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# Volumetric and refractive index behavior of L-valine with tetradecyltrimethylammonium bromide and cetyltrimethylammonium bromide at different temperatures

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## ABSTRACT

*Densities,$\rho$ and refractive indices, $n_D$ of L-valine (0.02-0.1m) in 0.01m aqueous solution of cationic surfactants, tetradecyltrimethylammonium bromide(TTAB) and cetyltrimethylammonium bromide (CTAB) have been measured at 298.15, 303.15 and 308.15 K. The density data has been utilized to calculate apparent molar volumes, $V_\phi$, partial molar volumes at infinite dilution, $V_\phi^\circ$ , its experimental slope, $S_v^*$, and partial molar volumes of transfer, $V_\phi^\circ$(tr) of amino acids. The refractive index, $n_D$ data has been used to evaluate molar refractivity, $R_D$. 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**: cetyltrimethylammonium bromide, tetradecyltrimethylammonium bromide and partial molar volume.

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## INTRODUCTION

Protein-surfactant interactions have been a focus of studies for a long time [1-4]. It is known that protein-surfactant interactions play very important role in industrial, biological, pharmaceutical, and cosmetic applications [5, 6]. Surfactants are used for molecular weight determination [7], membrane protein solublization [8], and crystallization [9]. Binding of surfactants to proteins alters intermolecular forces which maintain the secondary and tertiary structure, thereby producing conformational changes [10, 11]. Surfactants can interact directly or indirectly with proteins through different physicochemical mechanisms such as electrostatic or hydrophobic interactions [12-14]. Surfactants may either bind to protein or initiate its unfolding or only bind and retain its tertiary structure intact [15]. The conformational solublization of proteins in surfactants is related to the nature of solute-solute and solute-solvent interactions. Therefore a detailed understanding of the interactions of the intact proteins and the constituents of proteins with surfactants is essential. Studies on the interactions of model compounds such as amino acids and peptides with surfactants can help in understanding the fine details of protein-surfactant interactions [16-20].

In this work, we have investigated the effect of cationic surfactants CTAB (cmc 8. $2\text{x}10^{-4}$molkg$^{-1}$) and TTAB (cmc $3.7\text{x}10^{-3}$ molkg$^{-1}$.) on amino acid L-valine. We report apparent molar volumes, partial molar volumes, its experimental slopes and volumes of transfer of amino acids from water to aqueous solution of surfactants. These data can throw light on interactions of biomolecules in aqueous CTAB and TTAB solutions.

## EXPERIMENTAL SECTION

L-valine was procured from s. d. fine Chem., India. CTAB and TTAB were purchased from s. d. fine Chem., Thomas Baker. L-valine, CTAB, TTAB were dried over $P_2O_5$ in vacuum desiccator. Solutions were made using deionized and triply distilled water. The weighing was done on an analytical balance (Mettler Toledo) having an accuracy of $1.0x10^{-5}$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 refractive indices were measured with the aid of an Abbe-refractometer to an accuracy of ±0.0001. The calibration of the refractometer was done by measuring the refractive indices of pure water and benzene at known temperatures.

## RESULTS AND DISCUSSION

The experimental values of densities and refractive index of L-valine (0.02-0.1m) in 0.01m aqueous micellar solutions of CTAB and TTAB at 298.15, 303.15 and 308.15 K are listed in table 1, 2, 3 and 4.

Volumetric Study

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

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

where m is the molality of solute (L-valine), $\rho$ 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 $V_\emptyset$ values for L-valine in the aqueous surfactant solutions and at different temperatures are graphically presented in Fig. 1and 2.

**Table 1**. **Values of density, ρ, of L-valine in 0.01m aqueous CTAB at different temperatures**

| | ρ(kgm$^{-3}$) | | |
|---|---|---|---|
| m/(molkg$^{-1}$) | 298.15K | 303.15K | 308.15K |
| 0.00 | 997.708 | 996.106 | 994.311 |
| 0.02 | 998.299 | 996.687 | 994.884 |
| 0.04 | 998.878 | 997.249 | 995.439 |
| 0.06 | 999.438 | 997.795 | 995.976 |
| 0.08 | 999.981 | 998.322 | 996.493 |
| 0.1 | 1000.492 | 998.818 | 996.989 |

