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Solvation behavior of some vitamins in aqueous solutions of sodium chloride at different temperatures and at atmospheric pressure

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ABSTRACT

Densities ρ, and viscosities η, of aqueous solutions of L-ascorbic acid, nicotinic acid, thiamine hydrochloride and pyridoxine hydrochloride have been determined in different concentrations of sodium chloride at temperatures 288.15–318.15 K. These data were used to calculate apparent molar volumes $V_{2,\phi}$, partial molar volumes at infinite dilution V_2°, and viscosity *B*-coefficient (*B*). The corresponding transfer parameters at infinite dilution ($\Delta_{tr}V_2^\circ$ and $\Delta_{tr}B$) have been calculated using the data in water reported earlier on these vitamins. The d*B*/d*T* values have also been calculated. Results have been discussed in terms of solute–solute and solute–solvent interactions, which are found to be very complex in these systems. Activation free energy of viscous flow has also been calculated for these vitamins + sodium chloride + water systems.

1. Introduction

Biofluid contain small molecules like sugars, amino acids, vitamins, nucleotides, nucleosides and proteins along with inorganic salts of many metal ions. Enzymes (proteins) carry out the biochemical reactions in abundance in this fluid of life with the help of certain cofactors which could be metal ion or organic molecules (coenzyme) [1]. Coenzymes are derived from various vitamins which are essential constituents of animal diet. Vitamins neither produce energy nor get incorporated into tissues but may act or get converted into coenzyme to maintain the health of immune system.

Water soluble vitamins: L-ascorbic acid (vitamin C), thiamine (vitamin B_1), nicotinic acid (vitamin B_3) and pyridoxine (vitamin B_6) help in the catalysis of several biochemical reactions and also add to the balance of Na^+ and K^+ ions and promotion of RBC. A large section of population gets affected with the deficiency diseases when there is imbalance in the intake of vitamins. These features prompt to carry out the studies on vitamins in aqueous solutions of electrolytes in vitro. Thermodynamic and transport studies provide the parameters which are helpful in understanding the solute–solute and solute–solvent interactions in aqueous media. Various workers [2–9] used these approaches to study the interactions of these organic compounds (vitamins) in the presence of different aqueous and mixed aqueous media. As these organic molecules seem to possess molecular dissociation in aqueous media, interactions studies have been reported [2] in acidic media to suppress their dissociation and thermodynamic relations have been modified [3] to treat such data. Viscosity studies (transport property) are important for the transport across the biomembrane, but data for viscometric studies on these biomolecules are scarce in aqueous media. Therefore we planned to carry out thermodynamics and transport studies on L-ascorbic acid, nicotinic acid, thiamine hydrochloride and pyridoxine hydrochloride (solutes) in aqueous solutions of sodium chloride (cosolute) at temperatures (288.15–318.15) K. The Partial molar volumes at infinite dilution from density data, viscosity *B*-coefficient from viscosity data have been calculated which are further used to calculate transfer partial molar volumes at infinite dilution ($\Delta_{tr}V_2^\circ$) and viscosity *B*-coefficient of transfer ($\Delta_{tr}B$). The d*B*/d*T* values, activation free energy of viscous flow and related parameters have also been derived from these data. The results have been discussed in terms of various interactions occurring in these solutions.

2. Experimental

The vitamins used are: L-ascorbic acid (0.99), nicotinic acid (0.99), thiamine hydrochloride (0.98) and pyridoxine hydrochloride (0.98) of AR grade and were procured from Sisco Research Laboratories, India (parenthesis contain the mass fraction

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purities). These were used without further purification, however before use these were dried for 24 h in vacuum desiccator. Densities and viscosities of these solutions have been measured using vibrating-tube digital densimeter (DMA 60/602, Anton Paar, Austria) and Ubbelohde type capillary viscometer with the Automatic Viscosity measuring unit (SCHOTT AVS 350) respectively. The preparations of solution, working of density meter and viscometer have been discussed elsewhere [10,11].

3. Results and discussion

3.1. Apparent molar volumes

The densities, ρ, for aqueous solutions of vitamins increase with concentration but decrease with temperature as shown in Fig. 1 (plot of ρ vs molality, m_A (molality of vitamin), for L-ascorbic acid as a function of temperature at $m_B = 0.2\ \text{mol kg}^{-1}$) ($m_B$ is the molality of sodium chloride in water). The apparent molar volumes, $V_{2,\phi}$, of L-ascorbic acid, nicotinic acid, thiamine hydrochloride and pyridoxine hydrochloride in aqueous solutions of sodium chloride at $m_B = 0.2$, 0.4, 0.6, 0.8, 1.0 and $1.5\ \text{mol kg}^{-1}$ and temperatures (288.15–318.15) K have been calculated (Table 1) from the experimentally measured densities using the following relation:

$$V_{2,\phi} = \frac{M}{\rho} - \left[\frac{\rho - \rho_0}{m_A \rho \rho_0}\right] \qquad (1)$$

where M is the molar mass of solute, i.e. vitamins, ρ and ρ_0 are the densities of the solution (vitamins + sodium chloride + water) and solvent (sodium chloride + water) respectively.

