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Apparent Molal Volumes of Urea and Its Derivatives in Aqueous Alkali Chloride Solutions

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The apparent molal volumes (ϕ_v) at 25 °C have been measured for the following urea derivatives in aqueous alkali chloride solutions (from density measurements) using a digital densimeter: urea, methylurea, ethylurea, 1,1-dimethylurea, 1,3-dimethylurea, 1,1-diethylurea, and 1,3-diethylurea. The limiting values (ϕ_v°) were obtained by a linear extrapolation using the least-squares method. A notable feature of the transfer volumes found in this study was that hydrophobic urea derivatives, such as dimethylureas and diethylureas, had negative values for transfer from water to lithium chloride solutions. For the remainder, however, all transfer volumes were positive.

In a previous paper,[1] we reported on the apparent molal volumes of urea derivatives measured in several water–methanol mixtures. Due to abnormalities of the water–methanol mixtures regarding their properties, such as viscosity–composition and ultrasonic velocity–composition relationships, each plot of ϕ_v° vs. X_2, mole fraction of methanol, showed a minimum at a lower methanol concentration where the solvent is more structured than the water itself, except for unsubstituted urea which had no minimum.

The volumes of transfer from water to a more structured solvent for the more hydrophobic urea were more negative. On the other hand, the reverse order was observed for those from water to methanol, a less structured solvent than water.

Though the properties of the lithium ion are somewhat different from those of the other alkali ions, volume data measured in aqueous lithium salt solutions have been rather few. We have felt that it would be very interesting to know, particularly, the interactions between lithium ions and a hydrophobic solute. We thus determined the apparent molal volumes of urea and its derivatives in an H_2O–MCl mixed solvent (M=Li, Na, and K) from density measurements. Since the limiting values (ϕ_v°) are determined mainly by the respective intrinsic volume of the solute and the solute–solvent interactions, they can provide useful clues regarding solute–solvent interactions. In the present work the densities were measured at 25 °C for the urea (alkylurea)–alkali chloride–water ternary system at various concentrations. The alkali chloride was thought of as being a co-solvent; in other words, an aqueous alkali chloride solution was considered to be a "solvent". We used 0.5, 1, and 2 molal solutions for each of three chlorides as solvents in this study. For the 1 and 2 molal solutions, the adiabatic compressibilities of the "solvent" were determined in order to find the relationship between the adiabatic compressibility of the "solvent" and the apparent molal volume of the urea obtained in it.

Experimental

The alkali chlorides used in this study were of guaranteed reagent grade from Wako Chemical Industries, Ltd., and were used without any further purification, except for lithium chloride which was used after drying for several hours at ca. 150 °C. As for urea and its alkyl derivatives, the same reagents were employed as in the previous study, some of them being recrystallized from a suitable solvent.[1]

All urea derivative solutions were prepared by weight in the concentration range 0.1—1.0 mol kg^{-1} (the number of moles of urea derivative per kg of the mixed solvent whenever the mixed solvents were used), except for the more hydrophobic urea derivatives; these urea derivatives measurements were carried out below 0.5 mol kg^{-1}, as mentioned below. The density and ultrasonic velocity measurements have been described previously.[2] The temperature control of the thermostated bath system for the densimeter was better than ±0.005 °C

Results

The apparent molal volumes of the urea derivatives were obtained by using

$$\phi_v=\frac{M}{d}+\frac{1000\,(d_0-d)}{md_0\,d}, \tag{1}$$

where M is the molecular weight of the urea; m, its molal concentration; and d_0 and d, the densities of the solvent and the solution, respectively. The data were fitted to the equation

$$\phi_v=\phi_v^\circ+S_v m, \tag{2}$$

where ϕ_v° is the infinite-dilution apparent molal volume and S_v is the experimental slope. Although the apparent molal volumes of nonelectrolytes in dilute solutions, below 1.0 mol kg^{-1} are commonly expressed as in Eq. 2, those for the more hydrophobic urea derivatives studied in alkali chloride solutions deviate from Eq. 2, even at such low concentrations as ca. 0.5 mol kg^{-1}. The limiting apparent molal volumes of 1,3-dimethylurea (1,3-DMU) and 1,3-diethylurea (1,3-DEU) were thus calculated using data for a concentration range of ca. 0.1—0.5 mol kg^{-1}. This is discussed later.

