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Interaction of Glycylglycine with Cationic Surfactants—Cetylpyridinium Chloride and Cetylpyridinium Bromide: A Volumetric, Ultrasonic and Conductometric Study

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Abstract

The interactions of glycylglycine (di-peptide of glycine) also known as 2-[(2-aminoacetyl)amino] acetic acid with cationic surfactants cetylpyridinium chloride (CPC) and cetylpyridinium bromide (CPB) as a function of temperature in aqueous medium has been studied by well-know permutation of volumetric, ultrasonic and conductometric techniques. These measurements have been used to evaluate some useful thermodynamic parameters viz. apparent molar volumes, ϕ_v, partial molar volumes, ϕ_v^o, transfer volumes, $\phi_v^0(tr)$, partial molar expansibility, ϕ_E^0, hydration number, n_H, apparent molal compressibility, ϕ_K, limiting partial molal adiabatic compressibility, ϕ_K^0. The specific conductivity (κ) was used to calculate the critical micellar concentration (cmc) and other physicochemical parameters of micellization of CPC/CPB with glycylglycine. The critical micelle concentration, cmc and limiting molar conductivity, Λ_m^o of the two surfactant systems were determined by using the conductivity data at 298.15 K, 303.15 K, 308.15 K and 313.15 K. The acquired data have been discussed as per various interactions taking place in the ternary system of CPC/CPB, glycylglycine and water.

Keywords Density · Intermolecular interactions · Partial molar volumes · Specific conductivity · Ultrasonic velocities

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1 Introduction

Proteins are extremely important from a biological point of view because they are fundamental parts of organisms and have a great contribution practically in all process in cells [1]. The expression of the protein performance is displayed by their interactions with the neighboring environment. Studies of interactions of protein with surfactants are of particular interest because protein interactions with cationic and anionic surfactants are used cooperatively in formulated complexes. Surfactant solutions have a broad affinity to solubilize a definite quantity of additives that is related with their structural organization and mutual interactions. The mechanisms for the protein—surfactant interactions are polyelectrolyte absorption [2], hydrophobic [3] and ionic interactions [4], depending on the substrate and type of proteins involved. In view of the fact due to the complex structural organization of proteins, it is difficult to study them directly therefore the amino acids/peptides which incorporate several structural features of protein molecules act as model compounds of protein and initiate significant information that direct better understanding of biological macromolecules or proteins [5–9]. In this work, the object of the study was the simplest di-peptide, i.e., glycylglycine contains complex structure and has more components of proteins than amino acids. (Di-Peptide in aqueous solution generally behaves as zwitterions with $NH4^+$ and COO^- groups at two ends of the molecule. The Na^+ ions provided through electrolytes interact electrostatically through $NH4^+$ and COO^- groups of di-peptide zwitterions. Moreover, the water dipoles are strongly associated to the cations/anions and also with the di-peptide zwitterions with the electrostatic forces. These interactions comprehensively introduce the cohesion into the solution under investigation). A number of workers have studied the thermodynamic properties of glycylglycine in different solvents [10–13]. However, studies on glycylglycine in aqueous media with surfactant solution are rare [14]. Keeping these considerations in mind, from the experimental densities, ultrasonic velocities and specific conductivities, the apparent molar volumes, partial molar volumes, transfer volumes, partial molar expansibility, hydration number, apparent molal compressibility, partial molal adiabatic compressibility and limiting molar conductivity were evaluated. In the present study, the interactions of glycylglycine (i.e., in molality (m) ranges from 0.02 to 0.10) in the presence of 0.005 m aqueous cetylpyridinium chloride (CPC) and aqueous cetylpyridinium bromide (CPB) solutions at temperature range (298.15–313.15) K were determined.

2 Materials and Methods

Biochemical reagent grade glycylglycine ($C_4H_8N_2O_3$) (Acros Organics, Belgium, mass fraction > 0.99), analytical reagent grade cetylpyridinium chloride (CPC) ($C_{21}H_{38}ClN$) and cetylpyridinium bromide (CPB) ($C_{21}H_{38}BrN$) (both from Sisco Research Lab., India, each having mass fraction > 0.98) were used after recrystallization from ethanol–water mixtures and drying in vacuum over P_2O_5 at room temperature for at least 10 h before use. Water, with conductivity 1.07×10^{-6} S·cm^{-1} at 298.15 K, was used for preparation of solutions and was obtained by distilling deionized water from alkaline potassium permanganate ($KMnO_4$) to remove organic matter, if any.

