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Solvent effects on the thermodynamic functions of dissociation of anilines and phenols

Barkat A. Khawaja
University of Wollongong

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SOLVENT EFFECTS ON THE
THERMODYNAMIC FUNCTIONS OF DISSOCIATION OF
ANILINES AND PHENOLS

A thesis submitted in fulfilment of the requirements
for the award of the degree of

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Barkat A. Khawaja, M.Sc.(U.S.)

Department of Chemistry
1982
ABSTRACT

For a systematic series of phenols and some anilines, the thermodynamic functions of proton dissociation have been determined in a 50 weight per cent water-methanol solvent system. The technique used was the e.m.f.-spectrophotometric method. The results obtained have been compared against those obtained for the same compounds in water solvent alone.

For phenols, the change in free energy on transferring from water to the mixed solvent system has been found to arise from a change in entropy - and therefore to a change in solvation - assuming entropy effects are primarily due to solvation effects.

In the case of anilines, solvation effects are minor, because of no anion solvation, both in water and mixed solvent systems.
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SECTION 1

INTRODUCTION
SECTION 1 - INTRODUCTION

The thermodynamic functions of proton dissociation of acids and bases have been extensively measured and evaluated in recent years. Much interest in such studies stemmed from the celebrated Hammett rho-sigma equation\(^{(1)}(2)\) which predicted the magnitude of the effect of a substituent on the strength of an acid. Hammett's original work, of course, used benzoic acid itself as the reference acid, and "\(\rho\)" was termed the reaction constant and "\(\sigma\)" the substituent constant. The thermodynamic parameter involved was the free energy change value and the relationship between \(\Delta G\) and \(\sigma\) has been widely studied and discussed as the linear Free Energy Relationship.\(^{(3)}\)

Not unexpectedly, not all acids and substituents conformed, so that other \(\sigma\) values have been introduced and the significance of enthalpy and entropy on \(\Delta G\) carefully considered. But to quantify the relationship given by \(\Delta G = \Delta H - T\Delta S\), it is necessary to measure and/or evaluate the values for \(\Delta G\), \(\Delta H\) and \(\Delta S\).

\(\Delta H\) can frequently be determined directly by calorimetric means. Solubility of the acid can be a limiting factor to the calorimetric method.

\(\Delta G\) can be, and has been, determined by a variety of methods; the main techniques, however, are potentiometry, conductivity and an e.m.f.-spectrophotometric method. Potentiometry involving, for example, a pH titration is a simple, if not a very accurate, method. Conductance\(^{(4)}\) is a very precise technique but is limited to relatively strong weak acids, due to the proton contribution from the solvent water. The e.m.f.-spectrophotometric method first described by Robinson\(^{(5)}\) and later used extensively by Bolton, Hall et al.,\(^{(6)}\) is
also capable of great precision and is not so limited by solubility problems. Its limitation is that only aromatic acids and bases give a convenient spectral peak. This technique, though, requires the use of buffers whose pH is precisely known and approximates closely to the pKa of the acid under study, that is, pH ≈ pKa.

As mentioned above, ΔH may be directly measured. It may, however, be evaluated from the Van't Hoff equation:

\[
\frac{d\ln k}{dT} = \frac{\Delta H}{RT^2}
\]

and to do so, Ka has to be determined over a range of temperature. This is the technique used in this current study, because there are available suitable buffers over a range of temperature, and it has been shown in earlier studies\(^{(7)}\) that a spectrophotometer can be readily thermostatted with sufficient precision to enable precise ΔG values to be determined over an appropriate range of temperature. The ΔH values so obtained, by appropriate modification of the Van't Hoff equation\(^{(8)-(10)}\) compare more than favourably with direct calorimetric measurements.
SECTION 2

THE ROLE OF THE SOLVENT IN ACID-BASE SYSTEMS
SECTION 2 - THE ROLE OF THE SOLVENT IN ACID-BASE SYSTEMS

It is customary to define acid and base in terms of some structural concept. But it is helpful if such concept can simplify the quantitative treatment of acid-base equilibria. Three concepts that have attained the widest acceptance are those of Arrhenius, Brønsted and Lewis. The Arrhenius concept is restricted to the solvent water, whereas the Brønsted concept, while it still requires the presence of a solvent, can be applied to any solvent system. The Lewis theory does not involve a solvent at all, and at best is only semi-quantitative in concept; for this reason, it will not be considered further; and since the Brønsted concept embraces the Arrhenius concept, it will be used in this present study.

In 1923, Brønsted proposed that an acid be regarded as a proton donor and a base as a proton acceptor, so that a proton transfer reaction can be represented as a combination of two conjugated acid-base pairs:

\[ \text{Acid}_1 + \text{Base}_2 \rightleftharpoons \text{Acid}_2 + \text{Base}_1 \]

where the strength of the acid is determined by the relative affinities for protons by the two competing bases, namely the conjugated base of the acid and the solvent.

Since proton transfer reactions are almost always studied in liquid solvents, then the solvent can be expected to play some role in the over-all process. Solvents can be classified as protophilic, protogenic, amphiprotic and aprotic, that is \textit{proton attracting, rejecting, attracting and rejecting}, and not interested respectively.
The extent to which such reactions do occur, however, depends on several properties of the solvent, namely, its dielectric constant, its ability to solvate ions and molecules of the acid or base, and its own acidic or basic character.

The dielectric constant (ε) of a solvent expresses its effect on the electrostatic force between ions. The work of separation of SH₂⁺ and X⁻ ions will vary inversely with the dielectric constant of the solvent. Thus this reaction:

\[
\text{SH} + \text{HX} \rightleftharpoons \text{SH}_2^+ + \text{X}^-
\]

would be expected to occur to a greater extent in water (ε = 78 at 25°C) than in methanol (ε = 33 at 25°C). When the dielectric constant is very low, as in benzene, it is possible that the ions may not separate at all, but remain as an ion pair SH₂⁺X⁻. In effect, then, the acid is not an acid. The solvent may also interact more specifically with ions and molecules of acids and bases. If solvent molecules are polar, interaction between ions and solvent dipoles helps to stabilize the ions. The solvent may also form hydrogen bonds and this is especially true for water and alcohols. The hydrogen groups of such compounds can either accept or donate hydrogen atoms to form hydrogen bonds.

Interactions in which protons are transferred from acid to solvent, or from solvent to base (Brønsted concept), call into play the basic or acidic nature of the solvent itself.

Waterlike or amphiprotic solvents include water and the alcohols. Self-ionization of the solvent:

\[
2\text{SH} \rightleftharpoons \text{SH}_2^+ + \text{S}^-
\]
produces an acid and base; and this is the strongest acid or base that can exist in that solvent. The value of this equilibrium is often referred to as the 'autoprotolysis constant' and the effect is known as the 'levelling effect of the solvent'. Thus, hydrochloric acid and acetic acid are considered strong and weak respectively in water, but both are strong in the basic solvent, liquid NH₃.

Water, because it is the most common liquid, is of course the most popular solvent, and most studies on acid-base equilibria are made in water. But it must be appreciated that the very properties of high dielectric constant, excellent solvating power and amphiprotic nature, make water exceptional in its effect on acids and bases.
ACIDITY CONSTANTS (Ka)

The equilibrium constant for an acid-base system is quantitatively expressed by the equilibrium constant, K, or by the related quantities, pKa and ΔG°:

where

\[ pKa = -\log K_a \]

\[ \Delta G^0 = -RT \ln K = RT(\ln 10)pK \]

and ΔG° is the change in Gibbs free energy at constant temperature and pressure when both products and reactants are in their standard states.

The absolute strength of a Brønsted acid, HX, can be expressed by the equilibrium constant for the reaction:

\[ HX \rightleftharpoons X^- + \text{proton} \]

In actual fact, the absolute strength cannot be measured because protons do not exist free, but in combination with bases such as solvent molecules. Thus it is usual to measure the strength of an acid, HX, when related to the solvent acid SH₂, and the equilibrium constant given by:

\[ HX + SH \rightleftharpoons SH_2^+ + X^- \]

is

\[ Ka = \frac{a_X a_{SH_2}}{a_{HX} a_{SH}} \]

where the "a" terms are relative activities of the indicated species. Generally the activity of the solvent in solution is virtually constant and equal to the activity of pure solvent; in which case the acidity constant can be rewritten as:

\[ Ka = a_X a_{SH_2}/a_{HX} \]
A major problem of interpretation in the use of acidity constants in solvents of low dielectric constant is that transfer of a proton may occur, but separation of the products may not follow because of ion pair formation. Reaction between acid and solvent is then represented by:

\[ \text{HX} + \text{SH} \rightarrow \text{SH}_2^+ \text{X}^- \] \hspace{1cm} \text{(Ki)}

\[ \text{SH}_2^+ \text{X}^- \rightarrow \text{SH}_2^+ + \text{X}^- \] \hspace{1cm} \text{(Kd)}

where the first step is truly ionization (Ki) and the second is dissociation (Kd). The experimentally determined acidity constant is neither Ki nor Kd, but:

\[ \text{Ka} = \frac{\text{KiKd}}{1 + \text{Ki}} \]
ACTIVITY COEFFICIENTS

Any activity can be written as the product of a concentration and an activity coefficient. The rational concentration unit is the mole fraction "x", and its associated coefficient is represented by "f". In the limit of infinite dilution activity coefficient becomes equal to unity; but in reality, when ionization of HX produces oppositely charged univalent ions, the mean activity coefficient bears the following relation to the ionic activity coefficients:

$$\gamma = (\gamma_{SH_2} \gamma_x)^{1/2}$$

and the acidity constant can then be written as:

$$K_a = \frac{[SH_2^+][X^-] \gamma^2}{[HX] \gamma_u}$$

where \(\gamma_u\) is the activity coefficient of ionized HX.

