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Interactions of L-alanine with anionic, cationic and nonionic surfactants at different temperatures: A volumetric and viscometric study

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ABSTRACT

Densities, ρ and viscosities, η of L-alanine (0.02-0.1m) in 0.01m aqueous sodium dodecyl sulphate (SDS) (anionic surfactant), cetyltrimethylammonium bromide (CTAB) (cationic surfactant) and triton X-100 (TX-100) (non-ionic surfactant) solutions have been measured at 298.15, 303.15, 308.15, and 313.15 K. The density data has been utilized to calculate apparent molar volumes, $\emptyset_v$, partial molar volumes at infinite dilution, $\emptyset_v^{\circ}$, its experimental slope, s_v^* and partial molar volumes of transfer, $\emptyset_v^{\circ}(tr)$ of amino acids. The viscosity data has been analyzed by means of Jones-Dole equation to obtain Falkenhagen coefficient, A, and Jones-Dole coefficient, B. The above calculated parameters were found to be sensitive towards the interactions prevailing in the studied amino acid-surfactant-water systems. The behavior of these parameters has been used to investigate the solute-solute and solute-solvent interactions.

Keywords: sodium dodecyl sulphate, cetyltrimethylammonium bromide, triton X-100, partial molar volumes and A and B-coefficients.

INTRODUCTION

The studies of interactions of proteins with amphiphilic molecules are of vast importance, not only in vivo but also in technical applications [1,2]. The interaction of surfactants with globular proteins attracts much attention of researchers [3-8]. Studies of these interactions favour understanding the denaturation and solubilisation action of surfactants on membrane proteins and lipids [9]. Due to the structural complexity of these bio molecules, direct thermodynamic study is somewhat difficult. Thus, amino acids are being extensively used as model compounds as they are structural units of proteins [10]. Surfactants at low concentrations in aqueous solutions behave much as normal electrolytes, but in more concentrated solutions they exhibit different behavior. Such behavior is due to the formation of aggregates consisting of many surfactant molecules. 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 2.5×10^{-3} $mol.kg^{-1}$, 8.2×10^{-4} $mol.kg^{-1}$ and 2.4×10^{-4} $mol.kg^{-1}$ respectively, 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 [11]. The physicochemical properties of surfactant solutions differ noticeably in solutions with concentrations higher and lower than the CMC. At concentrations below the CMC, the physicochemical properties of ionic surfactants resemble those of strong electrolytes. At concentrations exceeding the CMC, the properties of surfactants change considerably, indicating the formation of highly cooperative molecular associates [9].

Volumetric measurements have been reported to be a sensitive tool for analysis of interactions in solutions [12]. In the present work we evaluated various volumetric parameters, such as apparent molar volumes, partial molar volumes, its experimental slope and volumes of transfer of amino acids from water to an aqueous solution of surfactants. The viscosity A and B-coefficients were calculated by using Jones-Dole equation. All these parameters offer a convenient method to study the intermolecular interactions occurring between the various components of the ternary mixtures [13].

EXPERIMENTAL SECTION

L-alanine was procured from s. d. fine Chem., India. SDS, CTAB and TX-100 were purchased from s. d. fine Chem., Thomas Baker and s. d. fine Chem., respectively. L-alanine, SDS, 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 $1.0\text{x}10^{-5}$g.

The densities, ρ,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. The viscosity, η, was measured with Ostwald's viscometer which was precalibrated using triply distilled water. The accuracy of viscosity in this method was ±0.001Nsm^{-2}. A special thermostatic water bath arrangement was made for viscosity measurements, in which temperature variation was maintained within ±0.001ºC.

RESULTS AND DISCUSSION

The experimental values of densities and viscosities 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.

Volumetric study

The densities were used to evaluate the apparent molar volumes of glycine in aqueous surfactants solutions using the following relation:

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

where m is the molality of solute (L-alanine), ρ and $\rho_\circ$ 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.

