Potentiometric Determination of the Dissociation Constants of Some Monocarboxylic Acids in Various Hydroorganic Media

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The dissociation constant of acetic acid, benzoic acid, 3-phenylpropenoic acid, 2-methylpropionic acid, and pentanoic acid were determined at 25.0 °C ($I = 0.1$ mol dm^{-3} KNO_3) by potentiometric pH titration in pure water and water + methanol, water + ethanol, water + dimethylformamide, water + dimethyl sulfoxide, and water + acetonitrile. pK_a values increase with an increase in the concentration of the organic compounds. These results are discussed in terms of solvent characteristics. Solvent basicity and stabilization of the conjugate acid free base by hydrogen-bonding interactions in hydroorganic solvent media relative to pure aqueous media as well as proton–solvent interaction play an important role in the acid dissociation equilibrium.

Introduction

The determination of the dissociation constant of an acid in mixtures of organic oxygen compounds with water provides useful data for the theoretical understanding of the ionization process in these media. Acetic acid and benzoic acid and their alkali-metal salts have been of particular use as buffers for pH measurements in aqueous media as well as for pH*(s) measurements in mixed solvents (*1*). There have been extensive studies on the dissociation constants of acids and bases in various mixed and nonaqueous solvents (*2–16*). In this paper we determined the dissociation constants of the biologically important monocarboxylic acids acetic, benzoic, 3-phenylpropenoic, 2-methylpropionic, and pentanoic by potentiometric pH titrations in pure water and water + methanol, water + ethanol, water + dimethylformamide, water + dimethyl sulfoxide, and water + acetonitrile. The dependence of pK_a values on the composition of the solvent mixtures has been investigated in order to examine solute + solvent interactions.

Experimental Section

Chemicals. Acetic acid, benzoic acid, 3-phenylpropenoic acid, 2-methylpropionic acid, and pentanoic acid were BDH analytical grade. Methanol, ethanol, dimethylformamide, dimethyl sulfoxide, and acetonitrile were of high purity (analytical reagent or spectro grade products). All chemicals were used without further purification. Carbonate-free KOH was prepared and standardized by titration with standard potassium hydrogen phthalate. The molarity of HNO_3 was determined by titration with standard KOH solution. Generally, dilute solutions were prepared by appropriate dilution of the stock. The accuracy of the concentration in all mixed solvent mixtures has been checked by mass.

Procedure. pH potentiometric measurements were made on solutions in a double-walled glass vessel at 25.0 ± 0.1 °C with a commercial Fisher combined electrode. The pH was measured with a Fisher Accumet pH/ion meter, model 2301. The instrument was standardized against standard buffers of pH 4.0 and 9.20. The instrument was rechecked after each experiment. The electrode system was calibrated in terms of hydrogen ion concentrations instead of activities. Thus, all constants determined in this work are concentration constants. The temperature was controlled by circulation of water through the jacket from a VEB Model E3E ultrathermostat bath and maintained within ±0.1 °C. Purified nitrogen was bubbled through the solution to maintain an inert atmosphere. Efficient stirring of the solution was achieved with a magnetic stirrer. All test solutions (5×10^{-3} mol dm^{-3} carboxylic acid + 0.0127 mol dm^{-3} HNO_3) were prepared in a constant ionic medium, 0.1 mol dm^{-3} KNO_3, by mixing the appropriate amounts of monocarboxylic acid, nitric acid, potassium nitrate, and the proportion of the different organic solvents studied.

