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Intermolecular interaction studies in some amino acids with aqueous NaOH

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ABSTRACT

The ultrasonic Studies in liquids are great use in understanding the nature and strength of molecular interactions. The ultrasonic studies of biological materials in aqueous medium are ionized & can act as knowledge of the acid- base properties of proteins. The thermoacoustic analysis in biological medium would be interesting to discuss nonlinear behaviour with respect to concentrations and temperatures. Ultrasonic studies may throw more light on the molecular interactions to know the behaviour of biological macromolecules in aqueous solution. It is the key to solve the critical problems with the role and interaction of these substances in living organisms.Ultrasonic velocities, densities, viscosities, relaxation time and ultrasonic absorption of amino acids L-Histidine, L-Arginine, L-Cysteine, and L-Tyrosine in 1M Aqueous NaOH solutions have been measured as a function of amino acid concentration at different temperature (298.15K, 303.15K, 308.15K and 313.15K) using pulse echo overlap technique of frequency 2 MHz. Using density and ultrasonic velocity data, volume expansivity, reduced volume, Moelwyn-Hughes parameter, Bayer's nonlinearity parameter, Gruneisen parameters, fractional free volume, repulsive exponent, internal pressure, cohesive energy density, etc. values have been computed. The formation of Zwitterions Na^+/OH water dipole aggregates in solutions causes the release of water associated with Zwitterions to bulk water. The trends in the behaviour of said thermoacoustic properties with changes in the concentration of amino acids as well as in temperature have been discussed in terms of Zwitterions-ions, Zwitterions- water dipoles, ions-ions, ions-water dipole, intermolecular and interionic interaction operative in the said systems. The nonlinear variation of thermoacoustic parameters have been also discussed in light of complex formation in the solutions.

Keywords: Relaxation time, Zwitterions, Interionic interaction, Moelwyn-Hughes parameter, Bayers nonlinearity parameter, Gruneisen parameter

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INTRODUCTION

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Thermodynamic properties of amino acids i.e. proteins in electrolyte solution provide information about solute- solvent interactions, those are important in understanding the stability of Proteins. Some of these interactions are found applicable in several biochemical and physiological processses in a living cell [1]. A better understanding of the effect of electrolytes on the thermodynamic properties of amino acids in aqueous solution is of vital importance beacause such studies give useful information regarding protein unfolding [2] and the extent of hydrophobic interactions of nonpolar side chains [3]. Salt- protein interaction induced electrostatic forces are used to play a very important role in modifying the protein structure by affecting properties like solubility, denaturation and activity of enzymes[4].

Proteins are linear, large complex molecules, heterogeneous polymers genetically mandated with 20 different building blocks of all living organisms, which residues linked by covalent peptide bonds (-CO-NH-) into the polypeptide chain. Due to physiological conditions, the two terminals of amino acids are charged both positive charge (amino group NH_3^+) and negative charge (Carboxyl group, COO^-). Therefore the molecules has the properties of a "Zwitterion"[5].Volumetric properties [6] and thermodynamic properties[7] such as free energy, entropy and enthalpy of amino acids in aqueous electrolyte solution are the important tools to investigate the interaction between ionic salts and amino acids. These result lead to the conclusion that some of the electrolytes can stabilize the biological important molecule i.e. proteins. The effect of electrolytes on the structure and function of proteins and nucleic acids in terms of their structure- making or breaking property has been studied by number of researchers [8-11].

Due to the complex structure of proteins, a variety of different interaction with salt may occure, & it is difficult to resolve in a straightforward manner, the various interactions participating in protein hydration. Therefore to obtain more insight into the hydration of proteins and non-covalent forces i.e. hydrogen bonding and electrostatics interaction stabilizing their native structure [12].

According to exhastive literature survey, very few attentions have been given recently to the effect of electrolytes on the stability of proteins and polypeptides in aqueous solutions. However for completely understanding the influence of electrolytes on amino acids and their molecular interactions between salt & proteins functional group, more detailed investigations on thermodynamic behaviour are still needed.

