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# Physicochemical and friccohesity study of glycine, L-alanine and L-phenylalanine with aqueous methyltrioctylammonium and cetylpyridinium chloride from $T = (293.15 \text{ to } 308.15) \text{ K}$



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## ABSTRACT

Density  $\rho$ , sound velocity  $u$ , viscosity  $\eta$ , apparent molar volume  $V_\phi$ , isentropic compressibility  $\kappa_s$ , and apparent molar isentropic compressibility  $\kappa_{s,\phi}$  of glycine, L-alanine and L-phenylalanine: (0.05 to 0.15 mol · kg<sup>-1</sup>) with water, 0.002 mol · kg<sup>-1</sup> aqueous methyltrioctylammonium chloride (MTOAC) and cetylpyridinium chloride (CPC) are reported at  $T = (293.15, 298.15, 303.15 \text{ and } 308.15) \text{ K}$ . The data were regressed against composition and regression constants: apparent molar volume at infinite dilution  $V_\phi^0$ , apparent molar isentropic compressibility at infinite dilution  $\kappa_{s,\phi}^0$  and viscosity B-coefficient are studied. Surface tension  $\gamma$  and friccohesity  $\sigma$  data were calculated from density, pendant drop number and viscous flow time. The  $V_\phi^0$  values are found as  $V_{\phi(\text{gly,l-phal with water})}^0 < V_{\phi(\text{gly,l-phal with surfactant})}^0$ ,  $V_{\phi(\text{l-ala with surfactant})}^0 < V_{\phi(\text{l-ala with water})}^0$  and  $\kappa_{s,\phi}^0$  values as  $\kappa_{\phi(\text{gly,l-phal with water})}^0 < \kappa_{\phi(\text{gly,l-phal with surfactant})}^0$ ,  $\kappa_{\phi(\text{l-ala with surfactant})}^0 < \kappa_{\phi(\text{l-ala with water})}^0$ . Surface tension of the solvents are found as water > CPC > MTOAC. Amino acids with surfactants have produced higher friccohesity than with water whereas the friccohesity of amino acids with water and surfactants is found as l-phal > l-Ala > gly over the entire temperature range but with CPC at  $T = 298.15 \text{ K}$ , the order is l-phal > gly > l-Ala. The variations in physicochemical data with temperature and composition inferred structural changes with stronger solute–solvent interactions.

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## 1. Introduction

Currently, emphasis on harnessing the potential of an individual molecule is being considered as the most challenging and fascinating research area where temperature and chemical additives induced structures are of utmost importance. Many publications on the structural and dynamical properties of proteins are available in the literature, despite this; their thermodynamic properties in solutions remain unclear and needs further exploration [1–3]. Interactions of protein with functional molecules such as surfactant are of great interest for retrieval of the factors responsible for their structural changes. The study of structural interactions of protein through physicochemical inductions remains a challenging and tedious task considering their complex conformational and configurational 3D structures. The complexity associated with this task could be simplified by performing behavioural analysis with amino acids being the basic structural units of protein. The side chains of amino acids differ in size, shape, charge,

hydrogen-bonding capacity, hydrophobicity and chemical reactivity which control the structures and functions of a protein [4]. Thermodynamic properties of the amino acid side chain can be easily derived and a possibility of the additive effects of the chemical additives could be checked to estimate the properties of structurally complicated molecules in solution, such as unfolded proteins [5,6]. Because of an extensive use of surfactants in pharmaceutical and biotechnological processes such as drug delivery vehicles, emulsifiers, nanoemulsions, de-emulsifiers, wetting and foaming agents as well as in *in vivo* studies, the interaction of the protein with surfactants could be of critical significance [7–9]. Thus it becomes essential to study interactions between the amino acid and the surfactant where the data could hold computational significance for simulating behaviour of targeted proteins. Studies on physicochemical properties (PCP) could reveal valuable information on proteins stability based on amino acid interactions [10–12] in aqueous environment for biophysical processes [13–15]. Thus, efforts have been made to examine the effects of temperature and additives on interacting activities of basic unit of protein with aqueous surfactants. Thus, the effects of temperature and cationic surfactants (MTOAC and CPC) on glycine (Gly), L-alanine (L-Ala) and L-phenylalanine (L-Phe) have been chosen for study. The data obtained could throw light on the structural reorientations

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**TABLE 1**

Provenance and purity of the amino acids and cationic surfactants studied in this work.

Name	Mol. Formula	Mass fraction	Source	CAS No.
Glycine	C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>	≥0.98	Sigma	56-40-6
L-Alanine	C <sub>3</sub> H <sub>7</sub> NO <sub>2</sub>	≥0.98	Sigma	56-41-7
L-Phenylalanine	C <sub>9</sub> H <sub>11</sub> NO <sub>2</sub>	≥0.98	Sigma	63-91-2
Methyltrioctylammonium chloride	C <sub>25</sub> H <sub>54</sub> ClN	≥ 0.97	Sigma	5137-55-3
Cetylpyridinium chloride	C <sub>21</sub> H <sub>38</sub> ClN · H <sub>2</sub> O	USP Specification	Sigma	6004-24-6

**TABLE 2**Density ( $\rho$ ), viscosity ( $\eta$ ) and speed of sound ( $u$ ) of water and aqueous cationic surfactant at  $T = (293.15, 298.15, 303.15$  and  $308.15)$  K.

T/K	293.15	298.15	303.15	308.15
		$\rho \cdot 10^3 / \text{kg} \cdot \text{m}^{-3}$		
Water	0.998587	0.997425	0.996040	0.994425
MTOAC	0.998540	0.997375	0.995978	0.994348
CPC	0.998567	0.997407	0.996012	0.994387
		$\eta / 10^{-3} \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$		
Water	1.0020	0.8937	0.8001	0.7225
MTOAC	1.0430	0.9291	0.8195	0.7465
CPC	1.0039	0.9033	0.8137	0.7557
		$u / \text{m} \cdot \text{s}^{-1}$		
Water	1482.57	1496.58	1509.01	1519.54
MTOAC	1483.37	1497.31	1510.67	1520.15
CPC	1483.10	1497.19	1509.41	1519.79

Standard uncertainty: in temperature  $u(T) = \pm 0.01$  K, in density  $u(\rho) = \pm 2 \cdot 10^{-2} \text{ kg} \cdot \text{m}^{-3}$  and in speed of sound  $u(u) = \pm 1 \cdot 10^{-1} \text{ m} \cdot \text{s}^{-1}$ . The combined expanded uncertainty ( $k = 2$ ) for density  $U_c(\rho) = \pm 4 \cdot 10^{-2} \text{ kg} \cdot \text{m}^{-3}$ , speed of sound  $U_c(u) = \pm 2 \cdot 10^{-1} \text{ m} \cdot \text{s}^{-1}$  and  $U_c(\eta) = 2 \cdot 10^{-6} \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$ .

in protein caused by thermal energy and chemical environmental changes to elucidate changes in peptide bonds modelled as intramolecular multiple force theory (IMMFT). Proteins with peptide bonds undergo reorientation due to induced chemical and physical environment on dissolution. The peptide units have interacting domains acting as molecular force factors (MFF) with individual electrostatic forces confined and aligned based on Boltzmann energy distribution concept with certain intramolecular entropy (tentropy) because proteins having several interacting domains act as gradients that cause an effective environment facilitating the protein activity. Thus, the protein molecule acts as a significant interacting moiety involving dipole–dipole, dipole–induced dipole interactions, van der Waals forces, London dispersive forces and hydrogen bonding which, in protein moiety, is integrated as IMMFT. Considering the above mentioned facts, we hereby report the apparent molar volume, apparent molar isentropic compressibility, relative viscosity, surface tension and friccohesity of amino acids in aqueous cationic surfactants. To the best of our knowledge, a detailed study on interacting activities of the chosen amino acids with MTOAC and CPC at these temperatures has not yet been reported. However, Singh *et al.* [16,17] have reported volumetric properties of Gly and L-Ala in aqueous sodium dodecyl sulphate (SDS) at  $T = 298.15$  K. So, there is an urgent need to initiate an advanced understanding of protein interaction dynamics with several

surfactants using physicochemical inputs [18,19]. The regression data of mixtures have permitted the retrieval of critical information on the role of hydrophobic and hydrophilic interactions for the behaviour of biomolecules with MTOAC and CPC. Thus, the molecular structures develop critical solute–solute and solute–solvent interactions influenced by composition and temperature, which could be extended further to specified applications in the field of solution and biochemistry.

