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A study of molecular interactions of L-histidine with aqueous solutions of anionic and cationic surfactants at different temperatures

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Abstract

The density *(ρ)*, speed of sound *(u)*, viscosity *(η)*, refractive index *(n_D)* and specific conductivity *(κ)*, of L-histidine (0.02-0.1 mol kg^{-1}) in 0.02 m (mol kg^{-1}) aqueous surfactant solutions of sodium dodecyl sulphate (SDS) and dodecyltrimethylammonium bromide (DTAB) were obtained at temperatures (298.15, 303.15 and 308.15) K. The apparent molar volume *(V_ϕ)*, limiting apparent molar volume *(V_ϕ°)*, transfer volume *($\Delta_{tr}V_\phi^\circ$)*, isentropic compressibility *(K_S)*, apparent molar isentropic compressibility *($K_{S,\phi}$)*, limiting apparent molar isentropic compressibility *($K_{S,\phi}^\circ$)*, transfer compressibility *($\Delta_{tr}K_{S,\phi}^\circ$)*, relative viscosity *(η_r)*, Falkenhagen coefficient *(A)*, viscosity B-coefficient *(B)*, molar refraction *(R_D)*, molar conductivity *(Λ_m)* and limiting molar conductivity *(Λ°_m)*, were calculated. The results were used to identify the interactions of L-histidine with SDS and DTAB in terms of ionic-ionic, ionic-hydrophilic, hydrophilic-hydrophobic and hydrophobic-hydrophobic.

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Keywords Amino-acids, apparent molar volume, apparent molar isentropic compression, viscosity B-coefficient, transfer thermodynamic properties.

1. Introduction

Surfactant-amino acid systems have attracted the attention of the scientific community in the recent past all over the world as these interactions have important bearing in the field of industrial, pharmaceutical, biological and cosmetic applications [1-5]. Amino acids are biologically important compounds which have the unique property to exist as zwitter ion in solutions which have large electrical moment associated with them. In aqueous solutions systems, the hydrophobic tails flock to the interior in order to minimize their contact with water, and the hydrophilic heads remain on the outer surface in order to maximize their contact with water leading to the formation of surfactant–amino acid molecular complexes. Such complex formation is closely analogous to micellar solubilization, a phenomenon of potential practical importance in the field of detergency, [6] pharmaceuticals, [7] drug delivery [8] and solubilization of drugs, [9-14] besides being used to solubilize the otherwise insoluble substances in water [7].

L-histidine is an essential, basic amino acid that has many vital functions in all parts of body. It ensures the transmission of messages from the brain to various parts of the body. L-histidine is involved in the synthesis of haemoglobin and tissue repair. It has a proven effect on the production of histamine that is required by the immune system to know when the body is experiencing an allergic reaction and to produce gastric juices that are needed for normal digestion.

Therefore, keeping in mind the importance of surfactant-amino acid interactions in various systems in the present investigation volumetric, acoustic, rheological, refractive index and conductometric studies of L-histidine in aqueous surfactant solutions of sodium dodecyl sulphate (SDS) and dodecyltrimetylammonium bromide (DTAB) at different temperatures and concentrations have been undertaken for better understanding about the type of interactions present in these systems. Since surfactants consist of two distinct parts, polar head group and a polar hydrophobic tail group, the self aggregation of a polar hydrophobic groups leads to the formation of micelles above critical micelle concentration (cmc). The hydrophobic interaction acts as a vital driving force for the formation of micellar aggregates and for binding of surfactant to the proteins, however, the electrostatic repulsions between the polar head groups affects the size of micelle. The cmc of SDS is reported as 8 m mol L^{-1} [15] and DTAB as 15 m mol L^{-1} [16]. Thus, the surfactant used acts as micelles in the present study.

2. Experimental

SDS, DTAB and L-histidine (mass fraction purity 0.99) procured from s.d. fine. Chem. Ltd. India, were dried in vacuum desiccators over P_2O_5 for 72 hours and used without further purification. Freshly prepared triply distilled water (specific conductance 0.3×10^{-4} Sm^{-1} at 298.15 K) was used for preparing the solutions at different concentrations. The weighing of samples was done on an electronic single pan five digit analytic balance (Mettler Toledo, Model: ML204) with an uncertainty of ±0.01 mg. The solutions were stored in special air tight bottles to avoid contamination and evaporation. The densities and sound velocities of solutions were measured using Anton Paar DSA 5000 (Densimeter and sound velocity analyzer). The DSA 5000 is the first oscillating U-tube density and velocity sound meter which measures to the highest accuracy in the wide viscosity and temperature ranges. Both cells of instrument were temperature controlled by built-in Peltier thermostat which was stable to within 0.01K. The reproducibility of the density and ultrasound measurements were $\pm 10^{-6}$ g cm^{-3} and $\pm 10^{-2}$ m s^{-1} respectively. The viscosity measurement of solutions was done by using an Ubbelohde type suspended level viscometer. The viscometer containing test liquid was vertically immersed in thermostatic water bath for 45 min so that thermal fluctuation in viscometer was minimized. The

viscometer was calibrated with deionised distilled water at different temperatures (298.15-308.15 K). The efflux time of solutions were recorded three times with digital stop watch with an accuracy of ±0.01 s. The average of three sets of flow time for each solution was considered as the final efflux time for each sample and can be used for calculation of viscosity. The accuracy in viscosity measurements was found to be ±0.01 m Pa s. Refractive index of solutions was measured with the help Abbe's refractometer specially designed to measure the refractive index of the transparent liquids, solutions and solids ranging from 1.300 to 1.700 by direct reading was used. Initially the refractometer was calibrated with pure water and benzene at known temperature having precision of ±0.0001 unit. Conductance was measured with a (Control Dynamics, India) conductivity bridge having a cell constant 1.00 cm^{-1}. The temperature in all the experiments was maintained by circulating water from an electronically controlled water bath (Julabo, Germany) with a temperature stability of ±0.01 K. The readings were taken in triplicate and the numbers averaged.