But there are various expressions for activity coefficients in daily use. The Debye-Hückel limiting law (11) for the mean activity of an electrolyte is given by:

$$-\log y = z^+ | z^-| Ai^{1/2}$$

The factor, I, is the ionic strength and is defined in terms of the molar concentrations \(c_i\) and charge number \(z_i\) of all ions in the solution, i.e.:

$$I = 1/2 \Sigma_i c_i z_i^2$$

The limiting slope, A, is proportional to the dielectric strength of the solvent.
Davies\(^{(12)}\) simplified the Hückel equation thus:

\[-\log \gamma = \frac{AZ_i^2 \sqrt{u}}{(1 + \sqrt{u})} = \beta Z_i^2 U\]

On the other hand, Guggenheim\(^{(13)}\) used Brønsted's principle of specific ion interaction to formulate a different kind of linear term:

\[-\log yx = Z_i^2 A_{1/2}/(1 + I_{1/2}) - \sum M_i^B M_i^C M_i^H\]

Normally, each can be considered as equivalent to the other in this current text.
pH AND ITS SIGNIFICANCE TO DETERMINING ACIDITY CONSTANTS

Values of acidity constants are needed for quantitative treatment of acid-base equilibria. The method chosen for this present study involved an appreciation of those problems associated with the pH scale, buffer solutions, and spectrophotometric precision.

pH is one of the most popular parameters in modern experimental science, but it still remains an essentially empirical parameter. It can be precisely measured, but its interpretation in terms of activity or concentration of hydrogen ion is clouded by ambiguities associated with liquid junction potentials and single ion activities. Nonetheless, standardization of the pH scale is based on the hydrogen silver-silver chloride cell and standard buffer solutions have been devised.

A good buffer solution is any solution that maintains an approximately constant pH despite small addition of acid or base. Thus the effectiveness of a buffer depends primarily on changes in the buffer ratio \([HX]/[X]\), from which it is evident that all buffers contain weak acids and conjugate bases in approximately a 1:1 ratio and are effective over a range of about \(\pm 1.0\) pH units.

Values for a large range of buffer solutions are summarised by Bates and Gary, although the main reason for this publication was to derive the quantity \(p(\alpha_{HCl})\) for such buffers in aqueous solution over a range of temperature. Bolton, Hall et al., have made extensive use of such buffer tables in their studies on phenols, anilines and benzoic acid.
But what is the significance of the terms pH, pHs, paH and p(αHγCl)?

The pH of a solution is related to that of solution, S, by:

$$\text{pH}(X) - \text{pH}(S) = \frac{1}{k}(E_X - E_S)$$

where $k$ is the Nernst factor, $RT\ln 10/F$, and $E_X$ and $E_S$ are the electromotive forces of the two half cells, hydrogen and silver-silver chloride, when they are at the same temperature.

The value pHs is obtained, then, by assigning a pH value at each temperature to some standard solution. But this assignment is based on measurements of the familiar cell without liquid junction. The thermodynamic equation for such a cell given by:

$$\text{pH}(S) = -\log \rho_{H}$$

this differs from the experimental property by $-\log\gamma_{Cl}$. But, because the activity coefficient of a single kind of ion is devoid of thermodynamic significance, a reasonable assumption has to be made about $\gamma_{Cl}$ before we can relate pH(s) to $p(\alpha_{H}\gamma_{Cl})$. At low concentration, this is legitimately done by identifying ionic activity coefficient with the mean activity coefficient and using the Debye-Hückel concept, or modified form of it.
From the very definition of \( p(\alpha_{H\gamma Cl}) \) given by:

\[
p(\alpha_{H\gamma Cl}) = -\log(m_{H\gamma H\gamma Cl})
\]

it is evident that the hydrogen ion concentration, \( m_H \), is formally related to the acidity function as follows:

\[
-\log m_H = p(\alpha_{H\gamma Cl}) + \log(\gamma_{H\gamma Cl})
\]

\[
= p(\alpha_{H\gamma Cl}) - 2 \log \gamma_\pm
\]

In this equation, \( \gamma_\pm \) is the mean ionic activity coefficient of hydrochloric acid in the buffer solution for which the acidity function has been obtained.

This acidity function \( p(\alpha_{H\gamma Cl}) \) can be used to estimate \(-\log a_H\) when values of this quantity are needed. They are computed from the equation:

\[
pH_s = p(\alpha_{H\gamma Cl}) + \log \gamma_{Cl}
\]

\[
= p(\alpha_{H\gamma Cl}) - A \sqrt{u}/1 + 1.5 \sqrt{u}
\]

where \( A \) is the Debye-Hückel slope.
ACIDITY CONSTANTS AND MOLECULAR STRUCTURES

The prime question is why is one acid stronger or weaker than another? Or what structural features of the molecules and ions of the acid, its conjugated base and the solvent determine acid strength?

A simple and convenient classification is to divide the effects into two, viz.: internal and environmental. Internal effects are those intrinsic to the molecules and ions of the acid and base; and they would persist even in the ideal gaseous state. Inductive and resonance effects are familiar and popular examples of internal effects. Environmental effects are those which result from interaction of the molecules and ions of the acid and base with the solvent.

The strength of an acid is, of course, related to the standard Gibbs free energy:

$$\Delta G^0 = -RT\ln k$$

where the standard state, $\Delta G^0$, is a hypothetical solution in which the solutes are at unit concentration but solute-solute interactions are negligible. Because of this choice of standard state, the discussion of environmental effects is concerned only with solute-solvent interactions.

Solvation:

The transfer of a molecule or ion from the gas phase to a liquid solvent is associated with loss in potential energy and restriction on its motions. A simple way of calculating the loss of
The electrostatic potential energy in the solvation of an ion is given by the Born equation:

$$\omega_{el} = \frac{-Z^2 e^2}{2r} \left( 1 - \frac{1}{\epsilon} \right) = \frac{-C z^2}{r}$$

where $\epsilon$ is the dielectric constant of the solvent, $r$ is the radius of the ion, $Ze$ is the charge, and $C$ a constant of value $164.0 \times 4.184$ KJ A mol$^{-1}$. The order of magnitude of heats and entropies of solvation of pairs of univalent ions range from $-200$ to $-500$ KJ mol$^{-1}$ and entropies of hydration, $-40$ to $-120$ J deg$^{-1}$ mol$^{-1}$. The heat of hydration of the proton, because of its small size, is very large at $-1092$ KJ cal mol$^{-1}$.

But this description is very crude because it assumes ions are charged spheres immersed in a structureless dielectric. Other interactions can occur such as ion-dipole forces and hydrogen bonding, this latter being very important in water-solute interactions. Many anomalous sequences of acid strengths can be interpreted as resulting from hydrogen bonding.

**Inductive and Resonance Effects:**

Extensive literature discussions are available on this particular topic; therefore these effects will only be mentioned briefly here to illustrate their meaning. Inductive effects are transmitted along a chain by small shifts in electron density. Thus, when an aromatic ring is directly attached to the acidic group, the inductive effects will help make the acid stronger than the corresponding fatty acid. However, resonance effects arise from the ring so that over-all the inductive effect of the phenyl group is acid-strengthening but resonance stabilizes the molecular form.
Substituent Effects:

Substituent groups can change the electron density on an aromatic acidic group by polar interactions. There have been extensive attempts to divide these polar interactions into inductive effects (displacement of electrons along the chain or ring) and direct or electrostatic field effects which occur, at least in part, through the solvent. The problem, however, is that there is no real way to estimate one type of interaction independently of the other.

In aromatic acids, the electron density on the acidic group is changed, not only by induction, but also by resonance. Separation of these two effects is also difficult. But the inductive effect should be largest at the ortho-position and smallest at the para-position, and is so small in the remote meta- and para-position as often to be ignored. Most substituents enter into resonance with the aromatic ring, such conjugation being largest at the ortho- and para-positions.