## 2. Experimental

### 2.1. Materials and methods

Table 1 contains name, molecular formula, mass fraction purity, CAS no. and source of chemicals used. Gly (R=H), L-Ala (R=CH<sub>3</sub>), L-Phe (R=CH<sub>2</sub>–C<sub>6</sub>H<sub>5</sub>), MTOAC and CPC were used as received and were stored in P<sub>2</sub>O<sub>5</sub> filled vacuum desiccator. Their water contents were checked with anhydrous CuSO<sub>4</sub> which did not furnish blue colour with pinch of the chemicals. Molal solutions were prepared using Mettler Toledo New Classic MS with  $\pm 0.0001$  g precision. Millipore water of  $5 \cdot 10^{-6} \text{ S} \cdot \text{cm}^{-1}$  was used for solutions with  $\pm 2 \cdot 10^{-5} \text{ mol} \cdot \text{kg}^{-1}$  uncertainty in solution concentration. Solutions of (0.0502 to 0.1515) mol · kg<sup>-1</sup> Gly, (0.0503 to

**TABLE 3**Comparison table of density of water with literature values at  $T = (293.15, 298.15, 303.15$  and  $308.15)$  K.

T/K	$\rho / \text{g} \cdot \text{cm}^{-3}$		$\Delta \rho = \text{Exp.} - \text{Lit.} \Delta \rho / \text{g} \cdot \text{cm}^{-3}$	Percentage error %
	Experimental values	Literature values		
293.15	0.998587	0.998260 <sup>a</sup>	0.000327	0.032
298.15	0.997425	0.997100 <sup>b</sup>	0.000325	0.032
303.15	0.996040	0.995700 <sup>a</sup>	0.000340	0.034
308.15	0.994425	0.994100 <sup>c</sup>	0.000325	0.032

<sup>a</sup> Ref. [32].<sup>b</sup> Ref. [33].<sup>c</sup> Ref. [34].

**TABLE 4**

Apparent molar volumes at infinite dilution ( $V_{\phi}^0$ ) and slope ( $S_{\nu}$ ) of glycine, L-alanine and L-phenylalanine with water and aqueous 0.002 mol · kg<sup>-1</sup> surfactant solutions at  $T = (293.15, 298.15, 303.15 \text{ and } 308.15) \text{ K}$ .

T/K	Water		MTOAC		CPC		
	$V_{\phi}^0/10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$	$S_{\nu}/10^{-6} \text{ kg} \cdot \text{m}^{-3} \cdot \text{mol}^{-2}$	$V_{\phi}^0/10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$	$S_{\nu}/10^{-6} \text{ kg} \cdot \text{m}^{-3} \cdot \text{mol}^{-2}$	$V_{\phi}^0/10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$	$S_{\nu}/10^{-6} \text{ kg} \cdot \text{m}^{-3} \cdot \text{mol}^{-2}$	
	Lit <sup>a</sup>	Exp					
	<i>Glycine</i>						
293.15	42.8	42.75	3.64	43.06	2.26	44.53	-1.37
298.15	43.18	43.17	2.73	43.44	2.25	44.24	-1.35
303.15	43.89	43.84	0.77	44.14	-1.45	45.16	-1.35
308.15	43.9	43.98	1.96	44.23	-1.22	45.19	-1.35
	<i>L-Alanine</i>						
293.15	60.55	60.55	-0.41	60.1	3.17	59.63	7.1
298.15	60.48	60.76	0.63	60.31	2.98	59.76	8.23
303.15	60.63	61.13	-0.61	60.64	1.6	60.07	6.82
308.15	61.27	61.52	-1.9	60.98	0.55	60.29	6.96
	<i>L-Phenylalanine</i>						
293.15	117.14	120.3	5.01	121.21	3.14	120.92	-0.32
298.15	121.8	121.26	2.69	121.66	4.44	121.85	-2.6
303.15	119.52	122.18	1.47	122.85	0.07	122.47	-1.34
308.15	122.82	122.96	0.97	123.35	0.51	123.22	-2.84

The combined expanded uncertainty ( $k = 2$ ) for partial apparent volume  $U_c(V_{\phi}^0) = \pm 8 \cdot 10^{-8} \text{ m}^3 \cdot \text{mol}^{-1}$  and for slope  $U_c(S_{\nu}) = \pm 0.37 \cdot 10^{-6} \text{ kg} \cdot \text{m}^{-3} \cdot \text{mol}^{-2}$ .

<sup>a</sup> Ref. [9].

**TABLE 5**

Apparent molar isentropic compressibility at infinite dilution ( $\kappa_{s,\phi}^0/10^{12} \text{ m}^5 \cdot \text{N}^{-1} \cdot \text{mol}^{-1}$ ) and ( $S_k/10^{12} \text{ m}^4 \cdot \text{kg} \cdot \text{s}^2 \cdot \text{mol}^{-2}$ ) of amino acids with water and with aq. 0.002 mol · kg<sup>-1</sup> cationic surfactant at  $T = (293.15, 298.15, 303.15 \text{ and } 308.15) \text{ K}$ .

T/K	Water		MTOAC		CPC	
	$\kappa_{s,\phi}^0/10^{12} \text{ m}^5 \cdot \text{N}^{-1} \cdot \text{mol}^{-1}$	$S_k/10^{12} \text{ m}^4 \cdot \text{kg} \cdot \text{s}^2 \cdot \text{mol}^{-2}$	$\kappa_{s,\phi}^0/10^{12} \text{ m}^5 \cdot \text{N}^{-1} \cdot \text{mol}^{-1}$	$S_k/10^{12} \text{ m}^4 \cdot \text{kg} \cdot \text{s}^2 \cdot \text{mol}^{-2}$	$\kappa_{s,\phi}^0/10^{12} \text{ m}^5 \cdot \text{N}^{-1} \cdot \text{mol}^{-1}$	$S_k/10^{12} \text{ m}^4 \cdot \text{kg} \cdot \text{s}^2 \cdot \text{mol}^{-2}$
	<i>Glycine</i>					
293.15	-29.34	3.59	-29.13	2.80	-27.64	-1.14
298.15	-28.97	3.14	-28.74	3.05	-27.9	-1.12
303.15	-28.27	0.98	-27.97	-1.31	-26.92	-1.67
308.15	-28.18	2.57	-27.74	-0.74	-27.00	-0.63
	<i>L-Alanine</i>					
293.15	-26.72	-0.56	-27.11	-2.54	-27.53	6.15
298.15	-26.48	0.32	-26.88	2.18	-27.41	7.28
303.15	-26.13	-0.82	-26.61	1.25	-27.12	6.01
308.15	-25.80	-1.81	-26.32	0.22	-26.92	5.81
	<i>L-Phenylalanine</i>					
293.15	-40.05	5.63	-39.07	3.19	-39.31	-0.21
298.15	-39.10	3.41	-38.75	5.30	-38.43	-2.14
303.15	-38.16	1.95	-37.39	-0.24	-37.87	-0.50
308.15	-37.44	-0.05	-36.96	0.53	-37.10	-2.34

0.1519) mol · kg<sup>-1</sup> L-Ala and (0.0505 to 0.1532) mol · kg<sup>-1</sup> L-Phe were prepared with water and with 0.002 mol · kg<sup>-1</sup> aqueous MTOAC and CPC.