**Table 2. Values of density, ρ, of L-valine in 0.01m aqueous TTAB at different temperatures**

| | ρ(kgm$^{-3}$) | | |
|---|---|---|---|
| m/(molkg$^{-1}$) | 298.15K | 303.15K | 308.15K |
| 0.00 | 997.693 | 996.094 | 994.301 |
| 0.02 | 998.292 | 996.682 | 994.879 |
| 0.04 | 998.873 | 997.244 | 995.435 |
| 0.06 | 999.430 | 997.791 | 995.972 |
| 0.08 | 999.972 | 998.318 | 996.489 |
| 0.1 | 1000.481 | 998.815 | 996.986 |

**Table 3. Values of refractive index, $n_D$, of L-valine in 0.01m aqueous CTAB at different temperatures**

| m/(molkg$^{-1}$) | 298.15K | 303.15K | 308.15K |
|---|---|---|---|
| 0.00 | 1.3326 | 1.3319 | 1.3312 |
| 0.02 | 1.3338 | 1.3323 | 1.3318 |
| 0.04 | 1.3332 | 1.3326 | 1.3321 |
| 0.06 | 1.3336 | 1.3330 | 1.3325 |
| 0.08 | 1.3339 | 1.3334 | 1.3329 |
| 0.1 | 1.3345 | 1.3338 | 1.3332 |

**Table 4. Values of refractive index, $n_D$ of L-valine in 0.01m aqueous TTAB at different temperatures**

| m/(molkg$^{-1}$) 308.15K | 298.15K | 303.15K | 308.15K |
|---|---|---|---|
| 0.00 | 1.3321 | 1.3315 | 1.3308 |
| 0.02 | 1.3325 | 1.3319 | 1.3315 |
| 0.04 | 1.3330 | 1.3323 | 1.3318 |
| 0.06 | 1.3334 | 1.3327 | 1.3322 |
| 0.08 | 1.3337 | 1.3332 | 1.3326 |
| 0.1 | 1.3340 | 1.3335 | 1.3330 |

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

$$V_\emptyset = V_\emptyset^\circ + S_v^* m \qquad (2)$$

where $S_v^*$ is the experimentally determined slope, sometimes considered to be volumetric pairwise interaction coefficient and provides information regarding L-valine-L-valine interactions, while $V_\emptyset^\circ$ is the intercept and provides the information regarding L-valine–surfactant/water interactions. The values of $V_\emptyset^\circ$ of L-valine along with the $S_v^*$ values at different temperatures are given in Table 7. Table 7 reveals that the values of $V_\emptyset^\circ$ are large positive for L-valine in each aqueous surfactant solution, suggesting strong L-valine–surfactant/water interactions. The values (Table 7) increase with increase in temperature for both the L-valine–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-valine) in the bulk solution [21]. The reduction in electrostriction occurs with increase in temperature, hence, an increase in $V_\emptyset^\circ$ . The $S_v^*$ values (Table 7) for L-valine are found to be positive but smaller than $V_\emptyset^\circ$ 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 $V_\emptyset^\circ$ were computed using the equation:

$$\Delta_{tr} V_\emptyset^\circ\,(in\ aqueous\ surfactant) - V_\emptyset^\circ(in\ water) \quad (3)$$

where $V_\emptyset^\circ$ (in water) is the partial molar volume of L-valine in water. The $V_\emptyset^\circ$(tr) values at 298.15, 303.15 and 308.15 are summarized in Table7. A glance on the structure of L-valine and surfactant molecules studied reveals that the volumetric behavior of L-valine 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/hydrophilic-hydrophilic interactions between $Br^-$of CTAB/TTAB and the $NH_3^+$group of L-Valine and between $N^+$–$CH_3$ group of CTAB/TTAB and the COO−group of L-valine
2. Hydrophilic–hydrophobic/ion-hydrophobic interactions between the non-polar parts of amino-acid and polar head group of CTAB/TTAB and vice-versa.
3. Hydrophobic–hydrophobic interactions between the alkyl chain (hydrophobic tail) of the surfactants and the hydrophobic group (non-polar parts) of the amino acid.