The concentration of hydrogen ion was decreased by the addition of potassium hydroxide, prepared in the same medium used for the test solution. At each mixture, at least 6 titrations (35 measurements each) were performed. The concentration of free hydrogen ion, C_{H^+}, at each point of the titration was calculated from the measured emf, E, of the cell RE/TS/GE (RE and GE denote the reference and glass electrodes, respectively, and TS is the test solution) using the Nernst equation

$$E = E^\circ + Q \log C_{H^+} \qquad (1)$$

where E° is a constant which includes the standard potential of the glass electrode. It is to be assumed that the activity coefficient is constant, an assumption usually justified by performing the experiments with a medium of high ionic strength (0.1 mol dm^{-3} KNO_3). The value of E° for the electrode was determined from a separate titration of nitric acid with potassium hydroxide, both of known concentration, under the same temperature and medium conditions as for the test solution titration. The data obtained were analyzed by the program MAGEC (*17*). During the MAGEC calculation the autoprotolysis constant of water, K_w, was refined until the best value for Q was obtained. This refined K_w value is necessary as an adjustable parameter in pK_a calculation in pure water. The determination of E° and Q is only to determine K_w, and all the rest of the work is by pH titration with the different electrodes standardized in aqueous buffers. Values for K_w for water in water–organic solvent systems have been taken from the literature (*18–22*).

The pH-meter readings have been corrected in accordance with the method described by Douheret (*23, 24*). This was carried out to account for the difference in acidity,

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Table 1. pK_a* (Apparent Dissociation Constant) Values of Acetic Acid in Different Mass Fractions *w* for *w* Organic Solvent + (1 − w) Water Mixtures at 25.0 ± 0.1 °C and $I = 0.1$ mol dm^{-3} KNO_3

organic solvent	*w*	pK_a*	S^a
methanol	0.00	4.700	0.001
	0.20	4.923	0.002
	0.40	5.402	0.003
	0.55	5.954	0.002
ethanol	0.00	4.700	0.001
	0.20	5.052	0.003
	0.40	5.627	0.002
	0.55	6.054	0.001
DMF	0.00	4.700	0.001
	0.20	5.096	0.003
	0.40	5.951	0.004
	0.55	6.432	0.003
DMSO	0.00	4.700	0.001
	0.20	5.076	0.003
	0.40	5.606	0.004
	0.55	6.305	0.004
acetonitrile	0.00	4.700	0.001
	0.20	5.392	0.001
	0.40	6.096	0.001
	0.55	6.392	0.002

[a] *S* refers to standard deviation.

Table 2. pK_a* Values of Benzoic Acid in Different Mass Fractions *w* for *w* Organic Solvent + (1 − *w*) Water Mixtures at 25.0 ± 0.1 °C and $I = 0.1$ mol dm^{-3} KNO_3

organic solvent	*w*	pK_a*	S^a
methanol	0.00	4.210	0.002
	0.20	4.515	0.002
	0.40	5.303	0.006
	0.55	6.092	0.004
ethanol	0.00	4.210	0.002
	0.20	4.744	0.003
	0.40	5.486	0.005
	0.55	5.706	0.006
DMF	0.00	4.210	0.002
	0.20	4.571	0.002
	0.40	5.364	0.004
	0.55	6.008	0.002
DMSO	0.00	4.210	0.002
	0.20	4.235	0.005
	0.40	4.754	0.004
	0.55	5.443	0.004
acetonitrile	0.00	4.210	0.002
	0.20	4.696	0.003
	0.40	5.710	0.003
	0.55	6.292	0.003

[a] *S* refers to standard deviation.

Table 3. pK_a* Values of 3-Phenylpropenoic Acid in Different Mass Fractions *w* for *w* Organic Solvent + (1 − *w*) Water Mixtures at 25.0 ± 0.1 °C and $I = 0.1$ mol dm^{-3} KNO_3

organic solvent	*w*	pK_a*	S^a
methanol	0.00	4.440	0.002
	0.20	4.615	0.003
	0.40	5.203	0.002
	0.55	5.992	0.001
ethanol	0.00	4.440	0.002
	0.20	4.979	0.002
	0.40	5.546	0.001
	0.55	5.906	0.003
DMF	0.00	4.440	0.002
	0.20	4.671	0.001
	0.40	5.214	0.002
	0.55	5.808	0.002
DMSO	0.00	4.440	0.002
	0.20	4.535	0.001
	0.40	5.354	0.002
	0.55	5.743	0.002
acetonitrile	0.00	4.440	0.002
	0.20	4.596	0.001
	0.40	5.610	0.001
	0.55	6.292	0.002

[a] *S* refers to standard deviation.