In order to improve our understanding of the ionic salt effect on the aqueous amino acid solutions, the present study focussed on interactions between four amino acids (L-Histidine, L-Arginine, L-cysteine & L-Tyrosine) with 1M aqueous NaOH solutions via ultrasonic velocity, density, viscosity and ultrasonic absorption etc.Using these data, the adiabatic compressibility, volume expansivity, Moelwyn-Hughes parameter, Bayers nonlinearity parameter, Gruneisen parameter, repulsive exponent etc.as a function of solute concentration and temperature have been evaluated with a view to investigating the Zwitterions-ion, Zwitterions-water dipoles, ion-water dipole and ion-ion interactions operative in the systems.

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EXPERIMENTAL SECTION

The amino acids L-Histidine, L- Arginine, L-cysteine & L-Tyrosine and the salt sodium hydroxide (NaOH) used in the present study were of high purity(99%) were purchased from E.Merck(India). The amino acids and salt were used without further purification, and double distilled, deionised water was used. All the solutions were prepared by mass on electronic balance precise to within $\pm$ 0.0001 gm. Stock solutions of 1M aqueous NaOH were prepared in double distilled water and were used as solvents for the preparation of amino acid solutions of different molar concentrations at temperature range 298-313K. The solution were prepared with ultramost care and stored in special airtight bottles to avoid the exposure of solutions to air and evaporation.

The densities of the mixed solvent and the amino acid solutions were measured by using a hydrostatic plunger method. An Automatic ultrasonic attenuation recorder (AUAR-102), Innovative Instrument, Hyderabad, India based on Pulse Echo Overlap technique was used for the measurement of ultrasonic velocity at a frequency of 2 MHz at different concentrations and temperatures. Water from ultra-thermostate (Type U-10) was circulated through the brass jacket surrounding the liquid cell and the quartz crystal. The jacket was well insulated and the temperature of the solutions under study was maintained to an accuracy of $\pm$ 0.01^0C. The instrument was calibrated with the double distilled water.The viscosity of the solutions was measured using a Ostwald Viscometer. Time required for flow of water was measured using a racer digital stopwatch with an accuracy $\pm$ 0.01 Sec.An average of three readings was taken as the final value of time. The accuracy in the measurements of viscosity is 0.01%. The uncertainties in ultrasonic velocity and density measurements were found to be within $\pm$ 0.2 m/s and $\pm$ 0.0001 gm-cm^{-3} respectively. These experimental results have been used to calculate adiabatic compressibility, volume expansivity, Moelwyn-Hughes parameter, Bayers nonlinearity parameter, Gruneisen parameter, repulsive exponent etc.as a function of solute concentration and temperature with the help of standard formulae .

RESULTS AND DISCUSSION

The measured ultrasonic velocity (u), density (ρ) and viscosity (η), classical ultrasonic absorption(α/f^2), relaxation time(τ), adiabatic compressibility(β_a), volume expansivity(α), Moelwyn-Hughes parameter(C_1), Bayers nonlinearity parameter(B/A), Gruneisen parameter(Γ), fractional free volume(f), repulsive exponent(n), Internal pressure(Pi), cohesive energy density($\in$) values for four ternary systems:L-Histidine, L- Arginine, L-cysteine & L-Tyrosine with aqueous NaOH as a function of amino acid concentration at temperature of 303K are graphically represents in figures 1-12. All measured thermodynamic parameters are linearly increase or decrease with rise in temperature in all the systems under investigation.The density values in amino acids with aqueous NaOH have been found to be higher than those of water at all temperatures. The data for other temperatures are not shown due to similar variation.The variation of τ, (α/f^2)class, Pi, α, f, $\in$ with increase in molar concentration of all amino acids(C_m) in 1M aqueous NaOH shows similar behaviour whereas the variation of C_1, Γ, n, B/A shows exactly opposite behaviour in all the systems under investigation.

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From the figures, it is observed that all the systems seem to exhibit almost nonlinear behaviour in the variation of all thermodynamic parameters with rise in amino acid concentration. This may be the indication of complex formation [13-14] and molecular interaction [15] due to the possibility of hydrogen bond formation between water, NaOH and amino acid molecules.

