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Effect of magnesium acetate on the volumetric and transport behavior of some amino acids in aqueous solutions at 298.15 K

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Abstract

Densities, ρ, and viscosities, η, of glycine, DL-α-alanine, DL-α-amino-n-butyric acid, L-leucine and L-phenylalanine in 0.5, 1.0, 1.5 and 2.0 m_B of aqueous magnesium acetate solutions at 298.15 K have been measured as a function of concentration of amino acids using vibrating tube-digital densimeter and Ubbelohde capillary type viscometer, respectively. The apparent molar volumes, V_ϕ, and relative viscosities, η_r, of amino acids have been derived. The partial molar volume at infinite dilution, V_2^0, and viscosity B-coefficient obtained from these data have been used to calculate the corresponding transfer parameters, $\Delta_t V^0$, and $\Delta_t B$, for the studied amino acids from water to aqueous magnesium acetate solutions. The activation free energies, $\Delta\mu_2^{0\neq}$, for the viscous flow of solutions have been obtained by application of the transition-state theory to the viscosity B-coefficient data. The interaction coefficients and hydration number, n_H, of amino acids in aqueous solutions have also been calculated to see the effect of magnesium acetate on the hydration of amino acids. The contribution of the zwitterionic end groups (NH_3^+, COO^-) and (CH_2) group of the amino acids to V_2^0, viscosity B-coefficient and $\Delta\mu_2^{0\neq}$ have been calculated. These results have been rationalized in terms of the hydration of hydrophilic and hydrophobic parts of amino acids.

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1. Introduction

The knowledge about the origin of the stability of proteins in aqueous solutions is essential for the understanding of their structure and function. Protein hydration plays a crucial role in this matter. The stability of folded protein structure is marginal (only $20\ kJ \cdot mol^{-1}$ to $50\ kJ \cdot mol^{-1}$) under physiological conditions, which is due to the delicate balance among various powerful countervailing non-covalent forces such as hydrogen bonding, electrostatic interactions, hydrophobic interactions, etc. Salt solutions are known to produce remarkable effects on the conformation and properties of proteins like denaturation, solubility and

dissociation into subunits and the activity of enzymes, etc. [1,2]. Due to complex structure of proteins, a variety of different interactions with salts may occur and it is difficult to resolve straightaway the various interactions participating in protein hydration. Therefore, in order to obtain more insight into the hydration of proteins and non-covalent forces stabilizing their native structure, it is necessary to determine the effects of salts on the model compounds of proteins such as amino acids and peptides.

Various workers have studied the interactions between some amino acids and simple salts [3–15] (such as NH_4Cl, $NaCl$, KCl, Na_2SO_4, $KSCN$, $MgCl_2$, $CaCl_2$, etc.), which act as stabilizer/destabilizer, but very few studies are available about the behavior of amino acids in the presence of organic salts [16–20]. The volumetric and transport behavior of some amino acids in the presence of sodium acetate [16,17,20], sodium butyrate [18] and sodium caproate [19],

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which are known to influence the dissociation of proteins in solutions has been reported. Comparison of results has also shown that the interactions between carboxylate anion and the amino acids are stronger than those between chloride ion and amino acids. Further, the $\Delta_t V^0$ values [20] have shown that the acetate ion follows the same order as in the Hofmeister series. The size and nature of anion of organic salt also modulate the interactions. The caproate ions having bigger hydrophobic hydration sphere, have longer destructive effect on the hydration sphere of NH_3^+ group of the amino acids than butyrate and acetate ions. Most of this work on amino acids has been carried out in dilute electrolytes solutions. Recently Badarayani and Kumar [21,22] have studied some amino acids in concentrated ionic solutions and proposed a new method for the determination of ion–amino acid interaction parameters.

