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Determination of the Dissociation Constants of Salicylic Acid in Water-Ethanol Mixtures by Modified Conductometric Methods

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The dissociation constants of salicylic acid in water and ethanol–water mixtures (8—87.6 wt % of ethanol), have been determined by the modified conductometric method as suggested by Gelb. The results have been checked independently from the plot ΛC *vs.* $1/\Lambda$ of salicylic acid in mixed solvents. $\Lambda^\circ_{HClO_4}$ and $\Lambda^\circ_{\text{salicylic acid}}$ have also been determined.

The importance and limitations of the determinations of the dissociation constants of acids and bases in mixed solvents have been well-discussed.[1–4] In order to explore a suitable method for the determination of the dissociation constants in mixed solvents which could avoid the uncertainties due to liquid-junction potential and changed sensitivity of the glass electrode, we found the conductometric method as suggested by Gelb[5] with suitable modification can be utilized with success. The method is handy and less time consuming and ensures high accuracy. The method involves the assumption of complete dissociation of $HClO_4$ in mixed solvents—an assumption on which the measurement of H^+ ion concentration in mixed solvents is generally based. Until now the assumption has been regarded as being valid in mixed solvents containing fairly high percentages of organic solvents.

We report in this communication the dissociation constants of salicylic acid in a series of ethanol–water mixtures by the modified conductometric method. We are particularly interested in the determination of p*K* values of comparatively weak acids which may be useful for the preparation of suitable buffers, the lack of which is one of the strong handicaps for the measurement of H^+ ion concentrations in mixed solvents.

Experimental

Absolute ethanol was treated with the requisite quantity of calcium oxide, kept overnight, and then distilled. The middle fraction was collected and used without further treatment. The slight traces of water, if any, in the organic solvents were neglected. The weight percentages of the organic solvent and the relative permittivities of the solvent mixtures were determined in the same way as described before.[6] Salicylic acid (G. R. E. Merck) was recrystallized from alcohol. Perchloric acid and other reagents used for standardization were of E. Merck's reagent grade.

Conductance measurements were done with the aid of a Leeds and Northrup Model 4959 conductance bridge with a sensitivity of ±0.1%. A 50—60 cycle signal was employed. A dip-type Philips conductance cell with a cell-contant, $\theta = 0.815\ \text{cm}^{-1}$ was utilized. The cell constant was determined using accurately measured KCl (G. R. E. Merck) solutions and using the conductance values from the literature[7] and the value of the cell-constant was repeatedly checked during the course of the experiment. The measurements were done at $25 \pm 0.05\ ^\circ\text{C}$.

The initial conductance of a certain amount of the acid solution was measured. Definite amounts of perchloric acid in appropriate solvents were added at regular intervals. The mixtures were allowed sufficient time to attain equilibrium and the conductance of each solution was measured. The experiment was repeated with different concentrations of the salicylic acid and also in different percentages of mixed solvents. The ionic strengths of the solutions were kept as low as practicable ($\approx 10^{-3}$ M) so that the ionic strength correction was almost negligible. The blank titrations were performed in the same way as described above, the experimental solutions being replaced by the same amount of the appropriate solvent. The conductances of the solvents were taken to apply appropriate corrections.

Results and Discussion

The dissociation constant *K* for the reaction

$$HA \rightleftharpoons H^+ + A^- \qquad (1)$$

can be represented as

$$K = \frac{[H^+][A^-]}{[HA^-]} \times f_\pm^2 \qquad (2)$$

(f_{HA} may be regarded as unity).

However, if we take a mixture of completely dissociated $HClO_4$ and partly dissociated HA, Eq. 2 can be written as

$$K = \frac{\alpha(\alpha C_{HA} + C_{HClO_4}) \times f_\pm^2}{(1-\alpha)} \qquad (3)$$

C_{HA} = total concentration of HA
C_{HClO_4} = concentration of $HClO_4$ in the mixture
$f_\pm$ = mean activity coefficient
α = the degree of dissociation of HA in presence of $HClO_4$

The conductances of the mixtures (containing HA and $HClO_4$) and the blank solutions (containing $HClO_4$ only) are given by

$$\frac{1}{R} = \frac{1}{1000\theta}[C_{HClO_4}\Lambda'_{HClO_4} + \alpha C_{HA}\Lambda'_{HA}] \qquad (4)$$

[where $\Lambda'_{HA} = \lambda_{H^+} + \lambda_{A^-}$ at the appropriate ionic strength and $\Lambda = \alpha\Lambda'$, $\alpha = 1$ in the case of $HClO_4$] and

$$\frac{1}{R^*} = \frac{1}{1000\theta} C^*_{HClO_4}\Lambda^{*\prime}_{HClO_4} \qquad (5)$$

(* indicates quantities for blank solutions)

θ = cell constant.

