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ORIGINAL CONTRIBUTION

# Interaction of glycine with cationic, anionic, and nonionic surfactants at different temperatures: a volumetric, viscometric, refractive index, conductometric, and fluorescence probe study

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**Abstract** A number of thermodynamic parameters viz. apparent molar volumes, $\phi_v$, partial molar volumes, $\phi_v^0$, transfer volumes, $\phi_v^0(tr)$, Falkenhagen coefficients, $A$, Jones–Dole coefficients, $B$, free energies per mole of solute, $\Delta\mu_1^{0\#}$, and per mole of solvent, $\Delta\mu_2^{0\#}$, molar refraction, $R_D$, and limiting molar conductivity, $\overset{0}{\Lambda}_m$, have been calculated by using the experimentally measured densities, $\rho$, viscosities, $\eta$, refractive indices, $n_D$, and specific conductivities, $\kappa$, data of glycine (0.02–0.10 m) in 0.01 m aqueous sodium dodecyl sulphate, cetyltrimethylammonium bromide, and triton X-100 (TX-100) solutions at 298.15, 303.15, 308.15, and 313.15 K. The above calculated parameters were found to be sensitive towards the interactions prevailing in the studied amino acid–surfactant–water systems. Moreover, fluorescence study using pyrene as a photophysical probe has also been carried out, the results of which support the conclusions obtained from other techniques.

**Keywords** Density · Viscosity · Amino acid · Interactions · Surfactants

## 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]. However, due to the complex conformational and configurational three-dimensional structures of proteins, direct investigations of solute/solvent effect on these biological macromolecules are quite difficult [3]. Therefore, one convenient approach that reduces the degree of complex measurement techniques is to study the interactions in the systems containing simple model compounds, amino acids, which are the basic structural units of proteins [3, 4]. The side chains of these building blocks differ in size, shape, charge, hydrogen-bonding capacity, hydrophobicity, and chemical reactivity. Individually and collectively, these side chains contribute to the structure and function of proteins [5].

Keeping these considerations in mind, in this paper, we report the apparent molar volumes, $\phi_v$, partial molar volumes, $\phi_v^0$, transfer volumes, $\phi_v^0(tr)$, Falkenhagen coefficients, $A$, Jones–Dole coefficients, $B$, free energies per mole of solute, $\Delta\mu_1^{0\#}$, and per mole of solvent, $\Delta\mu_2^{0\#}$, molar refraction, $R_D$, and limiting molar conductivity, $\overset{0}{\Lambda}_m$, calculated by using the experimentally measured densities, $\rho$, viscosities, $\eta$, refractive indices, $n_D$ and specific conductivities, $\kappa$ data of glycine (0.02–0.10 m) in 0.01 m aqueous sodium dodecyl sulphate (SDS), cetyltrimethylammonium bromide (CTAB), and triton X-100 (TX-100) solutions at 298.15, 303.15, 308.15, and 313.15 K. Moreover, fluorescence measurements using pyrene as a photophysical probe have also been carried out for the present amino acid–surfactant systems. The ratio of the first over the third vibrational peak ($I_1/I_3$) of pyrene fluorescence has been measured which is very sensitive to the polarity of the probe microenvironment [6].

An exhaustive survey of literature reveals that no one has reported such extensive study on glycine in aqueous surfactants solutions at different temperatures, except the

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work of Singh et al. [7, 8], who have reported only volumetric properties of some amino acids and peptides in aqueous surfactants at a single temperature, 298.15 K.

## Experimental

Glycine was procured from s. d. fine Chem., India. SDS, CTAB, and TX-100 were of extra-pure analytical reagent grade purchased from s. d. fine Chem., Thomas Baker and BDH Chemicals, respectively. Purity of all the chemicals as reported by the vendors is 99%.

Glycine, SDS, and CTAB were dried over $P_2O_5$ in vacuum desiccators. TX-100 was kept over molecular sieves (0.4 nm Sigma union Carbide type) to reduce the water content, if any. Solutions were made using the deionized and doubly distilled water. The weighings were done on a digital electronic balance, Afcoset 120 A (Swiss make) having a precision of ±0.0001 g.

The densities of the solutions were measured using a single-stem pycometer made of Borosil glass with bulb capacity of $8\times10^{-6}$ $m^3$ by the method described elsewhere [9, 10]. The reproducibility in the density measurements, on the average, was ±0.05 $kg.m^{-3}$. Viscosities were measured by using an Ubbelohde-type suspended level viscometer with an accuracy of $\pm3\times10^{-6}$ $Nm^{-2}s$. Abbe refractometer was employed for refractive index measurements with a precision of ±0.0001 unit. Conductances were measured with a (Control Dynamics, India) conductivity bridge having a cell constant 1.02. 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.

Pyrene fluorescence measurements were carried out using a Fluorolog-3 modular spectrofluorometer (model FL 3-11) with single Czerny–Turner grating excitation and emission monochromators having 450 W Xe arc lamp as the excitation source and PMT as the detector (Horiba Jobin Yvon). The pyrene concentration was fixed at $1.0\times10^{-6}$ M, and the fluorophore was excited at a wavelength of 337 nm. The excitation slit width was 2.0 nm, while the emission slit was maintained at a width of 1.0 nm. The emission spectrum was scanned over the range 360–460 nm.

