

Short communication

Pressure dependence of the dissociation of acetic, benzoic, mandelic and succinic acids at 298.15 K

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Abstract

Dissociation constants for acetic, benzoic, mandelic and succinic acids have been measured at 298.15 K as a function of pressure up to 138.8 MPa. The spectrophotometric technique using Bromocresol Green as the optical indicator was employed up to ionic strength of 0.03 mol kg^{-1} in aqueous solution. Thermodynamic dissociation constants were calculated with the Davies activity coefficient equation. The pressure dependences of the ionization constants for the weak acids can be described by the equation of Lown, Thirsk and Wynne-Jones, application of which leads to accurate partial molal volume change on ionization, $\Delta \bar{V}^0$ and compressibility change, $\Delta \bar{\kappa}^0$ at 0.1 MPa.

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1. Introduction

Studies of the dissociation constant as a function of temperature and pressure offer a powerful tool to understand ion–solvent interactions. Useful information can be obtained by analyzing thermodynamics of ionization of weak acids and bases as a function of pressure. Temperature and pressure dependence of ionization of weak acids and bases have been investigated by several workers [1–22]. These workers have mainly employed density, conductance and potentiometric methods to investigate the dissociation behavior of these weak acids and bases. In the present work, we employ the spectrophotometric method to investigate the pressure dependence of dissociation of acetic, benzoic, mandelic and succinic acids.

Determination of $\Delta \bar{V}^0$ and $\Delta \bar{\kappa}^0$ from volumetric data requires highly accurate density, ρ and speed of sound, u -data extending much $<0.5 \text{ mol kg}^{-1}$. The apparent molar volumes and compressibility data are calculated from the expressions in which the concentration term appears in the denominator [2,23]. Thus, a small error in the concentration or ρ or u (u leads to adiabatic compressibility by $\beta = u^2 d^{-1}$) magnifies the errors in the determination of apparent molar properties. When the apparent molar properties are plotted against $M^{1/2}$ (where M is the molar

concentration) or $m^{1/2}$ leads to incorrect values of $\Delta \bar{V}^0$ and $\Delta \bar{\kappa}^0$, if high precision is not maintained during the measurements of mass, density and speed of sound [10,23,24]. For instance, if density of 0.01 mol kg^{-1} solution is measured with an error of 0.001 kg m^{-3} , it causes an error of $\pm 0.1 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ in apparent molar volume. The inaccurate apparent molar volumes when extrapolated as discussed above gives rise to larger errors in the determination of $\Delta \bar{V}^0$. Similarly, an error of 0.5 ms^{-1} in sound speed of 0.01 mol kg^{-1} solution with inaccuracy of 0.001 kg m^{-3} in density causes an error in apparent molar compressibility of $\pm 0.31 \times 10^{-14} \text{ m}^3 \text{ mol}^{-1} \text{ Pa}^{-1}$. This error is further magnified when $\Delta \bar{\kappa}^0$ is obtained by the extrapolation procedure discussed above [10,23,24]. Therefore it is of considerable advantage to determine $\Delta \bar{V}^0$ and $\Delta \bar{\kappa}^0$ values directly from measurements of the effect of pressure on the dissociation constants.

2. Experimental

Acetic, benzoic, mandelic and succinic acids (all from Aldrich) were used without further purification. The exact molality of the acids was determined by weight titration against standard NaOH solution. Anhydrous NaClO_4 (Aldrich) was used to adjust the ionic strength. A 0.04% solution of Bromocresol Green (Eastman Kodak) was prepared by the method of Clark [25]. The test solutions and the standards for the comparison

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possessed equal amount of indicator, in the proportion of 4.0 ml of 0.04% solution in a total volume of 50.0 ml.

Color comparisons were made by means of a Varian Cary 50 spectrophotometer equipped with a detachable high-pressure cell. The high-pressure cell was similar to that used by Mendez De Leo et al. [21]. For Bromosol Green the wavelength of maximum absorbance (λ_{max}) was observed to be 620 nm. The transmittance was measured with an accuracy of 0.2% at 298.15 K, corresponding to an accuracy of ± 0.0025 in $-\log \gamma_2[\text{H}^+]$. The uncertainties in $\text{p}K_1$ and $\text{p}K_2$ were estimated as ± 0.005 and ± 0.05 , respectively. Temperature of the constant temperature water bath (Julabo) was maintained at 298.15 ± 0.02 K.