When $1/R = 1/R^*$, we have

$$C^*_{HClO_4}\Lambda^{*\prime}_{HClO_4} = C_{HClO_4}\Lambda'_{HClO_4} + \alpha C_{HA}\Lambda'_{HA} \qquad (6)$$

Since $C_{\mathrm{HClO_4}}$ and $C^*_{\mathrm{HClO_4}}$ do not differ considerably and the ionic strengths of the solutions are equal, one can write $\Lambda'_{\mathrm{HClO_4}}=\Lambda^{*\prime}_{\mathrm{HClO_4}}$. However, approximations are made that $\Lambda'_{\mathrm{HClO_4}}=\Lambda'_{\mathrm{HA}}$ in aqueous as well as in mixed solvents. This is quite reasonable in view of the closeness of the mobility of $\mathrm{ClO_4^-}$ and anions on which the difference in equivalent conductances of $\mathrm{HClO_4}$ and organic acids ultimately depends. Thus,

$$C_{\mathrm{HClO_4}} + \alpha C_{\mathrm{HA}} = C^*_{\mathrm{HClO_4}} \tag{7}$$

from which α is obtained.

Modified equations[8)] can be used to take into account the variations of $\Lambda'_{\mathrm{HClO_4}}$ and Λ'_{HA} due to variations in ionic strengths; this, however, is not necessary in our case as the ionic strengths are kept low ($\approx 10^{-3}$ M) and the variation of ionic strengths is also too small to vitiate the assumption $\Lambda^{*\prime}_{\mathrm{HClO_4}}=\Lambda'_{\mathrm{HClO_4}}$ to a measurable accuracy.

Further modifications of K values are possible taking

$$\alpha = (C^*_{\mathrm{HClO_4}} - C_{\mathrm{HClO_4}})/\beta C_{\mathrm{HA}} \tag{8}$$

where $\Lambda'_{\mathrm{HClO_4}}=\Lambda^{*\prime}_{\mathrm{HClO_4}}$ and $\beta=\Lambda'_{\mathrm{HA}}/\Lambda'_{\mathrm{HClO_4}}$.
We have calculated β as suggested by Gelb but found the alternative procedure given below to be superior.

Equivalent conductance values of perchloric acid at different dilutions (5.0×10^{-2} M to 5.0×10^{-4} M) were obtained from conductance measurements. At low concentrations, $\Lambda'_{\mathrm{HClO_4}}$ values when plotted against $C^{1/2}$ gave good straight lines in aqueous as well as in mixed solvents. $\Lambda^\circ_{\mathrm{HClO_4}}$ values were obtained by extrapolation to zero dilution. $\Lambda_{\mathrm{HA}}^\circ$ and K values were obtained from the plot of $C\Lambda$ against $1/\Lambda$ of a number of dilute solutions of HA utilizing the equation[9)]

$$C\Lambda = -K\Lambda^\circ + K\Lambda^{\circ 2}/\Lambda \tag{10}$$

where the intercept gives ($-K\Lambda^\circ$) and the slope ($K\Lambda^{\circ 2}$). This, however, gives us an independent method of checking K values free from any assumption.

The β values were evaluated from $\Lambda^\circ_{\mathrm{HClO_4}}$ and $\Lambda^\circ_{\mathrm{HA}}$ values. Since the ionic strengths are very low, the slight differences of Λ' from Λ° values would not affect the value of β to any measurable extent. β value in water comes to be 400/415=0.96. The β values in mixed solvents also lie within 0.90 to 0.96, deviations occurring at higher percentages. However, evaluation of K and Λ° of the acid by the dilution method is liable to be erroneous at higher percentages of alcohols, where the dissociation constant decreases enormously.

The average values of $\Lambda^\circ_{\mathrm{HClO_4}}$, $\Lambda^\circ_{\text{salicyclic acid}}$, and p$K$ measured from several sets of experiments (using both the titration method and the dilution method) for each percentage of organic solvent are given in Table 1. The agreement of the K values suggests the accuracy of the titration method. The activity correction term from the Debye-Hückel limiting equations, making appropriate corrections for the change in the dielectric constant values, comes out to be about 0.02 (in 8 wt % of alcohol) to 0.09 (87 wt% of alcohol).

The values from the spectrophotometric measurements were also incorporated in Table 1 for comparison.[10)] The results are found to agree fairly well. The results obtained by the spectrophotometric method utilizing a glass–calomel electrode for measurement of $\mathrm{H^+}$ ions give higher values at higher percentages of alcohol. This may be due to uncertainties in $\mathrm{H^+}$ ion concentration measurements. The association of ions may be increasingly greater as the percentage of alcohol increases. However, it is noted that the pK values obtained by the modified conductivity method, when plotted against weight percentages and mole fractions of organic solvent, give excellent straight lines (up to 0.6 mole fraction); the plot of pK *vs.* $1/\varepsilon$ (ε=relative permittivity) gives deviations only at higher percentages of organic solvent.