## Results and discussion

The experimental values of densities, viscosities, refractive indices, and specific conductivities of glycine (0.02–0.10 m) in aqueous solutions of (0.01 m) SDS, CTAB, and TX-100 at 298.15, 303.15, 308.15, and 313.15 K are listed in Table 1.

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

$$\phi_v = \frac{M}{\rho} - \frac{1,000(\rho-\rho_0)}{m\rho\rho_0} \tag{1}$$

where $m$ is the molality of solute (glycine), $\rho$ and $\rho_0$ are the densities of the solution and the solvent (aqueous surfactant), respectively, and $M$ is the molar mass of the solute. The calculated $\phi_v$ values for glycine in all the aqueous surfactant solutions and at different temperatures are graphically presented in Fig. 1. For each system, $\phi_v$ vs $m$ plots (Fig. 1) were found to be linear, and thus, the partial molar volumes, $\phi_v^0$ at infinite dilution were obtained by least-squares fitting of the $\phi_v$ values to the following equation:

$$\phi_v = \phi_v^0 + S_v^* m \tag{2}$$

where $S_v^*$ is the experimentally determined slope, sometimes considered to be volumetric pairwise interaction coefficient [7, 11, 12] and provides information regarding glycine–glycine interactions, while $\phi_v^0$ is the intercept and provides the information regarding glycine–surfactant/water interactions. The values of $\phi_v^0$ of glycine along with the $S_v^*$ values at different temperatures are given in Table 2. A perusal of Table 2 reveals that the values of $\phi_v^0$ are large positive for glycine in each aqueous surfactant solution, suggesting strong glycine–surfactant/water interactions. The $\phi_v^0$ values (Table 2) increase with increase in temperature for all the glycine–water–surfactant systems under study. This may be attributed to the release of some water molecules from the loose hydration layers of the solute (glycine) in the bulk solution [13].

The thermodynamic transfer functions may be interpreted in terms of structure-making or breaking effects of the solute as has been postulated by Franks and Evans [14]. Thus, the volume of transfer of glycine from water to aqueous surfactant, $\phi_v^0(tr)$, was calculated by using the relation:

$$\phi_v^0(tr) = \phi_v^0(\text{in aqueous surfactant}) - \phi_v^0(\text{in water}) \tag{3}$$

where $\phi_v^0$ (in water) is the partial molar volume of the glycine in water and its values for the glycine at 298.15, 308.15, and 313.15 K have been taken from the literature [15, 16]. The $\phi_v^0(tr)$ values at the above temperatures are summarized in Table 2. A perusal of Table 2 indicates that $\phi_v^0$ values of glycine in aqueous surfactants are less than those in pure water at 298.15 K and become greater than those of water at subsequent temperatures, i.e., $\phi_v^0(tr)$ values increase from small negative to positive with temperature for all the three aqueous surfactant solutions. Further, $\phi_v^0$ and $\phi_v^0(tr)$ values have also been listed (Table 3)

**Table 1** Values of density, $\rho$, viscosity, $\eta$, refractive index, $n_D$, and specific conductivity, $\kappa$, of glycine in aqueous surfactant solutions at $T$=298.15, 303.15, 308.15, and 313.15 K

