



## Influence of surfactants on the solute-solvent interactions in aqueous solutions of $\alpha$ -alanine at different temperatures

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### ABSTRACT

Density ( $d$ ) values of 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 surfactants like TX-100, cetrimide and SDS. Partial molar properties of  $\alpha$ -alanine, e.g., apparent molar volume ( $V_{\Phi}$ ), limiting apparent molar volume ( $V_{\Phi}^{\circ}$ ), apparent molar expansibility ( $E_{\Phi}$ ), and limiting apparent molar expansibility ( $E_{\Phi}^{\circ}$ ) 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:**  $\alpha$ -alanine, TX-100, Cetrimide, Sodium dodecyl sulphate, ultrasonic velocity.

### INTRODUCTION

The study of surfactants – 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  $\alpha$ -alanine in aqueous solutions of (0.1, 0.2 and 0.3 wt.%) surfactants (TX-100, cetrimide and SDS) ranging from 298.15K to 313.15K at an interval of 5K. Various parameters such as apparent molar volume ( $V_{\Phi}$ ), limiting apparent molar volume ( $V_{\Phi}^{\circ}$ ), apparent molar expansibility ( $E_{\Phi}$ ), limiting apparent molar expansibility ( $E_{\Phi}^{\circ}$ ), 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  $\alpha$ -alanine 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 (Specific conductance  $\sim 10^6 \text{ Scm}^{-1}$ ) was used to prepare solutions of TX-100, cetrimide and SDS 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 elsewhere [3]. At least 5 observations were taken and the differences in any two readings did not exceed  $\pm 0.02\%$ . 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  $\pm 0.5 \text{ m/s}$ . The glycine content in the solutions varied over a concentration range of 0.006 to 0.08 mol  $\text{dm}^{-3}$  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 ( $V_{\phi}$ ) 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  $V_{\phi}$  varied linearly with concentration  $c^{1/2}$

The  $V_{\phi}$  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  $V_{\phi}^0$  (limiting apparent molar volume) and the slope  $S_E$

The apparent molar Expansibility,  $E_{\phi}$  was determined from equation [4]

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

The  $E_{\phi}$  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  $\alpha$ -alanine in aqueous TX-100, cetrimide and SDS 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]

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

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]

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

## RESULTS AND DISCUSSION

The values partial molar volume ( $V_{\phi}^0$ ), partial molar expansibility ( $E_{\phi}^0$ ), the slope ( $S_v$ ) of the plot of  $V_{\phi}$  vs  $c^{1/2}$  and the slope  $S_E$  of  $E_{\phi}$  vs  $c^{1/2}$  are given in Table 1 for  $\alpha$ -alanine in different compositions (0.1, 0.2 and 0.3 wt. %) of TX-100, cetrimide, and SDS in water at temperatures ranging from 298.15K to 313.15K at an interval of 5K.

The density values of the solutions of  $\alpha$ -alanine vary linearly with concentrations in all compositions of aqueous solutions of TX-100, cetrimide and SDS at different temperatures. It was found that the  $V_{\phi}$  values vary linearly with  $c^{1/2}$  for all the solutions at the experimental temperatures (a typical plot is given in figure 1 at 298.15K for 0.1 wt.% TX-100, cetrimide, and SDS). Since  $V_{\phi}^0$  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  $\alpha$ -alanine in the solutions of surfactants. As observed (Table-1) the  $V_{\phi}^0$  values of  $\alpha$ -alanine are higher in all compositions of TX-100 than in cetrimide and SDS solutions pointing to the fact that ion-solvent interactions take place strongly in TX-100 solution as compared to the solutions of cetrimide and SDS.

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 surfactants. As observed the magnitudes of  $V_{\phi}^0$  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.

**Table 1 : Values of  $V_{\phi}^0$  ( $\text{m}^3 \text{mol}^{-1}$ ),  $S_v$  ( $\text{m}^{3/2} \text{mol}^{-3/2}$ ),  $E_{\phi}^0$  ( $\text{m}^3 \text{mol}^{-1} \text{K}^{-1}$ ), and  $S_E$  ( $\text{m}^{3/2} \text{mole}^{-3/2} \text{K}^{-1}$ ) for  $\alpha$ -alanine in different compositions (0.1, 0.2 and 0.3 wt. % of TX-100, cetrimide and SDS solutions at different temperatures)**

