Available online at www.sciencedirect.com
ScienceDirect
J. Chem. Thermodynamics 39 (2007) 371–384
JCT
www.elsevier.com/locate/jct

Thermodynamic and transport properties of L-serine and L-threonine in aqueous sodium acetate and magnesium acetate solutions at $T = 298.15$ K

T.S. Banipal [a,*], Damanjit Kaur [a], P.K. Banipal [b], Gagandeep Singh [a]

[a] *Department of Applied Chemistry, Guru Nanak Dev University, Amritsar 143005, India*
[b] *Department of Chemistry, Guru Nanak Dev University, Amritsar 143005, India*

Received 5 June 2006; received in revised form 6 August 2006; accepted 7 August 2006
Available online 22 August 2006

Abstract

The apparent molar volumes, $V_{2,\phi}$, apparent molar adiabatic compressibilities, $\kappa_{S,2,\phi}$, and relative viscosities, η_r, of L-serine and L-threonine in different concentrations of aqueous sodium acetate and magnesium acetate solutions at $T = 298.15$ K have been obtained from the measurements of densities, speed of sound, and flow time, respectively. These data are used to derive the partial molar volumes, V_2°, partial molar adiabatic compressibilities, $\kappa_{S,2}^\circ$ (at infinite dilution), and viscosity B-coefficients. The corresponding quantities of transfer, ($\Delta_t V^0$, $\Delta_t \kappa_{S,2}^\circ$, and $\Delta_t B$), have been obtained. The activation free energy, $\Delta\mu_2^{\circ\neq}$, for viscous flow has been calculated for L-serine and L-threonine in aqueous solutions. The hydration numbers, n_H, side chain contributions, and interaction coefficients have also been calculated. The values of V_2°, $\kappa_{S,2}^\circ$, viscosity B-coefficient, and $\Delta\mu_2^{\circ\neq}$ for viscous flow increase with the concentration of sodium acetate and magnesium acetate solutions. The influence of magnesium acetate on the transfer properties is greater than sodium acetate in aqueous solutions. A comparison of $\Delta_t V^0$, $\Delta\kappa_{S,2}^\circ$, and $\Delta_t B$ values for L-serine and L-threonine with the reported data for DL-α-alanine and DL-α-amino-*n*-butyric acid in aqueous sodium acetate and magnesium acetate solutions shows that the values are greater for L-serine and L-threonine at the same concentration of sodium acetate and magnesium acetate.

Keywords: Apparent molar volume; Apparent molar adiabatic compressibility; Viscosity *B*-coefficient; Interaction coefficients; Activation parameters; Amino acids; Sodium acetate; Magnesium acetate

1. Introduction

Knowledge of the interactions responsible for stabilizing the native state of a globular protein in aqueous solution is essential to understand its structure and function. The study of these interactions provides an important insight into the conformational stability and unfolding behaviour of globular proteins [1]. Due to complex structure of proteins, the study of conformational stability and unfolding behaviour of globular proteins has proved quite challenging and still remains a subject of extensive investigations [2,3]. The thermodynamic properties of a completely unfolded protein system can be estimated by adding together the thermodynamic property contributions of the small structural units that constitute its molecular sequence. Therefore, protein model compounds such as amino acids and peptides, which are basic components of proteins, have been investigated in detail with respect to their thermodynamic properties in aqueous and mixed aqueous solutions [4–21].

Salt solutions are known to influence the stability and structure of proteins [22,23]. Remarkable experimental work has been reported on the thermodynamic and transport properties of amino acids in aqueous salt solutions [4–21], but very few studies exist on the volumetric and transport properties of amino acids in aqueous organic salt solutions [24–31], probably due to the complex nature of

* Corresponding author. Fax: +91 183 2258819/8820.
E-mail address: tsbanipal@yahoo.com (T.S. Banipal).

0021-9614/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jct.2006.08.003

their interactions. Moreover, no systematic studies are available on the thermodynamic and transport properties of amino acids having polar side group (chain) in the presence of organic salt solutions.

In view of the above and in continuation of our studies [29–31], we have undertaken a systematic study on the volumetric (volume and compressibility) and viscometric properties of amino acids in aqueous sodium acetate and magnesium acetate solutions. In the present paper, apparent molar volumes, $V_{2,\phi}$, apparent molar adiabatic compressibilities, $\kappa_{S,2,\phi}$, and viscosity B-coefficients of L-serine and L-threonine in water and in different concentrations of sodium acetate (SA) and magnesium acetate (MA) solutions have been determined by measuring the densities, speed of sound, and flow time using vibrating-tube digital densimeter, multi-frequency ultrasonic interferometer and Ubbelohde type capillary viscometer, respectively, at $T = 298.15$ K. These data have been used to calculate the transfer parameters such as $\Delta_t V^0$, $\Delta_t \kappa^\circ_{S,2,\phi}$, and $\Delta_t B$ for the studied amino acids from water to aqueous SA and MA solutions. The hydration numbers, n_H, side chain contributions, interaction coefficients, and activation free energy of viscous flow have also been calculated. The effects of size of the cation and concentration of SA and MA have also been discussed.

