INVESTIGATION OF MOLECULAR INTERACTION OF AMINO ACIDS IN AQUEOUS n-PROPANOL SOLUTIONS AT 308.15 K

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Abstract

The physical properties that has been investigated are, density (ρ),viscosity (η), and ultrasonic velocity (U) of L-valine, L- leucine and L-glutamine in aqueous n-propanol solution (0%-30%) in steps of 10% at 308.15K have been measured. The derived acoustical parameters namely adiabatic compressibility (β), apparent molal compressibility (ϕ_K), apparent molal volume (ϕ_V), limiting apparent molal compressibility(ϕ°_K), limiting apparent molal volume(ϕ°_V) and their constants (s_k, s_v), transfer adiabatic compressibility ($\Delta\phi^\circ_K$), transfer volume($\Delta\phi^\circ_V$) , and viscosity B-coefficient are calculated using the experimental data. The change that has been observed in the parameter with respect to molality of the solute has been interpreted in terms of ion-ion and ion- solvent interactions.

Key words: *Molecular interaction, solute-solvent interaction, ion-ion interaction, ion-solvent interaction.*

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1. INTRODUCTION

In recent years, the Physicist wished to understand the structure of liquid molecules. The only means they had of investigating these structures were by chemical reaction that led to the changes which themselves were known. The liquids and liquid mixtures help chemical physicist to explore the "dynamic behavior" of rigid molecules, using both physical and chemical methods. Denaturation of globular proteins in aqueous solutions is a fundamental biological process which till date is not completely understood and continues to be a subject of extensive investigations [1]. Knowledge of various solute-solute and solute-solvent interactions is very important to understand various fundamental phenomena like stability of proteins, folding/unfolding processes, denaturation of proteins etc., in aqueous solutions [2]. It is rather difficult to study the interaction of protein molecules because it has got a nature of complex structure. It is quite interesting to study the physio- chemical behavior of the non-electrolyte like propanol with amino acids [3].

The physical properties of dilute aqueous solutions of non-electrolytes depend on the solute and solvent i.e., water whose structure acts as breaker or maker. The influence of small quantity of amino acids over the hydrogen bonded structure of water in the solution may expect to yield good results. It will also help to study the nature of molecular interactions between the organic solute with water which act as a solvent [4].

2. MATERIALS AND METHODS

In the present study, the spectroscopic reagent (SR) and analytical reagent (AR) grades of minimum assay of 99.9% are used and obtained from E-Merck, Germany and Sd Fine chemicals, India. Water used in the experiment was deionized, distilled and are degassed to making solutions. An aqueous solution of n-propanol 0% - 30 % mol. dm^{-3} in steps of 10 % is prepared by volume and has been used for the present study. The amino acids in the concentration range of 0.02 - 0.1 mol dm^{-3} has been made by volume on the molality concentration with a precision of ± 1×10^{-4}g on an electronic digital balance (Model: Shimadzu Ax - 200). The density has been measured by using the relative measurement method with an accuracy of ± 0.01 kg m^{-3}, and obtained by using a specific gravity bottle. An Ostwald's viscometer (5ml) has been used for the viscosity measurements. Efflux time has been determined using a digital chronometer within ± 0.01 s. For velocity measurements, Ultrasonic interferometer having a frequency of 3 MHz (Mittal Enterprises, New Delhi, Model: F-18) with an overall accuracy of 0.1% has been used. A digital electronic constant temperature bath has been used for experimental purpose. The accuracy of the temperature measurement is ± 0.1 K.

3. RESULT AND DISCUSSION

The values of ultrasonic velocity (U), density (ρ), and viscosity (η), for different molar concentrations of L- valine, L-leucine and L-glutamine in aqueous n-propanol (0% - 30%) M solution at 308.15K is reported in Table1. The values of adiabatic compressibility (β), apparent molal compressibility (ϕ_k), apparent molal volume (ϕ_v), limiting apparent molal compressibility (ϕ°_k), limiting apparent molal volume (ϕ°_v) their constants (S_k, S_v), are reported in Table 2, 3. The volumetric, compressibility and transport parameter have been calculated using the standard relations,

Adiabatic compressibility

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

The apparent molar compressibility

$$\varphi_k = \frac{1000}{M\rho_0}(\rho_o\beta - \rho\beta o) + \left(\frac{\beta o M_w}{\rho_o}\right) \quad (2)$$

where, M is the molal concentration of the solute and M_w the molecular weight of the solute. φ_k is the function of M as obtained by Gucker (1993) [5] from Debye Huckel [6] and is given by

$$\varphi_k = \varphi^o_k + S_k M^{1/2} \quad (3)$$

where, φ^o_k is the limiting apparent molar compressibility and S_k is a constant.

