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Full length article

Micelle formation of Tyr-Phe dipeptide and Val-Tyr-Val tripeptide in aqueous solution and their influence on the aggregation of SDS and PEO–PPO–PEO copolymer micelles

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ABSTRACT

The aggregation properties of Tyr-Phe dipeptide and Val-Tyr-Val tripeptide were studied in aqueous solution and in the presence of SDS and SDS–polymer environments using UV–visible, surface tension, fluorescence and circular dichroism (CD) techniques. Both the peptides formed micelles. The *cmc* values obtained for dipeptide and tripeptide are 2×10^{-5} and 4×10^{-5} M, respectively in aqueous solution at 25 °C. The presence of additives (SDS and polymer) hindered the micelle formation of peptides. The *cmc* values obtained by various methods are in good agreement with each other. Effect of peptides on the aggregation properties of SDS also was investigated. The *cmc* of SDS was decreased in presence of peptides and were reduced with increase in temperature. Using monophasic micellization concept, the association constant (K_A) for the SDS–peptide mixed micellar systems was determined. Using biphasic model, the thermodynamic parameters viz; ΔG°_{m}, ΔH°_{m} and ΔS°_{m} for SDS–water and SDS–peptide–water mixed micellar systems, the standard free energy for transfer of SDS from aqueous to peptide additive environments were estimated at various temperatures. These results suggest that the SDS is more stable in micellized form in the SDS–water–peptide ternary systems compared to the situation in the corresponding SDS–water binary systems.

1. Introduction

Proteins and peptides have notable advantages in the field of research. Due to their wide spread interests in science, researchers have been continuously establishing a number of applications in various fields. The aggregation of a variety of active small molecular peptides in solutions is found to be valuable in modeling of some interactions. Identification of these interactions will lead to the molecular assembly of peptides. Self-aggregation of biomolecules is the process by which specific components of the concerned molecules assemble into well-defined aggregates. Peptide self-assembly is very similar to the modular assembly involved in protein folding in terms of compactness, the core of the non-polar alkyl side chains and internal architecture [1]. The strong and directional nature of hydrogen bonds between –NH–CO– groups in the peptides contribute to their wide spread involvement in self-assembling systems. Especially in an apolar medium, the solvophobic nature of amide groups is an advantage because of their low solubility in polar liquids [2,3].

Many smaller peptides exhibit a wide variety of biological activities [4]. The molecular recognition of the peptides is very important during self-assembly processes, which result in micelles, vesicles and liquid crystals [5]. Few peptides [6–11], most phospholipids and some biologically relevant molecules are known to exhibit such behavior [12]. These surface-active molecules exhibit a wide variety of biological activity [1]. As membrane bound receptors, proteins play several important roles in mediating their functions; the aggregation of membrane-active peptides in apolar media is valuable in the modeling of some interactions [13]. Ordered aggregates of the peptides in apolar media are also useful for obtaining information about the physicochemical nature of the interactions operating during self-assembly processes [14]. The micelle formation of various collagens was investigated in acetate and citrate buffers at various temperatures, as well as the interaction of collagen micelles with various surfactant micelles and urea additives [15,16] had been made earlier. The interaction of surfactants with protein appears to influence the hydrodynamic and physicochemical characteristics of the proteins [15–17]. The molecular structure and conformations of various biologically active peptides such as

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gramicidin analogs, lactoferricin B, platypus venom C-type natriuretic peptide and the cell penetrating peptide 'penetratin' were studied with SDS micelles [18–21] using various techniques.

The synthesis and characterization of a micelle-forming tetrapeptide TFA, Tyr-Gly-Phe-Ala-OBz were reported [6] using various spectroscopic techniques. The aggregation, hydrogen bonding and thermodynamic studies on the micelles of the above tetrapeptide have been reported in the light of NH···O=C– hydrogen bond formation and forces implicated in micellization [22]. The self-assembling properties of Boc-Lys(Z)-Tyr-NHNH$_2$ dipeptide was studied by Mandal et al. [7] in the absence and presence of ionic surfactants using UV–visible, fluorescence and FTIR spectroscopic and conductometric techniques. The evidence for micelle formation of Boc-Val-Val-Ile-OMe tripeptide in chloroform [23] was obtained from UV–visible, fluorescence, NMR, FT-IR and Raman scatter fluorescence spectroscopic techniques. The thermodynamic studies on the above tripeptide indicate that the driving force for micellization is entirely enthalpic in nature and the aggregates of the peptide in chloroform are ordered [24].

Although many polymers, peptides and proteins have been well characterized, we are only now beginning to obtain a better understanding of interaction of small molecular peptides with amphiphilic polymers and surfactants. In this respect, polymer–peptide interaction is an area that needs new focus in the future [25]. The aggregation properties of Tyr-Phe dipeptide and Val-Tyr-Val tripeptide have been studied in the present investigation. The effect of PEO–PPO–PEO triblock copolymer and SDS on the self-assembling properties of these peptides was also investigated at different temperatures. The critical micelle concentration, aggregation number, fluorescent lifetimes, etc. of the peptides were determined in aqueous solution and in the presence of various surfactants at different temperatures using various techniques [7]. The interactions of the above triblock copolymer with SDS and various physicochemical properties of the mixed micelles have recently been studied by us [26,27]. The investigated PEO–PPO–PEO copolymer is insoluble in water. However, SDS micelles was used to solubilize the above polymer in aqueous solution and this is the most essence in the present investigation where the above micellization/aggregational properties have been dealt with in detail in order to attract the attention of the scientists in the advance field of colloids and surface sciences.

2. Experimental details

2.1. Materials

The Tyr-Phe dipeptide and Val-Tyr-Val tripeptide obtained from ICN Biomedicals Inc. and were used as such. Poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) triblock copolymer of molecular weight 2800 was obtained from Aldrich and used without further purification. This triblock copolymer contained 19.3% poly(ethylene oxide) by weight and is insoluble in water. Sodium dodecylsulfate (SDS) was obtained from Aldrich, recrystallized twice from 95% ethanol, rinsed with ethanol and anhydrous ether at 0 °C and dried under vacuum for 10 days. All the other reagents used in the experiments were of analytical grades of the highest purity. Double distilled water of specific conductance 2–3 μS cm^{-1} at 25 °C was used as the solvent medium throughout the experiments.

