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ORIGINAL CONTRIBUTION

Animesh Kumar Rakshit
Bhaskar Sharma

The effect of amino acids on the surface and thermodynamic properties of poly[oxyethylene(10)] lauryl ether in aqueous solution

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A.K. Rakshit (✉) · B. Sharma
Department of Chemistry,
Faculty of Science, M.S. University
of Baroda, Vadodara 390 002, India
E-mail: rakshitak@indiatimes.com

Abstract The interfacial and thermodynamic properties of a non-ionic surfactant, poly[oxyethylene(10)] lauryl ether, $[C_{12}H_{25}(OCH_2CH_2)_{10}OH]$, in aqueous solution in the presence of amino acids have been investigated. Critical micelle concentrations (cmcs) were determined by surface tension measurements at different additive concentrations and temperatures using a du Nouy tensiometer. From the surface tension data, the surface excess concentration (τ), the minimum area per molecule (A_{min}), and the surface pressure at the cmc(π_{cmc}) were evaluated. Thermodynamic parameters of adsorption and micellization were evaluated and discussed. The other solution properties of this surfactant like the cloud point viscosity, and foaming have been determined in the presence of different concentrations of alanine and glycine.

Keywords Nonionic surfactants · CMC · Aggregation number · Thermodynamic parameters · Amino acids

Introduction

The investigation of interfacial and thermodynamic properties of surfactants in solution, both in the presence and absence of additives, can provide information about solute-solvent interactions of the surfactants in solution. These studies are also important for enhanced oil recovery and in froth floatation processes for metal ore concentration [1]. The interfacial and micellar properties of these solutions are governed by a delicate balance of hydrophobic and hydrophilic interactions [2]. Hence, such studies seem to be important [3]. Because of the importance of nonionic surfactants in industry as well as our own interest in these substances [4, 5, 6, 7, 8, 9], we studied the thermodynamics of micellization of poly[oxyethylene(10)] lauryl ether in the presence of two amino acids – glycine and alanine. As these amino acids have significant influence on the aqueous system and are referred to as water structure influencing molecules [10] and also have biological significance, we decided to look at the effect of these molecules on the properties of $C_{12}E_{10}$ aqueous solutions. The various solution properties such as surface tension and associated properties, cloud point; foaming, and viscosity of the nonionic surfactant $[C_{12}H_{25}(OCH_2CH_2)_{10}OH]$ (i.e. poly[oxyethylene(10)] lauryl ether) in aqueous media at different temperatures have been studied and are presented here.

Materials and experimental methods

Poly[oxyethylene(10)] lauryl ether (i.e. $[C_{12}H_{25}(OCH_2CH_2)_{10}OH]$, Sigma) molar mass 626, was used without any further purification. Glycine (AR) and *dl*-Alanine (AR) were obtained from Suvidhinath Laboratories, Baroda, India and were used without any further treatment. All solutions were prepared in doubly distilled water.

Critical micelle concentration measurements

The critical micelle concentration (cmc) was obtained by the surface tension method using a du Nouy tensiometer (S.C.Dey and Co., Kolkata, India). Measurements were made at 35, 40, 45, and 50 °C. The temperature was maintained constant (±1 °C) by

circulating thermostated water through a jacketed vessel containing the solution. The concentration of the solution was varied by adding aliquots of concentrated stock solution to the known volume of solution in the jacketed vessel by means of a Hamilton microsyringe. The platinum ring was cleaned before each measurement of surface tension. The reproducibility in γ was never more than 0.5%. The measured surface tension (γ) values were plotted as a function of the logarithm of the surfactant concentration (logC), and the cmc was estimated from the breakpoint in the resulting curve. Representative plots of surface tension vs. logarithm of surfactant concentration (logC) are shown in Fig. 1. The reproducibility of the surface tension-concentration curves was checked by duplicate runs and in general was very good. The error in the break point, i.e. in cmc, was found to be less than 1%. The cmc values are presented in Table 1.

