BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2052—2056 (1973)

# Ionic Equilibria in Mixed Solvents. VIII. Solvent Effects on the Dissociation of Diprotic Acids in Aqueous Methanol Mixtures

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(Received December 11, 1972)

Dissociation constants of protonated 1,6-hexanediamine, 1,8-octanediamine, 1,10-decanediamine, 1,11-undecanediamine, and 1,12-dodecanediamine in aqueous mixtures of 0 to 90% (w/w) methanol were determined potentiometrically at 25 °C, 0.1 M sodium chloride being used as an ionic medium. Values of $pK_2-pK_1$ of diamines were practically independent of the solvent composition in contrast to those of dicarboxylic acids, which increase monotonously with methanol concentration. Variations of $pK_1$, $pK_2$, and $pK_2-pK_1$ of diamines with solvent composition were discussed in comparison with those of dicarboxylic acids.

It is known that the acid dissociation constant of a monoprotic acid of neutral type (*e.g.* acetic acid or phenol) decreases with an increase in the concentration of an organic solvent in aqueous organic mixtures.[1–11] The solvent effect on dissociation constants of dicarboxylic acids[9,11–18] is similar to that of monocarboxylic acids. This can be explained qualitatively in terms of the electrostatic interaction between a leaving proton on an acid group and the conjugate base radical. On the other hand, the dissociation of a charged acid such as ammonium ion as well as other protonated mono- and diamines is enhanced by the addition of an organic solvent into aqueous solution, decreasing steeply after passing through a maximum.[1,5,9,10,14,19–21]

Kotaka and others[22] studied the association of ammonia in aqueous propanol solution by conductometry and confirmed that the association constant of the reaction

$$NH_4^+ + OH^- = NH_3 + H_2O$$

increases monotonously with solvent composition, and the variation of the dissociation constant of ammonium ion in mixed solvents described in terms of the reaction

$$NH_4^+ + H_2O = NH_3 + H_3O^+; \quad K = \frac{[NH_3][H^+]}{[NH_4^+]}$$

is essentially attributed to the variation of the autoprotolysis constant of the solvent with solvent composition.

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In a previous paper[10] we showed that the variation of dissociation constant of a monoprotic acid with solvent composition in aqueous alcoholic solutions, regardless of neutral or charged type, could be explained in terms of free energy changes of transfer of species from water to a mixed solvent taking into account the equilibrium between hydronium and alkoxonium ions:

$$H_3O^+ + ROH = H_2O + ROH_2^+ \qquad (1)$$

For protonated diamines we found that dissociation constants vary in the same manner as those of monoamines.[21] A remarkable difference was observed between variations of $pK_2-pK_1$ for diamine and carboxylic acid. For the latter not only $pK_1$ and $pK_2$ but also $pK_2-pK_1$ increase with solvent composition, as predicted from electrostatic theories.[23-26] On the other hand, values of $pK_2-pK_1$ for diamines remain practically constant, or in some cases decrease with an increase of the methanol content.

We have attempted to clarify these phenomena of dissociation reactions of diprotic acids in mixed solvents.

## Experimental

*A. Reagents.* Dihydrochlorides of 1,6-hexanediamine, 1,8-octanediamine, 1,10-decanediamine, 1,11-undecanediamine, and 1,12-dodecanediamine (Aldrich Chemical Co., Inc., Milwaukee, Wis., U.S.A.) were prepared by the method described previously.[21] Recrystallization of the salts was repeated three times from water. When a salt was colored, the colored substance was removed with active charcoal before recrystallization. The salts thus prepared were dried *in vacuo* at room temperature and kept in the dark.

*Sodium Chloride* (ultra pure) from E. Merck Co. was dried at 500 °C.

*Sodium Hydroxide* was prepared by the method described previously[21] and was stored in a polyethylene bottle under nitrogen. Transfer of the sodium hydroxide solution from the bottle to a buret was carried out under an atmosphere of nitrogen gas.

*Methanol.* Reagent grade methanol was distilled and stored in a glass bottle.

*B. Apparatus.* Beckman glass electrodes (No. 40495 and 39301) were used. No difference was observed between two types of electrodes in pH measurements. A silver-silver chloride electrode was prepared according to Brown[27] and was set in the "Wilhelm" type of a reference half-cell.[28] A Radiometer PHM-4d pH-meter (Copenhagen) was used.