2.2. Methods

UV–visible and steady state fluorescence measurements were made on Shimadzu UV-160A spectrometer and Hitachi Model No. 650-40 fluorimeter, respectively. Circular dichroism (CD) experiments were performed in a Jasco-715 spectrometer.

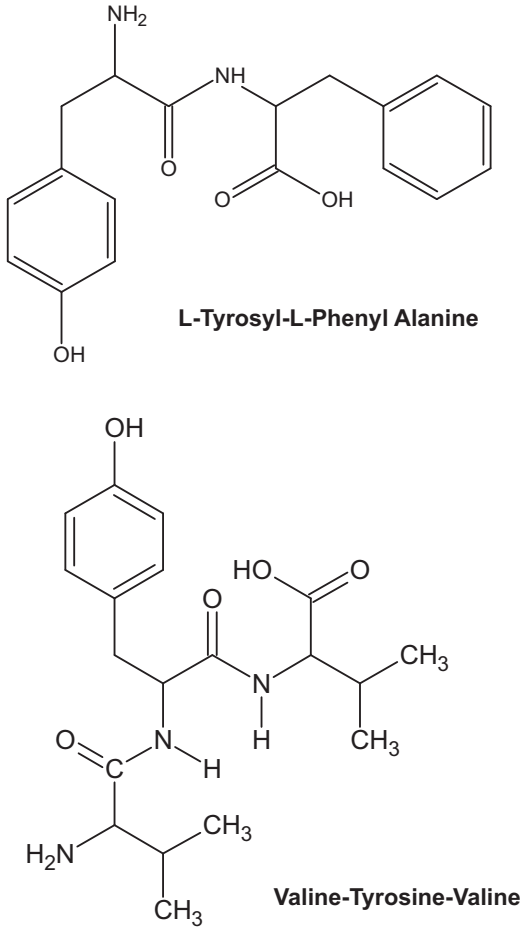

Fig. 1. Structure of Tyr-Phe dipeptide and Val-Tyr-Val tripeptide.

A NIMA model DST 9005 dynamic surface tensiometer was used to measure the surface tension. Extra care was taken to avoid disturbing the interface during measurements. The conductance measurements were taken in a Global digital conductivity meter, Model No. DCM 900, made at Chennai, India. A dip type cell of cell constant 1.0 cm^{-1} was used. The uncertainty in the conductance measurement was within ±0.4%. Zeta potential measurements were carried out in a Malvern Instruments Zetasizer 3000HS$_A$ by taking the average of five measurements at equilibrium. The cell used was 5 mm × 2 mm rectangular quartz capillary. The temperature was maintained at 25 ± 0.1 °C, controlled by a proportional temperature controller.

2.3. Determination of cmc

For the determination of the *cmc* of peptides in the absence and presence of additives (SDS or polymer as the case may be), a series of solutions were made at a particular concentration (fixed) of each additive, varying the concentration of peptide. Similarly, the *cmc* of SDS in the absence and presence of fixed concentration of peptides were also determined. The physicochemical properties viz., surface tension, specific conductance, absorbance, zeta potential, emission intensity and molar ellipticity of each solution were measured and plotted as a function of concentration in the absence and presence of additives. The abrupt change in the value of initial slope at a particular concentration was considered as *cmc*. Details regarding *cmc* determination are described in earlier publications [6,7,23,24,28].

Table 1
The *cmc* of Tyr-Phe dipeptide and Val-Tyr-Val tripeptide in aqueous solution, SDS and SDS–polymer environments at 25 °C.

System	*cmc* of peptide/10^{-5} M			
	UV–visible	Fluorescence	Surface tension	CD
Dipeptide alone	2.5	3.0	2.8	2.5
Dipeptide + SDS (25 mM)	5.5	5.8	6.0	6.0
Dipeptide + SDS (25 mM) + polymer (0.5 mM)	7.0	7.7	7.8	7.2
Tripeptide alone	4.0	3.8	4.1	4.0
Tripeptide + SDS (25 mM)	7.5	7.8	8.0	8.2
Tripeptide + SDS (25 mM) + polymer (0.5 mM)	9.0	9.5	9.0	8.8

The measurements were made at investigated temperatures, for the specified concentration of sample solutions. Prior to the experiments, all the solutions were thermostated for more than 20 min at the investigated temperatures. The temperature reproducibility was in the range ±0.05 °C.

3. Results and discussion

3.1. Structure of peptides

The structure of Tyr-Phe dipeptide and Val-Tyr-Val tripeptide are shown in Fig. 1.

3.2. Critical micelle concentration of the peptides in aqueous solution and in the presence of SDS and PEO–PPO–PEO triblock copolymer

The UV spectra of various concentrations of Tyr-Phe dipeptide and Val-Tyr-Val tripeptide in aqueous solutions have been recorded at 25 °C. There are two absorption maxima observed for the tripeptide (225 and 273 nm), whereas the dipeptide shows only one peak in aqueous solution (i.e., at 273 nm). The peak at 273 nm is assignable to the tyrosine residue present in the peptides. The absorption spectra of various concentrations of dipeptide and tripeptide in aqueous solution are given in Fig. 2. The presence of SDS or polymer and increasing concentration of peptide did not alter the absorption wavelength maxima. The optical density (OD) value corresponding to each peptide concentration is plotted against the concentration of the peptide to get the critical micelle concentration (*cmc*) value. The abrupt change in the OD values gave the *cmc*. The *cmc* values obtained are presented in Table 1. The fluorescence intensity of the peptide solutions was recorded and plotted against the peptide concentration to obtain the *cmc* of the peptides (Fig. 3). The aggregation numbers of peptide micelles were determined using steady state and time resolved fluorescence spectroscopic techniques and they are found to be 11 and 8 for dipeptide and tripeptide, respectively at 25 °C.

