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Partial molar volumes and compressibilities of glycine betaine in aqueous NaCl solutions at temperatures $T=(288.15–318.15)$ K

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ABSTRACT

The partial molar volumes, partial molar isentropic compressibilities, transfer molar volumes and transfer molar isentropic compressibilities of the system: glycine betaine in aqueous (0.1, 0.2, 0.3, 0.4 and 0.5 mol kg^{-1}) NaCl solutions at different temperatures were determined using the experimental values of density and speed of sound. The positive transfer molar volumes of the systems indicated the presence of strong solute–solvent interactions. The electrostatic charge–charge interactions (among Na^+/Cl^- ions and amino/carboxylic groups of glycine betaine) were found to be predominant over the ionic–hydrophobic interactions (among Na^+/Cl^- ions and —CH_2/—CH_3 groups of the glycine betaine) in aqueous solutions. Size of the metal ion was found to influence the volumetric properties to an appreciable extent.

1. Introduction

Biomolecules play an important role in modern science. Interactions of such molecules with the environment can be understood by their thermodynamic studies. The environment being aqueous, non-aqueous, mixed aqueous media, the biomolecules behave accordingly. The stability and structural features of such systems can also be revealed by these studies [1–3].

Volumetric properties such as partial molar volumes and compressibility properties such as isentropic compressibilities, isothermal compressibilities, partial molar isentropic compressibilities, etc., are some of the major tools in visualizing the interactions taking place in any system. These are determined by measuring the solution properties such as density, viscosity, speed of sound, refractive index, heat capacity, etc. [4–7]. A vast volume of literature mentions the extensive volumetric studies of amino acids and related compounds in aqueous and mixed aqueous media [8–18]. Also, there are some reports on the study of amino acid related compounds in aqueous solutions of metal salts [19–22].

Betaine is one of such biomolecules which still deserves exploration in volumetric point of view. It functions as osmo-protector in bio-systems and finds applications in various other fields [23–27]. Sodium on the other hand, is an essential nutrient that plays a major role in osmotic equilibrium, blood volume and blood pressure regulations in bio-systems [28]. The effect of KCl and $MgCl_2$ on the volumetric and acoustic properties of glycine betaine has been discussed in our earlier publication [29]. The results showed that the size of metal ions influences the solution properties of the solute to an appreciable extent. However the varying concentration of metal ion in such systems could also have an impact on the molecular interactions prevailing in the system. Thus in order to study the effect of NaCl on the solution properties of aqueous glycine betaine solutions, in the present paper, we report the density, refractive index and the speed of sound values in aqueous solutions of glycine betaine-NaCl at different temperatures $T=(288.15–318.15)$ K which have been utilized to calculate the derived parameters.

2. Experimental

Table 1 provides the specifications of the samples used in present study. The samples were dried over anhydrous P_2O_5 at room temperature for more than 72 h. Different solutions of betaine in aqueous (0.1, 0.2, 0.3, 0.4 and 0.5 mol kg^{-1}) NaCl solvents were prepared using demineralized, double distilled water with low specific conductance ($<1.6\times10^{-6}\ \Omega^{-1}\cdot cm^{-1}$). To record the weights of the samples, a Mettler balance with ±0.01 mg precision was used. The samples were kept in temperature bath manufactured by Raaga Industries, Chennai with ±0.01 K temperature control. An ultrasonic interferometer (Mittal make, model F-05) with a fixed frequency generator of 2 MHz was used to determine the speed of sound in each solution. The estimated maximum error in this was

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Table 1
Sample specifications.

Chemical name	Source	Initial mass fraction purity	Method of analysis	Final mass purity
Glycine betaine (CAS No. 107-43-7)	Sigma	0.990	GC[a] HPLC[b]	0.990
Sodium chloride (CAS No. 7647-14-5)	Sigma–Aldrich	0.995	None	0.995

[a] Gas–liquid chromatography.
[b] High pressure liquid chromatography.

$\pm 0.2\,\mathrm{m \cdot s^{-1}}$. The interferometer was calibrated by analytical grade benzene and carbon tetrachloride. The density measurement was carried out by Mettler Toledo Densito 30PX digital densitometer having an uncertainty of $\pm 2 \times 10^{-4}\,\mathrm{g\,cm^{-3}}$. It was calibrated using double-distilled-deionized water and dry air. Atago 7000α digital refractometer was used to record the refractive indices of the samples. The uncertainty of which was estimated to be 0.00011 and the temperature of refractometer was controlled by an internal peltier unit.

A temperature range of $T = (288.15–318.15)$ K was chosen for the current work with an interval 10 K. The concentration of betaine was varied from 0 to 3 mol kg^{-1} while keeping that of NaCl from 0.1 to 0.5 mol kg^{-1}. The average of triplicate measurement of density, speed of sound or refractive index has been reported as a final value.

3. Result and discussions

The experimental density, speed of sound and refractive index of glycine betaine in aqueous NaCl solutions at temperatures $T = (288.15–318.15)$ K are presented in Table 2 .