Table 4. pK_a* Values of 2-Methylpropionic Acid in Different Mass Fractions *w* for *w* Organic Solvent + (1 − *w*) Water Mixtures at 25.0 ± 0.1 °C and $I = 0.1$ mol dm^{-3} KNO_3

organic solvent	*w*	pK_a*	S^a
methanol	0.00	4.850	0.002
	0.20	5.223	0.002
	0.40	5.902	0.001
	0.55	6.354	0.002
ethanol	0.00	4.850	0.002
	0.20	5.152	0.001
	0.40	5.827	0.003
	0.55	6.354	0.002
DMF	0.00	4.850	0.002
	0.20	5.496	0.002
	0.40	6.251	0.001
	0.55	6.732	0.002
DMSO	0.00	4.850	0.002
	0.20	5.276	0.001
	0.40	5.906	0.003
	0.55	6.605	0.002
acetonitrile	0.00	4.850	0.002
	0.20	5.592	0.002
	0.40	6.396	0.001
	0.55	7.192	0.003

[a] *S* refers to standard deviation.

basicity, permittivity, and ion activity in partially aqueous solutions relative to the pure solvent.

Initial estimates of pK_a values were refined with the ESAB2M computer program (*25*) by minimizing the error squares sum

$$U_V = \sum_i W_i (V_i - V_{\mathrm{calc},i})^2 \qquad (2)$$

The weight is calculated by

$$1/W_i = S_i^2 = S_V^2 + (\delta V_i/\delta E_i)^2 S^2 \qquad (3)$$

Our calculation has been performed with a Gaussian error in *V* of $S_V = 0.005$.

Results and Discussion

The pK_a values of acetic, benzoic, 3-phenylpropenoic, 2-methylpropionic, and pentanoic acids in different solvent mixtures are given in Tables 1−5. The calculated pK_a values of the monocarboxylic acids studied in pure water agree well with the literature values (*1*). The differences in the pK_a values for acetic and benzoic acid in MeOH−H_2O (*24*) [pK_a of acetic acid in 0% MeOH, 4.754 (4.70); 20%, 5.076 (4.923); 40%, 5.452 (5.402); of benzoic acid 20%, 4.721 (4.515)] may be attributed to the different media and ionic strengths used. The data of the present paper are given in parentheses.

Effect of the Amphiprotic Solvents. Consider an acid HA at molality *m* in mixed amphiprotic solvent (SH). It is assumed that the permittivity of the mixed solvent is sufficiently large to permit a certain amount of ionization. The proton activity a_H, as a measure of acidity, can be expressed (*18*) in terms of K_{HA} and K_{SH}, which are, respectively, the acidity constants of HA and SH_2^+:

$$a_H = \left[m K_{HA} K_{SH} \frac{\gamma_{SH_2^+} \gamma_{HA}}{\gamma_{SH} \gamma_{A^-}} \right]^{1/2} \qquad (4)$$

Table 5. pK_a* Values of Pentanoic Acid in Different Mass Fractions w for w Organic Solvents + (1 − w) Water Mixtures at 25.0 ± 0.1 °C and I = 0.1 mol dm^{-3} KNO$_3$

organic solvent	w	pK_a*	S^a
methanol	0.00	4.800	0.002
	0.20	5.023	0.001
	0.40	5.702	0.002
	0.55	6.254	0.002
ethanol	0.00	4.800	0.002
	0.20	4.850	0.001
	0.40	5.212	0.002
	0.55	6.352	0.002
DMF	0.00	4.800	0.002
	0.20	5.396	0.002
	0.40	6.151	0.003
	0.55	6.732	0.001
DMSO	0.00	4.800	0.002
	0.20	5.276	0.001
	0.40	5.906	0.002
	0.55	6.605	0.003
acetonitrile	0.00	4.800	0.002
	0.20	5.392	0.002
	0.40	6.096	0.003
	0.55	6.792	0.001

