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RESEARCH ARTICLE

VOLUMETRIC, ULTRASONIC AND VISCOMETRIC BEHAVIOUR OF L-VALINE, L-THREONINE AND L-PHENYLALANINE IN AQUEOUS SODIUM BROMIDE SOLUTIONS AT DIFFERENT TEMPERATURES

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ABSTRACT

Ultrasonic speed (U), density (ρ) and viscosity (η) values for ternary systems (amino acid+ salt + water): L-valine/ L-threonine/L-phenylalanine in aqueous solutions of 0.0M, 0.025M and 0.050M sodium bromide have been measured for several concentrations of amino acids at 303, 308 and 313K. From these experimental results, apparent molal compressibility ϕ_k , limiting apparent molal compressibility ϕ_k^0 and the slope S_k, apparent molal volume ϕ_v , limiting apparent molal volume ϕ_v^0 and the slope S_v, transfer volume $\Delta\phi_v^0$,transfer compressibility $\Delta\phi_k^0$, Falkenhagen coefficient A and Jones Dole coefficient B were calculated. The results are used to establish the nature of solute-solute and solute-solvent interactions. The structure-making and the structure-breaking abilities of the solute in aqueous medium are also studied.

INTRODUCTION

Ultrasonic investigation in aqueous solutions of electrolytes and non-electrolytes with amino acids provides useful information in understanding the behavior of liquid systems, because intramolecular and intermolecular association, complex formation and related structural changes affect the compressibility of the system which in turn produces corresponding variation in the ultrasonic velocity. During the last two decades, the ultrasonic velocity has been carried out to investigate hydration of proteins through volumetric and ultrasonic measurements, since these properties are sensitive to the degree and nature of hydration. It is well known that electrolytes can influence the solubility behaviour of amino acids. Consequently, study of the volumetric properties of amino acids in aqueous salt solutions is very useful to obtain information about various types of interactions in solutions (Yan Z *et al.*, 2005; R.Badarayani and A.Kumar, 2003). The properties and behaviour of amino acids in solutions have always been a matter of interest mainly because amino acids are, among other compounds, the basic structural building units of biomolecules. Different techniques have been adopted for the understanding of the behaviour of amino acids in solutions (T.Vilarin *et al.*, 1996; A. Chaudhari *et al.*, 2004). The ultrasonic velocity and its derived parameters provide fruitful information regarding the nature of intermolecular/interionic interactions. Consequently, in view of the above, an effort is made to delineate the ion-ion and ion-amino acid interactions in the electrolytic solution from volumetric properties. This investigation therefore presents density and speed of sound data for systems comprising L-valine, L-threonine and L-phenylalanine in aqueous NaBr at three different temperatures.

Experimental methods

The amino acids L-valine, L-threonine and L-phenylalanine and the salt sodium bromide of high purity used in the present studies were purchased from S.D.Fines chemicals and E-Merck (India) .The claimed mass fraction purity for the chemicals was >0.995. Stock solution of 0M, 0.025M and 0.050M aqueous NaBr were prepared in doubly distilled water and were used as solvents for the preparation of amino acid solutions. All the solutions were stored in special airtight bottles to avoid the exposure of solutions to air and evaporation. All the solutions were weighed using an electronic digital balance (Model:SHIMADZU AX-200) with a precision of ±0.1mg. A single crystal variable path ultrasonic interferometer (Mittal Enterprises, New Delhi, Model:F-81) was used for the measurement of the ultrasonic velocity at a frequency of 3MHz with an accuracy of ± $2ms^{-1}$.The density was determined using a specific gravity bottle by relative measurement method with an accuracy of ± 0.01 kgm^{-3}. An Ostwald's viscometer (10 ml) was used for the viscosity measurement. Efflux time was determined using a digital chronometer within ± 0.01s. An electronically digital operated constant temperature bath (RAAGA industries, Madras 61) has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature.