The method however, cannot be used when the pK values are rather high (more than 4 or so). It is known that the dissociation constant is considerably suppressed with the addition of $\mathrm{HClO_4}$; as a result α becomes too small. For such cases, however, it is possible to take a large number of $1/R$ values from fairly concentrated to dilute solutions of HA (as dilute as measurable without impairing the accuracy). Suitable blank curves are obtained by addition of a dilute solution of perchloric acid to the appropriate solvents and the interpolated values of $1/R^*$ are determined from these blank curves. Under this condition, the equation reduces to $\alpha C_{\mathrm{HA}}=$

Table 1. Average values of Λ° and pK measured from several experiments (at 25 °C)

Wt % of ethanol	$1/\varepsilon\times10^2$	Mole fraction of ethanol	pK values			Λ° in $\mathrm{ohm^{-1}\cdot cm^2}$		Wt % of ethanol	p$K^{c)}$
			Titration method		From plot of ΛC *vs.* $1/\Lambda$	$\mathrm{HClO_4}$	Salicylic acid		
			(a)	(b)					
0.0	1.27	—	3.09	3.04	3.04	415.0	400.0	0.0	2.97
8.0	1.35	0.033	3.14	3.10	3.08	372.0	344.8	15.3	3.32
16.4	1.42	0.071	3.29	3.25	3.19	301.5	289.6	30.5	3.65
25.3	1.53	0.117	3.44	3.39	3.38	250.0	240.0	45.3	3.97
34.4	1.71	0.170	3.55	3.52	3.47	196.0	186.0	61.9	4.10
44.0	1.90	0.235	3.77	3.72	3.71	172.6	154.8	69.0	4.50
54.1	2.14	0.315	3.98	3.95	3.97	142.0	132.0	82.0	5.24
64.7	2.92	0.418	4.23	4.20	4.13	118.0	94.0	—	—
76.0	3.41	0.556	4.55	—	—	102.0	—	—	—
87.6	—	0.740	4.97	—	—	92.0	—	—	—

a) The pK-values before β-correction. b) The pK-values after β-correction. c) pK-Values from spectrophotometric data.[10)]

$C^*_{\mathrm{HClO_4}}$, from which α and hence pK values are calculated. Further refinements as suggested above are possible.

The method has the advantage that the accurate determination of cell constants is not at all necessary, provided the same cell is used, as the θ terms cancel.

The $\Lambda^\circ_{\mathrm{HClO_4}}$ in water has been found to be 415, in good agreement with the values in the literature ($\lambda^\circ_{\mathrm{H^+}}$= 349.8 and $\lambda^\circ_{\mathrm{ClO_4^-}}$=64.6[11] or 67.32)[12] at 25 °C. The $\Lambda^\circ_{\mathrm{HClO_4}}$ values decrease with increasing percentages of alcohol, as expected. The reliability of the results may be obtained from the comparison of $\Lambda^\circ_{\mathrm{HClO_4}}$ and $\Lambda^\circ_{\mathrm{HCl}}$ values ($\lambda^\circ_{\mathrm{Cl^-}}$=76.34 at 25 °C). The values of $\Lambda^\circ_{\mathrm{HCl}}$ in ethanol reported in the literature vary from 81.7 to 89.1[13] where $\Lambda^\circ_{\mathrm{HClO_4}}$ at 87.6 wt % of alcohol is 92.00. The values thus appear to be reasonable. The $\Lambda^\circ_{\text{salicylic acid}}$ (in water) comes out to be 400 ($\lambda^\circ_{\text{salicylate ion}}$= 35 at 25 °C).[11] A slight disagreement is thus apparent. It is, however, difficult to suggest the extent of reliability of the $\lambda^\circ_{\text{salicylate ion}}$ value. It is as yet inopportune to say something positively about the modified conductometric method. In comparison to the pH-metric method the assumptions involved in the determination of pK values by this method should not vitiate the result appreciably, even if association of $\mathrm{HClO_4}$ takes place at higher percentages of alcohol, as we are concerned with the conductivities.

Systematic studies by different techniques are necessary to make a definite statement about the reliability of this method in different mixed solvents.

References

1) S. C. Lahiri and S. Aditya, *J. Ind. Chem. Soc.*, **51**, 319 (1974).

2) R. G. Bates, "Determination of pH," John Wiley and Sons, New York (1964).

3) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed., Reinhold Publishing Corporation, New York (1958).

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

5) R. I. Gelb, *Anal. Chem.*, **43**, 1110 (1971).

6) S. C. Lahiri, G. Biswas, and S. Aditya, *Thermo Chim. Acta*, **9**, 369 (1974).

7) N. A. Lange, "Handbook of Chemistry," McGraw-Hill Book Company, New York, Toronto, London (1961).

8) T. Shedlovsky, *J. Am. Chem. Soc.*, **54**, 1405 (1932).

9) E. A. Moelwyn-Hughes, "Physical Chemistry," 2nd ed., Pergamon Press, Oxford (1964), p. 853.

10) S. K. Pal and S. C. Lahiri, *Z. Phys. Chem. (Leipzig)*, **246**, 81 (1971).

11) B. E. Conway, "Electrochemical Data," Elsevier Publishing Company, Amsterdam (1952), p. 45.

12) G. J. Janz and S. S. Danyluk, "Electrolytes," ed. by B. Pesce, Pergamon Press, Oxford, London (1962), p. 263.

13) G. Milazzo, "Electrochemistry," Elsevier Publishing Company, Amsterdam, London, New York (1963), pp. 60—61.