The apparent molar volumes ϕ_v and apparent molar isentropic compressibility, ϕ_k of glycine betaine in aqueous NaCl solutions with different concentrations were calculated using the expressions [30]:

$$\phi_v = \frac{\rho_0 - \rho}{m_A \rho \rho_0} + \frac{M_A}{\rho} \qquad (1)$$

$$\phi_k = \left[\frac{\kappa_S - \kappa_0}{m_A \rho_0}\right] + \kappa_S \phi_v \qquad (2)$$

where, m_A (mol kg^{-1}) is the molality of glycine betaine in aqueous solutions, M_A (kg mol^{-1}) is the molar mass of glycine betaine, ρ_0 and ρ (kg m^{-3}) are the densities of solvent (aqueous NaCl solution) and that of solution (Betaine + aqueous NaCl solution) respectively. $\kappa_0 (= 1/\rho_0 c_0^2)$ and $\kappa_s (= 1/\rho c^2)$ are the isentropic compressibilities (m^2 N^{-1}) of the solvent and that of the solution respectively. c_0 and c (m s^{-1}) are speeds of sound in solvent and solution, respectively.

The values of the apparent molar volume and apparent molar isentropic compressibility of glycine betaine in aqueous NaCl solutions at different temperatures are presented in Tables S1 and S2 respectively as supplementary material. The uncertainties of ϕ_v and ϕ_k were estimated using propagation of errors method [12,14] and included in Tables S1 and S2. As can be seen from the tables, the values of ϕ_v and ϕ_k increase with the concentration of the solute at a fixed NaCl concentration.

The method least-squares fit has been employed to fit ϕ_v and ϕ_k values:

$$\phi_v = \phi_v^0 + S_v m_A \qquad (3)$$

$$\phi_k = \phi_k^0 + S_k m_A \qquad (4)$$

where ϕ_v^0 (m^3 mol^{-1}) and ϕ_k^0 (Pa^{-1} m^3 mol^{-1}) are the partial molar volume and partial molar isentropic compressibility of the solute respectively. S_v and S_k are the experimental slopes and m_A is the molality of the solute. The values of ϕ_v^0 and ϕ_k^0 along with the slopes are listed in Tables S3 and S4 respectively as supplementary material. The so obtained values have been compared with those available in the literature. The infinite dilution properties (or partial molar quantities) are important because these values describe solely the interactions between glycine betaine and the solvent molecules, as the interactions among glycine betaine molecules are negligible at infinite dilution [31]. A close perusal of Tables S3 and S4 suggests that values of ϕ_v^0 and ϕ_k^0 are large and positive and are much larger than the values of S_v and S_k thereby, indicating the presence of strong solute–solvent interactions in the present systems. The variation of these derived properties of glycine betaine at different concentrations of NaCl are shown in Figs. 1 and 2. As depicted by the figures, with the temperature, ϕ_v^0 and ϕ_k^0 values follow an increasing trend. Further, the partial molar volumes and compressibilities of glycine betaine in 0.4 and 0.5 mol kg^{-1} NaCl aqueous solutions were found to be more positive than those in lower NaCl concentrations which hints much stronger solute-solvent interactions at higher NaCl concentrations.

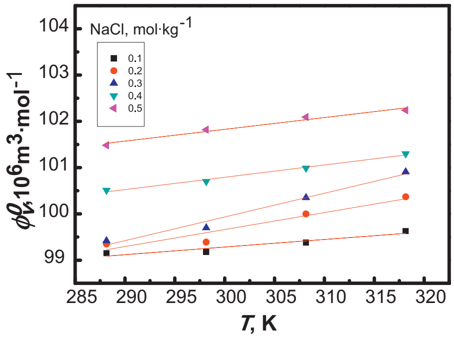

Fig. 1. Variation of ϕ_v^0 of glycine betaine in aqueous NaCl solutions with respect to temperature.

Glycine betaine can be regarded as a ‘doubly charged’ derivative of a peptide–‘glycine’ whose all the three hydrogen atoms in amino group are replaced by ($-CH_3$) groups. As a result of dissociation of amino and carboxyl groups of the molecule, it essentially behaves as a zwitterion. The solute–solvent interactins operative in this case can be explained as: (i) electrostatic hydration of charged terminals of the zwitter ion, and (ii) the overlap of hydration co-spheres of these terminal groups with that of $-CH_2$ group of glycine betaine thus contributing enhanced ϕ_v^0 values [32]. At higher temperatures,

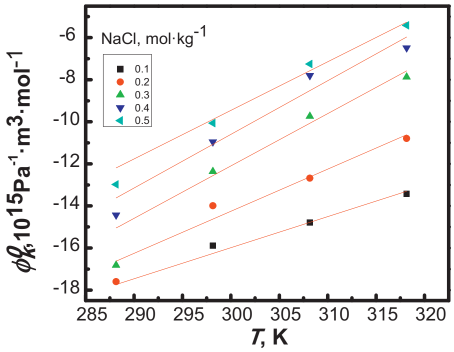

Fig. 2. Variation of ϕ_k^0 of glycine betaine in aqueous NaCl solutions with respect to temperature.