## 2.2. Experimental measurements

Densities and sound velocities were obtained with Anton Paar DSA 5000 M densimeter. The temperature inside the densimeter was controlled to  $\pm 1 \cdot 10^{-3} \text{ K}$ , built-in Peltier device. The sensitivity of the instrument corresponds to a precision in density and sound velocity measurements of  $1 \cdot 10^{-2} \text{ kg} \cdot \text{m}^{-3}$  and  $1 \cdot 10^{-2} \text{ m} \cdot \text{s}^{-1}$ . The combined expanded uncertainties ( $k = 2$ ) for density and sound velocity are  $\pm 4 \cdot 10^{-2} \text{ kg} \cdot \text{m}^{-3}$  and  $\pm 2 \cdot 10^{-1} \text{ m} \cdot \text{s}^{-1}$  respectively. The densimeter was calibrated with Millipore water and the densities are an average of three independent measurements reproducible to  $\pm 0.02 \text{ kg} \cdot \text{m}^{-3}$ . The density and sound velocity of water, aqueous surfactants along with their standard deviations are listed in table 2. Viscosity, surface tension and friccohesity were measured with Borosil Mansingh Survismeter [20](cal.no. 06070582/1.01/

C-0395, NPL, India) by flow time and pendant drop methods controlled by the Lauda Alpha KA 8 thermostat with  $\pm 0.05 \text{ K}$  control. After attainment of thermal equilibrium, viscous flow times were recorded with  $\pm 0.1 \text{ s}$  uncertainty. Viscosity and surface tension are an average of three replicate measurements with  $\pm 2 \cdot 10^{-6} \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$  and  $\pm 0.03 \text{ m} \cdot \text{Nm}^{-1}$  uncertainties in viscosity and surface tension respectively. The difference in densities of water from the literature are found as  $(3.27 \cdot 10^{-4}, 3.25 \cdot 10^{-4}, 3.40 \cdot 10^{-4}, \text{ and } 3.25 \cdot 10^{-4}) \text{ g} \cdot \text{cm}^{-3}$  at  $T = (293.15, 298.15, 303.15 \text{ and } 308.15) \text{ K}$  respectively, reported in table 3 with  $\pm 0.032\%$  deviation from the literature values covered within 95.5% CV.

## 3. Results and discussion

### 3.1. Density and speed of sound

Limiting densities  $\rho^0$  are given in table S1 (SI) (Supporting Information File) while F1–F9 (SI) illustrated, density increased with concentration but decreased with temperature. In general, from

**TABLE 6**

Relative viscosity ( $\eta_r$ ) of glycine, L-alanine and L-phenylalanine with water, 0.002 mol · kg<sup>-1</sup> aq. MTOAC and CPC solutions at T = (293.15, 298.15, 303.15 and 308.15) K.

m/mol · kg <sup>-1</sup>	293.15 $\eta_r$	298.15 $\eta_r$	303.15 $\eta_r$	308.15 $\eta_r$
<i>Glycine with Water</i>				
0.0502	1.0067	1.0064	1.0071	1.0076
0.0755	1.0103	1.0095	1.0104	1.0116
0.1007	1.0136	1.0135	1.0142	1.0147
0.1261	1.0173	1.0168	1.0181	1.0191
0.1514	1.0208	1.0213	1.0211	1.0223
<i>L-Alanine with Water</i>				
0.0503	1.0109	1.0117	1.0112	1.0191
0.0755	1.0163	1.0254	1.0121	1.0233
0.1009	1.0218	1.0375	1.0211	1.0307
0.1263	1.0267	1.0386	1.0314	1.037
0.1518	1.0327	1.0418	1.0392	1.0421
<i>L-Phenylalanine with Water</i>				
0.0505	1.021	1.03	1.032	1.0251
0.0759	1.0352	1.049	1.0459	1.0439
0.1015	1.0527	1.06	1.0584	1.0527
0.1273	1.0677	1.0763	1.0735	1.0608
0.1532	1.0782	1.0924	1.0896	1.0858
<i>Glycine with 0.002 mol · kg<sup>-1</sup> MTOAC</i>				
0.0502	1.004	1.0028	1.0095	1.0059
0.0755	1.0174	1.0112	1.0131	1.0126
0.1007	1.0259	1.0143	1.0156	1.0166
0.1261	1.0346	1.0217	1.0259	1.0184
0.1514	1.0457	1.0251	1.027	1.0259
<i>L-Alanine with 0.002 mol · kg<sup>-1</sup> MTOAC</i>				
0.0503	1.0103	1.0178	1.0033	1.0119
0.0756	1.0352	1.0221	1.0127	1.0189
0.1009	1.0394	1.0307	1.0149	1.0218
0.1263	1.0469	1.0327	1.0257	1.0319
0.1519	1.0601	1.0441	1.0292	1.0423
<i>L-Phenylalanine with 0.002 mol · kg<sup>-1</sup> MTOAC</i>				
0.0505	1.0215	1.0259	1.0226	1.0174
0.0759	1.0405	1.0381	1.0333	1.0244
0.1015	1.0533	1.049	1.0411	1.0348
0.1273	1.0621	1.0595	1.0606	1.0451
0.1532	1.0761	1.0713	1.0683	1.0584
<i>Glycine with 0.002 mol · kg<sup>-1</sup> CPC</i>				
0.0502	1.008	1.006	1.0004	1.0045
0.0755	1.011	1.0147	1.0016	1.0054
0.1007	1.0139	1.0237	1.0098	1.0066
0.1261	1.0197	1.0281	1.0246	1.0196
0.1515	1.0309	1.0401	1.0297	1.0249
<i>L-Alanine with 0.002 mol · kg<sup>-1</sup> CPC</i>				
0.0504	1.0157	1.0218	1.024	1.0232
0.0756	1.0273	1.0235	1.0274	1.0339
0.1008	1.0308	1.0265	1.0363	1.032
0.1264	1.0571	1.0306	1.0431	1.024
0.1518	1.0642	1.0486	1.0451	1.0249
<i>L-Phenylalanine with 0.002 mol · kg<sup>-1</sup> CPC</i>				
0.0505	1.01	1.0386	1.0258	1.0003
0.0759	1.0174	1.0373	1.0457	1.0114
0.1015	1.0412	1.0557	1.0551	1.0312
0.1273	1.0409	1.0758	1.066	1.0365
0.1532	1.0427	1.068	1.0761	1.0434

T = (293.15 to 298.15, 298.15 to 303.15 and 303.15 to 308.15) K, the  $\rho^0$  values decreased by 0.12%, 0.14% and 0.16% respectively. Dipoles, dipole moment, ionic charge, electronegativity or polarizability causes dipole–dipole, ion–dipole, dipole–induced dipole interactions, hydrogen bonding, van der Waals forces, Lorenz forces, London dispersion force and Columbic force to equilibrate the energy and referred as intermolecular forces (IMF). The IMF operative within the solvent molecules is depicted as a cohesive force (CF) whose nature and strength changes with addition of solute because new IMF (between solute and solvent) is developed

with change in density. Thus, zwitterionic amino acid, having certain electronegative atoms, develops interactions and in turns strengthens the IMF. Hence, IMF seems to be a fundamental driving force, stronger is the IMF; greater is the internal pressure with higher density. This led to propose two interacting models numbered 1 and 2.

SENF = More SEPS + SIP = SMI

= Higher Density and Lower AMV. (1)

SENF = stronger electronegative force, SEPS = shared electron pair shift, SIP = stronger internal pressure, SMI = stronger molecular interaction, AMV = apparent molar volume.

WENF = Less SEPS + WIP = WMI

= Lower Density and Higher AMV. (2)

WENF = weaker electronegative force, WIP = weaker internal pressure, WMI = weaker molecular interaction. Lorenz forces, van der Waals forces, London forces etc. are dispersive in nature because during interactions, reorientation and redistribution of electron clouds occur in hydrophobic part of surfactants to get dispersed over the whole alkyl chain and can not critically express the IMF. Columbic forces are developed due to polarization and electrostatic charges that critically define the intermolecular interaction as shown by equation (3) [21].

$$IMF = \pm(F_{H_2O} - F_{aa}) = \pm \frac{1}{4\pi\epsilon_0} \left[ \frac{q_{OH^-}q_H^+}{r_{H_2O}^2} - \frac{q_{COO^-}q_{NH_3^+}}{r_{aa}^2} \right]. \quad (3)$$

In general, on increasing amino acid concentration by 0.025 mol · kg<sup>-1</sup>, density increased by 0.079%, 0.071% and 0.109% with water; 0.083%, 0.071% and 0.107% with MTOAC and 0.083%, 0.070% and 0.118% with CPC for Gly, L-Ala and L-Phe respectively. Hence the strength of IMF is of a different strength for a given amino acid, greatly influenced by their side chain and might be quantitatively obtained by developing a computational model using equation (3). The limiting sound velocities  $u^0$  are given in table S2 (SI). Figures F1a–1i (SI) depict an increase in sound velocities with increase in concentration and temperature. An increase in density on strengthening the IMF on getting the solute and solvent to come closer with greater kinetic energy transfer that increases the sound velocity with increase in concentration. On a rise in temperature, molecules acquire more energy with greater vibration

**TABLE 7**

B-coefficients (B) of glycine, L-alanine and L-phenylalanine with water and with cationic surfactants MTOAC and CPC at T = (293.15, 298.15, 303.15 and 308.15) K.