Stock solutions of 0.005 m (mol·kg^{-1}) of CPC and CPB in water were prepared and used as solvents for preparation of 0.02 m, 0.04 m, 0.06 m, 0.08 m and 0.10 m Gly–Gly solutions. All the samples were prepared by weight on Precisa XB-220A (Swiss make) electronic balance precise to 0.0001 g. To avoid the evaporation and the contamination, all the samples were kept in special air-tight bottles. A single-stem pyconometer made of Borosil glass with a bulb capacity 8×10^{-6} m^3 was utilized for the density measurements of the ternary mixtures. The calibration of pycnometer was done using doubly distilled water. The uncertainty in the density measurements, on the average, was ±0.01 (kg·m^{-3}). The ultrasonic velocities of pure aqueous solvents and their ternary solutions were calculated by a single-crystal variable path-fixed frequency interferometer provided by Mittal Enterprises, New Delhi (Model F-05). The measurements of ultrasonic velocity were taken at a fixed frequency of 2 MHz. It is based on finding the wavelength, 'λ' in the medium. Ultrasonic speed is calculated by the relation $u = f \times \lambda$. The wavelength is calculated from the relation $d = (n-1)(\lambda/2)$ where d is the total distance moved by micrometer screw for a maximum or minimum deflection, n is the number of maxima (or minima) (≈ 17) of anode current for the distance d. The measured ultrasonic speeds were found to have a precision of ±0.8 m·s^{-1}. A minimum of three readings were taken for each sample, and the average values are used in all the calculations. The uncertainty in the ultrasonic speed measurements, on the average, was ±0.05 %. The calibration of the measurement cell was done by measuring the ultrasonic velocity in AR grade benzene, and the values of ultrasonic speeds were found to be 1307.3 m·s^{-1} at 298.15 K and 1281.5 m·s^{-1} at 303.15 K which compare well with the 1310.0 m·s^{-1} at 298.15 K and 1279.0 m·s^{-1} at 303.15 K found in the literature [15] and [16], respectively. Specific conductivities of the solutions were measured with a Control Dynamics conductivity meter, India, having a cell constant 1.01 cm^{-1}, and an uncertainty of 0.02 % was used. The conductivity meter was calibrated by measuring the conductivities of the solutions of potassium chloride (Merck, purity > 99 %) of different concentrations (0.01 N and 0.1 N). In whole experimental set-up, the temperature was retained by circulating water from electronically controlled water bath (Julabo, Germany) with a temperature stability of ±0.01 K. A minimum of triplicate reading was taken for each sample, and the average values were utilized for all the calculations.

3 Results and Discussion

In the present work, three sets of experiments were carried out. The densities, ultrasound speeds and specific conductivities of glycylglycine (0.02 m, 0.04 m, 0.06 m, 0.08 m and 0.10 m) in aqueous solutions of (0.005 m) CPC and CPB at different temperatures are presented in Table 1.

3.1 Volumetric Study

Densities of the solutions of the glycylglycine + aqueous CPC and glycylglycine + aqueous CPB were calculated at 298.15 K, 303.15 K, 308.15 K and 313.15 K. A variety

Table 1 Values of density, ρ, ultrasonic speed, u, specific conductance, κ and critical micelle concentration, *cmc*, of glycylglycine in aqueous CPC and aqueous CPB at different temperatures

m (mol·kg^{-1})	T (K)			
	298.15	303.15	308.15	313.15
Glycylglycine + aqueous CPC				
ρ (kg·m^{-3})				
0.00	997.0	995.4	993.5	990.7
0.02	998.0	996.3	994.2	991.4
0.04	998.9	997.1	994.9	992.0
0.06	999.8	997.9	995.6	992.5
0.08	1000.7	998.7	996.1	993.0
0.10	1001.5	999.4	996.7	993.5
u (m·s^{-1})				
0.00	1500.8	1510.6	1521.6	1530.8
0.02	1501.4	1511.7	1523.3	1533.2
0.04	1503.4	1514.2	1526.4	1536.8
0.06	1505.5	1516.8	1529.6	1540.7
0.08	1507.8	1519.8	1533.3	1544.9
0.10	1510.4	1523.0	1537.4	1549.1
κ (mS·cm^{-1})				
0.00	0.20	0.21	0.21	0.23
0.02	0.20	0.21	0.22	0.23
0.04	0.21	0.22	0.23	0.24
0.06	0.22	0.23	0.24	0.25
0.08	0.23	0.24	0.26	0.27
0.10	0.24	0.25	0.27	0.28
cmc (mol·kg^{-1})				
	0.02 101	0.02 192	0.02 315	0.02 468
Glycylglycine + aqueous CPB				
ρ (kg·m^{-3})				
0.00	997.1	995.7	994.1	992.3
0.02	998.2	996.8	995.1	993.2
0.04	999.2	997.7	996.0	994.1
0.06	1000.1	998.7	996.9	994.9
0.08	1001.1	999.5	997.7	995.6
0.10	1001.9	1000.4	998.4	996.3
u (m·s^{-1})				
0.00	1497.2	1511.7	1526.4	1535.3
0.02	1499.1	1513.5	1528.4	1537.7
0.04	1501.0	1515.2	1529.5	1539.0
0.06	1502.1	1516.8	1530.4	1540.2