The first type of these interactions gives a positive value of $\Delta_{tr} V_\emptyset^\circ$ since these lead to reduction in electrostriction of solvent resulting in strengthening of the structure of the water in the bulk. The last two types of interactions contribute negatively to $\Delta_{tr} V_\emptyset^\circ$ due to overall reduction in the structure of water upon the overlap of their hydration co-spheres.

The values of $\Delta_{tr} V_\emptyset^\circ$ for amino acid in aqueous surfactants can be explained by using the cosphere overlap model [22] in the light of this model hydrophilic-hydrophilic interactions between $Br^-$of CTAB/TTAB and the $NH_3^+$group of L-valine and between $N^+$–$CH_3$ group of CTAB/TTAB and the COO−group of L-valine would lead to positive values due to reduction in the electrostriction effect. On the other hand, hydrophilic–hydrophobic and hydrophobic–hydrophobic interactions between amino acid and surfactants lead to negative value because of the reduction in water structure that is formed around those groups as a result of the cosphere overlap.

**Table 5: Values of apparent molar volumes, $V_\emptyset$ , of L-valine in 0.01m aqueous surfactant solutions at different temperatures**

| $V_\emptyset$ . $10^{-6}$ ($m^3mol^{-1}$) | | | |
|---|---|---|---|
| m(molkg$^{-1}$) | 298.15K | 303.15K | 308.15K |
| L-valine + aqueous CTAB | | | |
| 0.02 | 87.6812 | 88.2789 | 88.7903 |
| 0.04 | 87.9315 | 88.7074 | 89.1955 |
| 0.06 | 88.3001 | 89.0864 | 89.6018 |
| 0.08 | 88.6739 | 89.4919 | 90.0347 |
| 0.1 | 89.2021 | 90.0304 | 90.4892 |
| L-valine + aqueous TTAB | | | |
| 0.02 | 87.2798 | 87.9265 | 88.5377 |
| 0.04 | 87.6803 | 88.5315 | 89.0440 |
| 0.06 | 88.1833 | 88.9523 | 89.5009 |
| 0.08 | 88.5990 | 89.3913 | 89.9591 |
| 0.1 | 89.1627 | 89.9399 | 90.4188 |

Further, $\Delta_{tr}V_\emptyset^\circ$ values of L-valine in both the surfactant solutions are negative. This indicates that hydrophobic-hydrophilic and hydrophobic-hydrophobic interactions dominate over hydrophilic- hydrophilic interactions in aqueous CTAB/TTAB-L-valine system The increase in $\Delta_{tr}V_\emptyset^\circ$ with rise in temperature in both the aqueous surfactant solutions may be due to release of some solvent molecules from the loose hydration spheres of the solute in solution [21]. It is worth mentioning that the values of $\Delta_{tr}V_\emptyset^\circ$ from water to aqueous surfactant solutions at all the studied temperatures follow the sequence: CTAB > TTAB

This suggests the sequence of the strength of interactions of L-valine with the surfactant molecules in the solution.
Refractive Index Study

**Table 6: Values of molar refractivity, $R_D$, of L-valine in aqueous surfactant solutions at different temperatures**

| $R_D.10^{-6}$ ($m^3mol^{-1}$) | | | |
|---|---|---|---|
| L-valine + aqueous CTAB | | | |
| m(molkg$^{-1}$) | 298.15K | 303.15K | 308.15K |
| 0.00 | | | |
| 0.02 | 3.7272 | 3.7283 | 3.7293 |
| 0.04 | 3.7355 | 3.7354 | 3.7386 |
| 0.06 | 3.7456 | 3.7458 | 3.7469 |
| 0.08 | 3.7549 | 3.7560 | 3.7570 |
| 0.1 | 3.7487 | 3.7641 | 3.7663 |
| L-valine + aqueous TTAB | | | |
| 0.00 | 298.15K | 303.15K | 308.15K |
| 0.02 | 3.7222 | 3.7222 | 3.7262 |
| 0.04 | 3.7335 | 3.7344 | 3.7334 |
| 0.06 | 3.7416 | 3.7407 | 3.7438 |
| 0.08 | 3.7508 | 3.7519 | 3.7519 |
| 0.1 | 3.7601 | 3.7612 | 3.7623 |

