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ABSTRACT

The present work deals with the interactions of biomolecules in mixed aqueous solvents of varied natures.

Chapter 1:- It provides a collection of most recent review on the interactions of biomolecules (amino acids) in aqueous and aquo- organic solvents. An exhaustive literature survey reveals that there have been a lot of thermodynamic and transport studies on amino acid- water, amino acid- aqueous electrolyte, and amino acid- aquo- organic mixtures. But, very few studies have been reported on interactions of amino acids in mixed solvents containing hydrophilic/hydrophobic solutes.

Chapter 2:- It describes, in detail, the experimental techniques for the purification and preparation of sample mixtures. Methods of determination of densities, viscosities and refractive indices of the solutions containing biomolecules. Further, necessary precautions were taken to get reliable experimental data.

Chapter 3:- Experimental values of densities, r , viscosities, h , and refractive indices, n_D of urea and D- glucose (0.01, 0.02 and 0.03 M) in aqueous glycine (Gly) (0.01, 0.03, 0.05, 0.07, 0.09, and 0.10 M) have been measured at 308 K. The experimental values of r , h , and n_D were used to compute limiting apparent molar volume (also known as partial molar volume), f^0_v, slope S^*_v of Masson's equation, Falkenhagen coefficient, A, viscosity B- coefficient (using Jones- Dole equation), free energy of activation per mole of solvent, D $m^{0\#}_1$, and per mole of solute, D $m^{0\#}_2$ (using transition- state theory), molar refractive index, R_D of the system. The results suggest that both urea and glucose behave as structure- makers in aqueous glycine and, also, solute- solute interaction is more pronounced than solute- solvent interaction.

Chapter 4:- Densities, viscosities, and refractive indices of (0.10 to 0.50 M) glycine in aqueous diols (1,2- ethanediol, 1,2- propanediol and 1,3- butanediol) (30 % v/v) were measured at 298, 303, 308, and 313 K. Using these values, the values of f^0_v and partial molar volumes of transfer of Gly from water to aqueous diol solution, f^0_v(tr), A and B- coefficients, D $m^{0\#}_1$, D $m^{0\#}_2$, activation enthalpies, D H^* and entropies, D S^* of viscous flow, and R_D were calculated. The derived values indicate that the electrostriction effect in

diols increases in the order: 1,3- BuD < 1,2- PrD < 1,2- EtD, which is also the order of the strength of interaction between Gly and diol molecules.

Chapter 5:- The values of r , h , and n_D were measured for 0.01, 0.02, 0.03, 0.04, and 0.05 M amino acids (Gly, DL- alanine (Ala), DL- valine (Val)) in 0.01 M aqueous tetramethyl/- ethylammonium bromide. These experimental data were used to evaluate the values of f^0_v, f^0_v(tr), side- chain contribution of amino acids, f^0_v(R), A and B- coefficients, D $m^{0\#}_1$, D $m^{0\#}_2$, contributions of zwitterionic end group (NH_3^+, COO-) and methylene group (- CH_2) of amino acids to f^0_v and D $m^{0\#}_2$, and R_D. f^0_v has been explained using cosphere overlap model in the light of the overlap of cosphere of two ionic species, overlap of hydrophobic- hydrophobic groups and ion- hydrophobic groups. The results indicate the presence of strong solute- solvent interaction, which follows the sequence: Gly < Ala < Val. Further, the interaction between R_4NBr and (NH_3^+, COO-) group is much stronger that between R_4NBr and CH_2 group.

Chapter 6:- Densities, viscosities and refractive indices were measured for 0.10, 0.20, 0.30, 0.40, and 0.50 M Gly, Ala, and L- serine (Ser) in aqueous 1- propanol (10 and 30 % v/v) at 308 K. The values of f^0_v, A and B- coefficients, D $m^{0\#}_1$, D $m^{0\#}_2$, and R_D were calculated for these ternary systems. These parameters suggest strong solute- solvent but weak solute- solute interactions in these systems.

Chapter7:- Densities, viscosities, refractive indices of Gly, Ala, DL- a - amino- n- butyric acid (Abu), Val, and L- leucine (Leu) in the concentration range 0.02 to 0.10 m in (5 % v/v) aqueous glycerol were measured at 298, 303, 308, and 313 K. From these experimental data, values of f^0_v, f^0_v(tr), A, and B- coefficients, D $m^{0\#}_1$, D $m^{0\#}_2$, D H^*, D S^*, f^0_v (NH_3^+, COO-), f^0_v (CH_2), f^0_v(R), B (NH_3^+, COO-), B (CH_2), D $m^{0\#}_2$ (NH_3^+, COO-), D $m^{0\#}_2$ (CH_2) and R_D were computed and analysed in order to get an insight into the solute- solute and solute- solvent interactions in these mixtures.

Some of the parameters used in this work and calculated by using the following relations:

$$\phi_V = \frac{1000(\rho_0 - \rho)}{C\rho_0} + \frac{M}{\rho_0} \quad (1)$$

$$\phi_V = \phi_V^0 + S_V^* \, C^{1/2} \quad (2)$$

$$\phi^0{}_v(\text{tr}) = \phi^0{}_v(\text{in ternary mixture}) - \phi^0{}_v(\text{in water}) \quad (3)$$

$$\phi^0{}_v(\text{R}) = \phi^0{}_v(\text{amino acid}) - \phi^0{}_v(\text{Gly}) \quad (4)$$

$$\phi^0{}_v = \phi^0{}_v(NH_3^+, COO^-) + n_C \, \phi^0{}_v(CH_2) \quad (5)$$

$$\frac{\eta}{\eta_0} = \eta_r = 1 + AC^{1/2} + BC \quad (6)$$

$$B = \frac{1}{1000}\left[\left(\bar{V}_1^0 - \bar{V}_2^0\right) + \frac{\bar{V}_1^0\left(\Delta\mu_2^{0\#} - \Delta\mu_1^{0\#}\right)}{RT}\right] \quad (7)$$

$$\Delta\mu_1^{0\#} = RT \ln\left[\frac{\eta_0 \bar{V}_1^0}{h\,N}\right] \quad (8)$$

$$\Delta\mu_1^{0\#} = \Delta\mu_1^{0\#} + \left[\frac{R\,T}{\bar{V}_1^0}\right]\left[1000\,B - \left(\bar{V}_1^0 - \bar{V}_2^0\right)\right] \quad (9)$$

$$\Delta\mu^{0\#}{}_2 = \Delta\mu^{0\#}{}_2(NH_3^+, COO^-) + n_C \, \Delta\mu^{0\#}{}_2(CH_2) \quad (10)$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (11)$$

$$\Delta S^* = \frac{-\,d\left(\Delta G^*\right)}{dT} \quad (12)$$

$$R_D = \left[\frac{n_D^2 - 1}{n_D^2 + 2}\right]\left[\sum_{i=1}^{3} \frac{x_i \, M_i}{\rho}\right] \quad (13)$$

where C is the molar concentration of solute (amino acid), n_C is the number of carbon atoms in alkyl chain of amino acid, (i =1,2) is the partial molar volume of the i^{th} component of the mixture, x_i and M_i are the mole fraction and molar mass of the i^{th} component,

respectively.