L-ascorbic acid has two pK values ($pK_1 = 4.10$ and $pK_2 = 11.6$). Simple analytical calculations show that at lower concentrations of L-ascorbic acid the maximum change in apparent molar volume will be $0.011\ \text{cm}^3\ \text{mol}^{-1}$ which is within the uncertainty limits of the measurements of apparent molar volume. But at higher concentrations of L-ascorbic acid the degree of hydrolysis decreases and consequently its effect on apparent molar volume will be almost zero. Nicotinic acid has isoelectric point at 4.75 and it exists in zwitterionic form in water as well as in aqueous solutions of sodium chloride (cosolute). Thus the behavior of nicotinic acid in water and in aqueous solutions of sodium chloride will be similar to the behavior of amino acids in aqueous solutions. In zwitterionic form acid groups remain fully deprotonated and basic groups remain fully protonated and there seems to be no effect of concentration on the degree of hydrolysis of nicotinic acid.

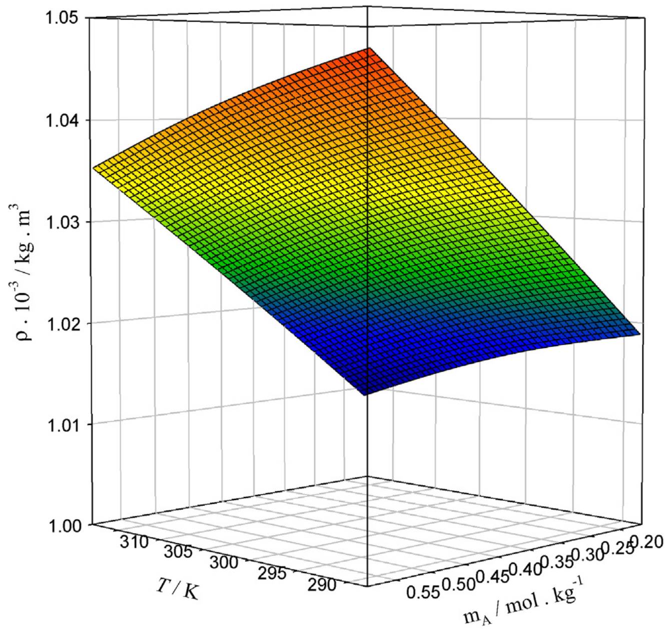
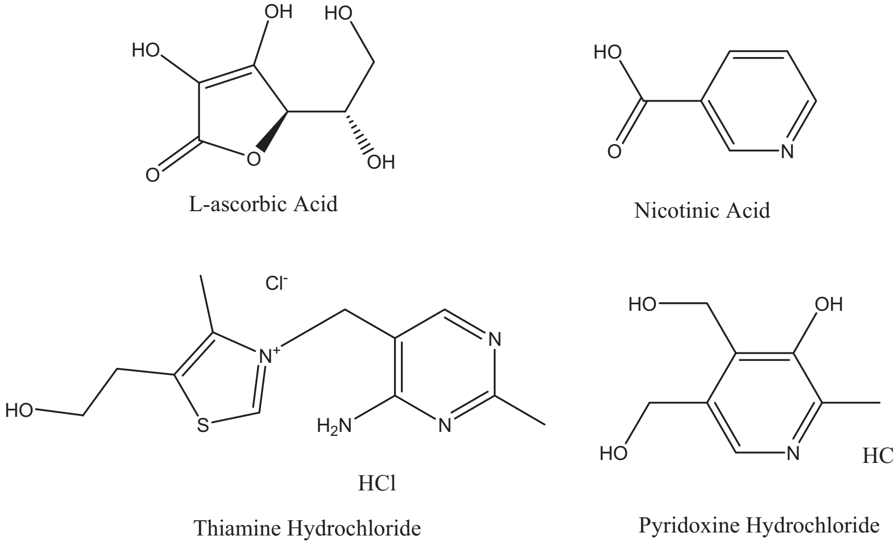


Fig. 1. Representative plot of density (ρ) vs molality (m_A) as a function of temperature for L-ascorbic acid in aqueous sodium chloride solutions at $m_B = 0.2\ \text{mol kg}^{-1}$. Densities of solutions (L-ascorbic acid + sodium chloride + water) increase with molality of the vitamin as the color on plot changes from blue → green → yellow → orange. The densities of the solutions decrease with increase in temperature as shown by large area under the blue region. Blue and orange regions represent the lower and higher density of the solution under study, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

At infinite dilution, the apparent molar volume, $V_{2,\phi}^{\circ}$ and standard partial molar volumes, V_2° become same, i.e. $V_2^{\circ} = V_{2,\phi}^{\circ}$. The V_2° values for L-ascorbic acid and nicotinic acid (treating them as non-electrolytes, Fig. 2) were calculated by the methods of least square using the following equation:

$$V_{2,\phi} = V_2^{\circ} + b_v m_A \qquad (2)$$



L-ascorbic Acid

Nicotinic Acid

Thiamine Hydrochloride

Pyridoxine Hydrochloride

Fig. 2. Structure of vitamins.