T/K	Water		MTOAC B/kg · mol <sup>-1</sup>	CPC B/kg · mol <sup>-1</sup>
	B/kg · mol <sup>-1</sup>	Exp		
<i>Glycine</i>				
293.15	0.1339	0.1389	0.3975	0.2158
298.15	0.1430	0.1464	0.2178	0.3225
303.15	0.1370	0.1413	0.1886	0.3231
308.15	0.1466	0.1455	0.1805	0.2171
<i>L-Alanine</i>				
293.15		0.2135	0.4388	0.5032
298.15	0.2520	0.2477	0.2498	0.2392
303.15	0.2460	0.2907	0.2553	0.2285
308.15	0.2363	0.2351	0.2909	-0.0257
<i>L-Phenylalanine</i>				
293.15		0.5723	0.5098	0.3463
298.15	0.5850	0.5926	0.4363	0.3784
303.15		0.5564	0.4629	0.4702
308.15		0.5391	0.4003	0.4336

<sup>a</sup> Ref. [33].

causing faster sound wave propagation which subsequently increases the sound velocity. The slopes for density are steeper than for sound velocity (Figures F1–F9) (SI). The less steep slope for sound velocity is due to acoustic resonance of acoustic system which absorbs more energy on increasing the solute concentration and thus, reducing the impact of concentration on sound velocity. The ratio of slope and limiting values for density and sound velocity is 0.03 indicating the strength of the solute–solvent interaction which is also similarly depicted with  $\rho^0$  and  $u^0$  values. The sound velocity of solvents is as MTOAC > CPC > Water. MTOAC with three octyl chains retracts the surrounding structured water to a greater extent than CPC with a single cetyl chain due to their larger hydrophobic domain. Thus, MTOAC develops a weaker IMF with water with a lower density and higher sound velocity than CPC. Probably the hydrophobic groups in surfactants are responsible for their weaker IMF with water with lower density and higher sound velocity than water. The  $\rho^0$  values with water and surfactants (table 3) are in the sequence as L-Phe > Gly > L-Ala (with water), L-Phe > L-Ala > Gly (with MTOAC) and L-Ala > L-Phe > Gly (with CPC). Due to the temperature effect, the trend for  $u^0$  is the reverse of  $\rho^0$ . It seems that the electrostriction at the polar heads of Gly zwitterion cause higher IMF than for L-Ala, since the latter is more hydrophobic than Gly, leads to a higher  $\rho^0$  value of Gly than L-Ala with water. The hydrophobic–hydrophobic interaction of L-Ala is stronger than Gly (no hydrophobic group) with MTOAC leading to a higher  $\rho^0$  value of L-Ala than Gly with MTOAC. For L-Phe, the  $C_6H_5CH_2^-$  group and its high molar mass lead to its highest  $\rho^0$  values with water and MTOAC. L-Ala, with its smaller size and strong (+I) methyl group forms stronger hydrophobic–hydrophobic interaction with CPC than L-Phe leading to its higher  $\rho^0$  value than L-Phe.

### 3.2. Apparent molar volume at infinite dilution and transfer volume

Apparent molar volume  $V_\phi$  was calculated using equation (4)

$$V_\phi = \frac{1000(\rho^0 - \rho)}{m\rho^0\rho} + \frac{M}{\rho} \quad (4)$$

The  $\rho$  and  $\rho^0$  are the density of solution and solvent respectively,  $m$  is the molal concentration of solute of molar mass,  $M$ . The apparent molar volume at infinite dilution  $V_\phi^0$  is obtained from regression of equation (5) [22]

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

where  $S_v$  is the slope that depicts information on solute–solute interactions while,  $V_\phi^0$  is the intercept furnishing information on solute–solvent interactions [23] and are given in table 4. The  $V_\phi^0$  and  $S_v$  values signify that they are inversely proportional to each other i.e., when solute–solute interaction decreases, solute–solvent interaction increases. With rise in temperature, electrostriction decreases resulting in increased  $V_\phi^0$  values. The positive  $V_\phi^0$  values for amino acids with water and surfactants are attributed to stronger solute–solvent interactions. The  $V_\phi^0$  values for Gly and L-Phe with surfactants are higher than water but lower for L-Ala. This trend can be due to the hydration behaviour [6,24] of amino acids which comprises of the following interactions in the present solvent:

- Hydrophilic–hydrophilic interaction (HHI) between the head groups of amino acid ( $-NH_3^+$  and  $-COO^-$ ) and  $=N^+$  group of surfactant weakens the electrostriction resulting in increased in  $V_\phi^0$  values with surfactant than with water [25].
- Hydrophilic–hydrophobic interactions (HH<sub>b</sub>I) between the head groups of amino acid and hydrocarbon chain of surfactants or  $=N^+$  of surfactant and non-polar moiety of amino acids strengthens the electrostriction with decreased  $V_\phi^0$  values with surfactant than with water.

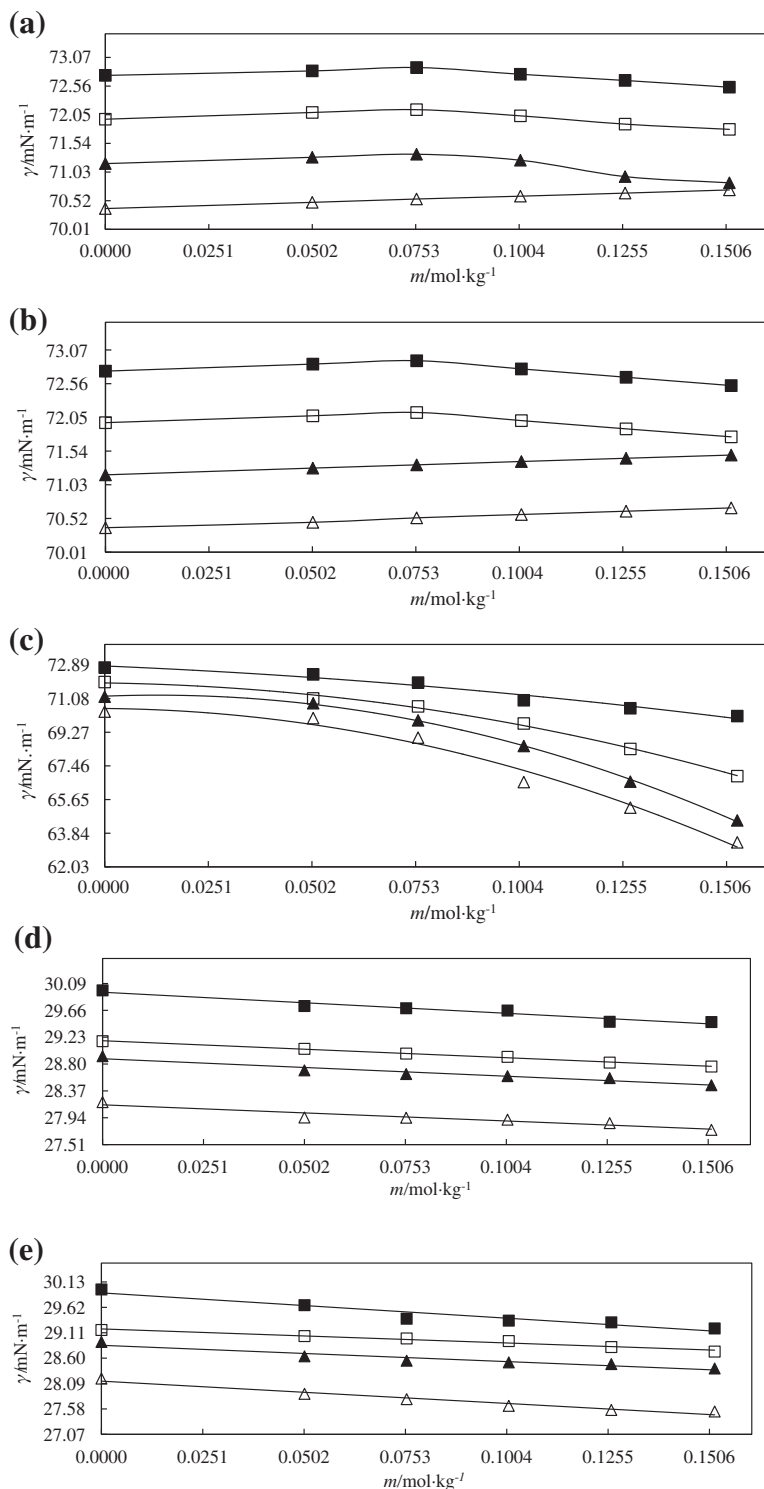
**TABLE 8**

Surface tension ( $\gamma$ ) of glycine, L-alanine and L-phenylalanine with water and with cationic surfactants MTOAC and CPC at  $T = (293.15, 298.15, 303.15 \text{ and } 308.15) \text{ K}$ .

