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The Dissociation Constants of Weak Acids in a Methanol-Water Mixture

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The theoretical expression of the Henry constant has been derived on the basis of the concept of an ideal associated mixture for the system in which a solute, M, exists as such clusters as $M\cdot(H_2O)_j\cdot(MeOH)_{z-j}$, which are related to each other by the equation:

$$M\cdot(H_2O)_{j-1}\cdot(MeOH)_{z-j+1} + H_2O \overset{K_j}{\rightleftarrows} M\cdot(H_2O)_j\cdot(MeOH)_{z-j} + MeOH$$

Making use of the theoretical expression, the transfer-free energies of halogen acids from water to water-methanol mixtures and the dissociation constants of weak acids in water-methanol mixtures have been analyzed and the following equilibrium constants have been obtained for a proton, assuming that a proton is in a higher free energy state in methanol than in pure water, while a counter ion is in the same free-energy state:

$$K_1 = 210,\quad K_2 \doteqdot 16,\quad K_3 \doteqdot 2,\quad K_4 \doteqdot 1$$

The maximum phenomena observed for the dissociation constants of charged acids in the same mixture could be reproduced by the combination of the above Henry constants; emphasis has been placed on the importance of the assumption of a multi-step solvation mechanism.

The solvation of electrolytes and related phenomena in mixed solvents have received very much attention and have been analyzed from various points of view. These may be classified into four categories: *i.e.*, the theoretical treatment developed by Debye[1] and refined recently by Padova,[2] the attempts taking into account the distribution of protons between water and alcohol,[3-8] Marshall's treatment of complete equilibrium constants,[9-12] and several modified forms of the Born equation.[13] A common feature of these attempts is that they all refer to some liquid state as the standard state.

In contrast to these treatments, taking an ideal gas state as the standard state, the present authors have developed a method of analyzing rate constants measured in mixed solvents from the view point of the theory of a nonelectrolyte solution.[14-16] Since the method is based on an equilibrium assumption between reactants and an activated complex, after a few modifications, it is, in principle, reasonable to apply it to the analysis of equilibrium constants measured in mixed solvents.

As will be discussed later, the behavior of dissociation constants in mixed solvents is more complex than that of rate constants. Therefore, several refinements were required for the method to be applicable to the analysis of equilibrium properties in mixed solvents. This paper is an extension of a previous series of works on the solvation of a solute in mixed solvents.[14-16]

Theoretical Expression of an Activity Coefficient in Mixed Solvents.

It is appropriate to define the following activity coefficient, β_{ij}, for the description of the partition of a component, i, between gas and solvent, j:[14]

$$\beta_{ij} = (m_{gi}/m_{li}) \tag{1}$$

where m_{gi} and m_{li} stand for the molar concentration of a component, i in the gas phase over the solution and that of the component, i, in solution.

The Henry constant of a component, i, in a solvent, j, H_{ij}, is defined by the equation:

$$H_{ij} = \lim_{x_i \to 0} (f_i/x_i)_j \tag{2}$$

where f_i and x_i stand for the fugacity and the mole fraction of a component, i, respectively.

At sufficiently low concentrations of a component, i, the following relations hold;

$$f_i = p_i \tag{3}$$

$$p_i = (n_{gi}/V) \times RT = m_{gi} \times RT \tag{4}$$

$$m_{li} = (n_{li}/\sum_i n_{li} \times V_i) = x_i \times V_j^{-1} \tag{5}$$

where f_i, P_i, n_{gi}, n_{li}, V_i, x_i, and V_j stand for the fugacity, the pressure, the number of moles in a gas phase, that in a solution, the partial molar volume, and the mole fraction, each of a component, i, and the molar volume of a solvent, respectively.

At sufficiently low concentrations of a component, i, by a combination of Eqs. (1), (2), (3), (4), and (5), we obtain:

$$\beta_{ij} = (H_{ij} \times V_j/RT) \tag{6}$$

where V_j stands for the molar volume of a solvent, j.

An electrolyte, M, can be expected to exist as such

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clusters as $\mathrm{M}\cdot(\mathrm{S}_1)_m\cdot(\mathrm{S}_4)_n$ in mixed solvents, where S_1 and S_4 stand for a solvent, 1 and 4; it has been suggested that the ratio of m to n changes with the composition of the solvent mixture (Refs. 25, 26, and *loc. cit*).

