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Ionic Equilibria in Mixed Solvents. IV.*[1] Solvent Effect on Dissociation Constants of Acids

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Equilibrium of hydronium ions with alkoxonium ions in water-alcohol mixtures being taken into account, solvent effects on dissociation constants of acids were quantitatively interpreted by the following: free energy changes on transferring ions from an aqueous solution to a mixed solvent and difference in standard states in different solvent compositions. Choosing suitable values for "effective ionic radii" for ions involved, satisfactory agreements were found between experimental and calculated values of ΔpK, the difference of pK in water and in an aqueous mixture, for positively charged acids (*e. g.*, ammonium, anilinium, *etc.*) as well as neutral acids yielding a negatively charged conjugate base (*e. g.*, acetic acid, benzoic acid, *p*-nitrophenol, *etc.*).

Numerous investigations have been made on dissociation equilibria in aqueous mixed solvents. Variation of a dissociation constant of an acid, HA (*e. g.*, acetic acid), was qualitatively interpreted in terms of the variation of activity coefficients of component ions in different media applying the Born solvation energy equation. Taking into consideration the variation of the concentration of water in the solution, the behavior of the dissociation constant was better expressed as a function of dielectric constant of bulk solutions.[1] However, the above treatment was not successful for positively charged acids, which dissociate as follows:

$$BH^+ \rightleftharpoons H^+ + B$$

A dissociation constant of the acid, BH^+, usually *increases* and then sharply *decreases* passing through a maximum with decreasing water concentration in the solvent. Paabo, Bates and Robinson[2] introduced a quantity not clearly defined which they called the "basicity effect" in their study of dissociation equilibria of ammonium ion in aqueous methanol solutions. Glover's assumptions[3] of formation of polymerized methanol molecules or somewhat unusual complexes of organic solvent molecules with water have not been confirmed.

Previous authors have paid little attention to the equilibrium between hydronium ion and an organic solvent molecule in their studies on the solvent effects on dissociation constants of acids. Equilibrium constants of a hydronium ion with a series of alcohol molecules have been determined by Conway, Bockris and Linton.[4] Equilibrium constants of the reaction

$$H_3O^+ + ROH \rightleftharpoons H_2O + ROH_2^+ \tag{1}$$

were found to be 0.23, 0.059 and 0.037 for R= $-CH_3$, $-CH_2CH_3$ and $-CH_2CH_2CH_3$, respectively.[4]

The present paper attempts a quantitative interpretation for the variation of dissociation constants of acids in aqueous methanol and ethanol solutions on the basis of the knowldege of hydronium-alkoxonium ion equilibria and of a suitable model for solvated ions in solution.

Standard Chemical Potential of Hydrogen Ion in an Aqueous Mixture. A chemical potential of hydrogen ion in a solution is formally described as:

$$\mu_H = \mu^\circ_H + \boldsymbol{R}T \ln(H^+) \tag{2}$$

where μ_H and μ°_H denote the chemical potential and the standard chemical potential of hydrogen ion, respectively. ( ) represents activity. The standard state is defined so that the activity coefficient of hydrogen ion, as well as those of any other ions present in the solution, tends to unity as the composition of the solution approaches the given solvent composition.

In an aqueous solution all protons exist as hydrated ones so that Eq. (2) may be described as:

$$\mu_H(w) = \mu^\circ_H(w) + \boldsymbol{R}T \ln(H_3O^+(w)) \tag{3}$$

the hydronium ion, H_3O^+, being assumed to be a unique entity of hydrated proton. Symbol (w) stands for water.

As seen in Eq. (1), however, in aqueous mixtures both hydronium and alkoxonium ions are considered to be thermodynamic entities which determine the chemical potential of hydrogen ion. Therefore, μ_H in aqueous alcohol mixtures must be

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* Part III, *Inorg. Chem.*, **7**, 1205 (1968).

[1] M. Yasuda, This Bulletin, **32**, 429 (1959).

[2] M. Paabo, R. G. Bates and R. A. Robinson, *J. Phys. Chem.*, **70**, 247 (1966).

[3] D. Glover, *J. Am. Chem. Soc.*, **87**, 5275, 5279 (1965).