$m/\text{mol} \cdot \text{kg}^{-1}$	293.15 $\gamma/\text{mN} \cdot \text{m}^{-1}$	298.15 $\gamma/\text{mN} \cdot \text{m}^{-1}$	303.15 $\gamma/\text{mN} \cdot \text{m}^{-1}$	308.15 $\gamma/\text{mN} \cdot \text{m}^{-1}$
<i>Glycine with Water</i>				
0	72.75	71.97	71.18	70.38
0.0502	72.83	72.09	71.29	70.49
0.0755	72.89	72.14	71.35	70.55
0.1007	72.77	72.03	71.24	70.60
0.1261	72.66	71.88	70.95	70.66
0.1514	72.54	71.79	70.84	70.71
<i>L-Alanine with Water</i>				
0	72.75	71.97	71.18	70.38
0.0503	72.86	72.07	71.28	70.46
0.0755	72.91	72.12	71.33	70.53
0.1009	72.78	72.00	71.38	70.58
0.1263	72.66	71.88	71.43	70.63
0.1518	72.53	71.76	71.48	70.68
<i>L-Phenylalanine with Water</i>				
0	72.75	71.97	71.18	70.38
0.0505	72.38	71.09	70.83	70.03
0.0759	71.94	70.66	69.91	68.98
0.1015	70.99	69.74	68.53	66.59
0.1273	70.56	68.37	66.61	65.22
0.1532	70.14	66.91	64.53	63.35
<i>Glycine with 0.002 mol · kg<sup>-1</sup> MTOAC</i>				
0	29.98	29.17	28.93	28.19
0.0502	29.73	29.04	28.70	27.94
0.0755	29.69	28.97	28.64	27.94
0.1007	29.66	28.92	28.61	27.91
0.1261	29.48	28.82	28.57	27.85
0.1514	29.47	28.76	28.46	27.75
<i>L-Alanine with 0.002 mol · kg<sup>-1</sup> MTOAC</i>				
0	29.98	29.17	28.93	28.19
0.0503	29.66	29.04	28.64	27.88
0.0756	29.39	29.00	28.55	27.78
0.1009	29.35	28.94	28.52	27.64
0.1263	29.32	28.82	28.48	27.56
0.1519	29.20	28.73	28.39	27.53
<i>L-Phenylalanine with 0.002 mol · kg<sup>-1</sup> MTOAC</i>				
0	29.98	29.17	28.93	28.19
0.0505	28.49	27.60	27.09	26.45
0.0759	28.36	27.33	26.90	26.31
0.1015	28.47	27.48	27.00	26.51
0.1273	28.51	27.62	27.11	26.61
0.1532	28.62	27.70	27.14	26.64
<i>Glycine with 0.002 mol · kg<sup>-1</sup> CPC</i>				
0	41.75	41.60	41.57	41.35
0.0502	41.64	41.49	41.46	41.07
0.0755	41.62	41.47	41.44	41.05
0.1007	41.71	41.56	41.53	41.14
0.1261	41.74	41.59	41.56	41.17
0.1515	41.77	41.62	41.59	41.20
<i>L-Alanine with 0.002 mol · kg<sup>-1</sup> CPC</i>				
0	41.75	41.60	41.57	41.35
0.0504	41.81	41.72	41.63	41.58
0.0756	42.19	42.11	42.01	41.96
0.1008	42.05	41.96	41.92	41.81
0.1264	41.53	41.44	41.37	41.20
0.1518	42.46	42.32	42.46	42.29
<i>L-Phenylalanine with 0.002 mol · kg<sup>-1</sup> CPC</i>				
0	41.75	41.60	41.57	41.35
0.0505	41.15	40.66	40.47	40.26
0.0759	40.52	40.05	39.07	38.89
0.1015	40.62	40.26	39.91	39.44
0.1273	40.61	39.98	39.74	39.28
0.1532	40.55	39.92	39.68	39.17

Standard uncertainty: in temperature  $u(T) = \pm 0.01 \text{ K}$  and in molality  $u(m) = \pm 2 \cdot 10^{-5} \text{ mol} \cdot \text{kg}^{-1}$ . The combined expanded uncertainty ( $k = 2$ ) in surface tension  $U_c(\gamma) = \pm 0.03 \text{ mN} \cdot \text{m}^{-1}$ .





**FIGURE 1.** (a)–(c) Effect of Concentration on Surface tension of (a) Gly (b) L-Ala and (c) L-Phe with water at  $T = (\blacksquare) 293.15 K, (\square) 298.15 K, (\blacktriangle) 303.15 K$  and  $(\triangle) 308.15 K$ , (d)–(f). Effect of Concentration on Surface tension of (d) Gly (e) L-Ala and (f) L-Phe with  $0.002 mol \cdot kg^{-1}$  MTOAC at  $T = (\blacksquare) 293.15 K, (\square) 298.15 K, (\blacktriangle) 303.15 K$  and  $(\triangle) 308.15 K$ , (g)–(i). Effect of Concentration on Surface tension of (g) Gly (h) L-Ala and (i) L-Phe with  $0.002 mol \cdot kg^{-1}$  CPC at  $T = (\blacksquare) 293.15 K, (\square) 298.15 K, (\blacktriangle) 303.15 K$  and  $(\triangle) 308.15 K$ .

(c) Hydrophobic–hydrophobic interaction ( $H_bH_bI$ ) between the hydrophobic group of amino acid and the non-polar tail of surfactants leads to increase in electrostriction resulting in decreased  $V_\phi^0$  values with surfactant than with water.

The HHI,  $HH_bI$  and  $H_bH_bI$  represent the fundamental interaction between solute and solvent which significantly explains the trends coming for density, sound velocity and other PCPs since the

electron clouds of the molecules are greatly reoriented or redistributed due to these interactions depending on the ionic, hydrophilic or hydrophobic domains in which they exist. Transfer volumes of amino acid from surfactant to water  $\Delta V_\phi^0$  were obtained from equation (6) and are given in table S3 (SI).

$$\Delta V_\phi^0 = V_{\phi(\text{in surfactant})}^0 - V_{\phi(\text{in water})}^0 \quad (6)$$

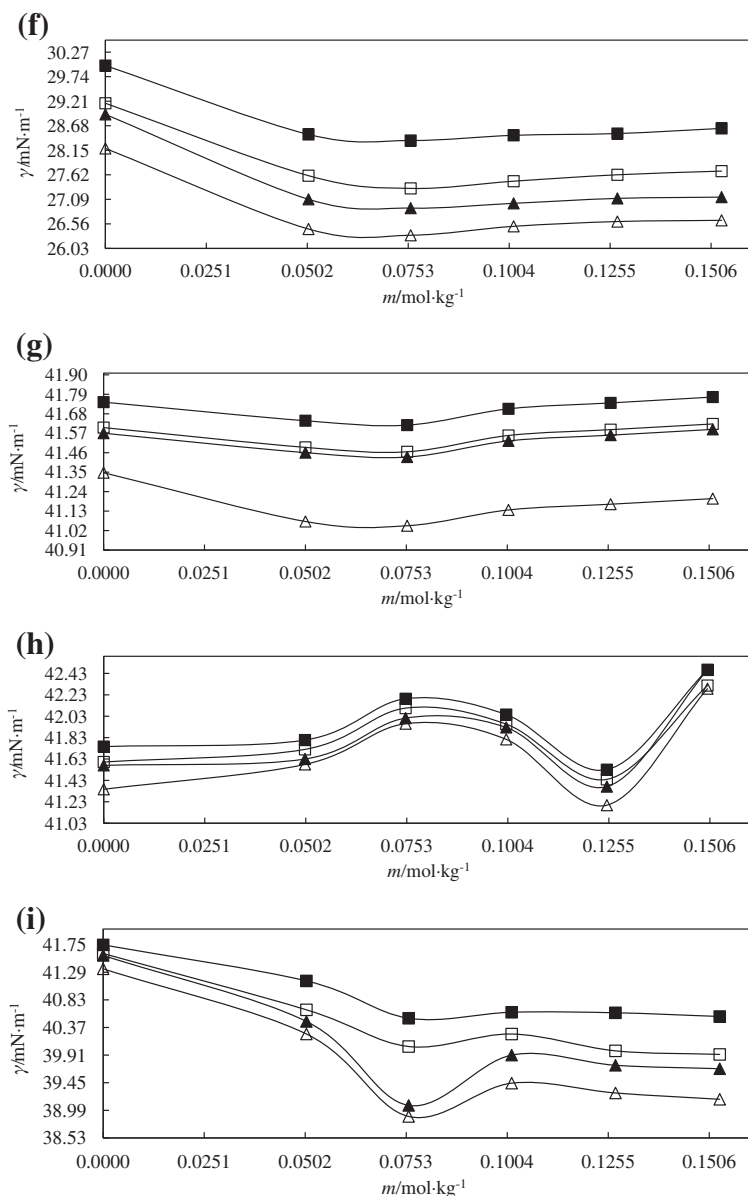


Fig. 1 (continued)

