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ARTICLE *in* THE JOURNAL OF CHEMICAL THERMODYNAMICS · NOVEMBER 2012

Impact Factor: 2.68 · DOI: 10.1016/j.jct.2012.05.031

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Contents lists available at SciVerse ScienceDirect

J. Chem. Thermodynamics

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Volumetric and calorimetric investigations of molecular interactions in some amino acids and peptides in the combined presence of surfactants and glycine betaine

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ARTICLE INFO

Article history:
Received 10 May 2012
Received in revised form 27 May 2012
Accepted 30 May 2012
Available online 7 June 2012

Keywords:
Amino acids
Polar interactions
Partial molar volume
Partial molar adiabatic compressibility
Enthalpy of dilution

ABSTRACT

The values of apparent molar volume $V_{2,\phi}$ and apparent molar adiabatic compressibility $K_{S,2,\phi}$ of amino acids glycine, L-alanine, DL-α-amino-n-butyric acid (ABA), L-valine, L-leucine and peptides diglycine and triglycine have been determined in the aqueous solutions of surfactants and glycine betaine by means of density and sound velocity measurements. The heat (Q) evolved or absorbed during the course of interactions of amino acids and peptides with the aqueous solution of surfactants and glycine betaine were determined by the calorimetric method at $T = 298$ K. The values of standard partial molar volume $V^0_{2,m}$ and standard partial molar adiabatic compressibility $K^0_{S,2,m}$ at infinite dilution were calculated from $V_{2,\phi}$ and $K_{S,2,\phi}$, and the values of limiting enthalpy of dilution $\Delta_{dil}H^0$ were calculated from the heat evolved or absorbed during the calorimetric experiments. The transfer values of partial molar volume $\Delta_{tr}V^0_{2,m}$, partial molar adiabatic compressibility $\Delta_{tr}K^0_{S,2,m}$ and limiting heat of dilution $\Delta_{tr}\Delta_{dil}H^0$ of amino acids and peptides from water to aqueous solution of surfactants and glycine betaine, in general, demonstrated a dominance of polar interactions. Furthermore, a specific trend in the involvement of different types of interactions was observed which varied as a function of size and hydrophobicity of different amino acids and peptides. The present study indicated that glycine betaine primarily exhibits polar interactions with the zwitterionic centres of the amino acids and peptide bonds of the peptides but might enhance the overall solvent structure in the presence of amino acids with bulkier alkyl groups. On the whole, the findings of volumetric and calorimetric studies in the present work precisely correlate and discuss the molecular mechanism on how glycine betaine might impart stability in the unfolded proteins induced by surfactants.

1. Introduction

In order to maintain the biological function and catalytic activity, it is desirous that proteins maintain their natively folded structures under physiological conditions. However, most proteins are sensitive to slightest changes in cellular and environmental conditions including temperature, pH, pressure, and the presence of salts and other chemical chaotropes [1–3]. In order to adapt to such agitations arising from extreme conditions, accumulation of small organic solutes, also known as "osmolytes" have been observed in certain plants and animals under stress [4–6]. The stabilization of protein in presence of osmolytes under adverse conditions of temperature, pressure and chemical chaotropes has been widely reported [6–9]. It has been speculated that most osmolytes like methylamines and polyols exert their influence by molecular crowding resulting in volume exclusion. This exclusion of the osmolyte termed as preferential exclusion from the protein backbone results in the formation of compact native state as opposed to extended conformations [10–12]. However, the physicochemical basis of the stabilization induced by the osmolytes in terms of solute-solute and solute-solvent interactions is still a matter of discussion.

In view of the above phenomenon, the determination of various thermodynamic, transport and surface properties of protein and model compounds which mimic some aspects of the former can provide creative insights into the solvent mediated effects and hydration properties operating in the system. Some of the compounds that can be made to mimic the proteins in such environments are amino acids and short peptides, which, being low molar mass molecules are extensively used as models for studying such systems [13,14]. The basic advantage of using such a system of amino acids and peptides is because of their side chain groups which represent a wide range of properties and can be selectively altered to investigate a range of interactions.

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http://dx.doi.org/10.1016/j.jct.2012.05.031

In this work, we investigated the effects of glycine betaine (GB), a widely known osmolyte [3,15], on amino acids and peptides in the presence of hexadecyl trimethyl ammonium bromide (HTAB, cmc-$0.92 \cdot 10^{-3}$ mol·dm^{-3}) [16] and sodium dodecyl sulphate (SDS, cmc-$8.2 \cdot 10^{-3}$ mol·dm^{-3}) [17] using densimetry, sound velocity and calorimetric techniques. Since HTAB and SDS are widely known to denature the proteins at low concentration [18,19], we considered the minimum post micellar concentration of HTAB ($m = 2 \cdot 10^{-3}$ mol·kg^{-1}) and SDS ($m = 10 \cdot 10^{-3}$ mol·kg^{-1}) in presence of GB ($m = 1.0$ mol·kg^{-1}), to study the present system comprising amino acids and peptides. Here 'm' represents molality of the solutes. However the above mentioned concentrations of surfactants might vary from protein to protein depending on its overall hydrophobicity, structural characteristics and pH of the solutions. The importance of studying such a system primarily arises from the fact that, apart from the participation of electrostatic interactions, the role of micelles during protein unfolding can also be predicted with accuracy. Historically, ionic surfactants at post micellar concentration are known to bind specifically and unfold proteins by mechanisms far different from the conventional chaotropes [20]. The volumetric data obtained from densimetry of amino acids and peptides in HTAB ($m = 1.0$ mol·kg^{-1}) and SDS ($m = 50 \cdot 10^{-3}$ mol·kg^{-1}) [21] have also been included for a comparative analysis of possible preferential interaction of GB ($m = 1.0$ mol·kg^{-1}) in the presence of HTAB ($m = 2 \cdot 10^{-3}$ mol·kg^{-1})/SDS ($m = 10 \cdot 10^{-3}$ mol·kg^{-1}). At HTAB ($m = 1.0$ mol·kg^{-1}) and SDS ($m = 50 \cdot 10^{-3}$ mol·kg^{-1}) the interactions of amino acids and peptides with the surfactants was shown to be predominantly polar in nature arising due to the micellar nature of HTAB/SDS at the above mentioned concentrations [21]. Furthermore, among various physical parameters, partial molar volume and partial molar adiabatic compressibility have been recognized as quantities which are sensitive to structural changes occurring in solutions. Thus, the overall volumetric and calorimetric data obtained have been interpreted in terms of types of intermolecular interactions, compressibility changes and thermodynamic properties to give a quantitative and qualitative insight on molecular interactions of building blocks of proteins with GB in presence of surfactants.

2. Materials and methods

2.1. Materials

The amino acids and peptides, glycine (mole fraction purity $x > 0.99$), L-alanine ($x = 0.99$), DL-α-amino-n-butyric acid ($x = 0.98$), L-valine ($x \geqslant 0.99$), L-leucine ($x = 0.98$), diglycine ($x \geqslant 0.99$), and triglycine ($x > 0.99$), and the surfactants HTAB ($x = 0.99$) and SDS ($x > 0.99$), and the osmolyte GB ($x \geqslant 0.99$) were all were procured from Sigma Aldrich Chemical Company, USA (table 1). All the amino acids and peptides were dried over P_2O_5 and used without further purification. The solutions of amino acids and peptides were prepared in double distilled water which was then deionised using a Cole-Parmer research mixed-bed ion-exchange column. This deionised water had a conductivity of 0.06 μS·cm^{-1}. All of the mass determinations were done on a Sartorius BP 211D digital balance that had a readability of 0.01 mg.

TABLE 1
Compounds used in this study with their empirical formula, molar mass (M_r) and mole fraction (x) purity as reported by the vendor (Sigma Aldrich Chemical Company, USA).

Compound	Empirical Formula	M_r/(g·mol^{-1})	x
Glycine	$C_2H_5NO_2$	75.07	>0.99
L-alanine	$C_3H_7\ NO_2$	89.09	=0.99
DL-α-amino-n-butyric acid	$C_4H_9\ NO_2$	103.1	=0.98
L-valine	$C_5H_{11}\ NO_2$	117.1	⩾0.99
L-leucine	$C_6H_{13}\ NO_2$	131.2	=0.98
Diglycine	$C_4H_8N_2O_3$	132.1	⩾0.99
Triglycine	$C_6H_{11}N_3O_4$	189.2	>0.99
HTAB	$C_{16}H_{33}(CH_3)_3NBr$	364.5	=0.99
SDS	$C_{12}H_{25}NaSO_4$	288.4	>0.99
Glycine Betaine	$C_5H_{11}NO_2.H_2O$	135.2	⩾0.99

2.2. Methods

2.2.1. Density and sound velocity measurements

Solution densities and sound velocities were measured using the digital density and sound velocity analyzer (DSA 5000 procured from Anton Paar Gmbh, Austria), which determines two independent physical properties within one sample. The chemical calibration of the densimeter was performed prior to the experiment by measuring the values of apparent molar volume and apparent molar adiabatic compressibility of aqueous NaCl at different molalities and comparing with the literature values, which had a good agreement [22].

The measured density (ρ) and adiabatic compressibility (k_S) of aqueous solutions of different amino acids and peptides in HTAB ($m = 2 \cdot 10^{-3}$ mol·kg^{-1})/SDS ($m = 10 \cdot 10^{-3}$ mol·kg^{-1}) and GB ($m = 1.0$ mol·kg^{-1}) were used to calculate the apparent molar volume ($V_{2,\phi}$) using equation 1 and apparent molar compressibility ($K_{S,2,\phi}$) using equation (2). The values of adiabatic compressibility of the solutions, k_S was calculated from sound velocity (u) using equation (3).

$$V_{2,\phi} = \frac{M}{\rho} - \frac{(\rho - \rho_0) \cdot 10^3}{m\rho\rho_0}, \tag{1}$$

$$K_{S,2,\phi} = \frac{\beta M}{\rho} - \frac{1000(\beta^0\rho - \beta\rho_0)}{m\rho\rho_0}, \tag{2}$$

$$k_S = \frac{1}{u^2\rho}. \tag{3}$$

Here, M is the molar mass of the amino acids and/or peptides in g·mol^{-1}, m is the molality of the solute in mol·kg^{-1}, ρ and ρ_0 are the densities of the quaternary system (water, HTAB/SDS, GB and amino acids) and reference solvent (aqueous HTAB/SDS and GB) in g·cm^{-3} respectively and $\beta^0 = 44.7733 \cdot 10^{-5}$ MPa^{-1} is the compressibility of water.