Theory

The apparent molal compressibility, ϕ_k and the apparent molal volume, ϕ_v of the amino acids in aqueous sodium bromide were calculated by using the relations (A N Kannappan and R Palani 2007):

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$$\phi_k = \frac{1000}{m\rho_0}(\rho_0\beta - \rho\beta_0) + \frac{\beta_0 M}{\rho_0} \qquad \ldots\ldots. 1$$

$$\phi_v = \frac{1000}{m\rho_0}(\rho_0 - \rho) + \frac{M}{\rho_0} \qquad \ldots\ldots. 2$$

Where m is the molal concentration of the solute (amino acid) ρ and ρ_0 are the densities of the solution and the solvent (aqueous NaBr) respectively. M is the molar mass of the solute and β and β_0 are the adiabatic compressibility of the solution and the solvent respectively. The values of apparent molal volume ϕ_v^0 (Gucker, 1923, Debye & Huckel, 1923) and apparent molal compressibility ϕ_k^0 (Masson 1929) were obtained using the relations:

$$\phi_v = \phi_v^0 + S_v m^{1/2} \qquad \ldots\ldots. 3$$

$$\phi_k = \phi_k^0 + S_k m^{1/2} \qquad \ldots\ldots. 4$$

Where the intercepts ϕ_v^0 or ϕ_k^0, by definition are free from solute-solute interactions and therefore provide a measure of solute-solvent interactions, whereas the experimental slope, S_v or S_k provides information regarding solute-solute interactions. The volume of transfer of amino acids from water to aqueous NaBr were calculated by using the relation,

$$\phi_V^{\ 0} = \phi_V^{\ 0}{}_{aqNaBr} - \phi_V^{\ 0}{}_{water} \qquad \ldots\ldots. 5$$

The viscosity results were analyzed by using the Jones-Dole (Jones and Dole, 1929) equation of the form

$$\frac{\eta}{\eta^0} = 1 + Am^{1/2} + Bm \qquad \ldots\ldots 6$$

Where η and η_0 are the viscosities of solution and the solvent (aqueous NaBr) respectively. A and B are the Falkenhagen and Jones-Dole (Jones and Dole, 1929) coefficients, respectively. Co-efficient A accounts for the solute-solute interactions and B is a measure of structural modifications induced by the solute-solvent interactions.

RESULTS AND DISCUSSION

The following observations have been made on ϕ_k (Fig.1) of the amino acids in aqueous solutions of NaBr:

- The values of ϕ_k are all negative over the entire range of molality and increase with increase in NaBr content.
- A linear relation between ϕ_k and solute has been observed throughout the concentration range.
- In all the amino acid systems, the maximum negative values of ϕ_k are recorded in 0.00M NaBr content.
- In all the systems, the maximum ϕ_k value is recorded for L-valine-NaBr aqueous solutions rather than for other two amino acids.

The above observations clearly suggest that the ϕ_k values for all the systems are comparatively higher than those of solvent, thereby indicating a solute-solvent interaction. The negative values of ϕ_k indicate electrostriction, hydrophilic and hydrophobic interactions occurring in these systems. Since more number of water molecules are available at lower NaBr content, the chances for the penetration of solute ions into the solvent molecules is highly favoured.The increasing values of ϕ_k in aqueous amino acids with lower NaBr (0.00M) content reveal the strengthening of solute-solvent interaction at lower rate than at its higher inclusions. The limiting apparent molal compressibility ϕ_k^0 and related constant S_k for all the systems have been computed using least square method. ϕ_k^0 values provide information regarding solute-solvent interaction and S_k, that of solute-solute interaction in the solution (A.K.Nain *et al.*, 2009).One can notice from Table 1 that ϕ_k^0 values are negative for all the systems indicating that the water molecules around ionic charged groups of amino acids are less compressible than the water molecules in the bulk solution. This further supports that there exist strong solute-solvent interactions in these systems (H.Rodriguez *et al.*, 2003). The values of S_k exhibit negative values for all the systems. This behaviour indicates the existence of ion-ion/solute-solute interaction. It is well known that the solute causing electrostriction leads to decrease in the compressibility of the solution. This is reflected by the negative values of ϕ_k of the systems. The following observations have been made on ϕ_v (Fig 2) of the amino acids in aqueous solutions of NaBr:

- The ϕ_v values are negative over the entire range of molality and increases with increasing NaBr content.
- There is a linear variation observed in ϕ_v with increase in molality of all the amino acids.
- In all the amino acid systems, the maximum negative values of ϕ_v are recorded in 0.00M NaBr content.
- The values of ϕ_v obtained in the systems vary in the order:

L-threonine >L-phenylalanine > L-valine

The limiting apparent molal volumes at infinite dilution ϕ_v^0 reflect the effects of solute–solvent interactions. It is inferred from Table 2 that the values of ϕ_v^0 in all the systems are negative. This enhances/reduces the electrostriction of water molecules. Increase in ϕ_v^0 with concentration is due to the reduction in electrostriction at the terminal groups of amino acids which increases the interaction between these polar ends and ions (A.Ali *et al.*, 2003). The ϕ_v^0 values decreases with rise in temperature due to the increase in the electrostrictions at the terminals and also it makes disruptions of side group hydration by that of the charged end.

Table 1 Limiting apparent molal compressibility Φ_k^0, slope S_k, transfer compressibility, $\Delta\Phi_k^0$ of L-valine, L-threonine and L-phenylalanine in aqueous solutions of NaBr at 303, 308 and 313K

Amino acids	Molality of NaBr(M)	Limiting apparent molal volume Φ_k^0 /(10^{-7} m^2 N^{-1})			Constant S_k /(10^{-7} N^{-1} m^{-1}.mol^{-1})			Transfer compressibility $\Delta\Phi_k^0$/(10^{-7} m^2 N^{-1})		
		303	**308**	**313**	**303**	**308**	**313**	**303**	**308**	**313**
L- valine	0.000	-0.90	-1.05	-0.94	-1.32	-1.20	-1.74	-	-	-
	0.025	-0.85	-0.97	-0.84	-0.68	-0.98	-1.71	0.05	0.08	0.1
	0.050	-0.78	-0.64	-0.60	-0.88	-1.68	-1.91	0.12	0.41	0.34
L- threonine	0.000	-1.05	-1.13	-1.15	-0.96	-0.74	-0.73	-	-	-
	0.025	-0.12	-1.06	-1.14	-0.33	-0.96	-0.68	0.93	0.07	0.01
	0.050	-0.58	-0.62	-0.75	-1.44	-1.88	-1.49	0.47	0.51	0.40
L- phenylalanine	0.000	-1.08	-1.04	-1.09	-0.68	-1.17	-0.80	-	-	-
	0.025	-0.48	-0.86	-1.08	-1.65	-1.52	-0.42	0.60	0.18	0.01
	0.050	-0.47	-0.50	-0.95	-2.06	-2.13	-0.45	0.61	0.54	0.14

Table 2 Limiting apparent molal volume Φ_v^0, slope S_v, transfer compressibility, $\Delta\Phi_v^0$ of L-valine, L-threonine and L-phenylalanine in aqueous solutions of NaBr at 303, 308 and 313K

Amino acids	Molality of NaBr(M)	Limiting apparent molal volume (Φ_V^0) /(m^3. mol^{-1})			Constant S_v /(m^3 $kg^{1/2}$. $mol^{-3/2}$)			Transfer volume $\Delta\Phi_v^0$/(m^3. mol^{-1})		
		303	**308**	**313**	**303**	**308**	**313**	**303**	**308**	**313**
L valine	0.000	-31.73	-44.33	-42.77	-117.20	-86.76	-134.16	-	-	-
	0.025	-22.78	-17.42	3.81	-87.74	-121.18	-262.39	8.95	26.91	46.58
	0.050	-18.70	-13.80	-6.97	-92.16	-126.14	-185.58	13.03	30.53	35.80
L- threonine	0.000	-63.23	-67.17	-65.25	-48.73	-46.70	-81.72	-	-	-
	0.025	-40.87	-43.64	-46.25	-88.30	-119.24	-131.67	22.36	23.53	19.00
	0.050	-16.50	-35.46	-31.84	-127.33	-111.24	-145.90	46.73	31.71	33.41
L- phenylalanine	0.000	-53.88	-56.37	-55.72	-49.58	-105.07	-103.68	-	-	-
	0.025	-48.68	-54.79	-62.60	-63.80	-63.78	-43.75	5.20	1.58	-6.88
	0.050	-6.61	-11.08	-39.21	-198.54	-159.46	-71.36	47.43	45.29	16.51

Table 3 Falkenhagen coefficients (A) and Jones-Dole coefficients (B) of L-valine, L-threonine and L-phenylalanine in aqueous solutions of NaBr at 303, 308 and 313K