^{a} S refers to standard deviation.

where $\gamma_{SH_2^+}$, γ_{HA}, γ_{SH}, and γ_{A^-} are the activity coefficients of the species SH$_2^+$, HA, SH, and A$^-$, respectively. A decrease in the permittivity usually causes $\gamma_{SH_2^+}/\gamma_{SH}$ and γ_{A^-}/γ_{HA} to increase, and it is possible that both of these ratios will increase by about the same amount (*26*). Hence, according to eq 4, a lowering of the permittivity due to addition of methanol or ethanol may have little effect on the acidity of an unbuffered solution of acetic, benzoic, 3-phenylpropenoic, 2-methylpropionic, or pentanoic acid. With respect to the solvent basicity effect, the autoprotolysis constant of water is slightly influenced by addition of methanol or ethanol (the pK_a of water changes from 14.0 to 14.90 for a 0.5 mass fraction ethanol + water mixture ($HA + SH \rightleftharpoons SH_2^+ + A^-$)). Thus, changing the medium basicity by addition of methanol or ethanol may result in a relatively low stabilization of the conjugate base of the monocarboxylic acids studied compared to that in a pure aqueous medium, thereby causing an increase in pK_a.

Effect of Dipolar Aprotic Solvents (Dimethylformamide and Dimethyl Sulfoxide). The observed increase in the pK_a values of the different monocarboxylic acids studied as the solvent is enriched in the dipolar aprotic solvent dimethylformamide or dimethyl sulfoxide can mainly be attributed to the expected low stabilization of the conjugate free base of acetic, benzoic, 3-phenylpropenoic, 2-methylpropionic, and pentanoic acids by a hydrogen bond donated from solvent molecules in dimethylformamide or dimethyl sulfoxide + water mixtures compared to that obtained in a pure aqueous medium. This in turn results in a high pK_a value.

Effect of a Low Basic Aprotic Acetonitrile Solvent. The presence of acetonitrile as coorganic solvent exerts a pronounced effect on the pK_a values of acetic, benzoic, 3-phenylpropenoic, 2-methylpropionic, and pentanoic acids as compared to the effect of the other coorganic solvents studied (methanol, ethanol, DMSO, and DMF). This behavior can be mainly attributed to the following effects.

(i) Solute−solvent interaction effect: Acetonitrile is considered to be both a poorer acceptor as well as donor of hydrogen bonds compared to water. Thus, one may expect a low stabilization of the free conjuate bases of the monocarboxylic acids studied by hydrogen-bonding interactions in the presence of this coorganic solvent. This leads to a higher pK_a value in such media than that obtained in pure aqueous solution.

(ii) Proton−solvent interaction effect: Since acetonitrile is a weakly basic solvent, one must expect that the H$^+$ ion becomes less stabilized in the presence of this coorganic solvent due to hydrogen ion−solvent interaction (*27*). Thus, increasing the acetonitrile proportion in the aqueous medium results in a high activity coefficient of the proton, i.e., a high pK_a value.

According to Bates (*18*) solvent effects on the dissociation equilibria of the monocarboxylic acids under investigation can be expressed by eq 5, where $\bar{r}$ is the common radius of

$$pK_a^* - pK_a = \frac{121.6n}{\bar{r}}\left(\frac{1}{D_2} - 0.0128\right) \qquad (5)$$

all the ions, D_2 is the permittivity of the organic solvent, n = 2 for HA,A pairs of the charge type A^{0}B$^-$, n = 4 for the charge type A$^-$B^{2-}, and n = 0 for the charge type A$^+$B^0. The pK_a for monocarboxylic acids as might be expected from eq 5 does indeed increase markedly as the permittivity decreases. Thus, the strong differences in the effect of a solvent on the protonation of the different acids investigated may be explained using the above eq 5.

