THE EFFECT OF DIELECTRIC CONSTANT ON ACID–BASE EQUILIBRIA[1, 2]

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Acid–base equilibria are usually represented by the equilibrium constant for the reaction

$$A^n + S \rightleftharpoons SH^+ + B^{n-1} \tag{1}$$

where A is an acid, S the solvent, SH^+ the solvated proton, and B the conjugate base. The change in the value of the equilibrium constant with electrolyte concentration depends upon the charge types involved and the solvent. For dilute aqueous solutions the concentration of solvent is usually considered constant, and the equilibrium constant is written

$$K_C = C_{H_3O^+} \frac{C_B}{C_A} \tag{2}$$

For the monosubstituted benzoic acids

$$\frac{K_C \ (\mu = 0.05 \text{ for solvent salt LiCl})}{K_C \ (\mu = 0)}$$

is found to be 1.45 in water, 5.5 in methyl alcohol, approximately 17 in ethyl alcohol, and 7.0 for a dioxane–water mixture of the same dielectric constant as ethyl alcohol. It has been reported that $\log K_C$ varies linearly with the reciprocal of the dielectric constant for glycerol–water and dioxane–water mixtures.

Instead of using the solvated proton as the standard acid to compare acid–base equilibrium constants in various solvents, it is more convenient to refer to a standard of the same charge type. This equilibrium constant $K_{A_xB_0}$ for the reaction

$$A_x + B_0 \rightleftharpoons A_0 + B_x \tag{3}$$

(where A_0 is benzoic acid for substituted benzoic acids and acetic acid for the aliphatic acids) is the ratio of the two dissociation constants as given in equation 2. $K_{A_xB_0}$ is approximately independent of the concentration of solvent salt over a considerable range in the solvents water, ethylene glycol, and methyl, ethyl, n-propyl, and n-butyl alcohols. The change in the constant $K_{A_xB_0}$ with dielectric constant can be represented for the pure solvent by the equation

$$\log K_{A_xB_0} = \log K_{a_xb_0} + \frac{L}{D} \tag{4}$$

where L is a constant specific to each acid. For the mixed solvents such as dioxane–water and alcohol–water, linearity with the reciprocal of the dielectric constant is not observed.

Acid–base equilibria are often represented by the equilibrium constant for the reaction

$$A_x^n + S \rightleftharpoons SH^+ + B_x^{n-1} \tag{1}$$

where A_x is an acid, S a basic solvent, SH^+ the solvated proton, B_x the conjugate base, and n the charge on the acid. This process involves a number of steps. When an uncharged acid A_x is introduced into the solvent S, the molecules of solvent orient themselves around the acid molecules under the influence of dipole or other forces; a proton is transferred from the acid A_x to the base S, and two ions, the solvated proton and the base B_x^-, are formed. In addition to this, the solvent molecules are now oriented about the ions and ionic atmospheres created. The equilibrium constant for such a process is given by the equation

$$K_{A_xS} = \frac{C_{SH^+}}{C_S} \cdot \frac{C_{B_x^-}}{C_{A_x}} \tag{2}$$

where the concentrations may be expressed in moles per liter, moles per 1000 grams of solvent, or mole fractions.

TABLE 1

Effect of electrolyte concentration on the reaction $A_0 + S \rightleftharpoons SH^+ + B_0^-$

Solvent	Water	Methyl alcohol	Ethyl alcohol	Dioxane-water
Dielectric constant	78.5	31.5	24.2	25
$\dfrac{K_C \ (\mu = 0.05, \text{ mostly LiCl})}{K_C \ (\mu = 0)}$	1.45	5.5	18	7

Since the concentration of solvent is considered constant, it is customary to write

$$C_S \cdot K_{A_xS} = C_{SH^+} \frac{C_{B_x^-}}{C_{A_x}} = K_c \tag{3}$$

where K_c is the familiar dissociation constant. Both K_{A_xS} and K_c vary with ionic strength, the change in sufficiently dilute solutions for solvents of sufficiently high dielectric constant being given by the relation

$$\log K_c = \log [K_c]^0 + A\sqrt{\mu} \tag{4}$$

where $A/2$ is the familiar Debye–Hückel constant. The values for A at 25°C. are 1.020 for water (dielectric constant $= 78.54$), 4.02 for methyl alcohol ($D = 31.5$), 5.97 for ethyl alcohol ($D = 24.2$), and 9.79 for butyl alcohol ($D = 17.4$). For more concentrated solutions no theoretical equation can be given, but it might be well to point out that the change in the equilibrium constant K_c is of considerable magnitude and depends on the solvent (10); see table 1.

