. It is seen that \( u_s^\ast(Q) \) cor-
responds, except for the factor 2.3 RT, to the log of the
degenerate activity coefficient ratio given in Equation 1.
Thus Grunwald's activity postulate becomes,

\[ \frac{u_s^\ast(Q)}{2.3 \text{ RT}} = \epsilon_Q y_S \]

We now define a function $\alpha_{SH}$ so that

$$\alpha_{SH} = u_w(H_2O) - u_{SH}(SH).$$  \hspace{1cm} (14)

The last term in this expression is

$$u_{SH}(SH) = -2.3 \text{ RT} \log \frac{a_{SH}}{a_{SH}^*}$$  \hspace{1cm} (15)

where the activities are referred to solvent $S$. The function $\alpha_{SH}$ is related to Grunwald's log $f_H$ by

$$\log f_H = \frac{\alpha_{SH}}{2.3 \text{ RT}} + \log a_{H_2O} - \log a_{SH}^*$$  \hspace{1cm} (16)

in which $a_{H_2O}$ is referred to water and $a_{SH}^*$ is referred to solvent $S$. Similarly, we define a function $\beta_{SH}$ such that

$$\beta_{SH} = u_w(OH) - u_{SH}(S^-)$$  \hspace{1cm} (17)

where

$$u_{SH}(S^-) = -2.3 \text{ RT} \log \frac{a_{S^-}^*}{a_{SH}}.$$  \hspace{1cm} (18)

This function is related to Grunwald's log $f_{OH}$ by the relation

$$\log f_{OH} = - \frac{\beta_{SH}}{2.3 \text{ RT}} + \log a_{H_2O} - \log a_{SH}^*.$$  \hspace{1cm} (19)

The difference in standard free energy changes for the reaction

$$QH + SH = Q + SH_2^*$$  \hspace{1cm} (20)
as measured in solvent S and water can then be written utilizing Equations 10, 12, 13, and 14

\[
\begin{align*}
\alpha_{SH}(Q) &= u_{SH}(Q, SH) - u_{w}(Q, H_2O) \\
&= u_{SH}(Q) - u_{w}(Q) - u_{SH}(SH) + u_{w}(H_2O) \\
&= \alpha_{SH}(Q) + \alpha_{SH} \\
&= -2.3 RT m_{Q}Y_{SH} + \alpha_{SH}
\end{align*}
\]

which is thus related to Equation 2 by a factor of 2.3 RT

\( \Delta pK = \log f_{H} + m_{Q}Y_{SH} \).

Let us examine more closely the function \( \alpha_{S} \). Adding the term \(-u_{w}(H_2O, SH)\) to both sides of Equation 14

\[
\alpha_{S} - u_{w}(H_2O, SH) = u_{w}(H_2O) - u_{SH}(SH) - u_{w}(H_2O, SH) \tag{22}
\]

\[
= u_{w}(H_2O) - u_{SH}(SH) - u_{w}(H_2O) + u_{w}(SH) \\
= -u_{SH}(SH).
\]

If solvent S is a pure compound one obtains

\[
\alpha_{S} = 2.3 RT m_{SH}Y_{SH}^{0} + u_{w}(H_2O, SH). \tag{23}
\]

If solvent S is a mixture, Equation 13 cannot be used since we could not expect to find a suitable constant value for \( m_{SH} \).

In this case \( u_{SH}(SH) \) is a more complicated function which will be derived farther on. If one adds and then subtracts the term \( u_{SH}(H_2O) \) on the right side of Equation 14, which
defines $\alpha_S$, one obtains

$$\alpha_S = u_w(\text{H}_2\text{O}) - u_{\text{SH}}(\text{SH}) + u_{\text{SH}}(\text{H}_2\text{O}) - u_{\text{SH}}(\text{H}_2\text{O})$$  \hspace{1cm} (24)

$$= u_{\text{SH}}(\text{H}_2\text{O}) + u_{\text{SH}}(\text{H}_2\text{O}, \text{SH})$$

$$= 2.3 \cdot \text{RT} \cdot \Sigma_{\text{SH}}(\text{S}) + u_{\text{SH}}(\text{H}_2\text{O}, \text{SH}).$$

It is seen that this relationship is valid regardless of whether or not $S$ is a pure compound or a mixture. Similar relations exist for the function $\beta_{\text{SH}}$. Thus

$$\beta_{\text{SH}} = - u_{\text{SH}}^*(\text{S}^-) + u_w(\text{OH}^-, \text{S}^-)$$  \hspace{1cm} (25)

and for pure solvent $S$

$$\beta_{\text{SH}} = 2.3 \cdot \text{RT} \cdot \Sigma_{\text{SH}}(\text{S}^-) + u_w(\text{OH}^-, \text{S}^-).$$  \hspace{1cm} (26)

Further,

$$\beta_{\text{SH}} = - u_{\text{SH}}^*(\text{OH}^-) + u_{\text{SH}}(\text{OH}^-, \text{S}^-)$$  \hspace{1cm} (27)

$$= 2.3 \cdot \text{RT} \cdot \Sigma_{\text{SH}}(\text{OH}^-) + u_{\text{SH}}(\text{OH}^-, \text{S}^-).$$

It should be noticed that the set of $Y_{\text{SH}}^0$ values in the relation for $\alpha$ is not the same as the set of $Y_{\text{SH}}^-$ values for the $\beta$ relation, but differ because the charge type of the base in question is different.

The problem now is to write an expression for standard free energy change of reaction

$$\text{H}_2\text{O} + \text{S}^- = \text{OH}^- + \text{SH}$$  \hspace{1cm} (28)
as measured in mixed solvent S such that said expression is a function of the m values of the solvent components, Y, and other readily measured or derivable quantities. These expressions then can be inserted into Equations 24 and 27 to obtain relations for comparison with Grunwald's data. This problem will be attacked by utilizing the fact that the molar free energy of a mixture can be considered as the sum of the contributions of each constituent.

$F_Q$ is the standard molar free energy of substance Q in a reference state of infinite dilute solution in solvent SH. However, if Q is a constituent of the solvent, $F_Q$ is the free energy per mole of Q at its particular concentration; thus it is the partial molar free energy of Q.

