Ultrasonic, viscometric and volumetric studies of some bioapplicable systems involving ZnCl$_2$, dextrose and methionine in water

A P Mishra
Inorganic Research Laboratories, Department of Chemistry, Dr. H.S. Gour University, Sagar (M.P.) 470 003
E-mail: apm19@rediffmail.com/panandma@sancharnet.in

Received 25 July 2002; revised 3 December 2003

Ultrasonic velocity, density, refractive index and viscosity of dextrose + methionine, ZnCl$_2$ + dextrose, ZnCl$_2$ + methionine and ZnCl$_2$ + methionine + dextrose in water have been determined. From these measured values, the apparent molar volume ($\phi_v$), partial molar volume ($\phi_v^0$), experimental slope ($S_v$), adiabatic compressibility ($\bar{B}_s$), apparent molar compressibility ($\phi_c$), viscosity coefficients $A$ and $B$ of Jones-Dole equation, have been calculated at 298.15 K. The observed and calculated values have been used to explain molecular association, ion-solvent and hydrogen bonding interaction. The above study may be helpful in understanding the dynamics between metal ions and biomolecules.

Materials and Methods
All chemicals used were of BDH and AR grade. The used distilled water had a specific conductivity of about $1 \times 10^{-6}$ $\Omega$cm$^{-1}$. Stock solutions of dextrose, methionine and ZnCl$_2$ (0.1 M) were prepared. The dilution method was used to get lower concentrations. Ultrasonic velocity (2 MHz) was measured by single crystal path interferometer with an accuracy of 0.03%.

Viscosity and density measurements were carried out at 298.15 K. The methodology has been described elsewhere. The viscosity and density data were found to be accurate within ± 0.02% respectively.

The apparent molar volume has been calculated from the density values using Eq. (1).

$$\phi_v = \frac{M}{d_0} + \frac{1000(d - d_0)}{Cd_0}$$  \hspace{1cm} (1)

where $d_0$, $d$ are the densities of solvent and solution respectively, $C$ is the molar concentration of solution and $M$ represents the molecular weight of the solute.

The experimental data were analysed in the light of Masson's$^9$ equation

$$\phi_v = \phi_v^0 + S_vC^{1/2}$$  \hspace{1cm} (2)
where $S_\nu$ is the experimental slope and $\phi_v^0$ the partial molar volume at infinite dilution.

The molar refraction of the solution was obtained from Eq. (3)

$$R_m = \frac{n_{soln}^2 - 1}{n_{soln}^2 + 2} \frac{M_{soln}}{d_{soln}} \quad \ldots \ (3)$$

where $M_{soln}$ is equal to $M_1X_1 + M_2X_2$. $M_1$ and $M_2$ are molar masses of solvent and solute, $X_1$ and $X_2$ being their respective mole fractions.

The molar refraction for the ideal binary solutions were deduced from the relation

$$R_{m12} = R_{m1}X_1 + R_{m2}X_2 \quad \ldots \ (4)$$

where $R_{m1}$ and $R_{m2}$ are the molar refractions of the pure solvent and solute, and $\Delta R_m$ is the change in molar refraction given by

$$\Delta R_m = R_{m(real)} - R_{m(idl)} \quad \ldots \ (5)$$

Adiabatic compressibility has been obtained from the relation

$$\beta_s = \left(\frac{U^2}{d}\right)^{-1} \quad \ldots \ (6)$$

Apparent molar compressibility is computed from the relation

$$\phi_k = \frac{1000}{C \cdot d} \left(\beta_s - \beta_0\right) + \beta_s \phi_v \quad \ldots \ (7)$$

where $\beta_s$ and $\beta_0$ are compressibility of the solution and solvent respectively, $C$ is the molar concentration and $d$ the density.

The viscosity data were analysed in the light of Jones-Dole equation:

$$\left(\frac{\eta}{\eta_0} - 1\right) = A + BC^{1/2} \quad \ldots \ (8)$$

where $A$ and $B$ are the viscosity coefficients characteristic of solute-solute and solute-solvent interactions respectively.

Results and Discussion

Experimental and calculated values of ultrasonic velocity, density, viscosity, adiabatic compressibility, apparent molar compressibility, apparent molar volume, partial molar volume, experimental slope and viscosity coefficients for ZnCl$_2$ + methionine, ZnCl$_2$ + dextrose and ZnCl$_2$ + dextrose + methionine are presented in Tables 1 and 2.

In the present studies, the hydration co-sphere i.e. the region occupied by water, is significantly affected by the presence of solute molecules viz. dextrose, methionine and zinc chloride. When the co-sphere of both of these molecules zinc chloride and dextrose/methionine overlap/interact due to their proximity caused by van der waals, hydrogen bonding or electrostatic interactions, some of the co-spherical molecular structures are displaced/distorted or disrupted, causing changes in parameters. When dextrose or methionine is dissolved in water, the solvent restructures or rearranges under the effect of solute i.e. dextrose and methionine. Similarly, on addition of zinc chloride solution to this solution, existing structure of dextrose + water, methionine + water also changes and get re-structured in the light of new solute; this is further reflected from the experimental data.

Zinc chloride + dextrose system

Apparent molar volume ($\phi_v$) values decrease with increase in concentration of zinc chloride. The interaction of carbonyl and hydroxyl groups of dextrose with zinc ions may be the reason for decrease in ($\phi_v$) values.

