Interactions of L-alanine with different types of surfactants at different temperatures.

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ABSTRACT

The interactions of L-alanine with aqueous solutions of surfactants, namely, sodium dodecyl sulphate (SDS) (anionic surfactant), cetyltrimethylammonium bromide (CTAB) (cationic surfactant) and triton X-100 (TX-100) (non-ionic surfactant) over a temperature range of (298.15, 303.15, 308.15, and 313.15) K were investigated using volumetric and acoustic approach. Partial molar volume, $\emptyset_v$, partial molar volume at infinite dilution, $\emptyset_v^\circ$, its experimental slope, S_v and partial molar volume of transfer, $\Delta_{tr}\emptyset_v^0$ of amino acid from water to aqueous surfactant solution were calculated from density data. The data of speed of sound was used to calculate apparent molar adiabatic compressibility ($\emptyset_{K_s}$), limiting apparent molar adiabatic compressibility ($\emptyset_{K_s}^0$), its slope S_{K_s} and transfer volume, $\Delta_{tr}\emptyset_{K_s}^0$. The results obtained were utilized in the qualitative analysis of the solute-solute and solute-solvent interactions present in the various systems under invetigation.

Keywords: apparent molar adiabatic compressibility, cetyltrimethylammonium bromide, partial molar volume, sodium dodecyl sulphate, triton X-100.

I. INTRODUCTION

The interactions between protein-surfactant find important applications in industrial, biological, pharmaceutical, and cosmetic applications [1,2]. Some of the applications of surfactants include molecular weight determination [3], membrane protein solublization [4], and crystallization [5]. When surfactants bind to proteins it alters intermolecular forces of proteins and hence produce some conformational changes in proteins [6,7]. The surfactants can interact with proteins either directly or indirectly involving different physicochemical mechanisms such as electrostatic or hydrophobic interactions [8-10]. Surfactants may either initiate the unfolding of proteins by binding to it or simply bind to proteins and the tertiary structure of proteins remain intact [11]. The nature of solute-solute and solute-solvent interactions influence the conformational solublization of proteins in surfactants. Therefore it is essential to understand various interactions present between proteins, constituents of proteins and surfactants. However, direct investigations between surfactants-proteins is quite difficult [12] due to the complex conformational and configurational three-dimensional structures of proteins. Therefore, one of the methods that reduces this complexity is to study the interactions of surfactants with amino acids, which are the basic structural units of proteins [12,13]. At specific concentration known as the critical micelle concentration (CMC), surfactant molecules undergo aggregation to form micelles. As the critical micelles concentrations (CMCs) of SDS, CTAB and TX-100 are reported as 8.2×10^{-3} mol L^{-1}, 8.2×10^{-4} mol L^{-1}

and 2.4×10^{-4} mol L^{-1} respectively[14], the concentrations of the surfactants used in this study are far above their CMCs; therefore, almost all the surfactant molecules in the present work are in the form of micelles.

Volumetric measurements have been reported to be a sensitive tool for analysis of interactions in solutions. In the present work we evaluated various volumetric parameters, such as partial molar volumes, limiting partial molar volumes, its experimental slope and volumes of transfer of amino acids from water to an aqueous solution of surfactants, apparent molar adiabatic compressibility, limiting apparent molar adiabatic compressibility, its slope S_{K_s} and transfer volume. All these parameters offer a convenient method to study the intermolecular interactions occurring between the various components of the ternary mixtures.

II. MATERIAL AND METHOD

L-alanine was procured from s. d. fine Chem., India. SDS, CTAB and TX-100 were purchased from s. d. fine Chem.. L-alanine, SDS and CTAB were dried over P_2O_5 in vacuum desiccators. TX-100 was kept over molecular sieves to reduce the water content, if any. Solutions were made using deionized and triply distilled water. The weighings were done on an analytical balance (Mettler Toledo) having an accuracy of 1.0×10^{-5} g.

The densities, ρ, and speed of sound, u, of the solutions were measured using (Density & Sound Analyzer) DSA 5000 (Anton Paar). The reproducibility in the density measurements was 0.001kg/m^3 and temperature was maintained within ±0.001ºC.