The standard free energy changes of Reactions 28 and 29 where solvent S is a pure compound, EH, are thus

$$\Delta_H^o (OH^-, E^-) = F_{OH^-} + F_{EH} - F_{H_2O}^0 - F_{E^-}$$

and

$$\Delta_H^o (H_2O, EH) = F_{H_2O}^0 + F_{EH^+} - F_{H_3O^+} - F_{EH}$$

When solvent S is a mixture of water and EH containing $X_E$ mole fraction of EH, the standard molar free energy of solvent S is

$$F_{SH} = X_W F_{H_2O} + X_E F_{EH}$$
This is true, of course, only when ionization of either of the components does not appreciably alter the composition of undissociated solvent. This would not be true, for instance, if EH were a strong acid because very few solvent molecules would consist of undissociated EH. In other words, the ratio of $X_E$ to $X_W$ must be effectively the same after EH is mixed with water as it was before they were mixed. The case of the standard molar free energy of $S^-$ and $S_{H^2}$ ion is not quite as simple. In general, we cannot expect that the ratio of $E^-$ to $OH^-$ ions will be the same as the composition of the bulk solvent. In whatever volume required, one mole of solvent anion (i.e., $E^- + OH^- = Avogadro's number) will contain more or less than mole fraction $X_W OH^-$ ions. If we represent the composition of one mole of solvent anion as being made of $X_W OH^-$ ions and $X_{Pe}E^-$ ions we may write

$$F_{S^-} = X_W^{0} F_{OH^-} + X_E^{0} F_{E^-}$$

(33)

A similar expression can be written for the solvent cation

$$F_{SH_{2}^+} = X_W^{0} F_{H_3O^+} + X_E^{0} F_{EH_{2}^+}$$

(34)

where $X_W^{0}$ and $X_E^{0}$ make up the composition of solvent cation. If $p$ is the difference between $X_W^*$ and $X_W$, then

$$X_W^* = X_W + p$$

(35)

and since
\[ X_W + X_E = 1 \]
\[ X_W^* + X_E^* = 1 \]

then
\[ X_E^* = X_E - p. \]

Similarly, if \( a \) is the difference between \( X_W^0 \) and \( X_W \) then
\[ X_W^0 = X_W + a. \] \hspace{1cm} (36)
\[ X_E^0 = X_E - a. \]

Thus Equations 33 and 34 become Equations 37 and 38 which define \( F_S^- \) and \( F_{SH2}^+ \)
\[ F_S^- = (X_W + p) F_{OH^-} + (X_E - p) F_{E^-} \] \hspace{1cm} (37)

and
\[ F_{SH2}^+ = (X_W + a) F_{H_3O^+} + (X_E - a) F_{EH2^+}. \] \hspace{1cm} (38)

Thus the expression for the standard free energy change of Reaction 28 for a mixed solvent becomes
\[ u_{SH}(OH^-, S^-) = F_{OH^-} + X_W F_{H_2O} + X_E F_{EH} - F_{H_2O} - (X_W - p) F_{OH^-} - (X_E - p) F_{E^-} \]
\[ = X_E (F_{OH^-} + F_{EH} - F_{H_2O} - F_{E^-}) - p(F_{OH^-} - F_{E^-}) \]
\[ = X_E u_{SH}(OH, E^-) - p(F_{OH^-} - F_{E^-}). \]
However, adding and subtracting $F_{EH}$ and $F_{H_2O}$ and using
Equation 30

$$u_{SH}(OH^-, S^-) = (X_E - p) u_{SH}(OH^-, E^-) + p(F_{EH} - F_{H_2O}). \quad (40)$$

This relationship merely states that the standard free energy for the transfer of proton from $OH^-$ to $S^-$ is proportional to the number of $E^-$ ions in the medium times the difference between the molar free energies of $OH^-$ and $E^-$ plus a term for the difference between the free energies of the solvent constituents.

By a similar treatment, it can be seen that

$$u_{SH}(H_2O, SH) = (X_E - q) u_{SH}(H_2O, EH) - q(F_{EH} - F_{H_2O}). \quad (41)$$

Substituting these relations into Equations 24 and 27 one obtains

$$\beta_S = -u_{SH}^*(H_2O) + (X_E - q) u_{SH}(H_2O, EH) - q(F_{EH} - F_{H_2O}). \quad (42)$$

and

$$\beta_S = -u_{SH}^*(OH) + (X_E - p) u_{SH}(OH^-, E^-) + p(F_{EH} - F_{H_2O}). \quad (43)$$

Utilizing the relationships,

$$u_{SH}(H_2O, EH) - u_{W}(H_2O, EH) = u_{SH}(H_2O) - u_{W}(H_2O) - u_{SH}(EH) + u_{W}(EH) \quad (44)$$

$$= u_{SH}^*(H_2O) - u_{SH}^*(EH)$$
and,
\[ u_{SH}(OH^-, E^-) - u_W(OH, E^-) = u_{SH}(OH) - u_{SH}(E) + u_W(E) \] (45)
\[ = u_{SH}^*(OH) - u_{SH}(E^-). \]

Equations 41 and 42 become
\[ \alpha_S = -u_{SH}^*(H_2O) + (X_E - q)(u_{SH}^*H_2O) - u_{SH}^*(EH) + u_W(H_2O, EH) - q(F_{EH} - F_{H_2O}) \]
\[ = (X_E - q) u_{SH}^*(H_2O) - (X_E - q) u_{SH}^*(EH) + (X_E - q) u_W(H_2O, EH) - q(F_{EH} - F_{H_2O}) \]

and
\[ \beta_S = -(X_W + p) u_{SH}^*(OH) - (X_E - p) u_{SH}^*(E^-) + (X_E - p) u_W(OH^-, E^-) + p(F_{EH} - F_{H_2O}). \] (47)

Except for the values of \( p \) and \( q \), we now have \( \alpha_S \) and \( \beta_S \) expressed in terms of measures of derivable quantities. The quantities \( u_{SH}(H_2O, EH) \) and \( u_{SH}(OH^-, E^-) \) are such derivable quantities and also, in principle at least, are measurable.

