VOLUMETRIC, VISCOMETRIC AND REFRACTIVE INDEX BEHAVIOURS OF AMINO ACIDS IN DMSO AT VARYING TEMPERATURES

SABIR, S. KUMAR, M.

Department of chemistry, Shivalik College of Engineering, Dehradun

Abstract— Density, viscosity and refractive index for alanine and leucine have been determine in aqueous solution of DMSO as a function of amino acid concentration at different temperature. The density data has been used to compute apparent molar volume. The partial molar volume (limiting apparent molar volume) was obtained by applying the Masson's Equation. The viscosity data have been analysed by means of Jones –dole equation. The value of Falkenhagen coefficient and Jones dole coefficient thus obtained are used to interpret the solute-solute and solute –solvent interactions respectively.. The transition state theory was applied to obtain the activation parameter of viscous flow i.e. free energy of activation per mole of solvent and solute. The enthalpy and entropy of activation of viscous flow were computed for the system. The refractive index was used to calculate the molar refractivity of the mixture. The results have been interpreted in the light of various interactions occurring between the components of the mixtures under applied experimental conditions

Index Terms— amino acids, DMSO, Falkenhagen coefficient, Jones dole coefficient, molecular interaction

INTRODUCTION

Amino acids are the building block of the entire living organism and contain intermolecular hydrogen bonding. Due its existence of dipolar ions in aqueous medium [1],[2],[3], [4] amino acid provide valuable information that lead to understand protein, amino acids are model well suited for estimation of several biological processes like fever which involve expansion and contraction of protein resulting from temperature and pressure changes in living system. The solvent is generally prepared by using water because its unique role in determining the structure and stability since it gives rise to hydrophobic force which stabilize the globular structure of protein [5] . The mixed solvents are of great importance as they provide wide range of solvent with appropriate composition and properties.

DMSO(dimethyl sulphoxide) is a is a highly polar and water miscible organic liquid and has a high boiling point due to which it is used as solvent in many chemical and biological process. It has large dipole movement and dielectric constant and is strongly associated aprotic solvent due to highly polar group S=O group in the molecules [6]. DMSO is used for various cancer treatments [7] and as an anti-flammatory agent for arthritic condition [8]. Thus interaction of amino acid in aqueous DMSO medium has its biological significance. In continuation to earlier studies [9], [10], [11], we report here the densities, viscosity and refractive index of (0.01, 0.02, 0.03, 0.04 and 0.05M) Leucine and alanine in aqueous DMSO (10% DMSO v/v) at 298.15, 303.15, 308.15, 313.15K. The density data have been used to calculate apparent molar volume $Ø_v$ and partial molar volume$Ø_v^0$. The viscosity data were analyzed by means of Jones dole equation. The activation parameter of viscous flow, namely free energies of activation per mole of solvent, $\mu_1^{0\#}$and per mole of solute $\mu_2^{0\#}$ respectively were obtained by using transition state theory. The refractive index Data was used to calculate molar refraction R_m for the amino acid in

DMSO solvent Mixture. These thermodynamic parameters are used to discuss the solute solvent /co solvent and solute-solute interaction in the aforementioned mixture.

EXPERIMENTAL:

The amino acids were recrystallized from ethanol-water mixture and dried over P_2O_5 in a desiccators for 72 hours before use. DMSO was used as such without further purification except drying over 0.4 nm molecular sieves. The mixed solvent aqueous DMSO (10 % v/v) was prepared using triple distilled water and was used to prepare various solution of amino acids

The densities of the solutions were measured using a pycnometer (Borosil glass, total volume of 8×10^{-6} m^3) having a graduated capillary of narrow bore (internal diameter 1×10^{-3} m). The capillary was provided with a well-fitted glass cap in order to avoid changes in composition due to evaporation. The marks on the pycnometer were calibrated at experimental temperatures using known densities of double distilled deionised water and extra pure ethanol (E. Merck, Germany, highly pure). The accuracy of the density measurement was checked by comparing the experimental values of the densities of water and ethanol and good agreement was found with the corresponding literature values [10]. Density measurements were made in triplicate and an average value was used for all the calculations. The uncertainty in density measurement was less than $\pm 5 \times 10^{-2}$ kg m^{-3}.