The Hammett equation is, of course, an attempt to show that a linear correlation is observed for substituents in the meta- and para-positions in benzoic acid derivatives.
Ka AS A FUNCTION OF TEMPERATURE

The effect of temperature changes on acid-base equilibria is related to the heat of ionization and dissociation by the Van't Hoff equation:

$$\left(\frac{\delta \ln K_a}{\delta T}\right)_p = \frac{\Delta H^0}{RT^2}$$

and because the changes in $K_a$ can go in either direction, that is, can increase or decrease, it is not wise to attach too much significance to relative acid strengths at a single temperature.

Various empirical equations have been proposed for expressing the acidity constant as a function of temperature, because many are parabolic. Such equations include the simple quadratic form:

$$\Delta G^0 = \tilde{A} - \tilde{B}T + \tilde{C}T^2 \text{ or } pK_a = \left(\frac{A}{T}\right) - B + CT$$

proposed by Harned and Robinson,$^{(8)}$ the proposal by Everett and Wynne-Jones,$^{(9)}$ based on the assumption that the change in heat capacity for ionization is independent of temperature, e.g.:

$$\Delta G^0 = \tilde{A} - \tilde{B}T + \tilde{C}T \log T \text{ or } pK_a = \left(\frac{A}{T}\right) - B + C \log T$$

and the more sophisticated expression proposed by Clarke and Glew.$^{(10)}$

The significant feature of the Van't Hoff equation, of course, is that, by determining $K_a$ over a range of temperature, the value of $\Delta H$ can be calculated and therefore $\Delta S$ evaluated, using the equation:

$$\Delta G = \Delta H - T\Delta S$$

It then becomes possible to discuss such effects as substituent and solvent upon $\Delta G$ in terms of $\Delta H$ and/or $\Delta S$. 
It is convenient, if somewhat arbitrary, to divide these thermodynamic properties into an internal part and an external part. The internal part is intrinsic to the molecules and ions of the acid itself, whereas the external or environmental part arises from the interaction of the molecules and ions with the solvent, i.e.:

$$
\Delta X^0 = \Delta X_{\text{internal}} + \Delta X_{\text{external}}
$$

\(\Delta H_{\text{int}}\) tends to be large and depends primarily on the proton affinity of the conjugate base of the acid.

The changes in entropy (and heat capacity) do not depend on the proton affinity. Contributions of translational, rotational and vibrational motions to \(\Delta S_{\text{int}}\) and \(\Delta C_p_{\text{int}}\) are small. But the changes in entropy and heat capacity will be largely caused by changes in the environment of the ions and molecules, for example, by the choice of solvent. The entropy change is sensitive to changes in molecular motions such as low frequency vibrations or restricted rotations;\(^{(25)}\) and so, in our current ignorance of such effects, we find \(\Delta S^0\) to be a rather complex function of structure, even though we know its numerical value with a precision of \(1\%\) or better in many cases.

The simplest point of view is to attribute change in entropy (and heat capacity) to the electrostatic action of the ions on the solvent. We assume that the internal part of the Gibbs function change \((\Delta G^0)\) for ionization is independent of temperature and that the environmental part is electrostatic in origin. The Born model of an ion as a conducting sphere of radius "r" immersed in a homogeneous medium of dielectric constant "\(\varepsilon\)" is the simplest approach. According to this model, the work done in increasing the charge on an ion from zero to Ze is:
\[ \omega_{el} = \frac{Z^2 e^2}{2r_e} \quad \text{(Eq. 1)} \]

and so, for a reaction, the Gibbs function change per mole is:

\[ \Delta G^0_{el} = \frac{Ne^2}{2e} \left[ \sum \text{products} \frac{Z^2}{r} - \sum \text{reactants} \frac{Z^2}{r} \right] \quad \text{(Eq. 2)} \]

and by defining a function, \( \phi \), by:

\[ \phi = \sum \text{products} \frac{Z^2}{r} - \sum \text{reactants} \frac{Z^2}{r} \quad \text{(Eq. 3)} \]

the other thermodynamic properties such as entropy for an acid-base equilibrium can then be obtained from (Eq. 3) by differentiation:

\[ -\left( \frac{\delta \Delta G_{el}}{\delta T} \right)_p = \Delta S^0_{el} = \frac{Ne^2 \phi}{2} \left( \frac{\delta (\frac{1}{e})}{\delta T} \right)_p - \frac{Ne^2}{2e} \left( \frac{\delta \phi}{\delta T} \right)_p \]

\[ -\left( \frac{\delta^2 \Delta G^0_{el}}{\delta T^2} \right)_p = \frac{\Delta C_p^0}{T} \]

**Medium Effects:**

Acid-base equilibria are disturbed by addition or removal of species foreign to the equilibria; for example, the nature of the solvent is changed when methanol is added to an aqueous solution of a weak acid.

The thermodynamic relation:

\[ \Delta G^0 = -RT \ln Ka \]

indicates that an acidity constant is associated with a particular standard state. Regardless of whether the acid is in pure water, or a mixture of solvents, if the chosen standard state for solutes is the hypothetical 1 molal solution in pure water, \( Ka \) is the same for all these media. However, there is available the option of choosing a different standard state for each medium, in which case there will be
different acidity constants for the different media. Because water is so important as a solvent, we then need to know how to relate the acidity constant in some solvent medium to the acidity constant based on the standard state in water.

The medium effects are those interactions which arise between the molecules and ions of the medium and those of the weak acid. But some minor change in the interaction of the acid with the medium may also occur as its concentration changes; for example, the weak acid may alter the dielectric constant of the medium. These concentration effects, however, disappear as concentration approaches zero.

By way of illustration, consider the partial molal Gibbs function of solute, R, in solvent, S. It can be expressed by:

\[ \bar{\mathcal{G}}_R = \bar{G}_R + RT\ln m_R + RT\ln(s\gamma R) \]

or it can equally well be referred to a standard state in water:

\[ \bar{\mathcal{G}}_R = \omega \bar{G}_R + RT\ln m_R + RT\ln(\omega \gamma R) \]

The two activity terms are, of course, not equal; the first approaches zero at infinite dilution in the solvent, and the second does not. The difference is given by:

\[ \ln(\omega \gamma R) - \ln(s\gamma R) = (\omega \bar{G}_R^0 - s\bar{G}_R^0)/RT \]

so it can be seen that \( \ln(\omega \gamma R) \) is greater than \( \ln(s\gamma R) \) by an amount that is independent of molality and is constant for any particular solvent at a given temperature and pressure. This difference can be termed the medium effect. It therefore is represented by:
Medium Effect $= \frac{s\xi_R - \omega_R}{RT} = \ln(m\gamma_R)$

and the sum of this medium effect and the concentration effect, $\ln(s\gamma_R)$ is the total effect given by $\ln(w\gamma_R)$, so that:

$\omega_{\gamma_R} = (m\gamma_R)(s\gamma_R)$

Medium and concentration effects can also be defined for weak acids and bases. In the solvent, $S$, the weak acid, $HX$, can be characterized by an equilibrium quotient $Q_a$, such that:

$\text{Limit } m \to 0 \quad Q_a = sK_a$

an activity coefficient factor can then be incorporated to give, ultimately,:

$\log(m\gamma_a) = -\log \frac{sK_a}{\omega K_a} = \Delta pK_a$

where the medium effect is proportional to the work of transfer of one mole of $H$ and $X$ from infinite dilution in water to infinite dilution in medium $S$ and simultaneous transfer of one mole of $HX$ in the opposite direction.
SOME CHARACTERISTICS OF WATER-ORGANIC SOLVENT MIXTURE

Mixtures of water with organic solvents, especially alcohols, are popular media for studying acid behaviour, not least because of solubility problems. Glass electrodes continue to function in such mixtures also. But there are disadvantages as well as advantages. For example, in methanol-water mixtures, the solvent acids include not only $\text{H}_3\text{O}^+$ and $\text{H}_2\text{O}$, but also $\text{CH}_3\text{OH}_2^+$ and $\text{CH}_3\text{OH}$; the solvent bases not only $\text{H}_2\text{O}$ and $\text{OH}^-$, but also $\text{CH}_3\text{OH}$ and $\text{CH}_3\text{O}^-$. In other words, both the water and methanol are amphiprotic solvents. The two components of the medium can also differ in their solvating power. It is, of course, widely assumed on the basis of electrostatic theory, that ions are preferentially solvated by water. The chemical potential of an ion varies inversely with the dielectric constant of the medium and most of the energy loss in transferring an ion from empty space to solution occurs in the immediate neighbourhood of the ion. The result is that the solvent component of higher dielectric constant (in this case, water) will concentrate about the ion in preference to methanol to make its chemical potential as low as possible. However, it is difficult to obtain experimental evidence of preferential hydration, even though the properties of acids in solvent mixtures should be sensitive to change in solvation of the proton, even though it is believed that the proton in a water-alcohol mixture is hydrated at least to $\text{H}_3\text{O}^+$. 
Medium Effects on Weak Acids in Mixed Solvents

The medium effect is measured simply by the change in pKa:

$$\Delta pK_a = p(sK_a) - p(wK_a) = \log(mY_H) + \log(mY_X) - \log(mY_{HX})$$

But it can be asked how pKa($\Delta G$) is effected: by change in $\Delta H$ or $\Delta S$?