| $m$/(mol.kg$^{-1}$) | 298.15 K | 303.15 K | 308.15 K | 313.15 K |
|---|---|---|---|---|
| Glycine+aqueous SDS | | | | |
| $\rho$/(kg.m$^{-3}$) | | | | |
| 0.00 | 997.8 | 996.2 | 994.7 | 993.1 |
| 0.02 | 998.4 | 996.7 | 995.1 | 993.4 |
| 0.04 | 998.9 | 997.1 | 995.4 | 993.6 |
| 0.06 | 999.3 | 997.4 | 995.6 | 993.7 |
| 0.08 | 999.6 | 997.6 | 995.8 | 993.8 |
| 0.10 | 999.9 | 997.8 | 996.0 | 993.9 |
| $\eta$/(Nm$^{-2}$s) | | | | |
| 0.00 | 0.8391 | 0.7597 | 0.6864 | 0.6278 |
| 0.02 | 0.8693 | 0.7845 | 0.7062 | 0.6438 |
| 0.04 | 0.8872 | 0.8006 | 0.7202 | 0.6553 |
| 0.06 | 0.9038 | 0.8147 | 0.7321 | 0.6651 |
| 0.08 | 0.9187 | 0.8286 | 0.7440 | 0.6757 |
| 0.10 | 0.9340 | 0.8414 | 0.7548 | 0.6863 |
| $n_D$ | | | | |
| 0.00 | 1.3321 | 1.3319 | 1.3311 | 1.3308 |
| 0.02 | 1.3325 | 1.3321 | 1.3315 | 1.3310 |
| 0.04 | 1.3329 | 1.3324 | 1.3318 | 1.3313 |
| 0.06 | 1.3332 | 1.3326 | 1.3321 | 1.3317 |
| 0.08 | 1.3334 | 1.3328 | 1.3325 | 1.3319 |
| 0.10 | 1.3336 | 1.3330 | 1.3328 | 1.3321 |
| $\kappa$/(mS.cm$^{-1}$) | | | | |
| 0.00 | 0.368 | 0.412 | 0.459 | 0.511 |
| 0.02 | 0.300 | 0.330 | 0.360 | 0.380 |
| 0.04 | 0.380 | 0.410 | 0.458 | 0.508 |
| 0.06 | 0.366 | 0.430 | 0.490 | 0.560 |
| 0.08 | 0.330 | 0.400 | 0.460 | 0.510 |
| 0.10 | 0.240 | 0.320 | 0.400 | 0.460 |
| Glycine+aqueous CTAB | | | | |
| $\rho$/(kg.m$^{-3}$) | | | | |
| 0.00 | 997.7 | 996.1 | 994.3 | 992.5 |
| 0.02 | 998.3 | 996.6 | 994.7 | 992.8 |
| 0.04 | 998.8 | 997.0 | 995.0 | 993.0 |
| 0.06 | 999.1 | 997.2 | 995.1 | 993.1 |
| 0.08 | 999.3 | 997.3 | 995.2 | 993.2 |
| 0.10 | 999.5 | 997.4 | 995.3 | 993.2 |
| $\eta$/(Nm$^{-2}$s) | | | | |
| 0.00 | 0.8488 | 0.7775 | 0.6914 | 0.6250 |
| 0.02 | 0.8550 | 0.7823 | 0.6953 | 0.6276 |
| 0.04 | 0.8587 | 0.7855 | 0.6980 | 0.6298 |
| 0.06 | 0.8622 | 0.7885 | 0.7005 | 0.6323 |
| 0.08 | 0.8656 | 0.7914 | 0.7030 | 0.6344 |
| 0.10 | 0.8682 | 0.7939 | 0.7055 | 0.6364 |
| $n_D$ | | | | |
| 0.00 | 1.3326 | 1.3319 | 1.3312 | 1.3308 |
| 0.02 | 1.3330 | 1.3322 | 1.3318 | 1.3315 |
| 0.04 | 1.3334 | 1.3328 | 1.3322 | 1.3319 |
| 0.06 | 1.3339 | 1.3331 | 1.3326 | 1.3321 |
| 0.08 | 1.3341 | 1.3336 | 1.3329 | 1.3324 |
| 0.10 | 1.3344 | 1.3338 | 1.3331 | 1.3326 |
| $\kappa$/(mS.cm$^{-1}$) | | | | |
| 0.00 | 0.369 | 0.418 | 0.471 | 0.528 |
| 0.02 | 0.310 | 0.350 | 0.410 | 0.440 |
| 0.04 | 0.390 | 0.440 | 0.510 | 0.550 |
| 0.06 | 0.400 | 0.440 | 0.490 | 0.560 |
| 0.08 | 0.330 | 0.410 | 0.460 | 0.530 |
| 0.10 | 0.300 | 0.400 | 0.400 | 0.500 |
| Glycine+aqueous TX-100 | | | | |
| $\rho$/(kg.m$^{-3}$) | | | | |
| 0.00 | 998.0 | 996.4 | 994.8 | 993.2 |
| 0.02 | 998.7 | 997.0 | 995.3 | 993.6 |
| 0.04 | 999.3 | 997.5 | 995.7 | 993.9 |
| 0.06 | 999.9 | 998.0 | 996.0 | 994.1 |
| 0.08 | 1000.5 | 998.4 | 996.3 | 994.3 |
| 0.10 | 1001.1 | 998.8 | 996.6 | 994.5 |
| $\eta$/(Nm$^{-2}$s) | | | | |
| 0.00 | 0.8618 | 0.7676 | 0.7024 | 0.6533 |
| 0.02 | 0.8821 | 0.7835 | 0.7157 | 0.6642 |
| 0.04 | 0.8920 | 0.7916 | 0.7224 | 0.6701 |
| 0.06 | 0.9003 | 0.7977 | 0.7275 | 0.6743 |
| 0.08 | 0.9061 | 0.8029 | 0.7326 | 0.6789 |
| 0.10 | 0.9124 | 0.8081 | 0.7365 | 0.6823 |
| $n_D$ | | | | |
| 0.00 | 1.3300 | 1.3296 | 1.3291 | 1.3288 |
| 0.02 | 1.3309 | 1.3301 | 1.3296 | 1.3293 |
| 0.04 | 1.3313 | 1.3303 | 1.3299 | 1.3296 |
| 0.06 | 1.3316 | 1.3306 | 1.3302 | 1.3299 |
| 0.08 | 1.3320 | 1.3312 | 1.3308 | 1.3305 |
| 0.10 | 1.3322 | 1.3316 | 1.3312 | 1.3309 |
| $\kappa$/(mS.cm$^{-1}$) | | | | |
| 0.00 | 0.006 | 0.008 | 0.009 | 0.010 |
| 0.02 | 0.008 | 0.010 | 0.012 | 0.0.13 |
| 0.04 | 0.012 | 0.014 | 0.016 | 0.018 |
| 0.06 | 0.013 | 0.016 | 0.018 | 0.019 |
| 0.08 | 0.015 | 0.018 | 0.020 | 0.022 |
| 0.10 | 0.016 | 0.018 | 0.020 | 0.022 |

as a function of cosolute (surfactant) concentration at 298.15 K. A perusal of Table 3 reveals that the values of both $\phi_v^0$ and $\phi_v^0(tr)$ increase with the increase in surfactant concentration and follow the sequence: SDS > CTAB > TX-100. Thus, our results are in good agreement with the one reported earlier [7, 8].

Franks et al. [17] suggested that the partial molar volume of a nonelectrolyte is the combination of intrinsic volume of the solute and the volume change due to its interaction with the solvent. Tarasawa et al. [18] pointed out that the intrinsic partial molar volume is considered to be made up of two types of contributions:

$$V_{\text{intrinsic}} = V_{\text{vw}} + V_{\text{void}} \tag{4}$$

where $V_{\text{vw}}$ is the volume occupied by the solute due to its van der Waals volume [19], and $V_{\text{void}}$ is the volume associated with the voids and empty spaces present therein

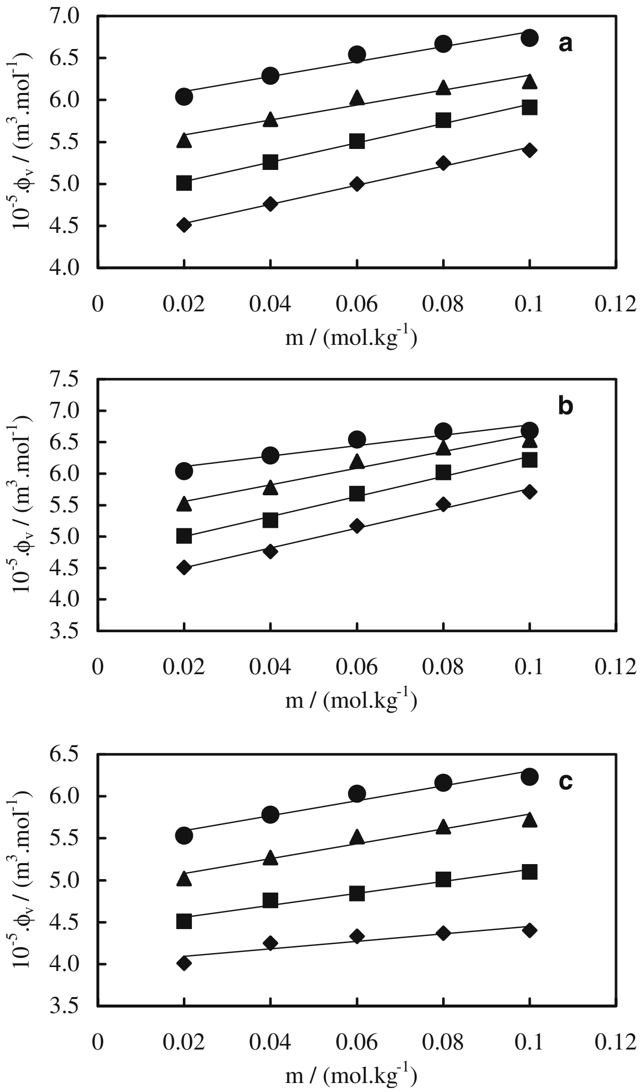

**Fig. 1** Plots of apparent molar volumes, $\phi_v$ vs $m$ of glycine in aqueous **a** SDS; **b** CTAB; **c** TX-100 at temperature $T$ [298.15 (*filled diamond*), 303.15 (*filled square*), 308.15 (*filled triangle*), and 313.15 K (*filled circle*)]

[20]. Shahidi et al. [21] modified the above equation to evaluate the contribution of a solute molecule to its $\phi_v^0$ as:

$$\phi_v^0 = V_{\mathrm{vw}} + V_{\mathrm{void}} - n\sigma_{\mathrm{s}} \tag{5}$$

where $\sigma_{\mathrm{s}}$ 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, $\phi_v^0$ of an amino acid can be viewed as:

$$\phi_v^0 = V_{\mathrm{vw}} + V_{\mathrm{void}} - V_{\mathrm{shrinkage}} \tag{6}$$

If it is assumed that $V_{\mathrm{vw}}$ and $V_{\mathrm{void}}$ are of the same magnitude in water and in aqueous surfactant solutions [8, 22], then the observed changes in $\phi_v^0$ or $\phi_v^0(tr)$ of the amino acid (glycine) can be explained in terms of the changes in the volume of shrinkage in the presence of surfactant molecules in aqueous solutions. As the critical micelles concentrations (CMCs) of SDS [23], CTAB [24], and TX-100 [25] are reported as $2.5\times10^{-3}$ mol.dm$^{-3}$, $8.2\times10^{-4}$ mol.dm$^{-3}$, and $2.4\times10^{-4}$ mol.dm$^{-3}$, 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.

