Dissociation Constants of Some Carboxylic Acids in Mixed Aqueous Solvents

By Motoo YASUDA

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The dissociation constants of carboxylic acids were determined by various authors in mixed solvents, such as water-methanol, water-ethanol and water-dioxane mixtures and the relationship between the dissociation constants of the acids and the dielectric constants of the mixed solvents was discussed. As the dissociation of an acid is influenced by the dielectric constant of the solvent, it may be reasonable to suppose that an acid has almost the same acidity, i. e., almost the same dissociation constant in mixed solvents having the same dielectric constant. However, both Speakman[1] and Dondon[2] observed that aqueous dioxane acted as if it had a higher effective dielectric constant than aqueous alcohol of the same bulk dielectric constant. In other words, the values of dissociation constants of several acids in aqueous dioxane were reported to be higher than those determined in aqueous alcohol with the same dielectric constant. The present paper deals with the problem whether a carboxylic acid has really different acidity in various mixed solvents having the same dielectric constant.

Calculation of the Dissociation Constants. — The dissociation of a carboxylic acid in mixed solvents is an equilibrium reaction of the type

$$\mathrm{HA+S} \rightleftarrows \mathrm{SH^+ + A^-} \qquad (1)$$

where HA is a monobasic acid and S is one of the components of the mixed solvent. Since water has an exceptionally high proton affinity, Eq. 1 may be written as Eq. 2, if the mixed solvent contains a sufficient quantity of water and the concentration of the acid is small.

$$\mathrm{HA+H_2O} \rightleftarrows \mathrm{H_3O^+ + A^-} \qquad (2)$$

The equilibrium constant of this dissociation, or the dissociation constant of an acid in aqueous mixed solvents should be given by Eq. 3:

$$K=[\mathrm{A^-}]\,[\mathrm{H_3O^+}]/[\mathrm{HA}]\,[\mathrm{H_2O}] \qquad (3)$$

where square brackets indicate activity. On the other hand, the strength of an acid in water is usually expressed in terms of the constant K_a, instead of K defined by Eq. 3,

$$K_a=[\mathrm{A^-}]\,[\mathrm{H^+}]/[\mathrm{HA}] \qquad (4)$$

In aqueous solution K_a may be used, for $[\mathrm{H_2O}]$ is nearly constant. But this is not true in mixed solvents containing a limited amount of water. Due consideration should be paid to the fact that the activity of water in mixed solvents changes with the molar fraction of organic solvents. Therefore, the constant K defined by Eq. 3 should be used for the estimation of the dissociation of an acid in mixed solvents, in place of K_a defined by Eq. 4.

Furthermore, K_a has a different numerical value in accordance with the unit of concentration used in calculation, whereas

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[1] J. C. Speakman, *J. Chem. Soc.*, **1943**, 270.

[2] M. -L. Dondon, *J. chim. phys.*, **54**, 290, 304 (1957).

K does not depend on the unit of concentration. The present author calculated the values of K from the values of K_a reported by previous workers. But, as the activity of water in mixed solvents containing electrolytes is not known, it was replaced by the concentration of water.

Results and Discussion

1) Benzoic, Adipic and Succinic Acids.— Speakman determined the dissociation constant K_a defined by Eq. 4 of some carboxylic acids in aqueous alcohols and dioxane by using a glass electrode in conjunction with a cell involving liquid-liquid potentials. Some of his results are listed in Table I together with the dielectric constants ε reported by him. As seen in Table I, the values of $pK_a(=-\log K_a)$ in aqueous dioxane are lower than those of pK_a in aqueous alcohol having the same dielectric constant. The present author calculated the values of pK defined by Eq. 3 considering the change in the amount of water in mixed solvents. The values of the first and the second dissociation constant, pK_1 and pK_2, recalculated in this way are listed in Table II.

The values of pK are plotted against $1/\varepsilon$ in Fig. 1. It is seen that all points fall on a straight line. This means that an acid has nearly the same acidity in the medium having the same dielectric constant, at least in the range of the dielectric constant studied.

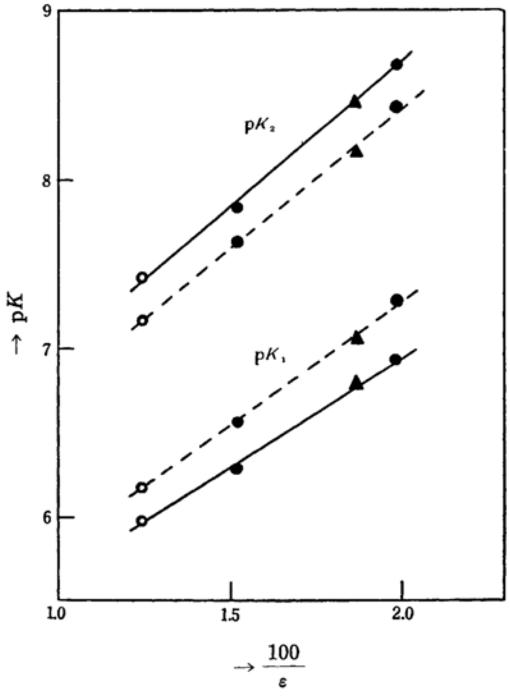

Fig. 1. Variation of pK values with the dielectric constant of the solution. Solid and broken lines indicate succinic and adipic acids, respectively. White and black circles and triangles show values in water, water-alcohol and water-dioxane mixtures, respectively.