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Table 1. Limiting Apparent Molal Volumes in Aqueous Alkali Chloride Solutions

Solvent		ϕ_v° / $cm^3\,mol^{-1}$					
	U	UM	1,1-DMU	1,3-DMU	EU	1,1-DEU	1,3-DEU
H_2O	44.24	62.40	78.53	80.32	79.26	111.63	113.74
0.5m LiCl	44.52	62.46	78.55	80.27	79.29	111.92	113.66
1.0m LiCl	44.80	62.63	78.46	80.16	79.36	111.67	113.47
2.0m LiCl	45.14	62.64	78.45	80.00	79.28	111.19	112.96
0.5m NaCl	44.63	62.62	78.83	80.45	79.52	112.09	113.86
1.0m NaCl	45.08	62.90	78.86	80.59	79.80	112.31	114.02
2.0m NaCl	45.44	63.10	79.08	80.75	80.06	112.47	114.13
0.5m KCl	44.63	62.59	78.77	80.43	79.52	112.16	113.95
1.0m KCl	45.00	62.93	78.91	80.55	79.79	112.54	114.08
2.0m KCl	45.37	63.13	79.16	80.72	80.00	112.64	114.17

Table 2. Adiabatic Compressibilities of Aqueous Alkali Halide Solutions

Solution	β_s / $10^{-4}\times bar^{-1}$
H_2O	4.477
1m LiCl	4.075
2m LiCl	3.750
1m NaCl	3.979
2m NaCl	3.588
1m KCl	4.015
2m KCl	3.660

Table 1 shows the limiting values (ϕ_v°) caluculated by a linear extrapolation (Eq. 2) using the least-squares method. In this Table, U, MU, 1,1-DMU, EU, 1,1-DEU denote urea, methylurea, 1,1-dimethylurea, ethylurea, and 1,1-diethylurea, respectively. In aqueous sodium and potassium chloride solutions the values of ϕ_v° of all urea and its derivatives studied here are larger than those measured in pure water, as can be seen from Table 1. On the other hand, in aqueous lithium chloride solutions some urea derivatives have negative transfer volumes. These are well known to be hydrophobic in nature.

The adiabatic compressibilities, β_S (bar^{-1}), of the "solvent" were calculated in order to determine the correlation with ϕ_v° using Eq. 3, where u is the velocity of sound ($m\,s^{-1}$) in the solvent. The density is expressed in $g\,cm^{-3}$.

$$\beta_s = \frac{1000}{d_0\, u^2}. \qquad (3)$$

The obtained values are given in Table 2; this subject will be further discussed later.

Discussion

The transfer volumes for the studied urea derivatives show that they increase in the following order:

$$Li^+ < K^+ \approx Na^+.$$

Until now, we have reported the transfer volumes of some amino acids[3] and polyalcohols[4] from water to aqueous alkali chloride solutions. The order of increasing transfer volume for these solutes was

$$Li^+ < K^+ < Na^+.$$

In the case of urea derivatives, there are no strong interactions, such as in the case of amino acids, with both the cations and anions in a mixed solvent; the absolute magnitudes of the transfer volumes are thus very small compared with those for amino acids. The lithium ion has the smallest value in each sequence; the sequence for the amino acids has been discussed by us previously.[3] While all transfer volumes were positive regarding hydrophilic solutes, such as amino acids and polyalcohols, those of the more hydrophobic urea derivatives to aqueous LiCl solutions have a negative sign.