Leaving the correction for the ionic atmosphere, it is seen that the solvent itself and the dielectric constant of the medium play important rôles in the process represented by equation 1. The formation of the ions involves a charg-

ing process, the transfer of the proton involves electrostatic work depending on the dielectric constant, and the solvation of the ions and molecules involves the dielectric constant and the structure of the solvent (4).

Equation 3 makes the standard acid the solvated proton, and equation 2 represents the ratio of the dissociation constant of the acid A_x to that of the acid SH^+. Since the solvated proton is a different acid in each basic solvent, one can hope to eliminate the solvent by choosing a standard acid other than the solvated proton (35). For example, if we choose benzoic acid as the standard acid, we have

$$K_c = C_{SH^+} \frac{C_{B_0^-}}{C_{A_0}} \tag{5}$$

and, dividing equation 3 by equation 5,

$$\frac{K_{C(A_x)}}{K_{C(A_0)}} = \frac{C_{B_x^-}}{C_{A_x}} \cdot \frac{C_{A_0}}{C_{B_0^-}} = K_{A_x B_0} \tag{6}$$

which is the equilibrium constant for the reaction

$$A_x + B_0^- \rightleftharpoons A_0 + B_x^- \tag{7}$$

This equilibrium constant will be less sensitive to changes in ionic strength, since there are equal numbers of equally charged ions on both sides. The effect of the nature of the solvent will be much less, and the rôles of the dielectric constant of the medium and the structure of the acids will be relatively more important. In any case, table 2 shows that the order of acid strength is not independent of the medium (6, 7, 8, 9, 10, 22, 23). In table 2 the order of acid strength decreases from top to bottom. The order will be the same in any particular solvent, whether we use the solvated proton or any other acid as the standard acid. The practice of using the thermodynamic dissociation constant in water at 25°C. as a basis of acid strength has been defended by Dippy (5), who claims that there is no proof that the dissociation constants in water are likely to give an ambiguous relative order. He recognizes exceptions in the case of the ortho-substituted benzoic acids. Since the equations

$$-RT \ln K^0 = \Delta F^0 = \Delta H_0 - T\Delta S^0 \tag{8}$$

and

$$\frac{d(\Delta H)}{dT} = \Delta C_p \tag{9}$$

connect the equilibrium constant, the free-energy change, the heat content change, the entropy change, and the change in heat capacity, a relationship between change of structure and any of these thermodynamic quantities might be sought. Harned and Embree (18) point out that in any discussion of dissociation constants in relation to constitution it will be essential to compare the values of the dissociation constants at their maxima or at their corresponding temperatures θ as given by the equation