The quantities \( q \) and \( p \) are related to these functions. Thus,
\[ u_{SH}(H_2O, EH) = 2.3 \, RT \, p_{K_{48}}^S \] (48)
where \( p_{K_{48}}^S \) is related to the reaction,
\[ H_3O^+ + EH = H_2O + EH_2^+ \] (49)
as measurable in solvent $SH$ and

$$u_{SH}(\text{OH}^-, E^-) = 2.3 \, RT \, pK_{50}^S$$

(50)

where $pK_{50}^S$ is related to the reaction,

$$H_2O + E^- = \text{OH}^- + EH$$

(51)

as measured in solvent $SH$. But, under conditions such that $c_w = a_w$

$$K_{48}^W = \frac{X_W(X_E - q)}{X_E(X_W + q)}$$

(52)

and

$$K_{50}^W = \frac{X_E(X_W + p)}{X_W(X_E - p)}$$

(53)

Thus

$$q = \frac{X_W X_E (1 - K_{48}^W)}{X_E K_{48}^W + X_W}$$

(54)

and

$$p = \frac{X_E X_W (K_{50}^W - 1)}{X_E + X_W K_{50}^W}$$

(55)

If these relations are valid we should be able to derive suitable $m$ values for water and ethanol, using Grunwald's data for this system. After dividing through by the factor $2.3 \, RT$, Equation 45 can be written
\[
\frac{\alpha_S}{2.3\ RT} \cdot q(\Delta G_{\text{H}_2O} - \Delta G_{\text{H}_2O}) - m_{H_2O}Y_{SH}^0 = \frac{(m_{EH} - m_{H_2O})Y_{SH}^0}{X_E - q} + pK_{48}^W
\]

where \( pK_{48}^W \) is associated with Reaction 49 as measured in water. Similarly Equation 47 can be written

\[
\frac{-\beta}{2.3\ RT} \cdot \frac{D(\Delta G_{\text{H}_2O})}{\Delta G_{\text{H}_2O}} + m_{OH}Y_{SH}^- = \frac{(m_{OH} - m_{E})Y_{SH}^-}{X_E - p} + pK_{50}^W
\]

where \( pK_{50}^W \) is associated with Reaction 51 as measured in water. It can be seen that the right hand side of Equation 56 is equal to \( pK_{48}^S \) since from Equation 43

\[
u_{SH}(H_2O, EH) = u_{SH}(H_2O) - u_{SH}(EH) + u_{W}(H_2O, EH)
\]

\[
pK_{48}^S = (m_{EH} - m_{H_2O})Y_{SH}^0 + pK_{48}^W
\]

Similarly, the right side of Equation 57 is equal to \( -pK_{50}^S \) since from Equation 45

\[
u_{SH}(OH^-, E^-) = u_{SH}(OH^-) - u_{SH}(E^-) + u_{W}(OH^-, E^-)
\]

\[
-pK_{50}^S = (m_{OH} - m_{E^-})Y_{SH}^- - pK_{50}^W
\]
Solution for the Solvent "m" Values

Utilizing Equations 58 and 54, Equation 56 can be written in the form

\[ a = (bz + c) 10^{-z} \quad (60) \]

where

\[ a = \frac{\beta S}{2.3 \, RT} x_w + x_{E}x_w \frac{(F_{EH} - F_{H2O})}{2.3 \, RT} - x_{W}^m H_{2O}Y_{SH} \]

\[ b = x_{E} \]

\[ c = \frac{-\alpha S}{2.3 \, RT} x_{E} + x_{E}x_{W} \frac{(F_{EH} - F_{H2O})}{2.3 \, RT} + x_{E}^{m} H_{E}Y_{SH} \]

\[ z = pK_{48}^{S} \]

Utilizing Equations 59 and 55, Equation 57 can be written in the form

\[ a' = b'z' + c'10^{z'} \quad (61) \]

where

\[ a' = \frac{\beta S}{2.3 \, RT} x_{E} - x_{E}x_{W} \frac{(F_{EH} - F_{H2O})}{2.3 \, RT} + x_{W}^{m} H_{Y}Y_{SH} \]

\[ b' = x_{E} \]

\[ c = \frac{\alpha S}{2.3 \, RT} x_{W} - x_{E}x_{W} \frac{(F_{EH} - F_{H2O})}{2.3 \, RT} - x_{E}^{m} H_{Y}Y_{SH} \]

\[ z' = - pK_{50}^{S} \]
The functions \( \frac{\lambda}{2.3 \, RT} \) and \( -\frac{S}{2.3 \, RT} \) are obtained from Grunwald's data and Equations 16 and 19. This is possible since in each case the applicable activity coefficients are equal to one. Therefore, one need only to calculate molar concentration of solvent form density data and the relation 62

\[
\sum_{SH} = \frac{1000 \, d}{18Xw + 46Xe}
\]  
(62)

These data are given in Table 1.

The function \( F_{EH} - F_{H2O} \) is obtained from the standard free energy of formation of pure ethanol and water from their elements, together with activity coefficients obtained from vapor pressure measurements according to the usual relations

\[
F_{EH} = F_{EH}^0 + 2.3 \, RT \log
\]  
(63)

\[
F_{H2O} = F_{H2O}^0 + 2.3 \, RT \log.
\]  
(64)

These data are tabulated in Table 2.

The data in Tables 1 and 2 can be utilized to calculate the parameters \( m_{H2O} \) and \( m_{EH} \) from Equation 60 subject to the restriction that

\[
z = (m_{EH} - m_{H2O})Ys^0 + \lambda_1 - m_{EH}
\]  
(65)

where \( \lambda_1 \) is the value of \( \frac{\lambda}{2.3 \, RT} \) for pure ethanol. This is so since Grunwald chose \( Ys^0 = 1 \) for pure ethanol. Therefore, in
Table 1. Data for calculation of $\alpha$ and $\beta$