2.2.2. Isothermal titration calorimetry

The calorimetric measurements were performed on Nano ITC micro calorimeter supplied by TA instruments. All the solutions were thoroughly degassed prior to the experiment. Titrations were carried out using a 0.250 cm^3 syringe containing aqueous amino acid and peptides with stirring speed kept constant at 300 rpm in all the experiments. The sample cell was filled with the solvent {HTAB ($m = 2 \cdot 10^{-3}$ mol·kg^{-1})/SDS ($m = 10 \cdot 10^{-3}$ mol·kg^{-1}) and GB ($m = 0.5$ mol·kg^{-1})}. Titration of aqueous amino acids and peptides were performed using 0.2 mol·kg^{-1} of glycine, alanine, and α-ABA, and 0.05 mol·kg^{-1} valine, leucine, diglycine and triglycine to HTAB ($m = 2 \cdot 10^{-3}$ mol·kg^{-1})/SDS ($m = 10 \cdot 10^{-3}$ mol·kg^{-1}) and GB ($m = 0.5$ mol·kg^{-1}). All the titrations consisted of 25 consecutive injections of aqueous amino acids or peptides with 20 s duration each and a 4 min interval between the successive injections. All the experiments were carried out at a constant temperature of $T = 298.15$ K. The ITC experiments provided a set of values for absolute heat (Q) liberated or absorbed at different molalities of the amino acids in the solution. From these values, the limiting heats of dilution ($\Delta_{dil}H^0$) was calculated, for respective amino acids and peptides by fitting the values of the measured heat (Q) to the following equation

$$Q = \Delta_{dil}H^0 + mS_V, \quad (4)$$

where m is the molality of the solute in solution and S_v is the empirical slope. The transfer enthalpy of dilution ($\Delta_{tr}\Delta_{dil}H^0$) from water to HTAB ($m = 2 \cdot 10^{-3}$ mol·kg^{-1})/SDS ($m = 10 \cdot 10^{-3}$ mol·kg^{-1}) in presence of GB ($m = 0.5$ mol·kg^{-1}) were calculated for all the five amino acids and two peptides.

3. Results and discussion

3.1. Contributions of zwitterionic end groups and methylene groups to standard partial molar volume $V^0_{2,m}$

The values of density (ρ), apparent molar volume ($V_{2,\phi}$), speed of sound (u) and adiabatic compressibility (k_S), and apparent molar adiabatic compressibility ($K_{S,2,\phi}$) of different amino acids at different molalities (m) and $T = 298.15$ K, in the combined presence of HTAB ($m = 2 \cdot 10^{-3}$ mol·kg^{-1}) and GB ($m = 1.0$ mol·kg^{-1}) are shown in table 2. These values in the combined presence of SDS ($m = 10 \cdot 10^{-3}$ mol·kg^{-1}) and GB ($m = 1.0$ mol·kg^{-1}) are shown in table 3. In case of amino acids where molality dependence of $V_{2,\phi}$ was found to have a definite trend, the values of standard partial molar volume at infinite dilution ($V^0_{2,m}$) were obtained by least square fitting of the data points to the following equation.

$$V_{2,\phi} = V^0_{2,m} + S_v m. \quad (5)$$

Here, S_V is the empirical slope, which is sometimes considered to be a volumetric pair-wise interaction coefficient [23,24]. In the other cases, $V^0_{2,m}$ was obtained by averaging all the data points. The standard partial molar volumes of amino acids and peptides in water [25–27] and in combination of HTAB ($m = 2 \cdot 10^{-3}$ mol·kg^{-1})/SDS ($m = 10 \cdot 10^{-3}$ mol·kg^{-1}) and GB ($m = 1.0$ mol·kg^{-1}) at $T = 298.15$ K are shown in table 4.

It is observed that the $V^0_{2,m}$ values of amino acids in presence of HTAB ($m = 2 \cdot 10^{-3}$ mol·kg^{-1}) and SDS ($m = 10 \cdot 10^{-3}$ mol·kg^{-1}) in similar concentration of GB, hardly change. But, interestingly on comparing the $V^0_{2,m}$ of amino acids in HTAB ($m = 1.0$ mol·kg^{-1})/SDS ($m = 50 \cdot 10^{-3}$ mol·kg^{-1}) with amino acids in the combination of HTAB ($m = 2 \cdot 10^{-3}$ mol·kg^{-1})/SDS ($m = 10 \cdot 10^{-3}$ mol·kg^{-1}) and GB ($m = 1.0$ mol·kg^{-1}), it was observed that the $V^0_{2,m}$ values increased for glycine and alanine while it decreased for valine and leucine (table 4). The values of $V^0_{2,m}$ in presence of HTAB/SDS only and in the combination of HTAB/SDS and GB, showed a linear variation with the number of carbon atoms in the alkyl side chain of the amino acids. Since the values of standard partial molar volume $V^0_{2,m}$, of an amino acid is a sum of contribution of the zwitter ionic end groups and the number of CH_2 groups in it, it can be represented by the following equation

$$V^o_{2,m} = V^o_{2,m}(NH_3^+, COO^-) + n_c V^o_{2,m}(CH_2), \quad (6)$$

where n_c is the number of carbon atoms in the alkyl chain of the amino acids and, $\mathbf{V^o_{2,m}(NH_3^+, COO^-)}$ and $\mathbf{V^o_{2,m}(CH_2)}$ are the values of the partial molar volume of the zwitterionic and methylene end group contribution to $V^0_{2,m}$, respectively. The values of $\mathbf{V^o_{2,m}(NH_3^+, COO^-)}$ and $\mathbf{V^o_{2,m}(CH_2)}$ for alkyl chains of different α-amino acids (CH_2-Glycine, CH_3CH-Alanine, CH_3 CH_2CH-α-amino-n-butyric acid, CH_3CH_2CHCH-Valine, $CH_3CH_2CHCHCH_2CH$-leucine) were calculated by the methods suggested by Hakin *et al.* [28] and are listed in table 5. The values of $\mathbf{V^o_{2,m}(NH_3^+, COO^-)}$ and $\mathbf{V^o_{2,m}(CH_2)}$ as reported by Singh *et al.* [21] for HTAB ($m = 1.0$ mol·kg^{-1}) are (28.38 ± 0.99) and (15.83 ± 0.29) respectively which is more or less similar to the values $\mathbf{V^o_{2,m}(NH_3^+, COO^-)}$ and $\mathbf{V^o_{2,m}(CH_2)}$ observed for SDS ($m = 50 \cdot 10^{-3}$ mol·kg^{-1}). The large values of $\mathbf{V^o_{2,m}(NH_3^+, COO^-)}$ as compared to $\mathbf{V^o_{2,m}(CH_2)}$indicates that both surfactants interact primarily with the zwitterionic centres of the amino acids. With the increase in

TABLE 2
Values of the density (ρ)[a], apparent molar volume ($V_{2,\phi}$), speed of sound (u)[a], adiabatic compressibility (k_S) and apparent molar adiabatic compressibility ($K_{S,2,\phi}$) of amino acids in $2 \cdot 10^{-3}$ mol·kg^{-1} hexadecyltrimethylammonium bromide and 1.0 mol·kg^{-1} glycine betaine in water at $T = 298.15$ K at various molalities (m).