Literature Cited

(1) Perrin, D. D.; Dempsey, B. *Buffers for pH and Metal ion control*; Chapman and Hall: London, 1979.
(2) Das, R. C.; Dash, U. N.; Panda, K. N. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76* (10), 2152.
(3) Shanbhag, P. M.; Bates, R. G. *Bull. Soc. Chim. Belg.* **1981**, *90* (1), 1.
(4) Hoefnagel, A. J.; Wepster, B. M. *J. Chem. Soc., Perkin Trans. 2* **1989**, 977.
(5) Niazi, M. S. K. *Bull. Chem. Soc. Jpn.* **1989**, *62* (4), 1253.
(6) Koppel, I. A.; Koppel, J. B.; Pihl, V. O. *Org. React. (Tartu)* **1988**, *25* (1), 77.
(7) Niazi, M. S. K.; Shah, S. S.; Ali, J.; Khan, M. Z. I. *J. Solution Chem.* **1990**, *19* (6), 623.
(8) Dash, U. N.; Mishra, M. K. *Thermochim. Acta* **1987**, *115*, 97.
(9) Amira, M. F.; El-Shazly, S. A.; Khalil, M. M. *Thermochim. Acta* **1987**, *115*, 1.
(10) Niazi, M. S. K.; Mollin, J. *Bull. Chem. Soc. Jpn.* **1987**, *60* (7), 2605.
(11) Rubino, J. T. *Int. J. Pharm.* **1988**, *42*, 181.
(12) Bhattacharya, D. C.; Basu, A. K.; Aditya, S. J. *Indian Chem. Soc.* **1984**, *61*, 956.
(13) Papanastasiou, G.; Stalidis, G.; Jannakoudakis, D. *Bull. Soc. Chim. Fr.* **1984**, 255.
(14) Niazi, M. S. K.; Ali, J. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3619.
(15) Gustavo, G. A., Rosales, D.; Gomez, J. L.; Fernandez, S. J. *Anal. Chim. Acta* **1990**, *228*, 301.
(16) Niazi, M. S. K.; Shah, S. S.; Ali, J.; Khan, M. Z. I. *J. Solution Chem.* **1990**, *19*, 569.
(17) May, B. M.; Wiliams, D. R. In *Computational Methods for the Determination of Formation Constants*; Leggett, Ed.; Plenum Press: New York, 1985; pp 37−70.
(18) Bates, R. G. *Determination of pH theory and Practice*; John Wiley & Sons, Inc.: New York, 1964.
(19) Woolley, E. M.; Hepler, L. G. *Anal. Chem.* **1972**, *44*, 1520.
(20) Woolley, E. M.; Hurkot, D. G.; Hepler, L. G. *J. Phys. Chem.* **1970**, *74*, 3908.
(21) Gutbezahl, B.; Grunwald, E. *J. Am. Chem. Soc.* **1953**, *75*, 565.
(22) Harned, H. S.; Fallon, L. D. *J. Am. Chem. Soc.* **1939**, *61*, 2374.
(23) Douheret, G. *Bull. Soc. Chem. Fr.* **1967**, 1412.
(24) Douheret, G. *Bull. Soc. Chem. Fr.* **1968**, 3122.
(25) De Stefano, C.; Princi, P.; Rigano, C.; Sammartano, S. *Ann. Chim. (Rome)* **1987**, *77*, 643.
(26) Hammett, L. P. *J. Am. Chem. Soc.* **1928**, *50*, 2666.
(27) Bates, R. G. In *Solute-Solvent interactions*; Coetzee, J. F., Ritchie, C. D., Eds.; Marcel Dekker: New York, 1969; pp 72, 51.

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