When NaOH is dissolved in water, the sodium ion (Na^+) has a stucture breaking effect, would first disrupt the water structure.This could be followed by structural reorganization leaving the molecules in closely fitting helical cavities[16]. This would cause an increase in closed packed structure as the cohesion between water molecules increases [17].This makes the liquid medium less compressible and hence the ultrasonic velocity increases above that of pure water value.

The increase in ultrasonic velocity values of L-Arginine, L-Histidine, L-Cysteine and L-Tyrosine-1M aqueous NaOH solution may be attributed to the overall increase of cohesion brought about by solute-solute, solute-solvent and solvent-solvent interaction in solution. Na^+ ions furnished by NaOH will have affinity for $-COO^-$ end group of Zwitterons of L-Arginine, L-Histidine, L-Cysteine and L-Tyrosine. Whereas the OH^- ion of salts may interact with $-NH_3$ group of Zwitterions of the said amino acids. In addition, the water dipoles are strongly aligned to the ions, i.e. Na^+ & OH^- as well as to the Zwitterions as the result of electrostatic forces.These interaction comprehensively introduce the cohesion into solutions. The added amount of amino acids/Zwitterions to 1M aqueous NaOH solution may have occupied the cavities of water clusters which may lead to the formation of denser medium of aqueous electrolyte solutions [18]. This process may have continued until a concentration of amino acids is reached at which all cavities are filled. Raman studies substantiate the view that the Zwitterions-water entities are formed in solutions increase on the addition of amino acids in solution. Kumar & Badrayani [19] reported that the ultrasonic velocity and density values of glycine –aqueous NaBr/KCL/KBr/ $MgCl_2$ increase with increase in concentration of solute and temperature. It appears that the rise in temperature causes the thermal rupture of the ice like structure of water, which in turn, enhances the cohesion in solution.It further seems that the cohesion factor dominate over the thermal expansion factor in solutions with increase in temperature.

Using the measured ρ & u values, the adiabatic compressibility values for the said systems have been calculated employing the following relation:

$$\beta_a = 1/\rho u^2$$

The decrease in β_a values for water on addition of the NaOH in it may be ascribed to the introduction of incompressible Na^+ & OH^- ions into water and the formation of Na^+ & OH^- water-dipole incompressible entities in salt solutions. The presence of these entities in the salt solutions makes them less compressible than that of pure water. The decrease in adiabatic compressibility values with rise in temperature in all the systems under study may be explained in terms of the changes occurred in water structure around Zwitterions and ions [20].Water is regarded as an equilibrium mixture of two structures such as an ice like structure and a closed packed structure [21].

Compressibility of a liquid water is expressed by $\beta_a = \beta_\infty + \beta_{relax}/(1+ w^2 \tau^2)$, where β_∞ is the instantaneous part of compressibility and β_{relax} a relaxational part of compressibility[22].The relaxational time τ, corresponding to β_{relax} is of the order of 10^{-11} Sec.The relation $w\tau < 1$ is

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assumed to be valid in the present study, where w is the angular frequency. Thus the adiabatic compressibility obtained is equal to ($\beta_\infty + \beta_{relax}$). With the rise in temperature β_∞ increases due to the thermal expansion and β_{relax} decreases due to the thermal rupture of the ice-like structure. Thus the decrease in adiabatic compressibility values with increase in temperature may be attributed to the corresponding decrease of β_{relax} , which is dominent over the corresponding increase of β_∞.

An increase in internal pressure (Pi) shows the orientation of the solvent (aqueous NaOH) molecules around the amino acid ions, which may be due to the influence of electrostatic field of ions.This means solution becomes less compressible. It indicates the associating tendency of the molecules in the amino acid solutions.Conversely, the reduction in Pi shows dissociating tendency of the molecules in the solutions.

The Moelwyn-Huges parameter (C_1) is found to be nearly equal to 11 in aggrement with the values of C_1 in other non-associated liquids[23].This signifies the nonlinear variation of volume expansivity(α) of the liquids with molar concentration C_m.In present amino acids with aqueous NaOH solutions the variation of C_1 shows opposite behaviour than α.This may be due to associating tendency of the solutions.

