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Densities and speeds of sound of L-valine in aqueous sodium bromide solutions at various temperatures

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ABSTRACT

Ultrasonic speed (U), density (ρ) and viscosity (η) values for ternary systems (amino acid+ salt+ water): L-valine in aqueous solutions of 0.0M, 0.025M, and 0.050M sodium bromide have been measured for several concentrations of amino acids at different temperatures (303, 308 and 313K). From these experimental data, derived thermodynamic parameters such as the adiabatic compressibility (β), change in adiabatic compressibility (Δβ), relative change in adiabatic compressibility (Δβ/β_0), acoustic impedance (Z) and relative association (R_a) have been computed using the standard relations. The results have been interpreted in terms of various intermolecular/interionic interactions existing in the systems.

KEYWORDS: Amino acids, adiabatic compressibility (β), acoustic impedance (Z), relative association (R_a).

INTRODUCTION

Amino acids and peptides are the fundamental structural units of proteins, dipeptide, certain types of hormones and many other compounds of biological relevance. Proteins play a vital role in nearly all biological processes. The three dimensional structure of proteins and nucleic acids provide critical information about the molecules but they provide no information about the stability of a molecule or the energetic of its importance [1]. Interactions of proteins with their surrounding environment play an important role in their conformational characteristics. These interactions are mainly those between the solute and solvent molecules. Most of these interactions such as hydrogen bonding, electrostatic interactions, hydrophobic interaction etc., are non-covalent. The study of these interactions provides important insight into the conformational stability and folding/unfolding behavior of globular proteins [2]. The influence of electrolyte on the behavior of protein is one of the important topics in physical chemistry of the substances. It has long been known that there is a strong interaction between electrolytes and proteins, which causes a departure from ideal behavior. Knowledge of the interactions responsible for stabilizing the native state of globular protein in aqueous solution is essential to understand its structure and function. To understand the fine details, the interactions of the building blocks of the protein with electrolytes [3, 4] must be studied owing to the complex structural organization of the biological macromolecules.

In this paper, we present results, the system consisting of L-valine in aqueous NaBr at different concentrations at different temperatures. Accurate thermodynamic data on electrolyte solutions are frequently needed. Sound velocity is a thermodynamic function. Many other thermodynamic properties of electrolyte solutions are determined from sound velocity [5]. Ultrasound velocity data do not provide significant information about the nature and strength of various types of intermolecular or interionic interactions between the components. Hence their derived parameters such as adiabatic compressibility (β), change in adiabatic compressibility (Δβ), relative change in adiabatic compressibility (Δβ/β_0), acoustic impedance (Z) and relative association (R_a) have been calculated to shed more light on such interactions.

EXPERIMENTAL DETAILS

The amino acids L-valine 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 AND CALCULATION

The various acoustical parameters such as adiabatic compressibility (β), change in adiabatic compressibility (Δβ), relative change in adiabatic compressibility (Δβ/β_0), acoustic impedance (Z) and relative association (R_a) have been calculated from the measured data using the following standard expressions:

Adiabatic compressibility [6] is given by

$$\beta = \frac{1}{\rho U^2} \qquad \ldots(1)$$

$$\Delta\beta = \beta_0 - \beta \qquad \ldots(2)$$

Relative change in adiabatic compressibility is determined by Δβ/β_0

$$Z = U\rho \qquad \ldots.(3)$$

Relative association parameter has been calculated using the following expression [7]

$$R_a = \frac{\rho}{\rho_0}\left(\frac{U_0}{U}\right)^{1/3} \qquad \ldots.(4)$$

where ρ and ρ_0 are the densities of their solution and solvent respectively while U and U_0 are their ultrasonic velocities.

RESULTS AND DISCUSSION

From the Fig.1, it is found that the density, viscosity and ultrasonic velocity increases with increase in molal concentration of amino acids as well as with NaBr content. But in all the cases, the ultrasonic velocity increases with increase in temperature while the density and viscosity decreases with rise in temperature.

Density is known to be a measure of ion–solvent and solvent-solvent interactions. The increase in the values of density may be attributed to the increase in hydrophilic interactions [8] or may be interpreted as structure making nature of the solvent due to the added solute.

Viscosity is one of the most important properties of many technological and scientific applications and therefore it has been a subject of enormous effort of the measurement and interpretation for liquid mixtures. The increasing trend of viscosity with increase in mole fraction of the amino acids indicates the existence of molecular interactions in these mixtures [9].