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

	ρ/(kgm^{-3})			
m/(molkg^{-1})	298.15K	303.15K	308.15K	313.15K
L-Alanine + Aqueous SDS				
0.00	997.899	996.322	994.714	993.109
0.02	998.515	996.923	995.301	993.682
0.04	999.095	997.489	995.853	994.219
0.06	999.646	998.023	996.373	994.726
0.08	1000.172	998.540	996.877	995.220
0.1	1000.680	999.036	997.362	995.692
L-Alanine + Aqueous CTAB				
0.00	997.708	996.106	994.311	992.518
0.02	998.360	996.743	994.934	993.127
0.04	998.973	997.343	995.519	993.698
0.06	999.557	997.910	996.074	994.239
0.08	1000.110	998.454	996.603	994.757
0.1	1000.650	998.983	997.123	995.265
L-Alanine + Aqueous TX-100				
0.00	998.012	996.416	994.817	993.207
0.02	998.743	997.132	995.517	993.893
0.04	999.427	997.800	996.172	994.533
0.06	1000.069	998.429	996.789	995.137
0.08	1000.690	999.039	997.382	995.719
0.1	1001.292	999.630	997.963	996.286

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 4. A perusal of Table 4 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.

Table 2 Values of viscosity,η, of L-alanine in aqueous surfactant solutions at different temperatures

$\eta.10^{-3}/(Nm^{-2}s)$				
m/(molkg^{-1})	298.15K	303.15K	308.15K	313.15K
L-Alanine + Aqueous SDS				
0.00	0.8399	0.7606	0.6872	0.6231
0.02	0.8729	0.7891	0.7114	0.6437
0.04	0.8937	0.8069	0.7268	0.6573
0.06	0.9128	0.8241	0.7419	0.6710
0.08	0.9306	0.8401	0.7564	0.6833
0.1	0.9470	0.8559	0.7700	0.6956
L-Alanine + Aqueous CTAB				
0.00	0.8497	0.7783	0.6921	0.6248
0.02	0.8597	0.7871	0.6997	0.6314
0.04	0.8680	0.7946	0.7062	0.6373
0.06	0.8756	0.8014	0.7123	0.6428
0.08	0.8830	0.8081	0.7181	0.6480
0.1	0.8901	0.8148	0.7242	0.6533
L-Alanine + Aqueous TX-100				
0.00	0.8626	0.7682	0.7029	0.6538
0.02	0.8935	0.7948	0.7264	0.6750
0.04	0.9083	0.8078	0.7382	0.6857
0.06	0.9206	0.8182	0.7474	0.6945
0.08	0.9310	0.8277	0.7558	0.7020
0.1	0.9406	0.8361	0.7637	0.7091

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 [11]. 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, $\emptyset_v^\circ$(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 $\emptyset_v^\circ$(tr) values at 298.15, 303.15, 308.15, and 313.15 K are summarized in Table 4. A glance on the structure of L-alanine and surfactant molecules studied reveals that the volumetric behavior of L-alanine in aqueous surfactant solutions can be explained by considering the following possible interactions, which are expected to occur in the present ternary systems:

1. Ion–ion interactions between $SO_4^{2-}$of SDS/Br^- of CTAB and the NH_3^+ group of L-alanine and between Na^+ of SDS/N^+–CH_3 group of CTAB and the COO^-group of L-alanine
2. Ionic–hydrophilic interactions between the charge centers (NH_3^+; COO^-) of L-alanine and the hydrophilic(polyoxyethylene) part of TX-100
3. Hydrophobic–hydrophilic group interactions between the hydrophobic group of the L-alanine and hydrophilic groups of the surfactants
4. Hydrophobic–hydrophobic interactions between the alkyl chain of the SDS/CTAB/TX-100 and the hydrophobic group of the L-alanine.

The changes in $\emptyset_v^\circ$(tr) of L-alanine in aqueous surfactant solutions (Table 4) can be interpreted by considering the cosphere overlap model [14, 15, 16]; according to which the overlap of hydration cospheres is destructive. In the light of this model, (1) and (2) type of interactions would lead to a positive $\emptyset_v^\circ$(tr) value due to reduction in the electrostriction effect. Because of the interactions of thecharge centers (NH_3; COO^-) of L-alanine with the ions of SDS/CTAB and with the hydrophilic part of TX-100, the electrostriction of water caused by the charge centers of L-alanine will be reduced, resulting in an increase in volume and, hence, positive $\emptyset_v^\circ$(tr) values.