$$\log K = \log K_m - p(t - \theta)^2 \tag{10}$$

TABLE 2

Order of acid strengths of substituted benzoic acids

SOLVENT		H₂O	(CH₂OH)₂	CH₃OH	C₂H₅OH	n-C₃H₇OH	n-C₄H₉OH	DIOXANE–WATER		
DIELECTRIC CONSTANT	∞ Extrapolated	78.5	37.7	31.5	24.2	20.1	17.4	55	40	15
Substituent groups...	o-NO₂	o-NO₂	o-NO₂	o-NO₂	o-NO₂	o-NO₂	o-NO₂	o-NO₂	o-NO₂	o-OH
	o-I	o-Br	o-OH	o-OH	o-OH	o-OH	o-OH	o-OH	o-OH	o-NO₂
	o-Br	o-I	o-Br	o-Br	m-NO₂	o-Br	p-NO₂	o-Br	p-NO₂	p-NO₂
	o-Cl	o-Cl	o-Cl	o-Cl	p-NO₂	m-NO₂	m-NO₂	o-Cl	o-Br	m-NO₂
	o-OH	o-OH	o-I	o-I	o-Br	p-NO₂	o-Br	o-I	m-NO₂	o-F
	o-F	o-F	p-NO₂	m-NO₂	o-Cl	o-I	o-Cl	o-F	o-Cl	o-Br
	p-NO₂	p-NO₂	m-NO₂	p-NO₂	o-I	o-Cl	o-I	p-NO₂	o-F	o-Cl
	m-NO₂	m-NO₂	o-F	o-F	o-F	o-F	o-F	m-NO₂	o-I	o-I
	o-CH₃	m-Br	m-Br	m-Br	m-Br	m-Br	m-Cl	m-Cl	m-Cl	m-Cl
	m-Br	m-Cl	m-Cl	m-Cl	m-Cl	m-I	m-Br	m-Br	m-Br	m-Br
	m-Cl	m-I	m-I	m-I	m-I	m-Cl	m-I	m-F	m-F	m-F
	m-F	m-F	m-F	m-F	m-F	m-F	p-Br	m-I	m-I	m-I
	m-I	o-CH₃	p-Br	p-Br	p-Br	p-I	m-F	p-F	p-Cl	p-Br
	m-OH	p-Br	p-I	p-Cl	p-I	p-Br	p-I	o-CH₃	p-I	p-Cl
	p-I	p-Cl	p-Cl	p-I	p-Cl	p-Cl	p-Cl	m-OH	p-Br	p-I
	p-Br	o-OCH₃	o OCH₃	p-F	o-OCH₃	o-OCH₃	o-OCH₃		p-F	p-F
	p-Cl	m-OH	o-CH₃	o-OCH₃	p-F	p-F	p-F			
	o-OCH₃	p-F	p-F	o-CH₃	o-CH₃	o-CH₃	o-CH₃			

Benzoic acid

	∞ Extrapolated	78.5	37.7	31.5	24.2	20.1	17.4	55	40	15
Substituent groups...	p-F	m-CH₃	m-OH	m-CH₃	m-CH₃	m-CH₃	m-CH₃	o-OCH₃	m-OH	m-OH
	m-CH₃	p-CH₃	m-CH₃	m-OH	m-OH	m-OH	m-OH	m-CH₃	o-CH₃	o-OCH₃
	p-CH₃	p-OCH₃	p-CH₃	p-CH₃	p-CH₃	p-CH₃	p-CH₃	p-CH₃	o-OCH₃	m-CH₃
	p-OCH₃	p-OH	p-OCH₃	p-OCH₃	p-OCH₃	p-OCH₃	p-OCH₃	p-OCH₃	m-CH₃	p-CH₃
	p-OH		p-OH	p-OH	p-OH	p-OH	p-OH	p-OH	p-CH₃	o-CH₃
									p-OCH₃	p-OCH₃
									p-OH	p-OH

where K_m is the dissociation constant at the maximum and θ the temperature of the maximum. The constant p was thought to be the same for many acids, but Walde (32) pointed out that $\log K$ is not a quadratic function of the temperature, and Harned and Robinson (20) state that p is a constant characteristic of each acid. More recently it has been shown that the properties of the solvent (water) almost completely determine the value of p (14, 28).

Everett and Wynne-Jones (13) show that the order is not always the same for the different thermodynamic functions; for example, for the toluic acids in water the order for $\Delta F_{298°}$ is

$$o\text{-toluic} > \text{benzoic} > m\text{-toluic} > p\text{-toluic}$$

while ΔH_0 gives

$$o\text{-toluic} > m\text{-toluic} > p\text{-toluic} \sim \text{benzoic}$$

It is also to be noted from table 2 that all three toluic acids are weaker than benzoic acid in dioxane–water mixtures of dielectric constants 40 and 15.

The effect of temperature on the relative strengths of carboxylic acids has been treated by several authors (2, 14, 15, 16), and a correlation of the two effects

$$\begin{array}{cc} \mathrm{I} & \mathrm{II} \\[6pt] \left(\dfrac{\mathrm{d} \ln K_{A_x B_0}}{\mathrm{d}D}\right)_{\text{Temperature shift}} & \left(\dfrac{\mathrm{d} \ln K_{A_x B_0}}{\mathrm{d}D}\right)_{\text{Solvent shift}} \\[10pt] \text{Same solvent} & \text{Same temperature} \end{array}$$

has been attempted. However, the two effects are not the same and should not be so considered. Following Baughan (2), for a given solvent,

$$\frac{\mathrm{d}}{\mathrm{d}T}[\ln K_{A_x B_0}] = \frac{\mathrm{d}}{\mathrm{d}T}\left[\frac{-\Delta F}{RT}\right] = \frac{\Delta H}{RT^2}$$

$$= \frac{1}{RT^2}\left\{[(\Delta H_x)_{A_x} - (\Delta H_x)_{A_0}] + \frac{e^2}{2D}\left(\frac{1}{r_{B_x^-}} - \frac{1}{r_{B_0^-}}\right)\left[1 + T\frac{\partial \ln D}{\partial T}\right]\right\} \quad (11)$$

where $r_{B_x^-}$ and $r_{B_0^-}$ are the radii of the two ions in equation 7, e is the charge on the ion, D is the dielectric constant of the medium, and $(\Delta H_x)_{A_x}$ and $(\Delta H_x)_{A_0}$ are the temperature-independent parts of the heats of reaction for the process represented by equation 1. Now for a given solvent we can regard D as a function of T, or *vice versa*. If we choose D as the independent variable, we write

$$\frac{\mathrm{d} \ln K_{A_x B_0}}{\mathrm{d}D} = \frac{\partial \ln K_{A_x B_0}}{\partial D} + \frac{\partial \ln K_{A_x B_0}}{\partial T}\frac{\mathrm{d}T}{\mathrm{d}D} \quad (12)$$

Now

$$\frac{\mathrm{d} \ln K_{A_x B_0}}{\mathrm{d}T} = \frac{\Delta H}{RT^2} \quad (13)$$

where

$$\frac{d \ln K_{A_zB_0}}{dT} \gtrless \frac{\partial \ln K_{A_zB_0}}{\partial T} \tag{14}$$

in equation 12.

Since (3)

$$\Delta F_{el} = \frac{e^2}{2D}\left(\frac{1}{r_{B_z^-}} - \frac{1}{r_{B_0^-}}\right) \tag{15}$$

and

I
$$\left(\frac{d \ln K_{A_zB_0}}{dD}\right)_{Temperature\ effect} = \frac{\Delta F_{el}}{RTD} + \frac{\partial}{\partial T}\left(\frac{-\Delta F}{RT}\right)\frac{dT}{dD} \tag{16}$$

and

II
$$\left(\frac{d \ln K_{A_zB_0}}{dD}\right)_{Solvent\ effect} = \frac{\Delta F_{el}}{RTD} \tag{17}$$

the criterion that I = II is not that $\Delta H = 0$, but that

$$\frac{\partial}{\partial T}\left(\frac{-\Delta F}{RT}\right)\frac{dT}{dD} = 0 \tag{18a}$$

or

$$\frac{1}{RT^2}\left\{[(\Delta H_z)_{A_z} - (\Delta H_z)_{A_0}] + \frac{e^2}{2D}\left(\frac{1}{r_{B_z^-}} - \frac{1}{r_{B_0^-}}\right)\right\}\frac{dT}{dD} = 0 \tag{18b}$$

If $dT/dD = 0$ (which means that the dielectric constant and temperature of a solvent are independent of each other), or in the event that the { } bracket in equation 18b is equal to zero, then effect I will be equal to effect II. But since $dT/dD \neq 0$ for most solvents, and since only one value of the dielectric constant satisfies the requirement that the { } bracket in equation 18b be equal to zero, it is evident that, in general, effects I and II will be unequal.

Baughan has shown that the variation with temperature of the heats of dissociation of a number of acids in water conforms to an equation similar to 11. However, it is to be noted that the mean radii of the ions used in the calculations are very small, being less than 1 Å. in most cases. Moreover, the substituted acetic acids have smaller radii than acetic acid. On the other hand, calculations for effect II from the equation

II
$$\left(\frac{d \ln K_{A_zB_0}}{dD}\right)_T = \frac{1}{RTD}\left(\frac{e^2}{2D}\left[\frac{1}{r_{B_z^-}} - \frac{1}{r_{B_0^-}}\right]\right) \tag{19}$$

yield values of the radii which are much larger (21). It is evident that the radii should not be considered to have any physical significance but should be regarded

as adjustable parameters in the equation. It is generally recognized that the Born equation (3) for the work done to create the field due to charges on two ions of radii r_+ and r_- in a medium of dielectric D

$$W = \frac{e^2}{2D}\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \tag{20}$$

is only an approximation. Everett and Wynne-Jones (15) have recognized the inadequacy of the Born equation to account for ΔC_p for the dissociation of acids, and Everett and Coulson (12) have attempted to evaluate the contribution of the orientation of the solvent to ΔC_p.

ACID STRENGTHS IN PURE SOLVENTS

In a comparison of the colorimetric and E.M.F. methods for the determination of the equilibrium constant of the reaction of equation 7, it was found that for the solvent methyl alcohol the equilibrium constant was essentially the same at
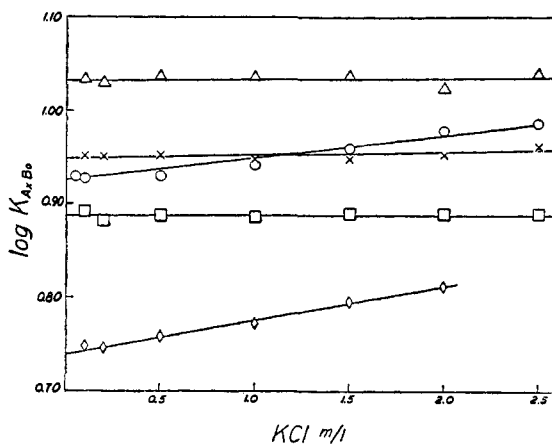

FIG. 1. Effect of electrolyte concentration. Standard acid, acetic acid. △, formic acid; ×, n-butyric acid (up 1.0); ○, monochloroacetic acid (down 1.0); □, propionic acid (up 1.0); ◇, trimethylacetic acid (up 1.0).

zero ionic strength as at $\mu = 0.05$ (mostly lithium chloride). Figure 1 shows that for the aliphatic acids (standard acid, acetic acid) there is no marked change in the value of the equilibrium constant, $K_{A_xB_0}$, over a considerable range of electrolyte concentration if the acids are similar and do not contain strongly polar groups. Examination of the literature shows that these examples are typical (24, 25, 26).

The results of the determination of the ratio of the dissociation constants of the substituted benzoic acids to the dissociation constant of benzoic acid in the solvents water, ethylene glycol, methyl alcohol, and ethyl alcohol can be represented by the equation

$$\log K_{A_xB_0} = \log K_{a_xb_0} + L\left(\frac{1}{D}\right) \tag{21}$$

where $K_{a_xb_0}$ is the intercept at $1/D = 0$; it has been called the "intrinsic acid strength" by Wynne-Jones (35). It is assumed that the intrinsic acid strengths are independent of solvent. Figure 2 presents a few typical results. An examination of the results for the twenty-three acids shows that equation 21 holds in all the pure solvents of dielectric constant > 24, the only exceptions being the ortho acids in the solvent ethylene glycol. Table 3 gives the slopes and intercepts of equation 21, as determined by the method of least squares for all the experimental results in the four solvents (5, 7, 8, 9, 10, 22, 23).
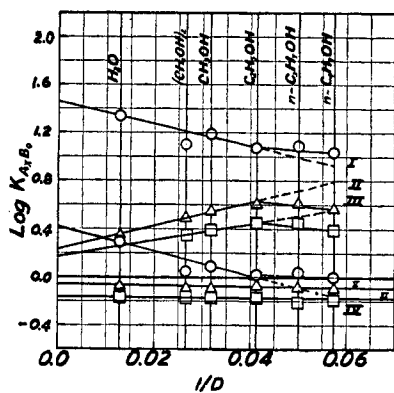

FIG. 2   FIG. 3

FIG. 2. Effect of substituents upon the acid strength of benzoic acid. Curve I, o-iodobenzoic acid; curve II, m-iodobenzoic acid; curve III, p-iodobenzoic acid; curve IV, o-methylbenzoic acid; curve V, m-methylbenzoic acid; curve VI, p-methylbenzoic acid.