Table 1 continued

m (mol·kg^{-1})	T (K)			
	298.15	303.15	308.15	313.15
0.08	1503.6	1517.6	1531.6	1541.5
0.10	1504.3	1518.4	1532.9	1543.2
0.00	1499.4	1515.3	1528.0	1537.1
0.02	1499.3	1515.5	1528.4	1537.7
0.04	1499.8	1516.2	1529.5	1539.0
0.06	1500.1	1516.8	1530.4	1540.2
0.08	1500.6	1517.6	1531.6	1541.5
0.10	1501.3	1518.4	1532.9	1543.2
κ (mS·cm^{-1})				
0.00	0.21	0.21	0.22	0.24
0.02	0.19	0.20	0.21	0.22
0.04	0.20	0.21	0.22	0.23
0.06	0.21	0.22	0.23	0.24
0.08	0.22	0.23	0.24	0.25
0.10	0.23	0.24	0.25	0.26
cmc (mol·kg^{-1})				
	0.02 007	0.02 070	0.02 161	0.02 223

of thermodynamic parameters have been estimated which reflects the solute–solute, solute–solvent and solvent–solvent interactions in different systems. An inspection on the structure of glycylglycine, CPC and CPB molecules reveals that the volumetric behavior of the CPC and CPB in glycylglycine solutions can be elucidated by taking into consideration the various feasible interactions taking place between these systems.

The apparent molar volume of glycylglycine in an aqueous CPC/CPB was calculated from the measured densities by using the following relation:

$$\phi_v = \frac{M}{\rho} - \frac{1000(\rho - \rho_0)}{m\rho\rho_0} \tag{1}$$

where m, M ρ and ρ_0 are the molality of solute (glycylglycine), molecular weight, densities of solution (glycylglycine + aqueous surfactant) and solvent (aqueous surfactant), respectively. Table 2 presented the ϕ_v values. As expected, the ϕ_v values illustrated in Table 2 are positive for both systems (glycylglycine + aqueous surfactant solutions), showing strong glycylglycine–surfactant interactions in aqueous media. Plots of ϕ_v against molal concentration of glycylglycine are linear (Fig. 1a, b). Therefore, partial molar volume, ϕ_v^0 (also known as apparent molar volume at infinite dilution) was acquired by utilizing the least-squares fitting method of the ϕ_v values to the following relation:

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

Table 2 Values of apparent molar volumes, ϕ_v, apparent molal compressibility, ϕ_K of glycylglycine in aqueous CPC and aqueous CPB at different temperatures

m (mol·kg^{-1})	T (K)			
	298.15	303.15	308.15	313.15
Glycylglycine + aqueous CPC				
$10^5 \times \phi_v$ (m^3·mol^{-1})				
0.02	8.2940	8.8649	9.3554	10.0390
0.04	8.3463	8.9759	9.5436	10.1490
0.06	8.4255	9.0501	9.7373	10.2680
0.08	8.5369	9.1469	9.8819	10.3880
0.10	8.6613	9.2528	10.0280	10.5090
$10^8 \times \phi_K$ (m^3·mol^{-1}·Pa^{-1})				
0.02	− 3.5088	− 4.4049	− 5.1474	− 6.1178
0.04	− 3.7992	− 4.5842	− 5.4996	− 6.4030
0.06	− 3.9933	− 4.8257	− 5.7195	− 6.7388
0.08	− 4.2362	− 5.1221	− 5.9922	− 7.0082
0.10	− 4.4675	− 5.3581	− 6.3220	− 7.3415
Glycylglycine + aqueous CPB				
$10^5 \times \phi_v$ (m^3·mol^{-1})				
0.02	7.9714	8.0560	8.2682	8.4876
0.04	8.0839	8.1789	8.4145	8.6550
0.06	8.1831	8.2987	8.5425	8.8244
0.08	8.2791	8.4178	8.6914	9.0073
0.10	8.4042	8.5470	8.8489	9.1754
$10^8 \times \phi_K$ (m^3·mol^{-1}·Pa^{-1})				
0.02	− 3.8128	− 4.2384	− 4.5745	− 5.0013
0.04	− 3.7597	− 4.1583	− 4.5258	− 4.9035
0.06	− 3.7031	− 4.1116	− 4.4567	− 4.8651
0.08	− 3.6891	− 4.0461	− 4.4461	− 4.8006
0.10	− 3.6156	− 3.9891	− 4.3526	− 4.7870

where S_v^* is the experimental slope, which is considered to be the volumetric pairwise interaction coefficient [17, 18]. At infinite dilution, m tends to 0, thus solute–solute interaction vanishes, ϕ_v becomes equal to ϕ_v^0, therefore, ϕ_v^0 reports about solute—solvent interactions [19], whereas, S_v^* is indicative of solute–solute interactions. The evaluated values of ϕ_v^0 and S_v^* are presented in Table 3. It is noticed from Table 3 the values of ϕ_v^0 are positive and are more than S_v^*, thus signifying the dominance of strong solute–solvent (glycylglycine–aqueous surfactant) interactions over solute–solute (glycylglycine–glycylglycine/surfactant–glycylglycine) interactions. It is evident from Table 3 that ϕ_v^0 values increase with temperature which may be attributed to the reduced electrostriction of water due to zwitterionic groups of glycylglycine. Our results are in agreement with the results reported by Ali et al. [20–22]. The increase in