TABLE I. VALUES OF pK_a AT 20°C REPORTED BY SPEAKMAN

Solvent % by wt.	ε	Adipic acid		Succinic acid		Benzoic acid
		pK_{a1}	pK_{a2}	pK_{a1}	pK_{a2}	pK_a
Water	80.4	4.43	5.42	4.22	5.67	4.24
25% Ethanol	65.7	4.93	6·00	4.65	6.19	4.83
50% Ethanol	50.4	5.83	6.98	5.48	7.24	5.87
30% Dioxane	53.3	5.45	6.55	5.19	6.84	5.35

TABLE II. RECALCULATED VALUES OF pK AT 20°C

Solvent % by wt.	Adipic acid		Succinic acid		Benzoic acid
	pK_1	pK_2	pK_1	pK_2	pK
Water	6.17	7.16	5.96	7.41	5.98
25% Ethanol	6.55	7.62	6.27	7.81	6.45
50% Ethanol	7.27	8.42	6.92	8.68	7.31
30% Dioxane	7.04	8.14	6.78	8.43	6.94

2) Succinic and Azelaic Acids. — In addition to the work of Speakman, Dondon reported recently the values of dissociation constants of several dibasic acids in water-methanol, water-ethanol and water-dioxane mixtures. A part of her results is shown in Fig. 2. She also reported that the dissociation of acids in aqueous dioxane is larger than in aqueous alcohols with the same dielectric constant. The values of pK_a determined by her in water-dioxane and in water-alcohol mixtures fall on two separate curves when they are plotted against $1/\varepsilon$. The range of the solvent composition studied for succinic acid by Dondon is wider than that by Speakman. She used the molarity basis for the calculation, but Speakman used the molality basis.

Now Dondon's values of pK_a are recalculated to give those of pK_1 and pK_2, which are listed in Table III. The values of density of the aqueous mixed solvents used for calculation were taken from Landolt-Börnstein's Tables[3] and the data

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[3] Landolt-Börnstein, "Physikalisch-Chemische Tabellen", Verlag J. Springer, Berlin, Hauptwerk (1923), p. 448 and Zweiter Ergänzungsband (1931), p. 287.

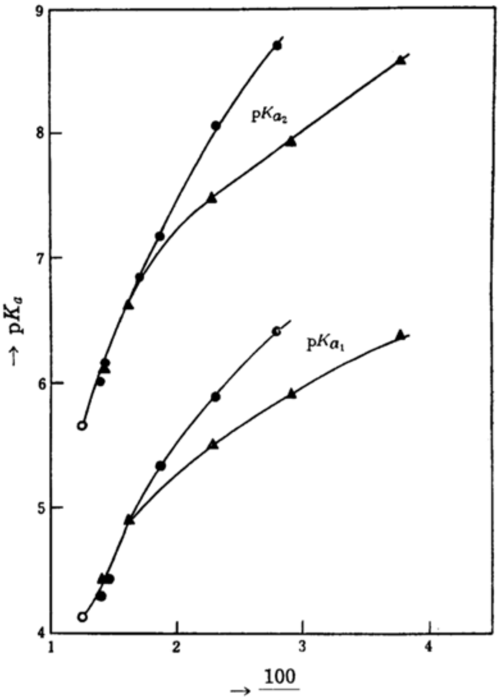

Fig. 2. Variation of pK_a values of succinic acid with the dielectric constant of the solution. White and black circles and triangles show values in water, water-alcohol and water-dioxane mixtures, respectively.

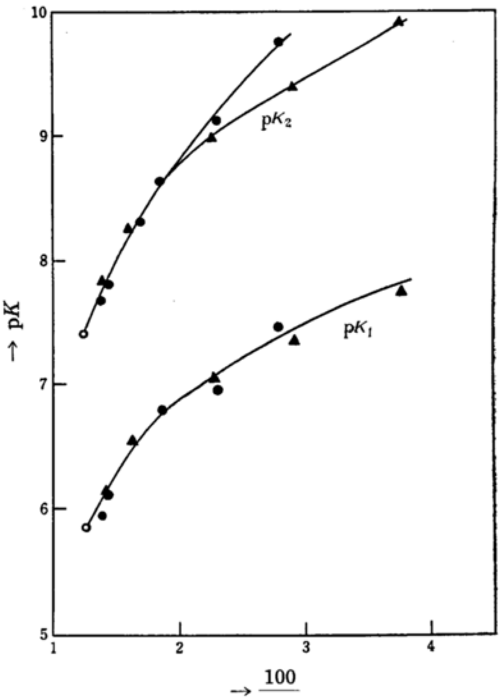

Fig. 3. Variation of pK values of succinic acid with the dielectric constant of the solution. White and black circles and triangles show values in water, water-alcohol and water-dioxane mixtures, respectively.

reported by Dunsmore and Speakman[4]. When the values of pK_1 and pK_2 are plotted against $1/\varepsilon$ (Fig. 3), all points of pK fall on a curve, except the points of pK_2 of succinic acid in the range of ε smaller than 40.