FIG. 3. Kirkwood-Westheimer model. Curve I, p-nitrobenzoic acid; curve II, p-chloro- and p-fluoro-benzoic acids; curve III, p-methylbenzoic acid. Experimental values: ×, p-nitrobenzoic acid; □, p-chlorobenzoic acid; △, p-fluorobenzoic acid; ○, p-methylbenzoic acid.
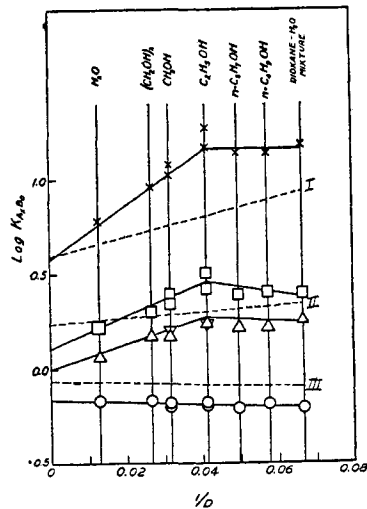
Eucken (11) and Schwarzenbach and Egli (31) have given a formula for the electrostatic effect of a substituent on the acid strength, of the form

$$\log K_{A_xB_0} = \frac{- em \cos \theta}{2.303kTD_E r^2} \tag{22}$$

where m is the dipole moment of the carbon-substituent bond (taken from the corresponding substituted benzene), θ the angle between the dipole and the line joining the mid-point of the dipole to the proton, r the distance from the proton to the mid-point of the dipole, and D_E the effective dielectric constant through which the electrostatic field operates. The difficulties of applying such an equation are that the calculated value of $K_{A_xB_0}$ is very sensitive to the value chosen for r, and that D_E must be evaluated. Kirkwood and Westheimer (34)

have evaluated D_E by considering the ions and molecules involved as ellipsoidal cavities of low dielectric constant with the charges along the focal line, and Westheimer (33) has recently evaluated log $K_{A_xB_0}$ for the para-substituted benzoic acids in aqueous solution. The calculations and comparison with experiment for the alcohols as solvent have been given elsewhere (9, 22, 23). Figure 3 shows that the observed relative acid strengths are more sensitive to the macrodielectric constant than the predictions of theory. Calculations are in progress with another model which approximates the benzenoid molecule more closely.[3] In this model the cavities are considered as oblate spheroids with the charges on the focal ring. This model permits calculation of the meta-substituted acids and may reveal the magnitude of the rôle of resonance in the benzene ring.

TABLE 3

Intercepts and slopes of equation 21

SUBSTITUENT	ORTHO		META		PARA	
	$\log K_{a_xb_0}$	L	$\log K_{a_xb_0}$	L	$\log K_{a_xb_0}$	L
NO$_2$	2.112	-8.9	0.491	17.4	0.575	14.
I	1.442	-8.0	0.225	10.0	0.141	8.2
Br	1.419	-5.5	0.281	9.3	0.128	8.7
Cl	1.342	-4.7	0.280	8.6	0.104	8.5
F	0.889	3.8	0.237	8.0	-0.009	6.5
CH$_3$	0.376	-8.7	-0.065	-0.4	-0.164	-0.6
OCH$_3$	0.056	4.0			-0.227	-3.5
OH	0.982	17.1	0.219	$-10.$	-0.270	-7.1

