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Determination of Partial Molar Properties of Amino Acids in Aqueous Methanol Solutions at Different Temperatures

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ABSTRACT

Density (d) values of amino acids have been measured at 298.15, 303.15, 308.15, and 313.15K in three different wt.%(5,10,and15 wt. %) of aqueous methanol solution. Partial molar properties of amino acids e.g., apparent molar volume (V_{ϕ}), limiting apparent molar volume (V_{ϕ}^0), apparent molar expansibility (E_{ϕ}), and limiting apparent molar expansibility (E_{ϕ}^0) have been evaluated in these solutions from the density data. The ultrasonic velocity (U) values in these solutions have been measured at 298.15K only. Acoustical parameters such as isentropic compressibility (K_s), apparent molar compressibility, ($K_{s,\phi}$) and solvation number (S_n) have been computed for these solutions from the values of ultrasonic velocity. The results are discussed in the light of molecular interactions in the solutions.

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1. Introduction

The study of alcohol- protein interactions is very important for immunology, pharmacology, and medicine. Due to complex molecular structure of proteins direct study is quite difficult. So the amino acids which are the building blocks of proteins are studied. In continuation of our previous work in aqueous medium¹, the present investigation aims at studying the molecular interactions of amino acids in aqueous solutions of (5,10,and15 wt.%) methanol ranging from 298.15K to 313.15K at an interval of 5K. Various parameters, such as apparent molar volume (V_{ϕ}), limiting apparent molar volume (V_{ϕ}^0), apparent molar expansibility (E_{ϕ}), limiting apparent molar expansibility (E_{ϕ}^0), isentropic compressibility (K_s), and

apparent molar compressibility($K_{s,\phi}$) have been calculated from the density (d) and ultrasonic velocity (U) data, respectively, which provide qualitative information regarding molecular interactions.

2. Experimental

All the chemicals used were of AnalaR grades and used as such. The solutions of amino acids were prepared on the molal basis and conversion of molality to molarity was done by using the standard expression ² using the density values of the solutions determined at 298.15K. Conductivity water (Specific conductance $\sim 10^6$ Scm⁻¹) was used to prepare solutions of methanol and the solutions were used on the same day. The densities of pure solvents and their solutions were determined by using a specific gravity bottle (25ml capacity) as described else where³. At least 5 observations were taken and the differences in any two readings did not exceed $\pm 0.02\%$.

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The ultrasonic velocity was measured by using Ultrasonic interferometer (Mittal Enterprises, New Delhi, Model No F-81) using a frequency of 2MHz. The precision of the ultrasonic velocity measurement was within ± 0.5 m/s. The amino acids content in the solutions varied over a concentration range of 0.006 to 0.08 mol dm⁻³ in various solvents. Measurement of density was done in the temperature range 298.15K to 313.15K and speed of sound at 298.15K only.

3. Theoretical aspects:

From the density data the apparent molar volume (V_ϕ) was calculated by using equation ⁴

$$V_\phi = 1000 (cd_0)^{-1}(d_0-d) + M_2d_0^{-1} \quad (1)$$

where d_0 is the density of solvent

It was found that the V_ϕ varied linearly with concentration $c^{1/2}$

The V_ϕ data were fitted by a method of least squares to Masson equation ⁴

$$V_\phi = V_\phi^0 + S_v c^{1/2} \quad (2)$$

to obtain V_ϕ^0 (limiting apparent molar volume) and the slope S_v

The apparent molar Expansibility, E_ϕ was determined from equation ⁴

$$E_\phi = \alpha_0 V_\phi + (\alpha - \alpha_0) 1000c^{-1} \quad (3)$$

The E_ϕ data were fitted by a method of least squares to the Masson equation [4]

$$E_\phi = E_\phi^0 + S_E c^{1/2} \quad (4)$$

The ultrasonic velocities 'U' of amino acids in aqueous methanol solutions at different concentrations were fitted to an equation of the form ⁵⁻⁷

$$U = U_0 + Fc + Gc^{3/2} + Hc^2 \quad (5)$$

U_0 is the sound velocity in pure solvent and F,G,H, are the empirical constants

$$U = (K_s d)^{-1/2} \quad (6)$$

The values of K_s obtained were fitted to an equation of the form

$$K_s = K_s^0 + A'c + B'c^{3/2} + C'c \quad (7)$$

where A' , B' and C' are the empirical constants.