The increase of Bayer's nonlinearity parameter(B/A) & Gruneisen parameter(Γ) shows the decrease in intra molecular modes of vibration and anharmonicity in all the systems under study.It also indicates the associating tendency and weak intermolecular forces in the amino acid solutions[24].The decrease in B/A and Γ shows the increase in intramolecular modes of vibration and harmonicity in the solutions.This indicate dissociating nature in all ternary systems is attributed to strong intermolecular forces.

The average values of fractional free volume (f) for all the systems are about 0.12 as compared to about 0.15 for fluorocarbon fluids & 0.20 for saturated hydrocarbon liquid [25]. This suggests that free (available) volume in the present solutions are less than fluorocarbon fluids. The increasing values of reduced volume ($\tilde{V}$) & f shows enhancement in disorder in the liquids beacause of increased mobility of the molecule.

The values of repulsive exponent (n) are found to be ~ 34, which of the same order as polymer & fluorocarbon fluids [26].The high value of 'n'shows the bulk nature of the molecules. The increase in repulsive exponent with molar concentration shows associating tendency of the molecules in the amino acid solutions.The low value of 'n' shows repulsive forces at the slightly larger distances in the liquids than in solids.

The molar concentration that corresponds to the maximum classical absorption may be called critical concentration. At critical concentration the solution is more structured due to the formation of hydrogen bond. This highly structured solution generally absorbs more ultrasonic energy. The maximum occur at particular concentration may indicate a remote possibility of the formation of an aggregate containing the molecules of amino acid, water and NaOH molecule. These molecular aggregates form large molecular clusters. This aggregation of many small molecules is bound together by cohesive forces [27].

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The cohesive energy of a material is the energy required to disassemble it into its constituent parts, also known as binding energy. The increase in cohesive energy density (Є) with increase in molar concentration shows associating tendency of molecules in the solutions.
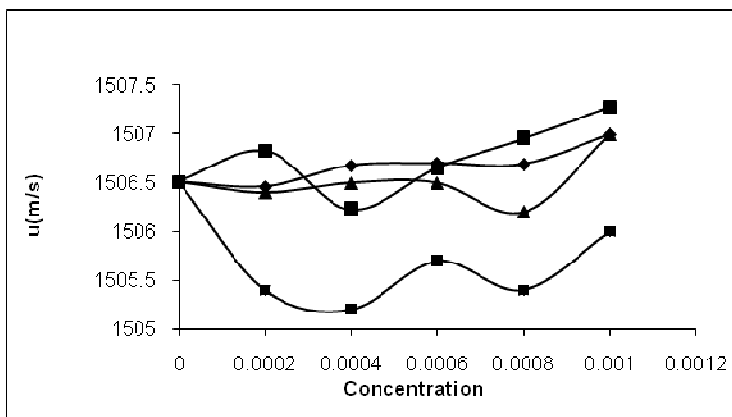
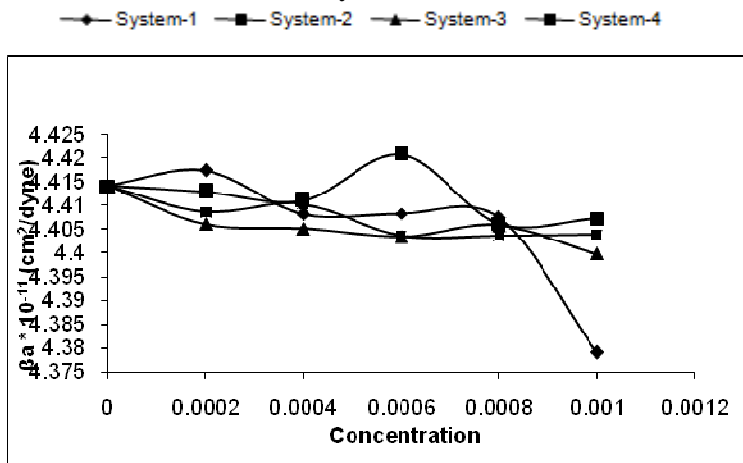**Fig. 1 Variation of Ultrasonic velocity with molar concentration of amino acids**
—◆— System-1 —■— System-2 —▲— System-3 —■— System-4