m (mol·kg^{-1})	ρ (g·cm^{-3})	$V_{2,\phi}$ (cm^3·mol^{-1})	u (m·s^{-1})	10^{-11} k_s (Pa^{-1})	10^{-8} $K_{S,2,\phi}$ (cm^3·mol^{-1}·Pa^{-1})
			Glycine		
0.0	1.016371		1579.75	39.4249	
0.206262	1.022600	44.35	1590.03	38.6797	−1.8376
0.315723	1.025794	44.55	1595.38	38.3011	−1.7947
0.539095	1.032187	44.76	1605.89	37.5673	−1.7086
0.749391	1.038023	44.93	1615.58	36.9093	−1.6442
0.842720	1.040679	44.86	1619.96	36.6163	−1.6362
1.033323	1.045726	45.06	1628.41	36.0624	−1.5765
1.168403	1.049249	45.16	1634.33	35.6814	−1.5408
1.345699	1.053760	45.29	1641.91	35.2014	−1.4932
			L-Alanine		
0.0	1.016414		1579.99	39.4113	
0.186917	1.021486	61.08	1591.82	38.6349	−1.7255
0.378252	1.026518	61.18	1603.69	37.8785	−1.6691
0.501012	1.029610	61.35	1611.02	37.4219	−1.6100
0.654287	1.033446	61.42	1619.77	36.8812	−1.5386
0.767967	1.036191	61.52	1626.55	36.4775	−1.5141
0.961456	1.040842	61.57	1637.44	35.8331	−1.4547
1.085473	1.043726	61.64	1644.34	35.4348	−1.4197
1.175009	1.045789	61.67	1649.08	35.1619	−1.3896
			α-Amino-n-butyric acid		
0.0	1.016378		1579.86	39.4192	
0.081824	1.018556	75.51	1586.40	39.0112	−1.9567
0.106304	1.019190	75.57	1588.32	38.8928	−1.9309
0.138573	1.020033	75.61	1590.89	38.7352	−1.9263
0.171522	1.020893	75.66	1593.50	38.5759	−1.9199
0.189259	1.021346	75.67	1594.93	38.4896	−1.9184
0.220146	1.022138	75.69	1597.30	38.3458	−1.8937
0.263692	1.023231	75.78	1600.62	38.1461	−1.8585
0.358759	1.025877	75.88	1607.83	37.7072	−1.8044
			L-Valine		
0.0	1.015395		1575.58	39.6720	
0.045258	1.016568	90.14	1580.02	39.4038	−2.2830
0.071447	1.017201	90.51	1582.40	39.2609	−2.1017
0.094408	1.017831	90.13	1584.71	39.1223	−2.2073
0.114442	1.018302	90.47	1586.48	39.0170	−2.1040
0.131169	1.018722	90.47	1588.18	38.9175	−2.1419
0.147779	1.019101	90.72	1589.70	38.8287	−2.0959
0.234966	1.021262	90.63	1597.74	38.3575	−2.0320
0.304267	1.022962	90.57	1604.22	37.9850	−2.0188
			L-Leucine		
0.0	1.016066		1578.51	39.4988	
0.051045	1.017241	106.70	1584.18	39.1712	−2.1385
0.064475	1.017552	106.64	1585.72	39.0832	−2.1748
0.076343	1.017783	107.15	1586.90	39.0163	−2.0392
0.085272	1.017976	107.22	1587.84	38.9627	−2.0111
0.094503	1.018225	106.76	1589.00	38.8963	−2.1194
0.105407	1.018422	107.22	1590.10	38.8350	−2.0336
0.109959	1.018561	106.88	1590.70	38.8004	−2.1014
0.123104	1.018818	107.18	1592.07	38.7239	−2.0443
			Glyclyglycine		
0.0	1.016267		1579.28	39.4524	
0.097166	1.021444	78.02	1586.95	38.8740	−2.8248
0.116122	1.022456	77.92	1588.44	38.7627	−2.8243
0.132799	1.023326	77.99	1589.84	38.6615	−2.8430
0.194601	1.026593	77.84	1594.59	38.3092	−2.7984
0.222748	1.027987	78.16	1596.65	38.1586	−2.7316
0.227887	1.028312	77.90	1597.22	38.1194	−2.7862
0.271799	1.030501	78.20	1600.34	37.8902	−2.6917
0.324834	1.033264	78.03	1604.52	37.5923	−2.7013
			Triglycine		
0.0	1.016099		1578.53	39.4965	
0.026882	1.018075	114.75	1581.09	39.2923	−2.9670
0.045863	1.019452	114.99	1582.89	39.1500	−2.9322
0.058339	1.020396	114.35	1583.99	39.0595	−2.9054
0.078062	1.021867	113.95	1585.91	38.9089	−2.9710
0.088022	1.022549	114.47	1586.71	38.8437	−2.8517

(*continued on next page*)

TABLE 2 (*continued*)

m (mol·kg^{-1})	ρ (g·cm^{-3})	$V_{2,\phi}$ (cm^3·mol^{-1})	u (m·s^{-1})	10^{-11} k_s (Pa^{-1})	10^{-8} $K_{S,2,\phi}$ (cm^3·mol^{-1}·Pa^{-1})
0.092527	1.022893	114.28	1587.29	38.8023	−2.9490
0.100532	1.02350	114.03	1588.05	38.7422	−2.9638
0.143524	1.026644	113.83	1592.22	38.4215	−2.9975

[a] The maximum uncertainties in density and velocity measurements were observed to be $3 \cdot 10^{-6}$ g·cm^{-3} and 0.03 m·s^{-1}, respectively.

the size of the alkyl group in the side chain, the contribution to the value of $V^0_{2,m}$ also increases as a result of combined effect of altered solvent structure and solute-solvent interactions. The detailed analysis of the intermolecular interactions has been done further where the thermodynamic properties of transfer from water to the mixed surfactant-GB solutions are discussed.

3.2. Number of water molecules hydrated to the amino acids (N_H) in aqueous solvents

The values of standard partial molar volume of amino acids were further used to calculate the number of water molecules hydrated to these solutes. In general, the hydration number depends on the alteration of structure of water in the bulk and orientation of water molecules around the solutes.

The number of water molecules hydrated by the homologous series of amino acids was calculated according to the following equation [29].

$$V^0_{2,m} = V^0_{2,m}(\text{int}) + V^0_{2,m}(\text{elect}), \tag{7}$$

where $V^0_{2,m}$(int) is the intrinsic partial molar volume of the amino acids and $V^0_{2,m}$(elect) is the electrostriction partial molar volume due to hydration of the amino acids. $V^0_{2,m}$(int) can be further divided into two terms, one for the van der Waals volume and other for the volume due to the packing effects which according to Millero *et al.* [25] can be expressed by the following relationship.

$$V^0_{2,m}(\text{int}) = \frac{0.7}{0.634}[V^0_{2,m}(\text{cryst})], \tag{8}$$

where 0.7 is the packing density of the molecules in an organic crystal and 0.634 is the packing density of random packed spheres. The molar volume of the crystal was calculated from the crystal densities of the amino acids at T = 298.15 K reported by Berlin and Pallansh [30]. The values of $V^0_{2,m}$(elect) were obtained from equation (7). The decrease in $V^0_{2,m}$(elect) can be related to the hydration number N_H of the amino acids by the following equation [30]

$$N_H = \frac{V^0_{2,m}(\text{elect})}{V^0_E - V^0_B}, \tag{9}$$

where V^0_E is the molar volume of the electrostricted water and V^0_B is the molar volume of the bulk water at T = 298.15 K. This model assumes that for every water molecule moved from bulk phase to the region near the amino acid, the volume is decreased by $V^0_E - V^0_B$. Using $(V^0_E - V^0_B) \sim -3$ cm^3 mol^{-1} [25] for electrolytes at T = 298.15 K, the hydration number (N_H) have been calculated and are reported in table 6.

The calculated values of *NH* are observed to vary according to the following order (leucine > valine > alanine > glycine) irrespective of the concentrations and types of co-solvents used. It is worth noting, that such a trend is a manifestation of increase in hydrophobicity with increasing alkyl chain length, resulting in increased electrostriction around the zwitter ionic end groups. But if observed keenly, the N_H for glycine, alanine and valine does not show a significant variation in the combination of surfactant and GB as compared to, in surfactants only. However, the N_H of leucine increases slightly in the combined presence of HTAB/SDS and GB as compared to HTAB/SDS only which might possibly be due to increase in the size of alkyl groups coupled with the altered solvent structure leading to increased electrostriction in leucine.

3.3. Standard partial molar volumes of transfer ($\Delta_{tr}V^0_{2,m}$) of amino acids from water to combinations of HTAB/SDS and GB solutions

The standard partial molar volume of transfer ($\Delta_{tr}V^0_{2,m}$) for the amino acids and peptides from water to surfactant solutions were calculated according to equation (10) and are represented in table 7.

$$\Delta_{tr}V^0_{2,m} = V^0_{2,m}(\text{aqueous HTAB/SDS and GB}) - V^0_{2,m}(\text{Water}). \tag{10}$$

According to Franks *et al.* [29], the $V^0_{2,m}$ of a non-electrolyte is explained as a combination of intrinsic volume of the solute and the volume changes due to interactions with the solvent. The intrinsic volume is considered to be consisting of two types of contributions:

$$V_{\text{intrinsic}} = V_{vW} - V_{\text{void}}, \tag{11}$$

where V_{vW} is the volume occupied by the solute due to its van der Waals volume [31] and V_{void} is the volume associated with the voids and empty spaces [32]. The above equation is further modified by Shaidi *et al.* [33] in order to evaluate the contribution of solute molecule towards $V^0_{2,m}$, wherein volume of shrinkage was incorporated, which is primarily produced by the interaction of hydrogen bonding groups present in the solute with water molecules. Finally, $V^0_{2,m}$ of an amino acid or a peptide can be viewed as:

$$V^0_{2,m} = V_{vW} + V_{\text{void}} - V_{\text{shrinkage}}. \tag{12}$$

Since the values of V_{vW} and V_{void} remain more or less constant in water and the aqueous surfactant solutions, the positive or the negative values of $\Delta_{tr}V^0_{2,m}$ for amino acids and peptides can be rationalized in terms of increase and decrease in the volume of shrinkage in the presence of co-solvents in aqueous solutions. The values of $\Delta_{tr}V^0_{2,m}$ further highlight the positive and negative modulation of solvent structure in the bulk upon solute co-solvent interactions. And since $V^0_{2,m}$ by definition is free from solute-solute interactions, it provides information about the solute solvent interactions. Furthermore based on the properties of the water molecules in the hydration co-sphere, which largely depends on the nature of the solute species, following different types of interactions can occur between the solute and solvent system: (A) Hydrophobic-hydrophobic interactions occurring between the non-polar side chains of amino acids and non-polar parts of HTAB/SDS and GB; (B) Hydrophilic-hydrophobic interactions between non-polar parts of amino acids and polar head group of HTAB/SDS and GB and vice-versa; (C) Ion-hydrophilic/hydrophilic-hydrophilic interaction occurring between zwitter ionic centers of amino acids and the and polar head group of HTAB/SDS and GB. The last of these type of interaction contribute positively to $\Delta_{tr}V^0_{2,m}$ since these lead to reduction in the electrostriction effect and the overall water structure in the bulk is enhanced, while the first two types contribute negatively to the $\Delta_{tr}V^0_{2,m}$, because the introduction of the alkyl group leads to reduction in the structure of water in the bulk, formed as a result of co-sphere overlap *i.e.* water moves from the hydration co-spheres (water more organized) to the bulk (water relatively less organized). Thus in simple terms, due to hydrophobic hydration of amino acids with bulky alkyl groups, water in the hydration shells is more organized as compared to that in the bulk. In contrast in amino acids with no or smaller alkyl groups, water in the hydration shell is less organized as compared to in bulk, primarily due to the effects of electrostriction. Upon solute solvent interaction, the water trapped in the hydration shells moves into