III. INDENTATIONS AND EQUATIONS

The experimental values of densities and speed of sound of L-alanine (0.02-0.1m) in aqueous micellar solutions of (0.01m) SDS, CTAB and TX-100 at 298.15, 303.15, 308.15, and 313.15 K are listed in table 1 and 2. The densities were used to evaluate the apparent molar volumes of L-alanine in aqueous surfactants solutions using the following relation:

$$\emptyset_v = \frac{M}{\rho} - \frac{1000(\rho - \rho_0)}{m\rho\rho_0} \qquad (1)$$

where m is the molality of solute (L-alanine), ρ and ρ_0 are the densities of the solution and the solvent (aqueous surfactant), respectively, and M is the molar mass of the solute. The calculated $\emptyset_v$ values for L-alanine in all the aqueous surfactant solutions and at different temperatures are graphically presented in Fig. 1, 2 and 3.

For each system, $\emptyset_v$ vs $m^{1/2}$ plots (Fig.1, 2 and 3) were found to be linear, and thus, the partial molar volumes at infinite dilution, $\emptyset_v^{\circ}$ were obtained by least-squares fitting of the $\emptyset_v$ values to the following equation:

$$\emptyset_v = \emptyset_v^{\circ} + S_v^* m^{1/2} \qquad (2)$$

where S_v^* is the experimentally determined slope, sometimes considered to be volumetric pairwise interaction coefficient and provides information regarding L-alanine– L-alanine interactions, while $\emptyset_v^{\circ}$ is the intercept and provides the information regarding L-alanine–surfactant/water interactions. The values of $\emptyset_v^{\circ}$ of L-alanine along with the S_v^* values at different temperatures are given in Table 5. A perusal of Table 5 reveals that the values of

$\emptyset_v^\circ$ are large positive for L-alanine in each aqueous surfactant solution, suggesting strong L-alanine–surfactant/water interactions. The $\emptyset_v^\circ$ values (Table 4) increase with increase in temperature for all the L-alanine–water–surfactant systems under study. This may be attributed to the release of some water molecules from the loose hydration layers of the solute (L-alanine) in the bulk solution [15]. The reduction in electrostriction occurs with increase in temperature, hence, an increase in $\emptyset_v^\circ$. The S_v^* values (Table 4) for all the amino acids are found to be positive but smaller than $\emptyset_v^\circ$ values, suggesting the presence of weak solute-solute interactions which decreases with increase in temperature.

The standard partial molar volumes of transfer of amino acid from water to aqueous surfactant, $\emptyset_v^\circ(\text{tr})$ were computed using the equation:

$$\emptyset_v^\circ(\text{tr}) = \emptyset_v^\circ(\text{in aqueous surfactant}) - \emptyset_v^\circ(\text{in water}) \qquad (3)$$

where $\emptyset_v^\circ$ (in water) is the partial molar volume of L-alanine in water. The $\emptyset_v^\circ(\text{tr})$ values at 298.15, 303.15, 308.15, and 313.15 K are summarized in Table 5.

$\emptyset_v^\circ(\text{tr})$ values of L-alanine in the surfactant solutions are negative. This indicates that hydrophobic-hydrophilic and hydrophobic-hydrophobic interactions dominate over ion-ion and ion-hydrophilic interactions in aqueous SDS, CTAB-L-alanine system and over ion-hydrophilic interactions in aqueous TX-100-L-alanine system. The increase in $\emptyset_v^\circ(\text{tr})$ with rise in temperature in all the three aqueous surfactant solutions may be due to release of some solvent molecules from the loose hydration spheres of the solute in solution. It is worth mentioning that the values of $\emptyset_v^\circ(\text{tr})$ from water to aqueous surfactant solutions at the studied temperatures is: SDS>CTAB > TX-100. This suggests the sequence of the strength of interactions of L-alanine with SDS are greater than in CTAB which in turn are greater than in TX-100 surfactant molecules in the solution.

Currently, the most accurate method of determining the apparent molar adiabatic compressibility, $\emptyset_{K_s}^\circ$ of a solute is based on Newton-Laplace equation which relates adiabatic compressibility, K_S, of a medium with its density, d and speed of sound, u as follows:

$$K_S = 1/u^2 d \qquad (4)$$

The apparent molar adiabatic compressibility, $\emptyset_{K_s}$ is calculated by:

$$\emptyset_{K_s} = \frac{K_s - K_s^0}{m\rho_0} + K_s \emptyset_v \qquad (5)$$

Where K_S^0 and K_S are the adiabatic compressibilities of solvent and solution respectively. ρ_0 is the density of solvent, m is the molality of solute and $\emptyset_v$ is the partial molar volume of the solution.

According to Gucker and Debye Huckel theory, $\emptyset_{K_s}$ is the linear function of molal concentration represented as:

$$\emptyset_{K_s} = \emptyset_{K_s}^0 + S_{K_S} m \qquad (6)$$

where m is the concentration of amino acid or any other solute, expressed usually in molality (mol kg^{-1}), $\emptyset_{K_s}^0$ is the limiting apparent molar compressibility at infinite dilution and is a measure of solute-solvent interactions. From $\emptyset_{K_s}^0$ data in aqueous and in mixed aqueous solutions, the corresponding transfer values, $\Delta_{tr}\emptyset_{K_s}^0$ have been summarized in table 5 and calculated as:

$$\Delta_{tr}\emptyset_{K_s}^0 = \emptyset_{K_s}^0 \text{(in aqueous surfactant)} - \emptyset_{K_s}^0 \text{(in water)} \qquad (7)$$

IV. Figures and Tables

Table 1: Values of density, ρ, of L-alanine in aqueous surfactant solutions at different temperatures.

ρ.10^{-3}/kgm^{-3}			
m/mol kg^{-1}	298.15K	303.15K	308.15K	313.15K
L-alanine + aqueous SDS				
0.00	0.9979	0.9963	0.9947	0.9931
0.02	0.9985	0.9969	0.9953	0.9937
0.04	0.9991	0.9975	0.9959	0.9942
0.06	0.9996	0.9980	0.9964	0.9947
0.08	1.0002	0.9985	0.9969	0.9952
0.1	1.0007	0.9990	0.9974	0.9957
L-alanine + aqueous CTAB				
0.00	0.9977	0.9961	0.9943	0.9925
0.02	0.9984	0.9967	0.9949	0.9931
0.04	0.9990	0.9973	0.9955	0.9937
0.06	0.9996	0.9979	0.9961	0.9942
0.08	1.0001	0.9985	0.9966	0.9948
0.1	1.0007	0.9990	0.9971	0.9953
L-alanine + aqueous TX-100				
0.00	0.9980	0.9964	0.9948	0.9932
0.02	0.9987	0.9971	0.9955	0.9939
0.04	0.9994	0.9978	0.9962	0.9945
0.06	10001	0.9984	0.9968	0.9951
0.08	1.0007	0.9990	0.9974	0.9957
0.1	1.0013	0.9996	0.9980	0.9963

Table 2: Speed of sound (u) of L-alanine in aqueous surfactant solutions at different temperatures.

u.10^{-2}/ms^{-1}			
m/mol kg^{-1}	298.15K	303.15K	308.15K	313.15K
L-alanine + aqueous SDS				
0.00	14.9778	15.0995	15.2078	15.2912
0.02	14.9906	15.1123	15.2203	15.3034
0.04	15.0036	15.1249	15.2331	15.3156
0.06	15.0163	15.1374	15.2454	15.3279
0.08	15.0289	15.1499	15.2576	15.3398
0.1	15.0409	15.1623	15.2695	15.3513
L-alanine + aqueous CTAB				
0.00	14.9799	15.1022	15.2120	15.2969
0.02	14.9922	15.1145	15.2241	15.3085
0.04	15.0049	15.1267	15.2363	15.3403
0.06	15.0172	15.1390	15.2482	15.3321

0.08	15.0293	15.1509	15.2600	15.3436
0.1	15.0408	15.1628	15.2714	15.3548
L-alanine + aqueous TX-100				
0.00	14.9857	15.1080	15.2303	15.3106
0.02	14.9971	15.1194	15.2414	15.3214
0.04	15.0089	15.1310	15.2527	15.3323
0.06	15.0204	15.1426	15.2641	15.3432
0.08	15.0319	15.1537	15.2750	15.3541
0.1	15.0427	15.1640	15.2856	15.3645

Table 3: Values of partial molar volumes, $\emptyset_v$, of L-alanine in aqueous surfactant solutions at different temperatures.