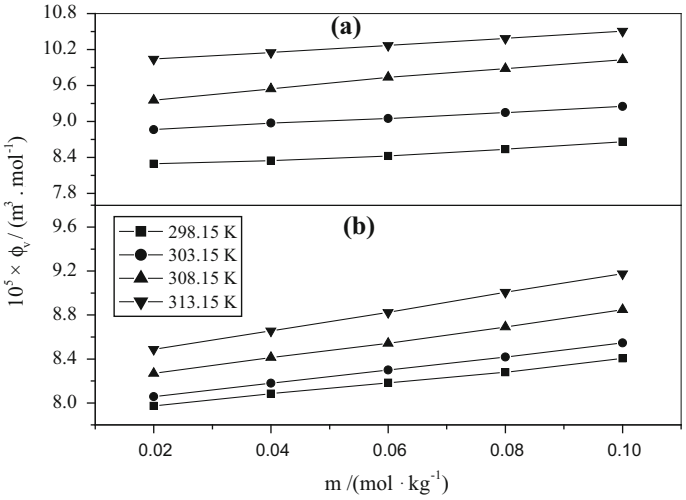

Fig. 1 Plot of apparent molar volume (ϕ_v), against molal concentration (m) of glycylglycine in (a) aqueous CPC and (b) aqueous CPB at different temperatures

ϕ_v^0 with temperature may be attributed to the release of some water molecules from the loose hydration spheres of Gly–Gly in bulk solution of CPC and CPB, respectively. A quantitative comparison of the magnitude of values shows ϕ_v^0 values for glycylglycine in the presence of aqueous CPC are higher than in the presence of aqueous CPB suggesting greater solute–solvent interaction in the presence of CPC than in the presence of CPB.

The volumes of transfer of glycylglycine from water to aqueous surfactant, $\phi_v^0(tr)$, were 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 ϕ_v^0(in water) is the partial molar volume of the glycylglycine in water and its value for glycylglycine at 298.15 K and 308.15 K has been taken from the literature [21]. The $\phi_v^0(tr)$ values at above-mentioned temperatures are summarized in Table 3. Table 3 shows that $\phi_v^0(tr)$ are positive in all the cases and it is higher in the presence of CPC than in the presence of CPB.

The positive values of ϕ_v^0 and $\phi_v^0(tr)$ with their tendencies in co-solutes can be explained by the following equation [22]:

$$\phi_v^0 = V_{VW} + V_{Void} - n\sigma_s \tag{4}$$

where V_{VW} is the van der Waals volume, and V_{Void} is the contribution due to the void or empty volume, σ_s is the shrinkage in volume caused by the interaction of a hydrogen bonding group with water molecules and n is the potential number of hydrogen bonding sites in a molecule. If we assume that V_{VW} and V_{Void} have no difference in pure water and aqueous surfactant solutions [23, 24], the positive volume change might

Table 3 Values of ϕ_v^0, S_v^*, ϕ_v^0 (aq.), ϕ_v^0 (tr), ϕ_E^0, n_H, ϕ_K^0, S_K^* and Λ_m^0 of Gly–Gly in aqueous cetylpyridinium chloride and cetylpyridinium bromide at different temperatures

	T (K)			
	298.15	303.15	308.15	313.15
Gly–Gly + aqueous CPC				
$10^5\ \phi_v^0$ ($m^3 \cdot mol^{-1}$)	8.1752	8.7741	9.2043	9.9167
$10^5\ S_v^*$ ($m^3 \cdot mol^{-2} \cdot kg$)	4.6261	4.7336	8.4134	5.8970
$10^5 \phi_v^0$ (aq.) ($m^3 \cdot mol^{-1}$)	7.6430[a]		7.7100[a]	
$10^5 \phi_v^0$ (tr) ($m^3 \cdot mol^{-1}$)	0.5322		1.4943	
$10^6\ \phi_E^0$ ($m^3 \cdot mol^{-1} \cdot K^{-1}$)	0.9607	1.0742	1.1876	1.3011
n_H	4.04		1.84	
$10^8 \phi_K^0$ ($m^3 \cdot mol^{-1} \cdot Pa^{-1}$)	− 3.2947	− 4.1257	− 4.8836	− 5.8061
$10^7\ S_K^*$ ($m^3 \cdot mol^{-2} \cdot Pa^{-1} \cdot kg$)	− 1.1772	− 1.2221	− 1.4209	− 1.5263
$10^3\ \Lambda_m^0$ ($S \cdot m^2 \cdot mol^{-1}$)	1.0100	1.0600	1.1110	1.1380
Gly–Gly + aqueous CPB				
$10^5\ \phi_v^0$ ($m^3 \cdot mol^{-1}$)	7.8661	7.9334	8.1216	8.3116
$10^5\ S_v^*$ ($m^3 \cdot mol^{-2}$ kg)	5.3037	6.1042	7.1916	8.6396
$10^5 \phi_v^0$ (aq.) ($m^3 \cdot mol^{-1}$)	7.6430[a]		7.7100[a]	
$10^5 \phi_v^0$ (tr) ($m^3 \cdot mol^{-1}$)	0.2271		0.4096	
$10^6\ \phi_E^0$ ($m^3 \cdot mol^{-1} \cdot K^{-1}$)	0.1209	0.2436	0.3663	0.4889
n_H	4.98		3.94	
$10^8 \phi_K^0$ ($m^3 \cdot mol^{-1} \cdot Pa^{-1}$)	− 3.8556	− 4.2919	− 4.6282	− 5.0310
$10^8\ S_K^*$($m^3 \cdot mol^{-2} \cdot Pa^{-1} \cdot kg$)	2.3250	3.0540	2.6175	2.6575
$10^3\ \Lambda_m^0$($S \cdot m^2 \cdot mol^{-1}$)	0.9656	1.0069	1.0524	1.1257

