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# Studies of Molecular Interactions of α-Amino Acids in Aqueous and Cationic Surfactant Systems Investigated from Their Densities and Apparent Molal Volumes at 283.15, 288.15 and 293.15 K

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**Abstract.** Density ($\rho/10^3$ kg m$^{-3}$) and molal volumes ($V_\phi/10^{-6}$ m$^3$ mol$^{-1}$) of glycine, valine and leucine from 0.03 to 0.07 mol kg$^{-1}$, and cetyl pyridinium chloride (CPC) and cetyl pyridinium bromide (CPB) were measured in 0.0497 mol kg$^{-1}$ aqueous surfactant solution systems at different temperatures. The data were regressed against molality, and constants were referred to as the limiting density ($\rho^0$) and apparent molal volumes ($V_\phi^0$) and denoted as solute-solvent interactions, while their slope constants indicated molecular interactions and influence of composition. It was observed that amino acids with a shorter alkyl chain, such as glycine, had weaker affinity to interact with cationic surfactants, in comparison with the longer alkyl chain amino acids, such as leucine. The CPB with larger-sized anion showed greater molecular interaction with amino acids.

**Keywords:** pyridinium ring, intermolecular forces, hydrophobic interactions, transfer volume, cationic surfactants

## Introduction

The limiting density ($\rho^0$) and apparent molal volume ($V_\phi^0$) are fundamental properties of binary and ternary solutions of non-ideal systems of amino acids and surfactants (Ali and Nain, 2002; Singh *et al.,* 2001). Such thermodynamic functions of biomolecules in mixed solvents are of significant interest as they influence their activity to a great extent (Apelblat and Manzurola, 1999). These properties can be used to obtain the desired polarity of solvents with surfactants (Creighton, 1990; Dill, 1990; Frank, 1973). The surfactant systems have been, therefore, drawing attention for the determination of their activity, and the activity coefficients of amino acids and peptides in aqueous and non-aqueous solvents (Mohammad and Wahab, 2002; Cabani *et al.,* 1972). Surfactants are of immense significance due to their interaction with hydrophobic and hydrophilic parts of the amino acids (Barbosa *et al*., 2001). They also assist in the partition of amino acids, if added to immiscible solvents in combination (Sandberg and Edholm, 2001; Key and Weitzman, 1987; Monica and Bufo, 1977; Frank, 1973). Further, the size of the anion associated with $N^+$ ion of the pyridine ring of the surfactants is seen to influence the activity of the surfactant itself, and of biomolecules (Mohammad and Wahab, 2002; Sandberg and Edholm, 2001). The polar head of α-amino acids (hydrophilic) is confined to one end, and the alkyl chain (hydrophobic) to another, similar to the alignment of hydrophilic and hydrophobic parts in surfactants (Singh, 2001). How does an increase in the alkyl chain of amino acids affects their interaction with water and aqueous surfactant solutions is of primary interest. Studies undertaken elsewhere, on different solvents, do not elucidate the mechanism of interactions of surfactants with amino acids (Frank, 1972-1983). As amino acids are also related to acetyl coenzyme-A (acetyl-CoA) of the Kreb's cycle (Key and Weitzman, 1987), it may be of interest to understand how the enzyme functions with amino acids in surfactant solutions in biological processes, since the enzyme catalyzes cellular reactions and amino acid interactions. Therefore, molar volumes of acids can be rationalized with the stability of proteins and the activity of an enzyme to recognize and bind its substrate. How do molal volumes of amino acids vary in surfactant solutions is not yet known (Barabosa *et al.,* 2001; Frank, 1972-1983), since molar expansion/contraction affect interactions of biofluids/biochemicals (Rialdi and Blitonen, 1973). Therefore, the density (ρ) and molal volume ($V_\phi$) properties of amino acids are helpful in elucidating the structural interactions and reorientations of enzymes with their substrates (Singh and Kumar, 2004; Goss, 2003; Sharma *et al.,* 1992; Crawford *et al.,* 1977; Nemethy and Scheraga, 1974). Also, the ρ and $V_\phi$ being state-related functions, these can depict transition of systems that may be of some use for non-ideal solutions (Singh, 2005; Parmar and Dhiman, 2002; Singh, 2001; Pandey *et al.,* 1998). Thermodynamic investigations on macromolecules and biomolecules in aqueous systems have always been a matter of interest (Singh, 2004), so as to focus the structural reorientation and conformational states regar-

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ded as valuable for the determination of activity and activity coefficients (Singh and Chand, 2005; Rialdi and Biltonen, 1973). Thus, the present studies were understood to have biological, biotechnological and biophysical significance, as such kinds of chemical species enter the cellular and intracellular matrix where their size could exert some pressure on the membrane systems. The molecules with hydrophobic-hydrophilic ends, like valinomycine protein, monitor the transport of various cations such as $Na^+$ and $K^+$ from aqueous to lipid phase through permeable membrane in the cells. The present studies may, therefore, be of some use to understand the carrier and channel mechanism for transporting of several ions performed by such molecules in the body.