The viscosity measurements were made by using a thoroughly cleaned Ubbelohde type suspended-level viscometer with a flow time of 300 s for pure water at 298.15 K. Since the flow time was greater than 100 s, kinetic energy corrections were not considered. The time of flow was recorded with a digital stop-watch, accurate to ±0.1 s. An average of four sets of flow times for each reading was taken and used for the calculation of viscosity of the solutions. The accuracy in viscosity measurement was found to be $\pm 3 \times 10^{-4}$ N s m^{-2}.

Refractive indices of the solutions were measured with the help of a thermostatic Abbe – refractometer. Before use, the refractometer was calibrated with double distilled deionised water and toluene (E. Merck, India, mass fraction 0.99) at experimental temperatures. The accuracy in refractive index measurement was up to ±0.0002 units. The temperature of the solutions during the measurements of ρ, η, and $n_D$was maintained (±0.02 K) in an electronically controlled thermostatic water bath (JULABO, G)

RESULT AND DISCUSSION

The experimental value of density ρ, viscosity η and refractive index n_D of 0.01, 0.02, 0.03, 0.04 and 0.05M L-leucine and L- alanine in aqueous DMSO (10%$^{V}/_{V}$) at different temperature are tested in table-1. The apparent in molar volume of amino acids in aqueous DMSO were calculated by using relation

$$\emptyset v = 1000(\rho_O - \rho)/c\rho_O + M_2/\rho_O$$

Where c is the molar concentration of the solute (amino acid), ρ and ρ_O are densities of the solution and solvent (aqueous DMSO), respectively and M_2 is the molar mass of the solute. The calculated value of as Øv a function of amino acid concentration and temperature are given in table2.

The value of $\emptyset v$ were plotted against $C^{1/2}$ and the plots were found to be almost linear in the concentration range studied. These plots are well represented by the equation,

$$\emptyset v = \emptyset_v^0 + s_v^* C^{½}$$

Where the intercept $Ø_v^0$ the partial molar volume of amino acid (which is a measure of solute – solvent interaction), and slope, S_v^* (which measure solute-solute interaction) were obtained by the least squares fitting of $Øv$ value to the above equation. The value of $Ø_v^0$ along with the slope S_v^* are listed in the table 3. The trends observed in the $Ø_v^0$ value of amino acids are due to their hydration behaviours. The hydration behaviours of amino acid are found to comprise of the following interaction [12], [13], [14], [15], [16] and [17]

a. The terminal group of zwitter ions of amino acid, NH_3^+ and $COO^-$are hydrated in an electrostatic manner, whereas, hydration of the intervening backbone depends on its nature that may hydrophobic, Hydrophilic or amphiphilic.
b. Electrostriction of NH_3^+ group is about 10times greater that COO^- group.
c. The overlap of hydration of co-sphere of terminal NH_3^+ and COO^- groups and of adjacent groups' results in volume change. The $Ø_v^0$ values increase due to reduction in the electrostriction at terminals and it decrease due to disruption of side group hydration by that of the charged end.

   The table 3 reveals that value of $Ø_v^0$ are large positive for the two amino acid in aqueous DMSO suggesting strong solute-solvent interaction. The $Ø_v^0$value are in the sequence alanine > leucine which is also the order of size of the side chain (hydrophobic group) of the two amino acid under study i.e. the increase in the $Ø_v^0$ may be attributed to the increased hydrophobic/ non polar character of the side chain of these amino acid causing a reduction in electrostriction at terminal charged groups.

   Similar trend in $Ø_v^0$ with increasing size of the side chain of amino acid in aqueous solution have also been reported by Banipal etal [18]. The $Ø_v^0$ value (table 3) increase with increase in temperature for all the amino acids studied. This increase can be explained by considering the size of primary and secondary solvation layer around the dipolar ions. At higher temperature the solvent from secondary solvation layer is release into the bulk of the solvent, resulting in expansion of the solution [19] as inferred from greater $Ø_v^0$ value of higher temperature.