The effect of change in solvent on the neutral species HX or X for a cation acid is not necessarily negligible, even though most interpretations of the solvent effect on weak acids have been focussed on the ions.

The medium effect on the proton is of considerable concern because the solvated proton can change from $H_3O^+$ to ROH$_2^+$ in going from water to solvent ROH.

Various attempts have been made to give an electrostatic interpretation of the medium effect. If $H_3O^+$ and $X^-$ are the ions, then the Born model simply expresses the medium effect by:

$$-\log\left(\frac{S_{K_a}}{w_{K_a}}\right) = \frac{e^2}{rkT\ln10} \left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_w}\right)$$

in which case the electrostatic theory predicts a linear relation between medium effect and the reciprocal of the dielectric constant of the solvent. But other factors have been found to affect such linearity, for example, the length of the alkyl chain in an alkyl carboxylic acid, and this is because the medium effect on the molecules of the acid has been neglected.

As another approach to this problem, Wynne-Jones$^{(27)}$ suggested that, if the relative acidity constants in two solvents were compared, the medium effect problem could be eliminated. This is
because the relative acidity of two acids of different charge types depends markedly on the dielectric constant of the solvent; whereas the relative acidity of two acids of the same charge type is less affected by the solvent. Indeed, if the two radii of the molecular acids are equal, the relative strengths of the two acids should then be independent of the solvent, i.e.:

\[ sK_r = \omega K_r \]

Unfortunately this is seldom true, and often the changes in relative strength are too large to be accounted for in simple terms of radii. This failure of simple electrostatic theory results from neglecting specific interactions of the solvent with the molecular acids and bases and with non-polar groups of the ions.

Of course other predictions have been made. The Bjerrum-Euchen theory predicts that \( \Delta pK \) defined as:

\[ \Delta pK = pK_a(\text{ref acid}) - pK_a(\text{given acid}) - \log \sigma \]

should vary inversely with the dielectric constant of the solvent, and the Kirkwood-Westhelmer theory\(^{28}\) predicts an inverse variation with the effective dielectric constant because much of the electrostatic interaction between dipole and ionizing proton occurs within the cavity of the molecule. The effective dielectric constant is then close to the internal dielectric constant and is virtually independent of the solvent.

But which theory is best? In all cases the scatter of points from experimental studies is so large that the question cannot be answered with certainty. What is certain, however, is that more accurate experimental work is needed to discuss with confidence the value of each theory.
SECTION 3

OBJECT OF THIS STUDY
SECTION 3 - OBJECT OF THIS STUDY

The object of this study was to observe the effect of solvent upon the various thermodynamic parameters of acid dissociation. $\Delta G$ is known to generally increase as the dielectric constant of the medium decreases. But is such change due to change in $\Delta H$ or $\Delta S$? And, if $\Delta S$ changes, as is predicted by external effects, can the effect of the medium be quantitatively assessed?

To this end, a systematic series of phenols and some anilines have been studied in a 50 weight % water-methanol medium, using the e.m.f.-spectrophotometric technique, as described originally by Robinson$^v$ and subsequently used extensively and successfully by Bolton, Hall and other workers.$^{(6)(18)(19)}$

Unfortunately there are only a limited number of precise buffers available in 50 weight % water-methanol solvent; these are described by Bates et al.$^{(29)}$ But it has placed a restriction on the compounds that can be studied. Another restriction is that precise thermodynamic data for the acid dissociation in water of the phenols and anilines under study must be available, because the mixed solvent values have to be compared against those values obtained in water.

On the other hand, a distinct advantage of the water-methanol system is that spectroscopic grade methanol is readily available at a moderate price, and the dielectric constant of methanol (32.6) and its autoprotolysis constant ($pK_a = 16.9$) ensure that, in this medium, the so-called acids under study are in fact acids.
SECTION 4

EXPERIMENTAL
The e.m.f.-spectrophotometric technique was used to determine the acidity constant for six phenols and two anilines over a range of temperature dictated by the buffers available in the mixed solvent system.

The actual experimental procedure may be briefly reiterated as follows:

(a) Preparation and/or purification of the acids under study. Purity, of course, may not be a problem if impurities do not absorb at the chosen wavelength.

(b) Preparation of 50 weight per cent water-methanol solvent using spectroscopically pure methanol.

(c) Selection and preparation of appropriate buffers in the water-methanol solvent. Ideally, pH of the buffer should have the same numerical value as the pKa of the acid under study.

(d) Preparation in suitable cells of the following solutions:

(1) A reference solution of the buffer in water-methanol, this corrects for buffer absorbance. However, aromatic compounds cannot be used as buffers due to their strong absorbance in the ultra-violet range usually required.

(2) A solution of the acid in the buffer solution of known ionic strength. The molality of the acid will normally be in the range $10^{-3}$ to $10^{-4}$ to give a suitable absorbance using a 10 mm cell system.

(3) A solution of fully protonated acid. This is achieved by adding $H_2SO_4$ to the acid under study. The concentration of acid must, however, be identical with that in (2).

(4) A solution of fully deprotonated acid. This is achieved by adding NaOH to the acid solution. Again the concentration of acid must be identical with that in (2) and (3).
(e) Spectrophotometric measurement on the solution at one fixed wavelength over the temperature range 5 to 45°. The wavelength chosen is normally that when molar absorbance (ε) is at a maximum for the base form and minimum for the acid form (see Fig. 1).

In broad terms, this information is then inserted into the equation:

\[ pK_a = pH - \log(\text{salt)/(acid}) \]

to evaluate pK\(_a\) at each temperature. pH, of course, is known from the buffer chosen, and the ratio (salt)/(acid) is measured spectrophotometrically.

(f) Assessment of best-fit experimental pK\(_a\) values at 5° intervals. At least four runs are necessary to obtain these results.

Thermodynamic pK\(_a\) values are obtained as described; then this data is applied into the Van't Hoff isochore - or a form of it - to evaluate ΔH. Subsequently ΔS is derived.

All spectrophotometric measurements were made on an Optica CF4 manual grating spectrophotometer. The cell compartment was thermostatted with a heater chiller system(7) and the temperature in the buffer cell was monitored, using a thermistor probe system as supplied by United System Corporation (Digitec HT series).

Various ionic strengths of the buffer system were employed in order to assess whether the pK\(_a\) values, as determined, were dependent, or independent, of ionic strength. Phenols, because of their charge type, give pK\(_a\) values which are
independent of ionic strength, \(^{(6)}\) whereas experimental values of pKa for anilines \(^{(30)}\) have been found to vary linearly with ionic strength. The thermodynamic pKa value can, of course, be found by extrapolation to zero ionic strength, or by using the Debye-Hückel, or similar equation from a single ionic strength determination.
Optica "$\text{CF}_4$" spectrophotometer and associated thermostating equipment.

Arrangement of cells, holder and thermistor probe.
Closer view of cells, holder and thermistor probe.
Fig. 1: Spectra of 2,4,6-Trichlorophenol (50 weight % water-methanol)

A = Deprotonated form
B = Phenol in buffer solution
C = Protonated form
DETERMINATION OF THERMODYNAMIC DISSOCIATION CONSTANT
FROM SPECTROPHOTOMETRIC MEASUREMENTS

The proton dissociation of phenols, which are acids of charge type -1, is represented by:

\[ HA + H_2O \rightleftharpoons H_3O^+ + A^- \]  \hspace{1cm} (Eq. 1)

the thermodynamic dissociation constant, pKa, is calculated from:

\[ pKa = p(\alpha_{H^+}) + \log \frac{m_{HA}}{m_A^-} + \log \frac{\gamma_{HA\gamma Cl}}{\gamma A^-} \]  \hspace{1cm} (Eq. 2)

where the term \( \frac{m_{HA}}{m_A^-} \) represents the ratio of the concentration of protonated and deprotonated forms of the acid in the buffered solution of HA. The term \( \frac{\gamma_{HA\gamma Cl}}{\gamma A^-} \) can cancel out if the assumption is that it is equal to unity. This can, however, be confirmed if need be by checking the constancy of pKa when measured over a range of ionic strength values up to about 0.1.

It has been found\(^{31}\) that experimental values for phenols are independent of ionic strength for solutions of ionic strength less than 0.1, so that it is now appropriate to modify Equation 2 to:

\[ pKa = p(\alpha_{H^+}) + \log \frac{m_{HA}}{m_A^-} \]  \hspace{1cm} (Eq. 3)

for phenols.

The fortuitous cancellation of activity coefficient terms for phenol type acids (i.e. negatively charged anions) does not, however, apply to ions of the anilinium type (positively charged ions).\(^{30}\) Thus, in dilute solutions of ionic strength less than 0.1, the activity coefficient terms do not cancel out, rather they become additive and a mean activity coefficient term can replace the individual values of all ionic species, chloride ions included,
present in the solution.

