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Volumetric and viscometric studies of amino acids in L-ascorbic acid aqueous solutions at $T = (293.15$ to $323.15)$ K

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ABSTRACT

Densities and viscosities of glycine, L-alanine, L-valine, L-threonine and L-arginine in aqueous solutions of (0.0, 0.1, 0.2, 0.3 and 0.4) mol · kg^{-1} L-ascorbic acid have been measured at $T = (293.15, 303.15, 313.15$ and $323.15)$ K under atmospheric pressure. The apparent molar volumes (V_φ), limiting partial molar volumes (V^0_φ), limiting partial molar volumes of transfer ($\Delta_{tr}V^0_\varphi$) and limiting partial molar expansibilities (E^0_2) were computed by densities. The extended Jones–Dole equation was used to correlate the viscosities in order to obtain viscosity *B*-coefficients and the free energies of activation per mole of solvent ($\Delta\mu^{0\neq}_1$) and solute ($\Delta\mu^{0\neq}_2$) were also calculated. The contributions of zwitterionic end group (NH^+_3, COO^-), CH_2 group, OH group and $CNHNHNH_2$ group to V^0_φ and viscosity *B*-coefficients were obtained through the group additivity analysis.

1. Introduction

The surroundings of most proteins are not only water but various kinds of organic and inorganic compounds which have great effects on the structures and properties of proteins including their solubility, denaturation, dissociation into subunits, and the activity of enzymes [1–2]. But it is rather difficult to conduct directly thermodynamic studies on proteins due to their complicated structures. Recently, researches on the model of proteins such as amino acids, peptides, amide, and their derivatives, have evoked a lot of interests [3–8].

Amino acids are the building blocks of proteins and often regarded as the ideal model for the studies of proteins. The thermodynamic properties and transport properties of amino acids in a variety of media can provide valuable information for the stability and denaturation of proteins, which could promote the progresses of medicine and human science [9–10]. Since the living organism is a complex system, it is of immense significance to study the thermodynamic properties of amino acids with functionally important bimolecule in aqueous solutions [11–12].

Polyhydroxy compounds have been known to be able to increase the stability of proteins or reduce their denaturation [13–15]. As a kind of polyhydroxy compounds, L-ascorbic acid (VC for short), is a ubiquitous and indispensable compound in living system, and also belongs to the natural surroundings of proteins. L-ascorbic acid is not only required for the metabolism of folic acids and mineral compouds but also essential to synthesize collagen which gives the structure of muscles, bones, and tendon. Except for its role in enhancing immunity function, improving metabolism, and maintaining health, L-ascorbic acid is also effectively used in skin-whitening and anti-aging processes.

There are extensive investigations of amino acids in aqueous and aqueous additive solutions, such as sugar, polyols and urea [15,16–20], but to our best knowledge, only limited reports are available on the volumetric and viscometric properties of amino acids in L-ascorbic acid aqueous solutions. Zhao *et al.* [21,22] reported the partial molar volumes, limiting partial molar volumes of transfer and viscosity *B*-coefficients of L-threonine and L-arginine in L-ascorbic acid aqueous solutions at $T = 298.15$ K through the density and viscosity data, while Banik *et al.* [23] measured the density, viscosity, refractive index and speed of sound of L-glycine, L-alanine, and L-valine in (0.010, 0.03, 0.05) mol · dm^{-3} aqueous ascorbic acid solutions at 298.15 K and computed the partial molar volumes, viscosity *B*-coefficients, molar refractions and adiabatic compressibilities. Since the previous investigations were usually restricted to two or three amino acids at the ambient temperature (298.15 K) and atmospheric pressure (1 atm) condition, therefore in this paper, we have undertaken a systematic study on the densities and viscosities of five typical amino acids (glycine, L-alanine, L-valine, L-threonine and L-arginine) in L-ascorbic acid aqueous solutions at $T = (293.15, 303.15, 313.15,$ and $323.15)$ K under atmospheric pressure. Here we have also presented various volumetric and viscometric properties like apparent molar volumes (V_φ), limiting partial molar volumes (V^0_φ), limiting partial molar volumes of transfer ($\Delta_{tr}V^0_\varphi$), limiting partial molar expansibilities (E^0_2),

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viscosity *B*-coefficients and the free energies of activation per mole of solvent ($\Delta\mu_1^{0\neq}$) and solute ($\Delta\mu_2^{0\neq}$). Moreover, V_φ^0 and viscosity *B*-coefficients were split into contributions from zwitterionic end group (NH_3^+, COO^-), CH_2 group, OH group and $CNHNHNH_2$ group. All these significant parameters give a deep insight into the solute-solvent interactions between amino acids and L-ascorbic acid in aqueous solution and also facilitate to study the substance conversion and transfer in living liquid system.

2. Experimental

2.1. Chemicals

The biochemical reagent-grade L-ascorbic acid was used to prepare the mixture solvents with the double-distilled water. The mass fraction purity of glycine, L-alanine, L-valine, L-threonine, and L-arginine are better than 0.99. The specifications of the studied chemicals are given in table 1. Prior to measurement, these chemicals were thoroughly dried in a vacuum desiccator at T = 313.15 K for more than 24 h. All solutions for the whole molality range at room temperature were prepared before use, with the help of an analytical balance with uncertainty of ±0.0001 g. The molality of amino acids was ranging from (0.0 to 0.7) mol · kg^{-1} except L-valine from (0.0 to 0.5) mol · kg^{-1}, while the molality of L-ascorbic acid aqueous solutions was from (0.0 to 0.4) mol · kg^{-1}. The uncertainty of molality for all solutions is ±0.0001 mol · kg^{-1}.

