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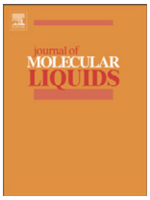

Studies of interionic interactions of L-serine/L-threonine in aqueous trilithium citrate solutions using density and speeds of sound measurements at different temperatures

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ABSTRACT

Densities and speeds of sound of L-serine and L-threonine in aqueous solutions of trilithium citrate have been measured at $T = 288.15$, 298.15, 308.15 and 318.15 K and atmospheric pressure. The apparent molar volume (V_ϕ), the partial molar volume ($V_\phi{}^0$) and standard partial molar volumes of transfer ($\Delta V_\phi{}^0$) for amino acids from water to aqueous trilithium citrate have been calculated from density data. Group contributions of amino acids to partial molar volume were determined. The limiting apparent molar expansibilities have also been calculated. Partial molar isentropic compression ($K_{\phi,s}$) and partial molar isentropic compression of transfer ($\Delta K^0_{\phi,S}$) have been calculated from speed of sound data. Hydration number (n_H) has also been calculated. The pair and triplet interaction coefficients have been calculated from both the properties. The results have been explained based on competing patterns of interactions of co-solvents and the solute.

1. Introduction

Hydration of hydrophobic, charged atomic groups and ions which are the components of almost every biological system plays an important role in the conformational stability of biopolymers. The stabilization of native confirmations of biological macromolecules (proteins) is related to several non-covalent interactions including hydrogen bonding; electrostatic and hydrophobic interactions [1,2] and these interactions are affected by the presence of surrounding solute and solvent molecules. Therefore, the physicochemical properties of proteins are strongly affected by the presence of these solutes. Because of direct solute–solvent interactions, these solutes can change many properties of globular proteins, such as their hydration, solubility and the activity of enzymes [3–5]. Extensive work [6–18] has been done on the thermodynamic properties of amino acids in aqueous electrolyte solutions, carbohydrates, surfactants etc. but, the biologically and industrially important citrate salts which found their applications in food, pharmaceutical, cosmetic industries and in many biochemical processes [19–21] have been included in few studies [22–26]. Our main aim is to study the interactional behavior of amino acids with these salts of biological and industrial importance to have better understanding of these classes of compounds. In continuation to our studies on citrate salts [27–31], in the present work, we report densities and speeds of sound of L-serine and L-threonine in aqueous trilithium citrate solutions at different temperatures $T = 288.15$, 298.15, 308.15, and 318.15 K and atmospheric pressure. The ultrasonic speed may be considered as a thermodynamic property, provided that a negligible amount of ultrasonic absorption of the acoustic waves of low frequency and of low amplitude is observed; in which case, the ultrasonic absorption of the acoustic waves is negligible. Trilithium citrate ($Li_3C_6H_5O_7$) (TLC) also known as lithium citrate, is a chemical compound of lithium and citrate. TLC is used as a mood stabilizer in psychiatric treatment of manic states and bipolar disorder. It is a chemical compound with extensive pharmacology of lithium, the active component of this salt. Investigations of the effect of TLC on hydration structure of the amino acids are important in view of solution chemistry. As per our knowledge, no data on densities and speeds of sound of amino acids with trilithium citrate mixtures has been reported, so far.

2. Experimental

2.1. Materials

L-Serine and L-threonine with mass fraction purities >0.99 procured from Merck, Germany and trilithium citrate with mass fraction purity of 0.985 purchased from SD Fine-Chem. Ltd, India were used as supplied. All the chemicals were vacuum dried and stored in desiccator over P_2O_5 for at least two days before their use. The specifications of the chemicals used in this study are also given in Table 1.

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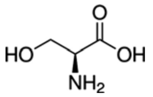
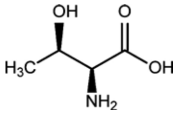
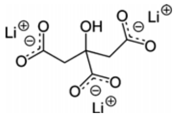
Table 1
Specification of chemical samples.

Chemical	CAS number	Source	Purification method	Mass fraction purity (supplier)	Structure
L-Serine	56-45-1	Merck, Germany	Used as such	>0.99	
L-Threonine	72-19-5	Merck, Germany	Used as such	≥0.99	
Trilithium Citrate	6080-58-6	SD Fine Chem. Ltd. India	Used as such	0.985	