**Table 7: Values of partial molar volumes at infinite dilution $V_\emptyset^\circ$ , its experimental slope $S_v^*$, partial molar volumes of transfer, $\Delta_{tr}V_\emptyset^\circ$, of L-valine in 0.01m aqueous surfactant solutions at different temperatures**

| L-valine + aqueous CTAB | | | |
|---|---|---|---|
| | 298.15K | 303.15k | 308.15k |
| $V_\emptyset^\circ$ $10^{-6}$ ($m^3mol^{-1}$) | 87.2225 ± 0.0931 | 87.8327 ± 0.0530 | 88.3512 ± 0.0208 |
| $S_v^*$ | 18.9210 ± 0.4022 | 21.4375 ± 0.8002 | 21.1850 ± 0.3129 |
| $V_\emptyset^\circ(aq)10^{-6}$ ($m^3mol^{-1}$) | 90.980$^a$ | - | 91.550$^a$ |
| $\Delta_{tr}V_\emptyset^\circ 10^{-6}$ ($m^3mol^{-1}$) | -3.757 | - | -3.199 |
| L-valine + aqueous TTAB | | | |
| $V_\emptyset^\circ$ $10^{-6}$ ($m^3mol^{-1}$) | 86.7757 ± 0.0502 | 87.4823 ± 0.0589 | 88.0889 ± 0.0182 |
| $S_v^*$ | 23.4225 ± 0.7568 | 24.4330 ± 0.8873 | 23.3685 ± 0.2737 |
| $V_\emptyset^\circ(aq)10^{-6}$ ($m^3mol^{-1}$) | 90.980$^a$ | - | 91.550$^a$ |
| $\Delta_{tr}V_\emptyset^\circ 10^{-6}$ ($m^3mol^{-1}$) | -4.204 | - | -3.461 |
| $^a$*Ref [23]* | | | |

The observed refractive index values are included in Table 3, 4 and are found to increase with concentration of solute. This indicates that the refractive index is directly related to the interactions present in the solutions. For mixtures of interacting components, the molar refractivity of each component is given by the equation:

$$R_D = 4\pi\alpha N_A$$

where α is the molecular polarizability. The $n_D$ data are utilized for the calculation of molar refractivity ($R_D$) using Lorentz Lorenz equation:

$$R_D = \left(\frac{n_D^2 - 1}{n_D^2 + 2}\right)\sum_{i=1}^{3} x_i M_i / \rho \qquad (4)$$

where $x_i$ and $M_i$ are the mole fractions and molar mass of the $i^{th}$ component of the mixture respectively. The calculated values of $R_D$ are shown in Table 6.The plots of $R_D$ vs L-valine concentration at 298.15 K, 303.15 K and 308.15 K for the studied systems are given in Fig. 3, 4. It is evident from Fig. 3, 4 that $R_D$ increases linearly with increasing amount of L-valine in both the systems. As $R_D$ is directly proportional to the molecular polarizability, Fig. 3 and 4 reveals that overall polarizability of the two systems under study increases with increasing amount of L-valine in the solutions. The polarizability is found to increase in the order: CTAB>TTAB (Fig. 3, 4). No significant effect of temperature has been observed on the $R_D$ values of the studied systems.

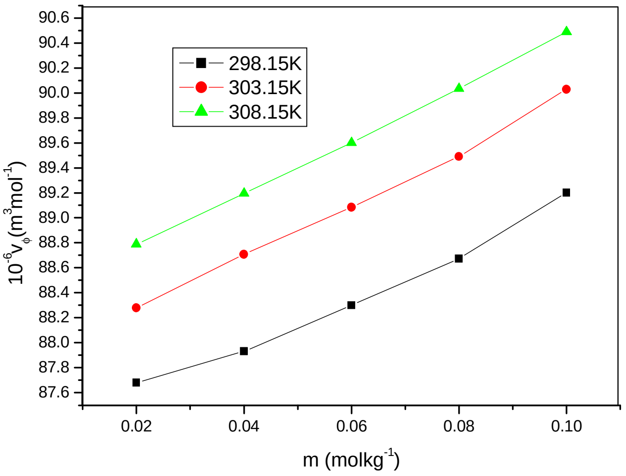

**Fig.1. Plot of apparent molar volume, $V_\Phi$, versus molality, m, of L-Valine in aqueous solutions of CTAB at different temperatures**

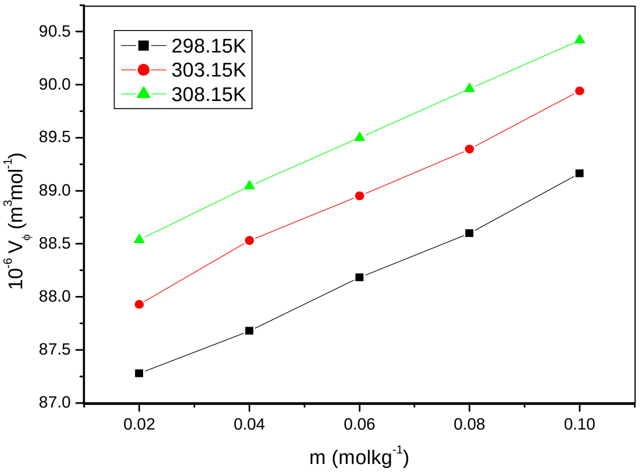

**Fig.2. Plot of apparent molar volume, $V_\Phi$, versus molality, m, of L-Valine in aqueous solutions of TTAB at different temperatures**

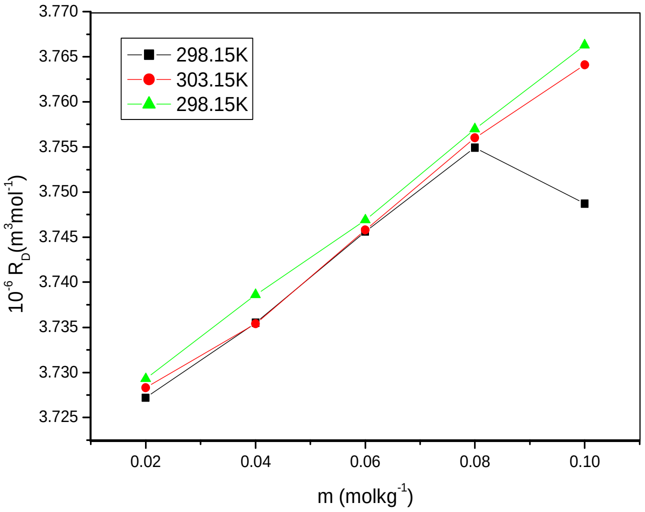

**Fig.3. Plots of molar refractivity, $R_{D,}$ versus molality, m, of L-Valine in aqueous solutions of CTAB at different temperatures**

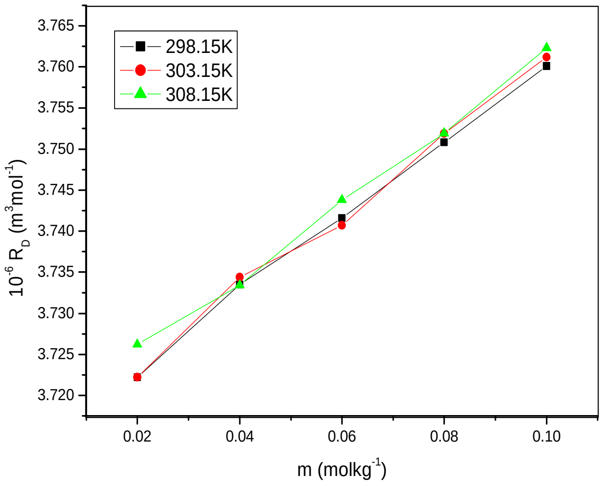

**Fig.4. Plots of molar refractivity, $R_D$, versus molality, m, of L-Valine in aqueous solutions of TTAB at different temperatures**

## CONCLUSION

The densities and refractive indices of L-valine in 0.01m aqueous solutions of CTAB and DTAB were measured at different temperatures. From the experimental data various parameters, viz., $V_{\emptyset}, V_{\emptyset}^{\circ}$, $S_v^*$, $\Delta_{tr}V_{\emptyset}^{\circ}$, $R_D$ were calculated. The results indicate that there exist strong hydrophilic–hydrophobic and hydrophobic–hydrophobic interactions between amino acid and surfactants which result in the reduction in water structure that is formed around these groups as a result of the cosphere overlap.

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