Amino acids	Molality of NaBr(M)	A/($dm^{3/2}$. $mol^{-1/2}$)			B/(dm^3.mol^{-1})		
		303	**308**	**313**	**303**	**308**	**313**
L-valine	0.000	-0.0814	-0.0973	0.0829	1.0907	1.1190	1.1740
	0.025	-0.0973	-0.0974	-0.1634	1.0153	0.9273	1.7505
	0.050	0.0373	-0.0834	0.0985	0.5104	1.1587	0.6978
L-threonine	0.000	-0.0781	0.0712	-0.0014	1.0823	0.6348	1.5522
	0.025	0.0108	0.0337	-0.0465	0.6952	0.6763	1.5292
	0.050	0.0176	-0.0488	0.0296	0.8256	0.9105	0.7783
L-phenylalanine	0.000	0.0149	0.0861	0.0991	0.9840	0.5014	0.7540
	0.025	-0.0783	-0.0807	-0.0147	1.1151	1.5161	1.3143
	0.050	0.1165	-0.1586	0.1538	0.5763	1.3996	0.7764

The negative values of S_v indicate the presence of stronger solute-solute interaction and less complex ion formation taking place in the systems (R Palani *et al.,* 2010). The thermodynamic transfer functions can be explained in terms of structure-making and structure-breaking effects of the solute as has been postulated by Frank and Evans (Frank *et al.*, 1945). $\Delta\phi_v^0$ values are positive (Table 2) for all the systems at all the temperatures thereby showing the presence of strong ion-solvent interactions (A.Pal 2004). The $\Delta\phi_v^0$ values can be explained on the basis of co-sphere overlap model (Gurney, 1953) in terms of solute-co solute interactions. According to this model, hydrophilic-ionic group interactions contribute positively, whereas hydrophilic-hydrophobic interactions contribute negatively to the $\Delta\phi_v^0$ values .The overlap of co solute ions and amino acids comes into play because of interactions between:

- The ($-NH3^+$, COO^-) charged ends of amino acids and ions of the co solute (NaBr).
- The hydrophobic parts of the amino acids and co solute ions, and the charged ends/hydrophilic parts of amino acids and hydrophobic parts of the co solutes (Banipal *et al.*, 2008, Banipal *et al.*, 2007).

As amino acids exist predominantly as zwitterions in pure water and there is an overall decrease in volume of the water due to the electrostriction of water near the end group. The observed positive $\Delta\phi_v^0$ values suggest that the ion-hydrophilic and hydrophilic- hydrophilic group interaction exist in these systems (A K Nain 2009). Viscosity is also an important parameter to understand the structure and molecular interaction occurring in the solutions and its variation is attributed to the structural changes. The co-efficient A is known to be a characteristic of a solute associated with the size and shape of the solute.