The apparent molar volume φ_v

$$\varphi_v = \left(\frac{M_w}{\rho}\right) - \left(\frac{1000(\rho-\rho_0)}{M\rho\rho_0}\right) \quad (4)$$

The apparent molar volume φ_v in according to empirical relation as:

$$\varphi_v = \varphi^o_v + S_v M^{1/2} \quad (5)$$

where, φ^o_v is the limiting apparent molar volume and S_v is a constant. The constant values have been evaluated by least square method.

The viscosity A and B coefficients has been calculated from the Jones - Dole equation [7].

$$\left(\frac{\eta}{\eta_o}\right) = 1 + AM^{1/2} + BM \quad (6)$$

where, η and η_o are the viscosities of the solution and solvent respectively.

Transfer adiabatic compressibility ($\Delta\varphi^o_k$) and transfer volume ($\Delta\varphi^o_v$) have been calculated as:

$$\Delta\varphi^o_y = \varphi^o_y \text{ (in aqueous n-propanol solution)} - \varphi^o_y \text{ (in water)} \quad (7)$$

Where, φ^o_y denotes limiting apparent molar compressibility φ^o_k, limiting apparent molar volume φ^o_v.

Table – 1: **Density (ρ), viscosity (η) and ultrasonic velocity (U) of the amino acids in aqueous solutions of n-propanol at 308.15 K**

M (mol.dm^{-3})	ρ/(kg.m^{-3})				η/(×10^{-3} Nsm^{-2})				U/(x10^{-10}m.s^{-1})			
	Water + n-Propanol + L-valine											
	0%	10%	20%	30%	0%	10%	20%	30%	0%	10%	20%	30%
0.00	994.0	980.1	966.2	952.9	0.7190	0.9614	1.0576	1.2861	1519.5	1537.6	1555.2	1575.7
0.02	994.7	981.0	967.3	954.2	0.8060	0.9926	1.0760	1.3062	1520.6	1540.2	1558.0	1579.2
0.04	995.5	982.2	968.8	955.2	0.8296	1.0001	1.0870	1.3322	1524.7	1542.6	1560.5	1584.2
0.06	996.5	983.6	970.4	957.2	0.8578	1.0128	1.1005	1.3516	1527.4	1545.0	1562.8	1586.2
0.08	997.8	985.1	971.9	959.0	0.8827	1.0255	1.1251	1.3878	1530.8	1547.8	1565.3	1590.3
0.10	999.2	986.8	973.6	960.8	0.9113	1.0360	1.1595	1.4044	1535.2	1552.3	1570.1	1594.2
Water + n-Propanol + L-Leucine												
0.00	994.0	980.1	966.2	952.9	0.7190	0.9614	1.0576	1.2861	1519.5	1537.6	1555.2	1575.7
0.02	996.7	983.4	971.0	958.7	0.7943	0.9711	1.1208	1.3292	1523.9	1540.9	1559.6	1579.1
0.04	998.2	985.4	973.0	960.6	0.8046	0.99s45	1.1372	1.3713	1526.6	1543.7	1562.2	1585.3
0.06	999.9	987.0	974.8	962.6	0.8122	1.0050	1.1530	1.3873	1529.1	1546.7	1565.0	1588.9
0.08	1001.6	989.2	976.8	964.4	0.8301	1.0274	1.1705	1.4059	1530.8	1549.7	1567.6	1593.2
0.10	1002.9	990.6	978.3	966.0	0.8360	1.0581	1.1839	1.4440	1533.9	1552.4	1570.9	1594.5
Water + n-Propanol + L-Glutamine												
0.00	994.0	980.1	966.2	952.9	0.7190	0.9614	1.0576	1.2861	1519.5	1537.6	1555.2	1575.7
0.02	997.2	984.6	972.0	959.4	0.7996	0.9711	1.2765	1.5215	1523.5	1542.3	1559.9	1579.8
0.04	998.3	985.8	973.3	960.8	0.8061	0.9842	1.3012	1.5423	1526.3	1545.0	1563.7	1586.2
0.06	1000.3	987.6	975.4	963.2	0.8161	1.0006	1.3068	1.5623	1529.6	1548.3	1567.0	1589.4
0.08	1002.2	990.0	977.8	965.6	0.8343	1.0156	1.3197	1.5754	1532.3	1551.9	1570.4	1592.2
0.10	1003.1	991.3	979.5	967.7	0.8537	1.0289	1.3397	1.5948	1535.2	1554.3	1573.4	1594.3

The density (ρ) increases with increase of molal concentration of amino acids and decreases with increase of concentration of n-propanol (Table 1), the values of ultrasonic velocity increase with increase in molal concentration of amino acids and also with n-propanol content. The observed results suggest a moderate strong electrolytic nature in which the solutes tend to attract the solvent molecules in the aqueous solution.

When amino acids are dissolved the water structure is disturbed initially, followed by a structural reorganization leaving the molecules in closely fitting helical cavities [8]. This will increase the density structure of water. Hence the density of medium is affected. The increase in the ultrasonic velocity may be attributed to the cohesion brought about by the hydration. When the amino acids are dissolved in aqueous alcohol, the cations NH_3^+ and anions COO^- are formed. The water molecules are attached to the ions strongly by the electrostatic forces which introduce a greater cohesion in the solution. The cohesion effect of medium generally increases with the increase of amino acid concentration. The increased associations observed in these solutions, may also be due to water structure enhancement brought by the increase of electrostriction in the presence of n-propanol.

The adiabatic compressibility (β) (Table-2) decreases with increase in the concentration of amino acids and also with the n-propanol content.

The decrease in adiabatic compressibility is attributed to the influence of the electrostatic field of ions (NH_3^+ and COO^-) on the surrounding solvent molecules ($C_3H_7^+$, OH^-).

The other observed results are on (ϕ_k) and (ϕ_v) (Table 2) of L-valine, L-leucine and L-glutamine in aqueous n-propanol solutions at 308.15K has been summarized as follows.

(i) All (ϕ_k) and (ϕ_v) values are negative over the entire system.

(ii) With increase in concentration of amino acids as well as n-propanol in system-I the values of (ϕ_k) and (ϕ_v) decreases. For system II and II the values of (ϕ_k) and (ϕ_v) increases with increase in concentration of amino acid but decreases with the increase in concentration of n-propanol.

(iii) For (ϕ_k) and (ϕ_v) values the magnitude are in the order L-valine > L-leucine > L-glutamine.

Table - 2 : Values of adiabatic compressibility (β), apparent molar compressibility (φ_k) and apparent molar volume (φ_v) of amino acids in aqueous n-propanol solutions at 308.15 K.

M (mol. dm^{-3})	β / (x 10^{-10} m^2 N^{-1})				-φ_k / (x 10^{-7} m^2 N^{-1})				- φ_v / (x 10^{-3} m^3 mol^{-1})			
	0%	10%	20%	30%	0%	10%	20%	30%	0%	10%	20%	30%
System - I Water + n-Propanol + L-valine												
0.00	4.3572	4.3156	4.2791	4.2267	--	--	--		--	--	--	
0.02	4.3474	4.3012	4.2589	4.2023	0.6653	0.9621	1.2535	1.3546	35.28	46.68	58.72	71.36
0.04	4.3206	4.2785	4.2387	4.1714	1.0903	1.1586	1.2978	1.5266	37.78	54.41	69.31	76.74
0.06	4.3013	4.2591	4.2193	4.1522	1.1362	1.1985	1.3066	1.6006	41.95	60.39	71.53	78.44
0.08	4.2766	4.2369	4.1993	4.1226	1.2102	1.2424	1.3130	1.6394	47.78	64.61	75.75	83.31
0.10	4.2461	4.2050	4.1660	4.0950	1.2293	1.3570	1.4321	1.6407	52.23	69.15	78.55	86.16
System - II Water + n-Propanol + L-Leucine												
0.00	4.3572	4.3156	4.2791	4.2267	--	--	--		--	--	--	
0.02	4.3203	4.2827	4.2340	4.1828	2.0595	2.3715	3.3179	3.4813	136.13	171.05	255.67	317.30
0.04	4.2986	4.2585	4.2112	4.1422	1.9252	2.0109	2.4503	2.9665	105.69	131.06	180.69	210.16
0.06	4.2773	4.2351	4.1884	4.1148	1.7627	1.8480	2.1464	2.5820	98.80	118.74	152.04	176.11
0.08	4.2601	4.2094	4.1660	4.0850	1.6301	1.8283	2.0005	2.4088	95.28	117.19	140.25	156.28
0.10	4.2378	4.1888	4.1421	4.0712	1.5841	1.7303	1.9058	2.1360	89.14	108.01	127.87	142.17
System - III Water + n-Propanol + L-Glutamine												
0.00	4.3572	4.3156	4.2791	4.2267	--	--	--		--	--	--	
0.02	4.3204	4.2697	4.2280	4.1763	2.4513	3.2857	3.5430	3.9615	161.27	233.01	308.64	355.34
0.04	4.2999	4.2496	4.2019	4.1365	1.9037	2.2774	2.7161	3.1310	108.18	147.33	188.57	215.56
0.06	4.2761	4.2238	4.1752	4.1102	1.8119	2.0804	2.4107	2.7031	105.45	128.99	162.54	186.88
0.08	4.2493	4.1940	4.1469	4.0850	1.7980	2.0648	2.2946	2.4754	102.74	127.39	153.33	172.38
0.10	4.2298	4.1756	4.1239	4.0652	1.6728	1.8931	2.1410	2.2714	91.12	115.12	140.38	160.34

The negative values of (ϕ_k) and (ϕ_v) indicates ionic and hydrophilic interactions occurring in these systems [10]. The magnitude of (ϕ_k) strongly supports our earlier view of the ultrasonic velocity and adiabatic compressibility. The negative values of (ϕ_v) indicate electrostrictive solvation of ions [11]. The value of (ϕv) shows that stronger molecular association has been found in L-valine.

Hence L-valine is a more effective structure maker than other two amino acids.

From Table 3, the changes observed in ($\phi°_k$) and (S_k) values with increase of amino acids concentration may be due to ion-solvent interaction and ion-ion interactions in the solution. The values of ($\phi°_k$) are negative and it decreases with increasing concentration of n-propanol in all the systems studied. It confirms the existence of ion-solvent interaction in the mixtures.

The magnitude of ($\phi°_k$) is in the order L-valine > L-leucine > L-glutamine. The values of (S_k) is negative for L-valine (Table 3), but it is positive for other two amino acids. The negative values of (S_k) Indicate weakening of ion-ion interaction and suggest the structure breaking effect of the amino acids.

It is well known that solutes causing electrostriction lead to decrease in compressibility of the solution. This is reflected by the negative values of the (ϕ_k) values of amino acids.

The volume behavior of the solute at infinite dilution is satisfactorily represented by ($\phi°_v$), which is independent of
the ion-ion interactions and provides information concerning ion-solvent interactions. Table 3 reveals that the values of ($\phi°_v$) are negative in all the three amino acids. From table 3, (S_v) values are negative for L-valine and positive for the other two amino acids. The negative (S_v) values for L-valine suggest the presence of weak ion-ion interactions [12]. Therefore it causes the complex ion formation in the systems. The values of transfer adiabatic compressibility ($\Delta\phi°_k$) and transfer volume ($\Delta\phi°_v$) (Table 3) are negative and it decreases with increasing concentration of n-propanol in all the three amino acid systems. It suggests that the existence of ion-solvent interaction in the mixtures.

Table - 3 Values of limiting apparent molal compressibility (φ°_k), limiting apparent molal volume (φ°_v), their constants S_k and S_v, transfer adiabatic compressibility ($\Delta\varphi^\circ_k$) and transfer volume ($\Delta\varphi^\circ_v$) of the a**mino acids in aqueous n-propanol solutions at 308.15 K**

