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Effect of temperature on viscometric properties of aliphatic amino acids glycine/L-alanine/L-valine in aqueous solutions of tetraethylammonium iodide

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ABSTRACT

Viscosities, η, for solutions of glycine, L-alanine and L-valine in (0.03, 0.05, 0.1, 0.15 and 0.2) mol·kg^{-1} aqueous tetraethylammonium iodide (TEAI) at temperature T = (288.15, 293.15, 298.15, 303.15 and 308.15) K have been measured as a function of molality of amino acids. The viscosity *B*-coefficients for the amino acids in aqueous TEAI solutions have been calculated at different temperatures employing the Jones–Dole equation. The trends of variation in viscosity values of amino acids with an increase in molal concentration of TEAI solutions and also with an increase in temperature have been ascribed to the solute–solvent interactions operative in the solutions. The contribution of the solute to the activation parameters ($\Delta\mu_2^{0*}$, ΔH^{0*} and ΔS^{0*}) for viscous flow of the solution has been obtained to throw light on the mechanism of viscous flow. The contributions of the charged end group (NH_3^+,COO^-) and (CH_2) groups of the amino acids to *B*-coefficient and $\Delta_t\mu_2^{0*}$ have also been estimated using the linear correlations between *B*-coefficient or $\Delta\mu_2^{0*}$ and the number of carbon atoms in the alkyl chains of the amino acids. All these parameters have been discussed in terms of the solute–solvent interactions in the ground and transition states.

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1. Introduction

Because of the complex structure of proteins, direct studies of solute–solvent effects on these biological macromolecules are quite difficult [1]. Therefore, to study the interactions of these macromolecules, some simple model compounds such as amino acids which are the basic structural units of proteins [1,2] are generally taken. There is a difference in the side chains of these model compounds due to the size, shape, charge, hydrogen-bonding capacity, hydrophobicity, and chemical reactivity, due to which these side chains contribute to the structure and function of proteins, individually and collectively [3].

Salt solutions have large effects on the structure and properties of proteins including their solubility, denaturation, dissociation into subunits, and the activity of enzymes [4,5]. Thermodynamic and transport properties of amino acids in aqueous electrolytic solutions provide information about the solute–solvent and solute–solute interactions. An understanding of the effect of electrolytes on transport properties of amino acid is a primary requirement in the separation and purification processes of the bio-molecules [6–8]. In the literature there are some reports [9–14] on the effect of various simple salts on the physicochemical properties of amino acids. However, there are only few studies about properties of amino acids in aqueous tetraalkylammonium salts [15–21], probably due to the complex nature of their interactions. The tetraalkylammonium salts with large size appear to have a promoting effect where water is encaging the alkyl chains with the result that water hydrogen-bonding network is stabilized as compared to bulk water [22]. The interaction of water and tetraalkylammonium salts with ions possessing asymmetrical apolar groups may provide evidence of the effect of a single hydrocarbon chain of the cation over the water structure [23,24]. In order to understand the interactions between amino acids and R_4NX, we [16] have very recently reported the densities and ultrasonic speeds of amino acids in aqueous tetraethylammonium iodide solutions and analyzed the volumetric and acoustic properties of amino acid.

The study of viscous behavior of macromolecules in solution is important in understanding the mechanism of transport processes. Viscosity and its derived parameters provide valuable information regarding the shape and size of these molecules [25]. As the viscosity of solution is a vital property in the process of separation, it would be of interest to examine the effect of electrolytes on the viscosity of aqueous amino acid solutions. A careful literature survey shows a complete lack of viscometric investigations of aqueous amino acids in R_4NX solutions, though the viscosities of some amino acids are reported in alkali

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chlorides [9], *KSCN* [10,11], NH_4Cl [12], urea [26], sodium butyrate [13] and sodium acetate [14]. In view of the above, it will be of interest to study the effect of these bulky ions on the viscosity of amino acids.

In continuation of recent work on these systems [15], we now report the viscosities of aqueous solutions of glycine, L-alanine and L-valine in R_4NI and delineate the effect of $(C_2H_5)_4N^+$ ions on the viscosities of these amino acids. We also correlate these viscosities by using a simple equation.