Fig. 2 Variation of adiabatic compressibility with molar concentration of amino acids
—◆— System-1 —■— System-2 —▲— System-3 —■— System-4
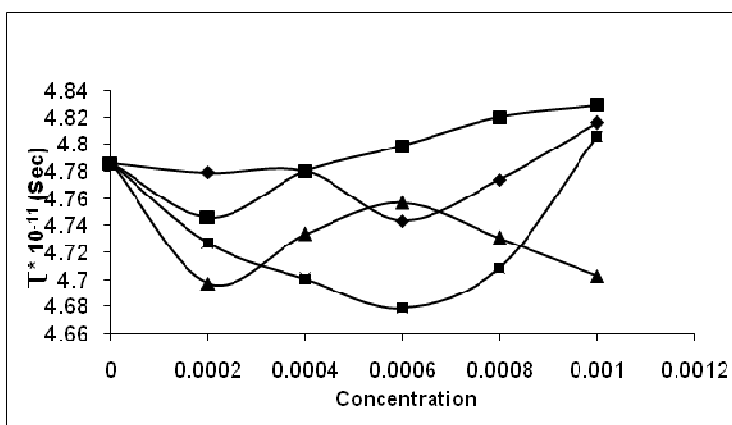
Fig. 3 Variation of relaxation time with molar concentration of amino acids
—◆— System-1 —■— System-2 —▲— System-3 —■— System-4
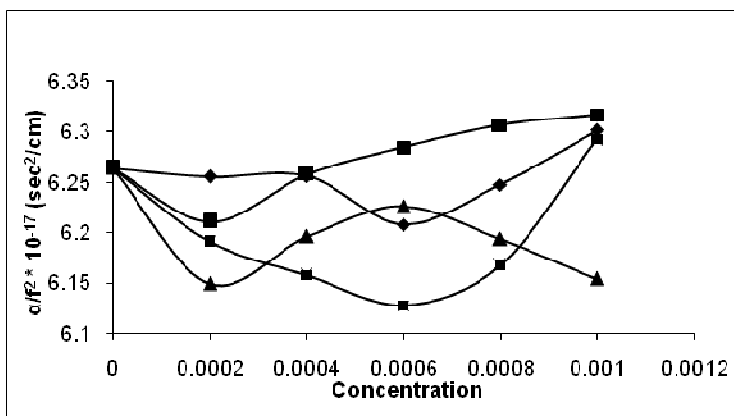
Fig. 4 Variation of ultrasonic absorption with molar concentration of amino acids
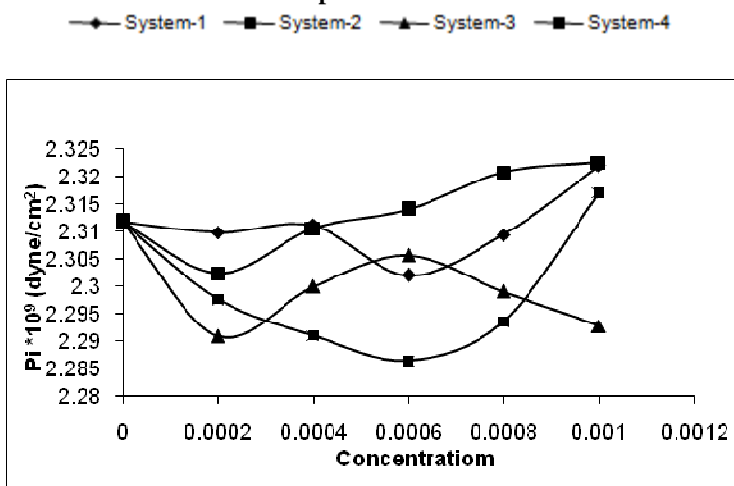