[4] B. E. Conway, J. O'M. Bockris and H. Linton, *J. Chem. Phys.*, **24**, 834 (1956).

described as:

$$\begin{aligned}\mu_{\mathrm{H}}(\mathrm{s}) &\equiv (1-x)\mu_{\mathrm{H_3O}}(\mathrm{s}) + x\mu_{\mathrm{ROH_2}}(\mathrm{s})\\ &= (1-x)\mu^\circ{}_{\mathrm{H_3O}}(\mathrm{s}) + x\mu^\circ{}_{\mathrm{ROH_2}}(\mathrm{s})\\ &\quad + \boldsymbol{R}T\ln(\mathrm{H_3O^+(s)})^{1-x}(\mathrm{ROH_2{}^+(s)})^{x} \qquad (4)\end{aligned}$$

when one mole of hydrogen ion produces fractions of $1-x$ of hydronium ion and of x of alkoxonium ion. The symbol (s) denotes the solvent of an aqueous alcohol mixture. Thus, the standard chemical potential of hydrogen ion in the aqueous alcoholic solution is defined as:

$$\mu^\circ{}_{\mathrm{H}}(\mathrm{s}) \equiv (1-x)\mu^\circ{}_{\mathrm{H_3O}}(\mathrm{s}) + x\mu^\circ{}_{\mathrm{ROH_2}}(\mathrm{s}) \qquad (5)$$

and hence, the activity of hydrogen ion, $(\mathrm{H^+})$, is denfied as:

$$(\mathrm{H^+(s)}) \equiv (\mathrm{H_3O^+(s)})^{1-x}(\mathrm{ROH_2{}^+(s)})^{x} \qquad (6)$$

Dissociation Constants of Ammonium Ion in Water-Methanol Solutions. One mole of proton liberated from a mole of ammonium ion is shared to both H_2O and ROH according to the equilibrium given in Eq. (1). Thus, the dissociation equilibrium of ammonium ion in a water-methanol mixture is described as:

$$\begin{aligned}&\mathrm{NH_4{}^+(s)} + (1-x)\mathrm{H_2O(s)} + x\mathrm{ROH(s)}\\ &\quad\rightleftharpoons \mathrm{NH_3(s)} + (1-x)\mathrm{H_3O^+(s)} + x\mathrm{ROH_2{}^+(s)} \qquad (7)\end{aligned}$$

Here x denotes a fraction of alkoxonium ion formed and is given by the following equation through the equilibrium constant, κ, of Eq. (1):

$$x = \frac{\kappa y}{1-y+\kappa y} \qquad (8)$$

activities of water and methanol being approximated to be equal to their mole fractions. y represents the mole fraction of methanol in the solvent.

The free energy change given as $(\mathrm{p}K\,(\mathrm{s}) - \mathrm{p}K\,(\mathrm{w}))\boldsymbol{R}T\ln 10$ corresponds to the free energy change of the transfer reaction:

$$\begin{aligned}&\mathrm{NH_4{}^+(s)} + (1-x)\mathrm{H_2O(s)}\\ &\qquad + x\mathrm{ROH(s)} + \mathrm{H_3O^+(w)} + \mathrm{NH_3(w)}\\ &\quad\rightarrow \mathrm{NH_4{}^+(w)} + (1-x)\mathrm{H_3O^+(s)}\\ &\qquad + x\mathrm{ROH_2{}^+(s)} + \mathrm{H_2O(w)} + \mathrm{NH_3(s)} \qquad (9)\end{aligned}$$

Thus, the difference of dissociation constants in an aqueous solution and in an aqueous methanol solution, $\Delta\mathrm{p}K = \mathrm{p}K\,(\mathrm{s}) - \mathrm{p}K\,(\mathrm{w})$, is given as:

$$\begin{aligned}\Delta\mathrm{p}K = &[(\mu^\circ{}_{\mathrm{NH_4}}(\mathrm{w}) - \mu^\circ{}_{\mathrm{NH_4}}(\mathrm{s})) + (\mu^\circ{}_{\mathrm{H_2O}}(\mathrm{w})\\ &- (1-x)\mu^\circ{}_{\mathrm{H_2O}}(\mathrm{s}) - x\mu^\circ{}_{\mathrm{ROH}}(\mathrm{s}))\\ &+ (\mu^\circ{}_{\mathrm{NH_3}}(\mathrm{s}) - \mu^\circ{}_{\mathrm{NH_3}}(\mathrm{w})) + ((1-x)\mu^\circ{}_{\mathrm{H_3O}}(\mathrm{s})\\ &+ x\mu^\circ{}_{\mathrm{ROH_2}}(\mathrm{s}) - \mu^\circ{}_{\mathrm{H_3O}}(\mathrm{w}))]/\boldsymbol{R}T\ln 10 \qquad (10)\end{aligned}$$