TABLE 3
Values of density (ρ)[a], apparent molar volume ($V_{2,\phi}$), speed of sound (u)[a], adiabatic compressibility (K_S) and apparent molar adiabatic compressibility ($K_{S,2,\phi}$) of amino acids in $10 \cdot 10^{-3}$ mol·kg^{-1} sodium dodecyl sulfate and 1.0 mol·kg^{-1} glycine betaine in water at $T = 298.15$ K at various molalities (m).

m (mol·kg^{-1})	ρ (g·cm^{-3})	$V_{2,\phi}$ (cm^3·mol^{-1})	u (m·s^{-1})	$10^{-11}\,k_s$ (Pa^{-1})	$10^{-8}\,K_{s,2,\phi}$ (cm^3·mol^{-1}·Pa^{-1})
		Glycine			
0.0	1.017101		1582.21	39.2742	
0.134734	1.021178	44.37	1588.90	38.7887	−1.8215
0.256688	1.024795	44.49	1594.90	38.3615	−1.7890
0.481684	1.031345	44.59	1605.61	37.6111	−1.7174
0.619624	1.035208	44.76	1611.94	37.1770	−1.6636
0.745759	1.038669	44.89	1617.61	36.7938	−1.6178
0.872627	1.042078	45.03	1623.16	36.4231	−1.5718
1.027786	1.046212	45.13	1630.05	35.9731	−1.5339
1.049721	1.046786	45.15	1630.91	35.9155	−1.5241
1.224756	1.051336	45.26	1638.54	35.4278	−1.4839
		L-Alanine			
0.0	1.016994		1581.77	39.3002	
0.104143	1.019830	61.10	1588.35	38.8669	−1.7141
0.221571	1.022970	61.16	1595.65	38.3939	−1.6726
0.260690	1.024001	61.19	1598.08	38.2387	−1.6641
0.404349	1.027711	61.33	1606.67	37.6943	−1.5934
0.524772	1.030761	61.40	1613.80	37.2514	−1.5510
0.572523	1.031951	61.43	1616.57	37.0810	−1.5327
0.811817	1.037775	61.59	1630.19	36.2594	−1.4497
0.892795	1.039723	61.60	1634.85	35.9854	−1.4337
0.990324	1.041996	61.67	1640.15	35.6752	−1.3989
		α-Amino-n-butyric acid			
0.0	1.016848		1581.15	39.3367	
0.056538	1.018353	75.55	1585.67	39.0549	−1.9455
0.098141	1.019443	75.64	1588.96	38.8518	−1.9198
0.132092	1.020328	75.67	1591.63	38.6880	−1.9002
0.148779	1.020748	75.77	1592.89	38.6109	−1.8701
0.171371	1.021322	75.83	1594.62	38.5055	−1.8498
0.189445	1.021785	75.83	1596.02	38.4206	−1.8406
0.218626	1.022531	75.84	1598.25	38.2855	−1.8236
0.230447	1.022820	75.90	1599.11	38.2335	−1.8048
0.239704	1.023055	75.90	1599.83	38.1903	−1.8033
		L-Valine			
0.0	1.016788		1580.96	39.3485	
0.0457926	1.017920	90.56	1585.10	39.0997	−1.9420
0.1169092	1.019746	90.48	1591.98	38.6930	−2.0124
0.1445535	1.020408	90.67	1594.55	38.5434	−1.9807
0.1776768	1.021290	90.51	1597.80	38.3536	−2.0430
0.2131960	1.02210	90.64	1600.83	38.1783	−1.9376
0.2596761	1.023223	90.67	1605.08	37.9347	−1.9138
0.3187454	1.024637	90.69	1610.44	37.6306	−1.8866
0.3924421	1.026406	90.65	1617.20	37.2523	−1.8759
		L-Leucine			
0.0	1.017030		1581.84	39.2953	
0.048882	1.018117	107.40	1587.09	38.9941	−1.8705
0.063164	1.018412	107.71	1588.61	38.9083	−1.8306
0.079418	1.018787	107.43	1590.41	38.8060	−1.8866
0.091394	1.019049	107.43	1591.64	38.7360	−1.8530
0.100376	1.019279	107.10	1592.70	38.6758	−1.9244
0.108167	1.019427	107.32	1593.45	38.6338	−1.8675
0.123485	1.019763	107.32	1595.21	38.5359	−1.9097
0.137503	1.020079	107.24	1596.57	38.4583	−1.8592
		Dilglycine			
0.0	1.016639		1580.24	39.3901	
0.014582	1.017416	78.37	1581.31	39.3068	−2.5385
0.041396	1.018843	78.29	1583.39	39.1487	−2.6706
0.153914	1.024794	78.07	1592.08	38.4976	−2.6981
0.179894	1.026125	78.21	1594.02	38.3541	−2.6633
0.217123	1.028052	78.22	1596.86	38.1462	−2.6499
0.232288	1.028827	78.25	1597.98	38.0640	−2.6405
0.269804	1.030707	78.42	1600.70	37.8656	−2.5882
0.306016	1.032545	78.44	1603.42	37.6701	−2.5729
0.360408	1.035265	78.51	1607.44	37.3834	−2.5406
		Triglycine			
0.0	1.016866		1581.24	39.3315	
0.019661	1.018345	113.09	1583.08	39.1831	−2.9906
0.029828	1.019099	113.36	1584.02	39.1077	−2.9460
0.040738	1.019891	113.86	1585.12	39.0231	−3.0016

(*continued on next page*)

TABLE 3 (*continued*)

m (mol·kg^{-1})	ρ (g·cm^{-3})	$V_{2,\phi}$ (cm^3·mol^{-1})	u (m·s^{-1})	$10^{-11}\,k_s$ (Pa^{-1})	$10^{-8}\,K_{s,2,\phi}$ (cm^3·mol^{-1}·Pa^{-1})
0.052173	1.020752	113.55	1586.12	38.9411	−2.9382
0.064227	1.021615	113.98	1587.30	38.8503	−2.9396
0.067681	1.021895	113.60	1587.64	38.8231	−2.9780
0.077195	1.022602	113.52	1588.51	38.7537	−2.9583
0.086814	1.023408	113.95	1589.44	38.6779	−2.8409

[a] The maximum uncertainties in density and velocity measurements were observed to be $3\cdot10^{-6}$ g·cm^{-3} and 0.03 m·s^{-1}, respectively.

TABLE 4
Standard partial molar volume ($V^0_{2,m}$) of amino acids in 1 mol·kg^{-1} of HTAB, $50\cdot10^{-3}$ mol·kg^{-1} SDS and in the combined presence of $2\cdot10^{-3}$ mol·kg^{-1} hexadecyltrimethylammonium bromide (HTAB)/$10\cdot10^{-3}$ mol·kg^{-1} sodium dodecyl sulfate (SDS) and 1.0 mol·kg^{-1} glycine betaine (GB) at T = 298.15 K.

Amino acids/peptides	V^0_2/(cm^3·mol^{-1})	$V^0_{2,m}$ /(cm^3·mol^{-1})			
	Water	‡HTAB[d]	†HTAB + GB$^{\psi}$	*SDS[d]	**SDS + GB$^{\psi}$
Glycine	43.14 ± 0.06[a]	44.07 ± 0.16	44.29 ± 0.05	43.46 ± 0.01	44.25 ± 0.03
L-Alanine	60.43 ± 0.04[a]	60.57 ± 0.03	61.01 ± 0.03	60.55 ± 0.01	61.04 ± 0.02
α-Amino-n-butyric acid	75.51 ± 0.02	–	75.43 ± 0.01	–	75.45 ± 0.02
L-Valine	90.39 ± 0.14[a]	90.70 ± 0.17	90.46 ± 0.21	90.99 ± 0.17	90.52 ± 0.08
L-Leucine	107.72 ± 0.24[a]	108.17 ± 0.23	106.97 ± 0.25	108.27 ± 0.13	107.37 ± 0.18
Diglycine	76.23 ± 0.07[b]	77.28 ± 0.07	78.01 ± 0.12	–	78.31 ± 0.14
Triglycine	111.81 ± 0.01[c]	–	114.34 ± 0.40	–	113.62 ± 0.31

‡HTAB (m = 1 mol·kg^{-1}); †HTAB (m = $2\cdot10^{-3}$ mol·kg^{-1}); *SDS (m = $50\cdot10^{-3}$ mol·kg^{-1}); **SDS (m = $10\cdot10^{-3}$ mol·kg^{-1}); $^{\psi}$GB (m = 1.0 mol·kg^{-1}).
[a] Reference [25].
[b] Reference [26].
[c] Reference [27].
[d] Reference [21]

TABLE 5
Contribution of zwitter ionic group and other alkyl chains to the standard partial molar volume ($V^0_{2,m}$) in 1 mol·kg^{-1} of hexadecyltrimethylammonium bromide (HTAB), $50\cdot10^{-3}$ mol·kg^{-1} sodium dodecyl sulfate (SDS) and in the combined presence of $2\cdot10^{-3}$ mol·kg^{-1} HTAB/$10\cdot10^{-3}$ mol·kg^{-1} SDS and 1.0 mol·kg^{-1} glycine betaine (GB) at T = 298.15 K.

Groups	V^0_2 /(cm^3·mol^{-1})	$V^0_{2,m}$ /(cm^3·mol^{-1})			
	Water[a]	‡HTAB[a]	†HTAB + GB$^{\psi}$	*SDS[a]	**SDS + GB$^{\psi}$
NH_3^+, COO^-	27.68 ± 1.12	28.38 ± 0.99	29.19 ± 0.74	27.80 ± 0.95	29.00 ± 0.81
CH_2–	15.91 ± 0.33	15.83 ± 0.29	15.48 ± 0.22	16.00 ± 0.28	15.58 ± 0.25
CH_3CH–	31.82 ± 0.40	31.66 ± 0.40	30.96 ± 0.44	32.00 ± 0.40	31.16 ± 0.49
CH_3CH_2CH–	47.73 ± 0.40	–	46.44 ± 0.66	–	46.74 ± 0.74
CH_3CH_2CHCH–	63.64 ± 0.40	63.32 ± 0.40	61.92 ± 0.88	64.00 ± 0.40	62.32 ± 0.92
$CH_3CH_2CHCH_2CH$	79.55 ± 0.50	79.15 ± 0.55	77.41 ± 0.80	80.00 ± 0.50	77.91 ± 0.70

‡HTAB (m = 1 mol·kg^{-1}); †HTAB (m = $2\cdot10^{-3}$ mol·kg^{-1}); *SDS (m = $50\cdot10^{-3}$ mol·kg^{-1}); **SDS (m = $10\cdot10^{-3}$ mol·kg^{-1}); $^{\psi}$GB (m = 1.0 mol·kg^{-1}).
[a] Reference [21].

TABLE 6
The number of water molecules hydrated (N_H) to the amino acids in water and in aqueous solutions of 1 mol·kg^{-1} of hexadecyltrimethylammonium bromide (HTAB), $50\cdot10^{-3}$ mol·kg^{-1} sodium dodecyl sulfate (SDS) and in the combined presence of $2\cdot10^{-3}$ mol·kg^{-1} HTAB/$10\cdot10^{-3}$ mol·kg^{-1} SDS and 1.0 mol·kg^{-1} glycine betaine (GB) at T = 298.15 K.

Co-solvents	N_H			
	Glycine	L-Alanine	L-Valine	L-Leucine
Water[a]	2.9	3.8	3.9	5.5
‡HTAB[a]	2.6	3.8	3.9	5.3
†HTAB+GB$^{\psi}$	2.6	3.6	3.9	5.7
*SDS[a]	2.8	3.7	3.7	5.3
**SDS+GB$^{\psi}$	2.6	3.6	3.8	5.6

[a] Reference [21].
‡HTAB (m = 1 mol·kg^{-1}); †HTAB (m = $2\cdot10^{-3}$ mol·kg^{-1}); *SDS (m = $50\cdot10^{-3}$ mol·kg^{-1}); **SDS (m = $10\cdot10^{-3}$ mol·kg^{-1}); $^{\psi}$GB (m = 1.0 mol·kg^{-1}).

the bulk, which is more organized due to the combined effects of reduction in electrostriction and hydrogen bonding by surrounding water molecules, thus resulting in the positive values of $\Delta_{tr}V^0_{2,m}$.

Thus, glycine, showing a high positive value of $\Delta_{tr}V^0_{2,m}$ in all the studied co-solvent is predominantly due to the polar interactions between the zwitter ionic centres and the co-solvent. However with the increase in the alkyl side chain / hydrophobic content in the amino acid, the value for $\Delta_{tr}V^0_{2,m}$ varies from (0.93 ± 0.16) cm^3·mol^{-1} for glycine to (0.85 ± 0.04) cm^3·mol^{-1} for leucine in presence of HTAB (m = 1.0 mol·kg^{-1}) and from (0.32 ± 0.06) cm^3·mol^{-1} for glycine to (0.55 ± 0.26) cm^3·mol^{-1} for leucine in presence of SDS (m = $50\cdot10^{-3}$ mol·kg^{-1}). Such an undulating behaviour in presence of HTAB/SDS has been explained, previously by our group [21] on the basis polar interactions between the zwitter ionic centres and micellar HTAB/SDS on the surface of the micelles. But interestingly, in combination study, the values for $\Delta_{tr}V^0_{2,m}$ varies from (1.15 ± 0.07) cm^3·mol^{-1} for glycine to (−0.75 ± 0.35) cm^3·mol^{-1} for leucine in the combined presence of HTAB (m = $2\cdot10^{-3}$ mol·kg^{-1}) and GB (m = 1.0 mol·kg^{-1}) and from (1.11 ± 0.07) cm^3·mol^{-1} for glycine to –(0.35 ± 0.30) cm^3·mol^{-1} for leucine in the combined presence of SDS (m = $10\cdot10^{-3}$ mol·kg^{-1}) and GB (m = 1.0 mol·kg^{-1}). These findings, in particular indicate that for smaller amino acids like glycine and alanine, polar interactions with surfactants and GB dominates.

TABLE 7
Standard partial molar volume of transfer ($\Delta_{tr}V^0_{2,m}$) of amino acids in 1 mol·kg^{-1} of hexadecyltrimethylammonium bromide (HTAB), 50 · 10^{-3} mol·kg^{-1} sodium dodecyl sulfate (SDS) and in the combined presence of 2 · 10^{-3} mol·kg^{-1} HTAB/10 · 10^{-3} mol·kg^{-1} SDS and 1.0 mol·kg^{-1} glycine betaine (GB) at T = 298.15 K.

Amino acids/peptides	$\Delta_{tr}V^0_{2,m}$ / (cm^3·mol^{-1})			
	‡HTAB	†HTAB+GB$^{\psi}$	*SDS	**SDS+GB$^{\psi}$
Glycine	0.93 ± 0.16	1.15 ± 0.07	0.32 ± 0.06	1.11 ± 0.07
L-Alanine	0.14 ± 0.03	0.58 ± 0.06	0.12 ± 0.05	0.61 ± 0.04
α-Amino-n-butyric acid	–	−0.08 ± 0.03	–	−0.04 ± 0.03
L-Valine	0.31 ± 0.19	0.07 ± 0.25	0.60 ± 0.19	0.13 ± 0.16
L-Leucine	0.45 ± 0.29	−0.75 ± 0.35	0.55 ± 0.26	−0.35 ± 0.10
Diglycine	0.85 ± 0.04	1.78 ± 0.14	–	2.08 ± 0.15
Triglycine	–	2.53 ± 0.40	–	1.81 ± 0.31

‡HTAB (m = 1 mol·kg^{-1}); †HTAB (m = 2 · 10^{-3} mol·kg^{-1}); *SDS (m = 50 · 10^{-3} mol·kg^{-1}); **SDS (m = 10 · 10^{-3} mol·kg^{-1}); $^{\psi}$GB (m = 1.0 mol·kg^{-1}).

TABLE 8
Values of the standard partial molar adiabatic compressibility ($K^0_{S,2,m}$) of amino acids and peptides in the combined presence of 2 · 10^{-3} mol·kg^{-1} hexadecyltrimethylammonium bromide (HTAB)/10 · 10^{-3} mol·kg^{-1} sodium dodecyl sulfate (SDS) and 1.0 mol·kg^{-1} glycine betaine (GB) and the corresponding standard partial molar adiabatic compressibility of transfer ($\Delta_{tr}K^0_{S,2,m}$) at T = 298.15 K.

Amino acids/peptides	10^{-8} $K^0_{S,2}$ Water	10^{-8} $K^0_{S,2,m}$ /(cm^3·mol^{-1}·Pa^{-1})		10^{-8} $\Delta_{tr}K^0_{S,2,m}$ /(cm^3·mol^{-1}·Pa^{-1})	
		†HTAB+GB$^{\psi}$	**SDS+GB$^{\psi}$	†HTAB+GB$^{\psi}$	**SDS+GB$^{\psi}$
Glycine	−27.0 ± 0.44[a]	−18.84 ± 0.01	−18.66 ± 0.06	8.16 ± 0.44	8.34 ± 0.29
L-Alanine	−25.23 ± 0.28[a]	−17.85 ± 0.01	−17.48 ± 0.05	7.38 ± 0.28	7.75 ± 0.28
α-Amino-n-butyric acid	−27.10 ± 0.60	−20.02 ± 0.01	−19.96 ± 0.06	7.08 ± 0.60	7.14 ± 0.60
L-Valine	−30.62 ± 0.23[a]	−21.23 ± 0.87	−19.49 ± 0.59	9.31 ± 0.90	11.13 ± 0.63
L-Leucine	−31.78 ± 0.56[a]	−20.83 ± 0.58	−18.75 ± 0.30	10.95 ± 0.80	13.03 ± 0.64
Diglycine	−40.20 ± 0.10[b]	−27.75 ± 0.59	−26.18 ± 0.59	12.45 ± 0.60	14.02 ± 0.59
Triglycine	−44.90 ± 0.01[b]	−29.42 ± 0.45	−29.49 ± 0.50	15.48 ± 0.45	15.41 ± 0.50

[a] Reference [25].
[b] Reference [35].
†HTAB (m = 2 · 10^{-3} mol·kg^{-1}); **SDS (m = 10 · 10^{-3} mol·kg^{-1}); $^{\psi}$GB (m = 1.0 mol·kg^{-1}).