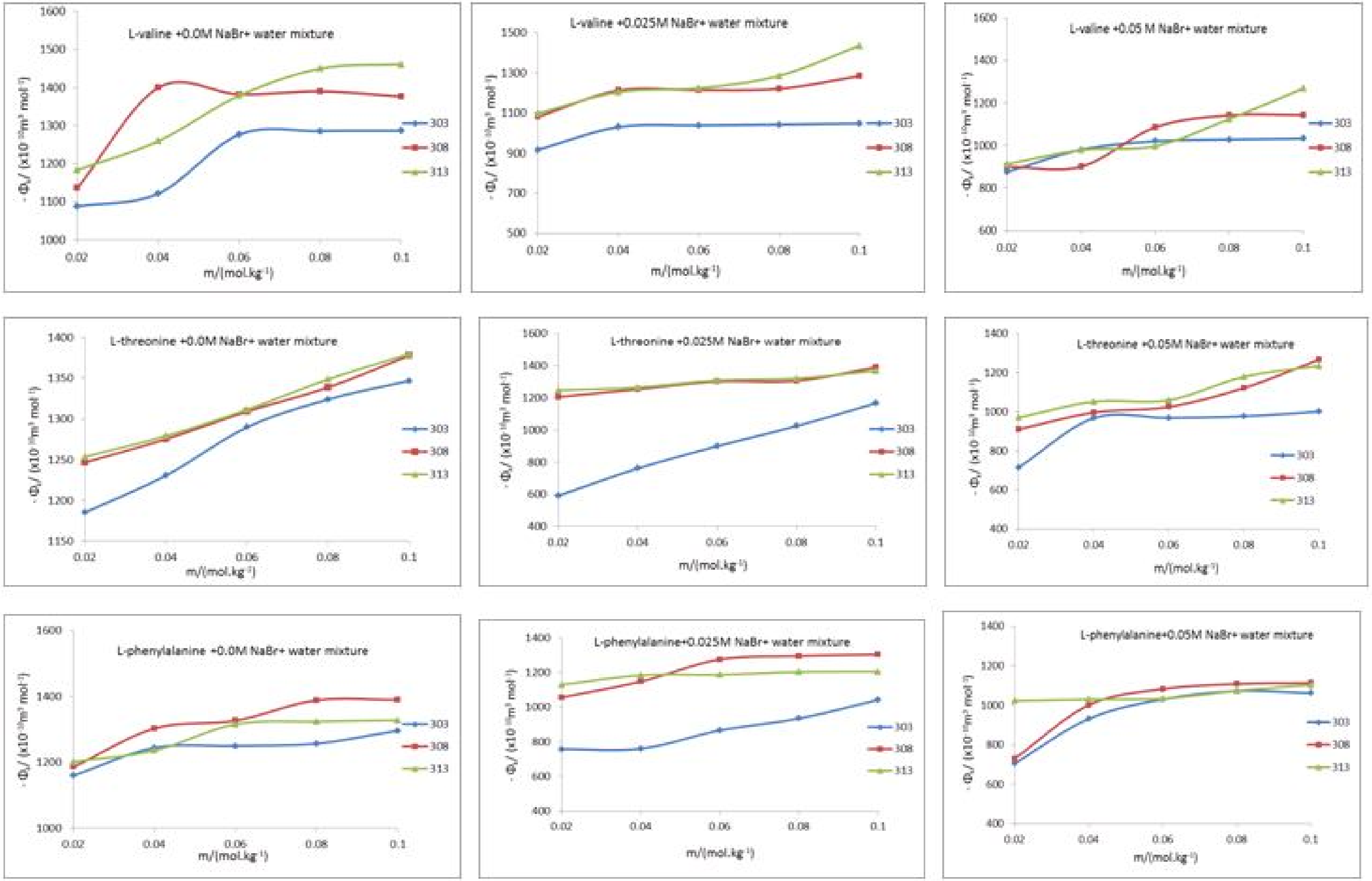

Fig 1 Values of apparent molal compressibility of L-valine, L-threonine and L-phenylalanine in aqueous solutions of NaBr at 303,308 and 313K