Interactions of type (a) produced positive  $\Delta V_\phi^0$  values because of reduction in electrostriction on an overlap of hydration co-sphere of the  $-\text{NH}_3^+$  and  $-\text{COO}^-$  with hydrophilic  $=\text{N}^+=$  group, whereas interactions of type (b) and (c) produced negative  $\Delta V_\phi^0$  values on strengthening electrostriction. For Gly and L-Phe,  $\Delta V_\phi^0$  is positive due to HHI and L-Ala, due to, its small size and stronger (+I) methyl group, electrostriction at its zwitterionic alpha position is increased with stronger HH<sub>b</sub>I and H<sub>b</sub>H<sub>b</sub>I. This causes contraction in volume with a lower  $V_\phi^0$  for L-Ala with surfactants than with water with negative values of  $\Delta V_\phi^0$ . The absence of a non-polar moiety in Gly and the existence of a smaller hydrophobic environment in CPC than MTOAC strengthen HHI between them, resulting in higher  $V_\phi^0$  values for Gly with CPC than MTOAC. L-Phe develops stronger H<sub>b</sub>H<sub>b</sub>I with MTOAC than with water with release of more water molecules to the bulk with its higher  $V_\phi^0$  values with MTOAC than CPC. L-Ala can easily approach the cetyl chain of CPC from all sides but faces a hindrance caused by the trifurcated octyl chain of MTOAC. This leads to a greater contraction in volume with CPC than with MTOAC with higher  $V_\phi^0$  values with MTOAC than with CPC. The  $V_\phi^0$  values increased with rise in temperature because binding the

solvent molecules from the second solvation sphere of zwitterions is weakened at higher temperature, releasing solvent into the bulk, with an expansion in volume causing increased  $V_\phi^0$ .

### 3.3. Apparent molar isentropic compressibility at infinite dilution and apparent molar isentropic compressibility of transfer at infinite dilution

Values of isentropic compressibility  $\kappa_s$  were calculated using Newton–Laplace equation (7)

$$\kappa_s = 1/\rho u^2. \quad (7)$$

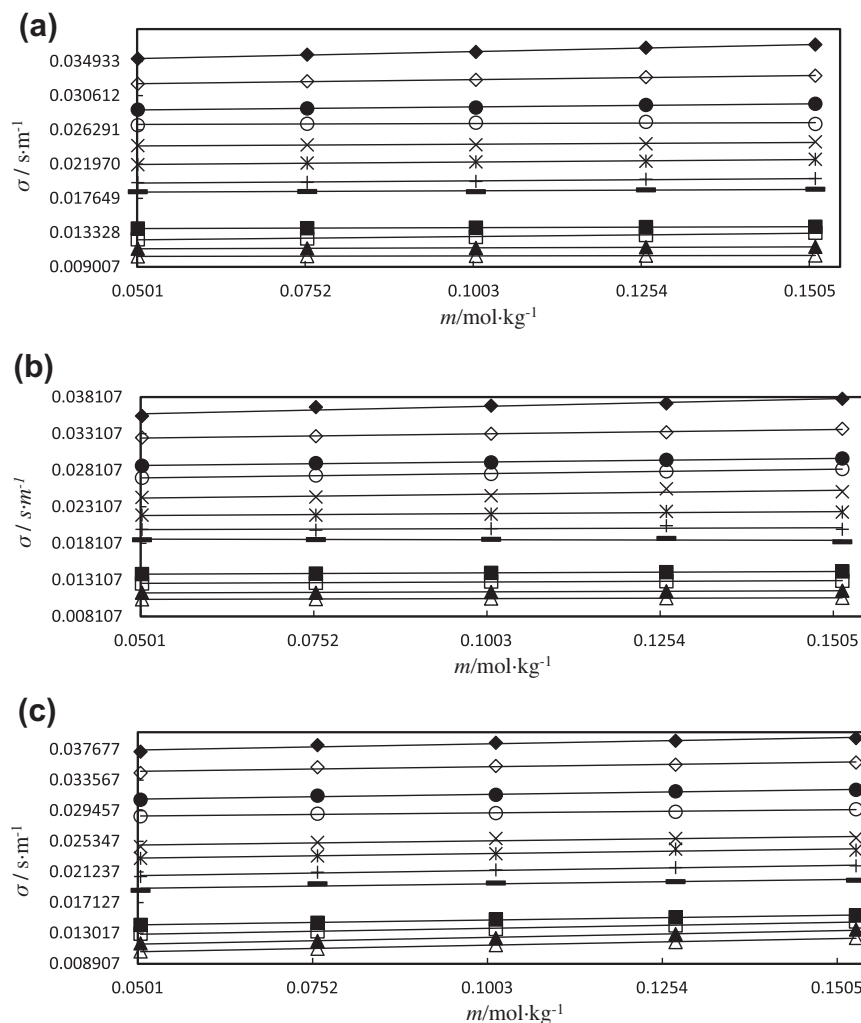
Apparent molar isentropic compressibility  $\kappa_{s,\phi}$  was calculated using equation (8)

$$\kappa_{s,\phi} = \{(\kappa_s \rho^0 - \kappa_s^0 \rho)/m\rho\rho^0\} + (\kappa_s M/\rho). \quad (8)$$

Apparent molar isentropic compressibility at infinite dilution  $\kappa_{s,\phi}^0$  was obtained from the regression analysis of equation (9)

$$\kappa_{s,\phi} = \kappa_{s,\phi}^0 + S_k m. \quad (9)$$





**FIGURE 2.** (a) Effect of Concentration on Frictional Coefficient of Gly with water at  $T = (\blacksquare)$  293.15,  $(\square)$  298.15 K,  $(\blacktriangle)$  303.15 K and  $(\triangle)$  308.15 K, with  $0.002 \text{ mol}\cdot\text{kg}^{-1}$  MTOAC at  $T = (\blacklozenge)$  293.15 K,  $(\circlearrowright)$  298.15 K,  $(\bullet)$  303.15 K and  $(\circ)$  308.15 K and with  $0.002 \text{ mol}\cdot\text{kg}^{-1}$  CPC at  $T = (\times)$  293.15 K,  $(*)$  298.15 K,  $(+)$  303.15 K and  $(\text{—})$  308.15 K, (b). Effect of Concentration on Frictional Coefficient of L-Ala with water at  $T = (\blacksquare)$  293.15 K,  $(\square)$  298.15 K,  $(\blacktriangle)$  303.15 K and  $(\triangle)$  308.15 K, with  $0.002 \text{ mol}\cdot\text{kg}^{-1}$  MTOAC at  $T = (\blacklozenge)$  293.15 K,  $(\circlearrowright)$  298.15 K,  $(\bullet)$  303.15 K and  $(\circ)$  308.15 K and with  $0.002 \text{ mol}\cdot\text{kg}^{-1}$  CPC at  $T = (\times)$  293.15 K,  $(*)$  298.15 K,  $(+)$  303.15 K and  $(\text{—})$  308.15 K, (c). Effect of Concentration on Frictional Coefficient of L-Phe with water at  $T = (\blacksquare)$  293.15 K,  $(\square)$  298.15 K,  $(\blacktriangle)$  303.15 K and  $(\triangle)$  308.15 K, with  $0.002 \text{ mol}\cdot\text{kg}^{-1}$  MTOAC at  $T = (\blacklozenge)$  293.15 K,  $(\circlearrowright)$  298.15 K,  $(\bullet)$  303.15 K and  $(\circ)$  308.15 K and with  $0.002 \text{ mol}\cdot\text{kg}^{-1}$  CPC at  $T = (\times)$  293.15 K,  $(*)$  298.15 K,  $(+)$  303.15 K and  $(\text{—})$  308.15 K.

Here,  $S_k$  is the slope depicting solute–solute interactions while  $\kappa_{s,\phi}^0$  is the intercept depicting solute–solvent interactions and are given in table 5. Apparent molar isentropic compressibility of transfer at infinite dilution of amino acids from surfactant to water  $\Delta\kappa_{s,\phi}^0$  is calculated using equation (10)

$$\Delta\kappa_{s,\phi}^0 = \kappa_{s,\phi}^0(\text{in surfactant}) - \kappa_{s,\phi}^0(\text{in water}). \quad (10)$$

Table 5 exemplifies that  $\kappa_{s,\phi}^0$  values for Gly and L-Phe with surfactants are greater than with water, with positive  $\Delta\kappa_{s,\phi}^0$  values (table S4) (SI), because of decreased electrostriction due to HHI. Increased electrostriction due to  $H_bH_bI$  developed between the hydrophobic group of L-Ala and the non-polar tail of surfactants with negative  $\Delta\kappa_{s,\phi}^0$  values.

### 3.4. Viscosity B-coefficient

The limiting viscosities  $\eta^0$  are reported in table S5 (SI) and figures F10–F12 illustrates that the  $\eta^0$  values decreased with rise in temperature because higher kinetic energy weakens the IMF operating on the viscous fluid flow with a net decrease in frictional force. The viscosity of CPC is lower than MTOAC at  $T = (293.15,$

298.15 and 303.15) K but at  $T = 308.15$  K is higher than MTOAC (table 2), may be due to more collisions at higher temperature. MTOAC, being larger in size than CPC, forms a larger moving entity with its three octyl groups, responsible for higher viscosity. The relative viscosity ( $\eta_r$ ) (table 6) increased with concentration because the average distance between the polar head of the amino acid and solvent or non-polar group of the amino acid and surfactant decreases causing stronger HHI and  $H_bH_bI$ . These strengthen the solute–solvent interactions with higher frictional resistance to the viscous flow. The  $\eta_r$  values are fitted in Jones–Dole equation, equation (11) [26].

$$\eta_r = 1 + Am^{1/2} + Bm. \quad (11)$$

Here,  $A$  and  $B$  are the Falkenhagen and viscosity B-coefficients respectively.  $A$ -coefficient specifies solute–solute interactions [27,28] and  $B$  is a measure of structural modifications induced by solute–solvent interactions [29,30]. For non-electrolytes,  $A$  is negligible [31] and for amino acids reduced Jones–Dole equation, equation (12) is used.

$$\eta_r = 1 + Bm. \quad (12)$$

**TABLE 9**  
Friccohesity ( $\sigma$ ) of amino acids with water and 0.002 mol · kg<sup>-1</sup> cationic surfactant solutions at T = (293.15, 298.15, 303.15 and 308.15) K.

$m/\text{mol} \cdot \text{kg}^{-1}$	293.15 $\sigma/\text{s} \cdot \text{m}^{-1}$	298.15 $\sigma/\text{s} \cdot \text{m}^{-1}$	303.15 $\sigma/\text{s} \cdot \text{m}^{-1}$	308.15 $\sigma/\text{s} \cdot \text{m}^{-1}$
<i>Glycine with Water</i>				
0	0.013773	0.012418	0.011241	0.010266
0.0502	0.013844	0.012478	0.011303	0.010327
0.0755	0.013882	0.012587	0.011330	0.010361
0.1007	0.013950	0.012777	0.011392	0.010383
0.1261	0.014023	0.013018	0.011482	0.010420
0.1514	0.014068	0.013312	0.011534	0.010445
<i>L-Alanine with Water</i>				
0	0.013773	0.012418	0.011241	0.010266
0.0503	0.013902	0.012610	0.011360	0.010449
0.0755	0.013967	0.012706	0.011353	0.010482
0.1009	0.014067	0.012877	0.011446	0.010552
0.1263	0.014159	0.012914	0.011553	0.010607
0.1518	0.014266	0.012976	0.011633	0.010652
<i>L-Phenylalanine with Water</i>				
0	0.013773	0.012418	0.011241	0.010266
0.0505	0.014133	0.012949	0.011659	0.010575
0.0759	0.014418	0.013267	0.011970	0.010934
0.1015	0.014860	0.013583	0.012357	0.011422
0.1273	0.015161	0.014068	0.012894	0.011829
0.1532	0.015404	0.014591	0.013510	0.012384
<i>Glycine with 0.002 mol · kg<sup>-1</sup> MTOAC</i>				
0	0.034861	0.031856	0.028333	0.026481
0.0502	0.035259	0.032084	0.028833	0.026871
0.0755	0.035775	0.032415	0.028992	0.027055
0.1007	0.036117	0.032597	0.029101	0.027191
0.1261	0.036646	0.032939	0.029427	0.027294
0.1514	0.037046	0.033121	0.029577	0.027033
<i>L-Alanine with 0.002 mol · kg<sup>-1</sup> MTOAC</i>				
0	0.034861	0.031856	0.028333	0.026481
0.0503	0.035522	0.032563	0.028717	0.027064
0.0756	0.036736	0.032754	0.029074	0.027384
0.1009	0.036931	0.03309	0.029172	0.027595
0.1263	0.037241	0.033292	0.029519	0.027952
0.1519	0.037870	0.033769	0.029710	0.028267
<i>L-Phenylalanine with 0.002 mol · kg<sup>-1</sup> MTOAC</i>				
0	0.034859	0.031856	0.028333	0.026483
0.0505	0.037391	0.034536	0.030935	0.028716
0.0759	0.038264	0.035298	0.031482	0.02906
0.1015	0.038583	0.035466	0.031596	0.029142
0.1273	0.038854	0.035643	0.032064	0.029317
0.1532	0.039215	0.035933	0.032263	0.029659
<i>Glycine with 0.002 mol · kg<sup>-1</sup> CPC</i>				
0	0.024048	0.021713	0.019573	0.018278
0.0502	0.024302	0.021901	0.019632	0.018485
0.0755	0.024391	0.022104	0.019668	0.018513
0.1007	0.024407	0.022250	0.019787	0.018494
0.1261	0.024526	0.022329	0.020061	0.018718
0.1515	0.024776	0.022571	0.020146	0.018801
<i>L-Alanine with 0.002 mol · kg<sup>-1</sup> CPC</i>				
0	0.024048	0.021713	0.019573	0.018278
0.0504	0.024389	0.021965	0.020014	0.018596
0.0756	0.024441	0.021956	0.019907	0.018621
0.1008	0.024611	0.022098	0.020111	0.018653
0.1264	0.025562	0.022464	0.020515	0.018778
0.1518	0.025159	0.022383	0.020025	0.018316
<i>L-Phenylalanine with 0.002 mol · kg<sup>-1</sup> CPC</i>				
0	0.024048	0.021713	0.019573	0.018278
0.0505	0.024643	0.023073	0.020626	0.018775
0.0759	0.025206	0.023394	0.021201	0.019654
0.1015	0.025732	0.023686	0.021511	0.019757
0.1273	0.025731	0.024308	0.021828	0.019942
0.1532	0.025814	0.024166	0.022064	0.020128

Standard uncertainty: In temperature  $u(T) = \pm 0.01$  K and in molality  $u(m) = \pm 2 \cdot 10^{-5}$  mol · kg<sup>-1</sup>.

The B-coefficient is the slope of the straight line on linear regression of equation (12) and is reported in table 7. From T = (293.15 to 298.15) K, the viscosity B-coefficient values with

water increases; with MTOAC, decreases whereas, with CPC, increases for Gly and L-Phe but decreases for L-Ala. On further rise in temperature no particular trend is observed. With CPC for Gly

and L-Phe, the  $B$  values are almost between those with MTOAC which depicts that the hydrophilic and hydrophobic effect remains functional during the flow.  $B$ -coefficient and size of the molecule are closely interlinked and both of them partially contribute to the active state of interaction. Increased  $\eta_r$  values with increase in concentration depict development of strong IMF with decreased hydration sphere size. On transfer of amino acids from water to surfactants, the  $B$  values of Gly and L-Ala increase and of L-Phe decrease (table 7). On hydrogen bonding, the surfactants act as structure-makers but this effect is stronger with  $\pi$ -conjugated L-Phe due to the shift in charge on  $sp^2$  hybridization.