The S_V^* values, as expected, are found to be negative [table 3] for all the amino acids and the negative follow the order alanine > leucine. The negative S_V^* values indicate weak solute-solute interaction in these systems. Generally, negative S_V^*values are associated with solute showing an overall hydrophobic character [20]as in the present case. For all amino acids studied, S_V^* value decrease with increase in temperature, indicating a decreased solute-solute interaction in the solution with rise in the temperature.

The volume of transfer of amino acid from water to aqueous DMSO, $Ø_v^0(tr)$are calculated by using the relation

$Ø_v^0(t_r) = Ø_v^0$ *(aqueous – DMSO)* - $Ø_v^0$ *(water)*

Where $Ø_v^0$ *(water)* is the partial molar volume of the amino acid in water and its values for the amino acid under study at 298.16, 303.15 and 313.15K have been taken from literature [18], [19], [20], [21]. The $Ø_v^0(t_r)$ value are summarised in table 3. A perusal of table 3 indicates that $Ø_v^0(t_r)$ valves are positive and increase with increase in temperature for the amino acid studied. When dissolved in waters, amino acids cause a decrease in volume of the water due to the electrostriction of water by zwitter ionic terminal group. The observed increase in $Ø_v^0(t_r)$ may be attributed to the decreased electrostriction of water by

($NH_3^+$and COO^-) group of amino acid in present of DMSO, because of the interaction of highly polar S=O group of DMSO with the polar end groups, particularlyNH_3^+group of amino acids. Similar explanation for increasing positive $\emptyset_v^0$ (tr) value of glycine, aniline and serine in aqueous glycerol solution were also proposed by Li and Co worker [22]. The increase in $\emptyset_v^0$ (t_r) values with rise in temperature may be due to release of some solvent molecules from the solvation layers, resulting in an expansion in volume of the solution.

The viscosity data were analyzed by using Jones Doles [23] equation.

$\eta_{r=}$ η/η_0 = 1+A$C^{½}$ + BC

Where η_r is the relative viscosity of the solution, η and η_0 are the viscosity of the solution and the solvent (aqueous DMSO), respectively, A and B are the Falkenhagan [24] and Jones Dole [23] coefficients, respectively. Coefficient A accounts for the solute – solute interaction and B is a measure of structural modification induced by the solute- solvent interaction[25],[26]. The value of A and B have been obtained from the intercept and slopes of the plot of $[\eta_r - 1/C^{1/2}]$ vs. $C^{1/2}$ The Value of A and B are including in table 3. Table 3 shows that the value of A coefficient are negative whereas those of B coefficient are large positive, suggesting weak solute-solute and strong solute- solvent interaction in the amino acid solutions under study. Thus, the value of coefficients A and B support the behaviours of $\emptyset_v^0$ and S_V^* which all suggest stronger solute- solvent interaction as compared to solute-solute interaction in these amino acids systems. The variations of B-Coefficient with temperature, $\frac{dB}{dT}$is found to provide the direct evidence regarding structure making and structure breaking ability of the solute in solution. The $\frac{dB}{dT}$ is negative for structure makes and positive for structure breaker [27]. The dB/dT are positive for all amino acids studied, indicating that these amino acids act as structure breakers in aqueous DMSO solvent.

Furthermore, the viscosity data were also examined in the light of transition state theory of the relative viscosity proposed by Feakins etal [25], [26], [27]. According to this theory the coefficient B is given as

$$B = \frac{[(V_1^0 - V_2^0) + V_1^0(\Delta\mu_2^0 - \Delta\mu_1^0)/RT}{1000}$$

Where V_1^0 (=$\emptyset_v^0$) and V_2^0 are the partial molar volume of the solute (amino acid) and the solvent (aqueous DMSO), respectively. The free energy of activation per mole of solvent, $\Delta\mu_1^{0\#}$has been calculated by using Eyring Viscosity [28] relation.