<table>
<thead>
<tr>
<th>Wt. % EtOH</th>
<th>0</th>
<th>20</th>
<th>35</th>
<th>50</th>
<th>65</th>
<th>80</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_e$</td>
<td>0</td>
<td>0.091</td>
<td>0.177</td>
<td>0.286</td>
<td>0.426</td>
<td>0.615</td>
<td>1.000</td>
</tr>
<tr>
<td>$d_{4/25}^1$</td>
<td>0.9971</td>
<td>0.9664</td>
<td>0.9415</td>
<td>0.9099</td>
<td>0.8753</td>
<td>0.8391</td>
<td>0.7851</td>
</tr>
<tr>
<td>$C_{SH}$</td>
<td>55.4</td>
<td>47.0</td>
<td>41.0</td>
<td>35.0</td>
<td>29.2</td>
<td>23.8</td>
<td>17.1</td>
</tr>
<tr>
<td>log $C_{SH}$</td>
<td>1.744</td>
<td>1.682</td>
<td>1.613</td>
<td>1.544</td>
<td>1.466</td>
<td>1.377</td>
<td>1.232</td>
</tr>
<tr>
<td>log $C_{H_2O} - log C_{SH}$</td>
<td>0</td>
<td>0.062</td>
<td>0.131</td>
<td>0.210</td>
<td>0.278</td>
<td>0.367</td>
<td>0.512</td>
</tr>
<tr>
<td>$y^{02}$</td>
<td>0</td>
<td>0.057</td>
<td>0.136</td>
<td>0.266</td>
<td>0.379</td>
<td>0.570</td>
<td>1.000</td>
</tr>
<tr>
<td>$-y^{-2}$</td>
<td>0</td>
<td>0.349</td>
<td>0.596</td>
<td>0.816</td>
<td>0.924</td>
<td>0.964</td>
<td>1.000</td>
</tr>
<tr>
<td>log $f_{H}^2$</td>
<td>0</td>
<td>0.01</td>
<td>0.04</td>
<td>0.25</td>
<td>0.54</td>
<td>1.15</td>
<td>4.71</td>
</tr>
<tr>
<td>log $f_{OH}^2$</td>
<td>0</td>
<td>0.32</td>
<td>0.53</td>
<td>0.63</td>
<td>0.75</td>
<td>0.76</td>
<td>0.80</td>
</tr>
<tr>
<td>$\alpha/2.3 , RT$</td>
<td>0</td>
<td>-0.052</td>
<td>-0.091</td>
<td>0.050</td>
<td>0.262</td>
<td>0.783</td>
<td>4.20</td>
</tr>
<tr>
<td>$-\beta/2.3 , RT$</td>
<td>0</td>
<td>0.258</td>
<td>0.399</td>
<td>0.430</td>
<td>0.472</td>
<td>0.393</td>
<td>0.288</td>
</tr>
</tbody>
</table>


Table 2. Data for Equations 60 and 61

<table>
<thead>
<tr>
<th>Wt. % EtOH</th>
<th>0</th>
<th>20</th>
<th>35</th>
<th>50</th>
<th>65</th>
<th>80</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\log \gamma_{EH} - \log \gamma_{W}$</td>
<td>0.576</td>
<td>0.471</td>
<td>0.351</td>
<td>0.295</td>
<td>0.015</td>
<td>-0.171</td>
<td>-0.339</td>
</tr>
<tr>
<td>$\mathcal{F}<em>{EH}^0 - \mathcal{F}</em>{H_2O}^{2.5 \mathcal{R} T}$</td>
<td>8.977</td>
<td>8.872</td>
<td>8.752</td>
<td>9.696</td>
<td>8.416</td>
<td>8.230</td>
<td>8.022</td>
</tr>
<tr>
<td>$a + X_{mEH}^0Y_0$</td>
<td>0</td>
<td>0.687</td>
<td>1.104</td>
<td>1.811</td>
<td>2.206</td>
<td>2.251</td>
<td>0</td>
</tr>
<tr>
<td>$c - X_{mEH}^0Y_0$</td>
<td>0</td>
<td>0.739</td>
<td>1.290</td>
<td>1.761</td>
<td>1.943</td>
<td>1.468</td>
<td>--</td>
</tr>
<tr>
<td>$a' - X_{mEH}^0Y_0$</td>
<td>0</td>
<td>-0.710</td>
<td>-1.203</td>
<td>-1.652</td>
<td>-1.867</td>
<td>-1.710</td>
<td>--</td>
</tr>
<tr>
<td>$c' + X_{mEH}^0Y_0$</td>
<td>0</td>
<td>-0.970</td>
<td>-1.603</td>
<td>-2.082</td>
<td>-2.308</td>
<td>-2.100</td>
<td>0</td>
</tr>
</tbody>
</table>


pure ethanol Equation 23 becomes

\[ l = m_{EH} + \frac{d K_{48}}{W} \]  

Substitution of this relation into the right hand side of Equation 56 which is equal to \( z \) gives Equation 65. Similarly, Equation 61 can be solved subject to the restriction

\[ z' = (m_{0H} - m_{E})Y_S^- - \beta_1 - m_E \]  

where \( \beta_1 \) is the value of \( \frac{-\beta}{2.3RT} \) for pure ethanol, since \( Y_S^- \) was chosen equal to minus one by Grunwald for pure ethanol.

Thus Equation 26 becomes

\[ l = -m_E + \frac{d K_{50}}{W} \]  

Substitution of this relation into the right side of Equation 57 which is equal to \( z' \) gives Equation 67.

The actual process used to solve the above expression was to solve Equation 60 for \( z \) with various arbitrary choices of \( m_{H_2O} \). These data are tabulated in Table 3 and plotted in Figure 2 at each mole fraction of ethanol. In Figure 3 are plotted values of \( z \) versus \( Y_S \) for each arbitrary choice of \( m_{H_2O} \). According to the restraint 65, this plot should be a straight line for proper choice of \( m_{H_2O} \). In addition, the intercept at \( Y = 1 \) must be equal to \( 1 - m_{H_2O} \). Except for the point of \( X_E = 0.091 \), this holds quite well for a value of \( m_{H_2O} \) equal to something slightly less than 3.9. Also, the intercept on \( Y = 0 \) should be equal to \( 1 - m_{EH} \). Thus \( m_{EH} \) is
Table 3. Values of $z$ for various values of $m_{H_2O}$

<table>
<thead>
<tr>
<th>$X_E$</th>
<th>.091</th>
<th>.177</th>
<th>.266</th>
<th>.426</th>
<th>.615</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m_{H_2O} = 0$</td>
<td>$z$</td>
<td>$z$</td>
<td>$z$</td>
<td>$z$</td>
<td>$z$</td>
</tr>
<tr>
<td>$m_{H_2O} = 0$</td>
<td>.033</td>
<td>.070</td>
<td>-.013</td>
<td>-.061</td>
<td>-.230</td>
</tr>
<tr>
<td>$m_{H_2O} = 1$</td>
<td>.073</td>
<td>.127</td>
<td>.058</td>
<td>.027</td>
<td>-.056</td>
</tr>
<tr>
<td>$m_{H_2O} = 2$</td>
<td>.116</td>
<td>.190</td>
<td>.143</td>
<td>.116</td>
<td>.089</td>
</tr>
<tr>
<td>$m_{H_2O} = 3$</td>
<td>.161</td>
<td>.260</td>
<td>.218</td>
<td>.210</td>
<td>.222</td>
</tr>
<tr>
<td>$m_{H_2O} = 4$</td>
<td>.210</td>
<td>.340</td>
<td>.312</td>
<td>.309</td>
<td>.352</td>
</tr>
<tr>
<td>$m_{H_2O} = 5$</td>
<td>.266</td>
<td>.432</td>
<td>.419</td>
<td>.418</td>
<td>.484</td>
</tr>
<tr>
<td>$m_{H_2O} = 6$</td>
<td>.332</td>
<td>.543</td>
<td>.550</td>
<td>.543</td>
<td>.626</td>
</tr>
<tr>
<td>$m_{H_2O} = 7$</td>
<td>.404</td>
<td>.678</td>
<td>.714</td>
<td>.678</td>
<td>.789</td>
</tr>
<tr>
<td>$m_{H_2O} = 8$</td>
<td>.484</td>
<td>1.057</td>
<td>1.151</td>
<td>.888</td>
<td>.992</td>
</tr>
</tbody>
</table>
Figure 2. $z$ versus $m_{H_2O}$. 
also about 3.9.

A similar treatment was carried out for Equation 61. The data are given in Table 4 and plotted in Figures 4 and 5. A value of $m_\text{OH}$ about equal to 0.32 quite adequately fits the requirements and $m_\text{E}$ is about equal to 0.43.

A More General Treatment

In general, the assumption involved in writing Equation 32 will not be valid. We can define a quantity $r$ in a manner similar to the definitions of $p$ and $q$, thus

$$F_{\text{SH}} = (X_W + r) F_{\text{H}_2\text{O}} + (X_E - r) F_{\text{E}_2\text{H}}.$$  \hspace{1cm} (69)

With this relation one can treat mixtures of water and strong or relatively strong acids.

It is also desirable to treat solutions of strong acids in mixed solvents. In order to do this, equations for $\lambda$ and $\beta$ must be obtained for at least three components. This is done in the Appendix, where the general case or $n$ components in the solvent is treated together with considerations mentioned above about ionization of the solvent. The treatment follows the same pattern as given previously for binary mixtures. One obtains for $\lambda$ and $\beta$ the relations

$$\lambda = -u_{\text{SH}}^*(\text{H}_2\text{O}) + \sum (X_1 + q_1) \left[ u_{\text{SH}}^*(\text{H}_2\text{O}) - u_{\text{SH}}^*(Q_1\text{H}) + u_{\text{W}}(\text{H}_2\text{O}, Q_1\text{H}) \right] - \sum (r_1 - q_1) F_{Q_1\text{H}}$$ \hspace{1cm} (70)
<table>
<thead>
<tr>
<th>$X_E$</th>
<th>.091</th>
<th>.177</th>
<th>.286</th>
<th>.426</th>
<th>.615</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m_{OH}$</td>
<td>$z'$</td>
<td>$z'$</td>
<td>$z'$</td>
<td>$z'$</td>
<td>$z'$</td>
</tr>
<tr>
<td>$m_{OH} = 0$</td>
<td>-.143</td>
<td>-.129</td>
<td>-.109</td>
<td>-.102</td>
<td>-.106</td>
</tr>
<tr>
<td>$m_{OH} = 0.1$</td>
<td>-.126</td>
<td>-.115</td>
<td>-.089</td>
<td>-.081</td>
<td>-.079</td>
</tr>
<tr>
<td>$m_{OH} = 0.2$</td>
<td>-.109</td>
<td>-.096</td>
<td>-.068</td>
<td>-.060</td>
<td>-.052</td>
</tr>
<tr>
<td>$m_{OH} = 0.3$</td>
<td>-.090</td>
<td>-.078</td>
<td>-.048</td>
<td>-.038</td>
<td>-.026</td>
</tr>
<tr>
<td>$m_{OH} = 0.4$</td>
<td>-.070</td>
<td>-.057</td>
<td>-.027</td>
<td>-.017</td>
<td>-.001</td>
</tr>
<tr>
<td>$m_{OH} = 0.5$</td>
<td>-.051</td>
<td>-.036</td>
<td>-.007</td>
<td>+.005</td>
<td>+.024</td>
</tr>
<tr>
<td>$m_{OH} = 0.6$</td>
<td>-.031</td>
<td>-.017</td>
<td>+.016</td>
<td>+.026</td>
<td>+.048</td>
</tr>
</tbody>
</table>
Figure 5: \( z^1 \) versus \( Y' \).
and

\[ \Theta = -u_{SH}(OH) + \sum (x_i + p_i) \left[ u_{SH}^*(OH) - u_{SH}^*(Q_i^-) \right] + u_W(OH^-, Q_i^-) \sum (r_i - p_i) F_{Q_iH} \]  

(71)

where the \( q_i, p_i, \) and \( r_i \) are subject to the restrictions.

**Ethanol-Water-Strong Acid Solution**

Let us now utilize the above equation to examine the case of a ternary mixture of water, ethanol, and a relatively small concentration of strong acid. The latter specification is made so that one will not be too far from the range in which calculation of ionic activity coefficients can be made by the Debye-Hückel laws, as may be necessary in calculating the quantities \( q_i, p_i, \) and \( r_i \). The following approximations can be made

\[ - (r_E + r_W) = r_A \approx -X_A \]  

(72)

\[ - (q_E + q_W) = q_A = -X_A \]  

(73)

\[ - (p_E + p_W) = p_r \approx X_E + X_W . \]

The first states that virtually all of the strong acid \( AH \) added to the mixture ionizes. The second states that no species \( AH_2^+ \) is formed, and the last states that virtually all of the anions in solution are \( A^- \) ions. Equation 70 can then
be written

\[
\kappa = -u_{\text{SH}}^*(\text{H}_2\text{O}) + (x_{\text{E}} + q_{\text{E}}) u_{\text{SH}}^*(\text{H}_2\text{O}) - u_{\text{SH}}^*(\text{EH}) + u_{\text{W}}(\text{H}_2\text{O}, \text{EH}) - (r_{\text{W}} - q)F_{\text{H}_2\text{O}} - (r_{\text{E}} - q_{\text{E}})F_{\text{EH}},
\]

(74)

However, from Equation 73

\[
(r_{\text{E}} + r_{\text{W}}) = (q_{\text{E}} + q_{\text{W}})
\]

(75)

or

\[
(r_{\text{E}} - q_{\text{E}}) = -(r_{\text{W}} - q_{\text{W}}).
\]

Thus Equation 74 becomes

\[
\kappa = -u_{\text{SH}}^*(\text{H}_2\text{O}) + (x_{\text{E}} + q_{\text{E}}) u_{\text{SH}}^*(\text{H}_2\text{O}) - u_{\text{SH}}^*(\text{EH}) + u_{\text{W}}(\text{H}_2\text{O}, \text{EH}) + (r_{\text{W}} - q_{\text{W}})(F_{\text{EH}} - F_{\text{H}_2\text{O}}).
\]

(76)

It is seen that this expression is essentially the same as Equation 46 except that \(-q\) is replaced by \(q_{\text{E}}\) in the second term, and \(-q\) is replaced by \((r_{\text{W}} - q_{\text{W}})\) in the last term. In general, for relatively dilute solutions of strong acid \((r_{\text{W}} - q_{\text{W}}) \sim q\) and \(q_{\text{E}} \sim q\) so that Equation 76 is essentially the same as Equation 46. For example, for a 0.1 molar solution of HCl in 65 per cent ethanol water, assuming the density of this solution to be equal to the density in the absence of HCl,
Examination of the Hammett Acidity Function

In order to find a relationship between the Hammett acidity function and Grunwald's treatment of acid–base reactions in mixed solvents, it will be convenient to examine closely the condition required in order that a Hammett acidity function be defined. This condition is stated as

\[ \log \frac{f_B}{f_{BH}} = d \]  

(77)

where \( f_B \) and \( f_{BH} \) are degenerate activity coefficients of base B and its conjugate acid, respectively, and \( d \) is a constant. This condition must be met for all bases, i.e., \( d \) is a constant independent of the base under consideration. There is, however, no restriction on \( d \) with regard to the solvent. Equation 1 can be rewritten

\[ \log \frac{a_B^*}{a_{BH}} - \log \frac{a_B^*}{a_B} = d \]  

(78)

where the \( a^* \) represents activities in any solvent \( S \) and the \( a \) represents activities in water. Thus the Hammett acidity function which is written

\[ H^0 = - \log \frac{a_H f_B}{f_{BH}} \]  

(79)
can also be written

$$H^0 = -\log f_H^* - d - \log c_H.$$  \hspace{1cm} (80)

For convenience let us define

$$H^* = \log f_H^* - d$$  \hspace{1cm} (81)

which is just the Hammett acidity function without the concentration term. The term by $f_H$ is degenerate activity coefficient of hydrogen ion in solvent $S$ and may be represented by

$$\log f_H^* = \log \frac{f_{SH}^*}{f_{SH}}$$  \hspace{1cm} (82)

or

$$\log f_H^* = \log \frac{a_{SH}^*}{a_{SH}} - \log \frac{a_{H2O}^*}{a_{H2O}}.$$  \hspace{1cm} (83)

Now, if Equation 78 holds for all bases, there seems to be no good reason to exempt water. Thus,

$$\log \frac{a_{H2O}^*}{a_{H2O}} - \log \frac{a_{H3O}^*}{a_{H3O}} = d.$$  \hspace{1cm} (84)

Substituting Equations 53 and 84 into Equation 81 one obtains

$$H^* = -\log \frac{a_{SH}^*}{a_{SH}^*} + \log \frac{a_{H2O}^*}{a_{H3O}^*} = pK_{S85}.$$  \hspace{1cm} (85)
Thus $H^*$ is equal to the pK for the reaction

$$H_3O^+ + SH = H_2O + SH_2^+$$

(86)

as measured in solvent $S$. Equation 80 may now be written

$$H^0 = pK_{85}^S - \log C_H.$$  \hspace{1cm} (87)

Thus, if $H^0$ is plotted versus $\log C_H$ for any solvent a straight line should be obtained with a slope of one. The intercept when $C_H = 1$ must be equal to $pK_{85}^S$. In Figure 6 is shown such a plot for water, ethanol, acetone, and dioxan taken from Braude (7). It is seen that for all solvents the slope is very close to one as predicted, except for dioxan which has a slope of 0.5. It is observed, however, that some of the lines deviate at higher acid concentration. This can be accounted for by $pK_{85}^S$ not being independent of the concentration of acid. Indeed, one would not expect this to be so. This point will be taken up again further on, but unfortunately with no completely satisfying explanation.

In the light of the discussion of the Hammett acidity function given in this section, it can be seen that this function is not necessarily a measure of the difference in proton activity between pure water and some other solvent $S$. Indeed, if the assumptions involved are valid, it is only generally true that the Hammett acidity function is a measure of the difference between the basicity of a water molecule in
Figure 6. Hammett acidity function versus logarithm HCl concentrate.
the case of mixed solvents.

If the quantity of $d$ in Equation 78 and Equation 84 is essentially constant under all conditions, then the two statements above are equivalent. However, it will be shown in the next section that $d$ is a function of the solvent, so that only the second statement is true.

Relations between Hammett Acidity Function and Grunwald Treatment of Acids and Bases

The quantity $pK_{85}^S$ can be obtained from Equation 24.

Thus,

$$pK_{85}^S = \frac{\alpha S}{2.3 RT} - m_{W} Y_{SH}^0 = H^*.$$  

(88)

It is seen from the above expression that $d$ is represented by the quantity $m_{W} Y$ from comparison with Equation 81, since the definition of $\log f_H^*$ in Equation 83 is essentially the same as the definition of $\alpha$ in Equations 16 and 7. Thus the $d$ will change with solvent as $Y_{SH}^0$.