Amino Acid	M/ (mol. Kg^{-1})	$-\varphi^\circ_k$ / ($\times10^{-7}$ m^2 N^{-1})	$-\varphi^\circ_v$ / ($\times10^{-3}$ m^3 mol^{-1})	S_k / ($\times10^{-7}$ N^{-1} m^{-1} mol^{-1})	S_v / ($\times10^{-3}$ m^3 $L^{1/2}$ $mol^{-3/2}$)	$\Delta\varphi^\circ_k$ /($\times10^{-7}$ m^2 N^{-1})	$\Delta\varphi^\circ_v$ / ($\times10^{-3}$ m^3 mol^{-1})	A / ($dm^{3/2}$. $mol^{-1/2}$)	B / ($dm^{3/2}$. mol^{-1})
L-Valine	0%	0.3522	20.46	-3.0117	-95.06	-	-	0.8210	-0.0349
	10%	0.7044	29.11	-2.0216	-126.25	-0.3522	-8.65	0.1982	0.1168
	20%	1.1286	45.41	-0.8096	-106.97	-0.7764	-24.95	-0.0384	0.9700
	30%	1.1663	59.85	-1.6285	-81.62	-0.8141	-39.39	-0.0357	1.0517
L-Leucine	0%	2.4107	164.68	2.6080	251.72	-	-	0.8746	-1.2209
	10%	2.7867	209.04	3.4966	336.75	-0.376	-44.36	-0.1051	1.2781
	20%	4.2240	338.96	7.8453	707.24	-1.8133	-174.28	0.4427	-0.2459
	30%	4.5015	429.68	7.5367	969.18	-2.0908	-265.00	-0.1546	0.6913
L-Glutamine	0%	3.0022	197.5	4.4574	0.3534	-	-	0.8882	-1.1238
	10%	4.0460	297.7	7.2800	0.6226	-1.0438	-0.1002	-0.0500	0.8670
	20%	4.4470	404.3	7.7035	0.9013	-1.4448	-0.2068	1.9129	-3.6004
	30%	5.1630	467.1	9.5105	1.0505	-2.1608	-0.2696	1.6619	-3.0269

In the case of amino acids + n-propanol + water, when the solute-cosolute molecules come close enough, their cospheres overlaps and the following types of interactions are possible:

(1) Ion-hydrophilic interactions occurring between zwitterionic centers of amino acids and the –OH group of n-propanol,

(2) Hydrophobic - hydrophilic interactions between nonpolar parts of amino acids or n-propanol and –OH group of n-propanol or zwitterionic centers of amino acids, and

(3) hydrophobic-hydrophobic interactions occurring between the nonpolar parts of amino acids and the nonpolar parts of n-propanol.

Anwar Ali [13] was also suggested the similar types of interactions in the study of some amino acids with salts in aqueous medium.

On the basis of co-sphere overlap model [14] the ($\Delta\phi^\circ_v$) values can also be explained in terms of solute-cosolute (ion-ion) interactions. According to this model, ion-ion group interactions contribute positively whereas ion-non-polar and non-polar-non-polar interactions contribute negatively to the ($\Delta\phi^\circ_v$) values.

Therefore the negative values of ($\Delta\phi^\circ_k$) and ($\Delta\phi^\circ_v$) observed in all the three amino acids showed that the interaction contribution of type (ii) is stronger than that of type (i).

The study of Viscosity (η), helps to understand the structure as well as molecular interactions occurring in the solutions. It is observed that the values of viscosity increases with increasing in solute concentration. This increasing effect indicates the existence of ion-solvent interaction occurring in these systems (Table 1).

Further to confirm the effect, the role of viscosity (B) coefficient has been obtained from Jones-Dole equations [15]. The (A) coefficient is negative and (B) coefficient is positive for L-valine whereas a reverse trend is observed for the other two amino acids (Table 3). Since there is a weak ion-ion interaction is occurred in L-valine, because (A) is a measure of ionic interaction, which is indicated by the negative and smaller magnitude of (A) values [16] for L-valine and vice-versa for the other two amino acids.

The viscosity (B) coefficient [17] gives the effect of ion-solvent interactions on the solution viscosity. The positive (B) values suggest the presence of strong ion-solvent interactions vice-versa. The magnitude of (B) is in the order L-valine > L-leucine > L-glutamine. The larger value of (B) shows structure making capacity of the solute.

4. CONCLUSION

In summary, from the magnitudes of β, ϕ_k, ϕ_v and viscosity B coefficient, it can be concluded that L-valine in aqueous n-propanol solution possesses the strong ion-solvent interaction than the other two amino acids. The transfer volume ($\Delta\phi^\circ_v$) suggests an ionic hydrophobic group interaction which predominates over the ionic hydrophilic interactions and hydrophobic – hydrophobic interactions. From the co-sphere overlap model it can be concluded that ionic-hydrophobic interactions are dominating over the ion-ion and hydrophobic – hydrophilic interactions.

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