The apparent molar compressibility $K_{s, \phi}$ has been

computed from equation (8) ⁵⁻⁷

$$K_{s, \phi} = 1000 K_s c^{-1} - K_s^0 d_0^{-1} (1000c^{-1}d - M_2) \quad (8)$$

The $K_{s, \phi}$ data were fitted to Eqn. (9)

$$K_{s, \phi} = K_{s, \phi}^0 + F'c^{1/2} + G'c \quad (9)$$

to obtain $K_{s, \phi}^0$ (the limiting apparent isentropic compressibility)

The solvation number S_n can be related to K_s by equation (10)

$$S_n = n_1 n_2^{-1} [1 - V K_s (n_1 V_1^0 K_s^0)^{-1}] \quad (10)$$

where V is the volume of the solution containing n_2 moles of solute

V_1^0 is the molar volume of solvent and n_1 is the number of moles of solvent

The variation of solvation number with molar concentration of the solute leads to the limiting solvation number, S_n^0 which was obtained from the relation (11)

$$\lim_{c \rightarrow 0} K_{s, \phi} = -S_n^0 V_1^0 K_s^0 \quad (11)$$

From the density and sound velocity values, the magnitude of relative association, R_A was calculated from the relation ⁵⁻⁷

$$R_A = (d/d_0)(U_0/U)^{1/3} \quad (12)$$

4. Results and Discussion

The values of partial molar volume (V_ϕ^0), partial molar expansibility (E_ϕ^0), the slope (S_v) of the plot of V_ϕ vs $c^{1/2}$ and the slope S_E of E_ϕ vs $c^{1/2}$ are given in Table 1 for amino acids in different wt.%(5,10, and 15wt%) of methanol in water at temperatures ranging from 298.15K to 313.15K at an interval of 5K. The density values of the solutions of amino acids vary linearly with concentrations in all wt.% of aqueous solutions of methanol at different temperatures. It was found that the V_ϕ values vary linearly with $c^{1/2}$ for all the solutions at the experimental temperatures (a typical plot is given in Fig. 1 at 298.15K for 5wt.% of methanol). Since V_ϕ^0 value indicates the ion-solvent interactions at infinite dilution (as the ion-ion interaction vanishes at infinite dilution), the positive values indicate the presence of ion-solvent interaction which decreases with rise of temperature. The presence of ion-solvent interactions between the molecules promotes structure making effect of amino acids in the solutions of methanol.

As observed (Table-1), the V_{ϕ}^0 values of glycine is higher in all wt.% of methanol solutions pointing to the fact that ion-solvent interactions take place strongly in glycine as compared to the other amino acids in solutions. As the magnitude of S_v is a measure of ion-ion interaction, the positive value of S_v in most of the solutions, are the indicative of strong ion-ion interaction. However, they vary with change of temperature and the content of amino acids. As observed the magnitudes of V_{ϕ}^0 values are much greater than those of S_v for all the solutions which suggest that the ion-solvent interactions dominate over ion-ion interaction in all the solutions and at all

experimental temperatures. The values of limiting apparent molar expansibility E_{ϕ}^0 (Table 1) are also positive and decrease with increase of temperature, and the values are higher in 15wt.% of methanol solutions than in other wt.%. This may be due to the gradual disappearance of caging or packing effect in the solutions with increase of temperature. But, the higher E_{ϕ}^0 values in 15wt.% solutions as compared to those in other wt.% which suggest that the appearance of caging or packing effect occurs to a greater extent in the former solution than in the other wt.% of the solutions.

Table 1 : Values of V_{ϕ}^0 ($\text{m}^3 \text{mol}^{-1}$), S_v ($\text{m}^{3/2} \text{mol}^{-3/2}$), E_{ϕ}^0 ($\text{m}^3 \text{mol}^{-1} \text{K}^{-1}$), and S_E ($\text{m}^{3/2} \text{mole}^{-3/2} \text{K}^{-1}$) for amino acids in different wt.%(5,10,and15wt.%) of methanol solutions at different temperatures.

Solvent	Wt. %	Temperature (K)	V_{ϕ}^0	S_v	E_{ϕ}^0	S_E
Gly+methanol	5	298.15	90.2	23.6	45.3	46.2
		303.15	89.4	25.2	45.2	46.2
		308.15	87.2	14.6	44.8	46.4
		313.15	82.4	14.2	44.7	46.4
	10	298.15	81.9	11.6	46.7	43.1
		303.15	80.2	23.2	46.4	43.6
		308.15	79.4	12.1	46.4	43.1
		313.15	78.6	12.4	46.3	43.2
	15	298.15	76.8	23.8	48.8	40.1
		303.15	74.6	24.6	48.4	40.1
		308.15	72.4	24.2	48.3	40.2
		313.15	70.4	24.1	48.1	40.3
α -Ala+methanol	5	298.15	72.4	10.8	30.6	31.4
		303.15	70.6	11.2	30.2	31.5
		308.15	69.2	10.6	29.6	31.6
		313.15	67.4	10.2	29.4	31.6
	10	298.15	64.6	9.6	23.4	28.6
		303.15	63.7	8.5	33.6	28.5
		308.15	62.8	6.2	31.2	28.4
		313.15	63.6	6.6	30.6	28.2
	15	298.15	58.6	8.6	34.2	26.4
		303.15	57.2	7.7	34.5	26.3
		308.15	53.4	6.4	34.2	26.2