A glance on the structure of glycine and surfactant molecules studied reveals that the volumetric behavior of glycine 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 glycine and between Na$^+$ of SDS/N$^+$–CH$_3$ group of CTAB and the COO$^-$ group of glycine
2. Ionic–hydrophilic interactions between the charge centers $\left(NH_3^+, COO^-\right)$ of glycine and the hydrophilic (polyoxyethylene) part of TX-100
3. Hydrophobic–hydrophilic group interactions between the hydrophobic part of the glycine 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 glycine

The changes in $\phi_v^0(tr)$ of glycine in aqueous surfactant solutions (Table 2) can be interpreted by considering the cosphere overlap model [14, 26, 27]; 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 $\phi_v^0(tr)$ value due to reduction in the electrostriction effect. Because of the interactions of the charge centers $\left(NH_3^+, COO^-\right)$ of glycine with the ions of SDS/CTAB and with the hydrophilic part of TX-100, the electrostriction of water caused by the charge centers of glycine will be reduced, resulting in an increase in volume and, hence, positive $\phi_v^0(tr)$ values. On the other hand, interactions of type (3) and (4) would lead to a negative $\phi_v^0(tr)$ because of the reduction in water structure that is formed around those groups as a result of the cosphere overlap. Further, $\phi_v^0(tr)$ values of glycine in all the three surfactant solutions are small negative at 298.15 K and become increasingly positive as the temperature increases to 313.15 K. These results indicate that ion–ion and ion–hydrophilic group interactions are dominant over the hydrophobic–hydrophobic and hydrophilic–hydrophobic group interactions at higher temperatures, 308.15 and 313.15 K, while at lower temperature, 298.15 K, hydrophobic–hydrophilic and hydrophobic–hydrophobic interactions seem to dominate over ion–ion and ion–hydrophilic

**Table 2** Values of various calculated parameters of glycine in aqueous surfactant solutions at $T$=298.15, 303.15, 308.15, and 313.15 K

| | 298.15 K | 303.15 K | 308.15 K | 313.15 K |
|---|---|---|---|---|
| Glycine+aqueous SDS | | | | |
| $10^{-5} \cdot \phi_v^0 / (\mathrm{m}^3 \cdot \mathrm{mol}^{-1})$ | 4.30±0.04 | 4.80±0.04 | 5.41±0.08 | 5.92±0.08 |
| $10^{-4} \cdot S_v^* / (\mathrm{m}^3 \cdot \mathrm{mol}^{-3/2} \cdot L^{1/2})$ | 1.14±0.06 | 1.15±0.06 | 0.89±0.12 | 0.90±0.12 |
| $10^{-5} \cdot \phi_{v(\mathrm{water})}^0 / (\mathrm{m}^3 \cdot \mathrm{mol}^{-1})$ | 4.32[a] | | 4.38[a] | 4.40[b] |
| $10^{-5} \cdot \phi_v^0(\mathrm{tr}) / (\mathrm{m}^3 \cdot \mathrm{mol}^{-1})$ | −0.02 | | 1.03 | 1.52 |
| $10^{-1} \cdot A/(\mathrm{dm}^{3/2} \cdot \mathrm{mol}^{-1/2})$ | 1.70±0.03 | 1.42±0.02 | 1.16±0.05 | 0.88±0.05 |
| $10^{-1} \cdot B/(\mathrm{dm}^3 \cdot \mathrm{mol}^{-1})$ | 5.91±0.11 | 6.28±0.09 | 6.35±0.19 | 6.45±0.21 |
| $\Delta\mu_1^{0\#} / (\mathrm{kJ} \cdot \mathrm{mol}^{-1})$ | 9.15 | 9.06 | 8.95 | 8.87 |
| $\Delta\mu_2^{0\#} / (\mathrm{kJ} \cdot \mathrm{mol}^{-1})$ | 89.07 | 95.75 | 98.68 | 101.88 |
| $\Lambda_m^0 / (S\,\mathrm{cm}^2\,\mathrm{mol}^{-1})$ | 24.45 | 26.20 | 28.28 | 29.92 |
| Glycine+aqueous CTAB | | | | |
| $10^{-5} \cdot \phi_v^0 / (\mathrm{m}^3 \cdot \mathrm{mol}^{-1})$ | 4.19±0.07 | 4.69±0.07 | 5.29±0.10 | 5.88±0.05 |
| $10^{-4} \cdot S_v^* / (\mathrm{m}^3 \cdot \mathrm{mol}^{-3/2} \cdot 1^{1/2})$ | 1.57±0.10 | 1.58±0.10 | 1.32±0.15 | 1.00±0.08 |
| $10^{-5} \cdot \phi_{v(\mathrm{water})}^0 / (\mathrm{m}^3 \cdot \mathrm{mol}^{-1})$ | 4.32[a] | | 4.38[a] | 4.40[b] |
| $10^{-5} \cdot \phi_v^0(\mathrm{tr}) / (\mathrm{m}^3 \cdot \mathrm{mol}^{-1})$ | −0.13 | | 0.91 | 1.48 |
| $10^{-2} \cdot A/(\mathrm{dm}^{3/2} \cdot \mathrm{mol}^{-1/2})$ | 3.40±0.14 | 2.53±0.07 | 2.02±0.09 | 0.63±0.15 |
| $10^{-1} \cdot B/(\mathrm{dm}^3 \cdot \mathrm{mol}^{-1})$ | 1.24±0.06 | 1.33±0.03 | 1.39±0.04 | 1.64±0.06 |
| $\Delta\mu_1^{0\#} / (\mathrm{kJ} \cdot \mathrm{mol}^{-1})$ | 9.22 | 9.16 | 9.01 | 8.90 |
| $\Delta\mu_2^{0\#} / (\mathrm{kJ} \cdot \mathrm{mol}^{-1})$ | 27.89 | 29.95 | 31.67 | 36.03 |
| $\Lambda_m^0 / (S\,\mathrm{cm}^2\,\mathrm{mol}^{-1})$ | 24.90 | 27.43 | 32.64 | 34.40 |
| Glycine+aqueous TX-100 | | | | |
| $10^{-5} \cdot \phi_v^0 / (\mathrm{m}^3 \cdot \mathrm{mol}^{-1})$ | 4.00±0.09 | 4.41±0.05 | 4.90±0.08 | 5.41±0.08 |
| $10^{-5} \cdot S_v^* / (\mathrm{m}^3 \cdot \mathrm{mol}^{-3/2} \cdot 1^{1/2})$ | 4.51±1.28 | 7.18±0.75 | 8.87±1.20 | 8.92±1.20 |
| $10^{-5} \cdot \phi_{v(\mathrm{water})}^0 / (\mathrm{m}^3 \cdot \mathrm{mol}^{-1})$ | 4.32[a] | | 4.38[a] | 4.40[a] |
| $10^{-5} \cdot \phi_c^0(\mathrm{tr}) / (\mathrm{m}^3 \cdot \mathrm{mol}^{-1})$ | −0.32 | | 0.52 | 1.01 |
| $10^{-1} \cdot A/(\mathrm{dm}^{3/2} \cdot \mathrm{mol}^{-1/2})$ | 1.53±0.04 | 1.32±0.03 | 1.18±0.03 | 1.02±0.03 |
| $10^{-1} \cdot B/(\mathrm{dm}^3 \cdot \mathrm{mol}^{-1})$ | 1.05±0.17 | 1.11±0.12 | 1.17±0.11 | 1.26±0.13 |
| $\Delta\mu_1^{0\#} / (\mathrm{kJ} \cdot \mathrm{mol}^{-1})$ | 9.41 | 9.28 | 9.21 | 9.18 |
| $\Delta\mu_2^{0\#} / (\mathrm{kJ} \cdot \mathrm{mol}^{-1})$ | 23.30 | 25.62 | 27.26 | 29.19 |
| $\Lambda_m^0 / (S\,\mathrm{cm}^2\,\mathrm{mol}^{-1})$ | 0.58 | 0.73 | 0.88 | 0.96 |