### 3.5. Surface tension

Values of the surface tension  $\gamma$  of amino acids with water and surfactants are listed in table 8 and illustrated in figure 1a–i. The surface tension of CPC > MTOAC occurs because MTOAC with three octyl chains effectively cleaves the hydrogen bonding between water molecules whereas CPC weakly cleaves them because of only one cetyl chain. With water, for Gly and L-Ala, from (0.05 to 0.075) mol · kg<sup>-1</sup>, the  $\gamma$  values increase by (0.14 to 0.17) mN · m<sup>-1</sup> but decrease on further increase in concentration at  $T = (293.15, 298.15$  and  $303.15)$  K for Gly and  $T = (293.15$  and  $298.15)$  K for L-Ala. The  $\gamma$  values increase on increasing concentration for Gly at  $T = 308.15$  K and for L-Ala at  $T = (303.15$  and  $308.15)$  K. The development of weaker IMF between Gly/L-Ala with water from (0.05 to 0.075) mol · kg<sup>-1</sup> due to the weaker ion-dipole interaction on weakening the hydrogen bonding between water molecules with decreased  $\gamma$ . For Gly and L-Ala, probably at higher temperatures, weaker ion-dipole interactions get disrupted giving way for formation of new hydrogen bond between water molecules with increased  $\gamma$  values. Due to C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>-group, L-Phe may act as a surfactant with a steady decrease in surface tension with increased concentration with water.

The  $\gamma$  values of Gly/L-Ala with MTOAC decrease with increase in concentration. In the MTOAC solution, stronger IMF was developed with ion-dipole interaction between N<sup>+</sup> of MTOAC and O<sup>δ-</sup> of water. However, when Gly/L-Ala having neutralized charges was added, it replaced the MTOAC molecules that were interacting with water causing weakening IMF with decreased  $\gamma$  values. For (0.050 to 0.075) mol · kg<sup>-1</sup> L-Phe, the  $\gamma$  values decreased but increased on further rise in concentration. At lower concentration with the C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>-group, it acts as a surfactant but on further increase in concentration, its hydrophobic part engages the octyl chain of MTOAC, thereby releasing water from MTOAC leading to formation of hydrogen bonds between water molecules with a steady increase in surface tension.

For (0.050 to 0.075) mol · kg<sup>-1</sup> Gly/L-Phe with CPC, the  $\gamma$  values decreased but on further addition, the  $\gamma$  values steadily increased for Gly but again decreased for L-Phe. At lower concentrations, due to its neutralized charge, the Gly might have replaced CPC forming weaker IMF (HHI) with water, whereas on increasing its concentration, the Gly starts interacting with the CPC, releasing water on strengthening hydrogen bond between water molecules with increased  $\gamma$  values. For (0.075 to 0.100) mol · kg<sup>-1</sup>, the increased  $\gamma$  values are attributed to the  $\pi$ -conjugation in L-Phe inducing stronger IMF with water. Decreased  $\gamma$  values on further increase in L-Phe concentration produces an hydrophobically rich environment at the air–liquid interface which dominates over the effect of  $\pi$ -conjugation. For (0.05 to 0.075) mol · kg<sup>-1</sup> L-Ala with CPC, the  $\gamma$  values increased but with further increase in concentration, the  $\gamma$  values decreased, passed through a minimum around 0.100 mol · kg<sup>-1</sup> and again increased on further increase in concentration. Thus this infers that the development of stronger H<sub>b</sub>H<sub>b</sub>I between L-Ala and CPC from (0.05 to 0.075) mol · kg<sup>-1</sup> is responsible for higher  $\gamma$  values. For concentration 0.100 mol · kg<sup>-1</sup> onwards,

the interaction of COO<sup>-</sup> and NH<sub>3</sub><sup>+</sup> of L-Ala with water weakens as the charges tend to neutralize each other with lower  $\gamma$  values. From (0.100 to 0.150) mol · kg<sup>-1</sup>, the methyl group of L-Ala induces an hydrophobic effect and engages the cetyl chain of CPC and releases the water molecules from the CPC hydration sphere with a stronger hydrogen bond between water molecules with higher surface tension.

### 3.6. Friccohesity

Friccohesity  $\sigma$  is a product of cohesive and frictional forces (FF) within similar and dissimilar molecules respectively. The CF acts within water molecules and when amino acid or surfactant is added. The CF is weakened with development of FF in the same proportion. Thus the CF and FF are mutually interrelated and such a combination of forces or their product reflects a critical state of the interacting behaviour of the molecules. Friccohesity is calculated with the Mangsingh equation (13) [20]

$$\sigma = \sigma_0 \left[ \left( \frac{t}{t_0} \pm \frac{B}{t} \right) \left( \frac{n}{n_0} \pm 0.0012(1 - \rho) \right) \right], \quad (13)$$

where,  $t_0$  and  $t$  are the reference and sample flow times respectively,  $\sigma_0$  is reference friccohesity,  $n_0$  and  $n$  are the pendant drop number of reference and sample respectively,  $B/t$  is kinetic energy correction,  $\pm 0.0012(1 - \rho)$  is the buoyancy correction. The terms  $B/t$  and  $0.0012(1 - \rho)$  are of the order 10<sup>-7</sup> and are omitted, reducing Mangsingh equation to equation (14)

$$\sigma = \sigma_0 \left[ \left( \frac{t}{t_0} \right) \left( \frac{n}{n_0} \right) \right]. \quad (14)$$

Reference friccohesity is calculated from equation (15)

$$\sigma_0 = \frac{\eta_0}{\gamma_0}, \quad (15)$$

where  $\eta_0$  and  $\gamma_0$  are the viscosity and surface tension of the reference sample. Figure 2a–c illustrate that the  $\sigma$  values (table 9) increase with concentration and decrease with rise in temperature. The slopes for L-Phe are steeper than for Gly and L-Ala whereby the  $\sigma$  of L-Phe increases to a greater extent on increasing the concentration. This is due to an efficient inter conversion of the CF existing within the solvent molecules to FF at their own cost and directly reflects an engagement of solvent with solute. The  $\sigma$  values are higher with surfactants as compared to water and could be explained by stronger inter conversion of CF to FF due to bulkier surfactants. The  $\sigma$  values with water and aqueous surfactants are as L-Phe > L-Ala > Gly because development of stronger FF by L-Phe due to its bulkiness as compared to the least bulky Gly molecule. The  $\sigma$  values with CPC at  $T = 298.15$  K is as L-Phe > Gly > L-Ala and may be attributed to the dominance of HH<sub>b</sub>I and H<sub>b</sub>H<sub>b</sub>I over HHI resulting in efficient trapping of solvent with a net contraction and less friction. The  $\sigma$  values rise on increasing concentration because of the inter conversion of CF to FF. This leads to stronger FF at the cost of CF with stronger solute–solvent interactions or friccohesity–interaction. The decreased  $\sigma$  values with increased temperature depict weaker solute–solvent interactions at higher temperature due to weakening of FF between solute and solvent molecules as well as weakening of CF between solvent molecules with lower product of IMF.

## 4. Conclusions

Apparent molar volume at infinite dilution  $V_{\phi}^0$ , apparent molar isentropic compressibility at infinite dilution  $K_{s,\phi}^0$ ,  $B$ -coefficient, surface tension  $\gamma$  and friccohesity  $\sigma$  have inferred interacting activities of amino acids with cationic surfactants. These PCP's have

confirmed the development of weaker solute–solute interactions and stronger solute–solvent interactions. A higher  $\Delta V_{\phi}^0$  value with CPC than with MTOAC has established a stronger HHI between Gly and CPC than with MTOAC. The role of IMF (HHI, HH<sub>b</sub>I and H<sub>b</sub>H<sub>b</sub>I) is reflected through higher  $\Delta V_{\phi}^0$  values with MTOAC than with CPC for L-Ala and L-Phe. Higher  $\kappa_{s,\phi}^0$  values for Gly and L-Phe with surfactant than with water established development of stronger HHI. Lower  $S_v$  and  $S_k$  values proved weaker solute–solute interactions. Weakening of IMF with increased temperature is reflected through increased  $V_{\phi}^0$  and  $\kappa_{s,\phi}^0$  values. The higher  $\sigma$  values with increased concentration and decreased temperature further established the presence of stronger solute–solvent interactions. Surface tension, being a highly sensitive property, has shown much variation due to minor structural changes in hydrophobic and hydrophilic groups either on amino acid or the cationic surfactants.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jct.2013.05.037>.

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