$\emptyset_v.10^6/m^3mol^{-1}$			
m/mol kg^{-1}	298.15K	303.15K	308.15K	313.15K
L-alanine + aqueous SDS				
0.02	58.3113	59.1110	59.8657	60.6238
0.04	59.1809	59.9576	60.7155	61.5030
0.06	59.9334	60.7550	61.5159	62.2811
0.08	60.6076	61.3520	62.1027	62.8198
0.1	61.1794	61.9095	62.6349	63.3532
L-alanine + aqueous CTAB				
0.02	56.5074	57.3020	58.0563	58.8151
0.04	57.4518	58.1984	58.9815	59.7441
0.06	58.2279	59.0296	59.7731	60.5390
0.08	58.9893	59.7177	60.4819	61.2129
0.1	59.5636	60.2691	60.9845	61.7053
L-alanine + aqueous TX-100				
0.02	52.5331	53.3139	54.1502	54.8902
0.04	53.6752	54.4850	55.2497	56.0198
0.06	54.7348	55.5064	56.2327	56.9801
0.08	55.5105	56.2389	57.0099	57.7223
0.1	56.1521	56.8555	57.5836	58.3059

Table 4: Apparent molar adiabatic compressibility, $\emptyset_{K_s}$, of L-alanine in aqueous surfactant solutions at different temperatures.

$\emptyset_{K_s}.10^{14}/N^{-1}m^5mol^{-1}$			
m/mol kg^{-1}	298.15K	303.15K	308.15K	313.15K
L-alanine + aqueous SDS				
0.02	-2.6123	-2.4725	-2.2792	-2.0774
0.04	-2.5546	-2.3657	-2.2230	-2.0200
0.06	-2.4688	-2.2784	-2.1355	-1.9671
0.08	-2.3777	-2.2162	-2.0617	-1.8865
0.1	-2.2780	-2.1422	-1.9815	-1.8012
L-alanine + aqueous CTAB				
0.02	-2.6436	-2.5032	-2.3097	-2.1074
0.04	-2.5825	-2.3940	-2.2503	-2.0481
0.06	-2.4951	-2.3215	-2.1629	-1.9772

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0.08	-2.4002	-2.2383	-2.0706	-1.8951
0.1	-2.3003	-2.1646	-1.9936	-1.8235
L-alanine + aqueous TX-100				
0.02	-2.7216	-2.5287	-2.3830	-2.1781
0.04	-2.6511	-2.4826	-2.2902	-2.1095
0.06	-2.5509	-2.4094	-2.2196	-2.0315
0.08	-2.4674	-2.3031	-2.1239	-1.9586
0.1	-2.3614	-2.1831	-2.0440	-1.8804

Table 5: Values of limiting partial molar volume ($\emptyset_v^0$), limiting apparent molar adiabatic compressibility ($\emptyset_{K_s}^0$), their slopes (S_v, S_{K_s}), their transfer volumes ($\Delta_{tr}\emptyset_v^0, \Delta_{tr}\emptyset_{K_s}^0$), of L-alanine in aqueous surfactant solutions at different temperatures.