Estimation of the Variation of the Standard Chemical Potentials. The variation of the standard chemical potential corresponds to the variation of the free energy on transferring one mole of the relevant species from one medium to another. We estimate the variation of the standard chemical potentials of ions from an aqueous solution to an aqueous methanol solution on the basis of a model which is essentially similar to that proposed by Stokes[5] with a slight modification for hydronium ion: The hydronium ion, H_3O^+, is a sphere with a "crystal radius" of $r = 1.4$ Å and is surrounded by a layer of 2.8 Å (the diameter of a water molecule) thickness of the first hydration shell. This layer has a minimum dielectric constant of about 5[5-7] (ε_1). The first hydration shell is covered with the second hydration shell whose thickness is 2.8 Å. The dielectric constant in the second hydration shell (ε_2) is given as:[5]

$$\frac{1}{\varepsilon_2} = \frac{1}{2}\left(\frac{1}{\varepsilon_1} - \frac{1}{\varepsilon_0}\right) \qquad (11)$$

For values of dielectric constant of bulk solution, ε_0, a monograph by Harned and Owen[8] is referred to.

According to this model, the variation of the standard chemical potentials, or the free energy change of the transfer, of a hydronium ion, $\Delta\mu^\circ{}_{\mathrm{H_3O}}$ is evaluated from an aqueous solution to an aqueous methanol solution.

$$\begin{aligned}\Delta\mu^\circ{}_{\mathrm{H_3O}} &= \mu^\circ{}_{\mathrm{H_3O}}(\mathrm{s}) - \mu^\circ{}_{\mathrm{H_3O}}(\mathrm{s})(\mathrm{w})\\ &= \frac{\boldsymbol{N}e^2}{2}\left[\frac{2.8}{r(r+2.8)\varepsilon_1(\mathrm{s})} + \frac{2.8}{(r+2.8)(r+5.6)\varepsilon_2(\mathrm{s})}\right.\\ &\quad\left. + \frac{1}{(r+5.6)\varepsilon_0(\mathrm{s})}\right] - \left[\frac{2.8}{r(r+2.8)\varepsilon_1(\mathrm{w})}\right.\\ &\quad\left. + \frac{2.8}{(r+2.8)(r+5.6)\varepsilon_2(\mathrm{w})} + \frac{1}{(r+5.6)\varepsilon_0(\mathrm{w})}\right]\\ &= \frac{\boldsymbol{N}e^2}{2}\left[\left(\frac{0.0952}{\varepsilon_2(\mathrm{s})} + \frac{0.143}{\varepsilon_0(\mathrm{s})}\right) - 0.0112\right] \qquad (12)\end{aligned}$$

where $\boldsymbol{N}$ denotes the Avogadro number and e the charge unit.

For an alkoxonium ion, $ROH_2{}^+$, the corresponding radius of the ion is assumed to be the same as that of the hydronium ion, while it is assumed that the alkoxonium ion is not solvated. In the course of the transfer of $ROH_2{}^+$ ion from pure water to an aqueous methanol solution, the values of $\Delta\mu^\circ{}_{\mathrm{ROH_2}}$ are given as:

$$\begin{aligned}\Delta\mu^\circ{}_{\mathrm{ROH_2}} &= \mu^\circ{}_{\mathrm{ROH_2}}(\mathrm{s}) - \mu^\circ{}_{\mathrm{ROH_2}}(\mathrm{w})\\ &= \frac{\boldsymbol{N}e^2}{2}\left(\frac{1}{1.4\varepsilon_0(\mathrm{s})} - 0.00910\right) \qquad (13)\end{aligned}$$

The crystal radius of ammonium ion is reported to be 1.48 Å.[2,9] An assumption of unsolvated ammonium ion leads to the value of $\Delta\mu^\circ{}_{\mathrm{NH_4}}$ calculated by the following equation:

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5) R. H. Stokes, *J. Am. Chem. Soc.*, **86**, 979 (1964).

