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Viscometric Studies of L-Leucine, L-Asparagine and Glycylglycine in Aqueous Electrolyte Solutions

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Abstract

Viscosity ( ) values have been measured for ternary systems, (amino acid / di-peptide + salt + water): L-leucine / L-asparagine / glycylglycine each in 1.5M aqueous solutions of NaCl or $NaNO_3$ or KNO_3 used as solvents for several concentrations of amino acids / di-peptide at different temperatures in the range of 303.15 to 323.15K.

The viscosity values exhibit usual increasing trend with increase in amino acids / di-peptide concentration and decreasing trend with increase in temperature in all the nine systems under investigation. The trend of variation of calculated specific viscosity (η_{sp}) values with change in concentration of solute and temperature is similar to those of the viscosity values. It has been observed that η_{sp} values are more concentration dependent than temperature. The relative viscosity (η_r) data for all the systems have been fitted to the Jones-Dole equation in order to evaluate the B-coefficient values. The viscosity B-coefficient values for all the three solutes in all the three aqueous electrolyte systems have been found to be positive. The positive values of B-coefficient have been interpreted in terms of the solute-solvent iontermolecular / interionic interactions. The computed viscosity B-coefficient values have been compared with those of the literature values. A good agreement has been found between the observed and literature values.

Keywords: viscosity; viscosity B-coefficient; L-Leucine; L-Asparagine; Glycylglycine; NaCl; $NaNO_3$; KNO_3

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1. Introduction

The viscosity coefficient or simply the viscosity of a liquid, a measure of transfer of linear momentum down a velocity gradient, depends on the spacing between imaginary layers of the liquid and the on the intermolecular / interionic forces operative in it. Viscosity measurement provides valuable information about the size and state of solvation of molecules in solution [280]. The viscometric studies also provide useful information about various types of intermolecular / interionic interactions occurring in solutions [284,334,335] and are of great help in understanding the nature of action of metal ions with amino acids / peptide in body system. The viscosity of the solution increases with increase of concentration of solute.

Viscometric studies are useful for studying the transport properties of liquids. Viscosity is a measure of the resistance of a fluid to flow. The two primary factors that affect the viscosity of a liquid or solution at a given temperature are the molecular structure of the liquid or solution components and the intermolecular / interionic forces operating within the liquid or solution. Molecules with long chains and structures that allow entanglement with adjacent molecules will slow the progress or flow of liquid. The viscosity and its derived parameters such as relative viscosity, specific viscosity and intrinsic viscosity have been used to study the shape and size of the macromolecules, and the intermolecular / interionic interactions in solutions [33,180,249-254]. The specific viscosity data are also used to calculate the hydrodynamic volume of solute. The specific viscosity depends on concentration whereas the intrinsic viscosity is independent of concentration and characteristic of the solute alone [255]. The solute-solvent interactions and the extent of solute hydration can also be studied in terms of B-coefficient of Jones-Dole equation [256]. The B-coefficient is a measure of effective solvodynamic volume of solvated ions and is governed by the size and shape effects of solute and the structural effect induced by the solute-solvent interactions [257-279]. The effect of solute size on the B-coefficient is apparent from solvodynamic theories applicable to particles in a fluid continuum. In these theories, the increase in viscosity due to the presence of the particles arises from the fact that they lie across the fluid streamlines and are subject to torsional forces. They tend to rotate, and thus absorb energy, this energy absorption corresponding to an

increased viscosity for the solution. A 'structure-building' solute lowers the average effective kinetic energy of the solvent molecules and thus increases the viscosity of the solution, and leads to a high B-coefficient. Because of the exponential relationship between viscosity and temperature [280], a rise in temperature of the solution as a whole causes B-coefficient to fall, this fall being greater at low than at high temperatures. Such behaviour has been used to identify 'structure-forming' solutes [281]. Conversely, 'structure-breaking' solutes should have rather low B-coefficients, which increase with temperature [275,281].

In the case of electrolytes, the B-coefficient is a measure of the order or disorder introduced by ions into their co-spheres [282]. A positive B-coefficient indicates that the ions tend to order the solvent structure and increase the viscosity of the solution, whereas a negative B-coefficient indicates disordering and a decrease of viscosity. The partitioning of the B-coefficient into their ionic components was first proposed by Cox and Woefenden [283] and it was re-examined by Gurney [284] and Kaminsky [285].

The viscometric studies of amino acids and peptides have been carried out by a number of workers [33,233, 234, 251, 257, 258, 267, 269, 270, 272, 275, 279, 281] in aqueous solutions and mixed aqueous solutions. According to J. Daniel et al. [336] charge distribution in an amino acid / peptide is less important than the size and structure of hydrocarbon portion in determining viscosities of aqueous solution containing these solutes. The relative viscosity data is employed in Jones-Dole equation [231,256,262,263,265,266] for the calculation of viscosity B-coefficients. The coefficient B depends on the strength and extent of the solute-solvent interactions as well as on shape, size and charge of the solute molecules. Solutes, which disrupt the hydrogen bonded water structure in their vicinity and thus create a region of lower viscosity, have relatively low B-coefficients, which increase, as the temperature is raised [280]. Conversely, solutes, which enforce water structure, e.g., by hydrophobic hydration, have relatively large B-coefficients, which decrease as the temperature is increased [281].