Calibration curves were constructed to determine the hydrogen-ion concentration of the test solutions. Solutions of known concentration of perchloric acid, containing a fixed amount of indicator and NaClO_4 were neutralized to the desired extent by the addition of NaOH solutions. The acid solutions were neutralized to various stages between 20 and 80% by adding standard NaOH solution. The total ionic strength of these solutions was maintained constant at 0.01 mol kg^{-1} . The $-\log \gamma_2[\text{H}^+]$ values were then determined by comparing them with standard perchloric acid solutions of accurately known $-\log \gamma_2[\text{H}^+]$.

3. Basic equations and calculation procedure

The thermodynamic dissociation constants of monobasic acid, HA and the dibasic acid, H_2A were determined following the method described by Speakman [26] as revised by Jones and Stock [27]. Throughout this work, the concentration terms in square brackets are given on molal basis. The activity coefficients, γ of univalent ions are considered to be equal. The activity coefficient of a divalent ion is represented by γ_2 . When the colors in two solutions are equal, then the quantity $-\log a_{\text{H}^+}$ is equal.

The activity coefficients, γ_1 and γ_2 were calculated with the Davies equation [28] as

$$\log \gamma = -0.5z_i^2 \left\{ \frac{I^{0.5}}{(1 + I^{0.5})} - 0.2I \right\} \quad (1)$$

where z_i is the ionic charge and I , ionic strength on molal basis is given by $I = 0.5 \sum m_i z_i^2$.

4. Results

The thermodynamic dissociation constants for acetic, benzoic, mandelic and succinic acids at 298.15 K as a function of pressure are presented in Table 1. The values of $\text{p}K_1$ and $\text{p}K_2$ at 0.1 MPa agree with the accepted literature values [29–32]. Dissociation constants for weak acids increase with pressure owing to the volume contraction caused by electrostriction.

For the weak acid, HA the partial molal volume change of ionization is defined by

$$\Delta \bar{V}^0 = \bar{V}^0(\text{H}^+) + \bar{V}^0(\text{A}^-) - \bar{V}^0(\text{HA}) \quad (2)$$

where \bar{V}^0 is the partial molal volume at standard state for the hydrated species. The partial molal volume change, $\Delta \bar{V}^0$ for the dissociation process was determined from the isothermal pressure dependence of the equilibrium constant as $(\partial \ln K / \partial P)_T = -\Delta \bar{V}^0 / RT$. The second derivative of the equilibrium constant gives the compressibility change of the ionization as $RT(\partial^2 \ln K / \partial P^2)_T = -(\partial \Delta \bar{V}^0 / \partial P)_T = \Delta \bar{\kappa}^0$. Assuming that $\Delta \bar{\kappa}^0$ is independent of pressure, the following expression can be derived [33]:

$$\frac{RT}{(P - P^0)} \ln \left(\frac{K_P}{K_1} \right) = -\Delta \bar{V}^0 + 0.5 \Delta \bar{\kappa}^0 (P - P^0) \quad (3)$$

where $P^0 = 101.325 \text{ kPa}$. The values of $\Delta \bar{V}^0$ and $\Delta \bar{\kappa}^0$ calculated from Eq. (3) are listed in Table 2. The values of $RT/(P - P^0) \ln(K_P/K_1)$ abbreviated as LHS are plotted against $(P - P^0)$ in Fig. 1. As shown in Table 2, the values of $\Delta \bar{V}^0$ and $\Delta \bar{\kappa}^0$ are in good agreement with those reported in the literature [1,4,8,33].

North [5] modified Eq. (3) to include the hydration effect to take the following form:

$$\frac{RT}{(P - P^0)} \ln \left(\frac{K_P}{K_1} \right) = -\Delta \bar{V}^0 + nA V_W^0 \left(1 - \frac{B + P}{P - P^0} \ln \frac{B + P}{B + P^0} \right) \quad (4)$$

Table 1

The $\text{p}K$ values for acetic, benzoic, mandelic and succinic acids at 298.15 K and pressure up to 138.8 MPa; uncertainties in $\text{p}K_1 = \pm 0.005$ and in $\text{p}K_2 = \pm 0.05$

Acid	P					
	0.1 MPa	25.3 MPa	50.6 MPa	83.1 MPa	111.4 MPa	138.8 MPa
Acetic	4.760 (4.76) ^a	4.652	4.543	4.412	4.304	4.204
Benzoic	4.199 (4.20) ^b	4.089	3.979	3.849	3.743	3.644
Mandelic	3.410 (3.41) ^c	3.290	3.178	3.052	2.929	2.825
Succinic						
$\text{p}K_1$	4.200 (4.21) ^d	4.079	3.979	3.862	3.774	3.704
$\text{p}K_2$	5.68 (5.64) ^d	5.55	5.43	5.29	5.18	5.09

^a Ref. [29].

