Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2012, 4(9):4364-4369

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Influence of hydrotropic agents on the solute – solvent interactions in aqueous solutions of glycine at different temperatures

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ABSTRACT

Density (d) values of glycine have been measured at 298.15, 303.15, 308.15, and 313.15K in three different compositions (0.1, 0.2 and 0.3 wt. %) of aqueous solutions of hydrotropic agents like sodium benzoate, sodium bromide and nicotinamide.Partial molar properties of glycine, e.g., apparent molar volume (V_Φ), limiting apparent molar volume (V_Φ^o), apparent molar expansibility (E_Φ), and limiting apparent molar expansibility (E^o_Φ) 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.

Keywords: Glycine, Sodium benzoate, Sodium bromide, Nicotinamide, ultrasonic velocity.

INTRODUCTION

The study of hydrotropic agents – 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 medium [1], the present investigation aims at studying the molecular interactions of glycine in aqueous solutions of (0.1, 0.2 and 0.3 wt.%) hydrotropic agents (sodium benzoate (SB),sodium bromide (SBr) and Nicotinamide (N)) 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^o_Φ) , apparent molar expansibility (E_Φ), limiting apparent molar expansibility (E^o_Φ), isentropic compressibility (K_s), 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.

EXPERIMENTAL SECTION

All the chemicals used were of AnalaR grades and used as such. The solutions of glycine were prepared on the molal basis and conversion of molality to molarity was done by using the standard expression [3] using the density values of the solutions determined at 298.15K. Conductivity water (Specfic conductance ~10^6 Scm^{-1}) was used to prepare solutions of sodium benzoate, sodium bromide and nicotinamide 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 where [3]. At least 5 observations were taken and the differences in any two readings did not exceed ± 0.02%. 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 glycine 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.

Theoretical aspects:
From the density data the apparent molar volume (V_{Φ}) was calculated by using equation [4]

$$V_{\Phi} = 1000\ (cd_0)^{-1}(d_0-d) + M_2 d_0^{-1} \quad (1)$$

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]

$$V_{\Phi} = V^{o}_{\Phi} + S_v\, c^{1/2} \quad (2)$$

to obtain V^{o}_{Φ} (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]

$$E_{\Phi} = E^{o}_{\Phi} + S_E\, c^{1/2} \quad (4)$$

The ultrasonic velocities 'U' of glycine in aqueous sodium benzoate, sodium bromide and nicotinamide solutions at different concentrations were fitted to an equation of the form [5-7]

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

U_o 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

$$K_{s,\Phi} = K^{o}_{s,\Phi} + F'c^{1/2} + G'c \quad (9)$$

to obtain $K^{0}_{s,\Phi}$ (the limiting apparent isentropic compressibility)

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

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

Where V is the volume of the solution containing n_2 moles of solute
V_1^{o} 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)

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

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

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

RESULTS AND DISCUSSION

The values 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 Table1 for glycine in different compositions (0.1,0.2 and 0.3 wt. %) of SB,SBr, and N in water at temperatures ranging from 298.15K to 313.15K at an interval of 5K.

The density values of the solutions of glycine vary linearly with concentrations in all compositions of aqueous solutions of SB, SBr and N at different temperatures.It was found that the V_Φ values vary linearly with $c^{½}$ for all the solutions at the experimental temperatures (a typical plot is given in figure 1 at 298.15K for 0.1 wt.% SB, SBr, and N). 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 glycine in the solutions of hydrotropic agents. As observed (Table-1) the V_Φ^0 values of glycine are higher in all compositions of sodium benzoate than in sodium bromide and nicotinamide solutions pointing to the fact that ion-solvent interactions take place strongly in sodium benzoate solution as compared to the solutions of sodium bromide and nicotinamide.