Dissociation constants of the diprotonated diamines were determined in aqueous mixtures of 0—90% (w/w) methanol. Experimental conditions were the same as those mentioned previously.[21] The pH values never exceeded 10.4 in the course of measurements in all systems.

Hydrogen ion concentrations in solution at equilibrium were determined from emf measurements by application of the Nernst equation

$$E = E_0 + 59.15 \log [H^+]_s + 59.15 \log f_H + E_j \qquad (2)$$

TABLE 1. DISSOCIATION CONSTANTS OF 1,6-HEXANEDIAMINE, 1,8-OCTANEDIAMINE, 1,10-DECANEDIAMINE, 1,11-UNDECANEDIAMINE, AND 1,12-DODECANEDIAMINE IN VARIOUS WATER–METHANOL MIXTURES CONTAINING 0.1M NaCl

| Concn of methanol %(w/w) | $pK_1$ | $pK_2$ | $pK_2-pK_1$ |
|---|---|---|---|
| 1,6-Hexanediamine | | | |
| 0 | 10.08 | 10.79 | 0.71 |
| 10 | 9.98 | 10.67 | 0.69 |
| 20 | 9.87 | 10.55 | 0.68 |
| 30 | 9.72 | 10.40 | 0.68 |
| 40 | 9.56 | 10.21 | 0.65 |
| 50 | 9.49 | 10.12 | 0.64 |
| 60 | 9.29 | 9.93 | 0.64 |
| 70 | 9.18 | 9.95 | 0.77 |
| 80 | 9.16 | 9.94 | 0.78 |
| 90 | 9.43 | 10.13 | 0.70 |
| 1,8-Octanediamine | | | |
| 0 | 10.16 | 10.76 | 0.60 |
| 10 | 10.11 | 10.71 | 0.60 |
| 20 | 10.01 | 10.54 | 0.53 |
| 30 | 9.82 | 10.48 | 0.66 |
| 40 | 9.67 | 10.26 | 0.59 |
| 50 | 9.51 | 10.13 | 0.62 |
| 60 | 9.39 | 9.99 | 0.60 |
| 70 | 9.31 | 9.94 | 0.63 |
| 80 | 9.35 | 9.97 | 0.62 |
| 90 | 9.46 | 10.09 | 0.63 |
| 1,10-Decanediamine | | | |
| 0 | 10.36 | 10.93 | 0.57 |
| 10 | 10.19 | 10.75 | 0.56 |
| 20 | 10.04 | 10.62 | 0.58 |
| 30 | 9.88 | 10.44 | 0.56 |
| 40 | 9.70 | 10.28 | 0.58 |
| 50 | 9.54 | 10.12 | 0.57 |
| 60 | 9.40 | 10.01 | 0.61 |
| 70 | 9.28 | 9.93 | 0.65 |
| 80 | 9.29 | 9.94 | 0.65 |
| 90 | 9.56 | 10.16 | 0.60 |
| 1,11-Undecanediamine | | | |
| 0 | 10.37 | 10.95 | 0.58 |
| 10 | 10.22 | 10.77 | 0.55 |
| 20 | 10.08 | 10.64 | 0.55 |
| 30 | 9.89 | 10.42 | 0.53 |
| 40 | 9.69 | 10.34 | 0.65 |
| 50 | 9.55 | 10.10 | 0.55 |
| 60 | 9.43 | 9.97 | 0.54 |
| 70 | 9.36 | 9.98 | 0.62 |
| 80 | 9.37 | 10.03 | 0.66 |
| 90 | 9.60 | 10.18 | 0.58 |
| 1,12-Dodecanediamine | | | |
| 0 | 10.34 | 10.92 | 0.58 |
| 10 | 10.24 | 10.81 | 0.57 |
| 20 | 10.10 | 10.66 | 0.56 |
| 30 | 9.90 | 10.52 | 0.62 |
| 40 | 9.82 | 10.44 | 0.62 |
| 50 | 9.57 | 10.17 | 0.60 |
| 60 | 9.44 | 10.05 | 0.61 |
| 70 | 9.35 | 9.94 | 0.59 |
| 80 | 9.37 | 9.90 | 0.53 |
| 90 | 9.61 | 10.16 | 0.56 |

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and the liquid junction potential $E_j$ in 90% methanol–water mixture was corrected with the relation $E_j = -450 \pm 50$ mV/M·$[H^+]_s$, where $[H^+]_s$ denotes the concentration of hydrogen ion at equilibrium. In other solutions the liquid junction potential was corrected by the use of $E_j$ values reported previously.[21]