Although various studies of amino acids are available in the presence of electrolytes having divalent cations [12–14,21,22], but no report has been found in the presence of organic salts having divalent cations. Therefore, it has been planned to study the effect of carboxylate anion in the presence of a divalent cation on the volumes and viscosities of some amino acids. Magnesium acetate has been chosen as organic salt because magnesium found immense importance in biological chemistry [23]. In the present paper, we report the partial molar volumes, V_2^0, and viscosity B-coefficients of glycine, DL-α-alanine, DL-α-amino-n-butyric acid, L-leucine and L-phenylalanine in aqueous 0.5, 1.0, 1.5 and 2.0 m_B magnesium acetate (MA) solutions at 298.15 K, where m_B, is the molality (mol kg^{-1}) of MA in water. From these data, the partial molar volumes of transfer, $\Delta_t V^0$, viscosity B-coefficient of transfer, $\Delta_t B$, side chain contributions, hydration number, n_H, and volumetric interaction coefficients of amino acids have been calculated. The transition-state theory has been applied to calculate the activation parameters for viscous flow of amino acids in aqueous MA solutions. The results have been discussed in terms of the hydration of different parts of amino acids (hydrophilic and hydrophobic) in aqueous solutions.

2. Experimental

Glycine (G-7126), DL-α-alanine (A-7502), DL-α-amino-n-butyric acid (A-1754), L-leucine (L-8000) and L-phenylalanine (P-2126) were obtained from Sigma Chemical Co. and were dried for 24 h in a vacuum oven before use. Analytical reagent grade magnesium acetate tetrahydrate from Sisco Research Laboratory, India was used as such after drying in a vacuum desiccator at room temperature. Deionised, doubly distilled degassed water with specific conductance less than $1.29 \times 10^{-6}\,\Omega^{-1} \cdot cm^{-1}$ was used for the measurements. All solutions were prepared afresh by mass using a Mettler Balance having an accuracy of ±0.01 mg. The densities of the solutions were measured using a vibrating tube-digital densimeter (Model DMA 60/602) with precision of $\pm 1 \times 10^{-6}\,g \cdot cm^{-3}$ and having accuracy of $\pm 3 \times 10^{-6}\,g \cdot cm^{-3}$. The principle and experi-

mental procedure for the densimeter have been described elsewhere [24]. The temperature of water around densimeter cell was controlled within ±0.01 K. The densimeter was calibrated with dry air and pure water. The working of the densimeter was checked by measuring the densities of aqueous sodium chloride solutions that agree well with the literature values [25].

Viscosity measurements were carried out with a suspended level Ubbelohde type capillary viscometer, mounted in water thermostat which was calibrated with water at four different temperatures (288.15 K to 308.15 K) [9]. The flow time of a constant volume of liquid through capillary was measured with an electronic stopwatch with a resolution of 0.01 s. An average of at least four readings of flow time with a variation not exceeding ±0.1 s was taken for each solution. The temperature of the thermostat bath was controlled within ±0.01 K. The measured viscosities were found to be accurate within ±0.001 mPa s.

3. Results

The apparent molar volumes, V_ϕ of amino acids in 0.5, 1.0, 1.5 and 2.0 m_B of aqueous MA solutions have been obtained from the solution densities (table 1) using the following relation:

$$V_\phi = (M/\rho) - (\rho - \rho_0)10^3/(m \cdot \rho \cdot \rho_0), \tag{1}$$

where M and m are, respectively, the molar mass and molality of the amino acids, ρ_0 and ρ are the densities of solvent (MA and water mixture) and solution, respectively. At infinite dilution, the apparent molar volume, V_ϕ^0 becomes same as the standard partial molar volumes V_2^0. When V_ϕ show no significant concentration dependence, the average of all the data points has been taken as the standard partial molar volume. However, where finite concentration dependence was observed, V_2^0 was determined by the method of least squares using

$$V_\phi = V_2^0 + S_V m, \tag{2}$$

where S_V is the experimental slope. The V_2^0 values along with their standard deviations are listed in table 2. The uncertainty in the determination of V_ϕ occurring because of the measurement of various quantities has been calculated. The uncertainty values for the V_ϕ range from 0.062 cm$^3 \cdot$ mol^{-1} to 0.009 cm$^3 \cdot$ mol^{-1} for the lower ($\leqslant 0.04 m$) and higher concentration ranges for glycine, DL-α-alanine and DL-α-amino-n-butyric acid, respectively. The uncertainty for V_ϕ in case of L-leucine and L-phenylalanine are slightly higher because very dilute concentration range has been studied. The uncertainty values in these cases range from 0.331 cm$^3 \cdot$ mol^{-1} to 0.051 cm$^3 \cdot$ mol^{-1} for the lower ($\leqslant 0.009\,m$) and higher concentration ranges, respectively. To the best of our knowledge these data for the studied amino acids are being reported for the first time in aqueous MA solutions. The viscosities, η of the solutions were calculated using the following expression: