

Ultrasonic investigation of amino acids in aqueous sodium acetate medium

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The ultrasonic velocity (U), density (ρ) and viscosity (η) measurements have been carried out for four amino acids namely L-alanine, L-leucine, L-valine and L-proline in aqueous sodium acetate solution as a function of composition at 303, 308 and 313K. Experimental data have been used to estimate the adiabatic compressibility (β), change in adiabatic compressibility ($\Delta\beta$), relative change in adiabatic compressibility ($\Delta\beta/\beta_0$), apparent molal compressibility (φ_K), apparent molal volume (φ_V), limiting apparent molal compressibility (φ_K°), limiting apparent molal volume (φ_V°) and the constants (S_K , S_V), and viscosity B -coefficient. The results are discussed in terms of structure-making or structure-breaking effects of amino acids in the mixture.

Keywords: Ultrasonic velocities, Amino acids, Aqueous sodium acetate, Adiabatic compressibility, Apparent molal compressibility, Apparent molal volume

1 Introduction

Ultrasonic study on the amino acids with aqueous solution of electrolytes and non-electrolytes provides useful information in understanding the behaviour of liquid systems, intramolecular and intermolecular associations, complex formation and related structural changes. 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 hydration¹⁻⁷. Due to the complex molecular structure of proteins, direct study is somewhat difficult. Therefore, the useful approach is to study simpler model compounds, such as amino acids which are building blocks of proteins. Most of the studies on amino acids have been carried out in pure and mixed aqueous solution⁸⁻¹⁰.

Amino acids, the monomer units of protein molecule play an important role in all biological species. Since amino acids are zwitterions in aqueous solution¹¹, their volume and compressibility properties should reflect structural interactions with water molecules as in the case of electrolytes. Water and sodium acetate mixtures have proved to be most interesting owing to the strong hydrogen bond interactions of sodium acetate with water. Since volumetric, compressibility and viscosity studies are lacking in aqueous mixtures of amino acids L-alanine, L-valine, L-leucine and L-proline, an attempt has

been made to understand their behaviour in aqueous sodium acetate solution at 0.4 molality and varying temperatures of 303, 308 and 313K through ultrasonic velocity measurements. However, the ultrasound velocity data do not provide significant information about the nature and relative strength of various types of intermolecular or inter ionic interactions between the components. Hence their derived parameters such as adiabatic compressibility (β), change in adiabatic compressibility ($\Delta\beta$), relative change in adiabatic compressibility ($\Delta\beta/\beta_0$), apparent molal compressibility (φ_K), apparent molal volume (φ_V), limiting apparent molal compressibility (φ_K°), limiting apparent molal volume (φ_V°) and the constants (S_K , S_V) and viscosity B -coefficient have been obtained to shed more light on such interactions.

2 Experimental Details

All the chemicals used in present work are analytical (AR) reagent grade and spectroscopic (SR) reagent grade of minimum assay of 99.9% obtained from Aldrich, E-Merck and Sdfines. Fresh conductivity water is used throughout the investigation. An electronically operated constant temperature bath (RAAGA Industries) has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature. The accuracy in the temperature measurement is $\pm 0.1K$.

Since, density is one of the prime parameters characterising many physical properties of a liquid medium, the density of pure liquids, liquid mixtures and amino acids are determined using a specific gravity bottle by relative measurement method. A specific gravity bottle with 5ml capacity is cleaned well and dried and filled with reference liquid (conductivity water) and then suspended in a temperature controlled water bath. The temperature of the bath can be maintained at any desired value. The bottle with water is allowed to attain the temperature at which density is to be measured and the weight is determined with an accuracy of ± 0.1 mg (Model: SHIMADZU AX-200). An Ostwald's viscometer which is 10 ml capacity is used for the viscosity measurement of pure liquids, liquid mixtures and amino acids. The viscometer is calibrated with fresh conductivity water immersed in the water bath which is kept at the experimental temperature. The time of flow of water and the time of flow of solution are measured with digital stop clock having an accuracy of 0.01S (Model: RACER HS-10W) of the bath. By knowing the flow time of reference liquid (water), the viscosity of the mixture can be determined. The measured viscosity values are accurate to ± 0.001 NS m^{-2} . An ultrasonic interferometer (Model: F81) supplied by M/s Mittal Enterprises, New Delhi, having the frequency 3MHz with an overall accuracy of ± 2 ms^{-1} has been used for velocity measurement.

3 Theory

Adiabatic compressibility (β) is given by:

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

The change in adiabatic compressibility is calculated by:

$$\Delta\beta = \beta - \beta_0 \quad \dots (2)$$

Relative change in adiabatic compressibility is determined by:

$$\frac{\Delta\beta}{\beta_0} \quad \dots (3)$$

Apparent molal compressibility (ϕ_K) is given by:

$$\phi_K = \frac{1000}{m\rho_0} (\rho_0\beta - \rho\beta_0) + \left(\frac{\beta_0 M}{\rho_0} \right) \quad \dots (4)$$

where β , ρ and β_0 , ρ_0 are the adiabatic compressibility and density of solution and solvent respectively, m is the molal concentration of the solute and M the molecular mass of the solute. ϕ_K is the function of m as obtained by Gucker¹² from Debye Huckel theory¹³ and is given by:

$$\phi_K = \phi_K^0 + S_K m^{1/2} \quad \dots (5)$$

where (ϕ_K^0), is the limiting apparent molal compressibility at infinite dilution and S_K is a constant. (ϕ_K^0), and S_K were obtained by least square method.

Apparent molal volume (ϕ_V) is obtained by:

$$\phi_V = \frac{1000}{m\rho_0} (\rho_0 - \rho) + \left(\frac{M}{\rho_0} \right) \quad \dots (6)$$

The apparent molal volume has been found to differ with concentration according to Masson's empirical relation¹⁴ as:

$$\phi_V = \phi_V^0 + S_V m^{1/2} \quad \dots (7)$$

where (ϕ_V^0) the limiting apparent molal volume at infinite solution and S_V is a constant and these values were determined by least square method.

The entire viscosity data have been analysed in the light of Jones-Dole semi empirical equation¹⁵:

$$\frac{\eta}{\eta_0} = 1 + Am^{1/2} + Bm \quad \dots (8)$$

The same may be expressed as,

$$\left(\frac{\eta}{\eta_0} \right) - 1 = \frac{A + Bm^{1/2}}{m^{1/2}} \quad \dots (9)$$

where η and η_0 are the viscosities of the solution and solvent respectively and m is the molal concentration of the solute-solvent system. A and B are constants which are definite for a solute-solvent system. A is known as the Falkenhagen¹⁶ coefficient which characterises the ionic interaction and B is the Jones-Dole or viscosity B -coefficient which depends on the size of the solute and nature of solute-solvent interactions.

4 Results and Discussion

The experimental values of density, viscosity and ultrasonic velocity for different molal compositions of each of the amino acids viz, L-alanine, L-valine, L-proline and L-leucine in aqueous sodium acetate solution at different temperatures are presented in Tables 1-4. The values of adiabatic compressibility, change and relative change in adiabatic compressibility, apparent molal compressibility, apparent molal volume, limiting apparent molal compressibility, limiting apparent molal volume and the constants S_K and S_V and viscosity B -coefficient are given in Tables 5-14.

In all the amino acid systems (Tables 1-4), the values of density, viscosity and ultrasonic velocity increases with increase of molal concentration of amino acids. And the same, except ultrasonic velocity, decreases with rise in temperature. The ultrasonic velocity (U) in Tables 1-4, increases with increase in the concentration of the solute as well as

rise temperature. Such an increase in ultrasonic velocity (U) clearly shows that molecular association is being taking place in these liquid mixtures. The factors apparently responsible for such behaviour may be the presence of interactions caused by the proton transfer reactions of amino acids¹⁷⁻¹⁸ and hydrophilic nature of aqueous sodium acetate¹⁹.

Density (ρ) 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 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, the increase in density may be interpreted to the structure-maker of the solvent due to the added solute. Similarly, the decrease in density with concentration indicates structure-breaker of the solvent. It may also be true

Table 1 — Density (ρ), viscosity (η) and velocity (U) of L-alanine in aqueous sodium acetate

Molality m (mol.Kg ⁻¹)	Density ρ (kg/m ³)			Viscosity η ($\times 10^{-3}$ NSm ⁻²)			Velocity U (ms ⁻¹)		
	Temperature (K)								
	303	308	313	303	308	313	303	308	313
0.00	1007.03	1006.38	1005.12	0.9086	0.8209	0.7383	1542.06	1544.76	1560.70
0.02	1008.34	1007.78	1006.99	0.9144	0.8247	0.7482	1545.60	1549.20	1568.76
0.04	1009.65	1008.34	1007.25	0.9205	0.8331	0.7505	1548.30	1551.96	1570.80
0.06	1010.36	1009.66	1008.43	0.9247	0.8381	0.7565	1548.90	1552.35	1572.60
0.08	1011.29	1010.24	1009.70	0.9350	0.8418	0.7606	1549.68	1554.00	1573.44
0.10	1012.96	1011.85	1010.39	0.9461	0.8541	0.7669	1551.00	1556.40	1577.64

Table 2 — Density (ρ), viscosity (η) and velocity (U) of L-leucine in aqueous sodium acetate

Molality m (mol.Kg ⁻¹)	Density ρ (kg/m ³)			Viscosity η ($\times 10^{-3}$ NSm ⁻²)			Velocity U (ms ⁻¹)		
	Temperature (K)								
	303	308	313	303	308	313	303	308	313
0.00	1007.03	1006.38	1005.12	0.9086	0.8209	0.7383	1542.06	1544.76	1560.70
0.02	1007.37	1006.58	1006.25	0.9358	0.8412	0.7458	1544.40	1555.20	1561.20
0.04	1007.57	1006.71	1006.51	0.9368	0.8462	0.7557	1553.40	1558.80	1567.20
0.06	1007.90	1007.12	1006.95	0.9465	0.8494	0.7562	1561.80	1570.80	1573.20
0.08	1008.40	1007.73	1007.21	0.9492	0.8523	0.7677	1563.60	1573.80	1576.20
0.10	1009.35	1008.96	1008.14	0.9573	0.8588	0.7742	1569.60	1576.20	1579.20

Table 3 — Density (ρ), viscosity (η) and velocity (U) of L-valine in aqueous sodium acetate

Molality m (mol.Kg ⁻¹)	Density ρ /(kg/m ³)			Viscosity η /($\times 10^{-3}$ NSm ⁻²) Temperature (K)			Velocity U /(ms ⁻¹)		
	303	308	313	303	308	313	303	308	313
	0.00	1007.03	1006.38	1005.12	0.9086	0.8209	0.7383	1542.06	1544.76
0.02	1007.96	1007.86	1007.01	0.9320	0.8382	0.7407	1548.75	1556.70	1560.84
0.04	1008.12	1008.05	1007.04	0.9375	0.8427	0.7533	1555.08	1561.05	1566.60
0.06	1008.99	1008.88	1007.30	0.9476	0.8473	0.7585	1556.55	1564.80	1569.24
0.08	1009.43	1009.06	1008.96	0.9540	0.8535	0.7641	1561.44	1566.96	1571.10
0.10	1009.68	1009.32	1009.18	0.9591	0.8556	0.7680	1564.50	1569.30	1572.90

Table 4 — Density (ρ), viscosity (η) and velocity (U) of L-proline in aqueous sodium acetate

Molality m (mol.Kg ⁻¹)	Density ρ /(kg/m ³)			Viscosity η /($\times 10^{-3}$ NSm ⁻²) Temperature (K)			Velocity U /(ms ⁻¹)		
	303	308	313	303	308	313	303	308	313
	0.00	1007.03	1006.38	1005.12	0.9086	0.8209	0.7383	1542.06	1544.76
0.02	1008.26	1008.32	1007.48	0.9311	0.8326	0.7511	1551.15	1556.28	1560.84
0.04	1008.62	1008.50	1008.03	0.9435	0.8409	0.7579	1552.20	1557.66	1561.20
0.06	1008.90	1008.73	1008.36	0.9446	0.8438	0.7592	1554.15	1560.30	1562.85
0.08	1009.58	1009.00	1008.74	0.9462	0.8463	0.7606	1559.10	1562.25	1564.95
0.10	1009.81	1009.61	1009.42	0.9508	0.8523	0.7675	1561.05	1565.04	1566.60

that solvent-solvent interactions bring about a bonding, probably hydrogen bonding between them. So, size of the resultant molecule increases and hence there will be decrease in density. Usually the values of density and viscosity of any system vary with increase in concentration of solutions. The change in structure of solvent or solutions as a result of hydrogen bond formation or dissociation or hydrophobic (structure-breaking) or hydrophilic (structure-forming) character of solute. That is hydrogen bond forming or dissociating properties can thus be correlated with change in density and viscosity²⁰.

The increase in ultrasonic velocity (U) in these solutions may be attributed to the cohesion brought about by the ionic hydration. When the amino acids are dissolved in aqueous sodium acetate, the water molecules are attracted to the ions strongly by the electrostatic forces²¹, which introduce a greater cohesion in the solution. Thus, cohesion increases with increase of amino acid concentration in the solutions. The increased associations obtained in these solutions may also be due to water enhancement brought by the increase in electrostriction in the presence of sodium acetate. The electrostriction effect, which brings about the shrinkage in the volume of solvent is caused by the zwitterionic portion of the

amino acid. Such a similar effect was reported by earlier workers²¹⁻²³.

The values of β in all the amino acids systems show a decreasing trend. The adiabatic compressibility's values are larger in L-leucine system than those of other amino acid systems. This shows that the molecular association is greater in L-leucine 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

Tables 5-8 show the values of change in adiabatic compressibility ($\Delta\beta$) and relative change in adiabatic compressibility ($\Delta\beta/\beta^0$) of amino acids in aqueous sodium acetate solution at varying temperatures. The negative values of ($\Delta\beta$) increases with increasing molality of the solute in all the four systems.

The β , $\Delta\beta$ and ($\Delta\beta/\beta^0$) vary non-linearly with rise in temperature (Tables 5-8). Such a behaviour lends further support to the contention of having apparently ideal systems caused by solute-solvent interactions.

The values of apparent molal compressibility (ϕ_k) are all negative over the entire range of molality, which are given in the Tables 9-12. No systematic

Table 5 — Adiabatic compressibility (β), change in adiabatic compressibility ($\Delta\beta$) and relative change in adiabatic compressibility ($\Delta\beta/\beta^0$) of L-alanine in aqueous sodium acetate

Molality m (mol.Kg ⁻¹)	Adiabatic compressibility β ($\times 10^{-10}$ m ² N ⁻¹)			Change in adiabatic compressibility $-\Delta\beta$ ($\times 10^{-12}$ m ² N ⁻¹)			Relative change in adiabatic compressibility $-\Delta\beta/\beta^0$ ($\times 10^{-2}$ m ² N ⁻¹)		
	Temperature (K)								
	303	308	313	303	308	313	303	308	313
0.00	4.176	4.164	4.084	-	-	-	-	-	-
0.02	4.151	4.134	4.035	2.4532	2.9586	4.8336	0.5875	0.7105	1.1837
0.04	4.132	4.117	4.024	4.4370	4.6558	5.9853	1.0625	1.1181	1.4657
0.06	4.126	4.110	4.010	5.0455	5.3990	7.3764	1.2082	1.2966	1.8064
0.08	4.118	4.099	4.000	5.8393	6.5056	8.3083	1.3983	1.5623	2.0346
0.10	4.104	4.080	3.976	7.2180	8.4218	10.7044	1.7285	2.0225	2.6214