In order to make an explicit formula for an activity coefficient based on the above concept, let us assume the following equilibrium:

$$\mathrm{M} + z\mathrm{S}_4 \rightleftarrows \mathrm{M}\cdot(\mathrm{S}_4)_z;\ K_0$$

$$\mathrm{M}\cdot(\mathrm{S}_4)_{z-j+1}\cdot(\mathrm{S}_1)_{j-1} + \mathrm{S}_1 \rightleftarrows \mathrm{M}\cdot(\mathrm{S}_4)_{z-j}\cdot(\mathrm{S}_1)_j + \mathrm{S}_4;\ K_j$$

$$\mathrm{M}\cdot(\mathrm{S}_4)\cdot(\mathrm{S}_1)_{z-1} + \mathrm{S}_1 \rightleftarrows \mathrm{M}\cdot(\mathrm{S}_1)_z + \mathrm{S}_4;\ K_z$$

where M, z, and K_j stand for an unsolvated electrolyte, the solvation number, and the equilibrium constant of a relevant step, respectively.

Hereafter, subscripts 1 and 4 will be used for a solvent, subscript jz for a solute, and subscript jz for a cluster except for those of equilibrium constants.

One advantage of the discrete model is that it makes it possible to introduce a mathematical formalism expressing the variation in the standard-state free energy with respect to the composition changes in the solvents. Consistent results have been obtained based on the predictions of the model, as will be shown later. However, it would be safe to take the view that this does not necessarily prove the real existence of the clusters.

When the above equilibrium steps exist, for the mixture containing components 1, 2, and 4 the following material balances hold:

$$N_1 = M_1 + M_{1z} + 2\times M_{2z} + \cdots + j\times M_{jz} + \cdots + z\times M_{zz} \tag{7}$$

$$N_2 = M_2 + M_{0z} + M_{1z} + \cdots + M_{jz} + \cdots + M_{zz} \tag{8}$$

$$N_4 = M_4 + z\times M_{0z} + (z-1)\times M_{1z} + \cdots + (z-j)\times M_{jz} + \cdots + M_{z-1,z} \tag{9}$$

where N_i, M_i, and M_{jz} stand for the number of moles of a component, i, before mixing, that of a free component, i, in solutions, and that of such a cluster containing j molecules of a solvent 1, and $(z-j)$ molecules of a solvent 4, such as $\mathrm{M}\cdot(\mathrm{S}_4)_{z-j}\cdot(\mathrm{S}_1)_j$.

Three kinds of mole fraction will be used in the following calculations:

$$x_i = N_i/\sum_i N_i \tag{10}$$

$$y_i = M_i/(\sum_i M_i + \sum_j M_{jz}) \tag{11}$$

$$y_{jz} = M_{jz}/(\sum_i M_i + \sum_j M_{jz}) \tag{12}$$

where x_i, y_i, and y_{jz} stand for the mole fraction defined in terms of the number of moles of a component, i, before mixing and of the number of moles of a component, i, and of a cluster, jz, in solution.

For the above equilibria, the equilibrium constant of each step is defined as follows:

$$K_0 = (y_{0z}/y_2\times y_4^z) \tag{13}$$

$$K_j = (y_{j,z}\times y_4/y_{j-1,z}\times y_1) \tag{14}$$

From Eqs. (7), (8), (9), (10), (11), and (12), we obtain:

$$x_2 = (y_2 + \sum_{j=0}^{z} y_{jz})/(1 + z\times\sum_{j=0}^{z} y_{jz}) \tag{15}$$

$$(y_2/x_2) = (1 + z\times\sum_{j=0}^{z} y_{jz})/(1 + \sum_{j=0}^{z}(y_{jz}/y_2)) \tag{16}$$

At sufficiently low concentrations of a solute 2:

$$\lim_{x_2\to 0}(y_2/x_2) = 1/(1 + \sum_{j=0}^{z}(y_{jz}/y_2)) \tag{17}$$

From Eqs. (13), (14), and (17), we obtain:

$$\lim_{x_2\to 0}(y_2/x_2) = 1/(1 + \sum_{i=0}^{z}(\prod_{j=0}^{i}K_j)\times x_4^{z-i}\times x_1^{i}) \tag{18}$$

since $x_2\to 0$, $y_1\to x_1$, and $y_4\to x_4$.