[a]Ref. [21]

arise from the decrease in σ_s in aqueous surfactant solutions. Due to the presence of surfactants, the interactions of charged end/peptide bond groups of glycylglycine and ions (Cl^-, Br^- and N^+) of surfactants become stronger, and the number of hydrogen bond between the hydrogen bonding group of glycylglycine with water molecules decreases, thus causing decrease in σ_s. The volume changes accompanying the transfer of glycylglycine are positive. For different aqueous surfactant solutions, the differences arise from the influences of anions. Cl^- and Br^- have the same charge but Br^- has larger ionic radius than Cl^-. As ionic radius increases, the interaction between the charged end/peptide bond groups of glycylglycine and ions (Cl^-, Br^- and N^+) of surfactants becomes weaker. On the other hand, the same concentration of CPC/CPB, the weaker interactions cause the smaller ϕ_v^0 and $\phi_v^0(tr)$ of glycylglycine. So, ϕ_v^0 and $\phi_v^0(tr)$ of glycylglycine in aqueous CPB are smaller than in the presence of aqueous CPC.

These can also be explained by using the co-sphere overlap model [25, 26]. In general, the interactions which are expected to occur between glycylglycine and aqueous surfactant solutions can be classified as follows:

1. Hydrophilic–hydrophilic group interactions between NH_3^+ of glycylglycine and Cl^- of $C_{21}H_{38}NCl$/Br- of $C_{21}H_{38}NBr$ and COO^- group of glycylglycine and N^+ of $C_{21}H_{38}NCl/C_{21}H_{38}NBr$.
2. Hydrophilic–hydrophobic group interactions between the polar groups of $C_{21}H_{38}NCl/C_{21}H_{38}NBr$ and peptide group of glycylglycine, and also between zwitterionic centers of glycylglycine and hydrophobic part of $C_{21}H_{38}NCl/C_{21}H_{38}NBr$.
3. Hydrophobic–hydrophobic group interactions between hydrophobic group of glycylglycine and alkyl chain of $C_{21}H_{38}NCl/C_{21}H_{38}NBr$.

The negative values observed are because of the decrease in volume caused by hydrophilic–hydrophobic group and hydrophobic–hydrophobic group interactions. On the other hand, positive values are due to the increase in volume resulting from hydrophilic–hydrophilic group interactions [22, 23]. The positive values of $\phi_v^0(tr)$ in all the cases indicate that hydrophilic–hydrophilic group interactions are dominant over the hydrophilic–hydrophobic/hydrophobic–hydrophobic group interactions in the ternary solutions. The marked increased values of $\phi_v^0(tr)$ with the increase in temperature in both of aqueous surfactants solutions studied are because of the release of some solvent molecules from the loose hydration spheres of the solute in solution [27].

Partial molar volume is a useful property which provides information on solute—solvent interactions. However, its temperature dependence may still be more useful in the study of solvation effects as the intrinsic volume of solute is almost independent of temperature [28, 29]. The ϕ_v^0 data are utilized in estimating the precise values of $\left(\frac{\partial \phi_v^0}{\partial T}\right)_p$ and $\left(\frac{\partial^2 \phi_v^0}{\partial T^2}\right)_p$. The temperature dependence of ϕ_v^0 data has been fitted by least-squares method using the following equation [30],

$$\phi_v^0 = a + bT + cT^2 \tag{5}$$

where a, b and c are constants and T is the temperature. The isobaric expansibility, ϕ_E^0 is obtained by differentiating the above equation with respect to temperature,

$$\phi_E^0 = \left(\frac{d\phi_v^0}{dT}\right)_p = b + 2cT \tag{6}$$

The values of ϕ_E^0 are included in Table 3. With the help of Hepler's reasoning [31], the structure-making and structure-breaking ability of glycylglycine in aqueous CPC/CPB can be explained on the basis of the sign of the second differential of Eq. 6, that gives the heat capacity of the solute at infinite dilution,

$$\left(\frac{\partial \bar{c}_P^0}{\partial p}\right)_T = -T\left(\frac{\partial^2 \phi_v^0}{\partial T^2}\right)_P = -2cT \tag{7}$$

where $\bar{c}_p^0$ is the partial molar heat capacity at infinite dilution. The positive value of $\left(\frac{\partial \bar{c}_P^0}{\partial p}\right)_T$ implies the structure-making, whereas, negative value reflects the structure-breaking ability of the solute. It has been found that the values of $\left(\frac{\partial \bar{c}_P^0}{\partial p}\right)_T$ for glycylglycine are negative in the presence of aqueous CPC and aqueous CPB, indicating that glycylglycine acts as structure-breaker in the presence of both of the surfactants. The ϕ_E^0 values are positive, and the increase with the increase in temperature may be ascribed to the presence of caging effect [32]. On heating, some water molecules may be released from the hydration layer of glycylglycine. The ϕ_E^0 values in aqueous CPC are larger than those in aqueous CPB. This signifies the volume of ternary solutions of CPC increases little more rapidly than that of ternary solutions of CPB with the increase in temperature which results the strong interactions between the glycylglycine–aqueous CPC interactions.