Table 6 — Adiabatic compressibility (β), change in adiabatic compressibility ($\Delta\beta$) and relative change in adiabatic compressibility ($\Delta\beta/\beta^0$) of L-leucine in aqueous sodium acetate

Molality m (mol.Kg ⁻¹)	Adiabatic compressibility β ($\times 10^{-10}$ m ² N ⁻¹)			Change in adiabatic compressibility $-\Delta\beta$ ($\times 10^{-12}$ m ² N ⁻¹)			Relative change in adiabatic compressibility $-\Delta\beta/\beta^0$ ($\times 10^{-2}$ m ² N ⁻¹)		
	Temperature (K)								
	303	308	313	303	308	313	303	308	313
0.00	4.176	4.164	4.084	-	-	-	-	-	-
0.02	4.162	4.108	4.077	1.4050	5.6515	0.6165	0.3364	1.3572	0.1510
0.04	4.113	4.088	4.045	6.2993	7.6010	3.8379	1.5085	1.8254	0.9399
0.06	4.068	4.024	4.013	10.8413	13.9858	7.0897	2.5961	3.3587	1.7362
0.08	4.056	4.006	3.996	11.9819	15.7616	8.7209	2.8693	3.7852	2.1356
0.10	4.021	3.989	3.977	15.4559	17.4685	10.6063	3.7012	4.1951	2.5973

Table 7 — Adiabatic compressibility (β), change in adiabatic compressibility ($\Delta\beta$) and relative change in adiabatic compressibility ($\Delta\beta/\beta^0$) of L-valine in aqueous sodium acetate

Molality m (mol.Kg ⁻¹)	Adiabatic compressibility β ($\times 10^{-10}$ m ² N ⁻¹)			Change in adiabatic compressibility $-\Delta\beta$ ($\times 10^{-12}$ m ² N ⁻¹)			Relative change in adiabatic compressibility $-\Delta\beta/\beta^0$ ($\times 10^{-2}$ m ² N ⁻¹)		
	Temperature (K)								
	303	308	313	303	308	313	303	308	313
0.00	4.176	4.164	4.084	-	-	-	-	-	-
0.02	4.136	4.094	4.076	3.9827	6.9621	0.7351	0.9537	1.6720	0.1800
0.04	4.102	4.071	4.046	7.4108	9.3207	3.7417	1.7746	2.2384	0.9163
0.06	4.091	4.048	4.031	8.5382	11.6028	5.2049	2.0446	2.7864	1.2746
0.08	4.063	4.036	4.015	11.2742	12.7869	6.8191	2.6998	3.0708	1.6699
0.10	4.046	4.023	4.005	12.9586	14.0968	7.8253	3.1031	3.3854	1.9163

Table 8 — Adiabatic compressibility (β), change in adiabatic compressibility ($\Delta\beta$) and relative change in adiabatic compressibility ($\Delta\beta/\beta^0$) of L-proline in aqueous sodium acetate

Molality m (mol.Kg ⁻¹)	Adiabatic compressibility β ($\times 10^{-10}$ m ² N ⁻¹)			Change in adiabatic compressibility $-\Delta\beta$ ($\times 10^{-12}$ m ² N ⁻¹)			Relative change in adiabatic compressibility $-\Delta\beta/\beta^0$ ($\times 10^{-2}$ m ² N ⁻¹)		
	Temperature (K)								
	303	308	313	303	308	313	303	308	313
0.00	4.176	4.164	4.084	-	-	-	-	-	-
0.02	4.122	4.095	4.074	5.3844	6.9296	0.9248	1.2894	1.6641	0.2265
0.04	4.115	4.087	4.070	6.0894	7.7269	1.3341	1.4582	1.8556	0.3267
0.06	4.104	4.072	4.060	7.2357	9.2040	2.3284	1.7327	2.2104	0.5702
0.08	4.075	4.061	4.048	10.1130	10.3250	3.5679	2.4217	2.4796	0.8737
0.10	4.064	4.044	4.035	11.2220	12.0164	4.8980	2.6873	2.8858	1.1995

Table 9 — Apparent molal compressibility (Φ_k) and Apparent molal volume (Φ_v) of L-alanine in aqueous sodium acetate

Molality m (mol.Kg ⁻¹)	Apparent molal compressibility $-\Phi_k(\times 10^{-8} \text{ m}^2 \text{ N}^{-1})$			Apparent molal volume $-\Phi_v(\times \text{m}^3 \text{ mol}^{-1})$		
	Temperature (K)					
	303	308	313	303	308	313
0.02	14.9985	17.6928	27.9765	65.2525	69.4674	93.0845
0.04	13.8197	13.6685	17.1344	65.1284	48.5510	52.9897
0.06	10.7165	11.2598	14.5430	55.0740	54.1320	54.8966
0.08	9.5121	10.1274	12.7179	52.8149	47.7436	56.9445
0.10	9.6820	10.6879	12.8486	58.8276	54.2446	52.3331