^b Ref. [30].

^c Ref. [31].

^d Ref. [32].

Table 2

The values of ΔV_1^0 , $\Delta \bar{\kappa}^0$ and n at 298.15 K obtained from the present work and their comparison with the reported values

Acid	ΔV_1^0 ($\times 10^6$ m ³ mol ⁻¹)	$\Delta \bar{\kappa}^0$ ($\times 10^{14}$ m ³ mol ⁻¹ Pa ⁻¹)	n -values ^a
Acetic	-11.11 (-11.28 ^a , -11.2 ^b , -11.5 ^c)	-1.7 (-1.9 ^c)	2.3
Benzoic	-11.33 (-11.53 ^a , -11.7 ^b)	-2.0 (-2.3 ^d , -1.5 ^{e,f})	2.8
Mandelic	-11.61 (-11.65) ^a	-1.6 (-1.7) ^e	2.0
Succinic			
I ionization	-11.98 (-12.12 ^a , -12.86 ^g)	-4.5 (-4.9) ^c	5.9
II ionization	-13.63 (-13.73 ^a , -13.58 ^g)	-4.4 (-4.6) ^c	5.5

^a From Eq. (4), ref. [5].^b Ref. [4] experimental data.^c Ref. [34] experimental data, eq. (5).^d Ref. [35], eq. (5).^e Ref. [33] experimental data, eq. (5).^f Ref. [36].^g Ref. [8].

In the above equation, n is the number of water molecules in the hydration sheath, V_W^0 the molal volume of water. A and B are the pressure independent constants of the Tait equation [37]. If the left-hand side of Eq. (4) is plotted against $AV_W^0(1 - (B+P)/(P-P^0) \ln(B+P)/(B+P^0))$, the resultant plots are linear with intercept and slope giving the values of $\Delta \bar{V}^0$ and n , respectively. The n -values are listed in Table 2. Further, the $\Delta \bar{\kappa}^0$ value can be calculated by means of the relationship

$$\Delta \bar{\kappa}^0 = -\frac{nAV_W^0}{B+P} \quad (5)$$

It may be noted that Eq. (4) was first successfully tested against experimental results extending up to about 1200 MPa [38].

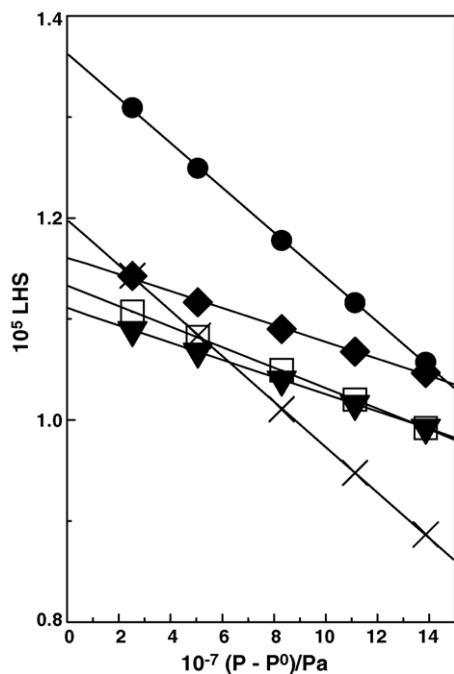


Fig. 1. Plots of LHS defined by $RT/(P - P^0) \ln(K_p/K_1)$ of Eq. (3) vs. $(P - P^0)$; (\blacktriangledown) acetic acid, (\square) benzoic acid, (\blacklozenge) mandelic acid, (\times) succinic acid (I ionization) and (\bullet) succinic acid (II ionization).

Using this equation and the values of n obtained from Eq. (4), we calculated the $\Delta \bar{\kappa}^0$ values. These values are also collected in Table 2. The values of $\Delta \bar{\kappa}^0$ calculated from Eq. (5) are pressure dependent.

5. Discussion

The value of n for acetic acid from this work agrees with that reported by other workers using a similar calculation method [5,7]. Benzoic and mandelic acids, being monobasic acids have approximately the same hydration numbers as acetic acid. The value of n for succinic acid is twice as large. Succinate⁻² ion forms a chelate with the hydrogen ion and is expected to release more water molecules than the monoanions. This is reflected in the magnitude of the entropy change, ΔS for the protonation reactions. The ΔS values on protonation of mandelate and succinate ions have been reported to be 62.7 and 100.3 kJ mol⁻¹, respectively [39].

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