Cloud points

Cloud points of poly[oxyethylene(10)] lauryl ether in all experimental solutions were determined. The surfactant concentration was 1%(w/v); the experimental method has been described earlier [11].The cloud points are presented in Table 1. These are averages of the appearance and disappearance temperatures. These temperatures did not differ by more than 0.6 °C under constant stirring.

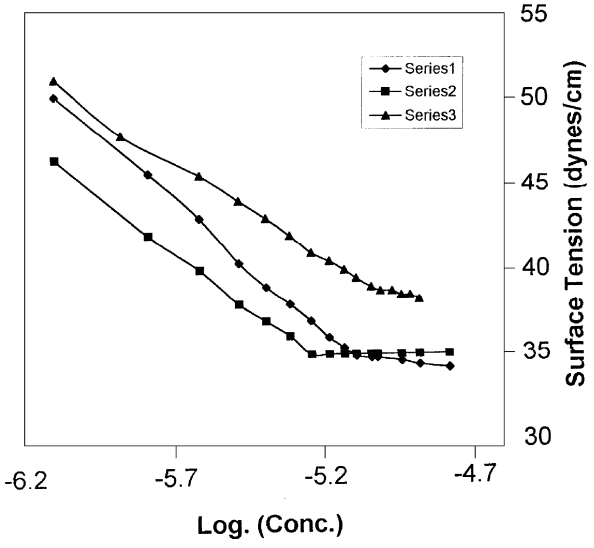

Fig. 1 Representative plots of surface tension vs. logarithm of surfactant concentration in presence of 1. 0.75% glycine at 40 °C, 2. 0.25% glycine at 50 °C, 3. 0.25% alanine at 35 °C

Fluorescence measurements

The micellar aggregation number of the pure surfactant, as well as in the presence of additives, was determined by steady-state fluorescence quenching measurements. Pyrene was used as probe and cetyl pyridinium chloride (CpyCl) as quencher. The excitation and emission wavelengths were 335 and 385 nm, respectively. All measurements were carried out at room temperature (~25 °C) using a Perkin Elmer LS-50B luminescence spectrophotometer.

An aliquot of stock solution of pyrene in acetone was transferred into a flask and the solvent was evaporated with nitrogen. The surfactant solution was added and the concentration of pyrene and surfactant were kept constant at 10^{-6} M and 5 mM, respectively. The quencher concentration was varied from zero to 12×10^{-5} M. The aggregation number (N_{agg}) was obtained from the following equation [12, 13]

$$\ln\ I = \ln\ I_0 - \{N_{agg}[Q]\}/\{[S] - cmc\} \quad (1)$$

where Q and S are quencher and surfactant respectively. The I_0 and I are the fluorescence intensities in the absence and presence of quencher in a given system.

Viscosity measurements

The viscosities of the surfactant solutions (5% w/v) were determined with the help of an Ubbelohde viscometer [14] at three temperatures, 35, 40, and 45 °C. The change in the viscosities of surfactant solutions in the presence of 0.25, 0.5, 0.75, and 1.0% (w/v) of glycine and alanine were also studied.

Foaming measurements

The foaming efficiency of the surfactants was determined by measuring the initial foam height. A method similar to Ross-Miles method [15] was used. The effect of glycine and alanine of different concentrations on the initial foam heights of surfactant solutions was also determined. The concentration of surfactant was 0.1% (w/v) and the reproducibility of the initial foam height was less than ±2%.

Table 1 The cmc (μM) of nonionic surfactant $C_{12}E_{10}$ in presence of additives at different temperatures. The cloud point (°C) of 1% solution in water

Additive (w/v)	Critical micelle concentration (μM)				Cloud point of 1% solution (°C)
% Glycine	35 °C	40 °C	45 °C	50 °C	
0.0[a]	11.8	10.0	8.9	7.1	93
0.25	6.4	7.0	8.1	8.3	85
0.50	4.9	6.3	7.2	7.4	84
0.75	4.5	5.7	6.6	6.9	82
1.0	3.9	4.8	5.6	5.7	80
% Alanine					
0.25	9.1	9.7	10.2	10.7	86
0.50	8.1	9.1	10.7	11.8	85
0.75	7.4	8.1	9.8	11.4	83
1.00	5.7	7.4	9.1	10.7	81

[a]Taken from reference 9

Results and discussion

In Fig. 1, some representative surface tension–logC plots are shown. In Table 1, the computed critical micelle concentrations of various systems at different temperatures are presented. It can be seen that, in general, the cmc decreases with an increase in additive concentration at any given temperature. The alanine system at 50 °C seems to be an exception. This type of observation was also seen earlier in the presence of PEG 400 and sucrose [9]. We noted (in reference 9) that the cmc decreases with increase in temperature, which is taken as characteristic of a nonionic surfactant within the narrow temperature range studied. However, the effect of additives seems to be different – both the systems, at all concentrations, show increase in cmc with increase in temperature. This was also seen earlier by us [9]. In the earlier case, the additives were nonionic hydrophilic substances. However, in the present case we have used two amino acids that are hydrophilic and zwitterionic. Overall behavior remains similar. It is well known that the micellization process occurs due to the hydrophobic interaction and that London dispersion force is the attractive force in the micelle formation. The effect of temperature on the dehydration process of the poly oxyethylene group of $C_{12}E_{10}$ is said to be responsible for the decrease of cmc with increase in temperature. However, this trend is not seen in the presence of additives. The question is why?

We have found it difficult to conclusively answer the above question with the limited experimental procedures at our disposal. In our earlier paper [9], we have shown that the variations in cmc with temperature in the presence of neutral additives (PEG 400 and sucrose) are similar to what we observe in the present case (zwitterionic, glycine, and alanine). The interaction – hydrogen bonding or otherwise between water and the additives – changes the solvent structure dramatically and we believe that the overall solvent structure (water plus soluble additive) controls the micelle formation.

The cloud point of 1% (w/v) $C_{12}E_{10}$ is 93 °C. The cloud point decreases with the addition of additives (Table 1). The cloud point can be looked as the temperature at which the phase separation occurs. The presence of additives, which are hydrophilic, probably decreases the available amount of water to be associated with $C_{12}E_{10}$. It is also known that the solutes, which get solubilized in the POE mantle of the micelle [13, 14, 15, 16], decrease the cloud point. Hence, we suggest that these additives are getting solubilized in the POE mantle and are not present deep inside the micellar core. Kjellander et al. [17] have suggested that the cloud point is highly entropy dominated. Hence, we expect that the entropy change is highly positive at the cloud point. This probably arises because the highly hydrophilic amino acid additives interact with water molecules and free these water molecules from their bound states in the nonionic micelles.

The free energy of micellization $\left(\Delta G_m^0\right)$ of the nonionic surfactants, both in the presence and in absence of additives, is presented in Table 2. It was computed by using the following equation [9]

$$\Delta G_m^0 = RT \ \ln \ cmc \tag{2}$$

where cmc is in mole fraction scale. The transfer process indicates the formation of micelles in the solvent medium from the solvated free monomer of unit mole fraction. In the presence of additives, the free energy of micellization is negative and it is more negative in the presence of glycine than in the presence of alanine. It is also to be noted that as the additive concentration increases, the ΔG_m^0 goes on decreasing – in other words the micelle formation becomes relatively more spontaneous. Though the variation of cmc with temperature in the presence of additives is different from that in absence of additives, the variations of ΔG_m^0 in both conditions are similar. The variation of ΔG_m^0 with temperature was used to compute the ΔH_m^0 and ΔS_m^0 by using the relation

$$\Delta G_m^0 = \Delta H_m^0 - T\Delta S_m^0 \tag{3}$$

Table 2 The free energy (ΔG_m^0), enthalpy (ΔH_m^0), and entropy (ΔS_m^0) of micellization of nonionic surfactant, $C_{12}E_{10}$, in presence of glycine and alanine

Additive (w/v)	$-\Delta G_m^0$ (kJ mol^{-1})				$-\Delta H_m^0$ (kJ mol^{-1})	ΔS_m^0 (J mol^{-1} K^{-1})
% Glycine	35 °C	40 °C	45 °C	50 °C		
0.0[a]	39.3	40.4	41.4	42.6	–27	220
0.25	40.0	41.3	41.6	42.2	15	84
0.50	41.4	41.6	41.9	42.5	19.1	72
0.75	41.8	41.8	42.1	42.7	23.0	60
1.00	42.2	42.3	42.6	43.2	21.7	66
% Alanine						
0.25	40.0	40.5	41.0	41.5	9.2	100
0.50	40.3	40.6	40.9	41.2	21.8	60
0.75	40.5	40.9	41.1	41.3	24.5	52
1.00	41.2	41.2	41.3	41.5	35.0	20

[a]Taken from reference 9

where ΔH^0_{rmm} and ΔS^0_m were taken to be independent of temperature. All systems show good straight lines except 1% alanine system. However, the points in the graph were reproducible. From Table 2 it can also be seen that in presence of amino acids, the micelle formation is exothermic and the entropy of micellization is positive. However, the micelle formation in pure water is endothermic. We therefore suggest that the interactions between the amino acids/water and/or amino acids/surfactant are exothermic. We have seen such behavior earlier also with other additives [8, 9]. However, it should be noted that this is not always the case. For example, in the presence of sucrose, the micellization process of Brij 35 was found to be endothermic at some concentrations [8]. In that case, the $\Delta G^0_m - T\Delta G_m{}^0$–T plot was not linear. Both ΔH^0_m and ΔS^0_m seem to be functions of the additive concentration. With more and more additive, the micellization process becomes relatively more exothermic which is quite different from our earlier observation [9]. The entropy change values are also quite different and are very low (20 J mol^{-1} K^{-1} for 1.0% alanine). Around this condition of 1% alanine solution, the micellization process becomes enthalpy dominated, whereas at lower concentrations of additives it is entropy dominated. These definite changes in ΔH^0_m and ΔS^0_m also indicate a remarkable change in the environment surrounding the hydrocarbon chains of the surfactant molecules in the presence of the amino acids. This is not unexpected as ion-dipole interaction should be a dominant factor here.

The ΔH^0_m–ΔS^0_m compensation plot was also evaluated. Both the systems individually show a very good straight line. Both the systems together also show a very good straight line with a correlation coefficient of 0.999. The slope of the line was found to be 310 K (Fig. 2), almost the same as observed for PEG–sucrose systems (312 K). This clearly shows once again that the micellization is controlled by the bulk structural property [9]. We also find that the intercept of the plot is –41.1 kJ mol^{-1}, which can be interpreted as the free energy of micellization ΔG^0_m of the $C_{12}E_{10}$ at 37 °C, where there is no effect of the entropy factor.

The free energy as well as enthalpy of transfer of micelles from water to amino acid solutions ΔG^{0tr}_m and $\Delta H^{0tr}_m \Delta H_m{}^{0tr}$, respectively were computed from the following relations

$$\Delta G^{0tr}_m = \Delta G^0_m(sol^n) - \Delta G^0_m(water) \quad (4)$$

$$\Delta H^{0tr}_m = \Delta H^0_m(sol^n) - \Delta H^0_m(water) \quad (5)$$

It can be easily seen that both the transfer quantities are negative. The micelle favors (relatively speaking) the solutions rather than pure water as was observed earlier. The hydrophilic group transfer from water to aqueous solutions was exothermic whereas the transfer of hydrophobic groups is endothermic. We find that the overall values are negative in our systems, indicating that the endothermic part of the transfer is dominant. The entropy of transfer of micelle can also be computed by following similar relations (cf Eq. 4 and Eq. 5) and the values are all negative. This indicates that in solution the micelle formation is not associated with that much bulk structural change as in pure water.

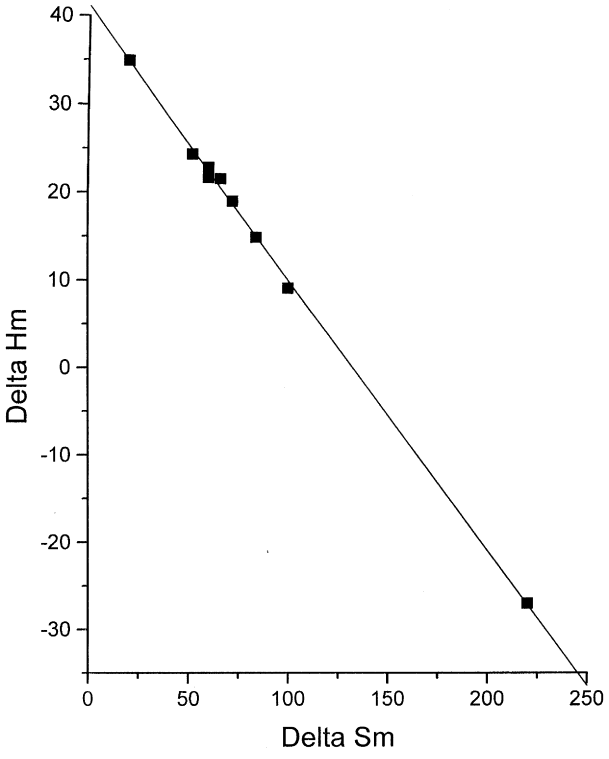

Fig. 2 Compensation plot of delta H_m and delta S_m, taking all systems together

We also looked at the air-solution interface as this interface is expected to be well-populated with surfactant molecules [18]. The Gibbs adsorption equation in a dilute solution is

$$\Gamma = (-1/RT)(d\gamma/d\ln C) \quad (6)$$

where Γ, γ, R, T, and C are surface excess, surface tension, gas constant, temperature, and concentration of surfactant, respectively. The plot of γ–lnC was a reasonably good straight line for all systems; the Γ is independent of surfactant concentration. The maximum error in the $d\gamma/d\ln C$ was less than 3%. The Γ_{cmc} ($=\Gamma_{max}$) i.e. the maximum possible surface excess concentration was also computed. It was observed that the surface excess concentration of the surfactant was higher in the presence of additives than in the absence of additives. It was also obvious that the Γ increases as the concentration of glycine increases only at 35 °C. At all other temperatures, as well as in the presence of alanine, the

Γ_{max} seems to remain more or less constant. The values of surface excess at 35 °C in presence of glycine (0, 0.25, 0.50, 0.75, and 1% w/v) are 2.3, 4.6, 5.2, 7.4, and 8.9×10^{-10} mol cm^{-2} respectively. However, for the other cases, the Γ was found to be $(5.5\pm0.1)\times10^{-10}$ mol cm^{-2}, which corresponds to 0.30 nm^2 molecule^{-1}. This suggests that the air-water interface is a closely packed one and that the orientation of the surfactant molecules is almost perpendicular to the surface [19]. As the amount of glycine increases at 35 °C, the tendency of the surfactant to locate at the air-water interface increases indicating dehydration of the surfactant molecules. This also suggests the possibility of a lower cloud point in the presence of additives, which has been observed and mentioned in an earlier paragraph.

The free energy of adsorption (ΔG^0_{ad}) can be calculated from the following relation

$$\Delta G^0_{ad} = \Delta G^0_m - N\Pi_{cmc}A_{cmc} \quad (7)$$

where N, Π_{cmc}, and A_{cmc} are Avogadro number, surface pressure at cmc (γ_o-γ_{cmc}), and area per molecule at cmc, respectively. As all these quantities are positive and ΔG^0_m is always negative, the ΔG^0_{ad} will always be more negative than ΔG^0_m. This indicates that adsorption at the air-water interface is more spontaneous. Therefore, the surfactant will always adsorb at the air-water interface before micelle formation occurs. In this present case where amino acids glycine and alanine are the additives, we found that A_{cmc} is almost constant (0.30 nm^2 molecule^{-1}) at all additive concentration and at all temperatures. Therefore $(\Delta G^0_m - \Delta G^0_{ad})$ will be equal to $180.6\times\Pi_{cmc}$ J mol^{-1}. The Π_{cmc} varies from system to system and the maximum and minimum values in the systems being studied are 33 and 16.5 mNm^{-1}. Hence, we find that in these cases (in presence of glycine and alanine) the free energy of adsorptions are less by about 6–3 kJ mol^{-1} from the free energy of micellization (i.e. ΔG^0_m) which is ~13% more negative. In case of PEG and sucrose, the ΔG^0_{ad} was about 20% more negative than ΔG^0_m [9].