2.2. Measurements

The solution densities were measured by means of a vibrating tube densimeter DMA 4500 (Anton Paar, Austria). The reproducibility of the measurement is $\pm 5.0 \times 10^{-5}$ g · cm^{-3}. The temperature stability of the densimeter was automatically controlled within ±0.03 K. The apparatus was calibrated with doubly distilled degassed water and dry air at atmospheric pressure before each series of measurements [23]. Triplicate measurements of each data were conducted to obtain the average value of density.

Viscosities of glycine, L-alanine, L-valine, L-threonine and L-arginine in L-ascorbic acid aqueous solutions were measured using an iVisc capillary viscometer (LAUDA, Germany) which was calibrated using the flow time of pure water at T = (293.15, 303.15, 313.15 and 323.15) K. A thoroughly cleaned and dried viscometer filled with experimental solutions was placed exactly vertical in a glass sided water thermostat (ET 15S, LAUDA, Germany) controlled to ±0.05 K. After the thermal equilibrium, the efflux time of liquids was recorded automatically by computer software connected to the viscometer. The uncertainty of the time measurement is ±0.01 s. The flow time for each sample was an average of at least four measurements within the deviation of ±0.2 s at a specified temperature. The viscosities η of the solutions were calculated from the following equation [24]:

$$\eta/\eta_w = \rho t/\rho_w t_w, \quad (1)$$

where η, ρ, t and η_w, ρ_w, t_w are viscosities, densities, and flow times of the solutions and pure water, respectively. The viscosity of pure water was obtained from Lange's Handbook of Chemistry [25]. The experimental viscosities were accurate up to ±0.0009 mPa · s.

3. Results and discussion

3.1. Volumetric properties

3.1.1. Apparent molar volume, and limiting partial molar volume

The experimental densities of glycine, L-alanine, L-valine, L-threonine and L-arginine in L-ascorbic acid aqueous solutions at T = (293.15, 303.15, 313.15 and 323.15) K are listed in table 2. The apparent molar volumes, V_φ of amino acids in solution have been computed by the following relation

$$V_\varphi = M/\rho - 1000(\rho - \rho_0)/m\rho\rho_0, \quad (2)$$

where M is the molar mass of the solute, m is the molality of the solute in mixture solvent, ρ and ρ_0 are the densities of the solution and the solvent, respectively. The calculated apparent molar volumes, V_φ, are also included in table 2.

The apparent molar volumes are found to vary linearly with the molar concentration of the solute. Consequently, the limiting partial molar volumes, V_φ^0 (*i.e.* apparent molar volumes at infinite dilution) could be obtained through the following equation:

$$V_\varphi = V_\varphi^0 + S_v C, \quad (3)$$

where S_v is the experimental slope and C is the molar concentration of amino acids in L-ascorbic acid aqueous solutions at T = 293.15 K. In this case, the values of V_φ^0 are obtained by the least-square regression analysis and listed in table 3. The values of V_φ^0 for glycine, L-alanine, L-valine, L-threonine and L-arginine in water at the temperatures studied show an excellent agreement with the data in the literature [26–29].

Clearly, from table 3, the V_φ^0 of amino acids are positive, implying the existence of solute-solvent interaction. It could be found that the V_φ^0 of amino acids increase with the increase of temperature. An increase of temperature may lead to a reduction of the electrostriction and a reinforcement of water structure, hence the limiting partial molar volumes increase. In addition, the V_φ^0 of amino acids except L-arginine in water are much smaller than in L-ascorbic acid aqueous solutions, which indicates the addition of L-ascorbic acid could enhance the solute-solvent interactions. Dramatically, the V_φ^0 of L-arginine decreases rapidly from water to L-ascorbic acid aqueous solutions, which is probably because L-arginine with the longer alkyl chain tends to be less favoured to interact with the solvent. Moreover, V_φ^0 of amino acids are diverse from each other and increase in the order: glycine < L-alanine < L-threonine < L-valine < L-arginine which could be explained through the group contribution in later Section 3.3.

TABLE 1
Specification of studied chemicals.

Chemical name	CAS No.	Molar mass /(g·mol^{-1})	Source	Mass fraction purity[a]
L-ascorbic acid	50-81-7	176.13	Aladdin Chemical Reagent Co., Ltd.	⩾0.997
Glycine	56-40-6	75.07	Zhengzhou Jianda Chemicals Inc.	⩾0.99
L-alanine	56-41-7	89.09	Zhengzhou Jianda Chemicals Inc.	⩾0.99
L-valine	72-18-4	117.15	Zhengzhou Jianda Chemicals Inc.	⩾0.99
L-threonine	72-19-5	119.12	Zhengzhou Jianda Chemicals Inc.	⩾0.99
L-arginine	74-79-3	174.20	Zhengzhou Jianda Chemicals Inc.	⩾0.99

[a] Declared by the supplier.