Thus, for the equilibrium reaction for the anilinium ion, where charge type is now zero:

\[
\text{AH}^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}
\]

the thermodynamic dissociation constant is given by:

\[
p\text{Ka} = p(a_H\gamma_{\text{Cl}}) - \log \frac{m_{\text{A}}}{m_{\text{AH}^+}} + 2\log \gamma_{\pm}
\]

where \(\gamma_{\pm}\) denotes the mean activity coefficient.

One method of calculating this mean activity coefficient correction is by means of the Debye-Hückel equation.\(^{(11)}\)

\[
-\log \gamma_{\pm} = AZ_i^2 \sqrt{T}/1 + \beta \sqrt{T}
\]

Modified forms of this equation, such as the Davies equation,\(^{(12)}\) can also be used with little variation in final results.

Having determined and evaluated thermodynamic pKa values over a range of temperature, \(\Delta H\) can be evaluated. However, the Van't Hoff equation is valid only for a linear relationship between pKa and 1/T, that is for an ideal-system. Our results show some curvature and to compensate for this, variations on the ideal equations are necessary.

Several such semi-empirical equations have been widely used:

(1) The Harned-Robinson equation;

(2) The Everett - Wynne-Jones equation; and

(3) The Clarke and Glew equation;

and their significance has been discussed earlier on.
Generally, over a limited range of temperature, heat capacity ($C_p$) can be assumed to remain constant and if the degree of curvature is slight, then each equation will give values of $\Delta H$ within experimental error.

The Clark and Glew equation\(^{(10)}\) has been used in these studies and $\Delta H$ and $\Delta S$ computed, using a computer program - that described by Associate Professor P.D. Bolton\(^{(53)}\) - using the Univac 1100/60 computer system installed at The University of Wollongong.
A TYPICAL EXAMPLE OF PROCEDURE

Two anilines and six phenols have been studied in this project, but full experimental data have been included for only one phenol. It is emphasised that the following example has not been selected on any special basis and that experimental data collected for each of the other anilines and phenols came from work following the same pattern.

2,4,6 trichlorophenol is taken as the typical example of the phenols studied. Absorbance data have been included for only one run, in Table 1.

Absorbance data was used to calculate raw pKa values, using equation:

\[ pKa = p(a_{H^+Cl}) - \log \frac{salt}{acid} \]

Raw pKa values for three experimental runs are recorded in Table 2. These data have been plotted in Figure 4 and the curve of best fit has been drawn manually. Experimental pKa values for 2,4,6 trichlorophenol were obtained by taking raw pKa values at 5° intervals from the graph, in Table 3.

The values of the thermodynamic functions of ionisation for our typical example, 2,4,6. trichlorophenol, have been evaluated by Clark and Glew equation, and are recorded in Table 4.
### TABLE 1

2.4.6. - Trichlorophenol (50 weight % water-methanol)

Molal Concentration of phenol: $1 \times 10^{-4}$

Buffer: $KH_2PO_4/Na_2HPO_4/NaCl$ Table 1 Ref 29

Ionic Strength: $I = 0.04$

Wave Length: 314 nm

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$p(a_{H^+}Cl)$</th>
<th>Absorbance Buffered Form</th>
<th>Absorbance Protonated Form</th>
<th>Absorbance Deprotonated Form</th>
<th>Raw pKa</th>
</tr>
</thead>
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<td>7.501</td>
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<td>0.458</td>
<td>0.019</td>
<td>0.530</td>
<td>7.379</td>
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</tbody>
</table>
**TABLE 2**

RAW pKa VS TEMPERATURE

Ionisation of 2.4.6. - Trichlorophenol (50 weight% water-methanol)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Raw pKa</th>
<th>Temperature</th>
<th>Raw pKa</th>
<th>Temperature</th>
<th>Raw pKa</th>
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</thead>
<tbody>
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<td>6.6</td>
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</table>
Fig. 4: Raw pKa versus temperature

2.4.6 Trichlorophenol in 50% water-methanol
Buffer: KH$_2$PO$_4$/Na$_2$HPO$_4$/NaCl  Table 1, Ref. 29
Ionic Strength:  I = 0.04
Molal Concentration of Phenol:  $1 \times 10^{-4}$
Wave Length of Measurement:  314 nm
TABLE 3
pKa DATA FOR 2,4,6 TRICHLOROPHENOL
IN 50% WATER-METHANOL

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Raw pKa</th>
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TABLE 4
THERMODYNAMIC FUNCTION OF IONISATION
OF 2,4,6 TRICHLOROPHENOL

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<tr>
<th>No. Variables</th>
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<td>124.12</td>
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</table>

Key:  * KJ/mol\(^{-1}\)
      # Jd\(^{-}\)/mol\(^{-1}\)
SECTION 5

THERMODYNAMIC RESULTS FOR THE COMPOUNDS STUDIED
TABLE 5

O-NO₂ - phenol

Molar Concentration of phenol: 1 \times 10^{-3}

Buffer: KH₂PO₄/Na₂HPO₄/NaCl Table 1 Ref 29

Wave Length of Measurement: 420 nm

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<th>Thermodynamic pKa</th>
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<th>ΔH° KJ/mol</th>
<th>ΔS° J mol⁻¹ K⁻¹</th>
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</table>
TABLE 6

p-NO₂ - phenol

Molal Concentration of phenol: $1 \times 10^{-3}$

Buffer: KH₂PO₄/Na₂HPO₄/NaCl Table 1 Ref 29

Wave Length of Measurement: 400 nm

| Temperature | Best-fit Experimental pKa $I = 0.04$ | Thermodynamic pKa | $\Delta G_{25}^{0}$/mol | $\Delta H_{25}^{0}$/mol | $\Delta S_{25}^{0}$/mol J/mol
<table>
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TABLE 7

2.6. Di-Cl-phenol

Molal Concentration of phenol: $1 \times 10^{-4}$

Buffer: $\text{KH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4/\text{NaCl}$ Table 1 Ref 29

Wave Length of Measurement: 300 nm

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<th>Best-fit Experimental pKa $I = 0.04$</th>
<th>Best-fit Thermodynamic pKa</th>
<th>$\Delta G_{25} \text{ KJ/mol}$</th>
<th>$\Delta H_{25} \text{ KJ/mol}$</th>
<th>$\Delta S_{25} \text{ Jd}^{-1}\text{mol}^{-1}$</th>
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</table>
2.4.6. Tri-Cl-phenol (Water)

Molal Concentration of phenol: $1 \times 10^{-4}$

Buffer: $\text{KH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$  

Table 11 Ref 17

Wave Length of Measurement: 314 nm

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<th>Temperature</th>
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<th>Thermodynamic pKa</th>
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<th>$\Delta H_{25}$ KJ/mol</th>
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<td>6.432</td>
<td>6.439</td>
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</tr>
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</table>
TABLE 9

2.4.6. Tri-Cl-phenol (50% water-Methanol)

Molar Concentration of phenol: $1 \times 10^{-4}$

Buffer: $\text{KH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4/\text{NaCl}$  Table 1  Ref 29

Wave Length of Measurement: 314 nm

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<tr>
<th>Temperature</th>
<th>Best-fit Experimental pKa $I = 0.04$</th>
<th>Experimental pKa</th>
<th>Thermodynamic pKa</th>
<th>$\Delta G_{25}^{\circ}$ KJ/mol</th>
<th>$\Delta H_{25}^{\circ}$ KJ/mol</th>
<th>$\Delta S_{25}^{\circ}$ J K$^{-1}$ mol$^{-1}$</th>
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2.6. di-Cl-4-acetyl phenol

Molar Concentration of phenol: $2.5 \times 10^{-4}$

Buffer: HAc/NaAc/NaCl Table 1 Ref 29

Wave Length of Measurement: 334 nm

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<th>Thermodynamic pKa</th>
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<td>6.003</td>
<td>6.013</td>
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TABLE 11

Aniline

Molal Concentration of aniline: $5 \times 10^{-4}$

Buffer: HAc/NaAc/NaCl Table 1 Ref 29

Wave Length of Measurement: 285 nm

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<th>Temperature</th>
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TABLE 12

p-Methylaniline

Molal Concentration of aniline: $5 \times 10^{-4}$

Buffer: HAc/NaAc/NaCl  Table 1  Ref 29

Wave Length of Measurement: 290 nm

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<th>Thermodynamic pKa</th>
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<td>( \delta \Delta G )</td>
<td>( \Delta H ) KJ mol(^{-1})</td>
<td>( \delta \Delta H )</td>
<td>( \Delta S ) Jdeg mol(^{-1})</td>
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</tr>
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<td>( H_2O )</td>
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<td>( H_2O )</td>
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SECTION 6

DISCUSSION OF RESULTS FOR PHENOLS
The free energy of transfer of an uncharged species or of a neutral electrolyte from one solvent to another is a concept with rigorous thermodynamic definition. However, thermodynamics offers no assistance in separating this free energy into the individual contributions of the ions making up the electrolyte. Nevertheless, in the case of hydrochloric acid, it is the medium effect $m\gamma_H$ of hydrogen ion that is the key to a single scale of electrode potentials and to a single scale of hydrogen-ion activity in a series of solvent media of different composition. Attempts to evaluate this individual medium effect must rest on non-thermodynamic procedures.