## Materials and Methods

Glycine, valine and leucine (AR, Sigma), and cetyl pyridinium chloride (CPC) and cetyl pyridinium bromide (CPB) (E. Merck) were dried and stored on $P_2O_5$ in a dessicator, before use. Solutions (w/w) were prepared in triple-distilled, deionised and degassed water, which was prepared by distilling deionized water in the presence of $KMnO_4$ and KOH twice and degassed by boiling. Densities and volumes were measured with a $25x10^{-3}dm^3$ capacity bicapillary pyknometer at constant temperature within ±0.1 °C. The temperature was maintained by an automatic electric relay attached to a contact thermometer and a 25-watt immersion rod, together with circulation of cold water through a copper coil immersed in a waterbath. The pyknometer with solutions was weighed within an accuracy of 0.01 mg using Dhona balance, model 100 DS. The pyknometer was calibrated with water of $1x10^{-7}\Omega^{-1}$conductivity. The reproducibility in weights was checked immediately after taking the measurement and was found to be $1x10^{-5}/10^3 kg/m^3$.

## Results and Discussion

The density ($\rho$) and molal volume ($V_\phi$) data were calculated from weights as:

$$\rho = W \times \rho_{solv}/W_0 + 0.0012\,(1 - W/W_0) \quad (1)$$

$$V_\phi = 1/\rho\,[M_2 - (1000/m)\,(W - W_0)/(W_0 - W_e)] \quad (2)$$

where:

$\rho$ and $\rho_{solv}$ = densities of the solution and solvent, respectively

$0.0012\,(1-W/W_0)$ = buoyancy correction of air

m = molality of the solution

$M_2$ = mol wt of the solute

$W_e$, $W_0$, W = wts of empty, with solvent-, and with solution-filled pyknometer, respectively

Uncertainty in $V_\phi$ data was computed from equation (3) given below:

$$V_\phi = (1000/m)\Delta\rho \quad (3)$$

where:

m = molality

$\Delta\rho$ = a calculated value of $1/10^{-5}$, representing uncertainty in wt measurements

Uncertainties were found within the permissible range of the standard deviation. The obtained data were regressed as:

$$\rho = \rho^0 + S_d m \quad (4)$$

$$V_\phi = V_\phi^0 + S_v m \quad (5)$$

where:

$\rho^0$ ($10^3 kg\,m^{-3}$) and $V_\phi^0$ ($10^{-6} m^3 mol^{-1}$) = limiting values of density and molal volumes, respectively

$S_d$ ($10^3 kg^2 m^{-3} mol^{-1}$) and $S_v$ ($10^{-6} m^3 kg\,mol^{-2}$) = the slope constants of density and molal volumes, respectively, as given in Tables 1 and 2

$V_\phi^0$ and $S_v$ = solute-solvent dipole-dipole interactions, respectively, depending on the amount of charge of the solute and the nature of solvent molecules

The transfer limiting densities ($\rho^0 tr$) and transfer limiting molal volumes ($V_\phi^0 tr$) from aqueous to aqueous surfactant solution systems were calculated as:

$$\rho^0 tr = \rho^0\,(\text{ternary}) - \rho^0\,(\text{binary}) \quad (6)$$

$$V_\phi^0 tr = V_\phi^0\,(\text{ternary}) - V_\phi^0\,(\text{binary})\ \text{systems} \quad (7)$$

The calculated values are given in Table 3 and the contribution of the $-CH_2$ group to $\rho^0$ and $V_\phi^0$ was evaluated from equation (8) given below:

$$\rho^0 = \rho^0\,(\text{leucine}) - \rho^0\,(\text{valine});\ \text{and}$$

$$V_\phi^0 = V_\phi^0\,(\text{leucine}) - V_\phi^0\,(\text{valine}) \quad (8)$$

The values calculated from equation (8) are shown in Table 4. The constants of regression of the limiting data against temperatures are given in Table 5. For binary systems, the density of water was taken from literature (Apelblat and Manzurola, 1999). The $V_\phi^0$ of the amino acids in the surfactant solutions are drawn in Fig. 1. The $\rho$ of 0.05 to 1.25 mol $kg^{-1}$ aqueous NaCl was measured for $V_\phi^0$ values, which were reproduced to $\pm 0.05/10^{-6} m^3 mol^{-1}$ as compared to the data available in lite-

rature (Apelblat and Manzurola, 1999), which authenticated the measurements. The water densities were taken from literature and an increase and decrease in the ρ values with concentration and temperature indicated the forming and breaking of the hydrogen bonds. The $\rho^0$ values of aqueous glycine as related with temperature was noted as 293.15 > 288.15 > 283.15 K, with reverse order of $S_d$, and $\rho^0$ values of the amino acids at each temperature were noted as glycine > valine > leucine. The order of $\rho^0$ of amino acids proved that α-amino acids with the increase in their alkyl chain resulted in lowering in $\rho^0$ due to larger hydrophobic interactions with the addition of $-CH_2$ group in the amino acid molecules. It proved that α-amino acids in aqueous solutions had greater force of attraction between dipoles of water and their polar group, as compared to the hydrophobic part, which lacked the possession of such forces. Similarly, the trend of $S_d$ values was seen as leucine > glycine > valine, which predicted a greater composition dependence of leucine at each temperature. It indicated stronger hydrophobic interactions of the amino acids with the larger alkyl chain. However, prominent hydrophilic interactions of glycine seemed to be strengthened with composition, yet still remained weaker than that of leucine and valine. This behaviour of amino acids could be attributed to the distance between hydrophobic and hydrophilic heads due to the size of the alkyl chain.

The surfactants in aqueous systems was observed to have an order of ρ as CPB > CPC, which showed that pyridinium surfactants of the same composition with $Br^-$ anion destabilized the water structure to a larger extent as compared to $Cl^-$ (Table 2). It showed that an induced dipole of larger anion remained effective even when it was associated with $N^+$ ion of the pyridinium ring of the cationic surfactants. On transfer of amino acids in aqueous cationic surfactant solutions, the order of their $\rho^0$ values differed from the values of aqueous systems and were noted as leucine > valine > glycine at each temperature, which was reverse as compared to the values for amino acids in the aquous systems. From this it may be concluded that there existed a stronger force of attraction between water and glycine, indicating glycine to be a stronger structure breaker in the aqueous medium, as dipoles of water and zwitterion of glycine are of smaller size, thereby stronger hydrophilic interactions occurred. But with surfactant systems, the glycine was found to attain the lowest and leucine the highest $\rho^0$ values, which proved that surfactants dubbed the hydrophilic interaction of glycine and strengthened the hydrophobic interaction of leucine in the same proportion. This explains how the cetly chain (alkyl chain of sixteen carbon atoms) of surfactants developed considerably stronger

**Table 1.** Regression analysis of density (ρ) and molal volume ($V_\phi$) data of aqueous amino acids and surfactants against molality, and of amino acids-aqueous surfactant systems, their limiting constants at infinite dilution and slope constants at different temperatures

| Temperature (K) | Limiting density | | Limiting molal volume | | Slope constant ($1x10^4$) |
|---|---|---|---|---|---|
| | $\rho^0$ | $S_d$ | $V_\phi^0$ | $S_v$ | $S_V'$ |
| **Aqueous glycine** | | | | | |
| 283.15 | 0.99965 | 0.0043 | 41.92 | 0.46 | |
| 288.15 | 0.99916 | 0.0065 | 42.37 | 0.47 | |
| 293.15 | 0.99887 | 0.0066 | 42.91 | 0.53 | |
| **Aqueous valine** | | | | | |
| 283.15 | 0.99900 | -0.2003 | 170.56 | -763.21 | |
| 288.15 | 0.99930 | 0.0053 | 147.38 | -197.78 | |
| 293.15 | 0.99870 | -0.0030 | 141.99 | -158.63 | |
| **Aqueous leucine** | | | | | |
| 283.15 | 0.99740 | 0.0489 | 344.17 | -4112.90 | |
| 288.15 | 0.99650 | 0.0477 | 413.53 | -4766.70 | |
| 293.15 | 0.99680 | 0.0147 | 579.04 | -13256.00 | 10.38 |
| **Glycine in 2% CPC** | | | | | |
| 283.15 | 0.99740 | 0.0415 | 4741.80 | -114280.00 | 83.58 |
| 288.15 | 0.99640 | 0.0484 | 2970.40 | -65957.00 | 44.49 |
| 293.15 | 0.99590 | 0.0405 | 1597.80 | -35713.00 | 23.93 |
| **Valine in 2% CPC** | | | | | |
| 283.15 | 0.99790 | 0.0237 | 3932.10 | -81435.00 | 53.65 |
| 288.15 | 0.99740 | 0.0025 | 2641.80 | -53626.00 | 35.80 |
| 293.15 | 0.99600 | 0.0455 | 1606.80 | -36142.00 | 24.65 |
| **Leucine in 2% CPC** | | | | | |
| 283.15 | 0.99820 | 0.0134 | 3909.60 | -80883.00 | 53.90 |
| 288.15 | 0.99770 | 0.0199 | 2392.90 | -48723.00 | 32.07 |
| 293.15 | 0.99690 | 0.0231 | 1239.30 | -26720.00 | 18.56 |
| **Glycine in 2% CPB** | | | | | |
| 283.15 | 0.99840 | 0.0426 | 3608.30 | -147682.00 | 200.00 |
| 288.15 | 0.99710 | 0.0417 | 2821.40 | -119075.00 | 200.00 |
| 293.15 | 0.99700 | 0.0436 | 1892.80 | -79585.00 | 100.00 |
| **Valine in 2% CPB** | | | | | |
| 283.15 | 0.99960 | 0.0334 | 3401.80 | -144219.00 | 200.00 |
| 288.15 | 0.99830 | 0.0133 | 2512.20 | -105186.00 | 100.00 |
| 293.15 | 0.99800 | 0.0158 | 1684.70 | -70365.00 | 95.67 |
| **Leucine in 2% CPB** | | | | | |
| 283.15 | 0.99880 | 0.0347 | 3718.80 | -152616.00 | 200.00 |
| 288.15 | 0.99850 | 0.0320 | 2247.50 | -91844.00 | 100.00 |
| 293.15 | 0.99740 | 0.0512 | 1663.30 | -66873.00 | 81.69 |

$\rho^0 = 10^3\,kg\,m^{-3}$; $S_d = 10^3\,kg^2\,m^{-3}\,mol^{-1}$; $V_\phi^0 = 10^{-6}\,m^3\,mol^{-1}$; $S_v = 10^{-6}\,m^3\,kg\,mol^{-2}$; $S_V' = 10^{-6}\,m^3\,kg^2\,mol^{-3}$; $\rho^0$ = limiting density; $S_d$ = slope constant for limiting density; $V_\phi^0$ = limiting molal volume; $S_v$ = slope constant for limiting molal volume; $S_V'$ = slope constant of m, molality of surfactants

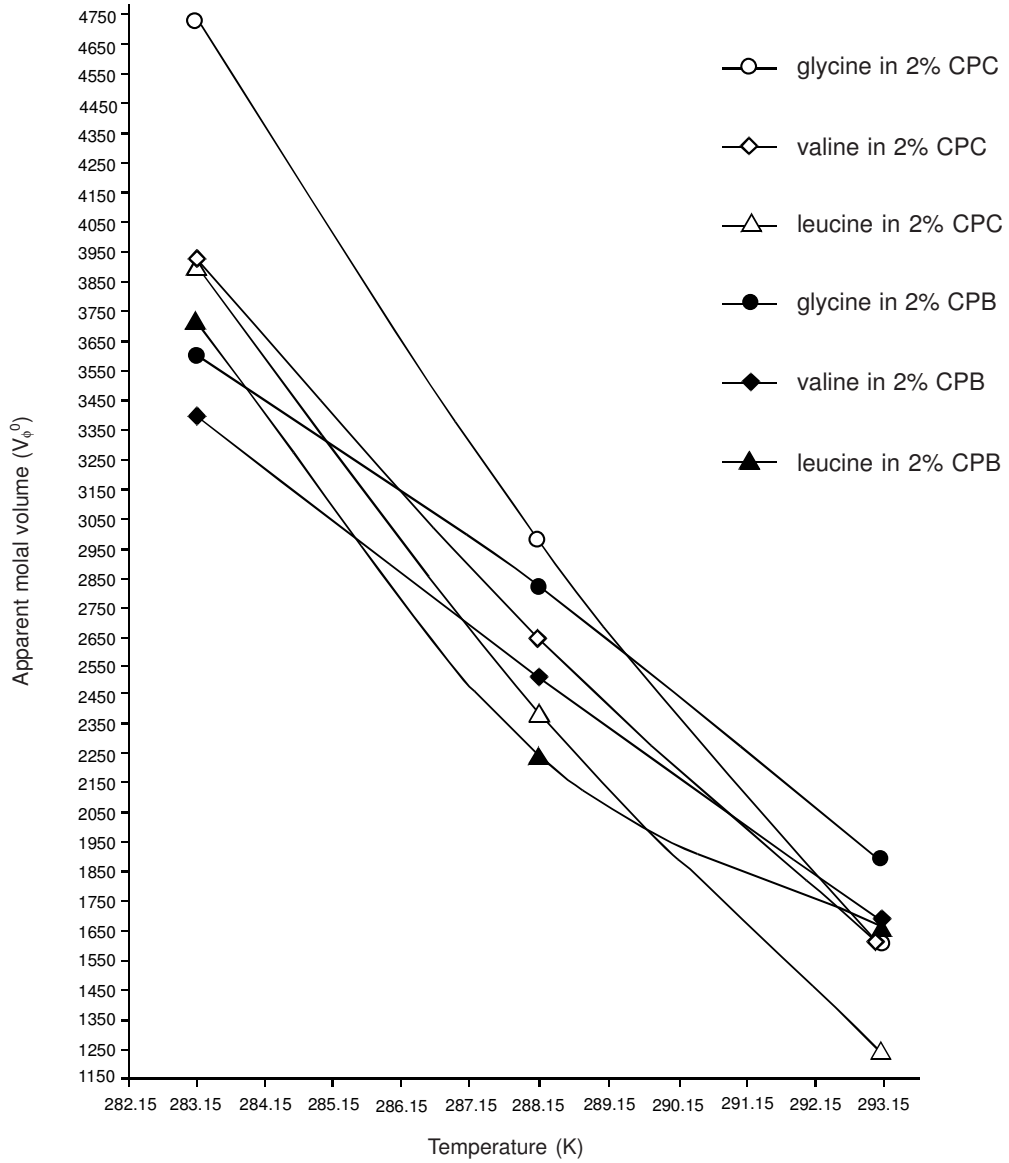


**Fig. 1.** The apparent molal volume ($V_\phi^0$) of amino acids in surfactant solutions at different temperatures (CPC = cetyl pyridinium chloride; CPB = cetyl pyridinium bromide).

hydrophobic interactions with the alkyl chain of leucine than of hydrophilic chain of glycine. These states of hydrophobic interactions among them developed stronger force of attraction between the dipoles of water and glycine, and the change in the behaviour of leucine in the surfactant systems was attributed to the -$CH_2$ group.

Comparison of the values of $\rho^0$ of amino acids in the surfactant systems have shown that they were higher by 0.00043/$10^3$ kg/m$^3$ for CPB than for CPC at each temperature. The values of $\rho^0$ of the aqueous amino acids were higher by 0.00022/$10^3$ kg/m$^3$ than of surfactant solutions, which indicated that surfactants weakened the intermolecular forces that existed between the amino acids and water. Thus, surfactants behaved as structure breakers for amino acids in aqueous solutions and proved that α-amino acids, with larger alkyl chain in the surfactant solutions, developed stronger hydrophobic-hydrophobic and hydrophilic hydrophilic interactions with surfactants. These interactions were noted to cause certain forces between the alkyl part of the amino acids and surfactants, and the polar part of the amino acids and surfactants, respectively. These molecular forces caused an additional internal pressure resul-ting in shrinkage or contraction among the acid-surfactant complexes with an increase in $\rho^0$. It may thus be concluded that amino acid-

surfactant and amino acid-water-surfactant interactions seem to be integrated. Further, the larger magnitude of $\rho^0$ values of α-amino acids in CPB surfactant with $Br^-$ anion showed that larger-sized anion was effective and gene-rated higher intermolecular forces. Probably, the induced dipole of $Br^-$ anion, due to its larger size and 4d empty orbital, stronger London or dispersive forces were generated and led to polar centre on the outer surface of $Br^-$ anion.

Apart from the order of $\rho^0$ values, which demarcated the solute-solvent interactions, the $S_d$ values of the amino acids in CPC and CPB surfactants were noted as glycine > valine > leucine at each temperature, which with temperature was 283.15 > 288.15 > 293.15 for each amino acid, respectively. Such trends of $S_d$ values proved a weaker effect of composition on amino acid-amino acid interactions with the size of alkyl chain. Perhaps, the stronger hydrophobic interaction of the larger-sized alkyl chain dominated over the interaction of amino acids caused by their polar centres. Thus, it may be concluded that an over-weighing of hydrophobic interactions weakened the composition effect on homomolecular interactions. In general, the $S_d$ values of amino acids with CPB were found to be higher than that of CPC at each temperature and indicated that the effect of composition on interactions was greater at the lower temperature, which weakened with temperature for each amino acid. This can be correlated to the fact that thermal energy too had structure-breaking influence, and hence the thermal factor became an additive to destabilizing the water structure and for the establishment of molecular interactions. Also, $Br^-$, a larger-sized anion in a state of induced dipoles, facilitated a structure-breaking influence of surfactants on water. A contribution of the $-CH_2$ group to $\rho^0$ of α-amino acids (Table 4) with temperature was: 283.15 > 293.15 > 288.15 K; and for surfactants as 293.15 > 288.15 > 283.15, and 288.15 > 293.15 > 283.15, for CPC and CPB, respectively. This proves that an addition of $-CH_2$ group to α-amino acids decreased the $\rho^0$ as it was noted that leucine had negative values as compared with valine, which denoted that more were the $-CH_2$ groups in the alkyl chain, less was the $\rho^0$ value, thus a decrease was greater at 288.15 K. But CPC had changed this behaviour of $-CH_2$ group as the $\rho^0$ values were found to be positive for the amino acids indicating a stronger hydrophobic interaction of the cetyl chain of CPC with that of the $-CH_2$ group of leucine.

The CPB produced higher $\rho^0$ values, which followed the same trend for the amino acids in aqueous systems except at 288.15 K, and the $\rho^0$ values of amino acids from aqueous to aqueous surfactants was found as: leucine > valine > glycine. But $\rho^0$tr of CPC was greater than of CPB with a

**Table 2.** Limiting density ($\rho^0$) and apparent molal volumes ($V_\phi^0$) of cetyl pyridinium chloride (CPC) and cetyl pyridinium bromide (CPB) surfactants in aqueous solution systems at different temperatures

| Molality (mol $kg^{-1}$) | Temperature (K) | | | | | |
|---|---|---|---|---|---|---|
| | 283.15 | | 288.15 | | 293.15 | |
| | $\rho^0$ | $V_\phi^0$ | $\rho^0$ | $V_\phi^0$ | $\rho^0$ | $V_\phi^0$ |
| **Aqueous CPC** | | | | | | |
| 0.0497 | 1.00564 | -53.59 | 1.00224 | 141.96 | 0.99905 | 301.20 |
| **Aqueous CPB** | | | | | | |
| 0.0497 | 1.00623 | -106.59 | 1.00289 | 108.30 | 1.00103 | 183.48 |

**Table 3.** Transfer volume, $V_\phi^0$tr ($10^{-6}m^3\ mol^{-1}$) and transfer limiting density, $\rho^0$ tr ($10^3$ kg $m^{-3}$) of glycine, valine and leucine from aqueous to aqueous CPC and CPB surfactant solutions

| Temp (K) | $V_\phi^0$tr | $\rho^0$tr | $V_\phi^0$tr | $\rho^0$tr | $V_\phi^0$tr | $\rho^0$tr |
|---|---|---|---|---|---|---|
| | **Amino acids from aqueous to aqueous CPC surfactant** | | | | | |
| | glycine | | valine | | leucine | |
| 283.15 | 4699.88 | - 0.00225 | 3761.54 | - 0.0011 | 3565.43 | 0.0008 |
| 288.15 | 2928.03 | - 0.00276 | 2494.42 | - 0.0019 | 1979.37 | 0.0012 |
| 293.15 | 1554.89 | - 0.00297 | 1464.81 | - 0.0027 | 660.26 | 0.0001 |
| | **Amino acids from aqueous to aqueous CPB surfactant** | | | | | |
| | glycine | | valine | | leucine | |
| 283.15 | 3566.38 | - 0.00125 | 3231.24 | 0.0006 | 3374.63 | 0.0014 |
| 288.15 | 2779.03 | - 0.00206 | 2364.82 | - 0.001 | 1833.97 | 0.002 |
| 293.15 | 1849.89 | - 0.00187 | 1542.71 | - 0.0007 | 1084.26 | 0.0006 |

CPC = cetyl pyridinium chloride; CPB = cetyl pyridinium bromide

**Table 4.** The apparent molal volume ($V_\phi^0$) and limiting density ($\rho^0$) values of $-CH_2$ group of amino acids at different temperatures, obtained by deducting the $V_\phi^0$ and $\rho^0$ values of leucine from valine as:

$(-CH_2-) = [(CH_3)_2CH_2CH(NH_2)COOH)]-[(CH_3)_2CH\text{-}CH(NH_2)COOH]$

| 283.15 K | | 288.15 K | | 293.15 K | |
|---|---|---|---|---|---|
| $V_\phi^0$ | $\rho^0$ | $V_\phi^0$ | $\rho^0$ | $V_\phi^0$ | $\rho^0$ |
| **$-CH_2-$ values evaluated from (leucine - valine) in aqueous systems** | | | | | |
| 173.61 | - 0.0016 | 266.15 | - 0.0028 | 437.05 | - 0.0019 |
| **Amino acids in aqueous surfactant systems** | | | | | |
| **Aqueous CPC** | | | | | |
| - 22.50 | 0.0003 | - 248.90 | 0.0003 | - 367.50 | 0.0009 |
| **Aqueous CPB** | | | | | |
| 317.00 | - 0.0008 | - 264.70 | 0.0002 | - 21.40 | -0.0006 |

difference of $\pm 2 \times 10^{-4} / 10^{3}$ kg/m$^3$. The $\rho^0$ and the $V_\phi^0$ values, calculated together from the weights of solutions, were considered as independent measurements and hence the trend of $V_\phi^0$ values was considered useful for the investigation. In general, the $V_\phi^0$ values of glycine and leucine in aqueous systems were found to increase with temperature, while valine reported a considerable decrease. For instance, for glycine, the $V_\phi^0$ value was $\pm 2.04/10^{-6}$ m$^3$ mol$^{-1}$ and for leucine it was $\pm 100/10^{-6}$ m$^3$ mol$^{-1}$. However, the order of decrease in $V_\phi^0$ values for valine from 283.15 to 288.15 K was $\pm 23$, and between 288.15 and 293.15 K was $\pm 5/10^{-6}$ m$^3$ mol$^{-1}$. It confirms that in the case of glycine molecule, sandwiching of its hydrophobic sphere of -$CH_2$ group by the hydrophilic sphere of polar -$COO^-$ and -$NH_3^+$ groups occurred, while the sandwiching effect for leucine hydrophobic interactions was weaker because of slightly stronger hydrophobic interactions due to its longer [-CH ($CH_3$)$_2$] chain. Thus, hydrophobic interaction of leucine dominated over those of glycine.

At each temperature, $V_\phi^0$ values of amino acids for the aqueous and surfactant systems were found to have a linear relationship with the composition. From 0.03 and 0.05 mol/kg surfactant, however, the $V_\phi^0$ of amino acids decreased, whereas for 0.07 mol/kg the values increased. This trend of values fits to the polynomial relation of $V_\phi^0$ values against the composition of surfactants. Table 1 shows that the $S_v'$ values (slope constant of m, molality of surfactants) were positive, ranging from 18 to $83 \times 10^4 / 10^{-6}$ m$^3$ kg$^2$ mol$^{-3}$, which indicate that surfactants developed micelle of mild nature with amino acids. Not-ably, the $S_v'$ values for CPB were found to be higher than for CPC, thus predicting comparatively dominating micelle for-mation with the former. The $V_\phi^0$ values decreased continuously with temperature by almost $1000/10^{-6}$m$^3$/mol. With temperature, a change in the trend of $V_\phi^0$ values weakened the intermolecular forces due to thermal energy, which seemed to be least effective for valine as it had almost a balance between the interactions of polar groups [-($NH_3^+$)($COO^-$)] and its hydrophobic [-CH($CH_3$)$_2$] groups. Such kinds of arrangements of molecular forces have shown a strengthening of the forces in aqueous solutions with its composition. Similarly, the magnitude of $S_v$ value of glycine was positive and increased with temperature, whereas the values for valine and leucine were negative, which for valine, however, increased with temperature while decreased for leucine. The magnitude of increase of values for glycine was $\pm 0.03$, whereas for valine it was $\pm 55/10^{-6}$ m$^3$/mol and for leucine it was $\pm 150/10^{-6}$ m$^3$/mol. These trends prove that for glycine, the temperature enhanced the glycine-glycine and aqueous-glycine interactions, which were weakened in the case of valine and leucine (Singh, 2004). Also, wea-ker valine-valine, aqueous-valine, leucine-leucine, and aqueous-lencine interactions, as related with temperature, lead to the the conclusion that valine and leucine strengthened cage formation of water around their alkyl chains. The larger $V_\phi^0$ values of valine and leucine too indicate that a cage formation around the chains was of structured water and partly hydrated water due to their polar groups. It seems that both the structured and hydrated waters have a grip over their hydropho-bic and hydrophilic parts, respectively, of these amino acids, thus establishing a better coordination among the caged and hydrated parts. Such an orientation of water around the amino acid molecules seems to result in larger values with valine and leucine, and a further trend of $V_\phi^0$ values proved that this grip was strengthened at the higher temperature in the case of leucine, while weakened for valine, due to the larger size of alkyl chains.

Similarly, amino acids in aqueous surfactants have larger $V_\phi^0$ values, which were in the range of $1000/10^{-6}$m$^3$/mol for amino acids (Fig. 1), than those in the aqueous medium only, resul-ting in higher transfer values (Table 3). The trend of $V_\phi^0$ for the amino acids with temperature in aqueous CPC was observed as glycine > valine > leucine, confirming a binding of polar group of glycine with $N^+$ of pyridine ring of CPC and cetyl chain surroundeding the glycine. Alternatively, the glycine could also surround the polar part of the surfactant. Yet another possibility is that hydrated water may also establish interaction with CPC and get attached with glycine. Such a complex must be of larger in size, as the amino acids have larger $V_\phi^0$ values in aqueous surfactant systems. Surprisingly, with temperature, the $V_\phi^0$ values of amino acids in aqueous surfactants marked an observable decrease of the same order for both the surfactants, i.e., $800/10^{-6}$m$^3$/mol. In general, molecules or the interconnected complexes expanded with temperature, but with surfactants there was noted a gradual decrease. This proved that with amino acid-surfactant interactions, thermal energy played a crucial role for the stability of interaction and the surfactant molecules associated with the amino acids. This indicated a thermal destabilization, thus detaching the surfactant molecules either from acids or the hydrated water, which after detachment may form smallersized interaction complexes. However, this decrease was higher with CPC than with

CPB, thus proving that surfactants with smaller anion $Cl^-$ had less stability with the amino acids, or hydrated water of acids. It can be attributed to an induced dipole of $Br^-$ with a slightly higher binding force than of $Cl^-$. Surfactants with $Cl^-$, therefore, do not apply stronger intermolecular force in the aqueous systems.

The composition of surfactants was noted to produce negative $S_v$ values for amino acids, which further increased with temperature for both the surfactants. But $S_v$ values of amino acids for CPB systems were found lower than those of CPC. The values were of the order of $-65x10^3/10^{-6}$ $m^3$ kg $mol^{-2}$, which indicated that composition of surfactants from 0.03 to 0.07 mol/kg established structure-making effect on water. It may be noted from Table 1, that glycine among amino acids had stronger structure making effect in surfactant solutions at each temperature. However, an increase in $S_v$ values with temperature proved that the cage effect decreased, with the thermal contents disrupting the cage formation/ geometry/ dyna-mics, and an influence was found in the order of glycine > valine > leucine in surfactants. It matched well with the structure of acids as there was least stability of the cage model of water with glycine. Surfactants, however, seemed to cement cage formation, which however did not remain stable with temperature.

The $V_\phi^0$tr values (Table 3) of amino acids indicated a greater effect at lower temperature, with a greater effect at 283.15 and 288.15 for CPC than for CPB. At 293.15, CPB caused greater decrease in $S_v$ values proving stronger caging of water aro-und amino acids, or the CPB molecule at the higher temperature. The $\rho^0$ and $V_\phi^0$ of amino acids, as affected by temperature in the aqueous medinium, were glycine > leucine > valine, and the aqueous surfactants as valine > glycine > leucine (Table 5). This proved that a greater effect of temperature, on glycine in aqueous systems, may be due to a greater attraction between polar groups. Additionally, surfactants decreased and increased $\rho^0$ and $V_\phi^0$ of glycine and valine, respectively, as compared with the aqueous systems, indicating a dominance of hydrophobic interactions with valine over hydrophilic interactions due to the presence of polar groups. The $S_d(T)$ for aqueous systems of acids was found in the order of : valine > leucine > glycine, whereas for CPC and CPB systems it was glycine = leucine > valine and glycine = valine = leucine, res-pectively. This points to the fact that temperature sensitized valine as it had polar and hydrophobic groups just adjacent to each other, thus leucine was the next to glycine in respect of the temperature effect on intermoleculer interactions.

**Table 5.** The limiting density ($\rho^0$) and apparent molal volume ($V_\phi^0$) data with slope constants for binary and ternary systems obtained by regressing against temperature

| $\rho^0(T)$ | | $V_\phi^0(T)$ | | |
|---|---|---|---|---|
| $\rho^0(T)$ | $S_d(T)$ | $V_\phi^0(T)$ | $S_v(T)$ | $S_v(T)$ |
| **Aqueous glycine** | | | | |
| 1.0217 | - $8.00x10^{-5}$ | 13.87 | 0.10 | |
| **Aqueous valine** | | | | |
| 1.0076 | - $3.00x10^{-5}$ | 976.55 | - 2.85 | |
| **Aqueous leucine** | | | | |
| 1.0142 | - $6.00x10^{-5}$ | 153313.00 | - 1084.70 | 1.92 |
| **Aqueous CPC** | | | | |
| 1.0122 | 0.0007 | - 402.00 | 35.48 | |
| **Aqueous CPB** | | | | |
| 1.0112 | - 0.0005 | - 955.54 | 112.84 | -2.79 |
| **Glycine in aqueous CPC** | | | | |
| 1.0361 | - 0.0001 | 85456.00 | - 286.13 | |
| **Valine in aqueous CPC** | | | | |
| 1.0460 | - 0.0002 | 63603.00 | - 211.51 | |
| **Leucine in aqueous CPC** | | | | |
| 1.0313 | - 0.0001 | 72478.00 | - 243.09 | |
| **Glycine in aqueous CPB** | | | | |
| 1.0350 | - 0.0001 | 47425.00 | - 155.14 | |
| **Valine in aqueous CPB** | | | | |
| 1.0412 | - 0.0001 | 47387.00 | - 155.84 | |
| **Leucine in aqueous CPB** | | | | |
| 1.0341 | - 0.0001 | 56879.00 | - 188.79 | |

$\rho^0(T) = 10^3$ kg $m^{-3}T^{-1}$; $S_d = 10^3$ $kg^2$ $m^{-3}$ $mol^{-1}$ $K^{-1}$; $V_\phi^0(T) = 10^{-6}$ $m^3$ $mol^{-1}$ $T^{-1}$; $S_v = 10^{-6}$ $m^3$ kg $mol^{-1}K^{-1}$; $S_v'(T) = 10^{-6}$ $m^3$ $kg^2$ $mol^{-1}$ $K^{-1}$; CPC = cetyl pyridinium chloride; CPB = cetyl pyridinium bromide

The amino acids in aqueous systems, in relation with temperature, showed $V_\phi^0$ as leucine > valine > glycine, and $S_v(T)$ as glycine > valine > leucine. $V_\phi^0$ in CPC and CPB were glycine > leucine > valine, and leucine > glycine > valine, respectively. However, $S_v(T)$ was valine > leucine > glycine in CPC, and glycine > valine > leucine in CPB (Table 5), Thus proving a compact linkage of leucine at the absolute zero degree temperature.

## Conclusion

The $\rho$ and $V_\phi$, and regressed data for a series of selected amino acids with an increase of $-CH_2$ group in their alkyl chains were noted to enhance the hydrophobic and weak-

ening of hydrophilic interactions of polar groups of the amino acids. A weak dependence of composition of amino acids on their structure-breaking behaviour was noted in aqueous and aqueous surfactant solutions. The surfactants were observed to produce mild micelle formation with amino acids resulting in exceptionally higher $V_\phi^0$ values for amino acids, with higher values for CPB. Additionally, the CPB was seen as an effec-tive structure-breaker than CPC, while amino acids also showed comparatively stronger structure-breaking effect of CPB than of CPC. An induced dipole of $Br^-$ was accountable for stronger interactions of CPC.

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