6) J. B. Hasted, D. M. Riston and C. H. Collie, *J. Chem. Phys.*, **16**, 1 (1948).

7) G. H. Haggis, J. B. Hasted and T. J. Buchanan, *ibid.*, **20**, 1452 (1952).

8) H. S. Harned and B. B. Owen, "The Physical Chemistry of the Electrolytic Solutions," 3rd ed., Reinhold Publ. Corp., New York (1964), p. 161.

9) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed., Butterworths, London (1959), p. 461.

$$\Delta\mu^\circ_{\mathrm{NH_4}} = \mu^\circ_{\mathrm{NH_4}}(\mathrm{s}) - \mu^\circ_{\mathrm{NH_4}}(\mathrm{w})$$
$$= \frac{\boldsymbol{N}e^2}{2}\left(\frac{1}{1.48\varepsilon_0(\mathrm{s})} - 0.00861\right) \tag{14}$$

A neutral ammonia molecule is expected to be subjected to the smallest change in free energy in the course of the transfer of the molecule from an aqueous solution to an aqueous methanol solution.

The free energy change caused by the variation of the standard state in each solution, which is given in terms of $\mu^\circ_{\mathrm{H_2O}}(\mathrm{w})-(1-x)\mu^\circ_{\mathrm{H_2O}}(\mathrm{s})-x\mu^\circ_{\mathrm{ROH}}(\mathrm{s})$ in Eq. (10), is given as:

$$\mu^\circ_{\mathrm{H_2O}}(\mathrm{w}) - (1-x)\mu^\circ_{\mathrm{H_2O}}(\mathrm{s}) - x\mu^\circ_{\mathrm{ROH}}(\mathrm{s})$$
$$= \boldsymbol{R}T\ln(\mathrm{H_2O(s)})^{1-x}(\mathrm{ROH(s)})^x/(\mathrm{H_2O(w)})$$
$$= \boldsymbol{R}T\ln(1-y)^{1-x}\cdot y^x \tag{15}$$

since the activity of water in aqueous solution is defined to be unity.

Table 1. Variation of dissociation constant of ammonium ion in water-methanol solutions at 25°C

Methanol, wt%	ΔpK(calcd)	ΔpK(obsd)[2]
0	—	—
10	−0.10	−0.099
20	−0.19	−0.201
33.4	−0.32	−0.352
50	−0.51	−0.558
60	−0.63	−0.654
70	−0.75	−0.674
80	−0.84	—
90	−0.71	—
100	+0.10	—

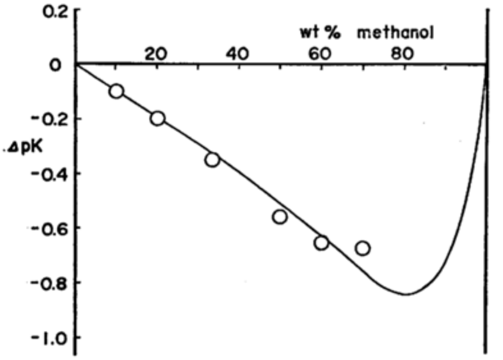


Fig. 1. Variation of ΔpK of ammonium ion as a function of the concentration of methanol. —— calculated; ○ experimental values by Paabo *et al.*[2]

In Table 1 are listed values of ΔpK of ammonium ion thus calculated by Eq. (10) and are compared with values of ΔpK reported by Paabo *et al.*[2] and the results are visualized in Fig. 1.

Dissociation Constants of Other Acids in Water-Methanol Solutions. Similar treatments were applied to systems of some acids in water-methanol solutions.