	298.15K	303.15K	308.15K	313.15K
L-alanine + Aq. SDS				
$10^6 \cdot \emptyset_v^0/(m^3mol^{-1})$	55.9313±0.0871	56.7936±0.0766	57.5757±0.0716	58.4008±0.0567
$10^6 \cdot S_v/(m^3mol^{-3/2}kg^{1/2})$	16.4988±0.3582	16.1285±0.3129	15.9927±0.2922	15.6728±0.2316
$10^6 \cdot \emptyset_{v(aq)}^0/(m^3mol^{-1})$	60.4784±0.0140	60.7332±0.0142	60.9464±0.0260	61.3649±0.0115
$10^6 \cdot \Delta_{tr}\emptyset_v^0 / (m^3mol^{-1})$	-4.5471	-3.9396	-3.3707	-2.9641
$10^{14} \cdot \emptyset_{K_s}^0/(N^{-1}m^5mol^{-1})$	-2.7119± 0.0151	-2.5380± 0.0162	-2.3632± 0.0087	-2.1562± 0.0142
$10^{14} \cdot S_{K_s}/(m^4s^2mol^{-2})$	4.2275±0.2268	4.0505±0.2435	3.7835±0.1312	3.4295±0.2141
$10^{14} \cdot \emptyset_{K_{s(aq)}}^0/(N^{-1}m^5mol^{-1})$	-2.6470± 0.0094	-2.4789± 0.0107	-2.3078± 0.0143	-2.1042± 0.0129
$10^{14} \cdot \Delta_{tr}\emptyset_{K_s}^0/(N^{-1}m^5mol^{-1})$	-0.0649	-0.0591	-0.0554	-0.0520
L-alanine+Aq. CTAB				
$10^6 \cdot \emptyset_v^0/(m^3mol^{-1})$	53.9693±0.0973	54.8278±0.0881	55.6273±0.0766	56.4296±0.0661
$10^6 \cdot S_v/(m^3mol^{-3/2}kg^{1/2})$	17.6273±0.3974	17.1920±0.3597	16.9926±0.3128	16.7622±0.2699
$10^6 \cdot \emptyset_{v(aq)}^0/(m^3mol^{-1})$	60.4784±0.0140	60.7332±0.0142	60.9464±0.0260	61.3649±0.0115
$10^6 \cdot \Delta_{tr}\emptyset_v^0 / (m^3mol^{-1})$	-6.5091	-5.9054	-5.3192	-4.9353
$10^{14} \cdot \emptyset_{K_s}^0/(N^{-1}m^5mol^{-1})$	-2.7450± 0.0144	-2.5742± 0.0121	-2.4010± 0.0105	-2.1865± 0.0073
$10^{14} \cdot S_{K_s}/(m^4s^2mol^{-2})$	4.3445±0.2173	4.1645±0.1823	4.0595±0.1588	3.604±0.1106
$10^{14} \cdot \emptyset_{K_{s(aq)}}^0/(N^{-1}m^5mol^{-1})$	-2.6470± 0.0094	-2.4789± 0.0107	-2.3078± 0.0143	-2.1042± 0.0129
$10^{14} \cdot \Delta_{tr}\emptyset_{K_s}^0/(N^{-1}m^5mol^{-1})$	-0.0980	-0.0953	-0.0932	-0.0823
L-alanine+Aq.TX-100				

