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 (φv) and apparent molal adiabatic compressibilities (φk) have been obtained. The results indicate that the φv versus m1/2 and φk versus m1/2 plots are linear for all the salts in the concentration range studied. The derived limiting apparent molal volumes (φvl) and limiting apparent molal adiabatic compressibilities (φkL) 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.

Results and Discussion

The φv(= V/l) of the sodium salts of benzoic, phenylacetic, m-toluic and m-nitrobenzoic acids at different temperatures are given in Table 1. The φv

Materials and Methods

Sodium salt of phenylacetic acid was prepared and purified as reported earlier. 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 ± 0.02°C. The average uncertainty in the density determination was ± 1 x 10^-5 g/cm^3.

Sound velocities in solutions were measured at the desired temperatures using an ultrasonic interferometer (Mittal, India, model, M 81) at a fixed frequency of 5 MHz. The uncertainty in sound velocity measurement was ± 0.5 ms^-1. The values of adiabatic compressibility (βo) were calculated using the Laplace equation.

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

φv = M/d - 1000 (d - d0) / m dd0

φk = 1000 (β - β0) / m d0 + βφv

where M is the molecular weight of the solute, m is the concentration of the solute in mol kg^-1; d and d0 are the densities and β and β0 represent the adiabatic compressibilities of solutions and pure water respectively.

Limiting apparent molal volumes (φvL) and limiting apparent molal adiabatic compressibilities (φkL) were obtained by extrapolating the plots of φv and φk versus the square root of molal concentration of the solutes to zero concentration.

Results and Discussion

The φvL of the sodium salts of benzoic, phenylacetic, m-toluic and m-nitrobenzoic acids at different temperatures are given in Table 1. The φkL
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 \(-\text{CH}_3\) group on the \(\varphi^0\) and \(\varphi^o\) are given by \(\varphi^0\) (m-toluic acid sodium salt) – \(\varphi^0\) (benzoic acid sodium salt) and \(\varphi^o\) (m-toluic acid sodium salt) – \(\varphi^o\) (benzoic acid sodium salt), respectively. These contributions at 25°, 35°, 45° and 55° are: to \(\varphi^0\) (in ml mol\(^{-1}\)), 18.0, 18.44, 19.11 and 19.81; and to \(\varphi^o\) (in ml mol\(^{-1}\) bar\(^{-1}\) × 10\(^4\)), –7.16, –5.98, –4.60 and –2.75 respectively. The corresponding effects of the \(-\text{NO}_2\) group are given by \(\varphi^0\) (m-nitrobenzoic acid sodium salt) – \(\varphi^o\) (benzoic acid sodium salt) and \(\varphi^o\) (m-nitrobenzoic acid sodium salt) – \(\varphi^o\) (benzoic acid sodium salt), respectively. These contributions at 25°, 35°, 45° and 55° are: to \(\varphi^0\) (in ml mol\(^{-1}\)), 21.52, 23.09, 24.18 and 24.95; and to \(\varphi^o\) (in ml mol\(^{-1}\) bar\(^{-1}\) × 10\(^4\)) 2.95, 2.45, 1.97 and 1.73 respectively. Similar contributions of \(-\text{CH}_3\) group to \(\varphi^0\) 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\(^{-1}\) × 10\(^4\)) respectively. The \(\varphi^0\) 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 \(\varphi^0\) is expected, since between benzoate and phenylacetate, the extra \(-\text{CH}_2–\) group in phenylacetate ensures extra hydrophobic hydration. In the sodium salt of m-toluic acid the \(-\text{CH}_3\) group being in the meta-position, is three bonds away from the \(-\text{COO}^-\) group and thus can cause greater hydration (hydration of the second kind or hydrophobic hydration).

The \(-\text{NO}_2\) group can form hydrogen bonds with water molecules due to its polar nature. Moreover the size of \(-\text{NO}_2\) group (intrinsic volume), is larger than that of \(-\text{CH}_3\) group. This is possibly why the \(\varphi^0\) of m-nitrobenzoate is higher than that of m-toluote.

The adiabatic compressibilities of all the salts are negative as expected. Among benzoate, phenylacetate and m-toluic 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 \(\varphi^0\) 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 numbers\(^8\).

That the nature of hydration in the presence of nitro and methyl groups is different is apparent from the contributions to \(\varphi^0\) values by the substitutions H →\(\text{CH}_3\) and H →\(\text{NO}_2\), being negative for the former and positive for the latter. This shows that hydrophobic hydration in the \(-\text{CH}_3\) group is less compressible than hydrophilic hydration in the \(-\text{NO}_2\) 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 \(\varphi^0\) 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 structure\(^8\).
Fig. 1—Plots of limiting apparent molal volumes ($\tilde{\psi}_o^0$) 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 (V—V)].

Fig. 2—Plots of limiting apparent molal adiabatic compressibilities ($\tilde{\gamma}_{ad}^0$) against temperature for sodium salts of aromatic monocarboxylic acids [Symbols used correspond to the salts in Fig. 1].

The high values of limiting slopes ($S_e$ and $S_Q$) of the plots of $\tilde{\gamma}_{ad}^0$ versus $m^{1/2}$ and $\tilde{\psi}_o^0$ versus $m^{1/2}$ (Tables I and II) indicate the existence of solute-solute interactions as envisaged by Gurney's sphere model. 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). (Even though we have used relatively concentrated solutions, our $\tilde{\psi}_o^0$ and $\tilde{\gamma}_{ad}^0$ values are fairly good and are comparable to literature data within the experimental errors.) The trend in variation in the numerical values of $S_e$ and $S_Q$ for this series of 1:1 electrolytes is in accordance with the variation in the size of the anion.

The $-\text{CH}_2-$ group contributions to the $\tilde{\psi}_o^0$ 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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References
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