TABLE III. RECALCULATED VALUES OF pK_1 AND pK_2 AT 20°C

Solvent % by vol.	ε	Succinic acid		Azelaic acid	
		pK_1	pK_2	pK_1	pK_2
Water	80.4	5.88	7.41	6.29	7.24
20% Methanol	72.3	5.96	7.68	6.48	7.76
50% Methanol	59.0	6.46	8.31	6.96	8.31
80% Methanol	43.5	6.95	9.10	7.60	8.98
20% Ethanol	70.5	6.12	7.82	6.53	7.86
50% Ethanol	54.0	6.82	8.64	7.49	8.82
80% Ethanol	36.0	7.48	9.75	8.12	9.65
10% Dioxane	71.0	6.15	7.82	6.39	7.77
20% Dioxane	62.0	6.57	8.27	6.67	8.05
40% Dioxane	44.0	7.04	8.99	7.67	9.00
50% Dioxane	34.5	7.34	9.36	8.18	9.57
60% Dioxane	26.5	7.71	9.92	8.80	10.26

For the irregularity of pK_2 of succinic acid, it is difficult to find the cause. One cause now suspected is the change of the distance between the secondly dissociating proton and the previously dissociated carboxyl group in different mixed solvents.

Although Dondon reported dissociation constants determined in 100% methanol, 100% ethanol and 80% dioxane, these data were not used in the calculation, for the dissociation of an acid in pure organic liquids is different from that shown by Eq. 2 and she reported that the data for 80% dioxane were least reliable.

3) Acetic Acid. — The dissociation constant of acetic acid in mixed aqueous solvents was determined by several authors[5-7]. The same situation as mentioned above was also found for acetic acid. The values of pK_a originally reported and those of pK recalculated for acetic acid are listed in Table IV and

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[4] H. S. Dunsmore and J. C. Speakman, *Trans. Faraday Soc.*, **50**, 236 (1954).

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

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

[7] H. S. Harned and G. L. Kazanjian, *J. Am. Chem. Soc.*, **58**, 1912 (1936).

these values of pK are plotted against $1/\varepsilon$ in Fig. 4. The dielectric constants, ε, of the mixed solvents were calculated by interpolation using the data of Gosting and Albright[8].

As shown in Tables II, III and IV, all the values of pK for acetic, benzoic, succinic, azelaic and adipic acids were calculated using the concentration of water instead of its activity. Nevertheless a carboxylic acid has almost the same dissociation constant in various mixed solvents having the same dielectric constant. The apparently greater acidity of a carboxylic acid in the water-dioxane mixture reported previously is due to the greater concentration of water in this mixture than in the water-alcohol mixture having the same dielectric constant.

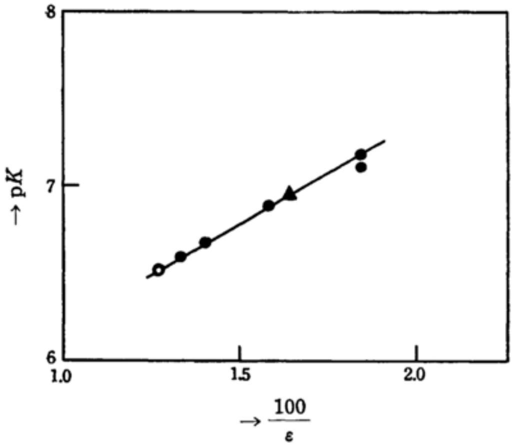

Fig. 4. Variation of pK values of acetic acid with the dielectric constant of the solution. White and black circles and triangle show values in water, water-alcohol and water-dioxane mixtures, respectively.

TABLE IV. THE DISSOCIATION CONSTANT OF ACETIC ACID AT 25°C

Solvent	ε	pK_a	pK
Water	78.5	4.76[5]	6.50
10% Methanol (by vol.)	75.0	4.88[5]	6.58
20% Methanol (by vol.)	71.3	5.02[5]	6.67
40% Methanol (by vol.)	63.2	5.34[5]	6.88
60% Methanol (by vol.)	54.4	5.74[5]	7.10
		5.81[6]	7.17
20% Dioxane (by wt.)	60.8	5.29[7]	6.94

Summary

Several authors determined dissociation constants of acids such as benzoic, succinic and azelaic acids in mixed solvents and reported that the dissociation constants determined in aqueous dioxane were higher than those determined in aqueous alcohols having the same dielectric constants. However, if the variation of the amount of water in mixed solvents is taken into consideration in calculating the dissociation constant, an acid has almost the same dissociation constant in various mixed solvents with the same dielectric constant.

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Chemical Institute, Nagoya University
Chikusa-ku, Nagoya

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[8] P. S. Albright and L. J. Gosting, ibid., 68, 1061 (1946).