For an ideal associated mixture, a fugacity of a component, 2, f_2, is related to the fugacity of that component in the pure state, f_2^0, by the equation:

$$f_2 = f_2^0\times y_2 \tag{19}$$

$$\lim_{x_2\to 0} f_2 = H_{2,\mathrm{mix}}\times x_2 \tag{20}$$

From Eqs. (18), (19), and (20), we obtain:

$$H_{2,\mathrm{mix}} = f_2^0/(1 + \sum_{i=0}^{z}(\prod_{j=0}^{i}K_j)\times x_4^{z-i}\times x_1^{i}) \tag{21}$$

$$H_{2,1} = \lim_{x_1\to 1} H_{2,\mathrm{mix}} = f_2^0/(1 + \prod_{j=0}^{z}K_j) \tag{22}$$

$$H_{2,4} = \lim_{x_4\to 1} H_{2,\mathrm{mix}} = f_2^0/(1 + K_0) \tag{23}$$

As is clear from Eqs. (13) and (23), the equilibrium constant, K_0, serves as a measure of the stability or of the solvation energy of a solute in a solvent 4.

By combining Eqs. (6) and (21), the activity coefficient of a solute in such a mixture is given by:

$$\lim_{x_2\to 0}\beta_{2,\mathrm{mix}} = \{f_2^0/(1 + \sum_{i=0}^{z}(\prod_{j=0}^{i}K_j)\times x_4^{z-i}\times x_1^{i})\}\times(V_{\mathrm{mix}}/\boldsymbol{R}T) \tag{24}$$

where V_{mix} means the molar volume of the mixed solvent.

Transfer-free Energy of a Solute from the Solvent 1 to a Mixed Solvent

The transfer-free energy of a solute 2 from the solvent 1 to a solvent mixture, ΔG_t°, can be defined as follows by making use of the above activity coefficient:

$$\begin{aligned}\Delta G_t^0 &= \boldsymbol{R}T\ln\beta_{2,\mathrm{mix}} - \boldsymbol{R}T\ln\beta_{2,1}\\ &= \boldsymbol{R}T\{\ln(1 + \prod_{j=0}^{z}K_j) - \ln(1 + \sum_{i=0}^{z}(\prod_{j=0}^{i}K_j)\times x_4^{z-i}\times x_1^{i})\}\\ &\quad + \boldsymbol{R}T\ln(V_{\mathrm{mix}}/V_1)\end{aligned} \tag{25}$$

where V_1 stands for the molar volume of a pure solvent 1.

Similarly, for the transfer of a solute from the solvent 1 to a solvent 4:

$$\begin{aligned}\Delta G_t^0 &= \boldsymbol{R}T\{\ln(1 + \prod_{j=0}^{z}K_j) - \ln(1 + K_0)\}\\ &\quad + \boldsymbol{R}T\ln(V_4/V_1)\end{aligned} \tag{26}$$

For grasping the concept of the above equations, numerical calculations were performed making use of the parameters in Table 1 for the case where $V_4 = V_1$, $(1 + K_0\times K_1\times\cdots\cdots\times K_z)/(1 + K_0) \fallingdotseq K_1\times K_2\times\cdots\cdots\times K_z$[17] $= 3{,}000$; then $\Delta G_t^\circ = 2.303\ \boldsymbol{R}T\ \log(\beta_4/\beta_1) = 4.74$(kcal mol^{-1}) at 25°C.

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17) Since the solvation energy of an electrolyte is very large in usual solvents, it is reasonable to assume $K_0 \gg 1.0$. Therefore, K_0 may be dropped out of the final equation.