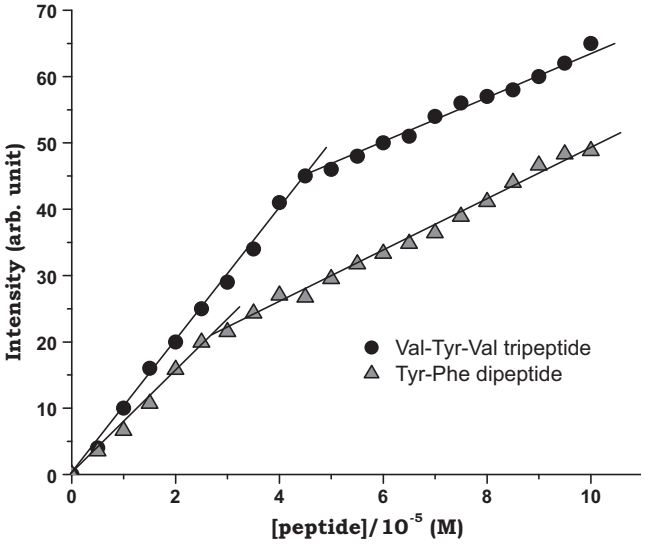

Fig. 3. Plot of fluorescence intensity *vs* concentration of peptides at 25 °C.

Figs. 4 and 5 show the CD spectra of different concentrations of the dipeptide and tripeptide, respectively. The CD spectra of dipeptide show peaks at 214 and 260 nm and tripeptide show peaks at 204, 229 and 254 nm. The molar ellipticity values were noted down at all the wavelengths for all the concentrations of the peptide solutions. By plotting the molar ellipticity values against corresponding

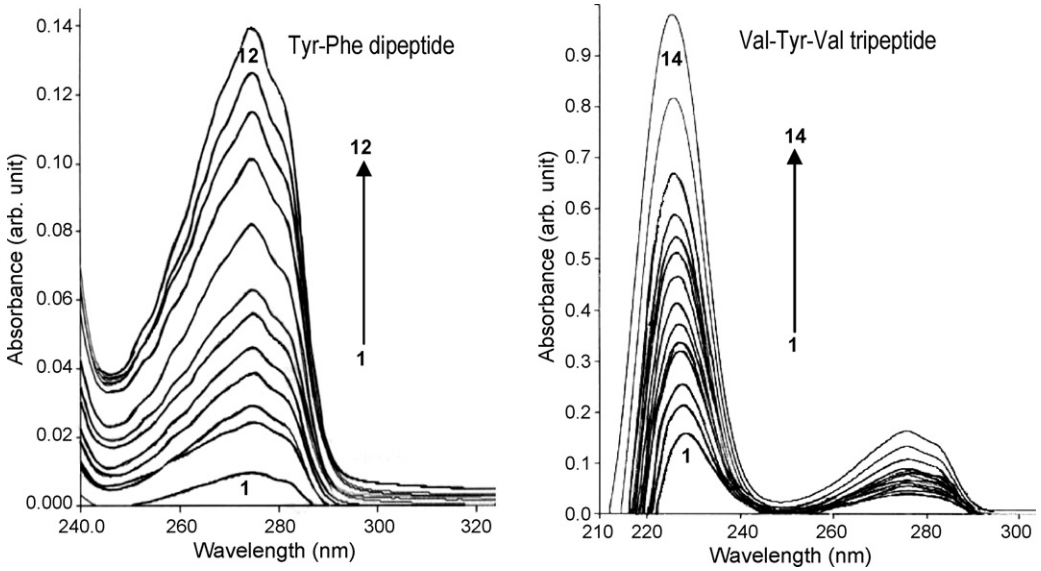

Fig. 2. UV–visible spectra of various concentrations of Tyr-Phe dipeptide and Val-Tyr-Val tripeptide in aqueous solution at 25 °C. In dipeptide: curve nos. 1–12: 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 5, 6, 7 and 8 × 10^{-5} M, respectively. In tripeptide: curve nos. 1–14: 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 7 and 8 × 10^{-5} M, respectively.

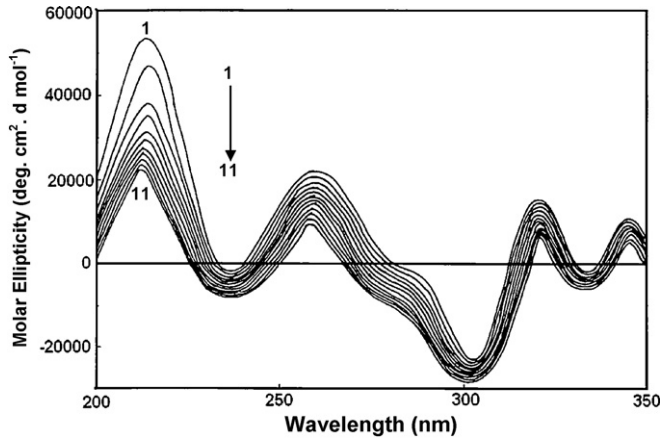

Fig. 4. CD spectra of Tyr-Phe dipeptide in water at 25 °C. Curve nos. 1–11 correspond to peptide concentrations of 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 5, 6 and 7×10^{-5} M, respectively.

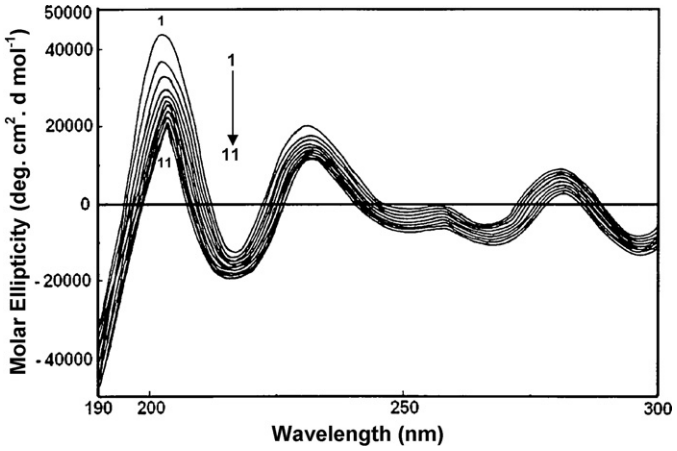

Fig. 5. CD spectra of Val-Tyr-Val tripeptide in water at 25 °C. Curve nos. 1–11 correspond to peptide concentrations of 0.5, 1.5, 2.5, 3, 3.5, 4, 5, 6, 7 and 8×10^{-5} M, respectively.

peptide concentration (Fig. 6), the *cmc* values for the peptides were obtained. Irrespective of the wavelength, the *cmc* values were found to be constant. Surface tension of various concentrations of peptide solutions was measured for the determination of *cmc* of the peptides. The plot of surface tension *vs* log[peptide] is shown in Fig. 7. The effect of SDS and PEO–PPO–PEO triblock copolymer on the *cmc* of the peptides is depicted in Fig. 8. When the peptide molecules are incorporated in the SDS surfactant micelle, and as a result, the mixed micelles may be formed. Generally, in surface tension experiment, one component may cause the impurity on the body of the other component in the mixed state, although both the individual components are in pure state. However, in the present case, the constant surface tension has been obtained at higher concentration indicates that the mixed micelles formed with homogeneous characteristics.