Table 10 — Apparent molal compressibility (Φ_k) and Apparent molal volume (Φ_v) of L-leucine in aqueous sodium acetate

Molality m (mol.Kg ⁻¹)	Apparent molal compressibility $-\Phi_k(\times 10^{-8} \text{ m}^2 \text{ N}^{-1})$			Apparent molal volume $-\Phi_v(\times \text{m}^3 \text{ mol}^{-1})$		
	Temperature (K)					
	303	308	313	303	308	313
0.02	7.7354	28.6670	5.3895	16.7512	9.5708	56.2310
0.04	16.3234	19.3484	11.0169	13.5155	8.0472	34.5669
0.06	18.6761	23.8226	13.0587	14.2829	12.0585	30.1644
0.08	15.6979	20.4041	11.9689	16.9923	16.6011	25.8863
0.10	16.4275	18.5411	11.8406	23.0037	25.4982	29.9655

Table 11 — Apparent molal compressibility (Φ_k) and Apparent molal volume (Φ_v) of L-valine in aqueous sodium acetate

Molality m (mol.Kg ⁻¹)	Apparent molal compressibility $-\Phi_k(\times 10^{-8} \text{ m}^2 \text{ N}^{-1})$			Apparent molal volume $-\Phi_v(\times \text{m}^3 \text{ mol}^{-1})$		
	Temperature (K)					
	303	308	313	303	308	313
0.02	21.8509	37.8605	7.5194	46.1586	73.0167	93.9023
0.04	19.6706	25.0342	11.3156	27.1516	41.3688	47.8020
0.06	15.5956	21.0669	10.1585	32.4597	41.2859	36.0981
0.08	15.3468	17.3704	10.4787	29.7978	33.0717	47.6390
0.10	14.0627	15.3185	9.4800	26.2072	29.1053	40.2878

Table 12 — Apparent molal compressibility (Φ_k) and Apparent molal volume (Φ_v) of L-proline in aqueous sodium acetate

Molality m (mol.Kg ⁻¹)	Apparent molal compressibility $-\Phi_k(\times 10^{-8} \text{ m}^2 \text{ N}^{-1})$			Apparent molal volume $-\Phi_v(\times \text{m}^3 \text{ mol}^{-1})$		
	Temperature (K)					
	303	308	313	303	308	313
0.02	29.4818	38.6578	9.4208	61.0665	96.0715	117.2349
0.04	16.8803	21.5088	6.2925	39.4468	52.4003	72.1904
0.06	13.3600	16.9653	6.0812	30.9112	38.8038	53.6602
0.08	13.9715	14.2614	6.3019	31.6272	32.3161	44.8802
0.10	12.3815	13.3543	6.8580	27.5382	31.9012	47.7695

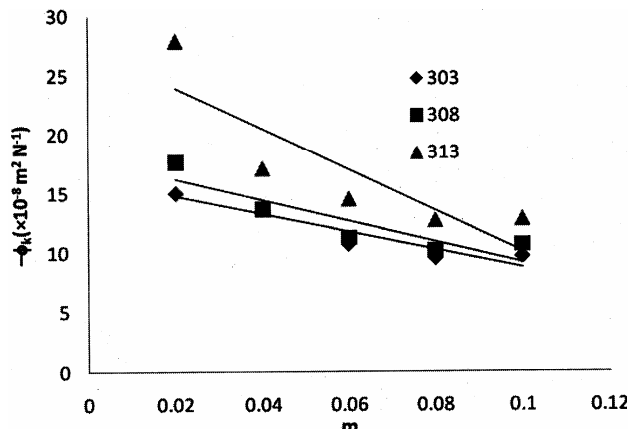


Fig.1 — Variation of apparent molal compressibility (ϕ_k) with molality of L-alanine in aqueous sodium acetate

variation between the ϕ_k and the solute over the entire range of composition as well as rise in temperature is observed (Fig. 1). The maximum value of ϕ_k is obtained for L-leucine system irrespective of molality and temperature indicates electrostriction and hydrophilic interactions accruing in these systems, thereby indicating solute-solvent (Fig. 2) interaction. The limiting apparent molal compressibility (ϕ_k^0) and the related constant S_K from the amino acids have been presented in Table 13. The limiting apparent molal compressibility (ϕ_k^0) provides information regarding solute-solvent interaction and the related constant S_K that of solute-solute interaction in the solution. From Table 13, one can observe that all ϕ_k^0 values are negative in all the systems. Appreciable negative values of (ϕ_k^0) for all the four amino acids systems reinforce the view that there exist solute-solvent interaction in the present systems. From the Table 13, the values are non-linear over the elevation of temperature.

The value of S_K exhibits positive values and also it is non-linear with increase of temperature in all the four systems. This behaviour indicates the existence of ion-ion/solute-solute interaction with increase in temperature. It is well known that solutes causing electrostriction led to decrease in compressibility of the solution, which is reflected by the negative values of (ϕ_k) of the amino acids.

