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Structure-making and Breaking Behaviour of Some α -amino Acids in Aqueous Sodium Butyrate Medium at 298.15K

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Abstract: The present study aims for the structure-making and structure-breaking behaviour of some amino acids in aqueous sodium butyrate solution at 298.15 K. The present investigation exploring the possible molecular interactions between the amino acids and organic salts such as sodium butyrate, which is known to have much dissociation of proteins in the solvent mixture. Experimental values of density, viscosity and ultrasonic velocities were carried out on the ternary mixtures of water+sodium butyrate+amino acids namely (L-asparagine, L-glutamine, L-serine and L-threonine) at 298.15 K. The present study was carried out by varying the different mass percentages of binary mixtures (water+sodium butyrate) varying from pure water to 20% (0, 5, 10, 15 and 20%) in increments of 5%. The related and relevant parameters correlated to our present study such as adiabatic compressibility (β), molar hydration number (n_H), apparent molar compressibility (ϕ_{β}), apparent molar volume (ϕ_V), limiting apparent molar compressibility (ϕ_{β}°), limiting apparent molar volume (ϕ_V°) and their associated constants (S_K, S_V), transfer volume ($\Delta\phi^{\circ}$) from water to aqueous solution viscosity B-Coefficient of Jones-Dole equations were meticulously evaluated. The molecular associations such as ion-ion, ion-solvent, solute-solvent, solute-solute etc are identified and critically discussed in terms of the structure-making and structure-breaking behaviour of amino acids in the solvent mixture.

Key words: Molar hydration number, adiabatic compressibility, structure-maker, viscosity B-coefficient, transfer volume, molecular interaction, amino acids

INTRODUCTION

Ultrasonic study on the amino acids with aqueous solution of electrolytes and non-electrolytes provides useful information in understanding the behaviour of intra-molecular and intermolecular associations, complex formation and related structural changes in liquid systems. For the past two decades, a considerable study has been carried out to investigate the hydration of proteins through volumetric and ultrasonic measurements, since these properties are sensitive to the degree and nature of hydration (Wang *et al.*, 2004; Sadeghi and Goodarzi, 2008). Due to the complex molecular structure of proteins, direct study is somewhat difficult. Therefore, an useful approach is to study simpler model compounds, such as amino acids which are building blocks of proteins. The investigation of volumetric and thermodynamic properties of amino acids and peptides in aqueous and mixed aqueous solvents (Riyazuddeen and Basharat, 2006; Banipal *et al.*, 2007b; Thirumaran and Kannappan, 2009) threw more light on the molecular interactions such as hydrogen bonding, ion-ion, ion-solvent solute-solvent etc. and eventually exhibited the behaviour of structure-making and breaking of studied amino acids in the solvent mixture.

More recent studies on salt solutions exploring the large effect on the structure and properties of proteins including their solubility, denaturation, distribution into subunits, and the activity of enzymes (Yan *et al.*, 2001; Palani and Geetha, 2007). Proteins are complex molecules and their behavior in solutions are governed by combination of many specific interactions. Ferreira *et al.* (2009) and Pal and Kumar (2005) have revealed that the presence of an electrolyte drastically affects the behavior of amino acids in solutions which can be used for their separation and purification. Several investigations so far carried out by the different workers on the partial molar volumes, adiabatic compressibilities, the heat capacity and Gibb's free energy of transfer volume and the Viscosity-B coefficient measurements on amino acids with organic salts such as CaCl_2 , Na_2SO_4 , KSCN (potassium thiocyanate) and (NH_4Cl) ammonium chloride solution (Kumar and Badarayani, 2003; Nain and Chand, 2009).

However, the authors noticed that there are a few measurements on interactions between amino acids and organic salt such as sodium butyrate, which is known to influence the dissociation of proteins in solutions (Yan *et al.*, 2001, 2009) and cause a salting-out of non-electrolytes. Hence, a systematic study of the effect of sodium butyrate on amino acids can be explained by

ultrasonic techniques bring a series of interest. The authors with an exhaustive literature survey carried out the present studies on the volumetric, viscometric and ultrasonic studies of amino acids having polar side group (chain) in the presence of organic salt solutions. In the present investigation, the authors studied the behavior of amino acids at neutral pH are L-asparagine, L-serine, L-glutamine and L-threonine are all polar R-groups.

Sodium butyrate possessing many biology characteristics which can promote growth of beneficial bacteria and inhibit the growth of harmful bacteria in the gastrointestinal tract. It is an energy source of cell differentiation and this salt is known to influence the dissociation of proteins in solution and cause a salting-out of non-electrolytes (Yan *et al.*, 2001).