2. Materials and methods

L-serine (S-4500), and L-threonine (T-8625) of highest purity grade procured from Sigma Chemical Company were used without further purification. However, these were dried for 24 h in a vacuum oven and then kept in a vacuum desiccator before use. Analytical reagent grade, sodium acetate trihydrate, and magnesium acetate tetrahydrate from Sisco Research Laboratories were used as such after drying in a vacuum desiccator at room temperature. The molalities of these salts have been calculated using molar mass of sodium acetate trihydrate and of magnesium acetate tetrahydrate by considering the constitutional water present in these salts. The specific conductivity of deionised, doubly distilled degassed water used for studies was less than $1.30 \cdot 10^{-6} \Omega^{-1} \cdot \mathrm{cm}^{-1}$. All solutions were prepared afresh on a mass basis using a Mettler Balance having an accuracy ± 0.01 mg. The solution densities were measured using a vibrating-tube digital densimeter, Anton Paar DMA 60/602. The reproducibility of the measurement on an average is $\pm 3 \cdot 10^{-6}\ \mathrm{g \cdot cm^{-3}}$. The details of its principle and working have been already described [29,30]. The densimeter was calibrated both with distilled water and dry air, respectively. The working of densimeter was checked by measuring the densities of aqueous sodium chloride solutions, which agreed well with the literature values [32].

Viscosities were measured using an Ubbelohde type capillary viscometer, which was calibrated using a flow time of water from $T = 298.15$ K to $T = 318.15$ K. The flow time of a constant volume of water through the capillary was measured with an electronic stopwatch, with a resolution of ± 0.01 s. An average of at least four readings was taken as the final value of time. The viscosity of a solution, η, is calculated by using following equation:

$$\eta/\rho = at - b/t,$$

where ρ is the density of the solution, t is the flow time, and a and b are the viscometer constants, obtained by measuring the flow time for water at four different temperatures. The measured viscosity values are accurate within ± 0.001 mPa · s.

A multi-frequency ultrasonic interferometer (Model M-82, Mittal Enterprises) was used to measure the sound velocities with the maximum uncertainty in velocity of $0.5\ \mathrm{m \cdot s^{-1}}$. The interferometer was calibrated by measuring the speed of sound of distilled water at $T = 298.15$ K, which agreed well with the literature value [33]. The sound velocities were precise within $0.1\ \mathrm{m \cdot s^{-1}}$. The average of at least 10 readings was taken as final value of sound velocity. The temperature of water around the densimeter cell, viscometer, and interferometer cell was maintained within ± 0.01 K.

3. Results

The apparent molar volumes, $V_{2,\phi}$, and apparent molar adiabatic compressibilities, $\kappa_{S,2,\phi}$, of amino acids (L-serine and L-threonine) in water and in different concentrations of SA and MA (co-solutes) solutions have been obtained from the solution densities and compressibilities, respectively, using the following equations:

$$V_{2,\phi} = (M/\rho) - [(\rho - \rho_0) \times 1000/(m_A \rho \rho_0)], \quad (1)$$

$$\kappa_{S,2,\phi} = (M\kappa_S/\rho) - [(\kappa^\circ_S \rho - \kappa_S \rho_0)/(m_A \rho \rho_0)], \quad (1a)$$

where M and m_A are the molar mass and molality of amino acids, respectively. The ρ_0 and ρ, κ°_S, and κ_S are the densities and adiabatic compressibilities of solvent (water or co-solute + water) and solution (water + amino acids or water + co-solute + amino acids), respectively. The adiabatic compressibility was determined from the sound velocity and density using the relation:

$$\kappa_S = 1/u^2\rho, \quad (2)$$

where u is the sound velocity. The densities, $V_{2,\phi}$, u, and $\kappa_{S,2,\phi}$ as a function of concentration of amino acids in aqueous SA/MA solutions are given in tables 1 and 2, respectively. The uncertainty in the determination of $V_{2,\phi}$ and $\kappa_{S,2,\phi}$ occurring because of the measurement of various quantities has been calculated. The uncertainty values for $V_{2,\phi}$ range from (0.05 to 0.007) $\mathrm{cm^3 \cdot mol^{-1}}$ for the lower ($\leqslant 0.05\ m_A$) and higher concentration range in aqueous SA/MA solutions for the studied amino acids, respectively. The uncertainty values for $\kappa_{S,2,\phi}$ range from (0.40 to 0.31) $\mathrm{m^3 \cdot mol^{-1} \cdot Pa^{-1}}$ for the lower ($\leqslant 0.05 m_A$) and higher concentration range in aqueous SA/MA solutions, respectively. As reported earlier [29–31], SA/MA being a salt of a weak acid and a strong base undergoes hydrolysis and