2.1. *Results and Discussions*

2.1.1 Volumetric studies

The experimental values of density of L-histidine (0.02, 0.04, 0.06, 0.08, 0.1 mol kg^{-1}) in aqueous surfactant solutions of SDS and DTAB (0.02 mol kg^{-1}) at 298.15, 303.15, 308.15 K were used to evaluate apparent molar volume (V_ϕ) of the solutions using equation (1):

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

where m is the molality (mol kg^{-1}) of solution (L-histidine + aqueous surfactant), ρ and $\rho_\circ$ are the densities (kg m^{-3}) of the solution and the solvent (aqueous surfactant), respectively, and M is the molar mass of the solute (kg mol^{-1}). The values of density and apparent molar volume at different temperatures are presented in Table 1. The linear variation of apparent molar volume against different molar concentrations of L-histidine in aqueous surfactant solutions of SDS and DTAB are presented in Fig. 1.

The values of limiting apparent molar (V_ϕ°) were obtained by least square fitting of the data points to the following linear equation (2):

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Table 1 Densities (ρ) and apparent molar volume (V_ϕ) of L-histidine in 0.02 m aqueous surfactant solutions of SDS and DTAB at different temperatures.

m/ (mol kg^{-1})	ρ/ (kg m^{-3})			$\mathbf{V_\phi} \times 10^6$/ (m^3 mol^{-1})		
	298.15 K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K
	L-histidine + 0.02 m aqueous SDS					
0.00	998.365	996.743	995.145			
0.02	999.481	997.849	996.244	99.31	99.88	100.30
0.04	1000.582	998.941	997.332	99.57	100.12	100.52
0.06	1001.668	1000.019	998.403	99.84	100.36	100.74
0.08	1002.738	1001.085	999.462	100.12	100.58	100.97
0.1	1003.797	1002.138	1000.509	100.36	100.80	101.19
	L-histidine + 0.02 m aqueous DTAB					
0.00	997.746	996.323	994.688			
0.02	998.874	997.447	995.800	98.73	98.99	99.67
0.04	999.989	998.559	996.900	98.94	99.18	99.86
0.06	1001.092	999.658	997.989	99.14	99.39	100.04
0.08	1002.182	1000.745	999.068	99.35	99.59	100.20
0.1	1003.261	1001.821	1000.137	99.55	99.78	100.35

Table 3 Speed of sound (u) and isentropic compressibility (K_s) of L-histidine in 0.02 m aqueous surfactant solutions of SDS and DTAB at different temperatures.

m/ (mol kg^{-1})	u × 10^{-2}/ (m s^{-1})			$\mathbf{K_s} \times 10^{10}$ / (m^2 N^{-1})		
	298.15 K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K
	L-histidine + 0.02 m aqueous SDS					
0.00	14.9842	15.1057	15.2089	4.4611	4.3968	4.3443
0.02	14.9992	15.1196	15.2228	4.4472	4.3838	4.3316
0.04	15.0136	15.1332	15.2361	4.4338	4.3712	4.3193
0.06	15.0273	15.1462	15.2489	4.4209	4.3590	4.3074
0.08	15.0405	15.1587	15.2613	4.4085	4.3472	4.2959
0.1	15.0532	15.1704	15.2730	4.3964	4.3359	4.2848
	L-histidine + 0.02 m aqueous DTAB					
0.00	15.0034	15.1228	15.2265	4.4527	4.3887	4.3362
0.02	15.0192	15.1375	15.2415	4.4381	4.3752	4.3229
0.04	15.0343	15.1517	15.2559	4.4242	4.3622	4.3100
0.06	15.0489	15.1652	15.2697	4.4108	4.3496	4.2975
0.08	15.0628	15.1783	15.2830	4.3979	4.3374	4.2854
0.1	15.0761	15.1906	15.2958	4.3854	4.3257	4.2736