TABLE 1. EQUILIBRIUM CONSTANTS USED IN THE CALCULATION

Model	z	K_1	K_2	K_3	K_4	K_5	K_6	Relations between $\Delta G_j°$ and ΔG°_{j-1}
I	4	3000	1.0	1.0	1.0	—	—	$\Delta G_j°=0, j\geq 2$
II	4	1000	1.88	1.37	1.165	—	—	$\Delta G_j°=(1/2)\Delta G^\circ_{j-1}\ j\geq 3$
III	4	222.0	6.06	1.82	1.225	—	—	$\Delta G_j°=(1/3)\Delta G^\circ_{j-1}$
IV	4	27.8	9.18	4.38	2.683	—	—	$\Delta G_j°=(2/3)\Delta G^\circ_{j-1}$
V	4	7.40	7.40	7.40	7.40	—	—	$\Delta G_j°=\Delta G^\circ_{j-1}$
VI	6	19.0	7.10	3.70	2.39	1.79	1.40	$\Delta G_j°=(2/3)\Delta G^\circ_{j-1}$

$(\Delta G_j° = -RT \ln K_j)$

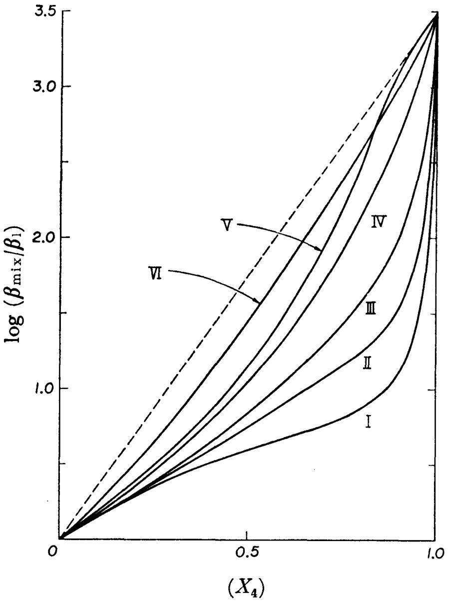

Fig. 1. Calculated values of log (β_{mix}/β_I) as a function of the solvent composition. Numbers in the figure correspond to the model number in Table 1.

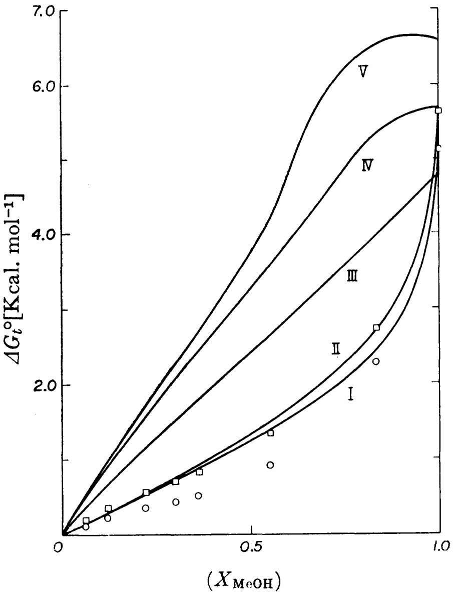

Fig. 2. Transfer-free energies of alkali metal halides and halogen acids from water to methanol-water mixtures.
Experimental results;[17] ○; HBr, □; HCl, III; LiCl, IV; NaCl, V; KCl
Theoretical values, I: HBr, II; HCl

The calculated values are shown in Fig. 1.

As is clear from Fig. 1, the negative deviation from the dotted line increases as the proportion of $\Delta G_1°$ to $\Delta G_t°$ increases. As $(\Delta G_{j-1}°/\Delta G_j°)\rightarrow 1.0$, and as the solvation number, z, increases, the transfer-energy curve approaches the dotted line. Thus, an important factor in controlling the shape of a transfer-energy curve may be concluded to be the ratio of $\Delta G_1°$ to $\Delta G_t°$.

In order to compare the above idea with the experimental results, the transfer-free energies measured by Feakins *et al.*[18,19] are shown in Fig. 2. For most of the electrolytes in Fig. 2, the transfer-free energies from water to methanol are fairly close to each other. However, there is a very sharp distinction between alkali metal halides and halogen acids concerning transfer-free energy curves. The phenomena clearly demonstrate the well-known inadequacies of the Born equation.

Provided that the above model applies to the present system, the difference in transfer-free energy curves reveals that the $(\Delta G_1°/\Delta G_t°)$ ratio of a proton is considerably larger than that of alkali metal ions.