The perusal of Tables 9-12, shows that the values of apparent molal volume (ϕ_v) are all negative over the entire range of molality. No systematic variation has been found in (ϕ_v) values with increase of molality of the solute as well as temperature. The maximum value of apparent molal

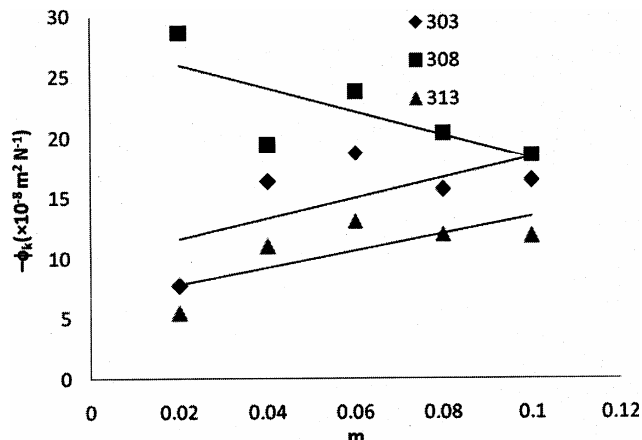


Fig. 2 — Variation of apparent molal compressibility (ϕ_k) with molality of L-leucine in aqueous sodium acetate

volume (ϕ_v) is obtained for L-leucine. These observations clearly suggest that the negative values of (ϕ_v) in all the four systems indicate the presence of solute-solvent interaction. The negative values of (ϕ_v) indicates electrostrictive solvation of ions²⁴. From Tables 9-12, the value of (ϕ_v) in all the systems are negative and vary irregularly. This enhances/reduces the electrostriction of water molecules. Thus, it can be concluded that the strong molecular association is found in L-leucine system than the other three amino acids and hence L-leucine is acting as effective structure-maker than other amino acids.

In the present amino acid systems, it may be presumed that the interactions may be taking place as: ion-dipolar/hydrophilic group interactions between the ions of sodium acetate (Na^+ , CH_3COO^-) and (NH_3^+ , COO^-), (-OH) group of amino acids¹⁹; ion-hydrophilic group interaction between the ions of sodium acetate and non-polar parts of amino acids¹⁹.

The values of the limiting apparent volume (ϕ_v^0) in all the four systems are non-linear with rise in temperature (Table 13). This enhances the electrostriction of water molecules. The negative value of (ϕ_v^0) indicates smaller solute-solvent interaction present in these systems.

The constant S_V exhibits positive values in all the systems suggesting the presence of ion-ion interactions (Table 13). Usually the negative values of S_V indicate weak ion-ion interaction whereas the positive values of S_V predict strong solute-solute interactions in the systems.

Table 13 — Limiting apparent molal compressibility (Φ_k^0), limiting apparent molal volume (Φ_v^0), and the constants S_k and S_v of amino acids

Amino acids	Limiting apparent molal compressibility Φ_k^0 ($\times 10^{-8} \text{ m}^2 \text{ N}^{-1}$)			Constant S_k ($\times 10^{-8} \text{ N}^{-1} \text{ m}^{-1} \text{ mol}^{-1}$)			Limiting apparent molal volume Φ_v^0 ($\times \text{m}^3 \text{ mol}^{-1}$)			Constant S_v ($\text{N}^{-1} \text{ m}^{-1} \text{ mol}^{-1}$)		
	Temperature (K)											
	303	308	313	303	308	313	303	308	313	303	308	313
L-alanine	-23.52	-25.41	-34.14	49.51	53.48	71.86	-118.84	-109.66	-124.10	250.62	231.25	261.72
L-leucine	-29.98	-44.37	-21.33	63.10	93.40	44.89	-33.82	-28.71	-70.73	71.32	60.55	149.15
L-valine	-34.66	-46.73	-19.60	72.95	98.36	41.25	-64.71	-87.14	-106.29	136.47	183.77	224.16
L-proline	-34.48	-41.96	-13.99	72.57	88.32	29.45	-76.24	-100.60	-87.40	160.78	212.15	184.32

Table 14 — Values of A and B parameters of Jones – Doles equation of amino acids

Amino acids	A ($\times \text{dm}^{-3/2} \text{ m}^{-1/2}$)			B ($\times \text{dm}^3 \text{ mol}^{-1}$)		
	Temperature (K)					
	303	308	313	303	308	313
L-alanine	-0.0275	-0.0308	-0.0604	0.2139	0.1891	0.4326
L-leucine	-0.2236	-0.1953	-0.0139	0.4668	0.4763	0.1723
L-valine	-0.1730	-0.1518	-0.0360	0.0033	0.0603	0.5617
L-proline	-0.2180	-0.0969	-0.1321	0.2262	0.0693	0.0501

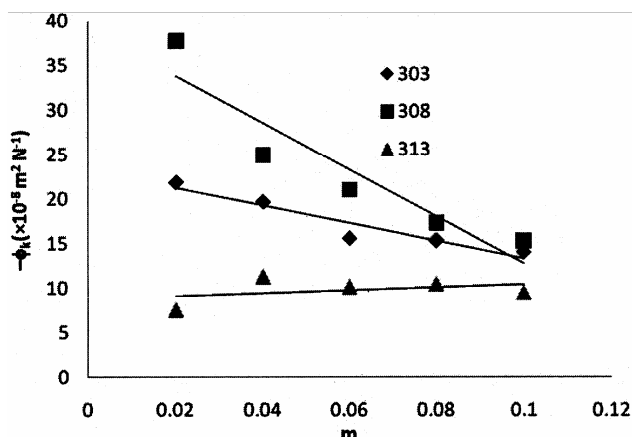


Fig. 3 — Variation of apparent molal compressibility (ϕ_k) with molality of L – valine in aqueous sodium acetate