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

	$\emptyset_V.10^{-6}/(m^3mol^{-1})$			
$m/(molkg^{-1})$	298.15K	303.15K	308.15K	313.15K
L-Alanine + Aqueous SDS				
0.02	58.311	59.111	59.866	60.624
0.04	59.181	59.958	60.715	61.503
0.06	59.933	60.755	61.516	62.281
0.08	60.608	61.352	62.103	62.820
0.1	61.179	61.910	62.635	63.353
L-Alanine + Aqueous CTAB				
0.02	56.507	57.302	58.056	58.815
0.04	57.452	58.198	58.981	59.744
0.06	58.227	59.029	59.773	60.539
0.08	58.989	59.718	60.482	61.213
0.1	59.564	60.269	60.985	61.705
L-Alanine + Aqueous TX-100				
0.02	52.533	53.314	54.150	54.890
0.04	53.675	54.485	55.250	56.020
0.06	54.735	55.506	56.233	56.980
0.08	55.510	56.239	57.010	57.722
0.1	56.152	56.855	57.584	58.306

On the other hand, interactions of type (3) and (4) would lead to a negative $\emptyset_v^\circ$(tr) because of the reduction in water structure that is formed around those groups as a result of the cosphere overlap. Further, $\emptyset_v^\circ$(tr) values of L-alanine in all the three 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 $\emptyset_v^\circ$(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 [11]. It is worth mentioning that the values of $\emptyset_v^\circ$(tr) from water to aqueous surfactant solutions at all the studied temperatures follow the sequence:

SDS > CTAB > TX-100. This suggests the sequence of the strength of interactions of L-alanine with the surfactant molecules in the solution.

Viscometric study

The viscosity data were analyzed by using Jones–Dole [17] equation:

$$\eta_r = {}^{\eta}/_{\eta_\circ} = 1 + Am^{1/2} + Bm \qquad (4)$$

where η_r is the relative viscosity of the solution, η and $\eta_\circ$ are the viscosities of the solution and the solvent (aqueous surfactant), respectively, and A and B are the Falkenhagen and Jones–Dole coefficients, respectively. Coefficient A accounts for the L-alanine–L-alanine interactions, and B is a measure of structural modifications induced by the L-alanine–surfactant/water interactions [11]. The values of A and B have been obtained from the intercepts and slopes of the plots of [η_r-1/$m^{1/2}$] vs $m^{1/2}$ (Fig 4, 5 and 6) and are included in Table 4. Table 4 shows that the values of B coefficients are large positive, while those of A coefficients are small positive in aqueous SDS and CTAB solutions, suggesting strong L-alanine–surfactant/water and weak L-alanine – L-alanine interactions in these ternary systems. However, in aqueous TX-100 solution, no appreciable difference in the values of B and A is noticed, indicating that the L-alanine–surfactant/water and L-alanine–L-alanine interactions are almost equally important. In addition, the increasing values of B coefficients and a reverse trend in A coefficients in different surfactant solutions with rise in temperature supports the variation of $\emptyset_v^\circ$ with temperature. The values of B coefficient in the studied systems at different temperatures follow the sequence: SDS > CTAB > TX-100. This reinforces our earlier conclusions drawn from volumetric study.

Table 4 Values of partial molar volumes at infinite dilution, $\emptyset_v^{\circ}$, its experimental slope, s_v^*, partial molar volumes of transfer, $\emptyset_v^{\circ}$(tr), Falkenhagen coefficient, *A*, and Jones-Dole coefficient, *B* of L-alanine in aqueous surfactant solutions at different temperatures