[a] Data taken from [15]
[b] Data taken from [16]

interactions in aqueous SDS/CTAB solutions. The increase in $\phi_v^0(tr)$ 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 [13]. Similarly, negative $\phi_v^0(tr)$ value in case of TX-100 at 298.15 K suggests the dominance of hydrophobic–hydrophilic and hydrophobic–hydrophobic interactions over the ion–hydrophilic interaction, while positive $\phi_v^0(tr)$ values at 308.15 and 313.15 K indicate that ion–hydrophilic interaction dominates over the hydrophobic–hydrophilic and hydrophobic–hydrophobic interactions.

It is worth mentioning that the values of $\phi_v^0(tr)$ from water to aqueous surfactant solutions at all the three studied temperatures follow the sequence: SDS > CTAB > TX-100. This, in turn, suggests the sequence of the strength of ion–ion or ion–hydrophilic interactions of glycine with the surfactant molecules in the solution.

The structure-making and breaking capacity of a solute may be interpreted with the help of Hepler's reasoning [28], i.e., on the basis of the sign of $\left(\frac{\partial^2 \phi_v^0}{\partial T^2}\right)_p$. It can be shown from general thermodynamic equation that

$$\left(\frac{\partial \overline{C}_p^0}{\partial p}\right)_T = -T\left(\frac{\partial^2 \phi_v^0}{\partial T^2}\right)_p \tag{7}$$

where $\overline{C}_p^0$ is the partial molar heat capacity at infinite dilution. From Eq. 7, it is clear that a structure-making solute should have a positive value of $\left(\frac{\partial^2 \phi_v^0}{\partial T^2}\right)_p$. For glycine, the $\left(\frac{\partial^2 \phi_v^0}{\partial T^2}\right)_p$ values in all the three aqueous surfactant solutions have been found to be positive (Table 4), and hence glycine acts as a structure-maker in all the three systems studied.

*Viscometric study* The viscosity data were analyzed by using Jones–Dole [29] equation:

$$\eta_r = \eta / \eta_0 = 1 + Am^{1/2} + Bm \tag{8}$$

where $\eta_r$ is the relative viscosity of the solution, $\eta$ and $\eta_0$ are the viscosities of the solution and the solvent (aqueous