$\Delta\mu_1^{0\#}$ = RT ln ($\eta_0 V_1^0$ /*hN*)

Where *h* and N are Planck's constant and Avogadro's number respectively, Eq (5) rearrange to give free energy of activation per mole of the solute, $\Delta\mu_2^{0\#}$

$$\Delta\mu_2^{0\#} = \Delta\mu_1^{0\#} + [RT/V_1^0][1000B/V_1^0 - V_2^0]$$

The value of $\Delta\mu_1^{0\#}$ and $\Delta\mu_2^{0\#}$ are included in table 3. It is evident from table 3 that for all the amino acid $\Delta\mu_2^{0\#}$ are positive and much larger than those of$\Delta\mu_1^{0\#}$ in aqueous DMSO. This suggests that the interaction between amino acids and solvent (aqueous DMSO) molecules in the ground state are stronger than in the transition state. Hence, in the transition state of the solvation of the solute molecules is unfavourable in free energy terms. The value of $\Delta\mu_2^{0\#}$increase in the

order analine < leu, indicating that the solvation of amino acid in the transition state become unfavourable as the hydrophobic character of this side chain increases. Thus the conclusion drawn from $\Delta\mu_2^{0\#}$is in good agreement with those concluded from the trends of $\emptyset_v^0$, S_V^* and B .

The experiment value of refractive index (table 1) show an increasing trend with measuring concentration of amino acid in the solution, indicating that refractive index is influenced by the interactions in the solution.

The refractive index data were used to calculate molar refraction R_m by using Lorentz – Lorentz equation.

$$R_m = \frac{(n^2-1)}{(n^2+2)} \sum_{i=1}^{n3} \frac{x_{iM_I}}{\rho}$$

Wherex_i and $M_i$are the mole fraction and molar mass of i[th] components of the mixture. The plots R_m vs. C values have been shown graphically in fig 1 at 298.15k. Fig 1 Indicates that R_m values increase almost linearly with increase in the concentration of solute for all the amino acids. Since R_m is directly proportional to molecular polarizability, from fig 1 it is clear that the overall 5 polarizability of the systems under study increase with concentration of amino acids in the solution

Table 1.

Density ρ, viscosities η and refractive index η_ρ solution of l alanine and L-leucine in aqueous DMSO (10% DMSO v/v) at different temperature.

Densityρ (kgm-3)				
C(5mol L^{-1})	T(K)			
	298.15	303.15	308.15	313.15
	L-isoleucine			
0.01	1010.5	1008.8	1007.1	1005.4
0.02	1010.7	1009	1007.3	1005.5
0.03	1010.9	1009.2	1007.5	1005.7
0.04	1011.1	1009.4	1007.6	1005.9
0.05	1011.3	1009.6	1007.9	1006.1
	L-analine			
0.01	1010.3	1008.5	1006.6	1004.8
0.02	1010.8	1009	1007	1005.1
0.03	1011.3	1009.4	1007.4	1005.5
0.04	1011.8	1009.9	1008	1006.1
0.05	1012.4	1010.4	1008.5	1006.5
	η(10^{-3} Nsm^{-2})			
	L-isoleucine			
0.01	1.1203	1.0009	0.9001	0.7852
0.02	1.1366	1.011	0.9089	0.7922
0.03	1.1512	1.0298	0.9259	0.8057
0.04	1.1667	1.0422	0.9359	0.8141
0.05	1.1838	1.0516	0.9431	0.5222
	L-analine			
0.01	1.133	1.0094	0.9064	0.785
0.02	1.1536	1.0183	0.9145	0.7886
0.03	1.1694	1.04	0.9296	0.799
0.04	1.181	1.0517	0.9401	0.8109
0.05	1.1964	1.0594	0.9473	0.8205
	n_D			
	L-isoleucine			
0.01	1.3442	1.3439	1.3432	1.3428
0.02	1.3445	1.344	1.3334	1.3429
0.03	1.3448	1.3443	1.3438	1.3432
0.04	1.3451	1.3449	1.3443	1.3439
0.05	1.3454	1.345	1.3447	1.3445

Table 1 *continued*

	L-analine			
0.01	1.3486	1.3472	1.3462	1.3459
0.02	1.349	1.3476	1.3465	1.3462
0.03	1.3494	1.3478	1.3469	1.3467
0.04	1.3499	1.3482	1.3472	1.3469
0.05	1.3508	1.349	1.3479	1.3472

Table 2 : Apparent molar volume $\emptyset_v$ (10^{-4} m^3mol^{-1}) of l alanine and L- leucine in aqueous DMSO (10% DMSO v/v) at different temperature.