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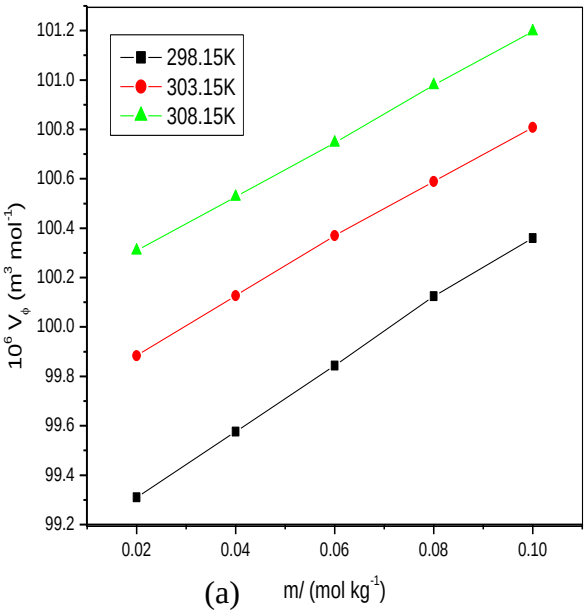
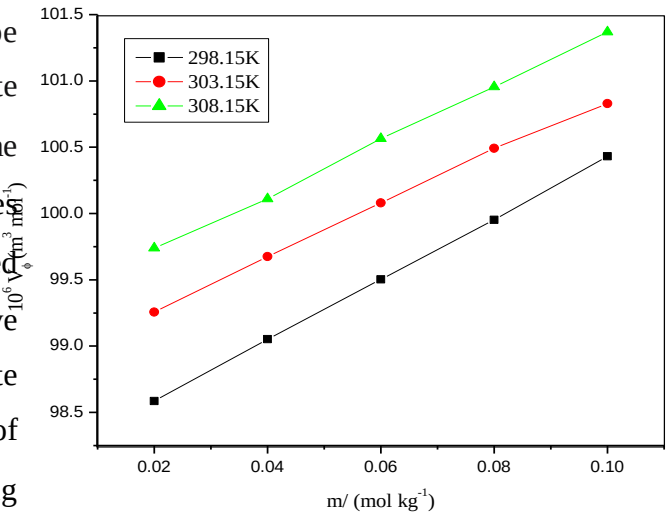
$$V_{\phi} = V_{\phi}^{\circ} + S_v m \qquad (2)$$

where S_V is the experimentally determined slope and provides information regarding solute-solute interactions, while V_{ϕ}° is the intercept showing the presence of solute-solvent interactions. The values of S_V, V_{ϕ}°, along with their standard errors, reported in Table 2. In the present systems the less positive behavior for Sv, suggests that solute–solute interactions are weak on the contrary, the values of V_{ϕ}° are large and positive and show an increasing behavior with increase in concentration of L-histidine as well as with increase in temperature. Thus, indicates dominance of solute-solvent interactions in the system. The V_{ϕ}° values (Table 2) increase with increase in temperature for both the L-histidine-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-histidine) in the bulk solution [17].



(a)



(b)

Fig.1 *Variation of apparent molar isentropic compressibility with molality for L-histidine in 0.02 m aqueous surfactant solutions of SDS (a) and DTAB (b) at different temperatures.*

The limiting apparent molar volume of transfer ($\Delta_{tr}V_{\phi}^{\circ}$) of L-histidine from water to aqueous surfactant solutions was evaluated using the following relation:

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

where V_{ϕ}°(in water) is the limiting apparent molar volume of L-histidine in water and its value for L-histidine has been taken from the literature [18]. The limiting apparent molar volume of transfer ($\Delta_{tr}V_{\phi}^{\circ}$) from water to aqueous surfactant solution is indicative of the nature of solute-solvent interactions, assuming that the volume occupied by the solute due to van der Waals volume and that due to voids and empty spaces present in the solution remain the same in both water and

aqueous solution [19,20]. The observed $\Delta_{tr}V_{\emptyset}^{\circ}$ are reported in Table 2.

The apparent molar volume of a non-electrolyte is the combination of intrinsic volume of the solute and the volume change due to its interaction with the solvent [21]. Tarasawa *et al.* pointed out that the intrinsic partial molar volume is considered to be made up of two types of contributions[20]:

$$V_{intrinsic} = V_{vw} + V_{void} \quad (4)$$

where V_{vw} is the volume occupied by the solute due to its van der Waals volume, and V_{void} is the volume associated with the voids and empty spaces present therein the above equation was modified to evaluate the contribution of a solute molecule to its $V_{\emptyset}^{\circ}$ as [22, 23, 19]:

$$V_{\emptyset}^{\circ} = V_{vw} + V_{void} - n\sigma_s \quad (5)$$

Table 2 Values of apparent molar volume ($V_{\emptyset}^{\circ}$), slope (S_V), limiting apparent molar volume of transfer ($\Delta_{tr}V_{\emptyset}^{\circ}$), apparent molar isentropic compressibility ($K_{S\emptyset}^{\circ}$), slope (S_K) and limiting apparent molar transfer compressibility ($\Delta_{tr}K_{S\emptyset}^{\circ}$) in aqueous surfactant solutions of 0.02 m SDS and DTAB at different temperatures.