A number of authors have investigated the viscosity B-coefficients of various amino acids and peptides in aqueous medium [231,258,269,275], aqueous-organic solvents

[231,233,234,267,270,276] and aqueous solutions of LiCl, NaCl, KCl, KBr [236, 249, 263], $BaCl_2$ [263], NH_4Cl [259], Na_2SO_4 [249], CH_3COONa [265,278], $CH_3CH_2CH_2COONa$ [262], KSCN [261,316], NaC_8 [266], and GuHCl [260,337].

Consequently, in the present work, the viscosities of ternary solutions, (amino acids / di-peptide + salt + water): L-leucine / L-asparagine / glycylglycine + (1.5M) NaCl / $NaNO_3$ / KNO_3 + water have been measured as functions of concentration of amino acids / di-peptide as well as of temperature. These measured viscosity data have been used to calculate the relative viscosity, specific viscosity and B-coefficients for the systems under investigation. The results have been discussed in the light of solute-solute and solute-solvent interactions and structural effects of solute in solutions.

2. Experimental

The amino acids: L-leucine, and L-asparagine hydrate and di-peptide: glycylglycine used in this work were obtained from SRL (Mumbai). The salts namely, sodium chloride, sodium nitrate and potassium nitrate were purchased from E. Merck (India). All the chemicals were of ≥99% purity. The amino acids and di-peptide were used as such without further purification. They were dried at ~110^oC and kept in vacuum desiccator over P_2O_5 for several hours before use. The salts were recrystallized twice in triply distilled water, dried in a vacuum oven and then kept over P_2O_5 in a vacuum desiccator at room temperature for a minimum of 24 hours. All the solutions were made by weight using a balance having an accuracy of ±0.1 mg. Stock solutions of 1.5 M concentration of NaCl, $NaNO_3$ and KNO_3 prepared in triply distilled water and used as solvents for the preparation of solutions. Various molal solutions of amino acids and di-peptide were prepared in 1.5 M aqueous solutions of NaCl, $NaNO_3$ and KNO_3. Pyknometer consisting of a small bulb with flat bottom of approximately 8.5 ml capacity having a graduated stem was used for the density measurements. The volume at each mark of the pyknometer was calibrated with the triple distilled water. The densities of pure water at various required temperatures were taken from literature for calibration purpose [286]. In order to check the reproducibility of calibration, the same process was repeated a number of times with different amounts of water. The reproducibility of density values was found to be within

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±0.0002 gm/cm^3. Cannon-Fenske viscometer was used for the viscosity measurement of various solutions under study. The viscometer consists of three parallel arms with a common base. The viscometer was calibrated with the triple distilled water. The viscosity coefficient values of water at different temperatures were taken from literature [287]. The reproducibility in viscosity measurements was found to be within ± 0.003x10^{-4} Nm^{-2}s.

3. Results And Discussion

The measured viscosity values of ternary systems: amino acids / di-peptide-electrolyte-water as functions of concentration and temperature have been listed in Table 1. These data have been least-squares fitted to the equation,

$$| = |_0 + |_1 m + |_2 m^2 \qquad (1)$$

where $|_o$, $|_1$ and $|_2$ are the fitted coefficients, and m is the molal concentration of amino acids / di-peptide in solution. The fitted coefficients alongwith standard deviations are listed in Table 2. The plots of viscosity data versus concentration (molality) have been shown in Figs. 1-9. The viscosity values increase with increase in concentration of amino acids / di-peptide and decrease with increase in temperature in all the systems under investigation. The increase in viscous behaviour of the solution with increase in concentration of amino acids / di-peptide may be attributed to an increase in intermolecular / interionic interactions in solutions, which in turn, may cause more frictional resistance to the flow of solutions. An increase in temperature may increase the kinetic energy of molecules and ions of solutions, which in turn may cause a decrease in the intermolecular / interionic forces operative in solutions consisting of the zwitterions, ions and water dipoles. This decrease in intermolecular / interionic forces seems to be responsible for the decreasing trend of variation in viscosity values with increase in temperature. The viscosity values for the amino acids / di-peptide (L-leucine, L-asparagine and glycylglycine), in an aqueous electrolyte solution, i.e., in 1.5M aqueous solution of either NaCl, $NaNO_3$ or KNO_3 vary as,

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L-asparagine < glycylglycine < L-leucine.

