

Apparent Molal Volumes & Compressibilities of Sodium Salts of Some Aromatic Monocarboxylic Acids in Water

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Sound velocities in aqueous solutions of sodium benzoate and sodium phenylacetate and densities of and sound velocities in aqueous solutions of sodium salts of *m*-nitrobenzoic and *m*-toluic acids have been measured at 25°, 35°, 45° and 55°C. From the data the apparent molal volumes (φ_v) and apparent molal adiabatic compressibilities (φ_k) have been obtained. The results indicate that the φ_v versus $m^{1/2}$ and φ_k versus $m^{1/2}$ plots are linear for all the salts in the concentration range studied. The derived limiting apparent molal volumes (φ_v^0) and limiting apparent molal adiabatic compressibilities (φ_k^0) increase with temperature for all the salts in the temperature range studied. An attempt has been made to explain these results in terms of solute-solvent and solute-solute interactions.

Temperature dependence of limiting apparent molal volumes (φ_v^0) of sodium benzoate and sodium phenylacetate has been recently studied by us¹. The limiting apparent molal adiabatic compressibility (φ_k^0) is shown by Kaulgud and Rao² to be a useful parameter in understanding solute-solute and solute-solvent interactions. Høiland *et al.*³ have reported the φ_v^0 and φ_k^0 values of the salts of aliphatic monocarboxylic acids in water at 25°C and laid stress only on the additivity of φ_k^0 . So far, not much attention has been paid to the trends in the $d\varphi_k^0/dT$, (ref. 4).

Methyl and nitro groups have different effects on the π -electron system of benzene ring, and such differences are likely to affect the hydration behaviour of salts of aromatic acids. The title investigation has been undertaken to study the effect of substitution of these two groups in the position *meta* to the carboxylic group on solute-solvent interaction.

Materials and Methods

Sodium salt of phenylacetic acid was prepared and purified as reported earlier¹. Sodium benzoate (AR) was used as such. Both the salts were dried at 110°C and then *in vacuo*.

Sodium salts of *m*-nitrobenzoic acid and *m*-toluic acid were prepared in the laboratory, washed thoroughly with acetone and ether, recrystallized from acetone-water, dried in an oven at 110°C and kept *in vacuo* for several days before use.

All the solutions were prepared by weight using deionised doubly distilled water. Densities of equilibrated (1 hr) aqueous solutions (0.1-0.7 molal) were measured with calibrated Ostwald-Sprengel type pycnometer (70 ml capacity) at the desired temperatures which could be controlled with an accuracy of

$\pm 0.02^\circ\text{C}$. The average uncertainty in the density determination was $\pm 1 \times 10^{-5} \text{ g/cm}^3$.

Sound velocities in solutions were measured at the desired temperatures using an ultrasonic interferometer (Mittal, India, model, M81) at a fixed frequency of 5 MHz. The uncertainty in sound velocity measurement was $\pm 0.5 \text{ ms}^{-1}$. The values of adiabatic compressibility (β_{ad}) were calculated using the Laplace equation.

The apparent molal volumes (φ_v) and apparent molal adiabatic compressibilities (φ_k) of aqueous solutions of salts at various concentrations and temperatures were calculated using Eqs (1) and (2), respectively.

$$\varphi_v = \frac{M}{d} - \frac{1000(d - d_0)}{m dd_0} \quad \dots (1)$$

$$\varphi_k = \frac{1000(\beta - \beta_0)}{m d_0} + \beta \varphi_v \quad \dots (2)$$

where M is the molecular weight of the solute, m is the concentration of the solute in mol kg^{-1} ; d and d_0 are the densities and β and β_0 represent the adiabatic compressibilities of solutions and pure water respectively.

Limiting apparent molal volumes (φ_v^0) and limiting apparent molal adiabatic compressibilities (φ_k^0) were obtained by extrapolating the plots of φ_v and φ_k versus the square root of molal concentration of the solutes to zero concentration.