The *cmc* of dipeptide and tripeptide were also determined in the presence of SDS and PEO–PPO–PEO triblock copolymer using UV–visible, fluorescence, CD and surface tension measurements. The effect of SDS and PEO–PPO–PEO triblock copolymer on the *cmc* of the peptides was established and the results obtained are given in Table 1. It is observed that the *cmc* values of dipeptide as well as tripeptide increased in the presence of additives. These results indicate that the presence of SDS and polymer additives hinder the micelle formation of the peptides.

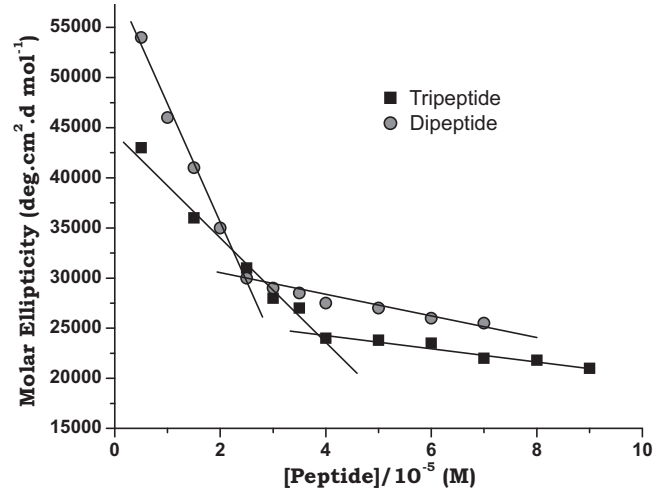

Fig. 6. Plot of molar ellipticity *vs* concentration of dipeptide and tripeptide in water at 25 °C.

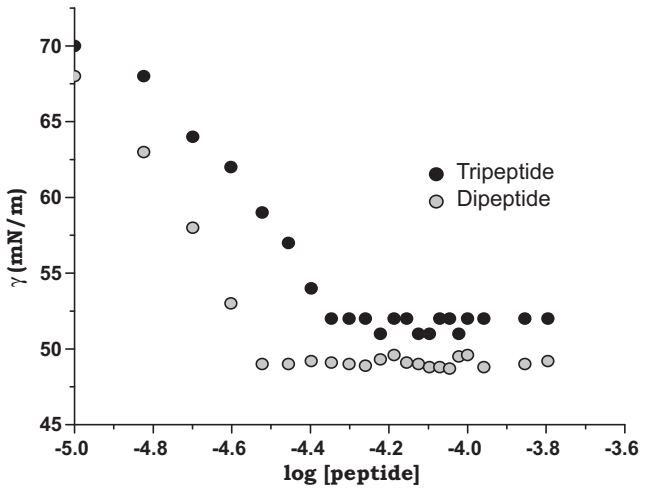

Fig. 7. Plot of surface tension *vs* log[peptide] on dipeptide and tripeptide in aqueous solution at 25 °C.

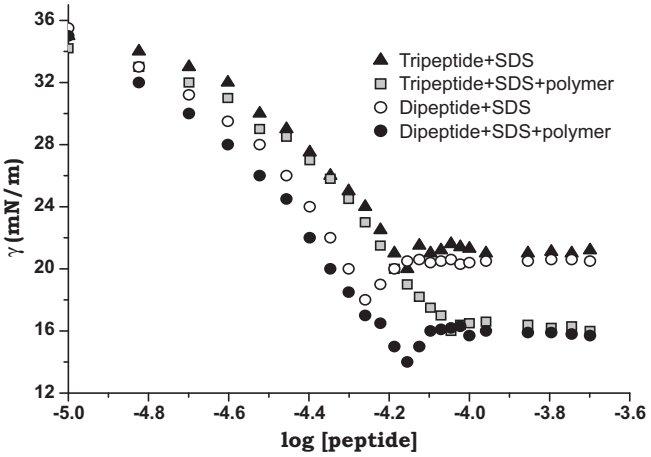

Fig. 8. Plot of surface tension *vs* log[peptide] on dipeptide–SDS, tripeptide–SDS, dipeptide–SDS–polymer and tripeptide–SDS–polymer at 25 °C. [SDS] = 25 mM (fixed) and [polymer] = 0.5 mM (fixed).