For an acid of BH$^+$ type, ΔpK is described in a form similar to Eq. (10); thus,

$$\Delta\mathrm{p}K = [(\mu^\circ_{\mathrm{BH}}(\mathrm{w}) - \mu^\circ_{\mathrm{BH}}(\mathrm{s})) + (\mu^\circ_{\mathrm{H_2O}}(\mathrm{w})$$
$$- (1-x)\mu^\circ_{\mathrm{H_2O}}(\mathrm{s}) - x\mu^\circ_{\mathrm{ROH}}(\mathrm{s})) + (\mu^\circ_{\mathrm{B}}(\mathrm{s})$$
$$+ \mu^\circ_{\mathrm{B}}(\mathrm{w})) + ((1-x)\mu^\circ_{\mathrm{H_3O}}(\mathrm{s}) + x\mu^\circ_{\mathrm{ROH_2}}(\mathrm{s})$$
$$- \mu^\circ_{\mathrm{H_3O}}(\mathrm{w}))]/\boldsymbol{R}T\ln 10 \tag{16}$$

and $\Delta\mu^\circ_{\mathrm{BH}}$ is given as:

$$\Delta\mu^\circ_{\mathrm{BH}} = \mu^\circ_{\mathrm{BH}}(\mathrm{s}) - \mu^\circ_{\mathrm{BH}}(\mathrm{w})$$
$$= \frac{\boldsymbol{N}e^2}{2r}\left(\frac{1}{\varepsilon_0(\mathrm{s})} - \frac{1}{\varepsilon_0(\mathrm{w})}\right) \tag{17}$$

the acid, BH$^+$, being assumed to be unsolvated. For terms of $\Delta\mu^\circ_{\mathrm{H_3O}}$, $\Delta\mu^\circ_{\mathrm{ROH_2}}$, $\Delta\mu^\circ_{\mathrm{H_2O}}$, $\Delta\mu^\circ_{\mathrm{ROH}}$ and $\Delta\mu^\circ_{\mathrm{B}}$, the same values as calculated in the preceding section were used.

For an acid of HA type, ΔpK is given as:

$$\Delta\mathrm{p}K = [(\mu^\circ_{\mathrm{HA}}(\mathrm{w}) - \mu^\circ_{\mathrm{HA}}(\mathrm{s})) + (\mu^\circ_{\mathrm{H_2O}}(\mathrm{w})$$
$$- (1-x)\mu^\circ_{\mathrm{H_2O}}(\mathrm{s}) - x\mu^\circ_{\mathrm{ROH}}(\mathrm{s}))$$
$$+ ((1-x)\mu^\circ_{\mathrm{H_3O}}(\mathrm{s}) + x\mu^\circ_{\mathrm{ROH_2}}(\mathrm{s}) - \mu^\circ_{\mathrm{H_3O}}(\mathrm{w}))$$
$$+ (\mu^\circ_{\mathrm{A}}(\mathrm{s}) - \mu^\circ_{\mathrm{A}}(\mathrm{w}))]/\boldsymbol{R}T\ln 10 \tag{18}$$

In Eq. (18) we put $\mu^\circ_{\mathrm{HA}}(\mathrm{s})-\mu^\circ_{\mathrm{HA}}(\mathrm{w})\simeq 0$, because HA is neutral. For the ion A$^-$

$$\Delta\mu^\circ_{\mathrm{A}} = \mu^\circ_{\mathrm{A}}(\mathrm{s}) - \mu^\circ_{\mathrm{A}}(\mathrm{w})$$
$$= \frac{\boldsymbol{N}e^2}{2r}\left(\frac{1}{\varepsilon_0(\mathrm{s})} - \frac{1}{\varepsilon_0(\mathrm{w})}\right) \tag{19}$$

Since "crystal radius" of any ion of these acids has not been evaluated, r of the ion was used as a parameter of calculation so that calculated results would best fit the experimental data. In this sense we shall call r the "effective ionic radius".