This trend of variation of viscosity values may be interpreted in terms of the size and structure of the hydrocarbon portion of the amino acids / di-peptide molecules rather than the charge distribution on them. The structure of hydrocarbon portion of L-leucine is more unsymmetrical than the hydrocarbon portion of glycylglycine and L-asparagine. On the other hand, the hydrocarbon portion of glycylglycine is larger than that of L-asparagine. Therefore, the viscosity of a solution having L-leucine is the maximum while a solution having L-asparagine is the minimum. This finding substantiates the view of J. Daniel et al. [336] that charge distribution in an amino acid / peptide is less important than the size and structure of hydrocarbon portion in determining viscosities of aqueous solution containing these solutes. However, the trend of variation in viscosity values of solutions containing an amino acid / di-peptide that is either L-leucine, L-asparagine or glycylglycine in 1.5M aqueous solutions of NaCl, $NaNO_3$ and KNO_3 is as follows:

$$NaCl > NaNO_3 > KNO_3.$$

This trend of variation of viscosity values may be attributed to the size of Na^+, K^+, Cl^-, NO_3^- ions. The electrostatic interactions of smaller ions (Na^+ and Cl^-) with zwitterions and water dipoles are stronger than those of larger ions (K^+ and NO_3^-). Hence, the viscosity of an aqueous solution of NaCl is maximum whereas that of KNO_3 is minimum due to the nature of interionic / intermolecular interactions.

The relative viscosities, η_r, for amino acids / di-peptide in 1.5M aqueous electrolyte solutions have been calculated using the following equation and are summarized in Table 4.3,

$$\eta_r = \eta / \eta_0 \qquad (2)$$

where η and η_0 are the viscosities of solution and solvent, respectively. There is an increasing trend of variation in relative viscosity values with increase in concentration of solutes in solutions. However, η_r values do not show a regular trend of variation with temperature.

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The specific viscosity, η_{sp}, which represents the relative increase in the viscosity of solution on addition of the solute, can be expressed as follows:

$$\eta_{sp} = (\eta - \eta_0) / \eta_0 \qquad (3)$$

where the terms have their usual meaning. The η_{sp} values have been presented in Table 4. The η_{sp} values increase with increase in concentration of amino acids / di-peptide in all the nine ternary systems. Similar to η_r values, the η_{sp} values also do not show a regular trend of variation with temperature. A close examination of Table 4 indicates that the η_{sp} values are found to be more concentration dependent as compared to temperature.

The dependence of viscosity on concentration for systems under investigation has been analyzed in terms of the semi-empirical Jones-Dole equation [231,262,263,265,266],

$$\eta / \eta_0 = 1 + Bc \qquad (4)$$

where B and c are the Jones-Dole coefficient, a characteristic of solute-solvent interactions, and concentration of solution in moles per litre, respectively. The B-coefficient values are equal to the slope values of linear plots of (η/η_o) versus c. These values have been computed by employing the least-squares fitting method. The computed values of B-coefficients are listed in Table 5. The typical plots of (η/η_0) versus c have been depicted in Figs.10-18. The. B-coefficient is a measure of order or disorder introduced by the ions or solute into the solvent. A close examination of the Table 5 shows that the B-coefficient values for L-leucine, L-asparagine and glycylglycine in all the electrolyte solutions are positive. The positive B-coefficient values indicate the strong solute-solvent interactions in the systems under investigation. The observed B-coefficient values of glycylglycine in all three aqueous electrolytes solutions are larger than the corresponding reported values in aqueous medium. The reported values of B-coefficient for glycylglycine in water are 0.315, 0.352 (at 298.15), 0.250 (at 303.15), 0.298 (at 308.15) and 0.337 (at 313.15K) [231,275]. The observed values of B-coefficients for L- leucine and L-asparagine could not be compared to the literature values as these are not available at the temperature: 303.15K or at higher temperatures. However, the reported values for L- leucine at 298.15 K are 0.453 [263], 0.576 [231], 0.537 [265] and 0.487 [258] in aqueous medium; 0.479

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in aqueous glucose solution [263]; 0.570 in aqueous sucrose solution [263]; 0.408 in aqueous KCl solution [263]; and 0.361 in aqueous KCl solution [263]. The literature values are quite close to the present observed values listed in Table 5. In addition, the literature values for L-leucine at 298.15K in aqueous solutions of n-propanol [231], 1,2-propanediol [267], 1,4-dioxane [234] and sodium acetate [265] are also in good agreement with the present observed values. The higher values of B-coefficients of L- leucine and glycylglycine in 1.5M aqueous solutions of NaCl, $NaNO_3$ and KNO_3 than those in water may be attributed to the enhancement of solution structure in the presence of electrolytes. This promotion of structure of solutions reflects the net structure effects of the charged ends and the hydrophobic $-CH_2$ groups of the L-leucine and glycylglycine on the said aqueous electrolyte solutions.