	298.15K	303.15K	308.15K	313.15K
L-Alanine + Aqueous SDS				
10^{-6}. $\emptyset_v^{\circ}$ /(m^3mol^{-1})	55.931±0.088	56.793±0.076	57.576±0.072	58.401±0.057
10^{-6}. s_v^*/($m^3mol^{-3/2}kg^{1/2}$)	16.499±0.358	16.130±0.312	15.993±0.295	15.671±0.231
10^{-6}. $\emptyset_{v(aq)}^{\circ}$/($m^3mol^{-1}$)	60.478±0.014	60.733±0.014	60.945±0.026	61.364±0.012
10^{-6}. $\emptyset_v^{\circ}$(tr) (m^3mol^{-1})	-4.547	-3.940	-3.369	-2.963
10^{-1}. A ($kg^{1/2}mol^{-1/2}$)	1.760±0.024	1.561±0.038	1.386±0.045	1.227±0.039
10^{-1}. B ($mol^{-1}kg$)	7.239±0.099	7.555±0.157	7.648±0.186	7.745±0.161
L-Alanine + Aqueous CTAB				
10^{-6}. $\emptyset_v^{\circ}$ /(m^3mol^{-1})	53.969±0.098	54.827±0.089	55.626±0.077	56.430±0.066
10^{-6}. s_v^*/($m^3mol^{-3/2}kg^{1/2}$)	17.629±0.398	17.193±0.362	16.997±0.314	16.762±0.271
10^{-6}. $\emptyset_{v(aq)}^{\circ}$/($m^3mol^{-1}$)	60.478±0.014	60.733±0.014	60.945±0.026	61.364±0.012
10^{-6}. $\emptyset_v^{\circ}$(tr) (m^3mol^{-1})	-6.509	-5.906	-5.319	-4.934
10^{-1}. A ($kg^{1/2}mol^{-1/2}$)	0.299±0.018	0.259±0.015	0.228±0.012	0.198±0.020
10^{-1}. B ($mol^{-1}kg$)	3.834±0.073	3.880±0.062	3.916±0.051	3.956±0.082
L-Alanine + Aqueous TX-100				
10^{-6}. $\emptyset_v^{\circ}$ /(m^3mol^{-1})	49.546±0.099	50.426±0.093	51.313±0.095	52.098±0.077
10^{-6}. s_v^*/($m^3mol^{-3/2}kg^{1/2}$)	20.987±0.403	20.475±0.380	19.964±0.389	19.766±0.315
10^{-6}. $\emptyset_{v(aq)}^{\circ}$/($m^3mol^{-1}$)	60.478±0.014	60.733±0.014	60.945±0.026	61.364±0.012
10^{-6}. $\emptyset_v^{\circ}$(tr) (m^3mol^{-1})	-10.932	-10.307	-9.632	-9.266
10^{-1}. A ($kg^{1/2}mol^{-1/2}$)	2.273±0.016	2.174±0.011	2.080±0.020	1.998±0.021
10^{-1}. B ($mol^{-1}kg$)	1.879±0.065	1.981±0.046	2.073±0.081	2.167±0.088
Aqueous L-Alanine				
10^{-6}. $\emptyset_{v(aq)}^{\circ}$/($m^3mol^{-1}$) (literature)	60.490 [Ref. 10]		61.010 [Ref. 10]	61.200 [Ref. 10]
10^{-1}. A ($kg^{1/2}mol^{-1/2}$)	-0.018±0.012	-0.048±0.013	-0.094±0.012	-0.120±0.013
10^{-1}. B ($mol^{-1}kg$)	2.502±0.052	2.359±0.056	2.233±0.048	2.117±0.053

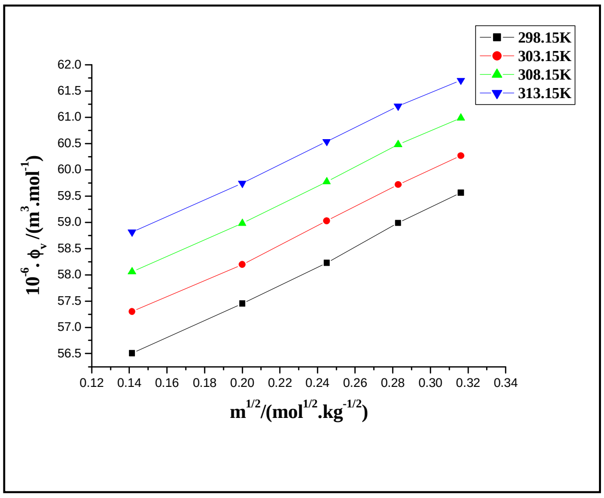


Fig 1 Plot of apparent molar volume,$\emptyset_v$ vs $m^{1/2}$ of L-alanine in CTAB at different temperatures.

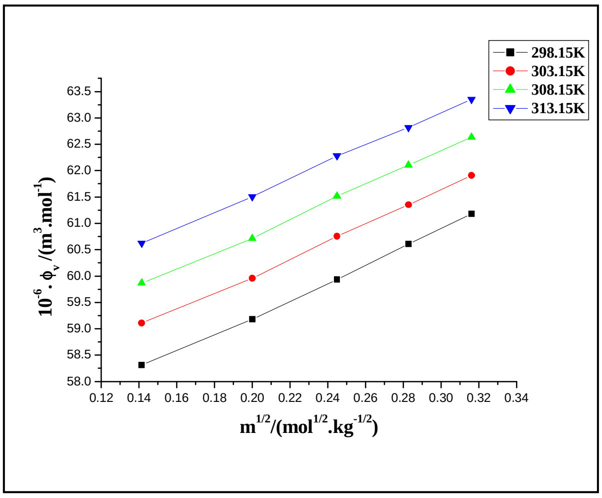


Fig 2 Plot of apparent molar volume,$\emptyset_v$ vs $m^{1/2}$ of L-alanine in SDS at different temperatures.