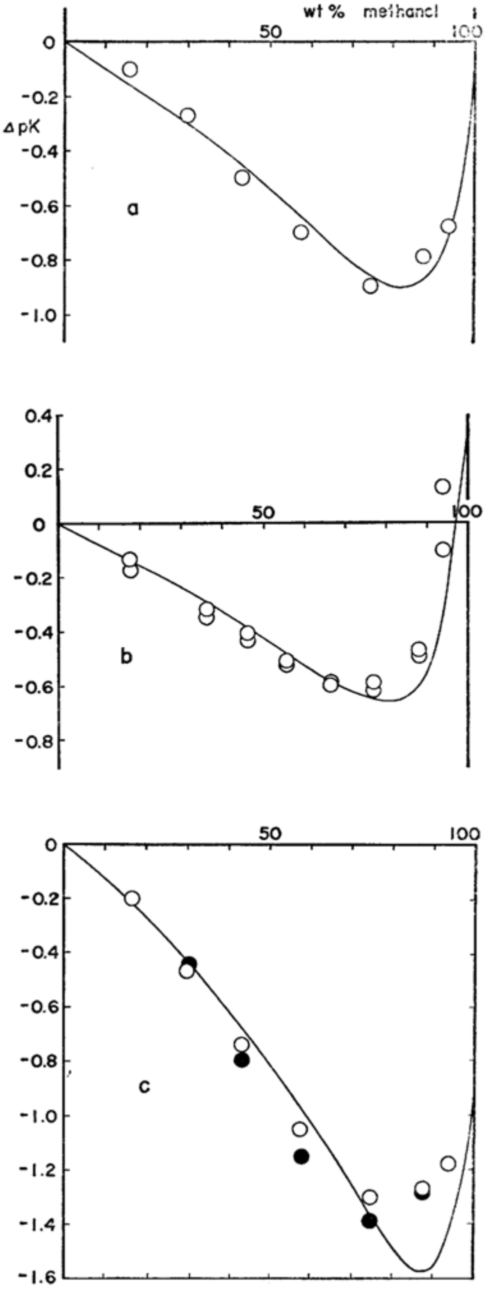
Table 2. Effective ionic radii of ions in water-methanol solutions

Ion	r (Å)	Ref.
Ammonium	1.48	2
Diethylethanolammonium	1.4	10
Anilinium	1.8	11, 12
Diethanolammonium	2.3	10
Piperidinium	1.1	10
Trimethylpyridinium	0.9	10
Pyridinium	0.9	10
Acetate	0.8	10, 11, 15
Mandelate	0.8 (0.7—0.9)*	10
p-Nitrophenolate	1.3	10
o-Nitrophenolate	1.1 (1.0—1.2)*	10
m-Nitrophenolate	1.1 (1.0—1.2)*	10
3, 4-Dinitrophenolate	1.4	10
2, 5-Dinitrophenolate	1.4	10
2, 4-Dinitrophenolate	1.3	10

* Values in brackets show the range of r spread.

Comparison of ΔpK values thus calculated with those observed are demonstrated for some aliphatic and aromatic amines, heterocyclic nitrogen compounds, aliphatic and aromatic carboxylic acids and phenols, and some examples are graphically represented in Fig. 2. The values of the "effective ionic radii" adopted are summarized in Table 2.

Dissociation Constants of Acids in Water-Ethanol Solutions. The validity of the present treatment was tested for dissociation equilibria of some acids in water-ethanol solutions. Resulting values of ΔpK in some examples are shown in Fig. 3 and values of r examined are tabulated in Table 3.



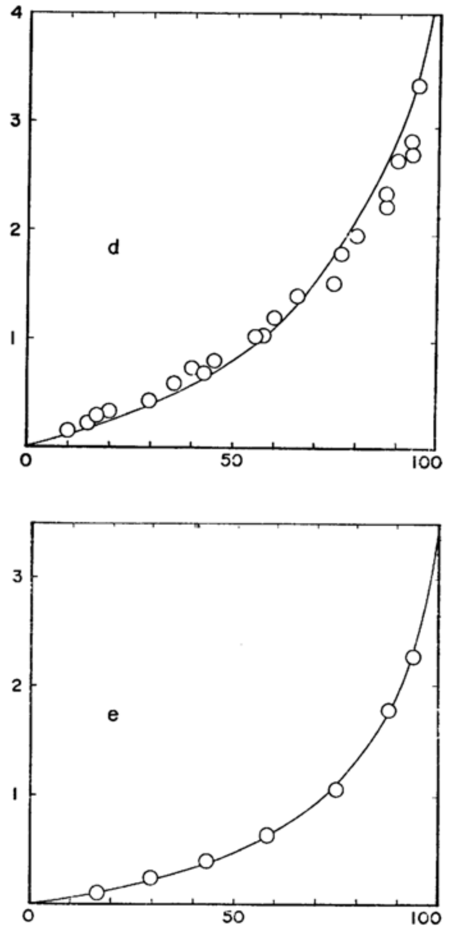


Fig. 2. Variation of ΔpK of various acids as a function of the concentration of methanol. Lines drawn show calculated values of ΔpK's using corresponding values of r in Table 2.