$10^6 \cdot \emptyset_v^0/(m^3 mol^{-1})$	49.5458 ± 0.0986	50.4256 ± 0.0932	51.3130 ± 0.0956	52.0980 ± 0.0774
$10^6 \cdot S_v/(m^3 mol^{-3/2} kg^{1/2})$	20.9877 ± 0.4025	20.4772 ± 0.3804	19.9620 ± 0.3903	19.7656 ± 0.3159
$10^6 \cdot \emptyset_{v(aq)}^0/(m^3 mol^{-1})$	60.4784 ± 0.0140	60.7332 ± 0.0142	60.9464 ± 0.0260	61.3649 ± 0.0115
$10^6 \cdot \Delta_{tr}\emptyset_v^0/(m^3 mol^{-1})$	-10.9326	-10.3076	-9.6334	-9.2669
$10^{14} \cdot \emptyset_{K_s}^0/(N^{-1}m^5 mol^{-1})$	-2.8217 ± 0.0108	-2.6426 ± 0.0295	-2.4654 ± 0.0065	-2.2555 ± 0.0030
$10^{14} \cdot S_{K_s}/(m^4 s^2 mol^{-2})$	4.5205 ± 0.1634	4.3535 ± 0.4439	4.2215 ± 0.0980	3.7315 ± 0.0454
$10^{14} \cdot \emptyset_{K_{s(aq)}}^0/(N^{-1}m^5 mol^{-1})$	-2.6470 ± 0.0094	-2.4789 ± 0.0107	-2.3078 ± 0.0143	-2.1042 ± 0.0129
$10^{14} \cdot \Delta_{tr}\emptyset_{K_s}^0/(N^{-1}m^5 mol^{-1})$	-0.1747	-0.1637	-0.1576	-0.1513
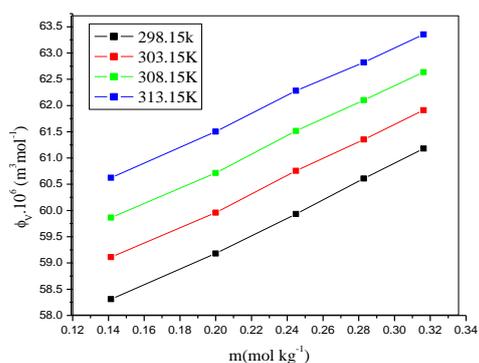
Fig. 1 Plots of partial molar volume versus concentration for L-alanine in aq. SDS solution at different temperatures.
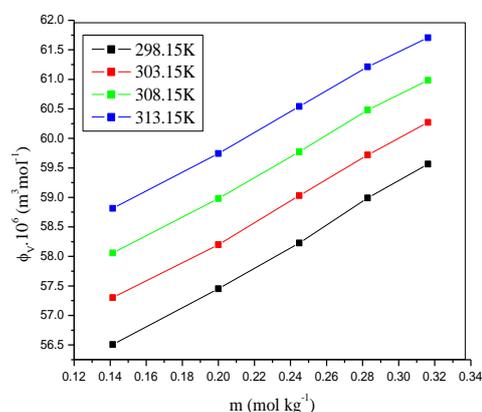
Fig. 2 Plots of partial molar volume versus concentration for L-alanine in aq. CTAB solution at different temperatures.
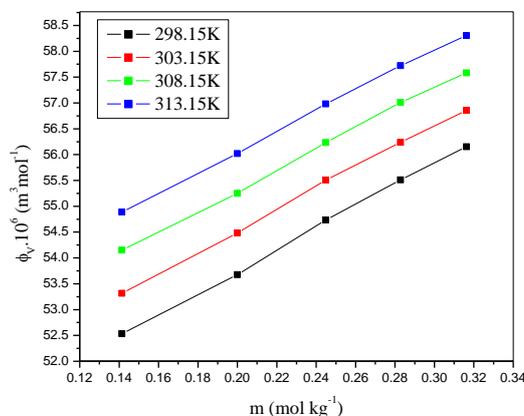
Fig. 3 Plots of partial molar volume versus concentration for L-alanine in aq. TX-100 solution at different temperatures.
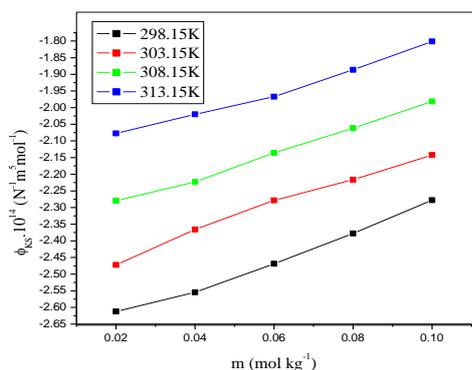
Fig. 4: Plots of apparent molar adiabatic compressibility versus concentration for L-alanine in aq. SDS solution at different temperatures
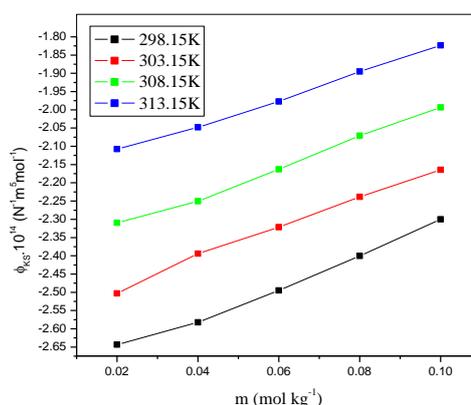
Fig. 5: Plots of apparent molar adiabatic compressibility versus concentration for L-alanine in aq. CTAB solution at different temperatures.
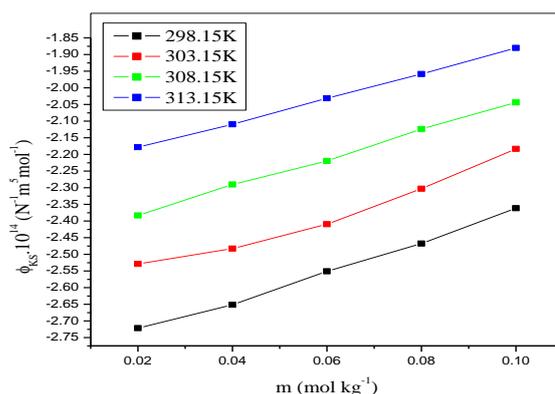
Fig. 6: Plots of apparent molar adiabatic compressibility versus concentration for L-alanine in aq. TX-100 solution at different temperatures.

V. CONCLUSION

From the various parameters evaluated it may be cocluded that:

➤ L-alanine shows maximum solute-solvent interactions with SDS in comparison to other two surfactants under study.

➤ With increase in temperature, the solute-solvent interactions increases.

➤ With increase in concentration, the solute-solvent interactions increases.

VI. ACKNOWLEDGEMENT

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