**Table 3** Variation of partial molar volumes, $\phi_v^0$ and transfer volumes, $\phi_v^0(\mathrm{tr})$ of glycine as a function of surfactant concentration in aqueous surfactants solutions at $T$=298.15 K

| [Surfactant]/ (mol.kg$^{-1}$) | $10^{-5}\cdot\phi_v^0/(\mathrm{m}^3\cdot\mathrm{mol}^{-1})$ | $10^{-5}\cdot\phi_v^0(\mathrm{tr})/(\mathrm{m}^3\cdot\mathrm{mol}^{-1})$ |
|---|---|---|
| Glycine+aqueous SDS | | |
| 0.01 | 4.30[a] | −0.02[a] |
| 0.05 | 4.35[b] | 0.03[b] |
| 0.50 | 4.41[b] | 0.10[b] |
| | 4.56[b] | 0.24[b] |
| Glycine+aqueous CTAB | | |
| 0.01 | 4.19[a] | −0.13[a] |
| 1.00 | 4.41[b] | 0.10[b] |
| Glycine+aqueous TX-100 | | |
| 0.01 | 4.02[a] | −0.32[a] |
| 0.05 | 4.29[c] | −0.03[c] |
| 0.10 | 4.34[c] | 0.03[c] |
| 0.40 | 4.34[c] | 0.03[c] |

[a] This work
[b] Data taken from [7]
[c] Data taken from [8]

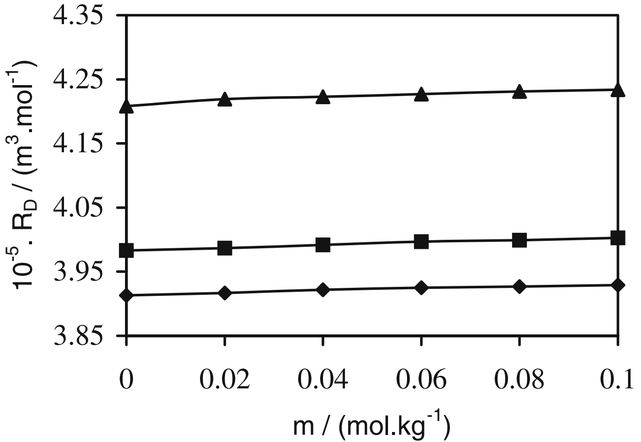

**Fig. 2** Plots of molar refraction, $R_D$ vs $m$ of glycine in aqueous SDS (*filled diamond*); CTAB (*filled square*); and TX-100 (*filled triangle*) at temperature $T$ (298.15 K)

surfactant), respectively, and $A$ and $B$ are the Falkenhagen [30, 31] and Jones–Dole [29] coefficients, respectively. Coefficient $A$ accounts for the glycine–glycine interactions, and $B$ is a measure of structural modifications induced by the glycine–surfactant/water interactions [32]. The values of $A$ and $B$ have been obtained from the intercepts and slopes of the plots of $\left[(\eta_r-1)/m^{1/2}\right]$ vs $m^{1/2}$ and are included in Table 2. Table 2 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 glycine–surfactant/water and weak glycine–glycine 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 glycine–surfactant/water and glycine–glycine interactions are almost equally important. In addition, the increasing values of $B$ coefficients and a reverse trend in $A$ coefficients with rise in temperature supports the variation of $\phi_v^0$ with temperature.

**Table 4** Values of $\left(\frac{\partial^2\phi_v^0}{\partial T^2}\right)_p$ of glycine in aqueous surfactant solutions

| | $10^{-3}\cdot\left(\frac{\partial^2\phi_v^0}{\partial T^2}\right)_p$ |
|---|---|
| SDS | 0.136 |
| CTAB | 1.622 |
| TX-100 | 1.986 |

The viscosity data have also been examined in the light of the transition state theory of the relative viscosity proposed by Feakins et al. [33, 34]. According to this theory, the $B$ coefficient is given by the relation:

$$B=\frac{\left[\left(\overline{V}_1^0-\overline{V}_2^0\right)+\left\{\overline{V}_1^0\left(\Delta\mu_2^{0\#}-\Delta\mu_1^{0\#}\right)\right\}/RT\right]}{1,000} \tag{9}$$

where $\overline{V}_1^0$ and $\overline{V}_2^0(=\phi_v^0)$ are the partial molar volumes of the solvent and solute, respectively. The free energy of activation per mole of solvent, $\Delta\mu_1^{0\#}$, has been calculated by using the Erying viscosity relation [35]:

$$\Delta\mu_1^{0\#}=RT\ln\left(\eta_0\overline{V}_1^0/hN_A\right) \tag{10}$$

where $h$ and $N_A$ are Planck's constant and Avogadro number, respectively. Equation 9 rearranges to give the contribution per mole of solute to the free energy of activation for viscous flow of the solution, $\Delta\mu_2^{0\#}$ as,

$$\Delta\mu_2^{0\#}=\Delta\mu_1^{0\#}+\left(RT/\overline{V}_1^0\right)\left[1,000B-\left(\overline{V}_1^0-\overline{V}_2^0\right)\right] \tag{11}$$

The values of $\Delta\mu_1^{0\#}$ and $\Delta\mu_2^{0\#}$ are also included in Table 2. It is evident from Table 2 that for all the three systems