ACID STRENGTHS IN MIXED SOLVENTS

When the solvent is composed of more than one base the reaction represented by equation 1 may be more complicated, owing to the fact that two bases are competing for the proton and two solvated protons may be formed. In addition to this, the solvent dipoles will be oriented differently around the ions and solute molecules, and in some cases, such as dioxane–water mixtures, there will be an unmixing of the solvent. In dioxane–water mixtures the envelope around the ions is poorer in dioxane than is the bulk of the solution (30). In the earlier work (29) a comparison of the values of $K_{A_xB_0}$ for the solvents ethyl alcohol and dioxane–water mixtures of the same dielectric constant showed quite good agreement, and it was concluded that the dielectric constant was the important factor. Further work (10) in dioxane–water mixtures of dielectric constants 55 and 40 has shown that the results are not in accord with equation 21. A few typical results are presented in figure 4, in which the dotted lines represent the line of equation 21 for the pure solvents. In general, for agreement with the results in pure solvents one would have to consider the dioxane–water mixtures

[3] These calculations are being carried out by J. N. Sarmousakis at the University of Pennsylvania.

to have lower dielectric constants than the experimental values. These results were obtained by the E.M.F. method and should be checked by the colorimetric.

From experimental determinations of the dissociation constant of acetic acid in glycerol–water mixtures of dielectric constant 81.1 to 73.3 at 18°C., Adell (1) concludes that the dissociation constant, expressed in moles per liter of solvent, can be represented by the equation

$$-\log K_0 = 2.878 + \frac{150.1}{D} \tag{23}$$

Lynch and La Mer (27), from determinations of the dissociation constants of acetic, propionic, butyric, and benzoic acids in dioxane–water mixtures, observe that the logarithm of the dissociation constant (expressed in moles per 1000 g.
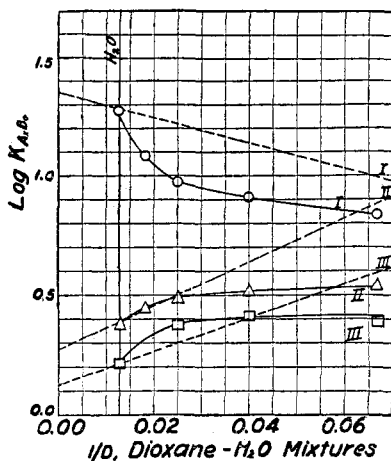

FIG. 4. Effect of substituents on the acid strength of benzoic acid. Curves I, o-chlorobenzoic acid; curves II, m-chlorobenzoic acid; curves III, p-chlorobenzoic acid.
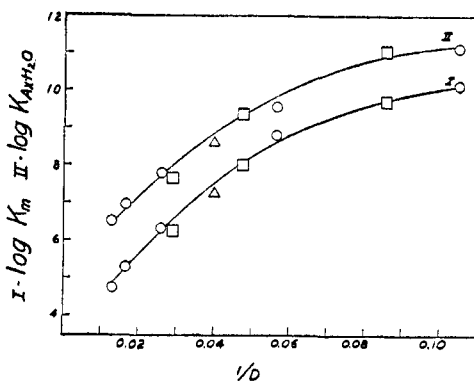
FIG. 5. Dissociation constant of acetic acid in dioxane-water mixtures. ○, Harned et al., □, Lynch and La Mer; △, Minnick and Kilpatrick.

of solvent) is a linear function of the reciprocal of the dielectric constant from $D = 78$ to $D = 21$. Harned (17) shows that log K for acetic acid is not a linear function of the reciprocal of the dielectric constant, and Harned and Fallon (19) show that the logarithm of the dissociation constant is nearly linear with the mole fraction of dioxane. Quite apart from the question of linearity with the reciprocal of the dielectric constant, it seems preferable to use equation 2 rather than the customary dissociation constant of equation 3. Provided there is only one solvated proton formed (H_3O^+), the actual process is

$$A_z + H_2O \rightleftharpoons H_3O^+ + B_z^- \tag{24}$$
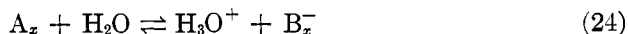
and the equilibrium constant

$$K_{A_x \cdot H_2O} = \frac{C_{H_3O^+}}{C_{H_2O}} \cdot \frac{C_{B_x}}{C_{A_x}} \tag{25}$$

takes account of the changing number of moles of water in the solution. In figure 5 a graph of log K_m and log $K_{A_x \cdot H_2O}$ *versus* $1/D$ is presented which indicates the difference in slope if an extrapolation to $1/D = 0$ is attempted.

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