2.2. Equipment and procedures

Freshly prepared triple distilled and degassed water (specific conductance < 10^{-6} S·cm^{-1}) was used for the preparation of solutions. The solutions were prepared by weighing on a balance having a precision of ±0.00001 g. The uncertainties in the molality of solutions are within $\pm 2 \times 10^{-5}$ mol·kg^{-1}. Density measurements were made on Anton Paar DSA 5000M densimeter. The speed of sound is measured using a propagation time technique. The sample is sandwiched between two piezoelectric ultrasound transducers. One transducer emits sound waves through the sample-filled cavity at a frequency of approximately 3 MHz; the second transducer receives those waves. Thus, the speed of sound is obtained by dividing the known distance between transmitter and receiver by the measured propagation time of the sound wave. A density check or an air/water adjustment was performed at 20 °C with triply distilled, degassed water, and with dry air at atmospheric pressure. Before each series of measurements, the densimeter was calibrated with triple distilled and degassed water, in the experimental temperature range. The density and speeds of sound values are extremely sensitive to temperature, so it was controlled to $\pm 1 \times 10^{-3}$ K by a built-in Peltier device. The sensitivity of the instrument corresponds to a precision in density and speeds of sound measurements of 1×10^{-3} kg m^{-3} and 1×10^{-2} m s^{-1}. The uncertainty of the density and speeds of sound estimates was found to be within $\pm 5 \times 10^{-3}$ kg m^{-3} and $\pm 5 \times 10^{-2}$ m s^{-1}, respectively.

3. Results and discussion

3.1. Apparent molar volume

The experimental values of solution densities, ρ of L-serine and L-threonine in 0.0, 0.2, 0.4 and 0.6 mol kg^{-1} aqueous solutions of trilithium citrate were measured at temperatures 288.15, 298.15, 308.15 and 318.15 K. These values of densities were used to calculate apparent molar volumes (V_ϕ) using the following equation:

$$V_\phi = M/\rho - (\rho - \rho_0)/m_A \rho \rho_0 \tag{1}$$

where m_A is the molality (mol·kg^{-1}) of the amino acids i.e. amount of solute (amino acids) per one kilogram of solvent (mixture of water + TLC), M is the molar mass of the solute (kg·mol^{-1}) and ρ_0 and ρ are the densities (kg·m^{-3}) of the solvent and solution. The values of apparent molar volumes along with densities are reported in Table 2. The experimental values of densities for aqueous solutions of L-serine and L-threonine at different temperatures are in good agreement with literature values [32–35] as shown in Figs. 1 and 2. The calculated values of apparent molar volume are graphically presented in Figs. 3 and 4. Fig. 3 represents the apparent molar volumes for L-serine at different temperatures in aqueous solutions of TLC while Fig. 4 represents the apparent molar volumes for L-serine and L-threonine in aqueous and aqueous solutions of TLC at different temperatures. The data reported in Table 2 and represented in Figs. 3 and 4, reveals that apparent molar volumes for L-serine and L-threonine increase with an increase in TLC concentration and temperature. Further, the values also increase with an increase in the number of alkyl groups present in amino acids i.e. from L-serine to L-threonine at all temperatures. Further, the positive values of V_ϕ are indicative of greater solute–solvent interactions, which increase from L-serine to L-threonine at all temperatures as shown in Scheme 1.

3.2. Partial molar volume

Partial molar volume V_ϕ^0, which is the limiting value of apparent molar volume, is calculated by least squares fitting of apparent molar volume V_ϕ by the following equation:

$$V_\phi = V_\phi^0 + S_V^* m_A \tag{2}$$

where S_V^* the experimental slope is the volumetric pair wise interaction coefficient and m_A is the molality of the amino acids in aqueous TLC solutions. The values of V_ϕ^0 and S_V^* together with standard errors derived by least squares fitting of the V_ϕ values to Eq. (2) are reported in Table 3. The positive V_ϕ^0 values increase with an increase in the TLC concentration and temperature for all amino acids as shown in Fig. 5. Further, at each temperature, the V_ϕ^0 values increase with size of alkyl group i.e. increase in chain length of alkyl part from L-serine to L-threonine.

As per co-sphere overlap model [36,37], an overlap of co-spheres of two ionic species causes an increase in volume, whereas overlap of hydrophobic–hydrophobic groups and ion–hydrophobic groups results in the volume decrease. The observed positive V_ϕ^0 values are due to ion–hydrophilic interactions, which dominate over ion–hydrophobic interactions and hydrophobic–hydrophobic interactions. Temperature dependence of standard partial molar property provides vital information on solute–solvent interactions i.e. ion–solvent or zwitterions–solvent interactions present in solutions, as, solute–solute interactions like ion–ion or zwitterion–zwitterion interactions at infinite dilution are negligible. The increase in V_ϕ^0 values with an increase in temperature for all amino acids may be explained as release of some solvation molecules from the loose solvation layers of the solutes in solution. This can also be explained by considering the size of primary and secondary solvation layers around zwitterions. At higher temperatures, the solvent from the secondary solvation layers of amino acid zwitterions is released into the bulk of the solvent, resulting into the expansion of solution, as inferred from larger values of V_ϕ^0 at higher temperatures. From Table 3, it is also observed that the magnitude of S_V^* is positive for all concentrations of TLC at all temperatures. The positive values of S_V^* indicate the presence of solute–solute interactions in solutions of amino acids in