On the other hand, under similar concentration of both surfactant and GB, $\Delta_{tr}V^0_{2,m}$ value of (−0.08 ± 0.03) cm^3·mol^{-1} for α-amino-n-butyric acid and (0.07 ± 0.25) cm^3·mol^{-1} for valine in presence of HTAB and GB, and –(0.04 ± 0.03) cm^3·mol^{-1} for α-amino-n-butyric acid and (0.13 ± 0.16) cm^3·mol^{-1} for valine in presence of SDS and GB, suggest a possible balance between polar and hydrophobic interactions. However in presence of leucine, negative $\Delta_{tr}V^0_{2,m}$ of a comprehensive magnitude implies prevalence of hydrophobic interactions in the combination of HTAB/SDS and GB. The values of $\Delta_{tr}V^0_{2,m}$ corroborates well with the N_H data where a slight decrease in N_H was observed in case of glycine and an increase was observed in case of leucine compared to N_H in water. Furthermore, on comparing the $\Delta_{tr}V^0_{2,m}$ values of amino acids in HTAB/SDS only and in the combination of HTAB/SDS and GB, it seems that the hydrophobic interaction increases in the combination study with the increase in alkyl side chain. The values of $\Delta_{tr}V^0_{2,m}$ of diglycine from water to a combination of HTAB (m = 2 · 10^{-3} mol·kg^{-1})/SDS (m = 10 · 10^{-3} mol·kg^{-1}) and GB (m = 1.0 mol·kg^{-1}) is (1.78 ± 0.14) cm^3·mol^{-1} and (2.08 ± 0.15) cm^3·mol^{-1} respectively. On introduction of a glycine residue to the dipeptide increases the value of $\Delta_{tr}V^0_{2,m}$ to (2.53 ± 0.40) cm^3·mol^{-1} in the combined presence of HTAB and GB. But interestingly the values of $\Delta_{tr}V^0_{2,m}$ remains almost unchanged (1.81 ± 0.31) cm^3·mol^{-1} in the combined presence of SDS and GB, after the introduction of glycine residue in diglycine. Such an increase in $\Delta_{tr}V^0_{2,m}$ values of diglycine and triglycine with respect to glycine can be attributed to the strengthening of polar interactions resulting from the introduction of peptide bond in the monomeric unit, leading to enhancement of water structure in the bulk.

Thus from the overall findings of zwitter ionic and methylene end group contribution, $\Delta_{tr}V^0_{2,m}$ and N_H, it can be proposed that GB in the combination of HTAB/SDS (post cmc) seems to positively modulate the polar interactions with the zwitterionic centres only and has least effects on hydrophobic-hydrophobic and/or ion-hydrophobic types of interactions. However the residual hydrophobic interactions as observed in α-ABA, valine and leucine might arise due to the interactions of isolated surfactant molecules (not part of the micellar system) with the alkyl groups of amino acids. Existence of such isolated surfactant molecules under equilibrium conditions at and above critical micelle concentrations have been reported to arise due to thermodynamic barrier and changes in the visco-elastic properties of the solvent [34]. Moreover, in contrast to the surfactants and GB system, in presence of surfactants only, due to extensive micellization arising from the high post micellar concentration, HTAB/SDS generally shows polar interactions (positive $\Delta_{tr}V^0_{2,m}$) irrespective of increase in the size of alkyl groups in amino acids (table 7).

3.4. Apparent molar compressibility ($K_{S,2,\phi}$) of amino acids in aqueous solution of HTAB (m = 2 · 10^{-3} mol·kg^{-1})/SDS (m = 10 · 10^{-3} mol·kg^{-1}) and GB (m = 1.0 mol·kg^{-1}) at T = 298.15 K

The values of speed of sound (u), adiabatic compressibility (k_S) and apparent molar adiabatic compressibility ($K_{S,2,\phi}$) of amino acids and peptides in combined presence of HTAB (m = 2 · 10^{-3} mol·kg^{-1})/SDS (m = 10 · 10^{-3} mol·kg^{-1}) and GB (m = 1.0 mol·kg^{-1}) are reported in tables 2 and 3. The values of apparent molar compressibility ($K_{S,2,\phi}$) at infinite dilution is an important property and provide valuable information on the interaction of HTAB/SDS and GB with amino acids. The standard partial molar adiabatic compressibility ($K^0_{S,2,m}$) of amino acids were obtained by fitting the values of $K_{S,2,\phi}$ against m according to the following equation

$$K_{S,2,\phi} = K^0_{S,2,m} + S_k m. \quad (13)$$

Here, S_k is the experimentally observed concentration dependence of $K_{S,2,\phi}$ at T = 298.15 K. In all other cases an average of all data

points was taken as $K_{S,2,\phi}$. The $K^0_{S,2,m}$ values for amino acids and peptides in the combined presence of HTAB ($m = 2 \cdot 10^{-3}$ mol·kg^{-1})/SDS ($m = 10 \cdot 10^{-3}$ mol·kg^{-1}) and GB ($m = 1.0$ mol·kg^{-1}) at $T = 298.15$ K are listed in table 8.

According to Franks *et al.* [26], the values of standard partial molar adiabatic compressibility $K^0_{S,2,m}$ can further be expressed by the following equation:

$$K^0_{S,2,m} = K^0_{S,2,m}(\text{int}) + K^0_{S,2,m}(\text{elect}), \tag{14}$$

where $K^0_{S,2,m}$(int) is the intrinsic partial molar adiabatic compressibility of the amino acids and $K^0_{S,2,m}$(elect) is the electrostriction partial molar adiabatic compressibility due to hydration of amino acids. Since the value $K^0_{S,2,m}$(int) is very small, it can be assumed as the first approximation [29], such that the value of $K^0_{S,2,m}$ becomes equal to $K^0_{S,2,m}$(elect). Further the standard partial molar adiabatic compressibility of amino acids and peptides in water ($K^0_{S,2}$) [25,35] and in presence of HTAB/SDS and GB ($K^0_{S,2,m}$) were used to calculate the standard partial molar adiabatic compressibility of transfer ($\Delta_{tr}K^0_{S,2,m}$) according to equation 15. The values of $\Delta_{tr}K^0_{S,2,m}$ are listed in table 8.

$$\Delta_{tr}K^0_{S,2,m} = K^0_{S,2,m}(\text{aqueous HTAB/SDS and GB}) - K^0_{S,2,m}(\text{Water}). \tag{15}$$

Thus, by definition, while $K^0_{S,2,m}$ indicates the compressibility of the overall solution, $\Delta_{tr}K^0_{S,2,m}$ indicates the contribution of electrostricted water in the hydration shells to the overall compressibility of the solution. So when hydrophobic interactions between the solute and solvent increases, as a rule $\Delta_{tr}K^0_{S,2,m}$ is negative as the water moves from more structured to less structured region (bulk). As opposed to this, in case of polar interactions between the solute and solvent, $\Delta_{tr}K^0_{S,2,m}$ is positive as water molecules moves from the hydration shells into the bulk (more ordered) thereby increasing the compressibility of the solution.

In the present study, the values of $K^0_{S,2,m}$ for all the studied amino acids and peptides are found to be negative in the combined presence of HTAB ($m = 2 \cdot 10^{-3}$ mol·kg^{-1})/SDS ($m = 10 \cdot 10^{-3}$ mol·kg^{-1}) and GB ($m = 1.0$ mol·kg^{-1}), as compared to in water, indicating movement of water from bulk into hydration shell of the ions. Furthermore the values of $K^0_{S,2,m}$ in general show a non linear increase in negativity with the increase in side chain length and branching of the amino acids and peptides in the presence of co-solvent. The small overall increase in negativity observed in $K^0_{S,2,m}$ of amino acids (-18.84 ± 0.01 to -20.83 ± 0.58)10^{-8} cm^3·mol^{-1}·Pa^{-1} in the presence of HTAB ($m = 2 \cdot 10^{-3}$ mol·kg^{-1}) and GB ($m = 1.0$ mol·kg^{-1}), and ($-18.66 \pm 0.06$to -19.96 ± 0.06)10^{-8} cm^3·mol^{-1}·Pa^{-1} in presence of SDS ($m = 10 \cdot 10^{-3}$ mol·kg^{-1}) and GB ($m = 1.0$ mol·kg^{-1}), fits our findings from $\Delta_{tr}V^0_{2,m}$. Such an increase in negativity in $K^0_{S,2,m}$ of amino acids with the increase in the side chain length can be justified on the basis of independent hydration of methylene group combined with their increasing distance from the zwitter ionic centres. However, under similar concentration of surfactant and GB, the $\Delta_{tr}K^0_{S,2,m}$ of amino acids shows a non-linear positive increase from $(8.16 \pm 0.44) \cdot 10^{-8}$ to $(10.95 \pm 0.80) \cdot 10^{-8}$ cm^3.mol^{-1}Pa^{-1} in presence of HTAB and GB, and from $(8.34 \pm 0.29) \cdot 10^{-8}$ to $(13.03 \pm 0.64) \cdot 10^{-8}$ cm^3.mol^{-1}Pa^{-1} in presence of SDS and GB. Such an unusual behavior observed in case of α-ABA, valine and leucine irrespective of hydrophobic interactions can be attributed to the strong water structure enhancing effects of GB. We thus propose that, upon solute solvent interaction, the structure released water from hydration shell is significantly enhanced in the bulk due to GB. This results in increased contribution of electrostricted water to the overall compressibility of the solution. This is possible as GB is known to form strong hydrogen bonds, thereby increasing the ordered organization of water molecules [36]. In contrary the large positive values of $\Delta_{tr}K^0_{S,2,m}$ for diglycine and triglycine as compared to glycine reinforce our findings from $\Delta_{tr}V^0_{2,m}$ and further confirm the prevalence of polar interactions arising due to addition of peptide bonds (table 8). The small overall increase in $\Delta_{tr}K^0_{S,2,m}$ in SDS and GB system as compared to HTAB and GB system might be due to the extensive micelle forming ability of SDS as compared to HTAB.

Thus in a nutshell, the findings of $\Delta_{tr}V^0_{2,m}$ and $\Delta_{tr}K^0_{S,2,m}$of amino acids in presence of surfactants and GB suggests a principal role of polar interactions. However with the increase in the size of the alkyl groups (valine and leucine) isolated surfactant molecules primarily interact hydrophobically resulting in the increase in negativity of $\Delta_{tr}V^0_{2,m}$ and $K^0_{S,2,m}$ of the overall solution. In addition, in valine and leucine due to the absence of significant polar interaction as observed in glycine and alanine, GB can significantly enhances structure of the electrostricted water in the bulk.