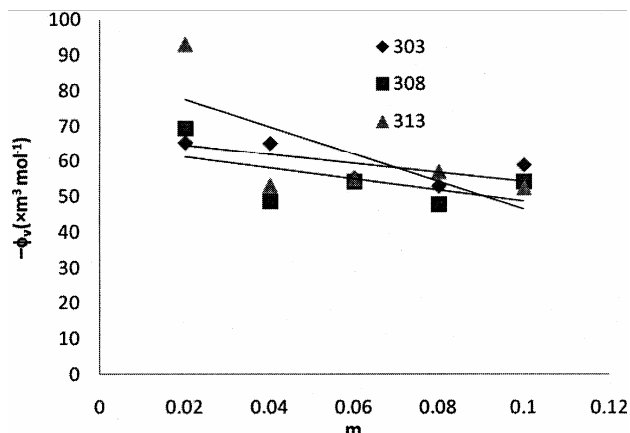


Fig. 5 — Variation of apparent molal volume (ϕ_v) with molality of L – alanine in aqueous sodium acetate

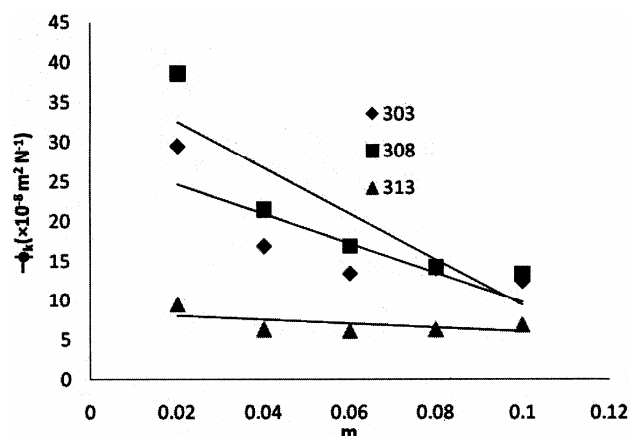


Fig. 4 — Variation of apparent molal compressibility (ϕ_k) with molality of L – proline in aqueous sodium acetate

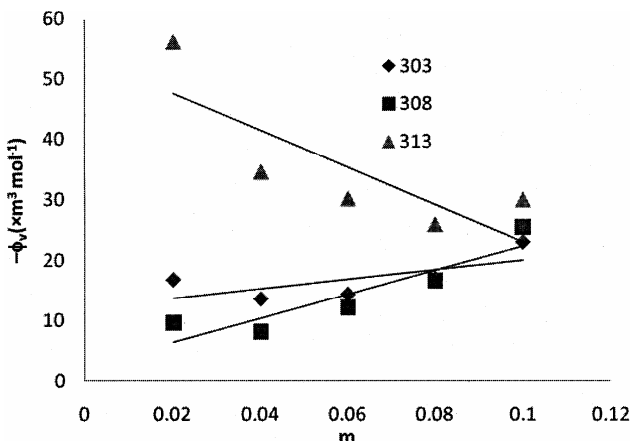


Fig. 6 — Variation of apparent molal volume (ϕ_v) with molality of L – leucine in aqueous sodium acetate

Viscosity is an important parameter in understanding the structure as well as molecular interactions occurring in the solutions. Viscosity variation is attributed to the structural changes. The structural changes influence the viscosity to a certain extent as compared to density and compressibility. From Tables 1-4, it is observed that the values of viscosity increase with increase in solute concentration in all the systems. This increasing trend indicates the existence of molecular interaction occurring in these systems.

In order to shed more light on this, the role of viscosity *B*-coefficient has also been obtained. From Table 14, it is observed that values of *A* are negative and *B*-coefficient are positive in all systems. Since *A* is a measure of ionic interaction²⁵ it is evident that there is a weak ion-ion interaction in the amino acids.

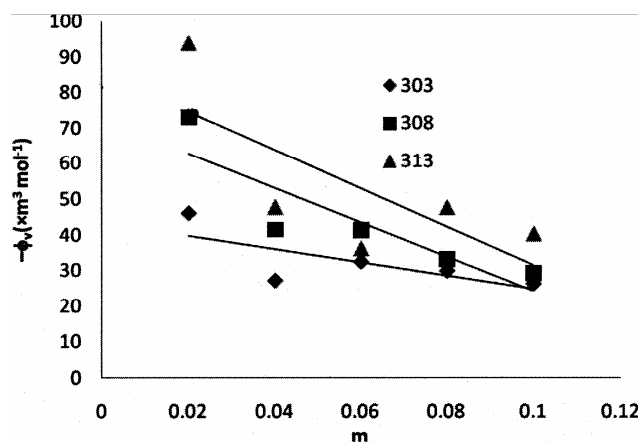


Fig. 7 — Variation of apparent molal volume (ϕ_v) with molality of L – valine in aqueous sodium acetate