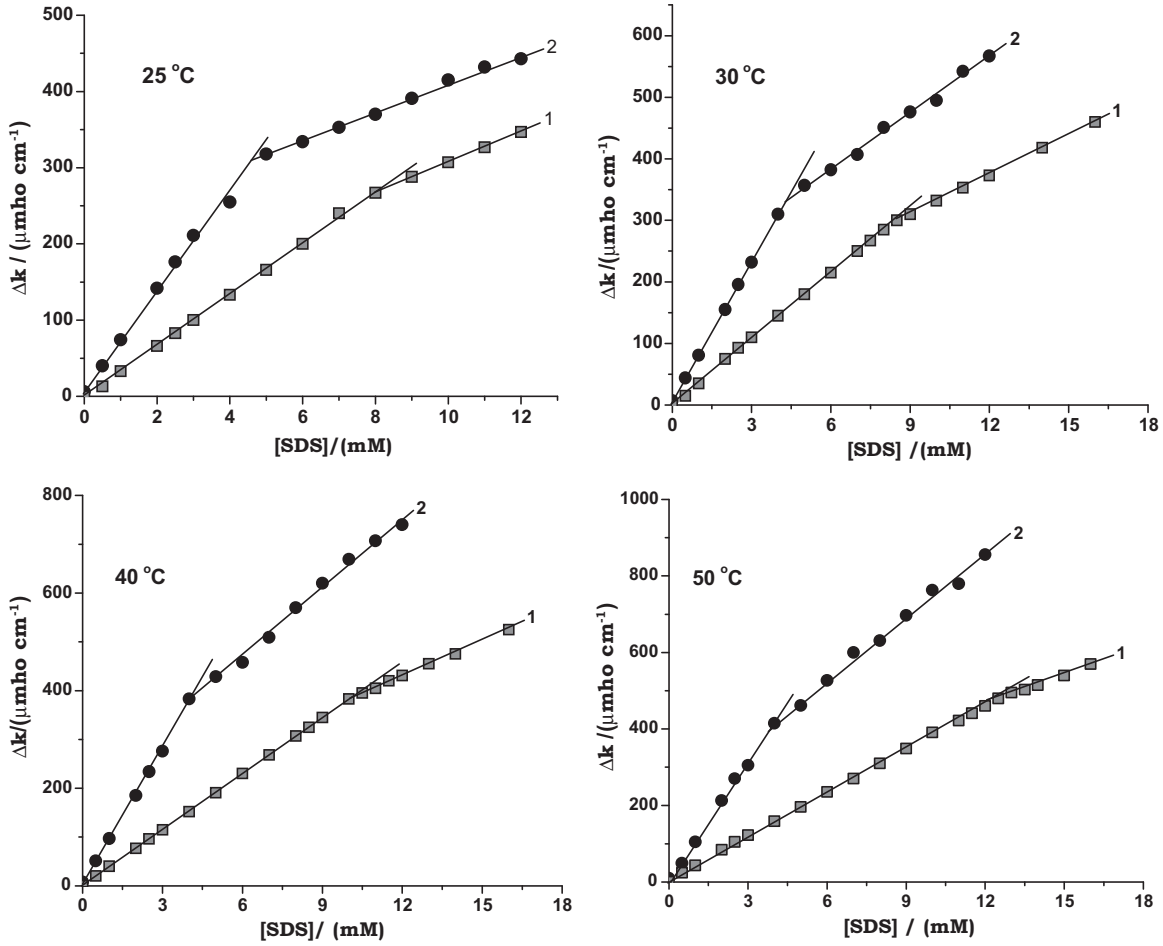

Fig. 9. Plot of difference in specific conductance, Δk *vs* [SDS] on SDS–water (curve 1) and SDS–dipeptide (curve 2) systems at various temperatures. [dipeptide] = 0.5 mM (fixed).

3.3. The cmc and counter ion association of SDS in aqueous and in the presence of Tyr-Phe dipeptide and Val-Tyr-Val tripeptide

The *cmc* values of SDS in aqueous solution and in the presence of dipeptide and tripeptide were determined by using conductance measurements at 25, 30, 40 and 50 °C. Surface tension and zeta potential measurements were also made to determine the *cmc* of SDS at various additive environments at 25 °C. The graphical representations of the conductance measurements are given in Figs. 9 and 10.

The *cmc* values obtained from all the three methods are in good agreement with each other (Table 2). The presence of 0.5 mM of dipeptide and tripeptide reduced the *cmc* of SDS from 8 mM to 4.7 and 6.0 mM, respectively at 25 °C. The *cmc* of SDS in aqueous solution was increased with increase in temperature, whereas the presence of peptides decreased the *cmc* of SDS with increase in temperature. From the specific conductance *vs* concentration of SDS plots, the degree of dissociation, α of the micelles was determined from which the counter ion association β was calculated [26]. The *cmc* by various methods, α and β values obtained for SDS micelles in the absence and presence of dipeptide and tripeptide at 25, 30, 40 and 50 °C are given in Table 2. Although the micelle formation of SDS was hindered at higher temperatures in aqueous solution (increased *cmc* and decreased β values), the presence of peptides facilitated the micelle formation of SDS (lower *cmc* and higher β values) (see Table 2) at higher temperatures [26]. Many systems are reported to have a decrease in *cmc* with increase in temperature [26,29,30].

3.4. Binding of (di/tri) peptide with SDS

In the presence of peptide additive, the conductance of SDS solutions increased at concentrations below *cmc*, which indicates the binding of the additive with SDS. However, a decrease in conductance was observed for SDS solutions at concentrations above its

Table 2
The *cmc*, degree of dissociation, α and counter ion association, β of SDS micelles in aqueous solution as well as in the presence of Tyr-Phe dipeptide and Val-Tyr-Val tripeptide (fixed concentrations) at various temperatures.

System	*cmc* of SDS/10^{-3} M	α	β
SDS–water			
25 °C	8.0, 8.0[a], 8.1[b]	0.59	0.41
30 °C	8.5	0.61	0.39
40 °C	10	0.63	0.37
50 °C	12.3	0.66	0.34
SDS–(0.5 mM) dipeptide			
25 °C	4.7, 4.5[a], 4.8[b]	0.48	0.52
30 °C	4.3	0.46	0.54
40 °C	4.0	0.45	0.55
50 °C	3.8	0.43	0.57
SDS–(0.5 mM) tripeptide			
25 °C	6.0, 6.3[a], 6.1[b]	0.55	0.45
30 °C	5.8	0.54	0.46
40 °C	5.6	0.53	0.47
50 °C	5.5	0.52	0.48

[a] *cmc* values determined by surface tension method.
[b] *cmc* values determined by zeta potential method.