The fluorescence quenching method was used to determine the aggregation number of surfactants in the micelle by using Eq. 1 and the values are presented in Table 3. From N_{agg} values it is clear that glycine and alanine have similar effects on the micellar aggregation. However, the first addition of additive seems to decrease the aggregation number before it increases once again. This is probably due to the demicellization property of amino acids. As the solvent structure is affected by the presence of amino acids (both water structure making and breaking occur simultaneously), it is difficult to pinpoint an exact reason for this decrease in N_{agg} before an increase. Moreover, the hydrophobic forces (the real reason for micelle formation) do also change in the presence of additives. The calculated I_1/I_3 values remain more or less constant at 1.09 for all systems, indicating that the micropolarity of the micellar system is rather high and hydrophilic. As the nonionic micelles are generally spherical in character we believe that the amino acid additives are present at the water–micelle interface.

The intrinsic viscosity, lηl, is a measure of solute-solvent interaction and is generally computed at infinite dilution. However, some researchers [9, 20] have used lηl to be equal to $(\eta_r$-1)/C without extrapolation to zero concentration. As given in Table 4, the lηl decreases with increase in temperature because of micellar dehydration. As the concentration of glycine increases, the lηl decreases at any given temperature. We can hence surmise that this is because of dehydration. However, for alanine it increased with the concentration of alanine. A similar discrepant result was obtained for PEG 400 and sucrose

Table 3 The micellar aggregation number of $C_{12}E_{10}$ in presence of additives glycine[a] and alanine[b] at room temperature (~25 °C)

% Additive	N_{agg}[a]	N_{agg}[b]
0.0	63	63
0.25	42.0	49.0
0.50	54.0	53.0
0.75	54.0	67.0
1.00	52.0	52.0

Table 4 The intrinsic viscosity $|\eta|$ (cm^3 g^{-1}), V_h, and V_{OE} of 5% $C_{12}E_{10}$ in presence of glycine and alanine at different temperatures

Additive concentration (w/v)	$\|\eta\|$			$V_A(\times10^4$ A$^3)$	$V_{OE}(\times10^4$ A$^3)$
% Glycine	35 °C	40 °C	50 °C	40 °C	40 °C
0.0	7.09	6.93	6.81	28.07	–
0.25	7.38	6.93	6.42	27.7	24.5
0.50	7.18	6.60	6.25	28.0	24.6
0.75	6.95	6.30	5.95	28.5	25.1
1.00	6.88	5.93	5.72	29.3	25.9
% Alanine					
0.25	7.18	6.84	6.30	28.0	24.6
0.50	7.25	6.93	6.38	26.7	23.3
0.75	7.40	7.05	6.50	25.5	22.1
1.00	7.50	7.24	6.56	24.0	20.6