a , diethylethanolammonium
b , anilinium
c , pyridinium (○) and trimethylpyridinium (●)
d , acetic acid
e , *p*-nitrophenol

Discussion

From Tables 2 and 3 it is seen that ammonium, diethylethanolammonium and anilinium ions have similar values of the effective ionic radius despite the fact that their pK values are widely spread (pK(ammonium)=9.245,²⁾ pK(diethylethanolammonium)=9.90¹⁰⁾ and pK(anilinium)=4.60¹¹⁾

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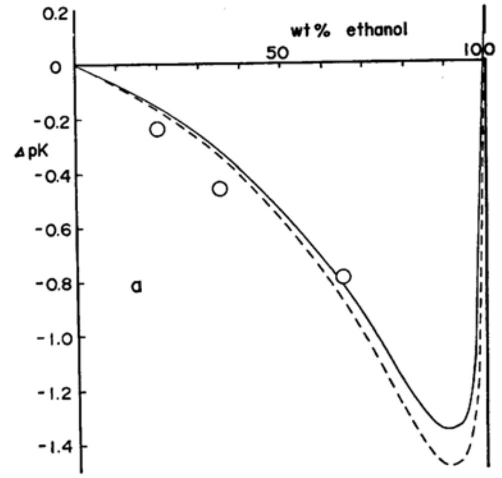
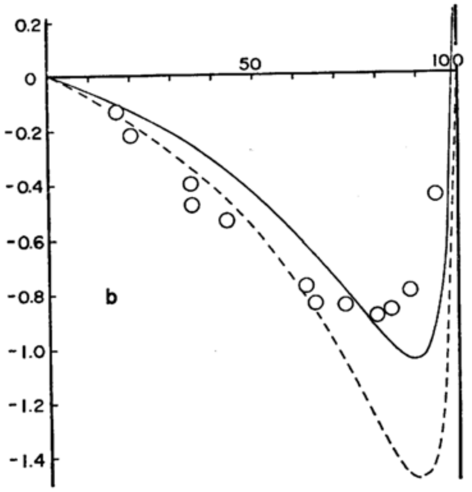
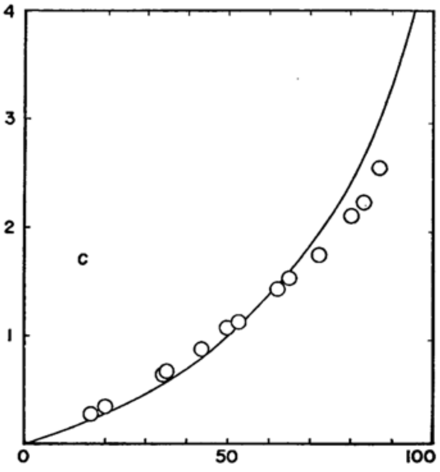
10) R. Gaboriaud, *Compt. Rend.*, **263**, 911 (1966).

11) G. Douheret, *Bull. Soc. Chim. France*, **1967**, 1412.







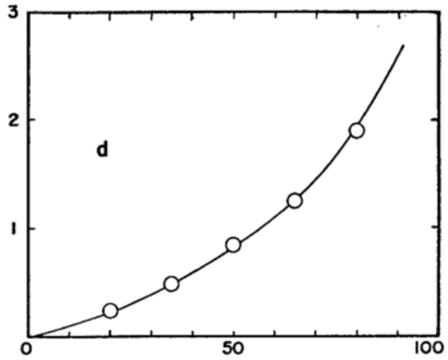


Fig. 3. Variation of ΔpK of various acids as a function of the concentration of ethanol. Lines drawn show calculated values of ΔpK's using corresponding values of r in Table 3.
a, ammonium (——, $r=1.4$ Å; ----, $r=1.5$ Å);
b, anilinium (——, $r=1.4$ Å; ----, $r=1.8$ Å);
c, acetic acid; d, formic acid.