The number of water molecules hydrated, n_H, by the glycylglycine can be estimated from the electrostriction partial molar volume $\phi_v^0(elect)$ [33] by the following equation:

$$n_H = \phi_v^0(elect)/\left(V_e^0 - V_b^0\right) \tag{8}$$

where V_e^0 is the molar volume of electrostricted water and V_b^0 is the molar volume of bulk water. This model assumes that for every water molecule taken from the bulk phase to the region near the peptide, the volume is decreased by $(V_e^0 - V_b^0)$. The value of $(V_e^0 - V_b^0)$ is approximately equal to -3.0 cm^3·mol^{-1} at 298.15 K and -4.0 cm^3·mol^{-1} at 308.15 K [34].

The $\phi_v^0(elect)$ values can be calculated [35, 36] from the standard partial molar volume, ϕ_v^0, of glycylglycine by using the relation:

$$\phi_v^0(elect) = \phi_v^0(glycyl\ glycine) - \phi_v^0(\text{int}) \tag{9}$$

where $\phi_v^0(int)$ is the intrinsic volume of glycylglycine. The $\phi_v^0(int)$ included the two terms: the vander der Waals volume and the volume due to packing effects.

According to Millero et al. [33], $\phi_v^0(int)$ for glycylglycine can be estimated from the crystal molar volume, $\phi_v^0(cryst)$:

$$\phi_v^0(int) = \left(\frac{0.07}{0.634}\right)\phi_v^0(cryst) \tag{10}$$

where 0.07 is the packing density for molecules in organic crystal and 0.634 is the packing density for randomly packed sphere. The $\phi_v^0(cryst)$ can be evaluated using the following relation:

$$\phi_v^0(cryst) = \frac{M}{\rho(cryst)} \tag{11}$$

where $\rho(cryst)$ is the crystal density of glycylglycine which is 1.534 g·cm^{-3} [34] at 298.15 K. Since crystal density has a very small change with temperature, we assume the $\rho(cryst)$ value at 308.15 K is approximately equal to the value at 298.15 K. The computed hydration numbers are presented in Table 3. The charged end groups of peptides have strong hydration ability. The hydration mainly arises from the electrostriction effect of the charged end/peptide bond groups of glycylglycine on water. Table 3 shows that n_H values for glycylglycine in both of aqueous surfactants are less than those of in water. This suggests that the interaction between ions of surfactants and the charged end/peptide bond groups is stronger and the electrostriction of water caused by the charged end/peptide bond groups of glycylglycine is largely reduced in the presence of surfactants, which results in the decrease in n_H. The n_H values of glycylglycine in the presence of aqueous CPC are less than in aqueous CPB indicating that interaction between ions of surfactants and the charged end/peptide bond groups is stronger in the presence of CPC than that of CPB. This is consistent with the observed values of $\phi_v{}^\circ$ and $\phi_v^0(tr)$.

3.2 Ultrasonic Study

The experimental density data and ultrasonic speed data were combined to calculate adiabatic compressibilities, β, using the Laplace equation:

$$\beta = u^{-2}\rho^{-1} \tag{12}$$

where ρ is the solution density and u is the sound speed of the solution. The apparent molal adiabatic compressibility ϕ_K of the solutions was determined from the relation:

$$\phi_K = \frac{M\beta}{\rho_0} + \frac{1000(\beta\rho_0 - \beta_0\rho)}{m\rho\rho_0} \tag{13}$$

where β_0 and β are the adiabatic compressibilities of solvent and solution, respectively, and m is the molality of the solution. The apparent molal adiabatic compressibility ϕ_K values are presented in Table 2 and its variation with molality is represented in (Fig. 2a, b). The limiting partial molal adiabatic compressibility ϕ_K^0 and the experimental slope S_K^* were determined by fitting ϕ_K against the molality of glycylglycine and were estimated by the following equation:

$$\phi_K = \phi_K^0 + S_K^* m \tag{14}$$

The compressibility behavior of solutes in solution presents the information concerning the solute–solvent and solute–solute interactions. The infinite dilution partial molal adiabatic compressibilities are, by definition, independent of solute–solute interactions and thus determined only by respective intrinsic value and the solute–solvent interactions. Accordingly, they can be used to examine solute–solvent interactions [37]. The slope S_K^* can be assumed to be an indicator of solute–solute interactions. The values of ϕ_K^0 and S_K^* are given in Table 3. The values of ϕ_K^0 (Table 3) are negative in both of aqueous surfactant solutions suggesting strong solute–solvent interactions.