	T (K)		
Property	298.15 K	303.15 K	308.15 K
L-histidine + 0.02 m aq. SDS			
$10^6.V_{\emptyset}^{\circ}$ /(m^3 mol^{-1})	99.04 (±0.01	99.66 (±0.01)	100.08 (±0.01)
$10^6.S_V$/(m^3 mol^{-2} kg)	13.23 (±0.18)	11.55 (±0.17)	11.14 (±0.06)
$10^6.V_{\emptyset(aq)}^{\circ}$ /(m^3 mol^{-1})	98.28 (±0.04)	98.52 (±0.05)	98.70 (±0.08)
$10^6.\Delta_{tr}V_{\emptyset}^{\circ}$ /(m^3 mol^{-1})	0.76	1.13	1.37
$10^{14}.K_{s,\emptyset}^{\circ}$ /(N^{-1} m^5 mol^{-1})	-2.66 (±0.01)	-2.24 (±0.00)	-2.13 (±0.01)
$10^{14}.S_K$/(m^4 s^2 mol^{-2})	6.01 (±0.11)	5.01 (±0.05)	4.96 (±0.07)
$10^{14}.K_{S\emptyset(aq)}^{\circ}$/($N^{-1}$ m^5 mol^{-1})	-3.00 (±0.04)	-2.66 (±0.08	-2.56 (±0.05)
$10^{14}.\Delta_{tr}K_{s,\emptyset}^{\circ}$/($N^{-1}$ m^5 mol^{-1})	0.34	0.41	0.42
L-histidine + 0.02 m aq. DTAB			
$10^6.V_{\emptyset}^{\circ}$ /(m^3 mol^{-1})	98.53 (±0.01)	98.79 (±0.01)	99.51 (±0.15)
$10^6.S_V$/(m^3 mol^{-2} kg)	10.21 (±0.10)	9.95 (±0.09)	8.51 (±0.22)
$10^6.V_{\emptyset(aq)}^{\circ}$ /(m^3 mol^{-1})	98.28 (±0.04)	98.52 (±0.05)	98.70(±0.08)
$10^6.\Delta_{tr}V_{\emptyset}^{\circ}$/($m^3$ mol^{-1})	0.25	0.27	0.81
$10^{14}.K_{S\emptyset}^{\circ}$/($N^{-1}$ m^5 mol^{-1})	-2.95 (±0.00)	-2.54 (±0.01)	-2.46 (±0.00)
$10^{14}.S_K$/(m^4 s^2 mol^{-1})	5.96 (±0.05)	5.44 (±0.09)	4.67 (±0.06)
$10^{14}.K_{S\emptyset(aq)}^{\circ}$/($N^{-1}$ m^5 mol^{-2})	-3.00 (±0.04)	-2.66 (±0.08)	-2.56 (±0.05)
$10^{14}.\Delta_{tr}K_{S\emptyset}^{\circ}$/($N^{-1}$ m^5 mol^{-1})	0.04	0.11	0.09

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where σ_s is the shrinkage in the volume produced by the interaction of hydrogen-bonding groups present in the solute with water molecules, and n is the potential number of hydrogen-bonding sites in the molecule. Finally, V_ϕ° of an amino acid can be viewed as:

$$V_\phi^\circ = V_{vw} + V_{void} - V_{shrinkage} \qquad (6)$$

If it is assumed that V_{vw} and V_{void} are of the same magnitude in water and in aqueous surfactant solutions [24, 25] then the observed changes in V_ϕ° or $\Delta_{tr}V_\phi^\circ$ of the amino acid can be explained in terms of the changes in the volume of shrinkage in the presence of surfactant molecules in aqueous solutions.

Using co-sphere overlap model, the following types of interactions are expected to occur in the present ternary systems of L-histidine, surfactants and water:

a) Ion-ion interactions between $SO_4^{2-}$of SDS/$Br^-$of DTAB and the NH^{3+}group of amino acids or between the Na^+ of SDS/N^+CH_3 group of DTAB and the COO^-group of amino acids

b) Ion-hydrophilic interactions between the ionic head group of the surfactants and the hydrophilic part of amino acid

c) Hydrophobic-hydrophilic interactions between the alkyl chain of the surfactants and the hydrophilic group of the amino acids and

d) Hydrophobic-hydrophobic interactions between the non-polar side groups of the surfactant and the amino acid.

The changes in $\Delta_{tr}V_\phi^\circ$ of L-histidine in aqueous surfactant solutions can be interpreted by considering the cosphere model [26-28]; according to which the overlap of hydration cospheres is destructive. According to this model, interactions between two ionic species or hydrophilic species, interaction between one hydrophobic and one hydrophilic species would lead to a positive $\Delta_{tr}V_\phi^\circ$, since there is a reduction in the electrostriction effect and overall water structure is enhanced. The charge centres (NH_3^+ ; COO^-**)** of L-histidine interact with the ions of SDS/DTAB, which results in the reduction of the electrostriction of water caused by the charge centres of L-histidine, leading to an increase in volume and hence, positive $\Delta_{tr}V_\phi^\circ$ values. Interactions between two hydrophobic species causes reduction of water structure that is formed around those groups as a result of the cosphere overlap leading to negative $\Delta_{tr}V_\phi^\circ$.

As we have used post micellar concentrations of SDS/DTAB, the interactions of amino acids with these co-solvents are mainly with the micelle. Further, the $\Delta_{tr}V_\phi^\circ$ values of L-histidine from water to 0.02 m DTAB and 0.02 m SDS are small positive at a temperature of 298.15 K but become large positive with increase in temperature this indicates that with rise of temperature (a) and (b) interactions become dominant over (c) and (d) type

of interactions but at lower temperature of 298.15K hydrophilic-hydrophobic and hydrophobic-hydrophobic interactions are dominant in the system. The release of some solvent molecules from the loose hydration spheres of the solute in the solution in both the aqueous surfactant solutions with the rise of temperature cause increase in $\Delta_{tr}V_{\emptyset}^{\circ}$. The $\Delta_{tr}V_{\emptyset}^{\circ}$ values from water to aqueous surfactant solutions at the studied temperatures of 293.15, 303.15 and 308.15 K follow the order: SDS > DTAB which indicates the sequence of the strength of ion-ion or ion-hydrophilic interactions of L-histidine with the surfactant molecules of SDS and DTAB in the studied systems.

2.1.2 Compressibility studies

The experimental values of speed of sound of different concentrations of L-histidine in 0.02 m aqueous surfactant solutions of SDS and DTAB measured at aforementioned temperatures, reported in Table 3**,** in order to evaluate apparent molar isentropic compressibilities, $K_{S\emptyset}$ using Equation (7).

$$K_{S\emptyset} = V_{\emptyset}K_s + \frac{K_s - K_s^{\circ}}{m\rho^{\circ}} \qquad (7)$$

K_s and K_s° are the isentropic compressibilities of the solution and solvent (aqueous surfactants) and was calculated using the relation:

$$K_s = 1/u^2\rho \qquad (8)$$

where u is the speed of sound. The isentropic compressibility (K_s), also reported in Table 3, is found to decrease with increase in concentration of L-histidine as well as with increase in temperature, the decrease in K_s values signifies electrostatic effect of amino acid on the surrounding medium [29], which makes the solution rather incompressible. This type of observation is characteristic of electrolytic behavior as found in literature [30-32]. Same kind of behavior has been reported for aqueous drug-surfactant, protein-surfactant system [33]. The variation of apparent molar isentropic compressibility, reported in Table 4, with molal concentration of L-histidine in 0.02 m aqueous surfactant solutions of SDS and DTAB at different temperatures has also been found to be linear and is presented in Fig.2.

It is observed that the values of apparent molar isentropic compressibility are negative at all the reported concentrations but become less negative with increase of concentration and temperature. The values of limiting molar isentropic compressibility ($K_{S\emptyset}^{\circ}$) and slope (S_K) are obtained by the least-square fitting using the following relation:

$$K_{S\emptyset} = K_{S\emptyset}^{\circ} + S_K m \qquad (9)$$

Here $K_{S,\emptyset}^{\circ}$ gives a measure of solute-solvent interactions while slope S_K depicts solute-solute interactions, the values of which along with standard errors are given in Table 2.

The values of standard partial molar adiabatic compressibility can be expressed by simple model:

$$K_{S\emptyset}^{\circ} = K_{S_{\emptyset(int)}}^{\circ} + K_{S_{\emptyset(elect)}}^{\circ} \qquad (10)$$

$K_{S_{\emptyset(int)}}^{\circ}$ is regarded as the intrinsic partial molar isentropic compressibility of the amino acid and $K_{S_{\emptyset(elect)}}^{\circ}$ is called as the electrostriction partial

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molar compressibility which is due to hydration of the amino acid. Since the value of $K^{\circ}_{S_{\emptyset(int)}}$ is very small [34], the value of $K^{\circ}_{S\emptyset}$ can essentially be considered to represent $K^{\circ}_{S_{\emptyset(elect)}}$. Hence, the value of $K^{\circ}_{S\emptyset}$ is mainly due to the hydration of polar and non-polar groups of amino acids. With increase of temperature for both the surfactant-amino acid systems under study there is increase in the compression of the hydration shell of the L-histidine which is responsible for the observed increase in the values of $K^{\circ}_{S\emptyset}$ [35]. The S_K values are positive and small, suggesting the presence of weak solute-solute interactions in the systems which decrease with increase of temperature.

The limiting apparent molar transfer compressibility ($\Delta_{tr}K^{\circ}_{S\emptyset}$) of L-histidine from water to 0.02 m aqueous surfactant solutions of SDS and DTAB was calculated using the following expression:

$$\Delta_{tr}K^{\circ}_{S\emptyset} = K^{\circ}_{S\emptyset}(\text{in aqueous surfactant}) - K^{\circ}_{S\emptyset}(\text{in water}) \quad (11)$$

Here $K^{\circ}_{S\emptyset}$ indicates compressibility of the overall solution, and $\Delta_{tr}K^{\circ}_{S\emptyset}$ indicates the contribution of electrostricted water in hydration shells to the overall compressibility of the solution. In the present systems under study, due to polar interactions between L-histidine and the surfactant solutions, the water molecules moves from hydration shell into the bulk (from less ordered to more ordered), the value of $\Delta_{tr}K^{\circ}_{S\emptyset}$ obtained, reported in Table 2, were positive resulting from increased compressibility of the solution. Also, with increase in temperature the values of $\Delta_{tr}K^{\circ}_{S\emptyset}$ also show an increase. This is attributed to the

Table 4 Apparent molar isentropic compressibility ($K_{s\emptyset}$) of L-histidine in 0.02 m aqueous surfactant solutions of SDS and DTAB of L-histidine at different temperatures.