Solvent	Wt. %	Temperature (K)	$V_{\phi}^0$	$S_v$	$E_{\phi}^0$	$S_E$
TX-100	0.1	298.15	130.2	53.6	45.3	46.2
		303.15	129.4	55.2	45.2	46.2
		308.15	127.2	44.6	44.8	46.4
		313.15	122.4	44.2	44.7	46.4
	0.2	298.15	121.9	51.6	46.7	43.1
		303.15	110.2	53.2	46.4	43.6
		308.15	110.4	42.1	46.4	43.1
		313.15	102.6	42.4	46.3	43.2
	0.3	298.15	112.8	53.8	48.8	40.1
		303.15	102.6	45.6	48.4	40.1
		308.15	100.4	54.2	48.3	40.2
		313.15	98.4	54.1	48.1	40.3
Cetrimide	0.1	298.15	112.4	40.8	30.6	31.4
		303.15	110.6	41.2	30.2	31.5
		308.15	109.2	40.6	29.6	31.6
		313.15	107.4	40.2	29.4	31.6
	0.2	298.15	104.6	32.6	23.4	28.6
		303.15	103.7	28.5	33.6	28.5
		308.15	102.8	26.2	31.2	28.4
		313.15	103.6	24.6	30.6	28.2
	0.3	298.15	98.6	28.6	34.2	26.4
		303.15	97.2	26.7	34.5	26.3
		308.15	93.4	22.4	34.2	26.2
		313.15	92.1	18.6	34.1	26.2
SDS	0.1	298.15	102.6	28.6	18.7	19.2
		303.15	100.8	29.2	17.8	19.6
		308.15	99.6	28.4	17.2	19.7
		313.15	96.2	27.8	16.8	19.6
	0.2	298.15	95.8	20.7	23.8	24.4
		303.15	94.7	21.2	23.6	24.6
		308.15	94.3	20.9	22.8	24.6
		313.15	93.8	19.8	21.6	24.8
	0.3	298.15	86.2	14.6	30.9	31.6
		303.15	85.6	14.8	30.4	31.5
		308.15	85.2	13.9	29.4	31.6
		313.15	84.8	13.2	27.2	31.7

The values of limiting apparent molar expansibility  $E_{\phi}^0$  (Table 1) are also positive and decrease with increase of temperature, and the values are higher in TX-100 solution than in cetrimide and SDS solutions. This may be due to the gradual disappearance of caging or packing effect in the solutions with increase of temperature. But the higher

$E_{\phi}^0$  values in TX-100 solutions as compared to those in cetrimide and SDS-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.

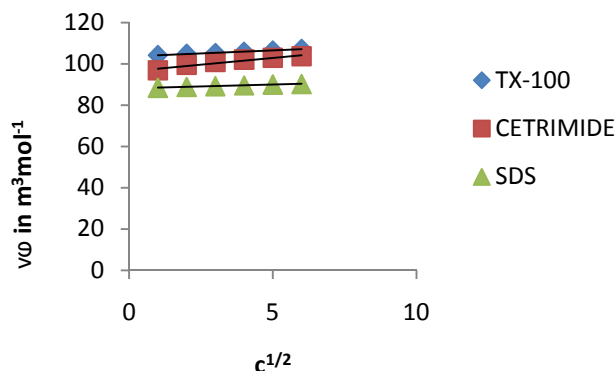


Fig.1:Plot of  $V_0$  vs.  $C^{1/2}$  in 0.1 wt% of TX-100, Cetrimide, SDS.

A study of ultrasonic behaviour of solutions of  $\alpha$ -alanine in different compositions of TX-100, cetrimide and SDS in water at 298.15K reveals that the sound velocity increases and the isentropic compressibility ( $K_s$ ) decreases as the contents of TX-100, cetrimide and SDS 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  $U_0$  ( $\text{ms}^{-1}$ ) and the constants F, G, H at 298.15K

$\alpha$ -alanine	Solvent	Wt. %	$U_0$ ( $\text{ms}^{-1}$ )	F	G	H
	Water	0.0	1510.0	386.41	582.48	1932.86
	TX-100	0.1	1616.0	612.8	229.2	1832.6
		0.2	1624.8	786.4	396.4	1541.6
		0.3	1632.0	823.2	191.2	1392.4
	Cetrimide	0.1	1552.0	938.2	-1931.0	712.8
		0.2	1564.0	526.2	-1365.2	623.4
		0.3	1572.0	465.4	-1024.6	1816.7
	SDS	0.1	1524.0	1022.4	627.4	-2022.2
		0.2	1536.8	812.2	-1413.2	-1914.6
		0.3	1544.0	413.4	-1028.4	-1128.2

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 TX-100, cetrimide and SDS. The values of sound velocities of  $\alpha$ -alanine are higher in TX-100 solutions than in the solutions of cetrimide and SDS. This is because of the higher mass of TX-100 as compared to cetrimide and SDS. (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 surfactants). The value of isentropic compressibility ( $K_s$ ) decreases with increase in concentration of the solutions in all the surfactants (a typical plot of  $K_s - K_s^0/c$  vs  $c^{1/2}$  are given in figure 3 for 0.3 wt. % of surfactants). As observed the values of  $K_s$  of  $\alpha$ -alanine are less in TX-100 solution than in cetrimide and SDS solutions and are in the reverse order to the sound velocities.