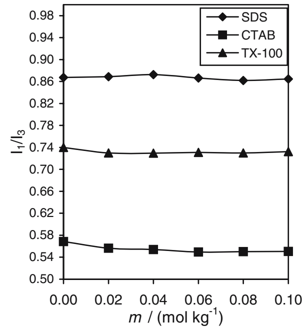

**Fig. 3** Effect of glycine concentration on $I_1/I_3$ ratio of pyrene fluorescence in aqueous SDS (*filled diamond*); CTAB (*filled square*); and TX-100 (*filled triangle*) under ambient conditions

investigated, the $\Delta\mu_2^{0\#}$ values are larger than those of $\Delta\mu_1^{0\#}$ values and increase with an increase in temperature for the glycine mixtures in all the three aqueous surfactants, thereby indicating that glycine behaves as net structure-maker in the present aqueous surfactant solutions. Thus, our finding is in good agreement with the results reported by Feakins et al. [33] for the study of activation parameters in aqueous electrolyte solutions. However, $\Delta\mu_2^{0\#}$ decreases in the order: SDS > CTAB > TX-100. Such a decrease in $\Delta\mu_2^{0\#}$ is attributed to a decrease in glycine-surfactant interactions. This reinforces our earlier conclusions drawn from volumetric study.

*Refractive index study* The experimental refractive indices presented in Table 1 show an increasing trend with increasing concentration of glycine in the mixtures. This indicates that the refractive index is directly related to the interactions present in the solutions. Similar view has also been proposed by Soto et al. [36]. For mixtures of interacting components, the molar refractivity of each component is given by the equation:

$$R_D = 4\pi\alpha N_A \tag{12}$$

where $\alpha$ is the molecular polarizability. The molar refractivity, $R_D$ of the mixtures can be calculated from the values of the refractive indices, $n_D$, by using Lorentz–Lorenz equation:

$$R_D = \left(\frac{n_D^2 - 1}{n_D^2 + 2}\right)\left(\sum_{i=1}^{3} x_i M_i/\rho\right) \tag{13}$$

where $x_i$ is the mole fraction and $M_i$ is the molar mass of the $i$th component of the solution. The plots of $R_D$ vs glycine concentration at 298.15 K for the studied systems are given in Fig. 2. It is evident from Fig. 2 that $R_D$ increases linearly with increasing amount of glycine in all the three systems. As $R_D$ is directly proportional to the molecular polarizability, Fig. 2 reveals that overall polarizability of the three systems under study increases with increasing amount of glycine in the solutions. The polarizability is found to increase in the order: SDS < CTAB < TX-100 (Fig. 2). No significant effect of temperature has been observed on the $R_D$ values of the studied systems.

*Conductometric study* The limiting molar conductance, $\overset{0}{\Lambda}_m$ for glycine in aqueous surfactant solutions were obtained by extrapolating the linear plots of molar conductance, $\Lambda_m$ vs $m^{1/2}$ to zero concentration. The $\overset{0}{\Lambda}_m$ values for glycine in aqueous surfactant solutions at different temperatures were recorded in Table 2. The $\overset{0}{\Lambda}_m$ has been regarded as a measure of glycine–surfactant/water interactions [37]; the greater the magnitude of $\overset{0}{\Lambda}_m$, the greater is the interaction. The large and positive values of limiting molar conductance of glycine in aqueous SDS and CTAB solutions and an increasing trend of $\overset{0}{\Lambda}_m$ with increase in temperature, show that glycine–surfactant/water interactions are stronger and increase with rise in temperature. However, for glycine in aqueous TX-100 solution, $\overset{0}{\Lambda}_m$ has very small values as compared to those in aqueous SDS and CTAB solutions, suggesting relatively weak glycine–surfactant/water interactions. This may be due to the nonionic nature of surfactant TX-100, which also seems to be responsible for very low values of specific conductances, $\kappa$ (Table 1) for glycine in aqueous TX-100 solutions.

*Fluorescence study* The ratio between the intensities of the first and the third of the major vibrational peaks in pyrene's fluorescence spectrum is quite sensitive to the probe microenvironment. As pyrene is hydrophobic in nature, the onset of micelle formation has been shown by a sudden decrease in the $I_1/I_3$ ratio, if a surfactant is added to aqueous solutions containing pyrene, due to the strong distribution of pyrene into micelles [38]. As the solutions in our study are micellar, the $I_1/I_3$ ratio is already much lower than in water (Fig. 3). It can be seen that the $I_1/I_3$ ratio is not affected much by increasing the concentration of glycine in all the aqueous surfactant solutions. This behavior can be supported by the results reported earlier [8] that the addition of glycine does not affect considerably the micellization of ionic surfactants. Furthermore, this behavior can be attributed to the contribution of solvophobic interactions, as glycine is the member of the neutral amino acid category [39] having no alkyl group attached to it.

Another interesting observation is that the $I_1/I_3$ ratio varies in the order: SDS > TX-100 > CTAB (Fig. 3). The results indicate that as the hydrophobicity increases, the ionic interaction decreases. The maximum $I_1/I_3$ value in case of SDS indicates enhanced polar/ionic interactions. On the other hand, CTAB shows a minimum $I_1/I_3$ ratio which indicates the dominance of hydrophobic–hydrophilic interactions over the ionic–hydrophilic or ionic–hydrophobic interactions. As TX-100 contains no ionic group, thereby, the $I_1/I_3$ ratio of TX-100 in presence of glycine lies in between the two ionic surfactants due to the presence of only hydrophobic and hydrophilic parts in the nonionic surfactant, TX-100.

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