Relative hydrogen-ion activities can be established experimentally in a considerable variety of non-aqueous and partially aqueous media. In most of these solvents, the hydrogen ion can normally be expected to have a fixed structure. Experimentally determined ratios of hydrogen-ion activity can then be interpreted in terms of ratios of hydrogen-ion concentrations, together with activity coefficients which are, in large part, a reflection of interionic forces in each particular solvent. No medium effect is involved.

On the other hand, estimates of the proton activity or escaping tendency, in a solution in solvent A with respect to that of a solution in solvent B are purely speculative. What is required is a knowledge of the difference of chemical potential of the proton in the standard reference states of the two solvents. This is, of course, $RT \ln m\gamma_H$. 
The change in the proton activity as solvent composition is altered can thus be attributed to the effect of the properties of the solvent on the free energy of the ions, that is, to ion-solvent interactions. In a qualitative way, such properties as dielectric constant, acidic strength, and basic strength of the solvent play a major, but not exclusive, role. According to simple electrostatic theory, the free energy of a charged spherical ion depends on the dielectric constant of the medium in which it is immersed, increasing as the dielectric constant is lowered.\(^{(32)}\) One mole of univalent ions should, according to the Born equation,\(^{(33)}\) experience an increase of free energy, \(\Delta G^0_t\) (el) when transferred from water to a medium of dielectric constant, \(D\), given by:

\[
\Delta G^0_t\ (\text{el}) = \frac{694.1}{r} \left( \frac{1}{D} - 0.0128 \right)
\]

where \(\Delta G^0_t\) (el) is in kilojoules per mole, and \(r\) is the radius of the spherical ion in Angstroms.

In addition to this electrostatic transfer energy, solvation of the ion will exert a profound influence on the energy required to remove one mole of ions from the standard reference state in one solvent and transfer it into the standard state in another solvent. In the case of the hydrogen-ion, a special type of solvation, namely, acid-base interaction with the solvent, must play a vital role; for example, a solvent with a pronounced basic property will hold the protons very firmly so that this transfer of protons from water to other solvents is possibly a good measure of the relative basicities of solvent.

The transfer free energy thus includes contributions of both electrostatic charging effects and solvation. Therefore, it
might be described by:

\[ \Delta G^0_t = \Delta G^0_t^{(el)} + \Delta G^0_t^{(solv)} \]

Although the \( \Delta G^0_t^{(el)} \) term can be estimated by the Born equation, this formula is usually of limited usefulness for quantitative calculations because it assumes the ions to be spherical and does not take solvation into account. Further, the effective dielectric constant close to an ion is probably quite different from that in the bulk of the solution and in mixed solvents. Then, to add to the problem, the effective radius (r) of the ion is not known.\(^{(34})(35)(36)\)

Predictably, there have then been several attempts to improve on the Born equation with the object of deriving a formula by which reliable values of transfer free energies could be obtained, but each approach leaves something to be desired, even though they are often useful for qualitative calculations of differences in the transfer free energy for various charged species, under conditions such that a uniform solvation pattern exists.
ION-SOLVENT INTERACTIONS

It is clear now that an acid-base equilibrium of the type:

\[ \text{HA} + \text{SH} \rightleftharpoons \text{SH}^+ + \text{A}^- \]

is markedly influenced by the dielectric constant of the solvent, as well as by the acid-base properties of the solvent. Other solvent interactions capable of stabilizing the anion \( \text{A}^- \) or the acid \( \text{HA} \) also affect the point of equilibrium. Broadly speaking, this is solvation effects.

An acid-base equilibrium of the type described above, then, will be affected if the solvation of the species \( \text{HA} \) and \( \text{A}^- \) is different in different solvents, and influences of this kind are revealed by comparing the strength of the two acids as the solvent is changed. The relative strength of the acids \( \text{HA} \) and \( \text{HB} \) in a given solvent is expressed by the magnitude of the equilibrium constant for the reaction:

\[ \text{HA} + \text{B}^- \rightleftharpoons \text{HB} + \text{A}^- \]

In general, it is to be expected that ion-solvent interactions will be stronger than interactions between the uncharged species and the solvent molecules. Consequently, any inequality in the solvation of the two anions \( \text{A}^- \) and \( \text{B}^- \) as the solvent is changed will affect the magnitude of the equilibrium constant and lead to the conclusion that the relative strengths of \( \text{HA} \) and \( \text{HB} \) are dependent on the solvent chosen.

Grunwald\(^{(37)}\) and Parker\(^{(38)}\) have made interesting contributions to an understanding of the role of anion solvation in
determining relative acidic strengths in various media. Grunwald suggests that delocalization of charge in some anions promotes interaction with localized dispersion centres in nearby solvent molecules. These delocalized dipole oscillators are the same ones responsible for the spectral absorption in the visible region observed with such anions as 2,4-dinitrophenolate, while the corresponding acid is colourless. Dispersion forces produce an interaction between the delocalized oscillators and the electronic oscillators localized in the atoms or bonds of the solvent molecules. The result is the free energy of those anions with delocalization of charge lowered, relative to that of ions such as benzoate which is a localized oscillator. The effective density of dispersion has been found\(^{(37)}\) to increase in the sequence \(\text{H}_2\text{O} < \text{CH}_3\text{OH} < \text{C}_2\text{H}_5\text{OH}\) and our results for phenols are in accord with this finding.

Parker, on the other hand, suggests that the free energy change is related to the medium effect activity coefficient \((m\gamma_i)\) and it may be convenient to regard \(m\gamma_i\) as a product of two partial medium effects; one embodying changes in chemical potential due to, for example, hydrogen bonding; the other including all other changes in transfer energy. The very good correlation between the hydrogen-bonding coefficient and the change of the equilibrium constant on transfer from dimethylformamide to methanol emphasizes the importance of solvent-anion interaction. It would appear, then, that hydrogen bonding solvation or stabilization of anions by methanol can account almost entirely for the changes in the position of the acid-base equilibrium found experimentally.

Unfortunately, however, in the present studies hydrogen bonding must occur in both water and methanol systems; and it can
only be assumed that the degree of hydrogen bond changes as the solvent changes from water to water-methanol. The extent of change can only be surmised.
SELECTIVE SOLVATION IN BINARY MIXTURES

The selective solvation of ions in binary mixtures, such as water/methanol, depends on the free energy of solvation of the ions in the two pure solvents. Because it is impossible to transfer a single ion between two phases, the free energy of one reaction alone cannot be measured directly. Using non-thermodynamic assumptions, however, it is possible to estimate the free energy of solvation of single ions. Several authors have discussed the primary hydration of ions by considering the interaction energy of an ion and the hydrating water molecules. Further, many experimental results have been discussed with the help of the Born equation and one of interest here is that the free energy of transfer of alkali ions and the hydrogen ion from water to the binary mixtures of methanol and water decreases with increasing mole fraction of methanol. At high methanol concentrations, the free energy values begin to increase. The inference drawn is that the cations are in lower free energy states in methanol-water mixtures than in water.
PREFERENTIAL SOLVATION

In mixed solvents, it has to be recognized that different types of solvent molecules may interact individually and to different extents with acidic and basic species present in the solvent medium.

Unfortunately, few studies have been made on this subject of selective solvation. It has been commonly assumed that ions in a binary solvent are predominantly surrounded by molecules of the more polar constituent, that is, by water rather than by methanol. The work of Grunwald\(^{(46)}\) on the other hand, shows that simple inorganic ions are appreciably solvated by dioxane in dioxane-water-solvents. Further, the solvation of large organic ions with low density of surface charge was found to resemble closely that of structurally similar uncharged molecules.

Thus, in the present studies, if solvation is a major contributor to the thermodynamic parameter \(\Delta G\) - arising through \(\Delta S\) - then it would appear that in water-methanol solvent systems, the phenolate ion is appreciably solvated by the methanol.

It is interesting to note that the various methods for estimating the free energy of transfer of individual ions from water to alcohols or water-alcohol systems usually agree that the free energies of transfer of cations and anions are of opposite sign and that the proton does not differ in this respect from other cations. Franks and Ives\(^{(45)}\) regard this as evidence that the failure of the Born treatment is complete and that the transfer free energies of ions must be largely determined by short-range interactions. That the Born equation by itself fails to account for transfer free energies is undeniable, but the view of Franks and Ives could be
extreme for the Born equation cannot do more than predict the electrostatic (coulombic) work of transferring the ion from one medium to another of different dielectric constant, and superimposed on this electrostatic energy is a solvation energy with which the Born equation cannot deal.