This idea is partly supported by the thermodynamic data for the following step-by-step addition of water to an ion, M^+, as measured by means of a mass spectrometer:

$$M^+\cdot(H_2O)_{n-1} + H_2O = M^+\cdot(H_2O)_n$$

For the reaction in the gas phase, it has been reported that the $(-\Delta H_{0,1})$ value of a proton is considerably larger than that of alkali metal ions and that, in addition, the rate of the decrease in $(-\Delta G°_{n-1,n})$ with an increase in n is smaller for larger ions.[20-23]

Also, the chemical intuition of a preferential solvation of a cation by water has been experimentally proved by Mills and King for the Cr^{3+} ion;[24] it has also been suggested from mass-spectroscopic studies of the competitive solvation of a proton in a water methanol vapor mixture.[21]

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TABLE 2. EQUILIBRIUM CONSTANTS OBTAINED FROM THE DISSOCIATION CONSTANTS AND TRANSFER-FREE ENERGIES IN MIXED SOLVENTS (25°C)

Acid	z	K_1	K_2	K_3	K_4	K_5	K_6
2,6-Dinitrophenol	4	210.	16.8	1.0	1.0	—	—
Benzoic acid	6	210.	17.0	4.0	2.0	2.0	1.2
Acetic acid	4	210.	17.0	5.0	1.8	—	—
Hydrochloric acid	4	210.	19.0	1.5	1.0	—	—
Hydrobromic acid	4	210.	12.0	1.0	1.0	—	—

Dissociation Constants of Neutral Acids and the Distribution of Clusters in Mixed Solvents

The importance of the entropy terms in determining the magnitude and the sign of the transfer-free energy of solutes from one solvent to another[27,28] has been demonstrated. However, the question of which of the constituents of the electrolyte, *i.e.*, the cation or the anion, is responsible for determining the magnitude of the transfer energy is still a matter of considerable discussion.

In the dissociation of a neutral acid, the perturbation effect brought about on a carbon skelton by the release of a proton may be expected to be small. Especially for the 2,6-dinitrophenolate anion, a negative charge is distributed over the aromatic ring and is partially prohibited from the approach of solvent molecules by two adjacent nitro groups. Also, the non-electrostatic effects by a carbon skelton may be expected to cancel each other out of the total transfer energy since the effect appears on both sides of equations. Thus, it is reasonable to assume that the dissociation constant of a neutral acid is mainly affected by the variation in the standard-state free energy of a proton accompanying the changes in the composition of the solvents.

The dissociation constant as measured in a mixed solvent, $K_{d,\mathrm{mix}}$, is given by;

$$\mathrm{HA} \rightleftarrows \mathrm{H}^+ + \mathrm{A}^-$$

$$K_{d,\mathrm{mix}} = K_g(\beta_{\mathrm{HA},\mathrm{mix}}/\beta_{\mathrm{H}^+,\mathrm{mix}} \times \beta_{\mathrm{A}^-,\mathrm{mix}}) \qquad (27)$$

where K_g is a dissociation constant in a gas phase at an ideal state.

Based on the above assumption, and from Eqs. (21), (22), (23), and (27):

$$\begin{aligned}\ln(K_{d,\mathrm{mix}}/K_{d,4}) &= \ln\Big(1+\sum_{i=0}^{z}\Big(\prod_{j=0}^{i}K_j\Big)x_4^{z-i}x_1^{i}\Big) \\ &\quad - \ln(1+K_0) + \ln(V_4/V_{\mathrm{mix}}) \\ &\doteqdot \ln\Big(x_4^{z}+\sum_{i=1}^{z}\Big(\prod_{j=1}^{i}K_j\Big)x_4^{z-i}x_1^{i}\Big) \\ &\quad + \ln(V_4/V_{\mathrm{mix}}) \qquad (28)\end{aligned}$$

$$\begin{aligned}(K_{d,1}/K_{d,4}) &= \Big\{\Big(1+\prod_{j=0}^{z}K_j\Big)/(1+K_0)\Big\}(V_4/V_1) \\ &\doteqdot \Big(\prod_{j=1}^{z}K_j\Big)(V_4/V_1) \qquad (29) \\ &(\because\ K_0 \gg 1)\end{aligned}$$