Table 1 : Values of V_Φ^0 (m^3 mol^{-1}), S_v($m^{3/2}$ $mol^{-3/2}$), E_Φ^0 (m^3 mol^{-1} K^{-1}), and S_E($m^{3/2}$ $mole^{-3/2}$ K^{-1}) for glycine in different compositions (0.1, 0.2 and 0.3 wt. %) of sodium benzoate (SB), sodium bromide (SBr) and nicotinamide (N) solutions at different temperatures)

Solvent	Wt. %	Temperature (K)	V_Φ^0	S_v	E_Φ^0	S_E
SB	0.1	298.15	90.1	21.6	15.3	16.1
		303.15	89.6	24.5	15.2	16.1
		308.15	87.7	12.9	15.1	16.3
		313.15	80.7	12.4	15.0	16.2
	0.2	298.15	82.1	19.6	16.6	13.1
		303.15	68.3	21.5	16.5	13.0
		308.15	64.5	11.2	16.4	13.1
		313.15	54.3	11.4	16.3	13.2
	0.3	298.15	74.2	21.2	17.6	10.2
		303.15	60.6	22.1	17.4	10.1
		308.15	54.2	10.3	17.3	10.3
		313.15	48.2	30.1	17.2	10.6
SBr	0.1	298.15	74.6	11.2	8.5	9.1
		303.15	60.3	37.1	8.4	9.2
		308.15	54.0	18.2	8.3	9.1
		313.15	48.1	16.1	8.2	9.0
	0.2	298.15	64.8	10.1	9.6	9.0
		303.15	58.6	27.2	9.4	9.1
		308.15	46.2	17.3	9.3	8.1
		313.15	39.6	15.8	9.2	8.2
	0.3	298.15	54.6	9.6	10.2	8.2
		303.15	48.2	29.2	10.1	8.0
		308.15	39.2	16.0	10.0	7.2
		313.15	34.2	16.5	10.0	7.1
N	0.1	298.15	82.8	18.4	12.6	14.2
		303.15	79.6	19.6	12.5	14.1
		308.15	72.6	11.4	12.3	13.8
		313.15	62.4	10.1	12.1	13.6
	0.2	298.15	73.7	16.2	13.4	10.4
		303.15	63.5	17.1	13.3	10.3
		308.15	58.4	10.2	13.1	10.2
		313.15	54.2	8.6	13.0	10.1
	0.3	298.15	66.4	14.4	14.5	9.6
		303.15	57.3	15.2	14.3	8.7
		308.15	46.3	9.6	14.2	8.6
		313.15	42.4	6.3	14.1	8.4

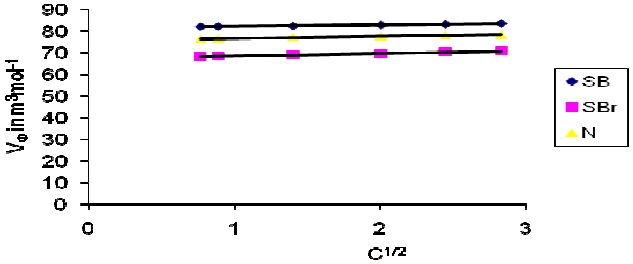

Fig 1: Plot of V_Φ vs $C^{1/2}$ In 0.1 wt. % of SB,SBr,N

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 hydrotropic agents. 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 sodium benzoate solution than in sodium bromide and nicotinamide solutions. 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 SB solutions as compared to those in SBr and N-solutions suggest that the appearance of caging or packing effect occurs to a greater extent in the former solution than in the latter two solutions.

A study of ultrasonic behaviour of solutions of glycine in different compositions of SB, SBr and N in water at 298.15K reveals that the sound velocity increases and the isentropic compressibility (K_s) decreases as the contents of SB, SBr and N in water increases. The values of U_0 and the empirical constants F, G and H are given in Table 2.