2. Experimental

Glycine (mass fraction > 0.99) and L-alanine (mass fraction > 0.99) were obtained from SD Fine Chem. Ltd., India and L-valine (mass fraction > 0.99) from Loba Chem. Pvt. Ltd. India. The amino acids were used after recrystallization from (ethanol + water) mixtures and dried in vacuum over P_2O_5 at room temperature for at least 72 h. Tetraethylammonium iodide (TEAI) (mass fraction > 0.98) was procured from Acros Organics, New Jersey, USA and purified by recrystallization to ensure maximum purity and dried in vacuum. The specifications and structures of the chemicals used in this study are given in Table 1. The solutions were prepared on molality basis. The concentrations of amino acids were in the range from 0 to 0.2 $mol \cdot kg^{-1}$ while concentration of TEAI varied from 0.03 $mol \cdot kg^{-1}$ to 0.2 $mol \cdot kg^{-1}$. The water used for making the solutions was doubly distilled and deionized by passing it through a Cole-Parmer Barnstead mixed-bed, ion exchange resin column followed by degassing. The weighings were done using an electronic balance precisely up to 0.00001 g. The standard uncertainty in molality as per stated purities is $u_r(m) = 0.01$. The solutions were prepared with utmost care and stored in special airtight bottles to avoid moisture contamination and evaporation.

The viscosity measurements were carried out using a Ubbelohde type suspended level viscometer, which was calibrated with doubly distilled deionized water at temperatures (288.15, 293.15, 298.15, 303.15 and 308.15) K. The efflux time was measured using an electronic watch with a resolution of 0.01 s. An average of three or four readings reproducible within 0.1 s was used as the final efflux time. The combined expanded uncertainties ($k = 2$) for the viscosity are, at least, 1%. A thermostatically controlled, well stirred water bath, whose temperature was controlled to ±0.01 K, was used for all of the measurements.

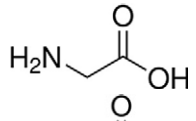
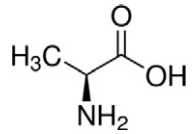
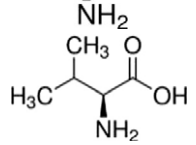
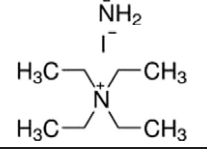
3. Results and discussion

The viscosities η of the solutions were determined from flow time, t, using the equation:

$$\frac{\eta}{\rho} = at - \left(\frac{b}{t}\right) \quad (1)$$

where a and b are viscometer constants and ρ and t are the density and flow time of solution, respectively. The experimentally measured viscosities of aqueous solutions of glycine, L-alanine and L-valine in (0.03, 0.05, 0.1, 0.15 and 0.2) $mol \cdot kg^{-1}$ tetraethylammonium iodide (TEAI) at temperatures T = (288.15, 293.15, 298.15, 303.15 and 308.15) K are listed in Table 2. The viscosity data has also been represented graphically in Figs. 1 and 2. Fig. 1 shows the experimental viscosities for glycine, L-alanine and L-valine in different TEAI solutions at 298.15 K. Fig. 2 represents the viscosity data for glycine in 0.05 $mol \cdot kg^{-1}$ TEAI, L-alanine in 0.1 $mol \cdot kg^{-1}$ TEAI and L-valine in 0.2 $mol \cdot kg^{-1}$ TEAI at different temperatures. Fig. 1 also shows the comparison of viscosities for amino acids in aqueous solutions of TEAI reported in the present study with viscosities for amino acids in aqueous solutions of tetramethyl ammonium iodide (TMAI) [17] and tetrabutyl ammonium iodide (TBAI) [15]. The comparison of the results shows that values of viscosities for all the amino acids increase with an increase in the molar mass of tetra-n-alkyl ammonium salt i.e. with an increase in the alkyl part. This shows that the C_4H_9- group being the most bulky (as compared to C_2H_5- and CH_3-) makes the amino acids more viscous. For all the systems investigated herein, the viscosity of glycine, L-alanine and L-valine is enhanced upon the addition of TEAI. This is due to the fact that with the increase of TEAI concentration, the number of collisions between the molecules also increases to result in a loss of kinetic energy, therefore the molecules tend to stack together to induce the increase in the viscosity. Further, the viscosity values also increase with an increase in the alkyl chain length of amino acids i.e. follows the order: glycine < L-alanine < L-valine. This is possible due to stronger hydrophobic–hydrophobic interaction at longer alkyl chain of amino acids. The viscosity values tend to increase with an increase in amino acid concentration. This may be attributed to an increase in the number of cations and anions like NH_3^+, COO^-, $(C_2H_5)_4N^+$ and I^- of amino acids and TEAI in solutions which may in turn lead to an increase in the

Table 1
Specification of chemical samples.

Chemical name	Provenance	[a]Mass fraction purity	Purification method	Structure
Glycine	SD Fine Chem. Ltd., India	>0.99	Recrystallization	
L-Alanine	SD Fine Chem. Ltd., India	>0.99	Recrystallization	
L-Valine	Loba Chem. Pvt. Ltd., India	>0.99	Recrystallization	
Tetraethylammonium iodide	Acros Organics, New Jersey, USA	>0.98 [b]0.998	Recrystallization	

[a] As declared by supplier.
[b] Mass fraction purity as per certificate of analysis provided by manufacturer.

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