In the present study, we reported the values of density, viscosity and ultrasonic velocity which have been measured for the amino acids, L-asparagine, L-glutamine, L-serine and L-threonine in aqueous sodium butyrate solution at 298.15 K. The relevant parameters which are related to our study such as adiabatic compressibility (β), molar hydration number (n_H), apparent molar compressibility (ϕ_k), apparent molar volume (ϕ_v), limiting apparent molar compressibility (ϕ_k^0) and its related constant (S_k), limiting apparent molar volume (ϕ_v^0) and its related constant (S_v), transfer volume ($\Delta\phi_v^0$) and Viscosity-B coefficients of Jones-Dole equations have been evaluated meticulously. The authors eventually analysed the possible molecular interactions of amino acids in the solvent mixture and they interpreted their findings in terms of structure-making and structure-breaking of these amino acids in the solvent mixture.

MATERIALS AND METHODS

The study was carried out during December 2010. AR/SR grade chemicals having a minimum assay of 99.9% were obtained from sigma aldrich, G merck and sd fine. Fresh conductivity water was used for preparing binary solvent mixture (water+sodium butyrate) at varying mass percentages such as 0, 5, 10, 15 and 20% - in 5% interval. Water used in the present investigation was deionised, distilled and was degassed prior to making solutions. Aqueous solutions were prepared by mass percentage and used on the day they were prepared. Required amount of water and sodium butyrate was taken to prepare varying composition of binary mixtures in a dry conical flask with a ground stopper. The required quantity of amino acids for a given molarity was dissolved in the binary mixture and similar procedure was adapted for different amino acids.

The chemicals were weighed in an electronic digital balance (SHIMADZU AX-100, Japan Make with a

precision of 0.0001 g. The density was determined using a specific gravity bottle by relative measurement method with an accuracy of $\pm 0.01 \text{ k g}^{-3}$. An Ostwald's viscometer of 10 mL capacity was used for the viscosity measurement. Efflux time was determined using a digital chronometer within $\pm 0.01 \text{ s}$. An Ultrasonic Interferometer having the fixed frequency of 3 MHz (Mittal Enterprises, New Delhi-Model: F-81) with an overall accuracy of 2 m sec^{-1} has been used for velocity measurement. An electronically digital operated constant temperature bath (RAAGA Industries, Chennai) has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at desired temperature, whose accuracy is maintained at $\pm 0.1 \text{ K}$. The pH values of the liquid mixtures were measured using a digital pH meter (Labtronics Delux pH meter. Model: LT-10) with a precision of 0.01.

THEORY AND CALCULATIONS

Adiabatic compressibility (β) is given by:

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

Molar hydration number (n_H) is given by:

$$n_H = \frac{n_1}{n_2} \left(1 - \frac{\beta}{\beta_0} \right) \quad (2)$$

where, β and β_0 are adiabatic compressibilities of solution and solvent, respectively, n_1 and n_2 are number of moles of solvent and solute respectively. Apparent molar compressibility (ϕ_k) is given by:

$$\phi_k = \frac{1000}{m\rho_0} (\rho_0\beta - \rho\beta_0) + \left(\frac{\beta_0 M}{\rho_0} \right) \quad (3)$$

where, β , ρ and β_0 , ρ_0 are the adiabatic compressibility and density of solution and solvent respectively, m is the molar concentration of the solute and M the molecular mass of the solute. ϕ_k is the function of m as obtained by Guckre (1933) and Debye and Hiickel (1923).

Apparent molar volume (ϕ_v) is obtained by:

$$\phi_v = \frac{1000}{m\rho_0} (\rho_0 \cdot \rho) + \left(\frac{M}{\rho_0} \right) \quad (4)$$

The apparent molar volume has been found to differ with concentration according to Masson's empirical relation (Masson, 1929).

Transfer volume ($\Delta\phi_v^\circ$), of each amino acid from water to aqueous sodium butyrate solution were calculated using the equation:

$$\Delta\phi_v^\circ = \phi_v^\circ(\text{in aqueous sodium butyrate}) - \phi_v^\circ(\text{in water}) \quad (5)$$

The entire viscosity data have been analysed in the light of Jones-Dole semi empirical equation (Jones and Dole, 1929).

RESULTS AND DISCUSSION

In the present study, one can observe that in all the amino acid systems, the values of density, viscosity and ultrasonic velocity increases with increase of molar concentration of amino acids as well as the increasing mass percentage of sodium butyrate. The increasing trend of ultrasonic velocity in the mixtures suggests a moderate strong electrolytic nature in which the solutes (amino acids) tend to attract the solvent (sodium butyrate) molecules (Yan *et al.*, 2001; Banipal *et al.*, 2007a). Further, the increasing values of density with the increasing molar concentration of amino acids and mass percentage sodium butyrate suggesting an enhanced molecular association in the solution. i.e., existence of molecular interaction between solute and solvent molecules. The above causes may also be the reasons for an increase in ultrasonic velocity in the mixtures. Such an increase in ultrasonic velocity in these solutions may be attributed to the cohesion brought about the ionic hydration.

It can be qualitatively ascribed that, when the amino acids are dissolved in water+sodium butyrate mixtures, the cations NH_3^+ and the anions COO^- are formed. The water molecules are attached to the ions strongly to the electrostatic forces, which introduce a greater cohesion in the solutions (Ragouramane and Rao, 1998) resulting the increasing of cohesion, whenever an increase of amino acid concentration in the solution. Such a increased association observed in these solutions may also be due to the water structure enhancement brought about by the increased electrostriction in the presence of sodium butyrate. The electrostriction effect which brings about the shrinkage in volume of solvent caused by the Zwitterionic portion of the amino acids is increased in mixed solvent. Similar effect was reported by earlier workers (Palani and Saravanan, 2008; Thirumaran and Sabu, 2009).

Incidentally, the density (ρ) which is a measure of solvent-solvent and ion-solvent interactions. Increase of density with concentration indicates the increase in solvent-solvent and solute-solvent interactions, whereas

the decrease in density indicates the lesser magnitude of solute-solvent and solvent-solvent interactions. Increase in density with concentration is due to the shrinkage in the volume which in turn is due to the presence of solute molecules. In other words, an increase in density may be interpreted to the structure-maker of the solvent due to the added solute and the decrease in density with concentration indicates structure-breaker of the solvent.

Interestingly, the sodium butyrate, being a salt of weak acids and strong bases undergo hydrolysis to give basic solution (Banipal *et al.*, 2007a). In the present study, the measured pH values of aqueous solution of these electrolytes were found to be less than 8.32, however the pH values decrease, while increasing the molarity of the amino acids and increases with increase in mass percentage of sodium butyrate. This can be inferred that at the pH of the solutions, the side-chains of the acidic amino acids remain fully deprotonated, which makes the acidic amino acids studies are considered to exist mainly as zwitterions in aqueous sodium butyrate, having the charged side chain.

The perusal of Table 1 illustrates the variation of adiabatic compressibility (β) with molar concentration of amino acids. The values of β in all the amino acids systems exhibit a decreasing trend with increasing molar concentration of amino acids as well as sodium butyrate content. Such compressibility's values are larger in L-serine system, comparing other amino acid systems, which suggest that the molecular association is greater in L-serine than that of other amino acid systems. It is known that amino acid molecules in the neutral solution exist in dipolar form and then have stronger interaction with the surrounding water molecules. The increasing electrostrictive compression of water around the molecules results in a larger decrease in the compressibility of the solutions.

The hydration number that reflects the electrostriction effect of the charged centre of the amino acids in the vicinity of the water molecules. From Table 1, it is noticed that the values of hydration number n_H are positive in all the four amino acids systems. The values n_H are found to be decreased with increase in molarity of the amino acids, (except in L-serine system) as well as content of sodium butyrate. Such a possession of positive values of n_H salvation of solutes. It can be taken as an added support for the structure promoting nature of solutes as well as the presence of dipolar interaction between the solute and water molecules. This parameter also suggests that the compressibility of the solution will be less than that of the solvent. As a result solutes will gain mobility and have more probability of contacting solvent molecules. This may enhance the interaction between

Table 1: Values of adiabatic compressibility (β) and molar hydration number (n_H) of amino acids in aqueous sodium butyrate solution at 298.15 K