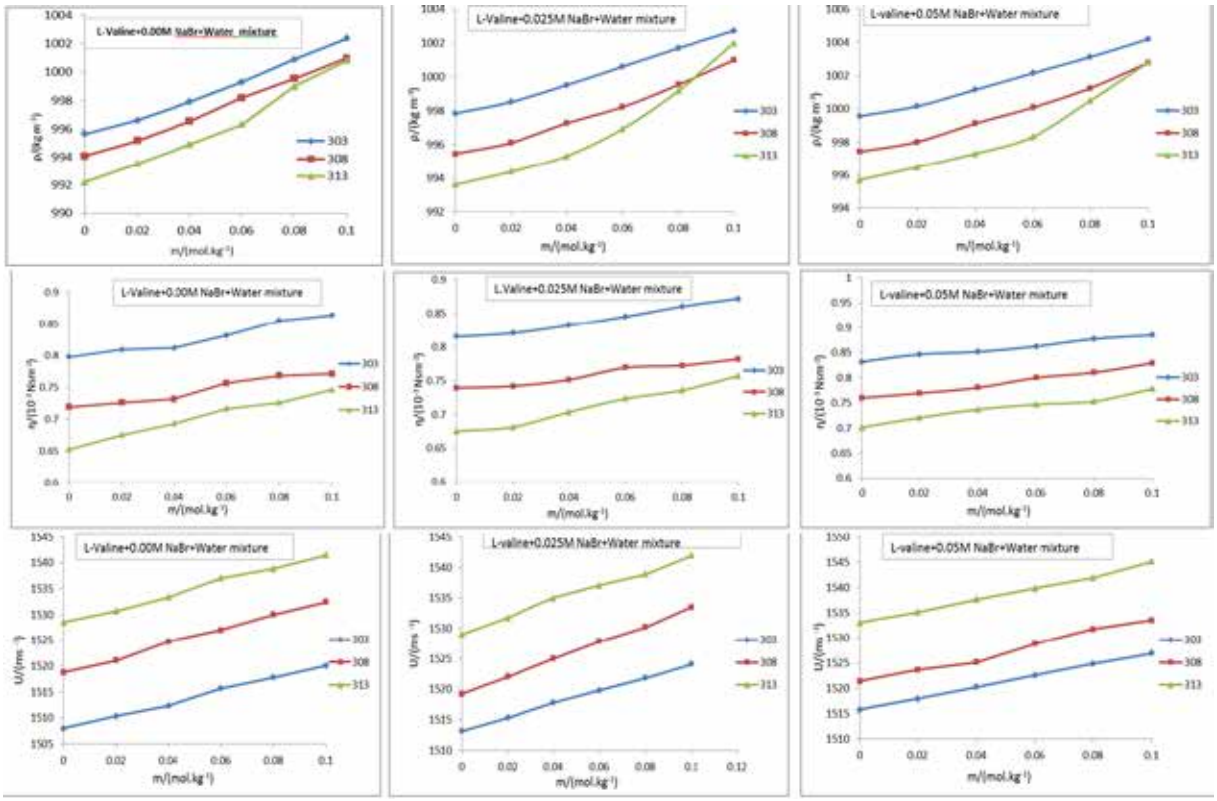

Fig.1: Values of density, viscosity and ultrasonic velocity of L-valine in aqueous NaBr at 303, 308 and 313K

From Table 1, it is observed that the adiabatic compressibility values are found to decrease with increase in the concentration of amino acids in all the systems [10] and the same decreases with rise in temperature. The decrease in adiabatic compressibility values with increase in concentration of amino acids in 0.00, 0.025 and 0.05 M aqueous solutions of NaBr may be ascribed to (i) the introduction of incompressible Na^+ and Br^- ions into water and (ii) the formation of Na^+/Br^- water dipole incompressible entities in salt solutions. The decrease in adiabatic compressibility values with increase in temperature in all systems under study may be explained in terms of the changes in water structure around zwitterions and ions.

Table 1: Values of adiabatic compressibility (β), change (Δβ) and relative change in adiabatic compressibility (Δβ/ β_0) of L-valine