Comparisons of the calculated values with the experimental results are shown in Fig. 3, where the subscript 1 refers to water and the subscript 4, to methanol, since $(K_{d,\mathrm{water}}/K_{d,\mathrm{MeOH}})>1$. Similar calculations were performed for the transfer energies of hydrochloric acid and of hydrobromic acid on the basis of Eqs. (25) and (26) (the molar volume of the mixture was calculated from the density data of the mixture).[29]

The parameters obtained from the calculations are listed in Table 2.[30]

The most interesting feature of the table is the fact that, for all five cases, the experimental results are fairly well reproduced by similar values of K_j.

The equilibrium constants of the following reaction have been measured by several people:

$$\mathrm{MeOH_2^+} + \mathrm{H_2O} = \mathrm{H_3O^+} + \mathrm{MeOH}$$

The values are *ca.* 110—140 on the pure methanol side[3,7,34–36] and *ca.* 0.20 on the pure water side.[4–6]

At first sight, our equilibrium expression looks a little different from the above equation. However, at each step the net reaction actually taking place is the substitution of water for methanol in the cluster; as a result, the other remaining molecules in the cluster do not appear in the mass-action equation. Therefore, there is no essential difference between the two approaches.

As may partly be inferred from Fig. 3, a proton would exist as $\mathrm{H^+\cdot(MeOH)}_n$ in methanol and as $\mathrm{H^+\cdot(H_2O)}_n$ in water. Thus, our value of K_1 and K_4 should correspond to the equilibrium constant measured on the pure methanol side and on the pure water side rescpectively. They agree with each other generally, but not completely.

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[29] International Critical Tables, Vol. III, p. 115.

[30] The calculations were performed as follws: the comparison of the theoretical values of Fig. 1 with the log $K_{d,\mathrm{mix}}$ *vs.* $x_{\mathrm{H_2O}}$ plot led to rough estimates of z and of the relation between equilibrium constants, *i.e.*, ΔG°_j and ΔG°_{j-1}, for the relevant system. For an assumed value of z (usually $z=3$), the value of $\prod_{j=1}^{z}(K_j)$ has been obtained on the basis of the boundary condition, *i.e.*, Eq. (29). After that, the values of $\log(K_{d,\mathrm{mix}}/K_{d,4})$ have been calculated on the basis of Eq. (28) for various sets of equilibrium constants. Similar calculations were repeated for several values of z until satisfactory agreements with the experimental results were attained. Similar procedures were adopted for the other systems.

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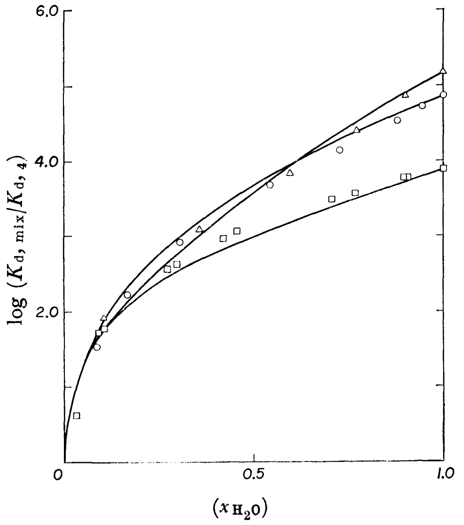

Fig. 3. Dissociation constants in water-methanol mixtures. Experimental results, □; 2,6-dinitrophenol,[31] ○; acetic acid,[32] △; benzoic acid,[33]
Theoretical values; ——

The results in the table are also of interest in showing the fall in equilibrium constants as the number of water molecules in a cluster increases.

A trend of the equilibrium constants similar to that obtained above, *i.e.*, $K_1 > K_2 > K_3 > K_4$, has been observed for the proton hydration equilibria in acetonitrile.[37–39]

Thus it may be seen that completely different procedures can lead to similar conclusion about the proton hydration equilibria in mixed solvents.