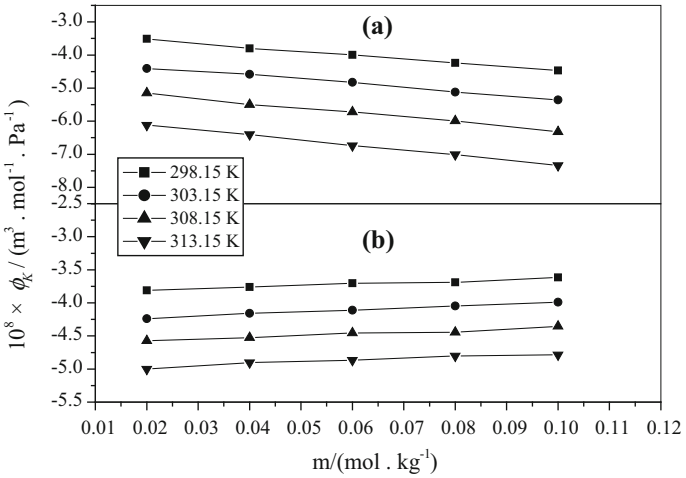

Fig. 2 Plot of partial molal adiabatic compressibility (ϕ_K), against molal concentration (m) of glycylglycine in (a) aqueous CPC and (b) aqueous CPB at different temperatures

However, ϕ_K^0 values in the presence of aqueous CPC are more negative than in the presence of aqueous CPB indicating strong glycylglycine–CPC interaction which supports our $\phi_v{}^\circ$, $\phi_v^0(tr)$ and Λ_m^0 data.

The limiting partial molal adiabatic compressibility ϕ_K^0 can also be represented as the sum of intrinsic and hydration contributions [38]:

$$\phi_K^0 = K_M + \Delta K_h = K_M + n_H\left(K_h^o - K_0^o\right) \tag{15}$$

where K_{M} is the intrinsic compressibility of the solute molecules; ΔK_{h} is the compressibility effect of hydration; K_0^{o} and $K_{\mathrm{h}}^{\mathrm{o}}$ are the partial molal adiabatic compressibilities of water in the bulk state and in the hydration shell of the solute, respectively; and n_{H} the "hydration number" is the number of water molecules with in the hydration shell of a solute.

For low molecular weight substances, the intrinsic compressibility term, K_{M}, in Eq. 15, is negligibly small since it is determined by the compressibilities of covalent bonds and external electron shells, which are close to zero [38]. Thus, the limiting partial molal adiabatic compressibility, ϕ_K^0, of low molecular weight substances primarily reflects solvents hydration changes as reflected by the reduced form of Eq. 15.

$$\phi_K^0 = n_H\left(K_h^o - K_0^o\right) \tag{16}$$

Since ϕ_K^0 for glycylglycine is less negative in the presence of aqueous CPB than aqueous CPC suggesting glycylglycine is more hydrated in the presence of aqueous CPB.

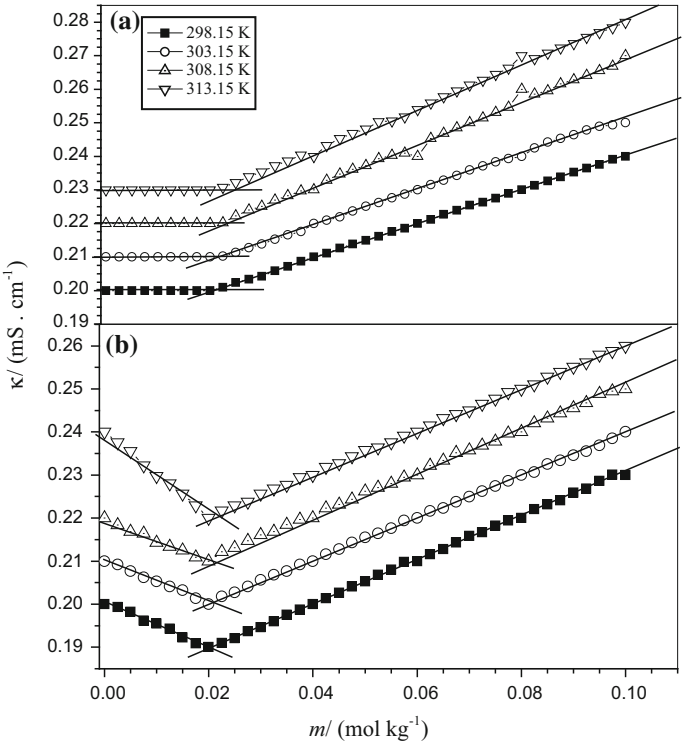

Fig. 3 Plots of specific conductivity (κ), against molal concentration (m) of glycylglycine in (a) aqueous CPC and (b) aqueous CPB at different temperatures

3.3 Conductometric Study

Surfactant–amino acid interactions are very essential in the view point of biotechnological and biopharmaceutical formulations. In the pre-micellar and post-micellar regions, the specific conductivity (k) is linearly correlated to the concentrations of the studied surfactants. The specific conductance of the mixtures of the glycylglycine + aqueous CPC and glycylglycine + aqueous CPB was measured at temperature 298.15 K, 303.15 K, 308.15 K and 313.15 K. The plot of specific conductance vs concentrations of CPC and CPB in aqueous medium of glycylglycine at different temperatures 298.15 K, 303.15 K, 308.15 K and 313.15 K is illustrated in Fig. 3, and the cmc values of two systems, glycylglycine + aqueous CPC and glycylglycine + aqueous CPB are presented in Table 1. These cmc values were acquired from the intersection point of the two straight lines of the conductivity versus concentration above and below the break points. The specific conductivity (k)-CPC/CPB concentrations plots give a clear change from the pre-micellar to the post-micellar regions with growing number of non-aggregated micelles in the pre-micellar region and at the break point the aggregation process starts in the post-micellar regions. The plot of specific conductivity vs surfactant concentrations (CPC, CPB) in the presence of glycylglycine gives two straight lines with a higher slope in pre-micellar region and