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

Glycine	Solvent	Wt.%	U_0 (ms^{-1})	F	G	H
	Water		1502.0	316.41	500.46	1898.89
	SB	0.1	1512.0	212.8	99.4	-1632.0
		0.2	1525.6	386.3	106.2	-1416.2
		0.3	1540.0	413.2	81.4	-1191.3
	SBr	0.1	1508.0	922.0	-1731.0	511.8
		0.2	1522.0	428.8	-1315.2	223.3
		0.3	1532.0	375.2	-1124.3	1416.7
	N	0.1	1509.6	812.2	82.6	-1817.6
		0.2	1524.8	312.4	215.2	-1512.2
		0.3	1536.0	613.6	318.4	-1022.4

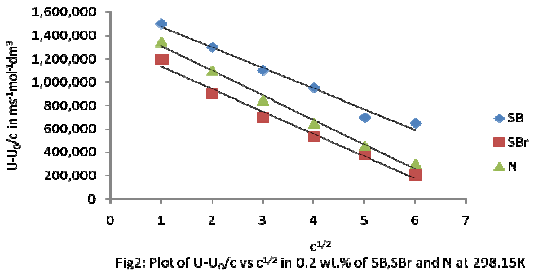

Fig2: Plot of $U-U_0/c$ vs $c^{1/2}$ in 0.2 wt.% of SB,SBr and N at 298.15K

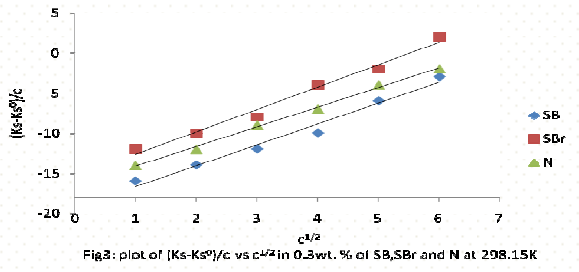

Fig3: plot of $(Ks-Ks^0)/c$ vs $c^{1/2}$ in 0.3wt. % of SB,SBr and N at 298.15K

Such changes are also reported by other workers in other aqueous solvent mixtures like water + methanol [10], water + PG [11]. As observed, the sound velocity increases with increase in concentrations of the solutions in SB, SBr and N. The values of sound velocities of glycine are higher in sodium benzoate solutions than in the solutions of sodium bromide and nicotinamide. This is because of the higher mass of benzoate anion as compared to bromide and

nicotinamide.(a typical plot of $U - U_0/c$ vs $c^{1/2}$ in different solutions is given in figure 2 for 0.2 wt.% of hydrotropic agents). The value of isentropic compressibility (K_s) decreases with increase in concentration of the solutions in all the hydrotropic agents (a typical plot of $K_s - K_s^0 / c$ vs $c^{½}$ are given in figure 3 for 0.3 wt. % of hydrotropic agents). As observed the values of K_s of glycine are less in sodium benzoate solution than in sodium bromide and nicotinamide solutions and are in the reverse order to the sound velocities.

The apparent isentropic molar compressibility $\mathbf{K_{s,\Phi}}$ increases with concentration of the solutions of glycine in all the hydrotropic agents. The values of $\mathbf{K_{s,\Phi}}$ are negative and so also the values of $\mathbf{K^0_{s,\Phi}}$ [18]. The negative values may be explained by two different phenomena, i.e., electrostriction and hydrophobic solvation.

The loss of compressibility of the sorrounding 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. A typical plot of $\mathbf{K_{s,\Phi}}$ Vs. $c^{1/2}$ for 0.2 wt.% of SB, SBr. and N solutions are given in figure 4.
The values of $\mathbf{K^0_{s,\Phi}}$ and S^0_n are given in Table3 for glycine in aqueous sodium benzoate, sodium bromide and nicotinamide solutions. Another property [12,13] which also can be studied to understand the ion-ion or ion-solvent interaction is relative association R_A(a typical plot of R_A vs. c in 0.2 wt. % of SB, SBr and N is shown in figure 5). The relative association is influenced by two factors : (i) the breaking up of the solvent structure on addition of solute to it and (ii) the solvation of solute. The former results in the decrease and the lattrer results in increase in R_A. The increase in R_A with conc.(Fig:5) suggests that the solvation of glycine in hydrotropic agents predominates over breaking-up the solvent structures. It is observed that R_A increases linearly with concentration of the solutions of glycine in SB,SBr and N.