## Results and Discussion

Dissociation constants for each diamine were determined from the formation function $\bar{n} = ([H^+]K_2^{-1} + 2[H^+]^2K_1^{-1}K_2^{-1}) / (1 + [H^+]K_2^{-1} + [H^+]^2K_1^{-1}K_2^{-1})$ by means of a generalized least-squares method with the aid of an electronic computer FACOM 230-60 in order to make the error square sum $(U = \sum(\bar{n} - \bar{n}_{\text{calcd}})^2)$ minimum for the set of dissociation constants $K_1$ and $K_2$. The results are summarized in Table 1.

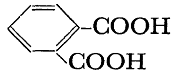
In order to assess the solvent effects on the dissociation of diprotic acids, the variation of the dissociation constants of dicarboxylic acids with the methanol concentration is discussed first, the values of p$K_1$ and p$K_2$ of the dicarboxylic acids being quoted from literature. Variations of p$K_1$ and p$K_2$ of diamines with solvent composition are treated next.

*(1) Variation of p$K_2$−p$K_1$ for Dicarboxylic Acids with the Solvent Composition.* In 1937 Kirkwood and Westheimer[25,26] proposed the following equation for the p$K_2$−p$K_1$ value of a diprotic acid in aqueous solution.

$$\mathrm{p}K_2 - \mathrm{p}K_1 = \frac{Ne^2}{a\varepsilon_e RT \ln 10} + \log \sigma \tag{3}$$

If we assume that the equation is applicable to a diprotic acid not only in aqueous solution but also in a mixed solvent and that Kirkwood-Westheimer's spherical model can be used, we can calculate from the data of p$K_2$−p$K_1$ the radius of the sphere $b$, the distance between a charge and the center of the sphere $r$, the angle between lines from the center to the charges $\theta$ and the distance between charges $a$ of the model. The values of p$K_2$−p$K_1$ found in literature are satisfactorily reproduced with the parameters best chosen by means of the least-squares method over the whole range of methanol concentration (Fig. 1). Parameters thus obtained are given in Table 2. The value of $\theta$ decreases as the methylene chain becomes longer. The value of $2r = l$ for an acid is very close to $l_{\text{max}}$. These results lead to a conclusion that a dicarboxylic acid is bent in a nearly V- or U-shape in solution and the bending may be enhanced with chain length. The fact that *p*-phthalic acid has a larger value of $\theta$ than that of *o*-phthalic acid supports the model we used. Values of $a$ obtained from p$K_2$−p$K_1$ values in aqueous solu-

Table 2. Parameters of various dicarboxylic acids

| | $a$ (Å) | $\theta$ (°) | $l=2r$ (Å) | $l_{\text{max}}$ (Å) |
|---|---|---|---|---|
| $HOOCCH_2COOH$ | 2.81 | 100 | 3.67 | |
| $HOOCCH(CH_3)COOH$ | 2.58 | 100 | 3.37 | |
| $HOOCC(CH_3)(C_2H_5)COOH$ | 2.12 | 100 | 2.77 | |
| $HOOCC(C_2H_5)_2COOH$ | 1.84 | 100 | 2.40 | |
| $HOOC(CH_2)_4COOH$ | 5.53 | 70 | 8.38 | 9.02[a], 6.65[b] |
| $HOOC(CH_2)_5COOH$ | 5.78 | 70 | 10.07 | 9.91[a], 7.40[b] |
| $HOOC(CH_2)_8COOH$ | 5.60 | 70 | 9.76 | 11.46[b] |
| $HOOC(CH_2)_{10}COOH$ | 7.10 | 70.2 | 12.37 | 13.93[b] |
|  | 2.72 | 100 | 3.55 | |
|  | 3.03 | 145 | 3.18 | |

a) Ref. 29.
b) Ref. 31.