$\mathbf{K_{s\emptyset}} \times 10^{14}$ / (N^{-1} m^5 mol^{-1})			
m/(molkg^{-1})	298.15 K	303.15K	308.15K
L-histidine + 0.02 m aqueous SDS			
0.02	-2.54	-2.14	-2.03
0.04	-2.42	-2.04	-1.94
0.06	-2.29	-1.94	-1.84
0.08	-2.17	-1.84	-1.74
0.1	-2.06	-1.73	-1.64
L-histidine + 0.02 m aqueous DTAB			
0.02	-2.83	-2.44	-2.37
0.04	-2.71	-2.32	-2.28
0.06	-2.59	-2.21	-2.18
0.08	-2.47	-2.10	-2.08
0.1	-2.35	-2.01	-2.00

strengthening of polar interactions between solute and solvent at higher temperature [36]. The trends in the value of $\Delta_{tr}K^{\circ}_{S\emptyset}$ also support the result obtained from $\Delta_{tr}V^{\circ}_{\emptyset}$ which suggest

the sequence of strength of solute-solvent interactions

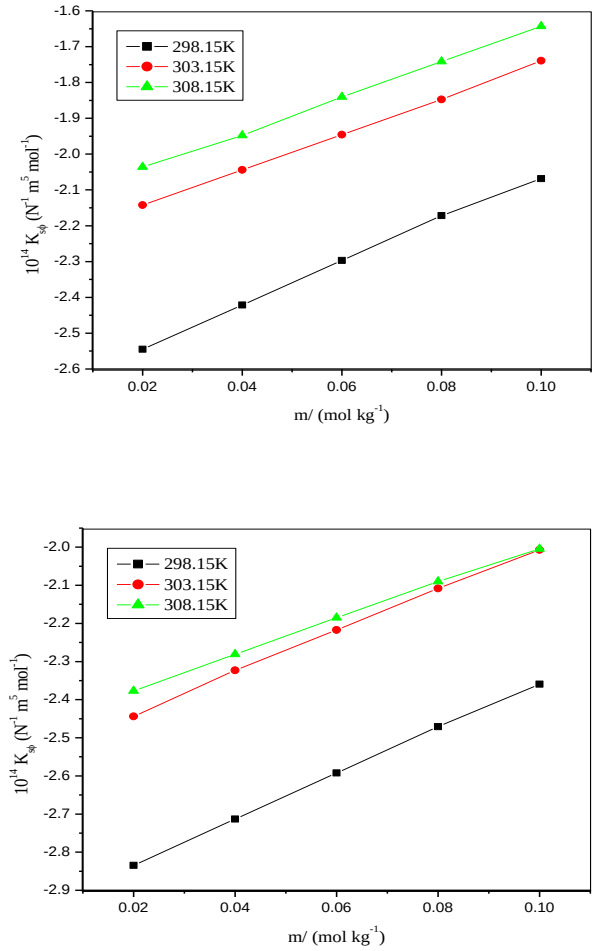

Fig.2 Variation of apparent molar isentropic compressibility with molality for L-histidine in 0.02 m aqueous surfactant solutions of SDS (a) and DTAB (b) at different temperatures as SDS>DTAB.

2.1.3 Viscosity

The experimentally determined values of viscosity, η, for L-histidine in 0.02 m aqueous solutions of SDS and DTAB at different temperature are reported in Table 5. The viscosity increases with increase in concentration of L-histidine and follows decreasing trend with increase in temperature. This increase in value of viscosity with increase in concentration is due to increase of solute-solvent interactions with concentration, which cause more frictional resistance to flow of solutions. It is observed that with rise of temperature, a decreasing trend in viscosity occurs due to decrease in extent of different intermolecular interactions. Rise of temperature is responsible for increase of kinetic energy of molecular species and ions present in the solution, which causes decrease in the solute-solvent interactions. Rise of temperature is responsible for the decrease of intermolecular forces of attraction which the moving molecules of solute and solvent and ions have to overcome and results in rapid movement of the molecules and ions into empty sites. Such a decrease in interactions causes decrease in viscosity with increase in temperature [37]. The viscosity data were evaluated by using Jones-Dole equation of the form [38]:

$$\eta_r = {}^{\eta}/_{\eta_\circ} = 1 + Am^{1/2} + Bm \qquad (12)$$

where, η_r denotes the relative viscosity of the solution, η and $\eta_\circ$ are the viscosities of solution (L-histidine + water + surfactant) and solvent (surfactant + water), respectively and m is the molality of L-histidine (Table 5). Falkenhagen coefficient A, represents solute-solute interactions and Jones-Dole coefficient

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Table5 Viscosity (η) and relative viscosity (η_r) of L-histidine in 0.02 m aqueous surfactant solutions of SDS and DTAB at different temperatures.

m/ (mol kg^{-1})	$\eta \times 10^3$/ (N m^{-2} s)			η_r		
	298.15 K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K
L-histidine + 0.02 m aqueous SDS						
0.00	0.8769	0.7831	0.7045			
0.02	0.9275	0.8277	0.7440	1.0577	1.0570	1.0561
0.04	0.9550	0.8521	0.7658	1.0891	1.0881	1.0870
0.06	0.9800	0.8743	0.7857	1.1176	1.1165	1.1153
0.08	1.0032	0.8948	0.8041	1.1440	1.1426	1.1414
0.1	1.0258	0.9150	0.8219	1.1698	1.1684	1.1666
L-histidine + 0.02 m aqueous DTAB						
0.00	0.8294	0.7557	0.6712			
0.02	0.8704	0.7924	0.7032	1.0494	1.0486	1.0477
0.04	0.8909	0.8112	0.7198	1.0741	1.0734	1.0724
0.06	0.9089	0.8276	0.7342	1.0959	1.0951	1.0939
0.08	0.9253	0.8422	0.7471	1.1156	1.1145	1.1131
0.1	0.9408	0.8560	0.7592	1.1343	1.1327	1.1311