The apparent enhancement of the stability of cations upon transfer from water to water-methanol solvents has been attributed\(^{(47)(48)}\) to changes in the structure of the primary solvation shell, in which the increased electron density on the oxygen of the solvating species plays a major role. This increase results from the inductive effect of the methyl group and may well be exerted both on the oxygen of the methanol molecule and that of water molecules hydrogen bonded to methanol. On the other hand, anions become less stable, because anion solvation is also influenced by a reduction in charge on the hydrogen atoms of the solvent OH groups, bringing about decreased coulombic interaction with the anionic charge. The presumed structure of the primary solvation shell in methanol-water solvents can be as shown in Figure 2 below.

The complexity of the ion-solvent interactions is well illustrated by the conflicting evidence concerning the relative basicities of water and methanol. As already indicated, the investigation of transfer free energies brings one to the conclusion that anions are in a higher free energy state in methanol-water mixtures than in water alone, whereas cations (the proton included) are in a lower free energy state.
Fig. 2: Structure of the primary solvent shells around alkali and halide ions in methanol-water solvents (R = methyl)

Note: The inductive effect of the methyl group (R) is indicated by the arrows.

Finally, it must be appreciated that the free energy of transfer of the proton from water to another solvent of identical \textit{basicity} would not be zero if the dielectric constants of the two solvents were different. There are other complications as well. Franks and Ives\textsuperscript{(45)} have discussed this situation in detail and they point out that it is often not meaningful, in a hydrogen-bonded liquid system, to assign intrinsic basic or acidic strengths to
species that exist under the strong influence of each other. They regard the primary solvation zone to dominate the free energy of transfer, but secondary zones are envisaged in which field-induced molecular orientation may be strongly assisted by hydrogen bonding with molecules in the primary solvation shell, where dielectric saturation may occur. However, as the radius of the ion becomes greater and the field becomes correspondingly weaker relative to thermal agitation, further contributions to the free energy of solvation are correctly estimated by the Born equation.

In spite of progress in this field, there is, as yet, no means of evaluating in a reliable way the proton affinity of one medium with respect to that of another. It is hoped, however, that the experimental values given above will help in a better appreciation of the problem.
SPECIFIC AND NON-SPECIFIC SOLVENT EFFECTS

It has now been established that there are a series of factors affecting the Hammett linear free energy relationship in mixed solvent systems. These include:

(1) The dielectric constant of the solvent;
(2) The acid-base strength of the solvent; and
(3) The solvation of the ions and molecules of the solute.

Solvent effects on rate and equilibrium constants are of major importance; in fact, no less in magnitude than structural effects. In addition, it is generally agreed that the problem of solute-solvent interaction is no less complicated than that of structural effects.

A general statement, however, can serve as a general principle. This is the conclusion that solvent effects on chemical reactivity and on various physical and physico-chemical phenomena such as spectra, activity coefficients, etc., are similar in their very nature. This similarity is considered to show that there are comparatively few mechanisms of physical interaction between solvent and solute. Thus, the problem can be reduced to finding general ways of treating the data in order to express these interactions quantitatively.

The following basic principles can be assumed:

(a) The free energy of any compound, including any solute, consists of two parts: an additive (non-perturbed) term and a contribution caused by different kinds of interaction (perturbation). The essence of this
principle is that any deviation from additivity is automatically identified with some kind of interaction.

(b) Any interaction so defined may be expressed as a sum of terms, each of which represents a definite formal interaction type.

(c) The factors (variable substituent, solvent, temperature, etc.) influencing the magnitude of interaction terms can be identified, so that each interaction term is considered to depend on several definite variable factors, and each factor can influence the magnitude of several interaction types.

Thus, the free energy \( G \) is expressed by:

\[
G = G_0 + \Sigma A_i;
\]

where \( G_0 \) is the additive part of the energy and \( A_i \) is the interaction term or contribution to free energy.

For free energy changes, then, this leads to:

\[
\Delta G = \Delta G_0 + \Sigma \phi_i(n) \chi_i n
\]

and practical use of this last equation is possible when the number of formal interaction types to be taken into account has been stated and the set of parameters \( \chi_i \) has been defined.

Historically, two basic alternative and complementary viewpoints on the influence of solvation on free energy change have been established.

In the first viewpoint, the solvent is considered as a homogeneous isotropic continuum which surrounds the molecules of the
solute. The intensity of solvent-solute interactions in solvents of this type is considered to be determined by macroscopic physical parameters of the solvent, e.g. dielectric constant, and by the molecular characteristics of the solute. Solvent effects of this type caused by long-range intermolecular forces are sometimes called 'non-specific' or 'universal' solvent-solute interactions.

According to the second alternative, the medium should be characterized as anisotropic and unhomogeneous, and these features determine the nature of the solvent-solute interactions. It is widely believed that such solvent-solute interactions are chemical (short-range) in nature and consist of the formation of solvation complexes through donor-acceptor bonds which are localized and directed in space in a definite manner. Sometimes strong dipole-dipole interactions, concentration fluctuations in multicomponent solvent-solute systems, etc., are also dealt with in this subdivision. Solvent effects of this type are usually called 'specific solvation effects'.

The nature of specific solvent-solute interactions may be considered in terms of a model involving the formation of donor-acceptor bonds between interacting molecules of solute and solvent, regarded as Lewis acid-base. To be more exact, the most important manifestation of a specific solvation is regarded as being connected with the behaviour of protic (Brønsted) acids as Lewis acids, when hydrogen-bonded solvent-solute complexes are formed. Solvent-solute interactions between acidic (electron accepting) solvent and basic (electron donating) solute, is often called 'electrophilic solvation'. The opposite case is called 'nucleophilic solvation'.

Besides these two concepts, the idea of so-called 'co-operative' solvent-solute interactions has also been suggested. In essence, this type of interaction is considered intermediate between the above specific and non-specific solvation mechanisms. It takes into account specific interaction of solute with solvent molecules beyond the first solvation shell.

The most elaborate amongst the theories of non-specific solvation are those which consider solvation processes as various types of electrostatic, induction or dispersion interactions. The intensity of these interactions depends on the static or induced distribution of charges (dipoles, point charges, etc.) of the molecules of the solute on the one hand, and on the macroscopic dielectric constant and polarisability of the solvent on the other hand. The basic principles of these theories were mainly worked out by Born, Kirkwood, and Onsager.

But it is noteworthy that, in general, numerous attempts to interpret solvent effects of all kinds on chemical reactivity and physical properties on the basis of the dielectric approach alone have failed.

The general failure of fundamentally classical theories, derived from non-specific solvent-solute interaction models, does not mean that chemical specific solvation theories have escaped a similar fate; hence the search for some new approach to the quantitative treatment of solvation problems. These include:

(a) polarity scales based on chemical processes;
(b) empirical solvent polarity parameters from shifts in electronic spectra;
(c) solvent polarity parameters based on the dependence on the solvent of infra-red stretching frequencies arising from attached groups;
(d) the N.M.R. solvent polarity P-scale; and
(e) Empirical Solvent Polarity Parameters devised on the basis of other model processes, e.g., Hildebrand's solubility parameter.

All such polarity scales are formally based on the assumption that it is necessary to take into account only one mechanism of solvent-solute interaction. Frequently, however, this fact is overlooked; and in addition, different empirical polarity parameters are wrongly linearly related to each other because there is only a limited range of solvents in general use. In principle, however, this does not exclude the possibility that solvent effects on certain processes, or in selected solvents, can be related to the alteration of the intensity of solvent-solute interaction, in the framework of a single interaction mechanism. Unfortunately, in practice, the number of processes depending on the influence of only one solvent property is very limited.

The quantitative treatment of solvent effects in mixed solvents presents a special problem. Additional problems arise when one of the components (Sk) of a binary solvent mixture interacts specifically with solute A, whereas the other does not solvate A by that mechanism.

Inevitably, there is a certain range of concentrations of the solvent components for which the solvation equilibrium:

\[ \text{A + Sk} \rightleftharpoons \text{ASk} \]

does not lie virtually either to the left or to the right. Specifically, non-solvated (A) as well as solvated (ASk) molecules of solute participate in the chemical reaction, and they react at different rates.
Besides this solvation equilibrium, similar equilibria may also involve the interaction of the components of mixed solvents and, as the concentration of the binary solvent changes, a shift in the solvent-solvent interaction could be expected:

$$Sk + Se \rightleftharpoons Sk Se$$

where k and e refer to the two solvents in the mixture.

In our present studies, it is of course evident that in 50 weight % methanol-water solvent, both solvents are solvating the molecule or anion of the phenols, for there is an increase in entropy (which is assumed to be external and therefore due to solvation) in going from pure water to the mixed solvent. But our studies do not allow any prediction regarding at what water-methanol ratio the methanol dominates the solvation process.