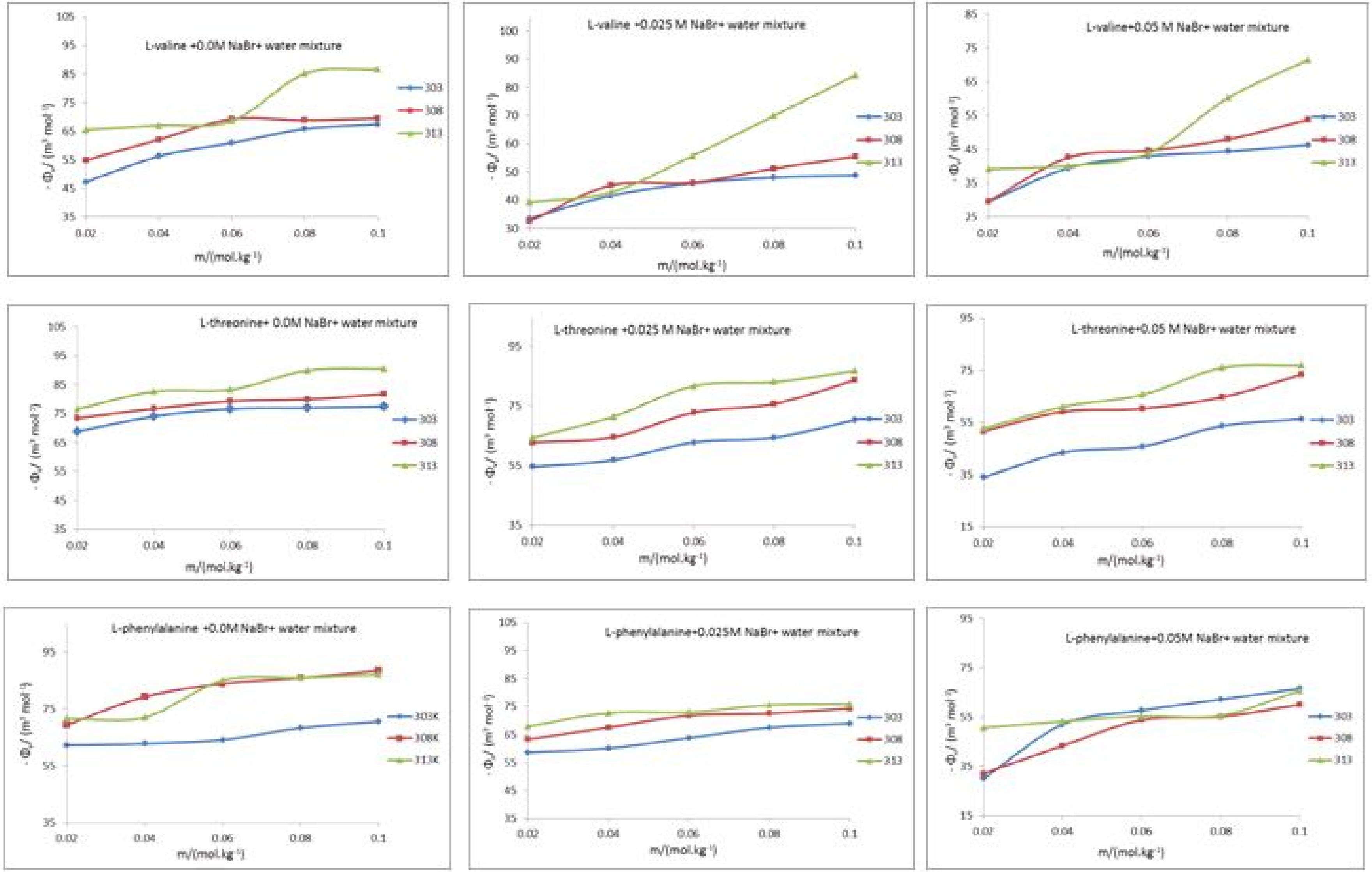

Fig 2 Values of apparent molal volume of L-valine, L-threonine and L-phenylalanine in aqueous solutions of NaBr at 303,308 and 313K

The negative values of the A co-efficient indicate the presence of very weak solute-solute interactions, the positive values of the A co-efficient found in the systems apparently indicate the presence of significant solute-solute interactions. On close scrutiny of the resultant values of both the A and B co-efficients, it has been found that the values of A are both negative and positive and B co-efficient values are positive for all the systems (Table 3). Since A is a measure of ionic interactions, it is evident that there is a weak ion-ion interaction in the solute molecule, which is indicated by the small magnitude of the A values. The B Co-efficient is known as a measure of the order or disorder introduced by the solute into the solvent. It also indicates ion-solvent interactions and it is directly dependent on the size, shape and charge of the solute molecules. Thus, B co-efficient values reflect the net structural effect of the solute on solvent molecule. The positive values of the B co-efficient in all the systems suggest the existence of strong ion-solvent interactions (A.P.Mishra et al 2001, A.Pal *et al.,* 2009). The larger values of the B co-efficient indicate the structure-making capability of the solute (Jamal Akhter *et al.,* 2012, A.Pal and Suresh Kumar 2004). The magnitude of B values is in the order of L-valine > L-phenylalanine >L-threonine.

CONCLUSION

In summary, viscometric and ultrasonic behavior of L-valine, L-threonine and L-phenylalanine in aqueous solutions of NaBr has been determined at 303, 308 and 313K. An appreciable existence of solute-solvent and solute-solute interaction present in the system with varying degrees and the presence of ion-solvent or solute-solvent interactions resulting in attractive forces promote the structure-making tendency while ion-ion or solute-solute interactions resulting in dipole-dipole, dipole-induced dipole and electrostrictive forces enhance the structure-breaking properties of amino acids. We conclude from the magnitude of the B co-efficient that L-valine shows stronger ion-solvent interactions than the other two studied amino acids and it is evident that the existence of molecular interactions is in the order L-valine > L-phenylalanine >L-threonine. Hence, L-valine behaves as a good structure-maker. Further, with rising of temperature, the ion-solvent interactions get weakened due to increase in the thermal energy of the system.

References

Yan Z, Wang J and Zhang H and Xuan X, **2005**.Volumetric and viscosity properties of α-amino acids in aqueous Sodium caproate Solutions. *J. Chem. Eng. Data,* 50: 1864-1870.

Badarayanai R and A Kumar, **2003**. Effect of temperature on the volumentric properties of the L-alanine(1)+KCl(2)+H_2O(3) system. *J.Chem.Eng.Data,* 48:664-668.