By making use of the equilibrium constants in Table 2, it is possible to calculate the distribution of each cluster, F_{iz}, over the full composition ranges of the solvent by means of Eq. (30):

$$\lim_{x_2\to 0} F_{iz} = \lim_{x_2\to 0} M_{iz}/\sum_{j=0}^{z} M_{jz} = (\prod_{j=0}^{i} K_j) x_4{}^{z-i} x_1{}^{i} / \sum_{i=0}^{z} (\prod_{j=0}^{i} K_j) x_4{}^{z-i} x_1{}^{i} \qquad (30)$$

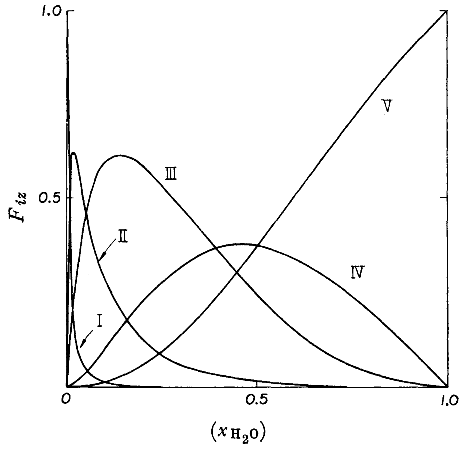

Fig. 4. Distributions of the clusters as a function of the solvent composition.
I: $H^+\cdot(MeOH)_4$, II: $H^+\cdot(MeOH)_3\cdot(H_2O)$, III: $H^+\cdot(MeOH)_2\cdot(H_2O)_2$, IV: $H^+\cdot(MeOH)\cdot(H_2O)_3$, V: $H^+\cdot(H_2O)_4$.

The calculated values of F_{iz} for the set of equilibrium constants of hydrochloric acid are plotted against the mole fraction of water in Fig. 4.

As may be inferred from the figure, such clusters as $H^+\cdot(MeOH)_4$ and $H^+\cdot(MeOH)_3(H_2O)$ exist only over quite narrow ranges of solvent compositions. In contrast, on the water side, the fraction of the $H^+\cdot(H_2O)_4$ cluster decreases nearly linearly with the composition of the solvent and the following relation holds over a fairly wide range.

$$F_{44} + F_{34} \doteqdot 1 \qquad (31)$$

These factors should be taken into account when attempts are made to correlate the solvation-related properties with the macroscopic properties of the mixed solvents.

Similar distribution curves of a hydrated proton were estimated by Chantooni and Kolthoff in acetonitrile-water mixtures.[39]

Dissociation Constants of Charged Acids in Mixed Solvents

There is a marked difference in the dissociation behavior of charged acids and uncharged acids as measured in mixed solvents. One of the main reasons for such a difference is the charge type of the acids. Since, for the charged acids, electrostatic charging effects appear on both sides of the equilibrium expression, most parts of the effects compensate one another. Thus, the result of such a compensation is a maximum in the plot of log K_d *vs.* the composition of the solvents.

As has been mentioned above, in contrast to the case of hydrogen halogenide acids, the transfer-free energy of alkali metal halides varies monotonously with the change in the composition of the solvents. Also, the

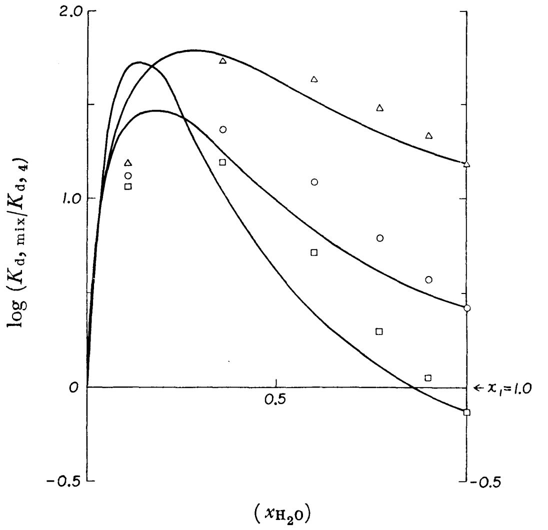

Fig. 5. Dissociation constants of charged acids in water-methanol mixtures.
Experimental results,[33] △; anilinium ion, ○; N-methyl anilinium ion, □; N,N-dimethyl anilinium ion
Theoretical values; ——

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[37] I. M. Kolthoff and M. K. Chantooni, Jr., *Anal. Chem.*, **39**, 1080 (1967).