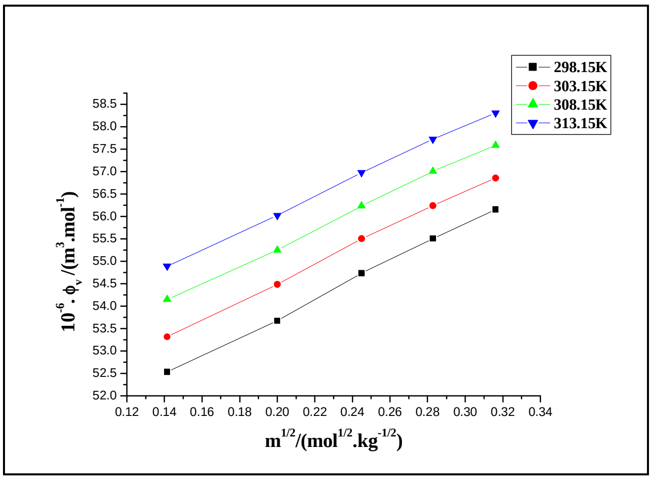
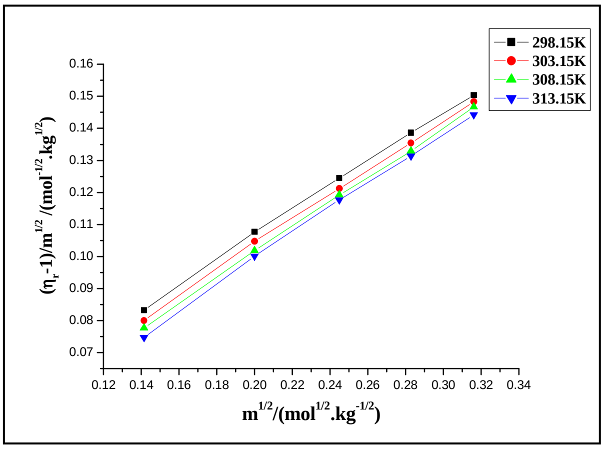


Fig 3 Plot of apparent molar volume,$\emptyset_v$ vs $m^{1/2}$ of L-alanine in TX-100 at different temperatures.



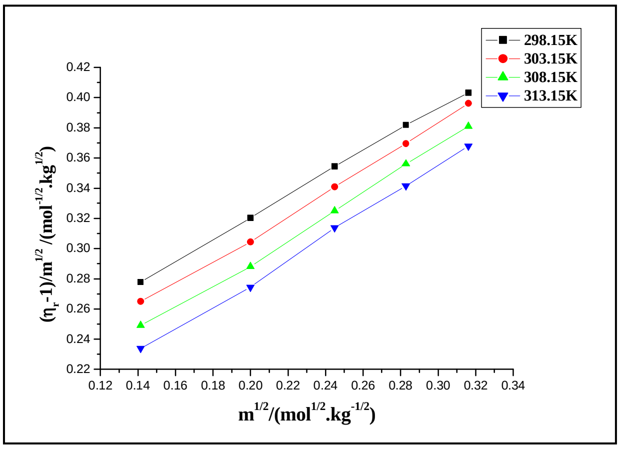


Fig 4 Plot of η_r-1/$m^{1/2}$vs $m^{1/2}$ of L-alanine in CTAB at different temperatures.

Fig 5 Plot of η_r-1/$m^{1/2}$vs $m^{1/2}$ of L-alanine in SDS at different temperatures.

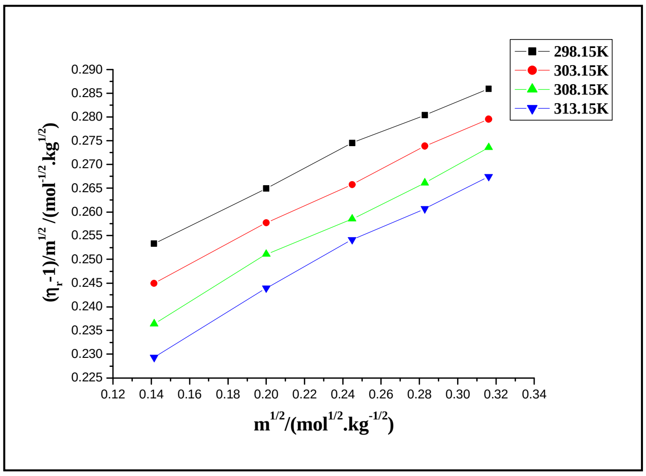


Fig 6 Plot of η_r-1/$m^{1/2}$vs $m^{1/2}$ of L-alanine in TX-100 at different temperatures.

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