		313.15	52.1	5.6	34.1	26.2
β -Ala+methanol	5	298.15	72.6	8.6	18.7	19.2
		303.15	69.8	8.2	17.8	19.6
		308.15	59.6	8.4	17.2	19.7
		313.15	56.2	7.8	16.8	19.6
	10	298.15	55.8	6.7	23.8	24.4
		303.15	54.7	5.2	23.6	24.6
		308.15	54.3	4.9	22.8	24.6
		313.15	53.8	9.8	21.6	24.8
	15	298.15	46.2	9.6	30.9	31.6
		303.15	45.6	8.8	30.4	31.5
		308.15	45.2	7.9	29.4	31.6
		313.15	44.8	7.2	27.2	31.7

Table-2 : Values of U_0 (ms^{-1}) and the constants F, G and H at 298.15K.

Solvent	Wt.%	U_0 (ms^{-1})	F	G	H
Water+methanol	0.0	1510.0	386.41	582.48	1932.86
gly	5	1616.0	612.8	229.2	1832.6
	10	1624.8	786.4	396.4	1541.6
	15	1632.0	823.2	191.2	1392.4
α -ala	5	1652.0	938.2	-1931.0	712.8
	10	1664.0	526.2	-1365.2	623.4
	15	1672.0	465.4	-1024.6	1816.7
β -ala	5	1650.0	1022.4	627.4	-2022.2
	10	1662.8	812.2	-1413.2	-1914.6
	15	1670.0	413.4	-1028.4	-1128.2

A study of ultrasonic behavior of solutions in different wt% of aqueous methanol solutions at 298.15K reveals that the sound velocity increases and the isentropic compressibility (K_s) decreases as the contents of methanol in water increases. The values of U_0 and the empirical constants F, G and H are given in Table 2. Such changes are also reported by other workers in other aqueous solvent mixtures like water + methanol¹⁰, water + PG¹¹. As observed, the sound velocity increases with increase in concentrations of the solutions.

The values of sound velocities of α -alanine are higher in methanol solutions than in the solutions of other aminoacids. The value of isentropic compressibility (K_s) decreases with increase in concentration of the solutions in all the amino acids. As observed, the values of K_s of α -alanine are less in different wt% of solution than in other amino acids and are in the reverse order to the sound velocities.

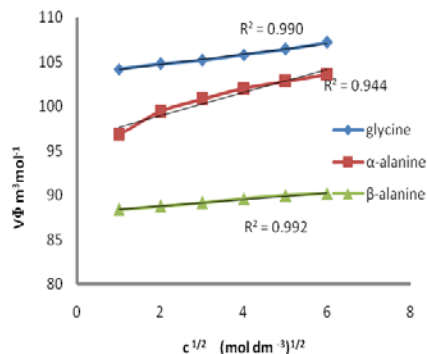


Fig.1. Plot of V_ϕ vs. $c^{1/2}$ in 5wt% of methanol.

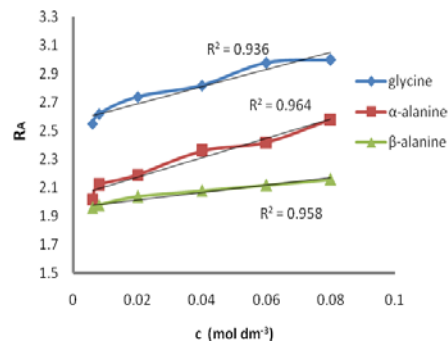


Fig. 4. Plot of R_A vs. c in 5wt% of methanol.

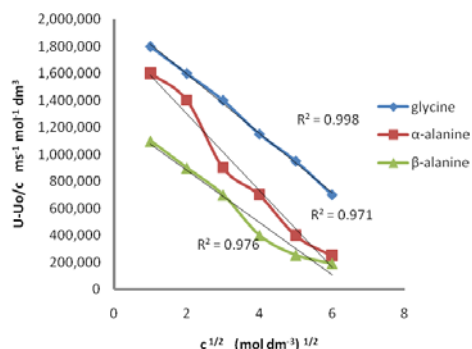


Fig.2. Plot of $U-U_0/c$ vs. $c^{1/2}$ in 10wt% of methanol at 298.15K.

The apparent isentropic molar compressibility $K_{s,\phi}$ increases with concentration of the solutions. The values of $K_{s,\phi}$ are negative and so also the values of $K_{s,\phi}^0$ ¹⁸. The negative values may be explained by two different phenomena, i.e., electrostriction and hydrophobic solvation. The loss of compressibility of the surrounding solvent molecules due to strong electrostrictive forces leads to the electrostrictive solvation. In other words, a tight solvation layer is formed around the ion for which the medium is little compressed by application of pressure.

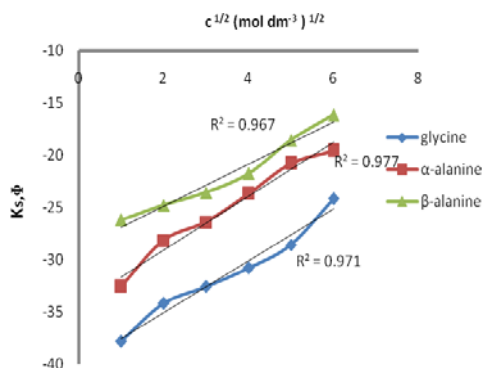


Fig.3: Plot of $K_{s,\phi}$ vs. $c^{1/2}$ in 5wt% of methanol.

Table – 3. Values of $K_{s,\phi}^0$ ($\text{m}^3\text{mol}^{-1}\text{Pa}^{-1}$) and S_n^0

Solvent	Wt.%	$K_{s,\phi}^0$ ($\text{m}^3\text{mol}^{-1}\text{Pa}^{-1}$ $\times 10^{-7}$)	S_n^0
Water	0.0	-3.00	7.31
gly	5	-8.00	6.42
	10	-6.00	6.48
	15	-6.00	6.72
α-ala	5	-4.00	5.46
	10	-0.8	5.48
	15	-6.00	5.84
β-ala	5	-8.00	4.92
	10	-0.2	4.96
	15	-7.00	4.98

The S_n values also increased with increasing methanol content in water. Higher S_n^0 values in aqueous glycine indicates strong electrostriction as compared to other aqueous amino acid solutions. However, the variation of S_n^0 as well as S_n values predicts the degree of hard electrostrictive solvation. It represents a structural effect of solute on solvent in a solution.

5. Conclusion

The results of the present investigations on amino acids in aqueous methanol solutions reveal that glycine shows high ion solvent interaction in solutions of methanol. The higher sound velocity values of α-alanine in aqueous methanol solutions than in other amino acids solutions are due to higher mass.

The decrease in value of K_s with increase in concentration of solutions may be due to occupation of the interstitial spaces of water by the solute molecules thereby making the medium less compressible. The increase in R_A values with increase in concentration of solution indicates that ion-solvent interaction

dominates over ion-ion interaction in all the solutions. The variation of S_n^0 values predicts the degree of hard electrostrictive solvation, i.e., it represents the structural effect of amino acids on aqueous solutions of methanol.

References

1. S. Pattnaik, U.N. Dash J.Chem. Pharm. Res., 4(9), 4364-4369, (2012).
2. R.A Robinson; R.H. Stokes, Electrolyte Solutions,
3. Butterworths, Scientific Publication, London, p.30, (1955).
4. U. N Dash, S.Supkar, Acoust. Letters, 16,135, (1992),
5. H.S. Harned, B.B. Owen., The Physical Chemistry of Electrolyte Solutions, 3rd, edn., Reinhold, New York, (1958)
6. P.S. Nikam, M. Hassan, Indian J. Pure & Appl. Phys., 24,502, (1986).
7. M. Kaminsky, Disc Faraday Soc. 24, 171, (1957).
8. A. Passinsky; Acta. Phys. Chem., USSR, 8, 835, (1930).
9. S.Thirumaran; R. Murugan; N. Prakash., J. Chem. Pharm., Res., 2(1), 53, (2010).
10. S .Thirumaran; S.Sudha, J. Chem.pharm Res, 2(1) 327, (2010).
11. A.K. Chattopadhyaya; S.C. Lahiri, Electrochem. Acta. 27, 269, (1982).
12. U.N.Dash; P.K. Padhi, The Research Network, 5(3), (2010).
13. H. Eyring; J.F Kincaid, J.Chem. phys., 6, 728, (1977).
14. Saneel K Thakur; Shivani Chauhan,J.Chem Pharm. Res., 3(2),657, (2011).
15. U. N. Dash; N.N. Pasupalak, J. mol. Liquids, 76, 97, (1998).
16. C. Sharma; Indian, J. Pure & Appl, Physics, 27,32, (1989).
17. Rose Venis; Rosario Rajkumar,J.Chem. Pharm. Res., 3(2), 878, (2011).
18. Alka Tadkalkar; Pravina Pawar;Govind K Bichile, J. Chem. Pharm. Res., 3(3), 165, (2011).
19. M. V Kaulgud; KSM Rao,India J.Chem., 27A, 12, (1988).