Table 3. Values of $a$ of dicarboxylic acids estimated by various authors

| | Tanford[30] (Westheimer Shookhoff)[29] | Peek and Hill[33] | Ninomiya and Tōei[32] | Present work |
|---|---|---|---|---|
| $HOOCCH_2COOH$ | 4.10 | | | 2.81 |
| $HOOCCH(CH_3)COOH$ | 4.05 | | | 2.58 |
| $HOOCC(C_2H_5)_2COOH$ | 3.75 | | | 1.84 |
| $HOOCC(CH_3)(C_2H_5)COOH$ | 4.10 | | | 2.12 |
| $HOOC(CH_2)_4COOH$ | 7.75 | 5.99 | 5.72 | 5.53 |
| $HOOC(CH_2)_5COOH$ | 8.30 | 6.57 | 6.79 | 5.78 |
| $HOOC(CH_2)_6COOH$ | 9.30 | 7.59 | 7.64 | |
| $HOOC(CH_2)_7COOH$ | 9.85 | 8.22 | 7.86 | |
| $HOOC(CH_2)_8COOH$ | 9.60 | 9.17 | 8.21 | 5.60 |
| $HOOC(CH_2)_{10}COOH$ | 11.20 | 10.37 | 8.81 | 7.10 |

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29) F. H. Westheimer and M. W. Shookhoff, *J. Amer. Chem. Soc.*, **61**, 555 (1939).

30) C. Tanford, *ibid.*, **79**, 5348 (1957).

31) H. M. Peek and T. L. Hill, *ibid.*, **73**, 5304 (1951).

32) A. Ninomiya and K. Tōei, *Nippon Kagaku Zasshi*, **90**, 655 (1969).

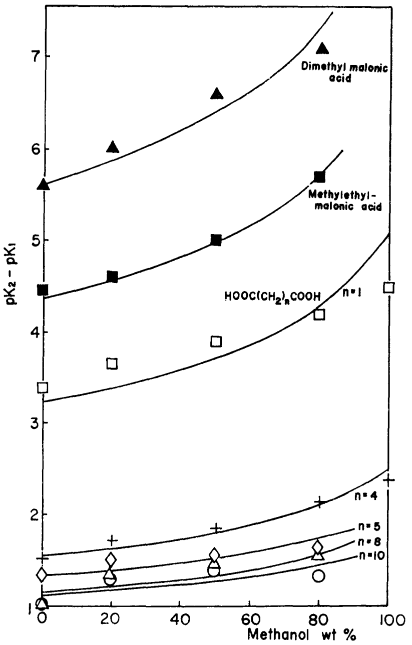
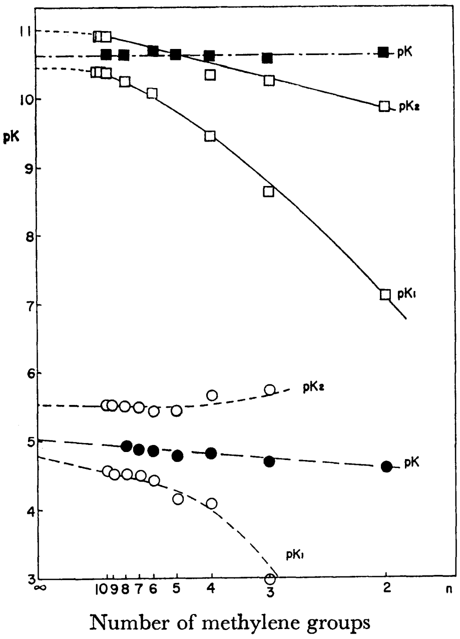


Fig. 1. $pK_2$—$pK_1$ of some dicarboxylic acids in water–methanol mixtures. Solid lines show calculated values of $pK_2$—$pK_1$ of the acids with parameters listed in Table 2.

tions are summarized in Table 3. The values calculated by the present method are slightly smaller than others but seem reasonable.

*(2) Variation of $pK_2$—$pK_1$ for Diamines with Solvent Composition.* The value of $pK_2$—$pK_1$ varied with solvent composition in a different manner from that of dicarboxylic acids; the $pK_2$—$pK_1$ value was practically independent of methanol concentrations. As $\varepsilon_e$ in Eq. (3) is expected to decrease with the increase of the methanol concentration, $a$ should increase in order to keep the $pK_2$—$pK_1$ value in solution constant independent of solvent compositions. Increase of $a$ caused by the addition of methanol into aqueous solution may be qualitatively interpreted in terms of the following effects: (1) Electrostatic repulsion between charged sites increases with the decrease of the effective dielectric constant. (2) It is known that hydrophobic groups in molecules tend to gather in hydrophilic solvent. However, the addition of methanol makes the solvent less hydrophilic so that hydrophobic coagulation of methylene groups may be reduced and the molecule turns out to be stretched. (3) The hydrogen bond between amino groups through water molecules may partly be broken by the addition of methanol, although no definite evidence for the hydrogen bond formation between amino groups in a molecule has been found.