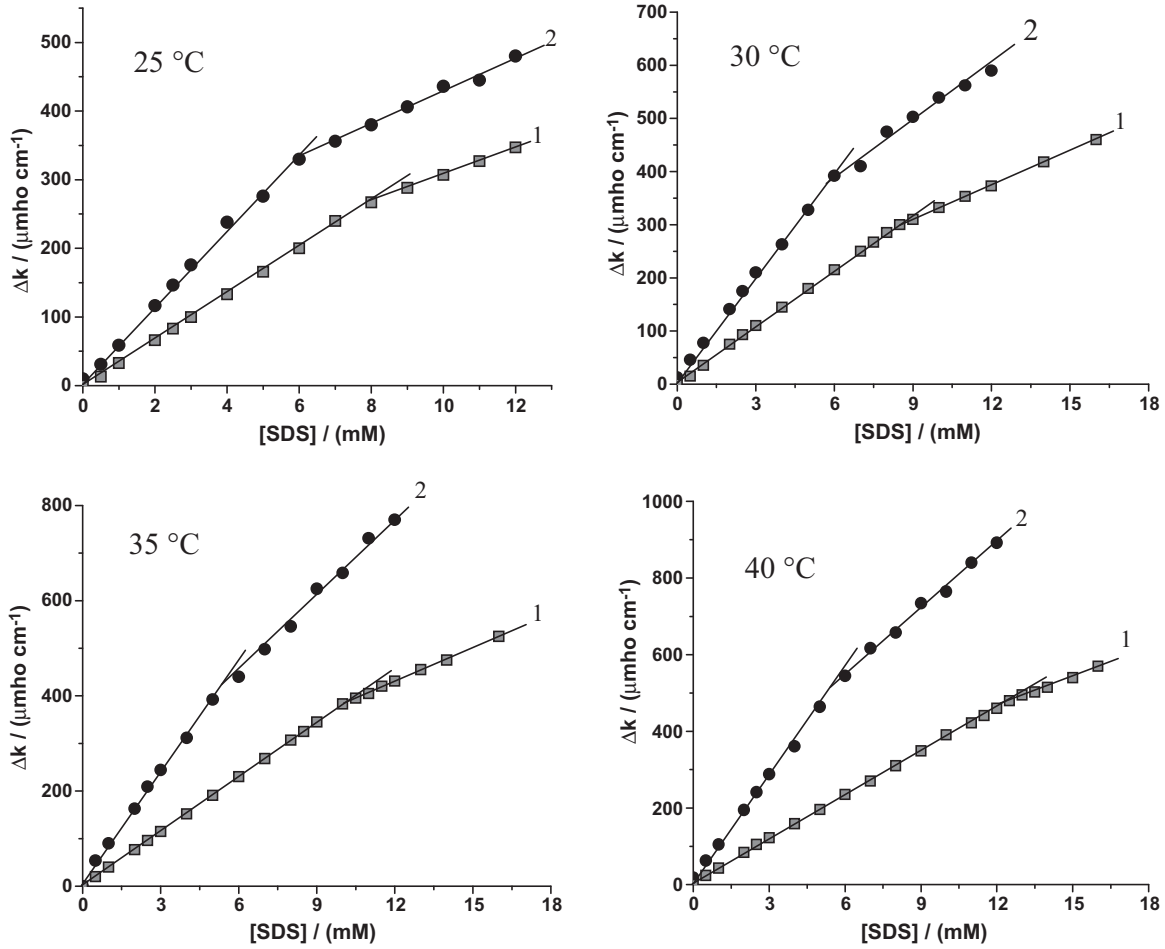

Fig. 10. Plot of difference in specific conductance, Δk *vs* [SDS] on SDS–water (curve 1) and SDS–tripeptide (curve 2) systems at various temperatures. [tripeptide] = 0.5 mM (fixed).

cmc, due to the breaking of the peptide micelles and the aggregation of SDS micelles upon complexation. The ionic obstruction and changes in dielectric constant are assumed to play negligible or very minor effects on the ionic conductance [31] as the compounds used were of very low concentration. The conductance was linearly proportional to concentration (Figs. 9 and 10). It is then apt to set up the following mass-action principle for the complexing system, assuming the following model:

$$\underset{\text{peptide molecules or micelles}}{(\text{Peptide})_{\text{M}}} + \underset{n\,(\text{ionic SDS})}{n(\text{SDS})^{\pm}} \overset{K_{\text{A}}}{\rightleftarrows} \underset{\text{Mixed micelle or complex}}{(\text{Peptide})_{\text{M}^-}(\text{SDS})_n^{\pm}} \quad (1)$$

In the above model, n number of molecules of ionic SDS with a single substrate (peptide) molecule form a mixed micelle (complex) with equilibrium association constant K_{A}. We can write the following equation [32–34]:

$$\log \quad \Delta[\text{SDS}^{\pm}] = \log\left(\frac{K_{\text{A}} n[\text{peptide}]}{\tilde{N}}\right) + n \quad \log[\text{SDS}^{\pm}]_{\text{free}} \quad (2)$$

where, $\tilde{N}$ designates the average aggregation number of peptide micelles. If $\tilde{N}$ is known for any system, it is possible to calculate K_{A} and n. Analysis and calculations were done in detail by referring to earlier publications [30,32–34]. From the slope and intercept of the plot of log Δ[SDS] *vs* log[SDS]$_{\text{free}}$ (Fig. 11), the n and K_{A} values are obtained and the results are given in Table 3. The validity of Eq. (2) has been demonstrated where well formed straight lines have been observed.

After plotting log K_{A} against $1/T$ (Fig. 12), ΔH°, ΔG° and ΔS° for the process are calculated and the values obtained also are depicted in Table 3. ΔH° and ΔG° are found to be positive, whereas the ΔS° values are negative.

3.5. Thermodynamics of SDS and SDS–peptide micelles formation

The thermodynamic analysis of the micellization process was made using the phase separation model and the monophasic mass-action model [22,32]. From the slope of the plot of ln *cmc* *vs* $1/T$, the standard enthalpy change for micelle formation, $\Delta H_{\text{m}}^{\circ}$ was estimated and found to be −13.78 kJ mol^{-1} for SDS–water system. The $\Delta G_{\text{m}}^{\circ}$, $\Delta H_{\text{m}}^{\circ}$ and $\Delta S_{\text{m}}^{\circ}$ values for SDS–water and SDS–peptide mixed micellar systems at various temperatures are calculated and the results are depicted in Table 4.

The entropy of formation of micelles was obtained as positive even in binary SDS–water system, which is one of the thermodynamic driving forces for micellization. The $\Delta H_{\text{m}}^{\circ}$ value estimated from the slope of the plot of ln [(*cmc*/288.4)/55.5] *vs* $1/T$ (Fig. 13), was also found to be −13.78 kJ mol^{-1} for SDS–water system, which indicates that the $\Delta H_{\text{m}}^{\circ}$ values remain constant irrespective of the reference state. However, the $\Delta G_{\text{m}}^{\circ}$ and $\Delta S_{\text{m}}^{\circ}$ values change with the reference states. The thermodynamic values obtained for SDS–water binary system are in good agreement with the recently reported values [35].