3.5. Enthalpy of transfer of amino acids from water to HTAB ($m = 2 \cdot 10^{-3}$ mol·kg^{-1})/SDS ($m = 10 \cdot 10^{-3}$ mol·kg^{-1}) in presence of GB ($m = 0.5$ mol·kg^{-1})

The heat liberated/absorbed (Q) during the titration of homologous amino acids and peptides in the combined presence of HTAB ($m = 2 \cdot 10^{-3}$ mol·kg^{-1})/SDS ($m = 10 \cdot 10^{-3}$ mol·kg^{-1}) and GB ($m = 0.5$ mol·kg^{-1}) are presented in table 9. The heats of dilution as a function of molality of amino acids in HTAB ($m = 2 \cdot 10^{-3}$ mol·kg^{-1}) and GB ($m = 0.5$ mol·kg^{-1}) are shown in (figure 1A) and in SDS ($m = 10 \cdot 10^{-3}$ mol·kg^{-1}) and GB ($m = 0.5$ mol·kg^{-1}) are shown in (figure 1B). The data thus obtained were fitted according to equation (4) to get the limiting heat of dilution ($\Delta_{dil}H^0$) presented in table 10. The values of limiting heats of dilution in water for the amino acids and peptides were also obtained according to equation (4). The enthalpy of transfer ($\Delta_{tr}\Delta_{dil}H^0$) of aqueous amino acid from water to a combined solution of HTAB ($m = 2 \cdot 10^{-3}$ mol·kg^{-1})/SDS ($m = 10 \cdot 10^{-3}$ mol·kg^{-1}) and GB ($m = 0.5$ mol·kg^{-1}) were calculated according to equation (16) and are presented in table 10.

$$\Delta_{tr}\Delta_{dil}H^0 = \Delta_{dil}H^0(\text{aqueous HTAB/SDS and GB}) - \Delta_{dil}H^0(\text{Water}). \tag{16}$$

It is observed that the $\Delta_{dil}H^0$ of the amino acids and peptides are all positive in the presence of HTAB/SDS and GB with the only exception of triglycine, which has a value of –(7.3 ± 1.7) J·mol^{-1} in presence of HTAB and GB. It is however worthy to note that the exothermicity and endothermicity of amino acids and peptides depends on a number of factors viz ion-polar, ion-hydrophobic, hydrophobic-hydrophobic interactions as well as solvent structure making and breaking effects. Out of these, the ion-polar interactions and the solvent structure making effects contributes exothermically while the ion-hydrophobic, hydrophobic-hydrophobic interactions and the solvent structure breaking effects contribute endothermically to the overall observed heat. The $\Delta_{dil}H^0$ of glycine and alanine (75.1 ± 1.1) J·mol^{-1} and (192.6 ± 1.7) J·mol^{-1}, respectively in presence of HTAB ($m = 2 \cdot 10^{-3}$ mol·kg^{-1}) and GB ($m = 0.5$ mol·kg^{-1}), and (158.1 ± 1.8) J·mol^{-1} and (197.6 ± 1.1) J·mol^{-1}, respectively in presence of SDS ($m = 10 \cdot 10^{-3}$ mol·kg^{-1}) and GB ($m = 0.5$ mol·kg^{-1}) visibly oppose our findings from volumetric and compressibility studies. However, it is known that, a considerable amount of heat is required to create a cavity to accommodate solute molecules upon their introduction into a stable solvent system. Thus taking the above assumption into consideration, the heat released during the structure breaking effect of solvent upon introduction of amino acids, the small positive values of $\Delta_{dil}H^0$ seems palpable in the combined presence of HTAB/SDS and GB. An increase in the endothermicity of $\Delta_{dil}H^0$ in alanine as compared to glycine might be due to the extensive structure

TABLE 9
Heat of dilution (Q) of amino acids and peptides against in the combined presence of $2 \cdot 10^{-3}$ mol·kg^{-1} hexadecyltrimethylammonium bromide (HTAB)/$10 \cdot 10^{-3}$ mol·kg^{-1} sodium dodecyl sulfate (SDS) and 0.5 mol·kg^{-1} glycine betaine (GB) at T = 298.15 K at various molalities (m).

$m/10^{-3}$mol·kg^{-1}	Q/J·mol^{-1}		$m/10^{-3}$mol·kg^{-1}	Q/J·mol^{-1}	
Amino acids/peptides	†HTAB+GB$^{\psi}$	**SDS+GB$^{\psi}$	Amino acids/peptides	†HTAB+GB$^{\psi}$	**SDS+GB$^{\psi}$
	Glycine			*L-Alanine*	
2.11	62.4	116.2	2.11	63.7	174.3
4.19	76.6	130.4	4.19	190.2	189.0
6.25	73.3	147.1	6.25	185.6	191.3
8.29	68.9	165.0	8.29	180.2	198.8
10.31	66.7	146.0	10.31	174.7	194.8
12.30	63.9	153.3	12.30	168.2	188.9
14.28	60.4	139.6	14.28	161.0	183.9
16.23	59.6	144.9	16.23	156.2	188.5
18.17	58.1	145.4	18.17	150.6	199.1
20.08	57.8	137.4	20.08	148.2	185.4
21.98	56.6	140.4	21.98	143.5	184.7
23.85	54.2	128.9	23.85	138.6	197.7
25.70	52.6	137.0	25.70	135.9	191.5
27.54	52.7	132.0	27.54	133.0	182.2
29.35	51.2	131.3	29.35	130.1	192.2
31.15	50.1	130.7	31.15	128.3	188.1
32.93	46.6	128.8	32.93	123.5	182.0
34.69	46.2	125.0	34.69	120.7	175.9
36.43	44.4	123.5	36.43	11	189.3
38.15	45.3	122.3	38.15	115.4	185.9
39.85	43.9	121.6	39.85	112.2	179.5
41.54	42.0	117.0	41.54	110.9	172.3
43.21	40.5	115.3	43.21	108.4	179.0
44.86	40.4	115.7	44.86	104.0	176.9
46.49	39.4	112.3	46.49	102.1	171.8
	α-Amino-n-butyric acid			*L-Valine*	
2.11	212.1	304.2	0.53	54.8	158.9
4.19	247.9	323.9	1.05	95.9	158.6
6.25	250.5	322.8	1.56	90.1	165.1
8.29	253.2	315.1	2.07	96.2	167.8
10.31	249.9	320.3	2.58	97.6	165.9
12.30	242.9	319.6	3.08	98.1	164.6
14.28	235.2	309.5	2.57	94.2	153.6
16.23	230.5	313.6	4.06	95.2	162.2
18.17	229.1	314.2	4.54	95.8	162.4
20.08	224.3	299.2	5.02	91.9	152.6
21.98	224.9	297.3	5.49	91.8	149.6
23.85	221.6	296.0	5.96	94.5	155.1
25.70	214.1	292.1	6.43	94.2	157.7
27.54	214.5	289.2	6.88	95.7	147.9
29.35	213.9	286.4	7.34	91.9	155.5
31.15	210.6	283.3	7.79	89.8	151.4
32.93	206.1	282.6	8.23	89.3	156.5
34.69	197.7	278.1	8.67	89.3	151.9
36.43	193.1	269.1	9.11	85.4	145.8
38.15	195.1	273.2	9.54	84.5	146.2
39.85	190.8	271.2	9.96	84.2	145.7
41.54	184.7	262.5	10.38	82.4	143.7
43.21	178.6	256.7	10.81	78.8	141.0
44.86	177.6	256.7	11.21	75.1	141.2
46.49	175.9	255.4	11.62	74.9	141.2
	L-Leucine			*Diglycine*	
0.53	54.4	166.2	0.53	1.5	77.4
1.05	96.3	184.1	1.05	−6.5	71.1
1.56	104.4	189.8	1.56	4.5	77.1
2.07	105.3	190.2	2.07	0.9	75.7
2.58	120.4	187.5	2.58	−0.9	74.1
3.08	112.4	197.7	3.08	0.3	72.4
2.57	110.1	183.9	2.57	1.1	65.8
4.06	104.5	182.2	4.06	−1.1	66.8
4.54	104.1	191.7	4.54	−3.5	69.7
5.02	105.1	186.1	5.02	−5.1	60.1
5.49	104.3	171.3	5.49	−4.8	58.1
5.96	102.9	166.5	5.96	−4.7	57.1
6.43	103.4	168.2	6.43	−4.8	57.1
6.88	102.1	179.3	6.88	−6.6	47.2
7.34	100.6	170.1	7.34	−6.2	51.3
7.79	99.3	158.9	7.79	−7.6	48.8
8.23	98.0	160.8	8.23	−11.3	48.4
8.67	96.7	167.7	8.67	−11.2	46.8

(*continued on next page*)

TABLE 9 (*continued*)

$m/10^{-3}$mol·kg^{-1}	Q/J·mol^{-1}		$m/10^{-3}$mol·kg^{-1}	Q/J·mol^{-1}	
Amino acids/peptides	†HTAB+GB$^{\psi}$	**SDS+GB$^{\psi}$	Amino acids/peptides	†HTAB+GB$^{\psi}$	**SDS+GB$^{\psi}$
9.11	92.8	166.5	9.11	−14.4	44.1
9.54	95.4	158.4	9.54	−13.2	44.7
9.96	90.2	154.4	9.96	−12.1	45.2
10.38	89.1	162.1	10.38	−14.8	39.2
10.81	86.2	155.1	10.81	−12.8	40.1
11.21	81.7	148.2	11.21	−15.2	42.8
11.62	84.2	143.0	11.62	−13.8	40.9
	Triglycine				
0.53	10.1	66.4			
1.05	−0.07	42.1			
1.56	−2.6	50.4			
2.07	−12.2	57.4			
2.58	−14.1	57.7			
3.08	−8.3	56.7			
2.57	−10.2	46.4			
4.06	−13.7	53.2			
4.54	−19.8	59.6			
5.02	−23.6	46.1			
5.49	−23.1	47.3			
5.96	−19.2	45.4			
6.43	−21.4	47.7			
6.88	−23.1	40.2			
7.34	−29.2	41.4			
7.79	−23.8	42.3			
8.23	−24.5	43.4			
8.67	−26.8	37.7			
9.11	−25.2	37.5			
9.54	−30.4	39.2			
9.96	−28.9	38.6			
10.38	−26.7	35.3			
10.81	−29.3	37.4			
11.21	−29.6	39.1			
11.62	−33.5	37.9			

†HTAB ($m = 2 \cdot 10^{-3}$ mol·kg^{-1});**SDS ($m = 10 \cdot 10^{-3}$ mol·kg^{-1}); $^{\psi}$GB ($m = 0.5$ mol·kg^{-1}).

