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Note

THERMODYNAMICS OF THE DISSOCIATION OF *ORTHO-*, *META-* AND *PARA-*SUBSTITUTED CHLORO-, NITRO-, HYDROXY- AND AMINO-BENZOIC ACIDS IN AQUEOUS MEDIUM FROM SOLUBILITY MEASUREMENTS

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Several physical methods, such as potentiometry, conductometry, spectrophotometry, and calorimetry, have widely been used for the determination of dissociation constants of acids in different solvent media. But very little work has been done on the determination of dissociation constants of acids by employing the solubility method. However, Li and Tulo [1] have reported the dissociation constant of iodic acid in aqueous medium from the solubility measurements of silver iodate in potassium nitrate and nitric acid solutions. Recently, Dash et al. in this laboratory have shown that the solubility method can be satisfactorily used for the determination of dissociation constants of both inorganic and organic acids in non-aqueous [2,3] and aqueous [4] media. As a further check on the method of determining the dissociation constants, the present work has been undertaken to redetermine the dissociation constants of a number of substituted benzoic acids in aqueous medium by employing the solubility method. It is seen that the present set of data are in reasonably good agreement with values reported in the literature [5].

EXPERIMENTAL

Silver salts of the substituted benzoic acids, sodium perchlorate and perchloric acid were of the same samples as used earlier [4,6]. The method of determination of solubility, the analysis of the solute contents and the accuracy of the analysis have been adequately described in our earlier studies [2,4,6,7].

RESULTS AND DISCUSSION

The dissociation constant of a substituted benzoic acid, HXBz, where X is any substituent, can be written as

$$K_a = \frac{c_{H^+}c_{XBz^-}}{c_{HXBz}} \times \frac{f_{H^+}f_{XBz^-}}{f_{HXBz}} = \frac{c_{H^+}c_{XBz^-}}{c_{HXBz}} f_{\pm}^2 \qquad (1)$$

where c and f are the molarity and activity coefficient, respectively (assuming $f_{H^+} = f_{XBz^-} = f_\pm$ and $f_{HXBz} = 1$). Using the Debye—Huckel limiting expression for the mean activity coefficient, $f_\pm$, eqn. (1) can be expressed as

$$\log K_a = \log K_c - \frac{2AI^{1/2}}{1 + a^0 B I^{1/2}} \tag{2}$$

where K_c is the dissociation constant in terms of concentration, I is the ionic strength, A and B are the Debye—Huckel constants and a^0 is the ion size parameter. The concentration dissociation constant, K_c was calculated from the expression [2,4]

$$K_c = \frac{c_{H^+} c_{XBz^-}}{c_{HXBz}} \tag{3}$$

where $c_{XBz^-} = s_s'^2/s_a$ (s_s' is the corrected solubility of the silver salt of the substituted benzoic acid in sodium perchlorate solutions, and s_a is that in perchloric acid solutions of the same ionic strength [2]), $c_{HXBz} = s_a - c_{XBz^-}$, $c_{H^+} = c_{HClO_4} - c_{HXBz}$, and $I = s_a + c_{H^+} = c_{HClO_4} + c_{XBz^-}$. Equation (3) is obtained from the concentrations of the species designated. As a first approximation, c_{XBz^-} was taken to be equal to s_s^2/s_a, where s_s is the observed solubility of the silver salt in sodium perchlorate solutions [6] having the same molarity as that of perchloric acid solutions, and I was calculated but subsequently a corrected value of s_s, which is written as s_s', was obtained by successive approximations and refinement [2] to a constant value of I. The values of the dissociation constant, K_a, were then calculated from eqn. (2) for each molarity of perchloric acid solution. As expected, these values did not remain constant with change of molarity and have been written as K_a'. The true dissociation constant, K_a, at any temperature for a particular acid was then obtained from the intercept of the log K_a' vs. $I^{1/2}$ plot.

The required values of A and B at different temperatures were taken from

TABLE 1

Values of pK_a of *ortho-*, *meta-*, and *para*-substituted chloro-, nitro-, hydroxy-, and aminobenzoic acids in water at different temperatures

Benzoic acid	pK_a [a]			
	20°C	25°C	30°C	35°C
o-Chloro	3.72	3.19	2.77	2.34
m-Chloro	3.53	3.70	4.01	4.33
p-Chloro	3.89	3.85	3.80	3.75
o-Nitro		2.06		
m-Nitro	3.56	3.51	3.43	3.41
p-Nitro	3.10	3.22	3.29	3.41
m-Hydroxy	4.18	4.14	4.08	4.06
p-Hydroxy	4.62	4.60	4.57	4.55
o-Amino	4.99	4.99	4.98	4.98
m-Amino	4.82	4.80	4.75	4.71
p-Amino	4.95	4.92	4.89	4.92

[a] Uncertainties in the pK_a values are of the order of ±0.007 units.