Results and Discussion

The $\varphi_v^0 (= \bar{V}_2^0)$ of the sodium salts of benzoic, phenylacetic, *m*-toluic and *m*-nitrobenzoic acids at different temperatures are given in Table 1. The φ_k^0

Table 1—Limiting Apparent Molal Volumes of Sodium Benzoate, Sodium Phenylacetate and Sodium Salts of *m*-Nitrobenzoic and *m*-Toluic Acids in Water at Different Temperatures

Salt	φ_v^0 (ml mol ⁻¹) at			
	25°	35°	45°	55°
C ₆ H ₅ COONa (0.1-0.7 <i>m</i>)	85.96 ^a (1.66) ^b	87.32 ^a (1.60)	88.07 ^a (1.53)	88.55 ^a (1.41)
C ₆ H ₅ CH ₂ COONa (0.1-0.7 <i>m</i>)	101.01 ^a (3.29)	103.31 ^a (2.43)	105.22 ^a (1.94)	106.25 ^a (1.36)
C ₆ H ₄ (<i>m</i> -CH ₃)COONa (0.1-0.6 <i>m</i>)	103.96 (1.92)	105.76 (1.65)	107.18 (1.33)	108.36 (1.17)
C ₆ H ₄ (<i>m</i> -NO ₂)COONa (0.1-0.6 <i>m</i>)	107.48 (2.95)	110.41 (2.33)	112.25 (1.82)	113.50 (1.66)

(a) From ref. 1; (b) values within parentheses represent the experimental limiting slopes (*S_v*)

Table 2—Limiting Apparent Molal Adiabatic Compressibilities of Sodium Benzoate and Sodium Salts of Phenylacetic, *m*-Nitrobenzoic & *m*-Toluic Acids in Water at Different Temperatures

Salt	$\varphi_k^0 \times 10^4$ (ml mol ⁻¹ bar ⁻¹) at			
	25°	35°	45°	55°
C ₆ H ₅ COONa (0.1-0.7 <i>m</i>)	-65.55 (20.22)*	-51.79 (15.59)	-42.88 (11.52)	-33.33 (6.57)
C ₆ H ₅ CH ₂ COONa (0.1-0.7 <i>m</i>)	-66.95 (22.11)	-53.57 (15.33)	-44.70 (12.77)	-35.58 (7.90)
C ₆ H ₄ (<i>m</i> -CH ₃)COONa (0.1-0.6 <i>m</i>)	-72.71 (35.99)	-57.77 (28.85)	-47.48 (23.35)	-36.07 (18.30)
C ₆ H ₄ (<i>m</i> -NO ₂)COONa (0.1-0.6 <i>m</i>)	-62.60 (30.41)	-49.34 (26.02)	-40.91 (24.78)	-31.60 (20.77)

*Values within parentheses represent the experimental limiting slopes (*S_k*).

values of these salts at different temperatures are given in Table 2. The effects of substituting the H-atom in the phenyl ring of benzoic acid at the *m*-position by -CH₃ group on the φ_v^0 and φ_k^0 are given by φ_v^0 (*m*-toluic acid sodium salt) - φ_v^0 (benzoic acid sodium salt) and φ_k^0 (*m*-toluic acid sodium salt) - φ_k^0 (benzoic acid sodium salt), respectively. These contributions at 25°, 35°, 45° and 55° are: to φ_v^0 (in ml mol⁻¹), 18.0, 18.44, 19.11 and 19.81; and to φ_k^0 (in ml mol⁻¹ bar⁻¹ × 10⁴), -7.16, -5.98, -4.60 and -2.75 respectively. The corresponding effects of the -NO₂ group are given by φ_v^0 (*m*-nitrobenzoic acid sodium salt) - φ_v^0 (benzoic acid sodium salt) and φ_k^0 (*m*-nitrobenzoic acid sodium salt) - φ_k^0 (benzoic acid sodium salt) respectively. These contributions at 25°, 35°, 45° and 55° are: to φ_v^0 (in

ml mol⁻¹) 21.52, 23.09, 24.18 and 24.95; and to φ_k^0 (in ml mol⁻¹ bar⁻¹ × 10⁴), 2.95, 2.45, 1.97 and 1.73 respectively. Similar contributions of -CH₂ group to φ_k^0 in going from sodium benzoate to sodium phenylacetate at 25°, 35°, 45° and 55° are -1.40, -1.78, -1.82 and -2.25 (ml mol⁻¹ bar⁻¹ × 10⁴) respectively. The φ_v^0 values (Table 1) at any given temperature increase in the order; sodium benzoate < sodium phenylacetate < sodium salt of *m*-toluic acid < sodium salt of *m*-nitrobenzoic acid. The trend in the variation of φ_v^0 is expected, since between benzoate and phenylacetate, the extra -CH₂- group in phenylacetate ensures extra hydrophobic hydration. In the sodium salt of *m*-toluic acid the -CH₃ group being in the *meta*-position, is three bonds away from the -COO⁻ group and thus can cause greater hydration (hydration of the second kind or hydrophobic hydration).