Molality m/(mol. kg^{-1})	**β/($\times10^{-10}$ m^2 N^{-1})**								
	0.0 M NaBr			0.025M NaBr			0.05 M NaBr		
	Temperature (K)								
	L-valine+Water								
	303	308	313	303	308	313	303	308	313
0.00	4.4166	4.3613	4.3138	4.3771	4.3525	4.3049	4.3543	4.3317	4.2734
0.02	4.3990	4.3433	4.2958	4.3617	4.3337	4.2863	4.3394	4.3162	4.2585
0.04	4.3817	4.3161	4.2750	4.3432	4.3119	4.2641	4.3220	4.3030	4.2411
0.06	4.3562	4.2965	4.2488	4.3269	4.2918	4.2459	4.3043	4.2781	4.2248
0.08	4.3370	4.2741	4.2272	4.3106	4.2727	4.2262	4.2875	4.2570	4.2040
0.10	4.3177	4.2540	4.2051	4.2936	4.2483	4.1977	4.2712	4.2406	4.1770
	-Δβ/($\times10^{-12}$ m^2 N^{-1})								
0.02	1.76	1.8	1.8	1.54	1.88	1.86	1.49	1.55	1.49
0.04	3.49	4.52	3.88	3.39	4.06	4.08	3.23	2.87	3.23
0.06	6.04	6.48	6.5	5.02	6.07	5.9	5.00	5.36	4.86
0.08	7.96	8.72	8.66	6.65	7.98	7.87	6.68	7.47	6.94
0.10	9.89	10.73	10.87	8.35	10.42	10.72	8.31	9.11	9.64
				-Δβ/ β_0/($x10^{-3}$)					
0.02	3.98	4.13	4.17	3.52	4.32	4.32	3.42	3.58	3.48
0.04	7.90	10.36	8.99	7.74	9.32	9.48	7.42	6.63	7.56
0.06	13.68	14.86	15.07	11.47	13.95	13.70	11.48	12.37	11.37
0.08	18.02	19.99	20.07	15.19	18.33	18.28	15.34	17.24	16.24
0.10	22.39	24.60	25.20	19.08	23.94	24.90	19.08	21.03	22.56

The change in adiabatic compressibility and relative change in adiabatic compressibility are negative and increase with increase in concentration of solute as well as temperature as shown in Table 1. The increase in Δβ and Δβ/β_0 values with increase in amino acid/zwitterion concentration may be attributed to an overall increase in the cohesive forces in solutions. These cohesive forces may be a result of zwitterions/ions and zwitterions-water

dipole interactions in solutions. In addition, the successive increase of amino acid concentration in the salt solution enhances the incompressible part of the solution [11]. The change and relative change in adiabatic compressibility values with temperature may be due to the thermal rupture of water structure as observed by Rajagopal et al.,2010 [12].

Relative association (R_a) is influenced by two factors.

- Breaking up of the associated solvent molecules on addition of solute in it.
- The solvation of solute molecule.

The former one leads to the decrease and later to the increase of relative association. The R_a values show an increasing trend of variation with increase in concentration of amino acids/dipeptide in aqueous electrolyte solutions. A close examination of the Table 2 reveals that the R_a values are either one or close to one. This indicates that the systems under investigation are essentially ideal in nature. Hence it is clear that the values of relative association parameter do not vary much from the value of unity as we move from 0.0M NaBr to 0.050M NaBr for all the concentrations of amino acids.

Table 2: Values of acoustic impedance (Z) and relative association (R_a) of L-valine in aqueous NaBr at 303, 308 and 313 K

Molality m/(mol. kg^{-1})	$Zx10^6$ Kg m^{-2} s^{-1}								
	0.0 M NaBr			0.025M NaBr			0.05 M NaBr		
	L-valine+Water								
	Temperature (K)								
	303	308	313	303	308	313	303	308	313
0.00	1.5014	1.5097	1.5166	1.5099	1.5123	1.5192	1.5151	1.5174	1.5264
0.02	1.5051	1.5137	1.5208	1.5130	1.5161	1.5231	1.5182	1.5206	1.5297
0.04	1.5091	1.5195	1.5255	1.5170	1.5208	1.5278	1.5220	1.5238	1.5335
0.06	1.5146	1.5242	1.5313	1.5207	1.5251	1.5323	1.5258	1.5289	1.5372
0.08	1.5191	1.5292	1.5373	1.5244	1.5295	1.5376	1.5296	1.5336	1.5427
0.10	1.5236	1.5339	1.5427	1.5282	1.5350	1.5450	1.5333	1.5378	1.5494
	R_a								
0.02	1.0004	1.0006	1.0008	1.0002	1.0000	1.0002	1.0001	1.0001	1.0003
0.04	1.0013	1.0012	1.0016	1.0006	1.0012	1.0004	1.0006	1.0001	1.0006
0.06	1.0020	1.0023	1.002	1.0013	1.0022	1.0016	1.0011	1.0010	1.0010
0.08	1.0031	1.0030	1.0045	1.0019	1.0035	1.0034	1.0016	1.0016	1.0029
0.10	1.0041	1.0039	1.0058	1.0025	1.0049	1.0056	1.0022	1.0027	1.0045

The acoustic impedance (Z) increases with increase in the concentration of solute, electrolyte content as well as temperature in all the systems under investigation (Table 2). In the case of amino acids, the increase in the value of acoustic impedance may perhaps be attributed to an apparent reduction in the repulsive forces (dissociation) with increase in temperature [13]. Such behavior reinforces the view that complex formation does not occur among the components of solutions. The trend in the values of acoustic impedance with variation in solute concentration and temperature are similar to those exhibited by the variation of ultrasonic velocity values [14].