lower slope value in the post-micellar region due to change in the specific conductivity of the studied systems. The plots clearly show an abrupt change in specific conductivity (κ) over a narrow concentration range, termed as the critical micelle concentration (cmc). It is well know that at below cmc, the amphiphilic molecules are unassociated and obey Debye–Huckel–Onsager equation [39, 40] while above the cmc the surfactant molecules aggregate and form micelles [41, 42]. The CPB + glycylglycine mixtures show decreased values of cmc than CPC + glycylglycine at different temperatures. It is recognized that micellization significantly depends on the nature of the medium and on the concentrations of additives, if any. On addition of glycylglycine, a structure-breaker molecule results the destruction in the equilibrium, established between the water molecules and in ions of CPC and CPB molecules. Glycylglycine molecules in surfactant solutions result the more disruption of H-bond associates in water molecules of CPC molecules than in CPB molecules. The distorted H-bond associates surround the hydrophobic head groups of the surfactant molecules, and this disfavors micellization, thereby, and an increase in cmc values of the CPC + glycylglycine is examined than in CPB + glycylglycine mixtures. One more convenient fact to inspect the increase in cmc values of CPC + glycylglycine mixtures is because of the pyridinium head groups of CPC and CPB molecules. These head groups act as chaotrope because of their large surface area and low charge density [43]. In the present study, the counterion Cl^- is more kosmotropic than Br^- ions, therefore, Cl^- are strongly associated with pyridinium head groups than Br^- ions which are weakly binded, resulting in the higher cmc values of CPC than CPB solutions.

It is apparent from Fig. 3, the cmc values increase with the increase in temperature. The effect of temperature on the magnitude of cmc values of surfactant is generally analyzed due to the presence of different components present in the mixtures. It is convenient that at higher temperatures the thermal motion increases which results the demicellization owing to the distraction of the palisade layer of the micelle, which subsequently enhances the cmc of the surfactants [44]. This is because of the facts that at increasing temperature high solubility of hydrocarbon stabilizes the surfactant monomers and, therefore, micelle formation is hindered, results the higher cmc of CPC and CPB. From Table 1, an increase in cmc values with increasing temperature is possibly due to the other factors such as ion–hydrophobic interactions have capability of forming the close packed ion pairs of CPC and CPB together with the charged end/peptide bond groups of glycylglycine. By utilizing the conductance data, the limiting molar conductance Λ_m^0 for glycylglycine in aqueous CPC and CPB systems has been measured. The values were acquired by extrapolating the linear plots of molar conductance, Λ_m versus $m^{1/2}$ to zero concentration. Table 3 presents the values of Λ_m^0 for glycylglycine in aqueous surfactant solutions at different temperatures. The Λ_m^0 has been observed as a measure of glycylglycine–surfactant/water interactions [45]. The greater the value of limiting molar conductance, Λ_m^0, greater is the interaction between the components of the mixtures. The positive values of Λ_m^0 (Table 3) of glycylglycine in aqueous CPC and CPB solutions show that glycylglycine–surfactant interactions are stronger and its value increases with the increase in temperature. The Λ_m^0 values for glycylglycine in aqueous CPC are larger than that in the presence of aqueous CPB

indicating that the interaction between glycylglycine and CPC/water is stronger than of glycylglycine–CPB/water interactions.

4 Conclusions

The densities, ultrasonic speeds and specific conductivities of glycylglycine in aqueous CPC and aqueous CPB solutions were measured at different temperatures. Using the experimental results, various parameters were calculated. The results indicate that the behavior of glycylglycine in aqueous CPC and aqueous CPB solution is a temperature-dependent property. A quantitative comparison of the magnitude of ϕ_v^0 and ϕ_E^0 values indicates that for glycylglycine in the presence of aqueous CPC is higher than in the presence of aqueous CPB suggesting greater solute–solvent interaction in the presence of CPC than in the presence of CPB. The n_H values of glycylglycine in the presence of aqueous CPC are less than in aqueous CPB indicating that interaction between ions of surfactants and the charged end/peptide bond groups is stronger in the presence of CPC than that of CPB. This is consistent with the observed values of $\phi_v{}^\circ$ and $\phi_v^0(tr)$. Glycylglycine shows the structure-breaker properties in both the solvent system at the temperatures studied from 298.15 K to 313.15 K. The compressibility behavior of solutes in solution can provide information concerning solute–solvent and solute—solute interactions. Similar information was reported by conductometric study which indicates that the interaction between glycylglycine–CPC/water is stronger than of glycylglycine–CPB/water interactions. The micellization of glycylglycine in aqueous CPC and CPB solutions reveals that both hydrophobic and hydrophilic interactions are the binding forces among CPC/CPB molecules and between amino acids and surfactant.

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