The apparent molal volumes of tetrabuthylammonium bromide have been measured by Desrosiers and Desnoyers in aqueous solutions of NaF, NaCl, NaAc, and NH_4Ac at 25 °C[5]. Since Bu_4NBr is dilute, but not the added electrolyte, they corrected the volume data for long-range coulombic forces in order to obtain more specific noncoulombic interactions between the solute and the mixed solvent. The observed transfer volumes from water to the electrolyte solutions, corrected for the Debye–Hückel interactions, were all negative at low concentrations. The same had been observed for the sign of the transfer volume of hydrophobic nonelectrolytes, such as argon and methane,[6] from water to aqueous electrolyte solutions. They thus concluded that the noncoulombic interactions between hydrophobic and hydrophilic ions resulted in negative contributions to the volumes. In this study, since the urea derivatives were used as solute nonelectrolytes, no long-range coulombic interactions existed between the solute and alkali chloride in the "solvent"; thus, no corrections for the Debye–Hückel interactions were necessary. As mentioned above, the more hydrophobic urea derivatives have negative transfer volumes only from water to an aqueous LiCl solution; this is in contrast to the most hydrophobic solutes, for example Bu_4NBr and argon, which have negative transfer volumes from water to aqueous NaCl and KCl solutions. Thus, the transfer volumes from water to electrolyte solutions corrected for the Debye–Hückel interactions may be used as a measure of the hydrophobicity of the solute.

The reason for the deviation in the ϕ_v data for 1,3-DMU and 1,3-DEU from Eq. 2 at low concentrations, (mentioned above) may be explained by the hydrophobicity of these solutes. In an aqueous alkali chloride solution a considerable number of water molecules are firmly combined to the alkali cations and chloride anions, so that it is likely that the concentration of the solute urea derivative virtually increases and an interaction between them (the so-called hydrophobic interaction) may result at an appreciably low solute concentration. As a result, Eq. 2 can be fitted to the data only below ca. 0.5 mol kg^{-1}. In this connection, it was reported by Wen and Saito that plots of ϕ_v *vs.* *c* for hydrophobic solutes, such as tetrapropylammonium and tetrabutylammonium bromides, go through a minimum at around 1 mol kg^{-1} at 15, 25, and 35 °C and then turn upward.[7)] They considered this phenomenon to be related to a strong structural influence of large tetraalkylammonium salts upon water, and described by the "formation of a clathrate-like structure". Further, the such terms as the iceberg effect,[8)] increase of ice-likeness,[9)] and tightening of hydrogen bonds of water molecules[10)] have been used to describe the structural influence.

The apparent molal volumes of urea were determined in several nonaqueous solvents as functions of the temperature by Hamilton and Stokes.[11)]. They pointed out that one noteworthy feature was the large variation in the limiting apparent molal volumes with a solvent, from 37 $cm^3 mol^{-1}$ in methanol to 45 $cm^3 mol^{-1}$ in formamide, the latter figure being close to the molar volume of solid urea. They found that of such properties as the cohesive energy density, the dielectric constant, the molar volume and the compressibility of the solvent, which might be expected to bear some relation to ϕ_v° the last one had the only clear correlation: ϕ_v° increases as the compressibility of the solvent decreases. Since the compressibility may be regarded as being a measure of the void space in the liquid, they argued that this means that the solute molecule does not have to create a hole for itself that has the full dimentions demanded by its intrinsic size. In this connection it may be interesting to see the relation between the compressibility coefficient of the solvent shown in Table 2 and ϕ_v° of urea measured in it. In this type aqueous electrolyte "solvent", the same rule mentioned by Hamilton and Stokes has held well; ϕ_v° increases as the compressibility of the solvent decreases. This, however, does not apply to such large and hydrophobic urea derivatives as 1,3-DMU and 1,3-DEU.

As reported by us, the assumption regarding the independent solvation of both sides of the urea derivatives produced a good approximation of the molal volumes in water–methanol mixtures in the same way as in pure water and methanol.[1)] An inspection of Table 1 shows that this assumption also holds to a good approximation to the apparent molal volumes in aqueous alkali chloride solutions.

In conclusion, the lithium ion shows a special behavior towards a hydrophobic solute. In order to clarify this, however, more data, especially for hydrophobic solutes in aqueous lithium salt solutions, are necessary.

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