In Figure 7 are plotted values of $H^*$ versus mole composition of water ethanol from data by Braude (8) at 0.1 molar and 1 molar HCl, together with values of the function $\alpha - m_{W} Y$ using Grunwald's data and a value of 3.9 for $m_{W}$. In a comparison of these data it is assumed that the $Y_{SH}^0$ values are not generally affected by small concentrations of
Figure 7. Comparison of H* and the function $\lambda_{mH_2OY^0}$ versus mole fraction ethanol.
strong acid.

It can be seen that agreement between the data for 0.1M and the calculated values are quite good up to \( X_E = 0.5 \). The values for 1 molar are all too high. This is probably in greater part correlated with the fact that a large deviation from linearity occurs for water in Figure 6 at this concentration. The lack of agreement of the calculated curve from experimental value for 0.1M HCl is significantly outside of experimental error. It was observed in the discussion of Equation 76 that \( \alpha \) is not entirely independent of the concentration of strong acid. The conditions are in the right direction but are much too small to be significant. The most likely explanation of this deviation is that the HCl is incompletely dissociated at higher concentrations of ethanol. If the HCl is not completely dissociated then Equation 76 is not valid, since assumptions in Equation 73 become

\[
- (r_W + r_E) = r_A \approx X_A + (1 - \gamma)X_A
\]

\[
- (q_W + q_E) = q_r = -X_A
\]

where \( \gamma \) is the degree of dissociation of strong acid. Equation 70 then becomes

\[
S = - u_{SH}^{*}(H_2O) + (X_E + q_E) u_{SH}^{*}(H_2O) - u_{SH}^{*}(EH) + u_W(H_2O, EH) + (r_W - q_r)(F_{EH} - F_{H_2O}) - (1 - \gamma)X_A
\]

\[
(F_{EH} - F_{AH})
\]
Thus Equation 89 differs from Equation 76 only by the addition of the last term. One can estimate the error introduced by neglecting this last term if a suitable value of \( F_{AH} \) is assumed. The standard free energy of formation of HCl from its elements is given in the International Critical Tables as about 22.7 kcal/mole. The standard free energy of HCl in infinitely dilute aqueous solutions is about 31.3 kcal/mole.

Assuming that it is in the neighborhood of 23 kcal/mole and using the value 45 kcal/mole for the standard free energy of ethanol, let us estimate the degree of association necessary to account for the deviation of the experimental values of Braude at 0.1M HCl in 80 per cent by weight ethanol. If the change in density on adding acid is ignored, the mole fraction of HCl is about 0.04. The deviation of Braude's data from the value calculated using Grunwald's data is about two tenths of a unit. Thus \( \alpha \) is

\[
0.2 = (1 - \alpha) \cdot 0.04 \cdot \frac{70000}{2.3 \cdot RT} \cdot (1 - \alpha) \cdot 0.04 \cdot 50.
\]

The value of \( \alpha \) is in the neighborhood of 0.9, which does not seem at all unreasonable.
Bibliography


Appendix

If $p_1$ is the difference between $X_i^*$ and $X_i$, where $X_i^*$ is the mole fraction of anion $Q_i^-$ in one mole of solvent anion and $X_i$ is the amount of $Q_iH$ added to form one mole of the total mixture, one can write,

$$F_5 = \sum_{i=1}^{n} (X_i + p_i)F_{Q_i^-}$$

where the $p_i$'s are subject to the restriction

$$p_j = -\sum_{i=1}^{n} p_i \sigma_j \quad \sigma_j = 1$$

or equivalently

$$\sum_{i=1}^{n} p_i = 0$$

Analogously for the solvent cation

$$F_{SH^2+} = -\sum_{i=1}^{n} (X_i + q_i)F_{Q_iH^2+}$$

in which the $q_i$ are restricted by

$$\sum_{i=1}^{n} q_i = 0$$
or
\[ q_j = \sum_{i=1}^{n} q_i \varepsilon_i^j \]  
(6)

and also for the undissociated molecules of the solvent
\[ F_{SH} = \sum_{i=1}^{n} (X_i + r_i)F_{Q_1H} \]  
(7)

where \( r_i \) is restricted by
\[ \sum_{i=0}^{n} r_i = 0 \]  
(8)

or
\[ r_j = - \sum_{i=1}^{n} r_i \varepsilon_i^j \]  
(9)

Thus one can write
\[ u_{SH}(OH, S^-) = F_{OH^-} + \sum_{i=1}^{n} (X_i + r_i)F_{Q_1H} - F_{H_2O} - \]  
\[ \sum (X_i + p_i)F_{Q_1}^- \]  
(10)

since
\[ X_i = 1 \]

\[ = \sum X_i F_{OH^-} + \sum X_i F_{Q_1H} - \sum X_i F_{H_2O} - \sum X_i F_{Q_1}^- + \]  
\[ \sum r_i F_{Q_1H} - \sum p_i F_{Q_1}^- \]
\[
= \sum x_i (F_{OH^-} + F_{Q_1} - F_{H_2O} - F_{Q_1^-}) + \sum r_1 F_{Q_1} - \sum p_1 F_{Q_1^-}
\]

\[u_{SH}(OH, S^-) = \sum x_i u_{SH}(OH^-, Q_1^-) + \sum r_1 F_{Q_1} - \sum p_1 F_{Q_1^-}.
\]

The term
\[
\sum p_1 F_{Q_1^-} = p_{OH} F_{OH} + \sum p_1 F_{Q_1^-} \sum_{OH} \tag{11}
\]

and since
\[
p_{OH} = - \sum p_1 \sum_{OH} \tag{12}
\]

\[
\sum p_1 F_{Q_1^-} = - \sum p_1 F_{OH} \sum_{OH} + \sum p_1 F_{Q_1^-} \sum_{OH} \tag{12}
\]

\[
= - \sum p_1 (F_{OH^-} - F_{Q_1^-}) \sum_{OH} \tag{12}
\]

However,
\[
F_{OH^-} - F_{Q_1} = F_{OH} + F_{Q_1} - F_{Q_1^-} - F_{H_2O} - F_{Q_1} + F_{H_2O}
\]

\[
= u_{SH}(OH^-, Q_1^-) + (F_{H_2O} - F_{Q_1^-}) \tag{13}
\]