The *cmc* of SDS increases with increase in temperature, whereas it decreases in the presence of peptide with increase in temperature (Table 2). The $\Delta H_{\text{m}}^{\circ}$ and $\Delta S_{\text{m}}^{\circ}$ values are negative and positive, respectively in SDS–water system (Table 4), whereas in the presence of peptide (i.e., in SDS–water–peptide system), these values

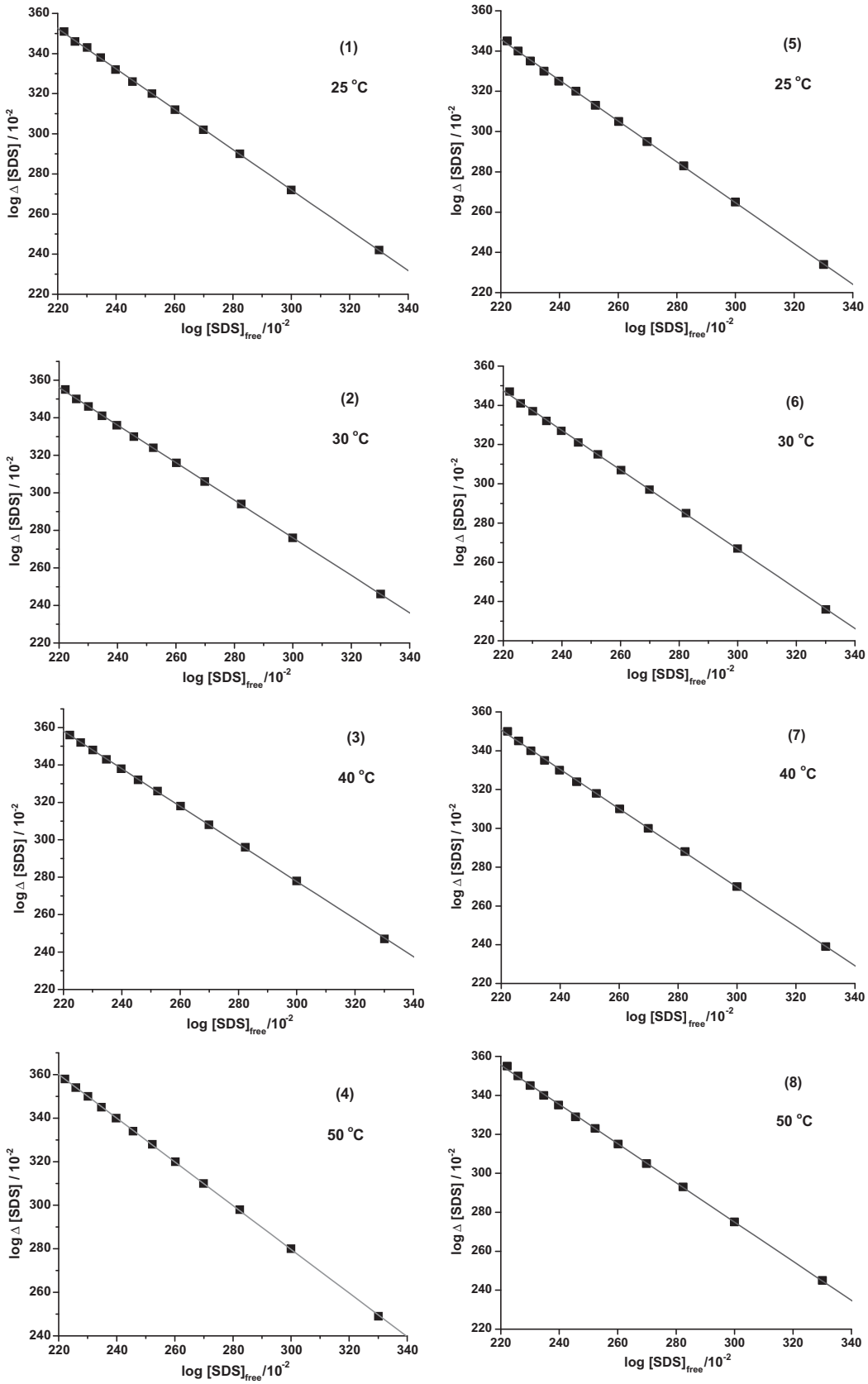

Fig. 11. Plot of log Δ[SDS] *vs* log[SDS]$_{free}$ at various temperatures. The concentration of peptide = 0.5 mM (fixed). Curves 1–4 and 5–8 correspond to SDS–dipeptide and SDS–tripeptide, respectively.

Table 3
Various physicochemical parameters of the complex SDS–(di/tri) peptide (0.5 mM, fixed) at various temperatures[a,b].

System	Temperature (T) (K)	$1/T \times 10^5$	n	K_A	$\log K_A$	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1})
SDS–dipeptide	298	335.6	−1.0053	0.0409	−1.3876	+7.92	5.71	−7.5
	303	330.0	−1.0010	0.0382	−1.4176	+8.22		−8.3
	313	319.5	−1.0041	0.0357	−1.4476	+8.67		−9.5
	323	309.6	−1.0041	0.0341	−1.4676	+9.08		−10.5
SDS–tripeptide	298	335.6	−1.0138	0.0334	−1.4758	+ 8.42	6.70	−5.8
	303	330.0	−1.0101	0.0319	−1.4959	+8.68		−6.6
	313	319.5	−1.0128	0.0291	−1.5358	+9.20		−7.9
	323	309.6	−1.0067	0.0272	−1.5659	+9.68		−9.2

[a] The n values obtained with different combinations of peptide concentrations at different temperatures are always close to 1.0. Non-integral values greater and lower than unity are due to experimental uncertainties. A fluctuation around a central value of unity has convinced us to consider $n = 1$ for the present systems.
[b] The negative values of n signify the non-interaction or non-binding of SDS with the corresponding peptide additives by desorption process. In other words, the binding of peptide with SDS by adsorption process.

Table 4
Thermodynamic parameters of SDS and SDS–peptide mixed micellar systems.