The -NO₂ group can form hydrogen bonds with water molecules due to its polar nature. Moreover the size of -NO₂ group (intrinsic volume), is larger than that of -CH₃ group. This is possibly why the φ_v^0 of *m*-nitrobenzoate is higher than that of *m*-toluate.

The adiabatic compressibilities of all the salts are negative as expected. Among benzoate, phenylacetate and *m*-toluate the degree of hydrophobic hydration would increase in this order and this kind of structure being less compressible^{5,6}, the apparent compressibility is more negative in this order. In the case of *m*-nitrobenzoate, the apparent compressibility is even less negative as compared to that of benzoate. This hydrophilic interaction of the nitro group with water would produce more compressible structural aggregates. From the φ_v^0 values (Table 1) the *m*-nitrobenzoate anion appears to be more hydrated than the *m*-methylbenzoate anion; this trend, however, is not corroborated by their hydration numbers⁸.

That the nature of hydration in the presence of nitro and methyl groups is different is apparent from the contributions to φ_k^0 values by the substitutions H → CH₃ and H → NO₂; being negative for the former and positive for the latter. This shows that hydrophobic hydration in the -CH₃ group is less compressible than hydrophilic hydration in the -NO₂ group. The methyl group is electron repelling whereas the nitro group is electron withdrawing. Thus they will affect the electron density of the benzene ring differently and their hydration will therefore be different.

The rate of increase in the φ_v^0 values with increase in temperature is more rapid in the present set of solutes (Fig. 1) than that for sodium salts of aliphatic acids^{1,7}. This may be due to differences (i) in the nature of the solutes and (ii) in the steric compatibility of the two sets of solutes with bulk water structure⁹. Different

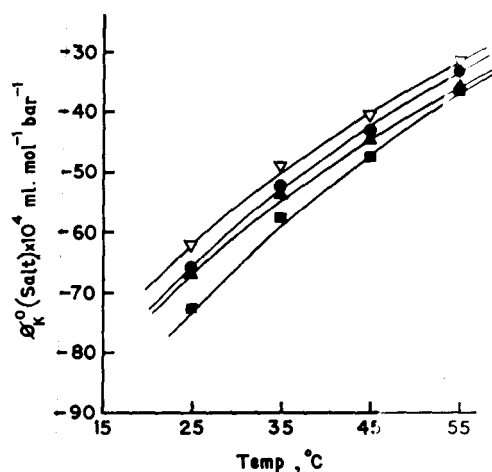


Fig. 1—Plots of limiting apparent molal volumes (ϕ_k^0) against temperature for sodium salts of aromatic monocarboxylic acids [Sodium benzoate (●—●); sodium phenylacetate (▲—▲); sodium salt of *m*-toluic acid (■—■); and sodium salt of *m*-nitrobenzoic acid (▽—▽)]

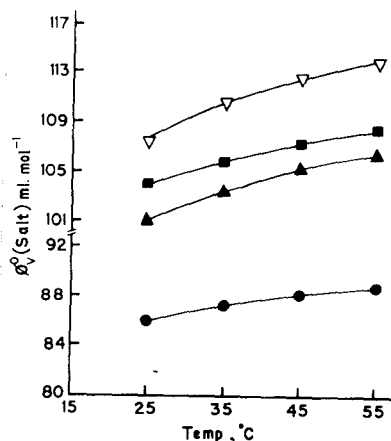


Fig. 2—Plots of limiting apparent molal adiabatic compressibilities (ϕ_V^0) against temperature for sodium salts of aromatic monocarboxylic acids [Symbols used correspond to the salts in Fig. 1]

hydration behaviour of compounds containing phenyl rings have also been suggested by French and Criss¹⁰.

The high values of limiting slopes (S_v and S_k) of the plots of ϕ_v versus $m^{1/2}$ and ϕ_k versus $m^{1/2}$ (Tables 1 and

2) indicate the existence of solute-solute interactions as envisaged by Gurney-cosphere model¹¹. This is expected because of the greater size of the anions (the cation is common) and also due to the fact that the solutions used are comparatively concentrated (0.1–0.7 molal)¹². (Even though we have used relatively concentrated solutions, our ϕ_v^0 and ϕ_k^0 values are fairly good and are comparable to literature data within the experimental errors^{1,8}). The trend in variation in the numerical values of S_v and S_k for this series of 1-1 electrolytes is in accordance with the variation in the size of the anion^{12b}.

The $-\text{CH}_2-$ group contributions to the ϕ_k^0 values at different temperatures are small but show a decreasing tendency with increase in temperature. At this stage it is difficult to suggest any explanation for this apparent trend. Further work in this direction is in progress in our laboratory.

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