Thus 12 becomes
\[
\sum p_1 F_{Q_1^-} = - \sum p_1 u_{SH}(OH, Q_1^-) \sum_{OH} - \sum p_1 (F_{H_2O} - F_{Q_1^-}) \sum_{OH} \tag{12}
\]
Since $u_{SH}(OH, OH) = 0$ the term
\[ + \sum_{i} p_{1} u_{SH}(OH, Q_{1}^-) \sum_{i} \quad = + \sum_{i} p_{1} u_{SH}(OH^-, Q_{1}^-) \] (15)

the term
\[ - \sum_{i} p_{1} (F_{H2O} - F_{Q_{1}H}) \sum_{i} \quad = - \sum_{i} p_{1} F_{H2O} \sum_{i} + \] (16)
\[ \quad \sum_{i} p_{1} F_{Q_{1}H} \sum_{i} \quad \]
\[ = p_{OH} F_{H2O} \sum_{i} \quad \sum_{i} p_{1} F_{Q_{1}H} \]
\[ = \sum_{i} p_{1} F_{Q_{1}H} \]

thus 14 becomes
\[ \sum p_{1} F_{Q_{1}^-} = - \sum p_{1} u_{SH}(OH^-, Q_{1}^-) * \sum p_{1} F_{Q_{1}H} \] (17)

and 10 becomes
\[ u_{SH}(OH, S^-) = \sum (x_{1} * p_{1}) u_{SH}(OH, Q_{1}^-) * \sum (r_{1} - \]
\[ p_{1})^{F_{Q_{1}H} ,} \] (18)
By a similar treatment one also obtains

\[ u_{\text{SH}}(H_2O, \text{SH}) = \sum (X_1 + q_1)u_{\text{SH}}(H_2O, Q_1 H) - \sum (r_1 - q_1)F_{Q_1 H}, \]  

(19)

Introducing these relations into Equations 24 and 27 of the text

\[ \alpha = - u_{\text{SH}}^*(H_2O) + \sum (X_1 + q_1)u_{\text{SH}}^*(H_2O, Q_1 H) - \sum (r_1 - q_1)F_{Q_1 H}, \]  

(20)

and

\[ \beta = - u_{\text{SH}}^*(\text{OH}) + \sum (X_1 + p_1)u_{\text{SH}}^*(\text{OH}, Q_1^-) + \sum (r_1 - p_1)F_{Q_1 H}, \]  

(21)

using the relation

\[ u_{\text{SH}}(H_2O, Q_1 H) = u_{\text{SH}}^*(H_2O) - u_{\text{SH}}^*(Q_1 H) + u_w(H_2O, Q_1 H), \]  

(22)

and

\[ u_{\text{SH}}(\text{OH}, H_2O) = u_{\text{SH}}^*(\text{OH}) - u_{\text{SH}}^*(Q_1^-) + u_w(\text{OH}^-, Q_1^-). \]  

(23)

Equations 20 and 21 become

\[ \alpha = - u_{\text{SH}}^*(H_2O) + \sum (X_1 + q_1) \left[ u_{\text{SH}}^*(H_2O) - u_{\text{SH}}^*(Q_1 H) + u_w(H_2O, Q_1 H) \right] - \sum (r_1 - q_1)F_{Q_1 H}, \]  

(24)

and
\[
\beta = - u_{SH}^{\#}(OH) + \sum (x_1 + p_1) \left[ u_{SH}^{\#}(OH) - u_{SH}^{\#}(Q_1^-) + u_w(OH, Q_1^-) \right] + \sum (r_1 - p_1) F Q_1 H ,
\]

(25)

The quantities \( q_1, p_1, \) and \( r_1 \) are not independent of each other. The \((n - 1)\) independent \( p_1 \)'s, the \((n - 1)\) independent \( q_1 \)'s and the \((n - 1)\) independent \( r_1 \)'s are related by equation of the type

\[
u_{SH}^{\#}(OH^-, Q_1^-) = - \log \frac{a_{OH^-} a_{Q_1 H}}{a_{H_2O} a_{Q_1^-}}
\]

(26)
of which there are \((n - 1)\)

\[
u_{SH}^{\#}(H_2O, Q_1 H) = - \log \frac{a_{H_2O} a_{Q_1 H^2+}}{a_{H_3O^+} a_{Q_1 H}}
\]

(27)
of which there are \((n - 1)\), and any \((n - 1)\) equation of the type

\[
u_{SH}^{\#}(Q_1^-, Q_j H) = - \log \frac{a_{Q_1^-} a_{Q_j H^2+}}{a_{Q_1 H} a_{Q_j H}}
\]

(28)
of which only \((n - 1)\) are independent of each other. In particular, one could choose Equation 28 such that \( Q_j H = H_2O \). If the concentration of ions is not too large one can write Equation 27 as

\[
u_{SH}^{\#}(OH, Q_1^-) = - \log \frac{(X_{OH} + p_{OH})(x_1 + u_1)}{(X_{H_2O} + r_{H_2O})(x_1 + p_1)}
\]

(29)
Similarly Equation 24 becomes

\[ u_{SH}(H_2O, Q_1H) = -\log \left( \frac{(X_{H_2O} + X_{H_3O^+})}{(X_{H_2O} + q_{H_3O^+})} \right) \]  (30)

However, in order to write Equation 28 as a function of the \( X_i \)'s, \( r_i \)'s, \( p_i \)'s, and \( q_1 \)'s one must first find suitable expressions for concentrations. This can be done by solving any 3n of the following equations for n terms \( X_{Q_1H} \), n terms \( X_{Q_1H_2^+} \) and n terms \( X_{Q_1^=} \) which all added together should total one mole.

\[ X_{Q_1H} + X_{Q_1H_2^+} + X_{Q_1^=} = X_1 \]  (31)

of which there are n

\[ \frac{X_i + p_i}{X_j + p_j} = \frac{X_{Q_1^=}}{X_{Q_j^=}} \]  (32)

of which there are \((n - 1)\) independent

\[ \frac{X_i + q_i}{X_j + q_j} = \frac{X_{Q_1H_2^+}}{X_{Q_jH_2^+}} \]  (33)

of which there are \((n - 1)\)

\[ \frac{X_i + r_i}{X_j + r_j} = \frac{X_{Q_1H}}{X_{Q_jH}} \]  (34)
of which there are \((n - 1)\), and

\[ X_{Q_1H_2^*} = X_{Q_1^-}. \]  \hspace{1cm} (35)