Viscosity B-coefficient (solute-solvent interaction) deduced from Jones-Dole equation has positive value for this system. This indicates a strong alignment among the molecules/ions of dextrose and zinc chloride with water. Viscosity A-coefficient (solute-solute interaction) is negative in this system. It is of less significance here i.e. interactions between ions/molecules of ZnCl$_2$-ZnCl$_2$ and dextrose-dextrose are weak.

Adiabatic compressibility ($\beta_s$) decreases with increase in concentration of ZnCl$_2$ in ZnCl$_2$+dextrose system. This may be attributed to a relatively closer packing of the components. For ZnCl$_2$+dextrose system the apparent molar isentropic compressibility has been found to decrease with increase in the concentration of ZnCl$_2$.

ZnCl$_2$ + methionine system

The values of apparent molar volume ($\phi_v$) decrease with increase in the concentration of zinc chloride. This indicates the stronger stacking interaction among
the molecules of solutes and solvent on adding zinc chloride.

Isentropic compressibility ($\beta_s$) value decreases with increase in the concentration of zinc chloride. This may also be attributed to the cohesion brought about by ionic hydration. Amino acids in water behave as zwitter ions having $\text{NH}_3^+$ and $\text{COO}^-$ groups. The water molecules are attached to the ions strongly by the electrostatic forces, which introduce a greater cohesion in solution. The increased association observed in these solutions, may also be due to increase in electrostriction effect. Another reason for decreasing compressibility with increasing concentration of zinc chloride, is strong interaction of $\text{ZnCl}_2$ with $\text{NH}_3^+$ and $\text{COO}^-$ groups of methionine. As per HSAB theory C-S group interaction should be weak with zinc ion.

The value of B-coefficient is positive and relatively higher for this system. This indicates the more ordered and favourable state of solution structure on adding the solute i.e. it disrupts the existing solvent structure and forms a new and thermodynamically more feasible arrangement. Viscosity A-coefficient value is negative indicating that the interaction between $\text{ZnCl}_2$-$\text{ZnCl}_2$ and methionine-methionine are weak.

**ZnCl$_2$+methionine + dextrose**

On mixing the $\text{ZnCl}_2$ solution to methionine + dextrose solution at various concentrations, the
apparent molar volume and compressibility increase. This indicates about the resultant interaction of ZnCl₂ with dextrose + methionine.

The values of (θ₂) are positive and small for ternary mixture containing zinc chloride, methionine and dextrose as compared to methionine + dextrose solution. This may be attributed to the decrease in electrostatic attraction between the molecules of dextrose and methionine on adding zinc chloride to it i.e. this salt does not contribute to the strengthening of interactions between methionine and dextrose.

Isentropic compressibility is higher for ternary system than the binary methionine + dextrose system. This may be attributed to the effect of electrolyte.

The value of A-coefficient is positive, while value of B-coefficient is lower in comparison to the value of methionine and dextrose. This may be attributed to the decrease in dextrose and methionine on adding zinc chloride to it. Here, zinc chloride acts as structure breaker.

The viscosity values decrease with increase in concentration of methionine and these values are small as compared to methionine + dextrose system. This effect may be interpreted in the light of following reasons: (i) The solute zinc chloride may have striking effect on the stacking interactions of methionine and dextrose molecules, (ii) H-bonding between methionine and dextrose are affected by zinc chloride; and (iii) cohesive forces among the molecules of solute and solvent result in a change in viscosity.

The values of molar refraction ΔRm of the binary solution of ZnCl₂ + methionine, ZnCl₂ + dextrose and methionine + dextrose indicate the extent of interaction among these chemical species.

The negative (θ₂) values in all the studied systems can be interpreted in terms of decrease in bulk of solvated molecular structure. The possible effects which a solute can exert on the solvent structure, and its role on solvent structure and molecular arrangement may be explained as follows:

(i) The solvated Zn²⁺ ions species have been believed to have comparatively smaller intermolecular free space, which is quite less to have any significant intrinsic compressibility; and
(ii) another cause may lie in penetration of the solvent molecules into the molecular free space. This electrostriction effect causes a decrease in the solution volume; thus resulting in a more compact and less compressible medium.

The values of partial molar volume (solute-solvent interaction) are higher for ZnCl₂ + methionine system in comparison to ZnCl₂ + dextrose, methionine + dextrose, ZnCl₂ + methionine + dextrose. This indicates the favourable interaction of ZnCl₂ salt, which may be accounted to comparatively smaller size of Zn²⁺ ions and fully filled d orbital (d¹⁰) system enabling the ion to penetrate easily into the molecular free space. The value of experimental slope S_v (solute-solute interaction) reflects that the solute-solute interaction is weak in all the systems.

On comparing all the systems, it has been found that the viscosity B-coefficients (solute-solvent interactions) are in order: ZnCl₂ + methionine > ZnCl₂ + dextrose > methionine + dextrose > ZnCl₂ + methionine + dextrose. On the other hand, the values of A-coefficient (solute-solute/ion-ion interaction) decreases in the order: ZnCl₂ + methionine + dextrose > methionine + dextrose > ZnCl₂ + dextrose > ZnCl₂ + methionine.

The above studies involving the interaction of metal ion, carbohydrate and amino acid may be helpful in understanding the molecular interaction of biopolymers in living systems. The excess/deficiencies of protein and carbohydrate in the body causes dysfunctioning or diseases. Metal ions also play a significant role in metabolic and physiological processes involving amino acids and sugars. It is reflected from present studies designed near to physiological pH, temperature and aqueous conditions, that zinc chloride decreases the interaction between these two biomolecules.

References