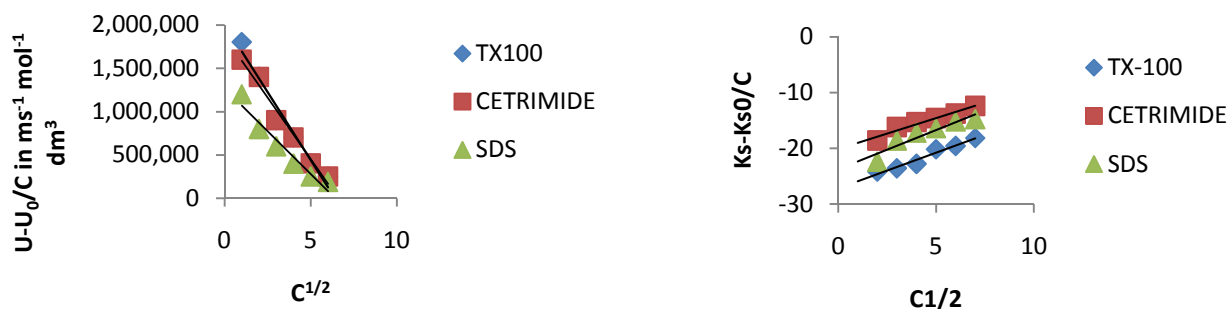


Fig.2:Plot of  $U - U_0/C$  vs.  $C^{1/2}$  in 0.1 wt% of TX-100, Cetrimide, SDS at 298.15K. Fig.3:Plot of  $K_s - K_s^0/C$  vs.  $C^{1/2}$  in 0.3 wt% of TX-100, Cetrimide, SDS at 298.15K.

The apparent isentropic molar compressibility  $K_{s,\phi}$  increases with concentration of the solutions of  $\alpha$ -alanine in all the surfactants. 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. A typical plot of  $K_{s,\phi}$  Vs.  $c^{1/2}$  for 0.2 wt.% of TX-100, cetrimide and SDS solutions are given in figure 4.

The values of  $K_{s,\phi}^0$  and  $S_n^0$  are given in Table 3 for  $\alpha$ -alanine in aqueous TX-100, cetrimide and SDS 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 TX-100, cetrimide and SDS 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 latter results in increase in  $R_A$ . The increase in  $R_A$  with conc. (Fig:5) suggests that the solvation of  $\alpha$ -alanine in surfactants predominates over breaking-up the solvent structures. It is observed that  $R_A$  increases linearly with concentration of the solutions of  $\alpha$ -alanine in TX-100, cetrimide and SDS.

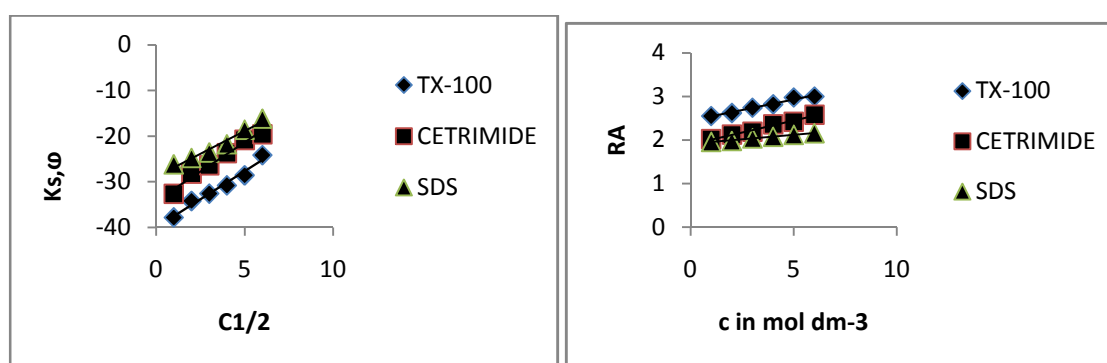


Table – 3: Values of  $K_{s,\phi}^0$  ( $\text{m}^3\text{mol}^{-1}\text{Pa}^{-1}$ ) and the  $S_n^0$

$\alpha$ -alanine	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
	TX-100	0.1	-8.00	6.42
		0.2	-6.00	6.48
		0.3	-6.00	6.72
	cetrimide	0.1	-4.00	5.46
		0.2	-0.8	5.48
		0.3	-6.00	5.84
	SDS	0.1	-8.00	4.92
		0.2	-0.2	4.96
		0.3	-7.00	4.98

The  $S_n$  values also increased with increasing TX-100, cetrimide and SDS content in water. Higher  $S_n^0$  values in aqueous TX-100 indicate strong electrostriction as compared to aqueous cetrimide and SDS 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  $\alpha$ -alanine in aqueous TX-100, cetrimide and SDS solutions reveal that  $\alpha$ -alanine shows high ion-solvent interaction in solutions of surfactants. The higher sound velocity values of  $\alpha$ -alanine in aqueous TX-100 solutions than in aqueous cetrimide and SDS solutions are due to the 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  $\alpha$ -alanine on the solutions of surfactants.

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