TABLE 3. EFFECTIVE IONIC RADII OF IONS IN WATER-ETHANOL SOLUTIONS

Ion	r (Å)	Ref.
Ammonium	1.4—1.5	13
Anilinium	1.4—1.8	11, 13
Acetate	0.8 (0.7—0.9)*	11, 13, 14
Formate	1.3	13, 14
Propionate	0.9 (0.8—1.0)*	13, 14
Benzoate	0.8 (0.7—0.9)*	13, 14

* Values in brackets show the range of r spread.

or 4.62[12] in aqueous solution at 25°). Similar phenomena may be found in systems of acetic acid ($pK=4.76$[10–12] in aqueous solution at 25°), propionic acid ($pK=4.87$,[13,14] benzoic acid ($pK=4.20$[13,14]) and mandelic acid ($pK=3.45$[10]). Thus the variation of pK may mainly be caused by the energy change of electrostatic interactions of charged atom with solvent moleculeus.

The effective ionic radius is found to remain unchanged when the solvent is changed from water-methanol to water-ethanol mixtures.

The fact that the effective ionic radius scarcely changes for various ions with the same functional group but with different molecular volumes may indicate that the effective ionic radius may not give the size of the whole molecule but that of a charged site such as oxygen in a carboxylate group and a phenolate or nitrogen in an ammonium group and a heterocyclic compound. A charge in

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12) A. Bacarella, E. Grunwald, H. P. Marshall and E. L. Purlee, *J. Org. Chem.*, **20**, 747 (1955).

13) R. G. Bates, "Determination of pH," John Wiley and Sons, Inc., New York (1964), p. 195.

14) E. Grunwald and B. J. Berkowitz, *J. Am. Chem. Soc.*, **73**, 4939 (1951).

an ion may be located on a specific site such as oxygen or nitrogen atom, and the electrostatic interaction of the ion with the surrounding medium may be described as a function of the distance from the charged atom in question. A hydrophobic group which occupies the major part of the volume of an ion may contribute to a lesser extent to the electrostatic interaction between the charged site in the molecule and the surrounding medium. Solvation of ions having hydrophobic groups may be smallest so that the relationships of Eqs. (17) and (19) may hold with a good approximation.

Similarly the assumption that the alkoxonium ion, $R-OH^{2+}$, has the same effective ionic radius as that of hydronium ion may be supported in spite of their different molecular volumes.

From results in Tables 2 and 3, the effective ionic radii are estimated as follows: 1.4—1.5 Å for $-NH_3^+$ in ammonium and aliphatic ammonium ions, 0.9—1.1 Å for $\rangle NH^+$ in hererocyclic compounds, 0.7—0.9 Å for $-O^-$ in carboxylic acids, 1.1—1.4 Å for $-O^-$ in phenols. Values of the effective ionic radii of diethanolammonium and formate ions are large as compared with the related compounds. This may be attributed to easier hydration of these ions: relatively hydrophilic ethanol groups in the former may allow water molecules to approach a charged nitrogen atom with electrostatic interactions, and the latter, formate ion, has no aliphatic radicals.

Some discrepancies observed in water-ethanol systems seem to be due to a more or less crude approximation that activities of water and ethanol are put equel to their mole fractions. Vapor pressure data show that water-methanol mixtures[16] are better approximated to the ideal mixtures than water-ethanol mixtures.[17]

The author wishes to thank Professors Motoharu Tanaka and Yutaka Miyahara for their helpful advice. The financial support given by the Ministry of Education is gratefully acknowledged.

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15) T. Shedlovsky and R. L. Kay, *J. Phys. Chem.*, **60**, 151 (1956).

16) J. Timmermans, ed., "The Physico-chemical Constants of Binary Systems in Concentrated Solutions," Vol. 4, Interscience Publ., Inc., New York (1960), p. 154.

17) E. A. Guggenheim, "Thermodynamics," 2nd Ed., North-Holland Publ. Co., Amsterdam (1950), p. 187.