Molarity M (mol.dm ⁻³)	Adiabatic compressibility β ($\times 10^{10}$ m ² N ⁻¹)					Molar hydration number (n_H)				
	0%	5%	10%	15%	20%	0%	5%	10%	15%	20%
Water+Sodium butyrate+asparagine										
0.00	4.4598	4.2525	4.1235	3.9772	3.8676	-	-	-	-	-
0.02	4.4353	4.2325	4.1032	3.9658	3.8573	0.1161	0.0946	0.0947	0.0523	0.0464
0.04	4.4258	4.2132	4.0880	3.9559	3.8460	0.0800	0.0933	0.0831	0.0493	0.0490
0.06	4.4158	4.1936	4.0749	3.9471	3.8375	0.0691	0.0930	0.0756	0.0463	0.0454
0.08	4.4045	4.1741	4.0557	3.9356	3.8289	0.0651	0.0929	0.0792	0.0481	0.0439
0.10	4.3927	4.1583	4.0467	3.9247	3.8181	0.0633	0.0893	0.0718	0.0485	0.0448
Water+Sodium butyrate+L-glutamine										
0.00	4.4598	4.2525	4.1235	3.9772	3.8676	-	-	-	-	-
0.02	4.4197	4.2206	4.0976	3.9591	3.8460	0.1707	0.1377	0.1092	0.0755	0.0882
0.04	4.4038	4.2041	4.0851	3.9501	3.8341	0.1192	0.1034	0.0809	0.0566	0.0683
0.06	4.3894	4.1861	4.0690	3.9364	3.8255	0.0998	0.0946	0.0766	0.0567	0.0573
0.08	4.3754	4.1634	4.0560	3.9227	3.8171	0.0898	0.0955	0.0712	0.0569	0.0516
0.10	4.3609	4.1449	4.0387	3.9109	3.8075	0.0843	0.0921	0.0716	0.0554	0.0492
Water+Sodium butyrate+L-serine										
0.00	4.4598	4.2525	4.1235	3.9772	3.8676	-	-	-	-	-
0.02	4.4506	4.2424	4.1146	3.9736	3.8623	0.0541	0.0601	0.0516	0.0209	0.0296
0.04	4.4397	4.2293	4.1012	3.9633	3.8539	0.0592	0.0688	0.0653	0.0401	0.0388
0.06	4.4333	4.2132	4.0872	3.9536	3.8464	0.0521	0.0777	0.0710	0.0457	0.0402
0.08	4.4227	4.1994	4.0724	3.9467	3.8378	0.0545	0.0784	0.0744	0.0439	0.0420
0.10	4.4158	4.1820	4.0590	3.9368	3.8315	0.0519	0.0836	0.0754	0.0468	0.0409
Water+Sodium butyrate+L-threonine										
0.00	4.4598	4.2525	4.1235	3.9772	3.8676	-	-	-	-	-
0.02	4.4415	4.2379	4.1085	3.9715	3.8596	0.0960	0.0769	0.0778	0.0293	0.0400
0.04	4.4307	4.2251	4.0978	3.9611	3.8518	0.0760	0.0722	0.0664	0.0414	0.0396
0.06	4.4205	4.2100	4.0833	3.9507	3.8395	0.0685	0.0743	0.0693	0.0453	0.0470
0.08	4.4106	4.1950	4.0746	3.9409	3.8316	0.0643	0.0755	0.0633	0.0464	0.0452
0.10	4.4048	4.1776	4.0540	3.9317	3.8232	0.0576	0.0788	0.0721	0.0467	0.0446

solute and solvent molecules. In the present study, the decreasing values of n_H indicating an increase in solute-co-solute interaction. It may also further inferred that butyrate ion has a bigger hydrophobic sphere and a larger destructive effect on the hydration sphere of NH_3^+ of the amino acids. The electrostrictive of water caused by NH_3^+ group of the amino acids will be largely reduced, which results in a larger increase in volume and this may be reason for a decrease in n_H values (Herskovits *et al.*, 1978).

The following observations noticed by the authors on apparent molar compressibility (ϕ_K) and apparent molar volume (ϕ_V) of L-asparagine, L-glutamine, L-serine and L-threonine in aqueous sodium butyrate solution at 298.15 K (Table 2).

The values of the (ϕ_K) and (ϕ_V) are all negative over the entire molarity range of amino acids. It is interesting to note that:

- The values of ϕ_K are found to be increased with increasing molarity of the amino acids, except for L-serine system whereas, a reverse trend is observed
- However, the same values of ϕ_K found to be increased with increase in mass percentage of sodium butyrate in all the four amino acids systems

- The ϕ_V values also increase with increasing molarity of amino acids in all the systems studied, except for L-serine system and increase with the increase in content of the sodium butyrate in all the four amino acid systems
- The present study observes that the maximum value of ϕ_K and ϕ_V obtained for L-serine system comparing the other three amino acids systems, which suggesting a strong molecular association is found in L-serine system
- The noticed maximum values of apparent molar compressibility (ϕ_K) as well as apparent molar volume (ϕ_V) are obtained for L-serine system, suggest electrostriction and hydrophilic interactions occurring in these systems, thereby indicating the presence of solute-solvent interactions
- From the magnitudes of (ϕ_K) and (ϕ_V), the molecular association between the four systems of amino acids are of the order: L-serine>L-threonine>L-asparagine>L-glutamine

All the observations clearly suggest that the negative values of ϕ_K and ϕ_V in all systems indicate the presence of ion-solvent interactions too. Further, the negative values of (ϕ_K) indicate electrostrictive solvation of ions (Dhanalakshmi and Vasantharani, 1999). The observed

Table 2: Values of apparent molar compressibility (ϕ_k) and apparent molar volume (ϕ_v) of amino acids in aqueous sodium butyrate solution at 298.15 K

Molarity (mol.dm ⁻³)	Apparent molar compressibility ϕ_k ($\times 10^{-8}$ m ³ N ⁻¹)					Apparent molar volume ϕ_v ($\times m^3$ mol ⁻¹)				
	0%	5%	10%	15%	20%	0%	5%	10%	15%	20%
Water+Sodium butyrate+L-asparagine										
0.00	-	-	-	-	-	-	-	-	-	-
0.02	15.639	13.456	14.054	8.1894	7.4929	76.0718	80.4977	94.0505	63.0707	60.7605
0.04	10.817	13.118	12.239	7.6401	7.3295	51.5059	77.0351	81.3631	58.0436	49.6690
0.06	9.3684	13.073	10.845	6.9596	6.6507	45.4898	76.3756	66.5611	48.8673	42.1960
0.08	8.8085	13.032	11.422	6.9794	6.5987	42.4817	75.9222	71.4816	44.8776	45.4212
0.10	8.4670	12.624	10.327	7.0698	6.6978	39.2731	75.1554	64.1863	45.8351	45.2796
Water+Sodium butyrate+L-glutamine										
0.00	-	-	-	-	-	-	-	-	-	-
0.02	24.953	21.997	17.934	12.222	17.257	109.6477	141.8208	120.8755	79.8141	166.9425
0.04	17.236	16.783	13.645	9.7112	12.335	72.2976	110.1630	98.1846	73.5901	102.7534
0.06	14.758	15.012	13.004	9.5032	10.026	67.8691	92.6853	95.0127	68.0045	78.0532
0.08	13.273	14.830	11.750	9.4291	8.9611	60.8921	86.6670	80.2515	65.6905	68.4169
0.10	12.482	14.338	11.603	9.2957	8.5051	58.1096	83.9464	75.6889	67.0789	64.6175
Water+Sodium butyrate+L-serine										
0.00	-	-	-	-	-	-	-	-	-	-
0.02	5.6448	6.6421	5.6471	2.6951	3.9226	22.9558	37.4629	29.1754	21.9221	33.4107
0.04	6.4186	7.4518	7.1348	4.6684	4.6856	31.2280	38.4784	37.4710	30.0611	32.4668
0.06	5.8438	8.5896	7.7943	5.3278	4.6045	31.9800	47.8768	42.3508	35.0084	27.7470
0.08	6.1594	8.7294	8.4429	5.1759	4.8940	34.1107	48.9897	49.6704	34.2503	30.3429
0.10	5.9727	9.1730	8.4657	5.4874	4.8906	35.2889	49.8554	48.8897	36.2851	33.1275
Water+Sodium butyrate+L-threonine										
0.00	-	-	-	-	-	-	-	-	-	-
0.02	12.865	9.7376	10.047	4.2213	5.9982	83.1036	57.2619	61.8567	34.3571	52.2772
0.04	9.2890	8.7775	8.0995	5.4677	5.4295	44.7508	45.1429	40.6298	36.2722	38.5898
0.06	8.3914	9.2105	8.6214	5.9779	6.2605	40.9907	50.0070	46.7295	39.1448	40.6350
0.08	7.8948	9.4144	8.2227	6.1461	6.0477	39.1107	52.3154	51.2432	40.5811	40.0057
0.10	7.1365	9.7265	9.1297	6.1984	5.8637	36.5789	52.4143	52.7804	41.4429	36.8907

Table 3: Values of limiting apparent molar compressibility (ϕ_k^0) and limiting apparent molar volume (ϕ_v^0) their associated constant S_k and S_v of amino acids in aqueous sodium butyrate solution at 298.15 K

Amino acids	Water+Sodium butyrate (%)	ϕ_k^0 ($\times 10^{-8}$ m ³ N ⁻¹)	S_k ($\times 10^{-8}$ N ⁻¹ m ³ mol ⁻¹)	ϕ_v^0 ($\times m^3$ mol ⁻¹)	S_v ($\times 10^{-8}$ N ⁻¹ m ³ mol ⁻¹)
L-asparagine	0	-20.0125	39.6162	-98.2472	199.4309
	5	-14.0081	3.9966	-83.7061	28.2971
	10	-16.4487	19.7028	-114.8422	165.8187
	15	-9.0353	7.0338	-78.6888	111.9836
	20	-8.2603	5.5103	-69.4579	87.6999
L-glutamine	0	-32.9998	69.4233	-139.4944	277.2436
	5	-26.5478	41.9921	-182.0918	333.3582
	10	-21.8922	35.0291	-154.0257	253.1678
	15	-13.6315	15.1813	-89.8076	80.0207
	20	-23.2611	49.9572	-232.8588	576.5877
L-serine	0	-5.7280	-1.1802	-15.4633	-66.0065
	5	-4.5998	-14.8357	-25.1068	-81.9349
	10	-3.5840	-16.5041	-12.8068	-121.0715
	15	-1.1420	-14.8843	-12.7125	-79.2653
	20	-3.3717	-5.1787	-33.5750	9.0938
L-threonine	0	-16.4147	30.7874	-106.5137	242.9760
	5	-9.1756	-0.8339	-54.1503	11.4810
	10	-10.0134	5.0165	-57.3498	28.2675
	15	-2.9479	11.1959	-28.1965	42.8666
	20	-5.7350	0.7798	-58.7365	71.9431

increasing behavior of ϕ_v may pointing towards the existence of strong ion-solvent interaction in all the systems studied. The negative values of (ϕ_k) indicate possible interactions such as ionic, dipolar and hydrophilic occurring in these systems. Since more number of water molecules are available at lower concentration of sodium butyrate, the chances for the penetration of solute molecules into the solvent.

The evaluated parameter Limiting apparent molar compressibility (ϕ_k^0) which provide information's

regarding the ion-solvent interactions and its related constant (S_k) of the ion-ion interactions in the solution, which are systematically tabulated in Table 3. It is noticed that the ϕ_k^0 values are negative in all the systems and increase with increase of mass percentage of sodium butyrate. Appreciable negative values of ϕ_k^0 for all the systems which suggest that the existence of ion-solvent interactions. The large values of ϕ_k^0 is noticed in L-serine system than other amino acid systems. Its related constant (S_k) whose values are positive in L-asparagine,

L-glutamine and L-threonine and these systems show a decreasing trend with increase of sodium butyrate and however, it finds a reverse trend in L-serine system, where it exhibits negative values and increases with increasing mass percentage of sodium molecules is highly favored. The decreasing values of (ϕ_k) in the present study revealing the weakening of ion-solvent interactions in these mixtures. From the magnitude of ϕ_k and ϕ_v , it can be concluded that a strong molecular interaction is found in L-serine than other three amino acids and confirming that the L-serine is a more effective structure-maker in the solvent mixture butyrate. The authors observed that such positive values of S_k indicate the strengthening of ion-ion interactions and suggest the structure-making effect of the amino acids.

The perusal of Table 3 represents the values of limiting apparent molar volume ϕ_v^0 exhibiting negative values in all the four systems and increase with increase in content of sodium butyrate in all the four systems. This may enhances/reduces the electrostriction of water molecules. Increase of ϕ_v^0 is due to enhancement in electrostriction at the terminal groups of amino acids, which result in decreasing of interaction between these polar ends and ions. The increase of ϕ_v^0 values in sodium butyrate solution may also be attributed to hydrophobicity/polar character of the side chains of the amino acids. Hence, such an increasing values of ϕ_v^0 in sodium butyrate solution clearly indicate the weakening of the ion-solvent interaction. It is evident from the Table 3 that the values of S_v are positive, except in L-serine system and almost decrease with increase of sodium butyrate content in the mixture. Such a possession of positive values of S_v clearly indicates the presence of strong ion-ion interactions in the solution.

The Co-sphere overlap model (Gurney, 1953) can be utilized to rationalize the transfer volume values in terms of solute-solute interactions. The overlap of co-solute ions and amino acids comes into play because of interactions between (1) the $(\text{NH}_3^+, \text{COO}^-)$ charged ends of amino acids and ions of the co-solute such as sodium butyrate, (2) 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; and (3) the hydrophilic parts of the amino acids and hydrophobic parts of ions of co-solutes. According to this model, ion-ion interactions result in positive transfer volume values, whereas, ion-hydrophobic and hydrophilic group interactions result in negative transfer volume values. Our present investigation reveals that, L-asparagine, L-serine and L-threonine systems exhibit positive values and L-glutamine amino acids system exhibit negative values. Hence, it is very obvious that

Table 4: Values of transfer volume ($\Delta\phi_v^0$), A and B co-efficient of Jones-Dole equation of amino acids in aqueous sodium butyrate solution at 298.15 K