*(3) Variation of $pK_1$ and $pK_2$ for Diamines with Chain Length and with Solvent Composition.* In aqueous solution both $pK_1$ and $pK_2$ of a diamine are smaller than the $pK$ of the corresponding monoamine when the chain is short, $pK_2$ increasing with chain length in such a way to cross $pK$'s of monoamines (Fig. 2). At a given solvent composition variations of $pK_1$ and $pK_2$ are similar to those of $pK$'s of monoamines. Since the interaction between charges, that is $pK_2$—$pK_1$, in a diamine molecule can be assumed to be practically constant, we can assume that free energy changes caused by the interaction between charges is independent of solvent composition and therefore, variations of $pK_1$ and $pK_2$ can be treated separately as if there were two independent acids, each having dissociation constants of $pK_1$ and $pK_2$. Therefore, equations proposed to monoamines can be used also for diamines. For an acid of $BH^+$ type, $\Delta pK = pK(s) - pK(w)$ is written as follows:



Number of methylene groups

Fig. 2. Variations of $pK_1$ and $pK_2$ of dicarboxylic acids[32] and diamines in aqueous solutions with the number of methylene groups in the molecule: ○ dicarboxylic acids, ● monocarboxylic acid, □ diamines, ■ monoamines.

$$\begin{aligned}\Delta pK = {} & [(\mu^\circ_{BH}(w) - \mu^\circ_{BH}(s)) + (\mu^\circ_{H_2O}(w) - (1-x)\mu^\circ_{H_2O}(s) \\ & - x\mu^\circ_{ROH}(s)) + (\mu^\circ_{B}(s) - \mu^\circ_{B}(w)) + ((1-x)\mu^\circ_{H_3O}(s) \\ & + x\mu^\circ_{ROH_2}(s) - \mu^\circ_{H_3O}(w))]/RT\ln 10 \qquad (4)\end{aligned}$$

where $\mu^\circ(w)$ and $\mu^\circ(s)$ stand for standard chemical potentials of a relevant species in water and an aqueous methanol solution, respectively, $x$ a fraction of meth-

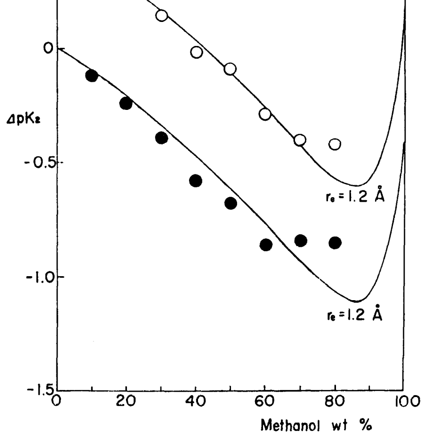


Fig. 3. Variations of $\Delta pK_1$ and $\Delta pK_2$ of 1,6-hexanediamine with the solvent composition.

oxonium ion formed from one mole of proton and is given by the equation

$$x = \frac{\kappa y}{1-y+\kappa y} \tag{5}$$

where $y$ represents the mole fraction of methanol in the solvent. $\kappa$ is the equilibrium constant of reaction (1).

By application of models proposed by one of the authors (H. O.),[10] we can calculate free energy changes of transfer of species from aqueous solution to a mixed solvent and thus $\Delta \mathrm{p}K$, assuming an effective size of a functional group $r_e$ in a diamine molecule. Typical results for $\Delta \mathrm{p}K_1$ and $\Delta \mathrm{p}K_2$ are shown in Fig. 3 for 1,6-hexanediamine. The effective sizes of each amino group in the diamine were evaluated to be $r_e = 1.2$ Å. The value 1.2—1.3 Å of $r_e$ was found for other diamines regardless of the chain length. For ammonium and diethylethanol ammonium ions, the effective sizes of the functional groups were estimated to be 1.4—1.5 Å. The slightly smaller values of $r_e$ for diamines than those for ammonium and diethylethanol ammonium ions may be due to the interaction between charged groups in diamine molecules, the solvent effect on which is neglected in calculation of $\Delta \mathrm{p}K$ of diamines. The different interactions between an ammonium ion or a tertiary amino group in diethylethanol ammonium ion and a primary amino group of a diamine with solvent molecules might give rise to different values of $r_e$.