[38] I. M. Kolthoff and M. K. Chantooni, Jr., *J. Amer. Chem. Soc.*, **90**, 3320 (1968).

[39] M. K. Chantooni, Jr., and I. M. Kolthoff, *ibid.*, **92**, 2236 (1970).

Table 3. Equilibrium constants for charged acids (25°C)

Acid	z	K_1	K_2	K_3	K_4	K_5	K_6	Relations between ΔG_j° and ΔG_{j-1}°
Anilinium	6	12.0	5.25	3.0	2.1	1.6	1.4	$\Delta G_j^\circ = (2/3)\Delta G_{j-1}^\circ$
N-Methylanilinium	6	13.53	7.05	4.3	3.0	2.3	1.8	$\Delta G_j^\circ = (3/4)\Delta G_{j-1}^\circ$
N,*N*-dimethylanilinium	6	5.15	5.15	5.1	5.1	5.1	5.1	$\Delta G_j^\circ = \Delta G_{j-1}^\circ$

behavior of the transfer energy of tris(hydroxymethylamine) hydrochloride, *i.e.*, a charged acid, has been reported to resemble that of LiCl.[13]

Thus, the following calculations have been performed from the point of view that the variation in the dissociation constants of charged acids in mixed solvents are mainly controlled by the dissimilarities of the transfer-energy behaviours between charged acid and a proton.

By a procedure similar to that used for uncharged acid, for the equilibria:

$$\mathrm{BH^+} \rightleftharpoons \mathrm{B} + \mathrm{H^+}$$

$$\begin{aligned}\ln(K_{d,\mathrm{mix}}/K_{d,4}) = {} & [\ln\{1+\sum_{i=0}^{z}(\prod_{j=0}^{i}K_j)x_4{}^{z-i}x_1{}^{i}\}-\ln(1+K_0)]_{\mathrm{H^+}} \\ & -[\ln\{1+\sum_{i=0}^{z}(\prod_{j=0}^{i}K_j)x_4{}^{z-i}x_1{}^{i}\}-\ln(1+K_0)]_{\mathrm{BH^+}} \\ & +\ln(V_4/V_{\mathrm{mix}}) \qquad (32)\end{aligned}$$

$$\begin{aligned}(K_{d,1}/K_{d,4}) = {} & [\{(1+\prod_{j=0}^{z}K_j)/(1+K_0)\}_{\mathrm{H^+}}/ \\ & \{(1+\prod_{j=0}^{z}K_j)/(1+K_0)\}_{\mathrm{BH^+}}]\times(V_4/V_1) \qquad (33)\end{aligned}$$

As is clear from Eqs. (32) and (33), it is necessary to determine two sets of equilibrium constants, *i.e.*, for a proton and for a charged acid. The set of equilibrium constants obtained from the transfer energy of hydrochloric acid has been substituted into Eqs. (32) and (33) for those of a proton; the other parameters used in the calculations are listed in Table 3. A comparison of the experimental results with the calculated values is shown in Fig. 5.

It may be seen from Fig. 5 that the general tendency of the dissociation behaviors of charged acids can be reproduced in mixed solvents by the procedure described above.

In several aqueous-organic mixtures, the acidity function, $-H_0$, goes through a minimum with changing water concentration at fixed concentration of the acid (which corresponds to the maximum in the log K_{BH^+} of the indicator used for the measurements); several attempts have been made to interpret this phenomenon.[40]

A similar maximum phenomenon has been observed for the rate of Wolff-Kishner reaction in mixed solvents.[41]

In previous works, the present authors developed theoretical methods for analyzing the rate constants in solvent mixtures and performed theoretical calculation for the rate constants based on several solvation patterns.[14–16] However, in none of these calculations could a maximum or a minimum phenomenon be simulated. Thus, it is inevitable to assume a multistep solvation mechanism for reproducing a maximum or a minimum phenomenon in solvent mixtures, although the necessary procedure is much more complicated.

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[40] C. H. Rochester, "Acidity Functions," Academic Press, London and New York (1970).

[41] H. H. Szmant and M. N. Roman, *J. Amer. Chem. Soc.*, **88**, 4034 (1966).