C(molL-1)	T(K)			
	298.15	303.15	308.15	313.15
	L-isoleucine			
0.01	1.1993	1.2706	1.2926	1.3048
0.02	1.1498	1.2012	1.2281	1.255
0.03	1.1333	1.1682	1.1867	1.2053
0.04	1.1251	1.1517	1.171	1.1804
0.05	1.1202	1.1418	1.1536	1.1655
	L-analine			
0.01	1.2384	1.4386	1.6397	1.7419
0.02	0.9415	1.0421	1.1928	1.2943
0.03	0.8425	0.943	1.0439	1.112
0.04	0.7931	0.8687	0.9198	0.9711
0.05	0.7436	0.8421	0.8652	0.9263

Table 3. partial molar volume $\emptyset_v^0$,slope S_v^* ,partial molar volume in water, $\emptyset_v^0\,(water)$,volume transfer from water to aqueous DMSO, $\emptyset_v^0\,(tr)$,Falkenhagen coeffient ,A,Jones dole coefficient B and free free energy of activation permole of solvent $\mu_1^{0\#}$ and solute $\mu_2^{0\#}$ for L-l alanine and L- leucine in aqueous DMSO (10% DMSO v/v) at different temperature.

C(molL-1)	T(K)			
	298.15	303.15	308.15	313.15
	L-isoleucine			
$\emptyset_v^0$ ($1o^{-4}m^3$/mol	1.25	1.36	1.394	1.418
S_v^*($1o^{-4}m^3/mol^{-3/2}L^{1/2}$	-0.623	-1.035	-1.12	-1.168
$\emptyset_v^0\,(water)1o^{-4}m^3$/mol	1.058	_	1.065	1.07
$\emptyset_v^0\,(tr)(1o^{-4}m^3$/mol	0.192		0.329	0.348
A($dm^{3/2}/mol^{1/2}$)	-0.8099	-0.8931	-0.9217	-0.9464
B(dm^3/mol	3.9123	4.1073	4.1367	4.164
$\mu_1^{0\#}$(Kj/mol)	9.82	9.72	9.62	9.43
$\mu_2^{0\#}$(Kj/mol	566.5	603.74	617.13	630.04
		L-analine		
$\emptyset_v^0$ ($1o^{-4}m^3$/mol	1.558	1.823	2.163	2.312
S_v^*($1o^{-4}m^3/mol^{-3/2}L^{1/2}$	-3.855	-4.77	-6.147	-6.581
$\emptyset_v^0\,(water)1o^{-4}m^3$/mol	0.826		0.831	0.836
$\emptyset_v^0\,(tr)(1o^{-4}m^3$/mol	0.732		1.332	1.476
A($dm^{3/2}/mol^{1/2}$)	-0.6425	-0.7853	-0.8233	-0.96
B(dm^3/mol	3.4019	3.7789	3.7552	4.1172
$\mu_1^{0\#}$(Kj/mol)	9.82	9.72	9.62	9.43
$\mu_2^{0\#}$(Kj/mol	500	564.1	573.66	636.23

Table 4:Molar refraction R_m ($10^{-6}m^3$ mol^{-1}) of L-l alanine and L- leucine in aqueous DMSO (10% DMSO v/v) at different temperature.

C(molL-1)	T(K)			
	298.15	303.15	308.15	313.15
	L-isoleucine			
0	3.7888	3.7889	3.7903	3.7917
0.01	3.7958	3.7991	3.7986	3.8011
0.02	3.8023	3.8037	3.8049	3.806
0.03	3.8088	3.8103	3.8127	3.8125
0.04	3.8153	3.8198	3.8212	3.8231
0.05	3.8219	3.8243	3.8288	3.8327
	L-analine			
0	3.7888	3.7889	3.7903	3.7917
0.01	3.8397	3.8326	3.8298	3.8337
0.02	3.8454	3.8384	3.835	3.8393
0.03	3.8512	3.8425	3.8412	3.8465
0.04	3.858	3.8483	3.8456	3.8499
0.05	3.8683	3.8581	3.8544	3.8551

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