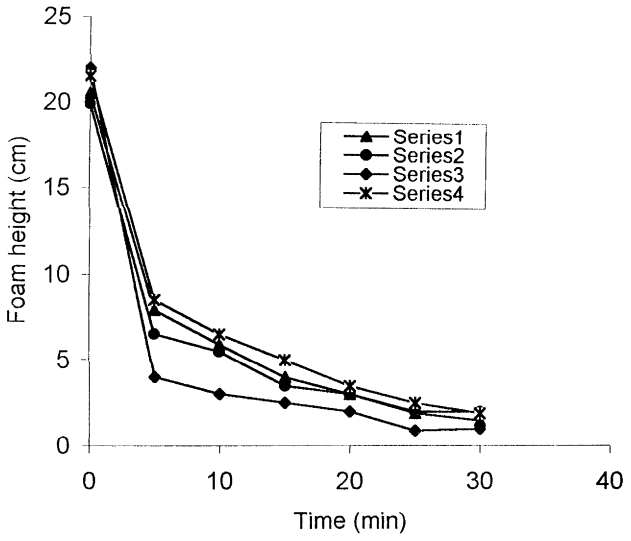

Fig. 3 Representative plots of foam heights vs. time. The surfactant concentration is 0.1% $C_{12}E_{10}$ .Additives are 1% glycine at 35 °C (series 1); 0.5% glycine at 40 °C (series 2); no additive at 35 °C (series 3); 0.5% alanine at 40 °C (series 4)

[9]. We are not quite sure why glycine and alanine behave somewhat differently.

The C_{12} E_n micelles are suggested to be spherical and the micellar molecular weight (M_m) of the oxyethylene chain of number n is given by [20]

$$M_m = A_n M = (1025/n - 5.1)\ M \tag{8}$$

where A_n is aggregation number and M is the molecular wt. of C_{12} E_n. When $n = 10$, M_m can be calculated from the above equation to be equal to 6.1×10^4. The hydrated micellar volume V_h, the volume of the hydrocarbon core V_c, and the volume of the pallisade layer of the oxyethylene unit V_{OE}, can be calculated by using the relations

$$V_h = \frac{l\eta l M_m}{2.5\ N};\ V_c = 10^{24}.\ An.\ M_e/d.N \tag{9}$$

and $V_{OE} = V_h - V_c$ where M_e and d are the molecular weight (170) and density (0.802 g cm^{-3}) of the corresponding liquid n-alkane at 25 °C. In Table 3, the computed values of V_h and V_{OE} are also presented. It is obvious from the computed data that with increase in temperature the hydrated micellar volume (V_h) and the volume of the pallisade layer V_{OE} go on decreasing in all systems. However, it is obvious that the variations of hydrated micellar volume with additive concentrations are not similar in all cases. Hence, we suggest that the effect of the additives on the micellar volume are different because of the ion-dipole interaction between water and amino acids, the solubilization of amino acids at the palliside layer, and probably some interaction between amino acids and the surfactants. In this calculation, the micellar molecular weights have been taken as the same both in the presence and absence of amino acids, which may not be correct. Moreover, the molecular weights calculated from the aggregation number are much lower than 6.1×10^4.

We have also studied the foaming property of the surfactant solution (0.1% w/v) in the presence of glycine and alanine. It was obvious that the foam height decreased very sharply in the initial 5 min (from ~22 cm to ~7 cm). However, after that the variation of foam height with time is slow. There was not much effect of temperature (within the range studied). However, both glycine and alanine had some effect on the foam height or the foam stability. A representative foam stability curve is presented in Fig. 3. Alanine increases the initial foam height and the foam is more stable at 0.75 and 1.0% w/v concentration. At lower concentration there is not much effect. Glycine also stabilizes the foam but not as much as alanine. At the beginning, dilute foams are formed. Due to a rather fast decrease of liquid, these change into more stable concentrated foams within about 5 min, in all cases. The drainage of liquids becomes slower and the foam height perceptibly changes though very slowly. The air bubbles here consist of polyhedral gas cells whereas at the beginning the gas bubbles were spherical.

Conclusions

The thermodynamics of micellization and adsorption of the nonionic surfactant $C_{12}E_{10}$ in aqueous medium in the presence of two amino acids, glycine and alanine, were studied. The foaming property was also determined. It was observed that the behavior of these additives was somewhat similar to nonionic PEG 400 and sucrose though in some cases there were differences e.g. in the magnitudes of ΔG^0_{ad}, in the constancy of A_{min} values, as well as in the variation of hydrated micellar volumes. The interaction of amino acids with water, the probable solubilization in the pallisade layer of the hydrated micelle, and surfactant-additive interactions are the possible reasons for the observed effects.

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