The problem of calculating the contribution of non-specific solvent-solute interaction, to gross solvent effects is of basic importance. By definition, all solvents are able to interact with the solute non-specifically, but the analogous statement for specific solvation is not true. Consequently, specific solvation is always accompanied by non-specific solvation, but not vice-versa.

The subtraction of the polarity ($yY$) and polarisability ($pP$) contributions from the total solvent effect automatically allows the definition of a contribution, $\Delta Asp$, from specific solvent-solute interactions. Thus:

$$\Delta Asp = A - Ao - yy - pp$$

where A is the solvent-sensitive characteristic for a given process. If for a given process the susceptibility parameters, y and p, can
be estimated by correlating the data for properly selected non-specifically interacting solvents only, the ΔAsp can be calculated for any specifically interacting solvent. Further, if the process is sensitive to a single kind of specific interaction only (e.g. nucleophilic or electrophilic solvation) the ΔAsp values can be regarded as a set of solvent parameters.

In practice, the calculation of Ao, y and p values involves a degree of uncertainty because the requirement of the presence of a single specific solvation mechanism is fulfilled only approximately.

Thus the general correlation equation for the simultaneous separate calculation of the contributions of different types of non-specific solvent effect (polarity and polarisability) and specific-solute interaction (electrophilic and nucleophilic solvation) can be represented by:

\[ A = A_0 + yY + pP + eE + bB \]

where e and b now characterize the sensitivity of a given process towards electrophilic and nucleophilic solvation effects respectively.

Unfortunately, however, such data is not available to allow numerical calculations for this present study.
SECTION 7

DISCUSSION OF RESULTS FOR ANILINES
SIGNIFICANCE OF THE SOLVENT EFFECT ON ANILINES

The effect of solvent on the Gibbs free energy change for the dissociation of a weak acid can, as mentioned earlier, be ascribed to a change in the electrostatic self energy of the ions; and the simplest expression for the electrostatic energy of a mole of univalent ions, which includes phenols and anilines, is that of Born:

$$\Delta G_{el} = \frac{N e^2}{2} \frac{1}{1/e r s}$$

where $N$ is Avagadro's number, $e$ the electron charge, $\varepsilon$ the dielectric constant of the medium, and $r_s$ the radius of the spherical ion (ideal system). It is assumed here that the solvent is a continuous medium with a dielectric constant equal at all points to the macroscopic dielectric constant.

The dissociation of anilinium ions is an isoelectric process:

$$BH^+ + SH = B + SH_2^+$$

The change in electrostatic energy on transfer from water to 50 weight % methanol is then:

$$\Delta G_{el} \leq \frac{N e^2}{2} \left( \frac{1}{\varepsilon} - \frac{1}{\varepsilon_{50\%methanol}} \right) \left( \frac{1}{r_{H^+}} - \frac{1}{r_{BH^+}} \right)$$

where $\varepsilon$ the dielectric constant of 50 weight % methanol is 56.3$^{51}$ and $\varepsilon$ the dielectric constant of water 78.4. Thus $\Delta G_{el}$ will have a positive value in $r_{BH^+} > r_{H^+}$.
Although the value assigned to the radius of the hydrogen ion may be uncertain because of solvation problems, it can reasonably be expected that the protonated anilinium ion could be larger than the hydrogen ion. In fact, a radius of 4 Å has been given to the tetraethyl ammonium ion and this could reasonably be taken as an estimate of the radius of the anilinium ion. An ion with this radius contributes about 0.9 kJ mol\(^{-1}\) to the electrostatic energy change on transfer from water to 50 weight % methanol.

The difficulty in applying the above equation to an acidic dissociation process lies in our ignorance of the effective radius of the hydrogen ion, even though considerable evidence points to the hydrogen ion associating with four water molecules in solvents containing a considerable amount of water. Thus it is reasonable to assign the tetra-hydrated hydrogen ion with the diameter of the water molecule, viz.: 2.8 Å. This size contributes 1.24 kJ mol\(^{-1}\) to the electrostatic energy.

The total electrostatic effect on dissociation of the anilinium ion should, therefore, be about 0.4 kJ mol\(^{-1}\). In fact, the experimental value of 0.8 kJ mol\(^{-1}\) assuming a diameter of 4 Å is substantially different, an anomaly seen in all protonated bases.

This anomaly has been ascribed to an increase in the basicity of the solvent on the addition of methanol and might be due to a breakdown of the water structure by the methanol.

A structure promoting entity is more effective in a methanolic solvent than in water because there are more opportunities for the water structure to be promoted. Hydrogen ion should be one of the best structure promoters and therefore we have a reasonable
explanation of the increase in acidity of the anilinium ion on addition of methanol. But the magnitude of the electrostatic effect is greater than that allowed for in the Born treatment; and this has led to assuming other than the simple Born model - for example, the model proposed by Ritson and Hasted. Three regions of solvent distribution around an ion are considered. From the surface of the ion of radius, $r_s$, to a distance $1.5 \AA$ from its centre is a region of dielectric solvation with a dielectric constant of $\varepsilon_{\text{sat}}$ for water solvents. $\varepsilon_{\text{sat}}$ may be taken as 5. At distances greater than $4 \AA$ from the centre of the ion, the solvent has its macroscopic dielectric, $\varepsilon_0$. In the intermediate region, the dielectric constant varies linearly with $r$.

The variation of the dielectric constant in water and in 50% methanol with distance from the centre of the ion is shown in Figure 3.

![Figure 3: Variation of the dielectric constant of water and 50% aqueous methanol in the vicinity of an ion; $r_s$ is the distance from the centre of the ion.](image-url)
Calculation on amines using this approach tend to illustrate that, no matter how doubtful some of the assumptions about the ionic radii may be, the basicity effect in the opposite direction must be of some magnitude - in fact, about 2 kJ mol$^{-1}$ - when methanol is added to water to make a 50 weight % mixture. All this, of course, illustrates that there is always a term of considerable magnitude for the basicity effect that does not figure in the electrostatic treatment.

In any solution system, the value $\Delta G$ is governed by both enthalpy and entropy effects. These may be additive or compensating. However, normally changes in $\Delta S$ are considered to arise mainly from solvation effects and, when considering our experimental values for phenols, it is significant that the increase in $\Delta G$ values arise primarily from an increase in $\Delta S$ values with $\Delta H$ values remaining substantially constant. This, then, is evidence that, even in the mixed solvent system, the methanol is certainly contributing to the overall solvation process, that is, the solvation effect is not dominated by water, as is often proposed. Quantitatively in fact, for the phenols, the $\delta \Delta S$ values are somewhat similar, which tends to suggest that solvation is of the same order of magnitude for this series.

However, in the case of anilines, solvation, even in water, is not very significant, so that it is not expected - nor indeed found - that mixed solvents significantly effect the solvation process for anilines.
BIBLIOGRAPHY


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PUBLICATION
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PUBLICATION

It is anticipated that publication based on the present study will follow shortly.
APPENDIX
APPENDIX

This is a general program for use with acids measured by the "standard buffer" technique. It evaluates raw experimental pKa values from measured optical absorbance, reading at each temperature of measurement:

C EXPERIMENTAL PKAS FROM ABSORBANCE READINGS.
DIMENSION Y(100),P(100),A(100),PKA(100),TEM(100)
CHARACTER*4 HEADS(7)
DATA HEADS/" NO',' TEM',' PH','BASE','BUFF','ACID','PKA"/
C NUMBER OF OPTICAL ABSORBANCE READINGS
READ(5,1)N
C NAME OF THE COMPOUNDS (FIRST FORTY SPACES)
READ(5,2)
C ANALYTICAL WAVELENGTH WHERE ABSORBANCE READINGS HAVE BEEN MEASURED.
READ(5,1)WL
C TEMPERATURE, PH VALUES, ABSORBANCE VALUE BASE FORM, VALUE BUFFER, VALUE ACID.
READ(5,3)(TEM(I),PH(I),BASE(I),BUFF(I),ACID(I),I = 1,N)
WRITE(6,6)WL
WRITE(6,4)HEADS
DO 10 I = 1,N
10 X(I) = BASE(I)-BUFF(I)
DO 20 I = 1,N
20 Y(I) = BUFF(I)-ACID(I)
DO 30 I = 1,N
30 A(I) = X(I)/Y(I)
DO 40 I = 1,N
40 P(I) = ALOG10(A(I))
DO 50 I = 1,N
50 PKA(I) = PH(I)+P(I)
WRITE(6,5)(I,TEM(I),PH(I),BASE(I),BUFF(I),ACID(I),PKA(I),I = 1,N)
1 FORMAT(I5)
2 FORMAT(40H)
3 FORMAT(5E10.4)
4 FORMAT(2X,2X,2X,2X,2X,2X,2X,2X,2X)
5 FORMAT(2X,2X,2X,2X,2X,2X,2X,2X,2X,2X,2X,2X,2X,2X,2X,2X,2X,2X,2X)
6 STOP
END