Fig. 5 Variation of Internal presssure with molar concentration of amino acids
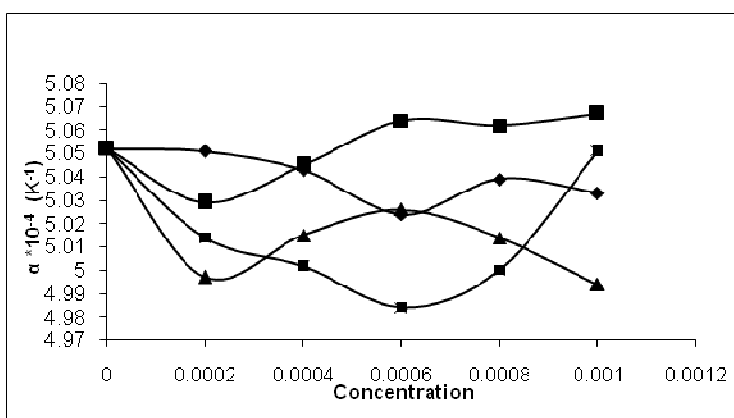
Fig.6 Variation of volume expansivity with molar concentration of amino acids
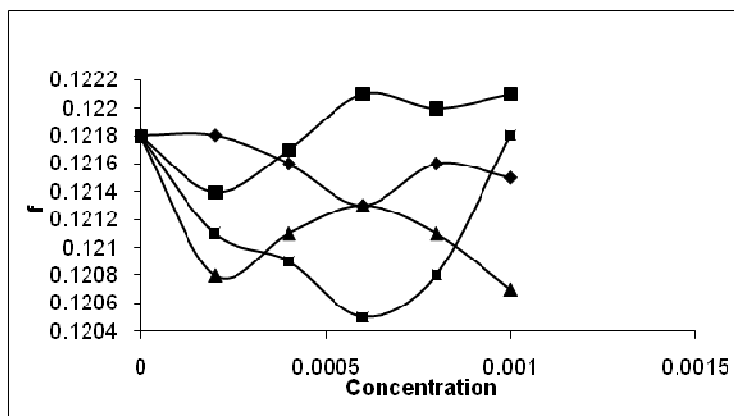
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Fig.7 Variation of fractional volume with molar concentration of amino acids
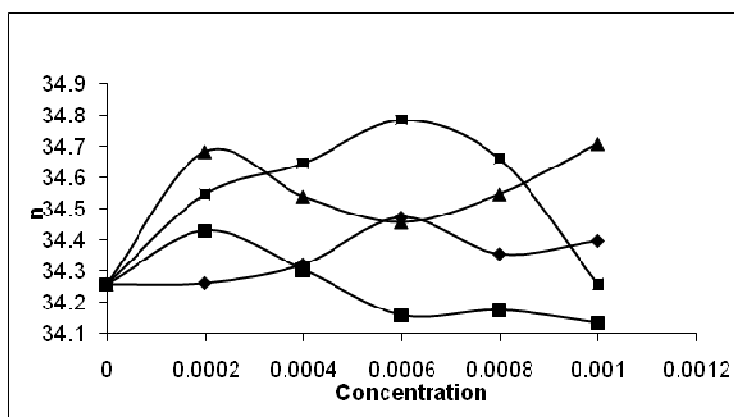
System-1 —■— System-2 —▲— System-3 —■— System-4