The values of coefficients A and B were obtained using plot between $(\eta_r-1)/m^{1/2}$ vs. $m^{1/2}$ by least square fitting, slope gives the values of B and intercept gives the values of A. The values of the A and B coefficients of the Jones-Dole Equation are reported in Table 8. It can be observed that the values of both the coefficients are positive but larger values of B-coefficient than coefficient A suggests stronger solute-solvent interactions as compared to solute-solute interactions. Similar behavior has also been reported by Kumar *et al.* for L-histidine in aqueous ketorolac tromethamine solutions at various temperatures [40]. The results obtained from viscosity data also support our results obtained from the volumetric studies.

2.1.4 Refractive index (n_D)

The experimental values of refractive indices are given in the Table 6 which show an increasing trend with increase in concentration of L-histidine in aqueous surfactant solutions which indicates the fact that refractive index gives a measure of the interactions present in the systems, same view was also proposed by Soto *et. al*. [41, 42]. The molar refractivity of each component in a mixture of interacting components is given by the equation:

$$R_D = \pi\alpha N_A \qquad (13)$$

where α is the molecular polarizability. The Lorentz-Lorenz equation was used to calculate the molar refractivity, R_D as follows :

$$R_D = \left(\frac{n_D^2-1}{n_D^2+2}\right)\left(\sum_{i=1}^{3} x_i M_i/\rho\right) \qquad (14)$$

where x_i and M_i is the mole fraction and the molar mass of the i^{th} component of the system respectively. The plots of R_D vs m (amino acid concentration) at different temperatures for the studied systems were plotted (Fig. 3). R_D is directly proportional to the molecular polarizability which indicates that the polarizability increases with increase in concentration of L-histidine in the solutions. Also the polarisability is found to increase in the order SDS>DTAB and no significant effect of temperature is observed on the R_D values [2].

2.1.5 Conductometric study

The experimental values of conductance and molar conductance of L-histidine in aqueous solutions were recorded in Table 7 which increase with increase in concentration as well as temperature. The limiting molar conductance for L-histidine in aqueous surfactant solutions were obtained by extrapolating the linear plots of molar conductance, Λ_m vs $m^{1/2}$ to zero concentration. The Λ_m° values for L-histidine in 0.02 m aqueous SDS and DTAB at different temperatures are presented in Table 8. At infinite dilution the solute-solute interactions are absent so the limiting molar conductance, Λ_m° indicates the strength of L-histidine-surfactant-water interactions [43]; the higher the value of Λ_m°, the greater are the interactions. As the values of limiting molar conductance of L-histidine in aqueous DTAB and SDS solutions are large and positive and show an increasing trend of Λ_m° with increase in temperature, suggest that L-histidine-surfactant-water interactions are strong and increase with increase in temperature supporting the results obtained from other parameters.

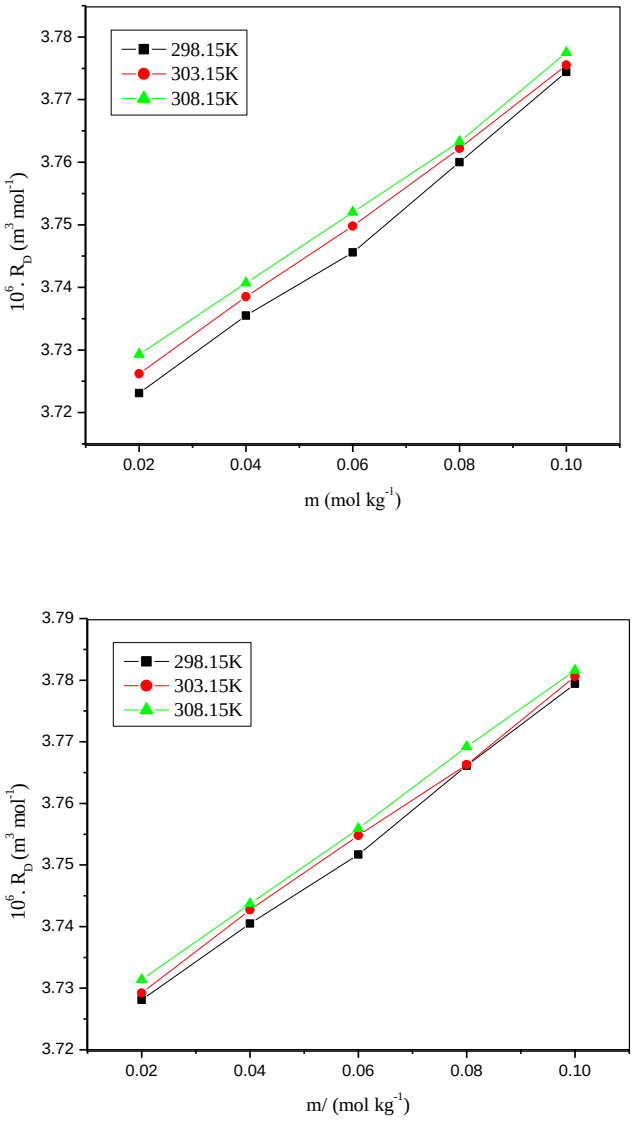

Fig.3 Variation of molar refractivity with molality for L-histidine in 0.02 m aqueous surfactant solutions of SDS (a) and DTAB (b) at different temperatures.