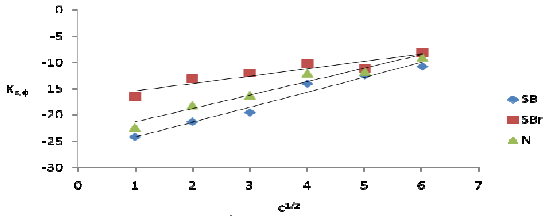

Fig1 : Plot of $K_{s,\Phi}$ vs $c^{1/2}$ in 0.2 wt. % of SB,SBr and N at 298.15K

Fig 5: Plot of R_A vs c in 0.2 wt.% of SB, SBr, N

Table – 3: Values of $K^0_{s,\Phi}$ (m^3mol^{-1} Pa^{-1}) and the S^0_n

Glycine	Solvent	Wt.%	$K_{s,\Phi}{}^0$ (m^3mol^{-1} Pa^{-1} x 10^{-7})	S^0_n
	Water		-2.00	6.21
	SB	0.1	-4.00	3.42
		0.2	-3.00	3.49
		0.3	-1.00	3.65
	SBr	0.1	-3.00	2.39
		0.2	-0.6	2.46
		0.3	-7.00	2.50
	N	0.1	-6.00	2.50
		0.2	-0.7	2.65
		0.3	-3.00	3.12

The S_n values also increased with increasing sodium benzoate, sodium bromide and nicotinamide content in water. Higher S_n^0 values in aqueous sodium benzoate indicates strong electrostriction as compared to aqueous sodium bromide and nicotinamide 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.

CONCLUSION

The results of the present investigations on glycine in aqueous sodium benzoate, sodium bromide and nicotinamide solutions reveal that glycine shows high ion solvent interaction in solutions of hydrotropic agents. The higher sound velocity values of glycine in aqueous sodium benzoate solutions than in aqueous sodium bromide and nicotinamide solutions are due to higher mass of benzoate anion in the solution. 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 glycine on the solutions of hydrotropic agents.

REFERENCES

[1] Sanjibita Das, U.N. Dash, *J. Chem. Pharm. Res.*, **2012**, 4(1) : 754-762.
[2] R.A Robinson; R.H. Stokes, *Electrolyte Solutions*, Butterworths, Scientific Publication, London, **1955**,p.30.
[3] U.N Dash; S.Supkar , *Acoust. Letters*, **1992**, 16,135.
[4] H.S. Harned; B.B. Owen., *The Physical Chemistry of Electrolyte Solutions*, 3rd, edn., Reinhold , New York, **1958**
[5] P.S. Nikam; M. Hassan, *Indian J. Pure & Appl. Phys.* **1986**, 24,502.
[6] M. Kaminsky; *Disc Faraday Soc.* **1957**, 24, 171.
[7] A. Passinsky; *Acta. Phys. Chem.*, USSR, **1930**,8,835.
[8] S.Thirumaran; R. Murugan; N. Prakash., *J. Chem. Pharm., Res.*, **2010**,2(1),(53).
[9] S .Thirumaran; S.Sudha, *J. Chem.pharm Res* **2010** 2(1) 327.
[10] A.K. Chattopadhya; S.C. Lahiri, *Eleetrochem. Acta.* **1982**, 27, 269.
[11] U.N.Dash; P.K. Padhi, *The Research Network*, **2010**, 5(3),1.
[12] H. Eyring; J.F Kincaid, *J.Chem. phys*, **1977**,6,728.
[13] Saneel K Thakur; Shivani Chauhan,*J.Chem Pharm. Res.*, **2011**,3(2),657.
[14] U.N.Dash; N.N. Pasupalak, *J. mol. Liquids*, **1998**, 76,97.
[15] C.Sharma; Indian, *J. Pure & Appl, Physics*, **1989**, 27,32.
[16] Rose Venis; Rosario Rajkumar,*J.Chem. Pharm. Res.*, **2011**,3(2),878.
[17] Alka Tadkalkar; Pravina Pawar;Govind KBichile, *J.Chem.Pharm.Res.*, **2011**,3(3),165.
[18] MV Kaulgud; KSM Rao,*India J.Chem.* **1988**,27A,12.