T. Vilarin o, M.E. Sastre de Vicente, **1996**.Protonation of glycine in saline media: Evaluation of the effect of the ionic strength by use of the mean spherical approximation, *J. Phys. Chem.* 100:16378–16384.

A. Chaudhari, A.G. Shankarwar, B.R. Arbad, S.C. Mehrotra, **2004**.Dielectric relaxation in glycine-water and glycine-ethanol-water solutions using Time domain reflectometry, *J.Solution Chem.* 33:23–31.

A N Kannappan & R Palani, **2007**.Ultrasonic investigations in amino acids with aqueous dimethyl formamide, *Indian Journal of chemistry* 46A: 54-59.

Gucker F.T, **1933.The** apparent molal heat capacity, volume and compressibility of electrolytes,Chem Rev,13:111-130.

Debye P and E.Huckel, **1923.**On the theory of electrolytes I. Freezing point depression and related phenomena, Phys Z, 24(9): 185-206.

Masson D O, **1929**.Solute molecular volumes in relation to solvation and ionization, Philosophical Magazine, 8, 218-235.

G Jones and M Dole, **1929**. Viscosity of aqueous solutions of strong electrolytes with special reference to barium chloride. *J.Am.Chem. Soc. 51,* 2950-2964.

Anil Kumar Nain, Dinesh Chand, **2009**.Volumetric, ultrasonic and viscomteric behaviour of glycine,DL-alanine and L-valine in aqueous 1,4-butanediol solutions at different temperatures. *J.Chem.Thermodyn* 41:243-249.

Hector Rodgriguez, Ana Soto, Alberto Arce and Mohammad K.Khoshkbarchi, 2003. Apparent molar volume, isentropic compressibility, Refractive index, and viscosity of DL-alanine in aqueous NaCl solutions, *Journal of Solution chemistry* 32(1):53-63.

Anwar Ali, Yasmin Akhter and Soghra Hyder, **2003**. Ultrasonic and volumetric studies of glycine in aqueous electrolytic solutions, *J.Pure Appl. Ultrason.*25:13-18.

Palani R, S Balakrishnan and K.A.Sudhamani**, 2010.** Molecular interaction studies of glycylglycine in aqueous sodium halide solutions at 303,308 and 313K.*ARPN Journal of Engg and Applied sciences*, 5(12):58-64.

Frank, H. S. & Evans, M. W. **1945**. Free Volume and Entropy in Condensed Systems III. Entropy in Binary Liquid Mixtures; Partial Molal Entropy in Dilute Solutions; Structure and Thermodynamics in Aqueous Electrolytes. *J. Chem. Phys.* 13, 11, 507-532.

Amalendu Pal, Suresh Kumar**, 2004**.Viscometric and volumetric studies of some amino acids in binary aqueous solutions of urea at various temperatures, *Journal of Molecular liquids* 109:23-31.

Gurney R.W,*Ionic processes in solution*,**1953.**McGraw Hill Book company,Inc.

Banipal T.S, Kultar Singh, Parampaul K.Banipal, Jasbir Kaur,**2008**.Study of interaction of L-aspartic acid and L-glutamic acid with some metal acetates through volumetric behaviour over the temperature range(288.15 to 318.15)K. *J.Chem.Thermodyn* 40:1166-1185.

Anil Kumar Nain, Dinesh Chand, **2009.Volumetric**, ultrasonic and viscometric behaviour of glycine, DL-alanine and L-valine in aqueous 1,4-butanediol solutions at different temperatures. *J.Chem.Thermodyn* 41:243-249.

Mishra A.P and S.K Gautam, **2001.Viscometric** and volumetric studies of some transition metal chlorides in glycine-water solution, *Indian Journal of chemistry*.40A:100-104.

A.Pal and Nalin Chauhan, **2009.Volumetric**, viscometric and acoustic behaviour of diglycine in aqueous saccharide solutions at different temperatures. *Journal of molecular liquids,* 149: 29-36.

Jamal Akhter Siddique, Saeeda Naqvi, **2012.** Viscosity behaviour of α-amino acids in acetate salt solutions at temperatures (303.15 to 323.15) K. *International journal of thermophysics,* 33:47-57.

Amalendu Pal, Suresh Kumar, **2004**.Viscometric and volumetric studies of some amino acids in binary aqueous solutions of urea at various temperatures, *Journal of Molecular liquids* 109:23-31.

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