TABLE 2

Constants of eqn. (4), and ΔG^0, ΔH^0, ΔS^0, and ΔC_p^0 values at 25° for the dissociation of the substituted benzoic acids

Benzoic acid	*A*	*B*	$C \times 10^2$	ΔG^0 (kJ mole^{-1})	ΔH^0 (kJ mole^{-1})	ΔS^0 (J deg^{-1} mole^{-1})	ΔC_p^0 (J deg^{-1} mole^{-1})
o-Chloro	28987.5	−152.34	22.91	18.31 ± 0.38	165.46 ± 2.55	493.78 ± 7.12	−2614.1 ± 24.2
m-Chloro	40620.5	−282.51	50.31	21.24 ± 0.29	−77.67 ± 3.15	−331.90 ± 21.11	−5740.43 ± 29.14
p-Chloro	2603.2	+24.06	−3.85	21.96 ± 0.05	15.62 ± 0.17	−21.28 ± 1.14	439.29 ± 1.61
o-Nitro				11.73 ± 0.21			
m-Nitro	7271.4	−41.78	7.01	19.93 ± 1.72	20.03 ± 0.17	−0.35 ± 0.12	−799.9 ± 8.9
p-Nitro	2874.3	−22.15	5.27	18.26 ± 0.21	−34.57 ± 0.06	−177.27 ± 0.41	−601.31 ± 0.44
m-Hydroxy	423.3	4.17	−0.49	23.58 ± 0.32	16.43 ± 0.19	−23.98 ± 0.10	56.91 ± 0.46
p-Hydroxy	−456.3	9.17	−1.02	26.23 ± 0.49	8.61 ± 0.12	−59.14 ± 1.20	116.38 ± 0.48
o-Amino	5562.1	−31.26	5.90	28.45 ± 0.46	6.14 ± 0.03	−75.01 ± 0.98	−673.43 ± 1.4
m-Amino	5339.6	−27.79	4.93	27.40 ± 0.16	18.48 ± 0.19	−29.93 ± 0.096	−562.02 ± 1.46
p-Amino	1693.19	−4.89	1.39	28.06 ± 0.32	8.07 ± 0.10	−64.40 ± 1.2	−158.05 ± 2.2

the literature [8]. The values of a^0 for different acids were the same as those used in our earlier paper [6]. At each temperature six to eight solubility measurements for each acid were made with $c_{NaClO_4} = c_{HClO_4}$ in the range 1.0—8.0 × 10^{-2} mole^{-1}, and I between 1.0 and 8.0 × 10^{-2}. The values of pK_a thus obtained are presented in Table 1 for the acids under investigation.

The pK_a values at different temperatures for each acid were fitted to the Harned—Robinson type expression

$$pK_a = A/T + B + CT \tag{4}$$

by the method of least-squares. The values of the constants, A, B, and C, for different acids are given in Table 2. The values obtained using eqn. (4) are reproducible within ±0.008 units of the observed values. The values of the thermodynamic quantities, viz., ΔG^0, ΔH^0, ΔS^0 and ΔC_p^0 for the dissociation of the acids at 25°C were computed from the constants of eqn. (4) and are given in Table 2.

The pK_a values of *ortho*-, *meta*-, and *para*-substituted chloro-, nitro-, hydroxy-, and amino-benzoic acids have earlier been reported in aqueous medium [5] by several workers either at a single temperature, 25°C, or at a number of temperatures by various physical methods. A comparison of the present set of data with the values available in the literature [5], however, shows that the agreement is very satisfactory, so lending support to the reliability of the solubility method for determining the dissociation constants of acids. Similar agreement was also noticed in the pK_a values of salicylic acid obtained from the solubility measurements [4]. With regard to the relative strength of the acids and the effect of substituents [9] reflected in the dissociation constants, the agreement is very satisfactory. The linear relationship between log sK_a and d^{-1} existing in aqueous medium [10] in the case of chloro-benzoic acids, where sK_a is the dissociation constant of three monochloro-benzoic acids, and d is the distance between the polar bond joining the carboxyl group to the benzene ring and the polar bond connecting the substituent to the ring, is also found in the present study and can be expressed as

$$-\log sK_a = -4.1306 + 0.9838/d \tag{5}$$

and the intercept for $d^{-1} \rightarrow 0$ is of the correct magnitude for the unsubstituted acid, i.e., benzoic acid [5,11]. Equation (5) fits the four points [12] to within ±0.08 logarithm units.

The values of ΔG^0, ΔH^0, and ΔS^0 for the dissociation of these substituted acids have earlier been reported in aqueous medium [5], but the ΔC_p^0 values have hitherto not been determined. The ΔG^0, ΔH^0, and ΔS^0 values as obtained in the present study are found to be in reasonably good agreement with the literature values, although in a few cases the absolute magnitudes of the respective quantities are altered to some extent, for obvious reasons [13]. Also, the thermodynamic quantities computed from Hepler's model [14,15], indicate a similar type of behaviour for the substituted benzoic acids in aqueous medium studied in the present work and give extra confidence to the present method of determining the dissociation constants of acids.

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