Fig. 8 Variation of repulsive exponent with molar concentration of amino acids

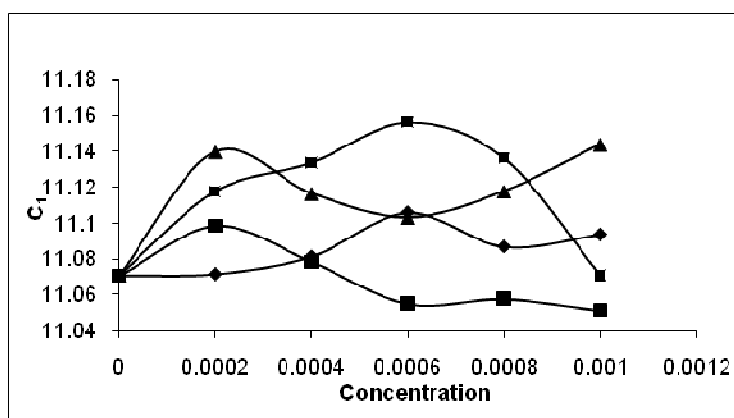System-1 —■— System-2 —▲— System-3 —■— System-4

Fig. 9 Variation of Moelwyn Hughes parameter with molar concentration of amino acids

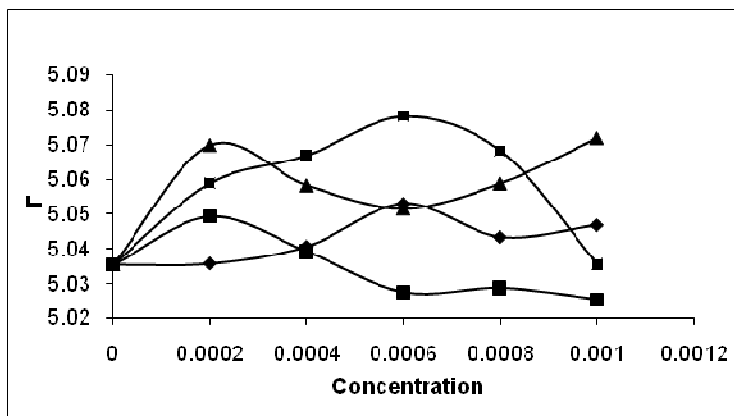System-1 —■— System-2 —▲— System-3 —■— System-4

Fig.10 Variation of Gruneisen parameter with molar concentration of amino acids
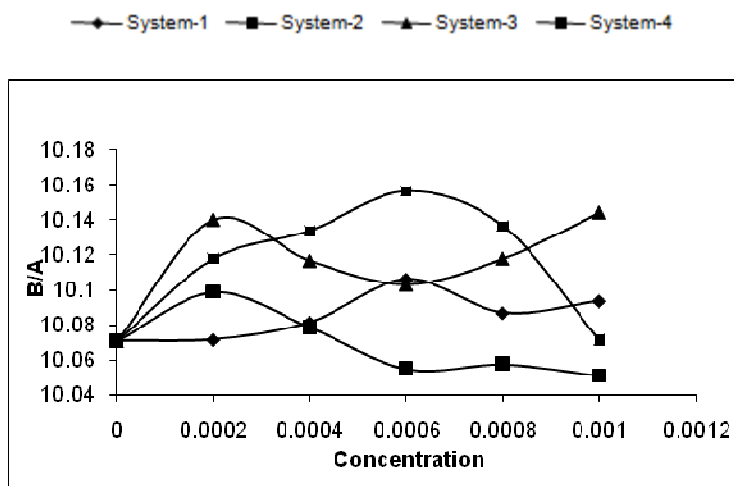

Fig. 11 Variation of Bayer's nonlinearity parameter with molar concentration of amino acids
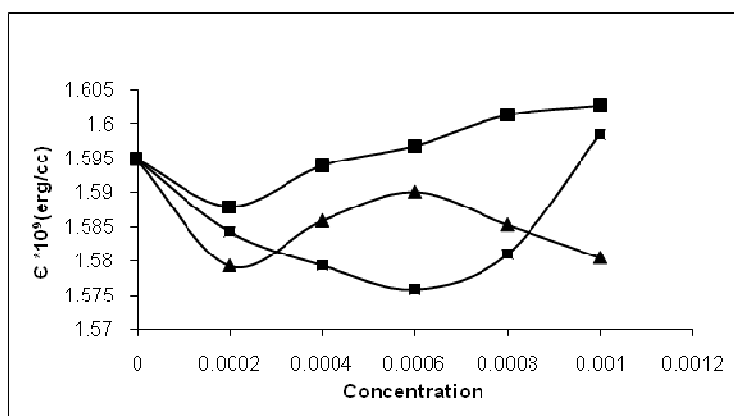

Fig. 12 Variation of Cohesive energy density with molar concentration of amino acids

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CONCLUSION

Thus nonlinearity confirms the presence of complex formation, solute- solvent interactions and weak association due to hydration.The existance of cohesive forces in the present systems may be the result of Zwitterions-ions and Zwitterions-water dipole interactions.Such behaviour extends support to the weak solute-solute and solute-solvent intermolecular/interionic interaction in these systems.

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