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Table 6 Refractive index (n_D) and molar refractivity (R_D) of L-histidine in 0.02 m aqueous surfactant solutions of SDS and DTAB at different temperatures.

m/ (mol kg^{-1})	$\mathbf{n_D}$			$\mathbf{R_D} \times 10^6$/ (m^3 mol^{-1})		
	298.15 K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K
L-histidine + 0.02 m aqueous SDS						
0.00	1.3325	1.3320	1.3316			
0.02	13.333	13.328	13.324	3.7281	3.7292	3.7314
0.04	13.339	13.335	13.330	3.7405	3.7427	3.7437
0.06	13.344	13.341	13.334	3.7517	3.7548	3.7559
0.08	13.352	13.346	13.343	3.7661	3.7663	3.7692
0.1	13.359	13.354	13.349	3.7794	3.7806	3.7816
L-histidine + 0.02 m aqueous DTAB						
0.00	1.3315	1.3311	1.3304			
0.02	13.326	13.323	13.320	3.7231	3.7262	3.7293
0.04	13.332	13.329	13.325	3.7355	3.7385	3.7407
0.06	13.336	13.334	13.330	3.7456	3.7498	3.7520
0.08	13.344	13.340	13.335	3.7600	3.7622	3.7633
0.1	13.352	13.347	13.343	3.7744	3.7755	3.7775

Table 8 Values of Falkenhagen coefficient (A), viscosity B-coefficient (B), and limiting molar conductance (Λ°_m) of L-histidine in aqueous surfactant solutions of 0.02 m SDS and DTAB at different temperatures.

m/ (mol kg^{-1})	T/ (K)		
	298.15 K	303.15 K	308.15 K
L-histidine + 0.02 m aq. SDS			
$A \times 10^1$/ (kg$^{1/2}$ mol$^{-1/2}$)	3.0054 (±0.0546)	2.9477 (±0.0531)	2.8800 (±0.0448)
$B \times 10^1$/ (kg mol^{-1})	7.3997 (±0.2228)	7.4423 (±0.2170)	7.5011 (±0.1830)
$\Lambda^{\circ}_m \times 10^{-1}$ (Sm^{2}mol^{-1})	3.3064±0.4421	3.5724 (±0.4779)	3.8821 (±0.5502)
L-histidine + 0.02 m aq. DTAB			
$A \times 10^1$/ (kg$^{1/2}$ mol$^{-1/2}$)	2.8633 (±0.0363)	2.8089 (±0.0162)	2.7382 (±0.0110)
$B \times 10^1$/ (kg mol^{-1})	4.3342 (±0.1481)	4.3816 (±0.0660)	4.4536 (±0.0450)
$\Lambda^{\circ}_m \times 10^{-1}$ / (Sm^{2}mol^{-1})	3.2365 (±0.4133)	3.4466 (±0.4266)	3.6934 (±0.4734)

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Table 7 Conductivity (κ) and molar conductivity (Λ_m) of L-histidine in 0.02 m aqueous surfactant solutions of SDS and DTAB at different temperatures.

m/ (mol kg^{-1})	κ (S m^{-1})			$\Lambda_m \times 10^{-1}$(S m^2 mol^{-1})		
	298.15 K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K
L-histidine + 0.02 m aqueous SDS						
0.00	0.295	0.341	0.373			
0.02	0.438	0.465	0.498	2.240	2.415	2.625
0.04	0.472	0.517	0.546	1.180	1.293	1.365
0.06	0.534	0.560	0.585	0.890	0.933	0.975
0.08	0.571	0.603	0.628	0.714	0.754	0.785
0.1	0.546	0.600	0.631	0.546	0.600	0.631
L-histidine + 0.02 m aqueous DTAB						
0.00	0.274	0.329	0.342			
0.02	0.423	0.452	0.481	2.115	2.260	2.405
0.04	0.453	0.498	0.531	1.133	1.245	1.328
0.06	0.500	0.535	0.564	0.833	0.892	0.940
0.08	0.539	0.570	0.602	0.6738	0.713	0.753
0.1	0.539	0.574	0.604	0.539	0.574	0.604

Conclusion

The current work leads to systematic experimental measurements of density (ρ), speed of sound (u), viscosity (η), refractive index (n_D) and conductivity (Λ), of solutions of L-histidine
in aqueous surfactant solutions of SDS and DTAB at different temperatures. From the experimental data, various thermodynamic parameters were calculated and the results were discussed in terms of solute-solvent interactions. Positive transfer values of $\Delta_{tr}V_{\phi}^{\circ}$, $\Delta_{tr}K_{S\phi}^{\circ}$, shows the dominance of ionic-ionic and ion-hydrophilic interactions over hydrophilic-hydrophobic and hydrophobic-hydrophobic interactions. Moreover from the study it was inferred that L-histidine interactions are stronger with surfactant SDS in comparison to DTAB.

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