CONCLUSION

In this study, we have determined density, viscosity and ultrasonic velocity of L-valine in aqueous solutions of sodium bromide at 303, 308 and 313K. On the basis of the above observations, it is concluded that the presence of ion-solvent interaction results in the structure-making property while ion-ion interaction is responsible for structure-breaking tendency of amino acids. The decrease in the values of adiabatic compressibility with increase in the solute concentration may be due to the occupation of the interstitial spaces of water by the solute molecules thereby making the medium less compressible. The increase in the relative association values with increase in the concentration of the solute indicates the solvation of the solute molecule i.e., it represents the structural effect of the amino acid on the solvent in the solution.

REFERENCES

1. Haq I, O'Brien R, Ladbury JE. (2001)General thermodynamic definitions and equations. In: Drug Receptor Thermodynamics: Introduction and Applications. Ed(s) Raffa RB. John Wiley & Sons Ltd. Chichester, UK, 61. | 2. Yan Z, Wang J, Kong W, Lu J(2004), "Effect of temperature on volumetric and viscosity properties of some α-amino acids in aqueous calcium chloride solutions", Fluid Phase Equilib., 215,143-150. | 3. Badarayani, R, Kumar, A. (2002) "Ionic interactions from volumetric investigations of l-alanine in NaBr, KCl, KBr and $MgCl_2$ up to high concentrations", Fluid Phase Equilib. 201, 321-333. | 4. Riyazuddeen and Sadaf Afrin (2010),"Viscosities of L-phenylalanine, L-leucine, L-glutamic acid or L-proline+ 2.0 $mol.dm^{-3}$ aqueous NaCl or 2.0 $mol.dm^{-3}$ aqueous $NaNO_3$ solutions at T= (298.15 to 328.15) K", J.Chem.Eng.Data 55(9) 3282-3285. | 5. Nikam P S, Mehdi Hasan, Pawar T B & Sawant A B, (2004) "Ultrasonic velocity and allied parameters of symmetrical tetraalkyl ammonium bromides in aqueous ethanol at 298.15K" Indian J Pure & Appl Phys., 42,172-178. | 6. R Palani, S Balakrishnan and K.A.Sudhamani (2010) "Molecular interaction studies of glycylglycine in aqueous sodium halide solutions at 303, 308 and 313K", ARPN J. Eng. Appl. Sciences, 5(12) 58-64. | 7. S. Nithiyanantham and L. Palaniappan (2012). "Ultrasonic investigation on some monosaccharides in aqueous media at 298.15", Arabian Journal of Chemistry, 5:25-30. | 8. Anjana and Rajinder K Bamezai, (2011). "Ultrasonic and volumetric investigations of L-threonine in aqueous and in mixed aqueous solution", Archives of applied science research,3(1):370-379. | 9. Palani R, S.Balakrishnan and G Arumugam, (2011)."Ultrasonic studies of amino acids in aqueous sucrose solution at different temperatures", Journal of Physical science, 22(1):131-141. | 10. Yasmin Akhtar, S F Ibrahim, (2011)."Ultrasonic and thermodynamic studies of glycine in aqueous electrolyte solutions at 303K", Arabian Journal of chemistry, 4: 487-490. | 11. Riyazuddeen, Riffat Basharat, (2006)."Intermolecular/interionic interactions in L-isoleucine-, L-proline-, L-glutamine-aqueous electrolyte systems", J.Chem.Thermodyn.38:1684. | 12. Rajagopal K, S.S Jayabalakrishnan, (2010)."Volumetric, ultrasonic speed, and viscometric studies of salbutamol sulphate in aqueous methanol solution at different temperatures", J.Chem.Thermodyn 42:984-993. | 13. Shahina Islam, B.N Waris, (2004). "Intermolecular interactions in leucine-NaCl, and KCl-aqueous urea systems", Thermochim. Acta 424:165-174. | 14. Riyazuddeen, G.K.Bansal, (2006)."Intermolecular/interionic interactions in L-leucine-, L-asparagine-, and glycylglycine-aqueous electrolyte systems". Thermochim. Acta, 445:40-48. |