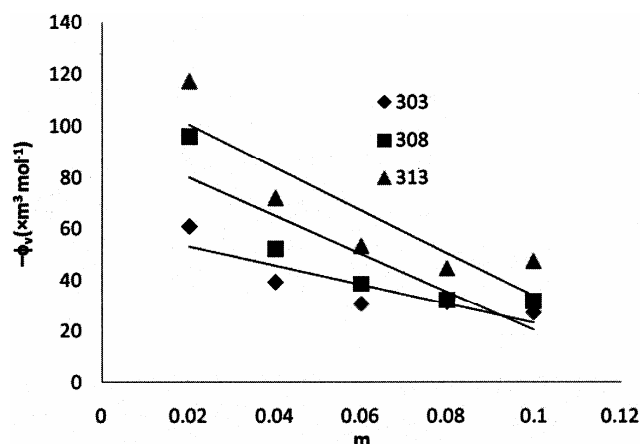


Fig. 8 — Variation of apparent molal volume (ϕ_v) with molality of L – proline in aqueous sodium acetate

B-coefficient which is known for measure of order or disorder introduced by the solute in the solvent. It is also a measure of solute-solvent interaction. The behaviour of *B*-coefficient in all the amino acids suggests the existence of strong solute-solvent interaction. The magnitude of *B*-values is higher in L-leucine which clearly confirms that the amino acid L-leucine is acting as an effective structure-maker in aqueous sodium acetate solution. Similar trends of interaction studies studied for other amino acids in aqueous sodium acetate solution have been reported earlier¹⁹, which supports the present investigation (Figs 3-8). From the magnitude of *B*-Coefficient, it can be concluded that the molecular interaction between the amino acids is of the order L-leucine > L-alanine > L-valine > L-proline.

5 Conclusions

Intermolecular interaction of electrostriction and hydrophilic nature exist in the systems studied in the

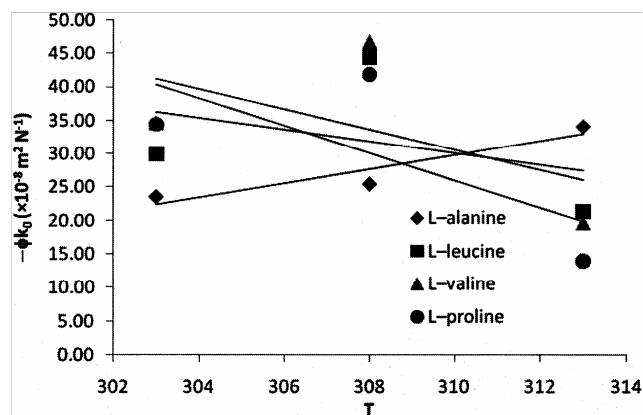


Fig. 9 — Variation of limiting apparent molal compressibility (ϕ_K^0) with temperature

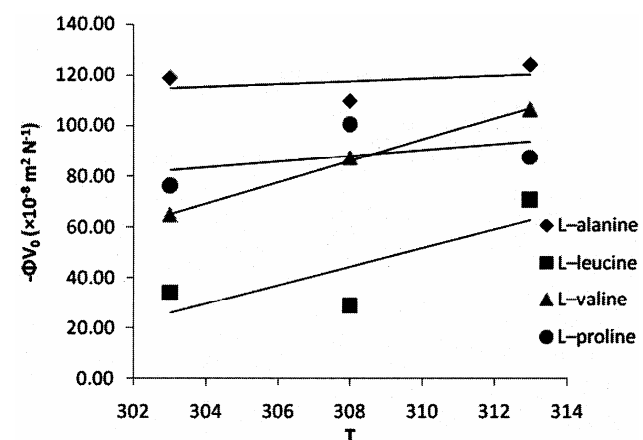


Fig 10 Variation of limiting apparent molal volume(ϕ_K^0) with temperature

present paper. The existence of ion-solvent or solute-solvent interactions resulting in attractive forces promote the structure-making tendency, while ion-ion or solute-solute interaction resulting dipole-dipole, dipole-induced dipole and electrostrictive forces enhance the structure-breaking properties of amino acids. And eventually, analysing all the evaluated parameters clearly suggest that L-leucine is a strong structure maker in aqueous sodium acetate solution over the other three amino acids. Hence, in the present study the molecular interaction follows the order L-leucine > L-alanine > L-valine > L-proline.

Ultrasonic velocity, density and viscosity have been measured for four amino acids viz, L-alanine, L-leucine, L-valine and L-proline in aqueous sodium acetate solutions at 303, 308 and 313K, which have biological and biochemical relevance (Figs 9 and 10). The dipolar (zwitterions) characteristics of these organic liquid molecules shed light on solute-solvent interactions in aqueous sodium acetate mixtures and have proved to be the most interesting owing to the strong hydrogen bond interactions with water. There is much scope for further studies in these systems by varying pH of the solution and temperature which may reveal more about hydrogen bonding interaction as well as other interaction existing between solute-solvent molecules. Hence it is evident that the ultrasonic velocity measurement in the given medium serves as a powerful probe in characterising the physio-chemical properties of that medium.

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