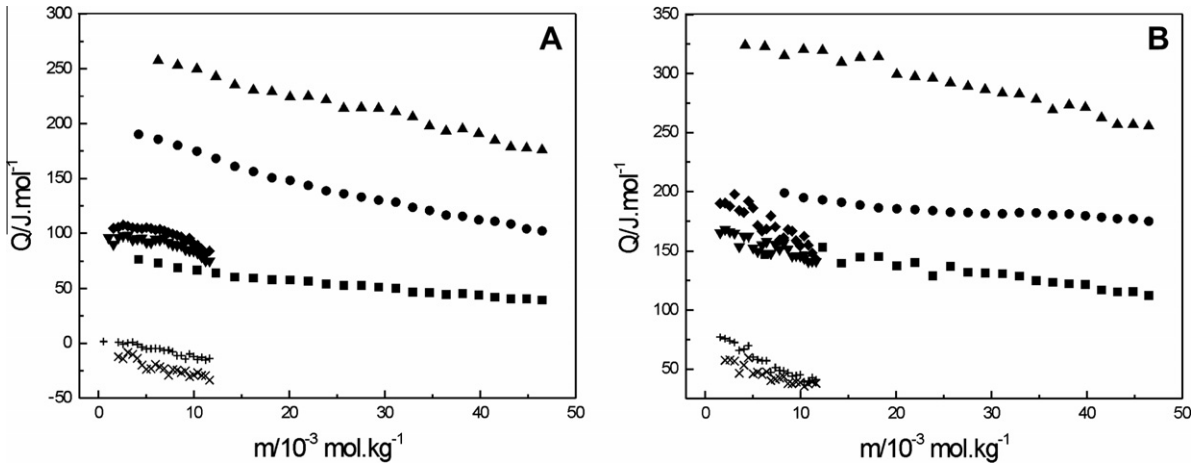

FIGURE 1. Plot of heat of dilution (Q) against molality for the homologous series of amino acids (■) glycine, (●) alanine, (▲) a-amino-n-butyric acid, (▼) valine and (♦) leucine, and peptides (+) diglycine and (x) triglycine upon titration against (A) $2 \cdot 10^{-3}$ mol·kg^{-1} of HTAB and 0.5 mol·kg^{-1} of glycine betaine (GB) and (B) $10 \cdot 10^{-3}$ mol·kg^{-1} sodium dodecyl sulfate (SDS) and 0.5 mol·kg^{-1} of GB at $T = 298.15$ K.

breaking effects of the solvent resulting form the comparatively large size of alanine. On the other hand, in case of α-ABA, as observed form the values of $\Delta_{tr}V^0_{2,m}$ there seems to be a balance of polar and hydrophobic interactions, which is why the sharp increase in endothermic contribution to the $\Delta_{dil}H^0$ primarily and predominantly comes from the structure breaking effects of solvent upon addition of α-ABA. Conversely, the immense dip in endothermic contribution towards $\Delta_{dil}H^0$ observed for valine (101.6 ± 1.7) J.mol^{-1} in HTAB and GB, and (170.1 ± 1.9) J·mol^{-1} in SDS and GB and leucine (114.1 ± 1.6) J·mol^{-1} in HTAB and GB, and (202.1 ± 3.1) J·mol^{-1} in SDS and GB suggests that the hydrophobic interactions of amino acids and isolated surfactant molecules are largely compensated by the solvent structure enhancing effects of GB in the bulk. Furthermore, as mentioned earlier, the strong water structure enhancing capability of GB also seems to override the contributions from endothermic heat arising from the structure breaking effects, upon addition of valine and leucine. However, the peptides diglycine and triglycine ($\Delta_{tr}\Delta_{dil}H^0 = 3.9 \pm 0.9$

TABLE 10
Limiting enthalpy of dilution ($\Delta_{dil}H^0$) of aqueous amino acids and peptides in the combined presence of $2 \cdot 10^{-3}$ mol·kg^{-1} hexadecyltrimethylammonium bromide (HTAB)/ $10 \cdot 10^{-3}$ mol·kg^{-1} sodium dodecyl sulfate (SDS) and 0.5 mol·kg^{-1} glycine betaine (GB) and the corresponding limiting transfer heats of dilution ($\Delta_{tr}\Delta_{dil}H^0$) at T = 298.15 K.

Amino acids/peptides	$\Delta_{dil}H^0$ / J·mol^{-1}			$\Delta_{tr}\Delta_{dil}H^0$ /J·mol^{-1}	
	Water	†HTAB+GB$^{\psi}$	**SDS+GB$^{\psi}$	Water → HTAB + GB	Water → SDS + GB
Glycine	59.1 ± 1.3	75.1 ± 1.1	158.1 ± 1.8	16.0 ± 1.7	99.0 ± 2.2
L-Alanine	−22.9 ± 1.0	192.6 ± 1.7	197.6 ± 1.1	215.5 ± 1.9	220.5 ± 1.5
α-Amino-n-butyric acid	−57.4 ± 1.9	267.5 ± 1.5	336.2 ± 1.8	324.9 ± 2.4	393.6 ± 2.6
L-Valine	−8.7 ± 0.3	101.6 ± 1.7	170.1 ± 1.9	110.3 ± 1.7	178.8 ± 1.9
L-Leucine	−11.2 ± 0.3	114.1 ± 1.6	202.1 ± 3.1	125.3 ± 1.6	213.3 ± 3.1
Diglycine	0.73 ± 0.3	4.6 ± 0.8	82 ± 1.6	3.9 ± 0.9	81.3 ± 1.6
Triglycine	13.1 ± 0.4	−7.3 ± 1.7	61.1 ± 2.0	−20.4 ± 1.7	48 ± 1.8

†HTAB ($m = 2 \cdot 10^{-3}$ mol·kg^{-1}); **SDS ($m = 10 \cdot 10^{-3}$ mol·kg^{-1}); $^{\Psi}$GB (m = 0.5 mol·kg^{-1}).

and −20.4 ± 1.7 J·mol^{-1}) in presence of HTAB ($m = 2 \cdot 10^{-3}$ mol·kg^{-1}) and GB (m = 0.5 mol·kg^{-1}), and ($\Delta_{tr}\Delta_{dil}H^0$ = 81.3 ± 1.6 and 48 ± 1.8 J·mol^{-1}) in presence of SDS ($m = 10 \cdot 10^{-3}$ mol·kg^{-1}) and GB (m = 0.5 mol·kg^{-1}) seems curious and far different from the $\Delta_{tr}\Delta_{dil}H^0$ of homologous amino acids. It is further observed that in the combined presence of HTAB/SDS and GB, the endothermic contribution to the $\Delta_{tr}\Delta_{dil}H^0$decreases drastically going from glycine to triglycine. However it is worthwhile to note that in case of diglycine and triglycine there is an increase in the number of peptide bonds which has the potential of extensive polar interactions with GB and HTAB/SDS micelles. Thus it can be asserted that the exothermic heat effects arising from the polar interactions dominate over the endothermic heat effects from hydrophobic hydration/structure breaking effects and hydrophobic interactions in the case of diglycine and triglycine. Furthermore, an overall increase in the heat of dilution in the presence of the SDS-GB system as compared to HTAB-GB system might be due to extensive micellization of HTAB resulting from its larger size. Under such circumstances, HTAB micelles can show enhanced polar interactions as compared to SDS. This assumption is further supported by the findings of $\Delta_{tr}V^0_{2,m}$ values as well.

4. Conclusions

A comparison of $\Delta_{tr}V^0_{2,m}$ demonstrated a good correlation with $\Delta_{tr}K^0_{S,2,m}$ suggesting that at HTAB ($m = 2 \cdot 10^{-3}$ mol·kg^{-1})/SDS ($m = 10 \cdot 10^{-3}$ mol·kg^{-1}), GB shows palpable domination of polar interactions with zwitter ionic centres of amino acids and peptide bonds in peptides. The $\Delta_{tr}\Delta_{dil}H^0$of amino acids and peptides further suggest that the structure making and breaking effects of solutes can significantly affect the course of solute-co-solvent interaction in the solvent milieu. The polar interactions of GB are greatly enhanced in the presence of amino acids with small –R groups. However as the size of the –R group increases as was observed in the case of valine and leucine the polar interactions diminishes significantly. The non-polar interaction with amino acids valine and leucine, if any, mainly arises from the interactions with the hydrophobic tail of the isolated surfactants which is not part of the integrated micellar system. Thus under such circumstances where polar interaction with GB is unfavourable, it enhances the water structure leading to a significant rise in the exothermicity of $\Delta_{dil}H^0$. Apart from the polar interactions of GB, both the surfactants at post micellar concentration show polar interactions with the zwiterionic centres of amino acids and with the peptide bonds in diglycine and triglycine. From the variable values of $\Delta_{tr}V^0_{2,m}$ and $\Delta_{tr}\Delta_{dil}H^0$, it can be concluded that GB in the presence of surfactants can show preferential polar interaction with amino acids with relatively smaller –R groups/peptide bonds present in the proteins and might shift the N (native) ↔ D (denatured) equilibrium more towards the right. However, for exposed hydrophobic residues of unfolded proteins, GB might not interact and instead enhance the solvent structure (preferential exclusion from the protein domain) resulting in volume exclusion finally manifesting in the stabilization of proteins.

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