Amino acids	Water+Sodium butyrate (%)	$\Delta\phi_v^0 (\times 10^{-3} \text{ m}^3 \text{ mol}^{-1})$	A ($\text{dm}^{3/2} \text{ mol}^{-1/2}$)	B ($\text{dm}^3 \text{ mol}^{-1}$)
L-asparagine	0	-	0.0072	0.5798
	5	14.5411	0.1665	0.1284
	10	16.5950	0.0763	0.2416
	15	19.5583	0.0613	0.1915
L-glutamine	20	28.7893	0.0497	0.1667
	0	-	0.0031	0.3789
	5	-42.5974	0.0981	0.2754
	10	-14.5313	0.0118	0.3950
L-serine	15	-49.6868	0.0032	0.3452
	20	-93.3644	0.0248	0.2203
	0	-	0.1060	0.3645
	5	-9.6435	0.3280	-0.2570
L-threonine	10	2.6565	0.2003	-0.0442
	15	2.7508	0.1655	-0.0437
	20	44.3220	0.1244	-0.1037
	0	-	0.0021	0.6515
L-threonine	5	52.3634	0.2264	0.0151
	10	49.1639	0.1375	0.0968
	15	78.3172	0.1107	0.0832
	20	47.7771	0.0951	0.0592

ion-ion interactions are dominating in the former systems, whereas ion-hydrophobic and hydrophilic group interactions are dominating in the latter case (Table 4). The overall positive values of transfer volume which are observed for the amino acids can be due to the effect (Yan *et al.*, 1999) of the zwitterionic portion of the amino acids dominating that of alkyl chain. Because of the interactions of the ions ($\text{Na}^+, \text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^-$) and the zwitterionic group of the amino acids, the electrostriction of water molecules lying in the vicinity of NH_3^+ and COO^- centres of the amino acids would get reduced and consequently lead to positive values of transfer volume.

In the present study of amino acid systems with binary [water + sodium butyrate] mixtures, it may be presumed that the interactions may be taking place as:

- Ion-ion interaction between Na^+ and the COO^- of the amino acids
- And then between $\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^-$ of NaC_4 and NH_3^+ group of the amino acids
- Interaction between ion and polar group of amino acids (Wang *et al.*, 2000)

Viscosity is another important parameter in understanding the structure as well as molecular interactions occurring in the solutions. One can notice from Table 5 that the values of viscosity increases with increase in solute concentration in all the systems. This increasing trend indicates the existence of molecular interactions occurring in these systems. In order to shed more light on this, the role of viscosity B-coefficient has also been obtained. From Table 4, it is observed that the

Table 5: Values of density (ρ), viscosity (η) and velocity (U) of amino acids in aqueous sodium butyrate solution at 298.15 K