Temperature (K)	ΔG°_m (kJ mol^{-1})	ΔH°_m (kJ mol^{-1})	ΔS°_m (J K^{-1} mol^{-1})
(A) SDS–water			
298	−35.95 ± 0.1	−13.78 ± 0.7	74.40 ± 0.8
303	−36.40 ± 0.1		74.65 ± 0.9
313	−37.17 ± 0.1		74.73 ± 0.8
323	−37.81 ± 0.1		74.40 ± 0.8
(B) SDS–(0.5 mM) dipeptide			
298	−37.29 ± 0.1	+4.98 ± 0.4	147.08 ± 1.0
303	−38.09 ± 0.1		147.29 ± 1.0
313	−39.56 ± 0.1		147.28 ± 1.0
323	−40.95 ± 0.1		147.03 ± 1.0
(C) SDS–(0.5 mM) tripeptide			
298	−36.67 ± 0.1	+2.47 ± 0.5	131.33 ± 0.9
303	−37.36 ± 0.1		131.44 ± 0.9
313	−38.70 ± 0.1		131.52 ± 1.0
323	−39.96 ± 0.1		131.35 ± 0.8

are highly positive (Table 4). The hydrophobic interactions provide a driving force for micellization, whereas electrostatic repulsion provides an opposing force [36–38]. Thus, it might be suggested that the increase in temperature with a concomitant increase in peptide concentrations results in decreased electrostatic repulsion of the SDS micelles, which helps in increasing the strength of the hydrophobic interaction for this temperature range and as a result the micellization tendency of SDS increases even in its presence of peptide. The heats of solvation–desolvation of the species, their ionization, molecular arrangement, mixing, etc. may contribute

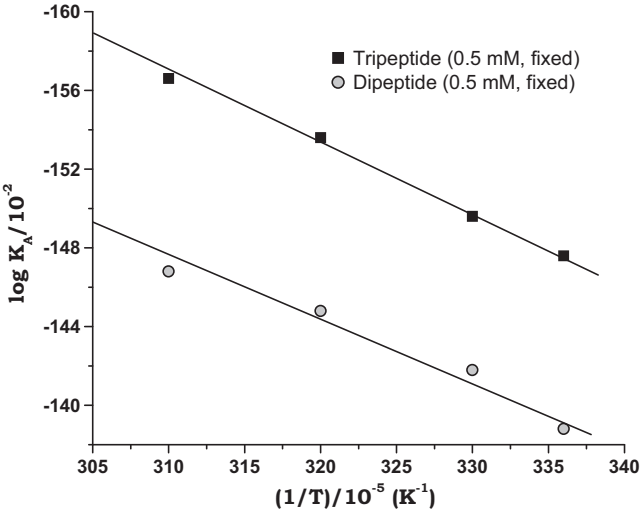

Fig. 12. Plot of $\log K_A$ *vs* $(1/T)$ on [SDS–dipeptide] and [SDS–tripeptide] systems.

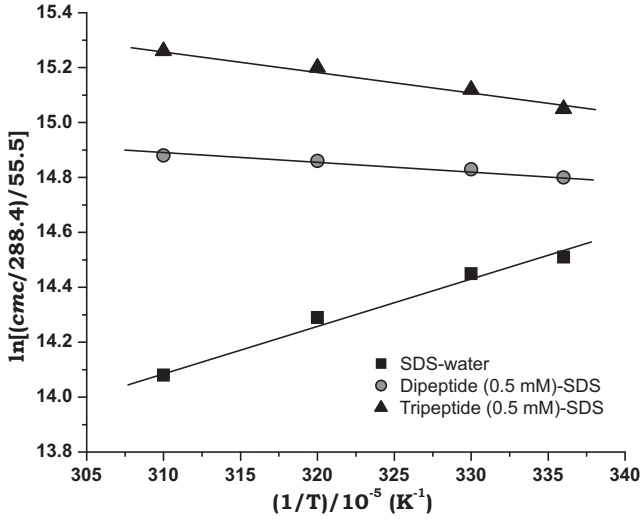

Fig. 13. Plot of ln[(*cmc*/288.4)/55.5] *vs* $1/T$ for SDS–water, SDS–dipeptide and SDS–tripeptide systems.

to their shares toward the overall enthalpy change in calorimetric measurements. These contributions are normally absent in the monophasic mass-action model. The large difference in ΔH°_m makes larger difference in ΔS°_m. The low β of SDS micelles (Table 2) and its decline at higher temperature can be the reason of low negative ΔH°_m. The decreased solvation of the shielded micellar head groups of the anionic SDS micelles by the presence of the peptide reduces the electrostatic repulsion in the peptide–SDS mixed micellar systems contributes to the positive ΔH°_m. The structural and solvation aspects in connection with enthalpy change are also applicable to the trend of ΔS°_m [35].

The standard free energy of transfer of SDS from water to the additive environments was calculated using biphasic model [30,32–34]. The values are given in Table 5. The transfer energies are negative at all the temperatures in the present investigation. The *cmc* for SDS solutions is lower in the presence of peptide additive, compared to binary SDS/water-solutions, indicating a gain in Gibb's

Table 5
Standard free energy for transfer of SDS from aqueous to dipeptide and tripeptide additive environments at various temperatures.

Temperature (K)	SDS to dipeptide (0.5 mM) environment $(\Delta G^\circ_m)_{tr}$/(kJ mol^{-1})	SDS to tripeptide (0.5 mM) environment $(\Delta G^\circ_m)_{tr}$/(kJ mol^{-1})
298	−1.318	−0.713
303	−1.717	−0.963
313	−2.384	−1.509
323	−2.685	−2.161

energy of transfer of SDS in the direction binary/ternary, meaning that this process is spontaneous in this direction. SDS is more stable in micellized form in the ternary systems (SDS–water–peptide) compared to the situation in the corresponding binary system (SDS–water).

4. Conclusion

The present study reports the micellization of Tyr-Phe dipeptide and Val-Tyr-Val tripeptide in aqueous solution, SDS and SDS–polymer environment using UV–visible, surface tension, fluorescence, conductivity, zeta potential and CD techniques. Both the peptides form micelles and the *cmc* values obtained for dipeptide and tripeptide are 2×10^{-5} and 4×10^{-5} M, respectively in aqueous solution at 25 °C, which indicates that dipeptide is more hydrophobic than tripeptide. It has been found that the presence of SDS and polymer hindered the micelle formation of peptides with the enhancement of *cmc* values of peptides. On the other hand the *cmc* values of SDS were decreased in the presence of peptides and were declined with increase in temperature. The counter ion association and thermodynamic results suggest that SDS is more stable in micellized form in the SDS–water–peptide ternary systems compared to the situation in the corresponding SDS–water binary systems.

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