Molarity M/ (mol.dm ⁻³)	Density ρ (kg m ⁻³)					Viscosity η (10 ⁻³ Nsm ⁻²)					Ultrasonic velocity U (m s ⁻¹)				
	0%	5%	10%	15%	20%	0%	5%	10%	15%	20%	0%	5%	10%	15%	20%
Water + Sodium butyrate + L-asparagine															
0.00	997.32	1010.81	1024.64	1044.35	1059.37	0.8906	1.1967	1.4598	1.8232	2.2428	1499.42	1525.25	1538.44	1551.63	1562.27
0.02	998.84	1012.44	1026.57	1045.67	1060.66	0.9019	1.2291	1.4832	1.8465	2.2668	1502.41	1527.63	1540.80	1552.87	1563.40
0.04	999.38	1013.93	1027.98	1046.78	1061.48	0.9124	1.2411	1.4955	1.8590	2.2792	1503.63	1530.00	1542.60	1554.00	1565.10
0.06	1000.05	1015.45	1028.74	1047.42	1062.06	0.9231	1.2531	1.5070	1.8706	2.2911	1504.82	1532.42	1544.50	1555.25	1566.40
0.08	1000.72	1016.96	1030.51	1048.11	1063.23	0.9338	1.2652	1.5199	1.8824	2.3043	1506.24	1534.85	1546.82	1557.00	1567.30
0.10	1001.25	1018.42	1031.23	1049.15	1064.18	0.9443	1.2773	1.5313	1.8948	2.3170	1507.87	1536.67	1548.00	1558.39	1568.80
Water + Sodium butyrate + L-glutamine															
0.00	997.32	1010.81	1024.64	1044.35	1059.37	0.8906	1.1967	1.4598	1.8232	2.2428	1499.42	1525.25	1538.44	1551.63	1562.27
0.02	999.51	1013.68	1027.12	1046.02	1062.91	0.8975	1.2205	1.4737	1.8366	2.2609	1504.56	1528.84	1541.43	1553.93	1564.04
0.04	1000.21	1015.27	1028.67	1047.43	1063.73	0.9032	1.2326	1.4862	1.8497	2.2734	1506.75	1530.63	1542.62	1554.66	1565.85
0.06	1001.39	1016.44	1030.49	1048.62	1064.34	0.9093	1.2442	1.4992	1.8623	2.2853	1508.32	1533.04	1544.31	1556.47	1567.16
0.08	1002.19	1017.83	1031.23	1049.85	1065.18	0.9151	1.2561	1.5106	1.8750	2.2978	1510.14	1536.17	1546.23	1558.28	1568.28
0.10	1003.13	1019.31	1032.41	1051.37	1066.23	0.9259	1.2681	1.5227	1.8882	2.3108	1511.93	1538.48	1548.65	1559.49	1569.47
Water + Sodium butyrate + L-serine															
0.00	997.32	1010.81	1024.64	1044.35	1059.37	0.8906	1.1967	1.4598	1.8232	2.2428	1499.42	1525.25	1538.44	1551.63	1562.27
0.02	997.78	1011.57	1025.24	1044.81	1060.08	0.9110	1.2484	1.5018	1.8660	2.2868	1500.63	1526.49	1539.65	1552.00	1562.81
0.04	998.57	1012.37	1026.18	1045.61	1060.75	0.9217	1.2595	1.5135	1.8779	2.2989	1501.87	1528.26	1541.47	1553.41	1564.03
0.06	999.24	1013.72	1027.25	1046.55	1061.14	0.9324	1.2714	1.5234	1.8901	2.310	1502.45	1530.15	1543.29	1554.62	1565.26
0.08	1000.05	1014.78	1028.72	1047.22	1061.95	0.9432	1.2829	1.5379	1.9018	2.3228	1503.64	1531.87	1545.00	1555.48	1566.41
0.10	1000.85	1015.86	1029.66	1048.15	1062.89	0.9540	1.2944	1.5496	1.9140	2.3355	1504.21	1534.23	1546.83	1556.75	1567.01
Water + Sodium butyrate + L-threonine															
0.00	997.32	1010.81	1024.64	1044.35	1059.37	0.8906	1.1967	1.4598	1.8232	2.2428	1499.42	1525.25	1538.44	1551.63	1562.27
0.02	998.98	1011.97	1025.91	1045.07	1060.48	0.9021	1.2387	1.4925	1.8560	2.2771	1501.26	1527.00	1540.29	1552.21	1563.06
0.04	999.11	1012.64	1026.31	1045.87	1061.01	0.9122	1.2417	1.5034	1.8679	2.2883	1503.00	1528.81	1542.00	1553.65	1564.25
0.06	999.78	1013.85	1027.52	1046.81	1061.96	0.9279	1.2613	1.5155	1.8801	2.3015	1504.23	1530.63	1543.82	1555.00	1566.07
0.08	1000.45	1015.05	1028.85	1047.75	1062.77	0.9335	1.2730	1.5278	1.8923	2.3139	1505.40	1532.46	1544.47	1556.22	1567.08
0.10	1000.98	1016.12	1030.06	1048.69	1063.29	0.9491	1.2846	1.5401	1.9045	2.3258	1506.00	1534.85	1547.49	1557.35	1568.41

values of A are almost positive and B-coefficients are positive in all systems, (except in L-serine system.) Since A is a measure of ionic interaction which may be presumed that there is a strong ion-ion interactions present in the liquid mixtures. The behaviour of B-coefficient in all the amino acids suggests the existence of strong solute-solvent interaction. Similar trends of interaction studies studied for other amino acids in aqueous sodium acetate solution have been reported earlier (Banipal *et al.*, 2007b), which supports the present investigation. Our present study clearly establishes that the behaviour of B values in these systems suggest that the existence of strong solute-solvent interactions. Hence, it can be concluded that the molecular interaction between the amino acids in the present investigation is of the order: L-serine>L-threonine>L-asparagine>L-glutamine.

The above conclusion is an excellent agreement which has observed from earlier parameters such as ϕ_{E} , ϕ_{v} , ϕ_{K}° and ϕ_{v}° .

CONCLUSION

By exhaustively analysing and critically examining the various related parameters, we briefly summarise our investigations as follows:

- In the present system of mixtures L-serine is a strong structure- maker in aqueous sodium butyrate solution over the other three amino acids
- The transfer volume studies predict that ion -ion interactions are prevailing in L-asparagine, L-serine and L-threonine systems and ion-hydrophobic and hydrophilic group of interactions are existing in L-glutamine amino acid system
- However, a weak ion-solvent interaction is noticed in the present system of mixtures
- The molecular interactions from this study follows the order: L-serine > L-threonine > L-asparagine > L-glutamine

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