

The Relationship between the Interfacial Free Energy and the Free Energy of Micellization of Triton X-100 and Sodium Dodecyl Sulfonate

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The contact angles for water and Triton X-100 on Teflon; for water, glycerol, formamide, and diiodomethane on Teflon covered with a Triton X-100 film and a sodium dodecyl sulfonate film and glass covered with a sodium dodecyl sulfonate film; and for water, glycerol, and diiodomethane on glass were measured. Also, the surface tension of Triton X-100 and the interfacial tensions of Triton X-100–*n*-dodecane and Triton X-100–diiodomethane were measured. From the results of these measurements, the Lifshitz–van der Waals component and the electron-acceptor and electron-donor parameters of the acid–base component of the apolar and polar moieties of Triton X-100 and sodium dodecyl sulfonate were determined. Next, taking into account the molecular dimensions of these surfactants, the free energy of interfacial interaction through water was calculated for the apolar and polar parts of Triton X-100 and sodium dodecyl sulfonate. Also, the electrostatic free energy of interactions between DS[−] ions was evaluated. Good agreement between the free energy of micellization obtained from the cmc data and the free energy of interaction between molecules of surfactant through water was found. © 1995 Academic Press, Inc.

Key Words: interfacial free energy; micellization; Lifshitz–van der Waals interactions; acid–base interactions; Triton X-100; sodium dodecyl sulfonate.

INTRODUCTION

Ionic and nonionic surfactants have a wide applicability from both biological and technological points of view. The sharp changes in such physical properties of the aqueous solutions of surfactants as surface tension, conductance, and intensity of scattered light have been attributed to the formation of micelles in equilibrium with their monomeric species in the solution. The critical micelle concentration (cmc) plays an important role in the description of the physical behavior of the surfactant solutions in such phenomena as adsorption and solubilization.

Although a great number of attempts have been made to describe the mechanism of the formation of micelles, this

problem has not been decisively solved as yet (1–7). Particularly, the correlation between the different kinds of interfacial interactions and the cmc has not been clearly explained.

Taking into account the electrostatic, the Lewis acid–base, and the Lifshitz–van der Waals interfacial interactions in aqueous media, it becomes possible to calculate the critical micelle concentrations for various types of surfactants from the molecular dimensions of their apolar and polar moieties and from the free energies between these moieties and water (8, 9).

Among other surfactants, the nonionic Triton X-100 and the anionic sodium dodecyl sulfonate are used in many branches of industry and their properties have been extensively investigated (1, 7, 10–14). But it is very interesting to study the relationship between the components of the surface free energy of Triton X-100 and sodium dodecyl sulfonate and their free energy of micellization.

Thus the purpose of our paper is to determine the Lifshitz–van der Waals component and the electron-acceptor and electron-donor parameters of the acid–base component of the surface free energy of the apolar and polar moieties of these surfactants using measurements of contact angles and interfacial tensions in proper systems and then to calculate the free energy of micellization of Triton X-100 and sodium dodecyl sulfonate.

EXPERIMENTAL

Materials

Triton X-100 (TX-100) is a *p*-(1,1,3,3-tetramethylbutyl) phenoxy polyoxyethylene glycol containing an average of 9.5 oxyethylene units per molecule. TX-100 and sodium dodecyl sulfonate (SDSs) were supplied by Merck with a high grade of purity (99%, for tenside tests). The following liquids were used for the contact angle measurements: doubly distilled and deionized water (W) from a Milli-Q system, glycerol anhydrous (G) (Fluka, purity > 99.5%), formamide (F) (Fluka, purity > 99%), and diiodomethane (D) (Fluka, purity > 98%). For the interfacial tension measurements, diiodomethane and *n*-dodecane (Fluka, pure) were used.

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Preparation of the TX-100 and SDSs Films

The glass slides used for the preparation of the SDSs film were cleaned in chromic acid, washed many times with doubly distilled water, and placed in an ultrasonic bath for 15 min. Then the SDSs film was prepared by spreading a 10% aqueous solution of SDSs on the glass plates, air-drying for 24 h, and a final drying in a desiccator filled with a dehydrating agent.

The Teflon plates were polished, boiled for a few minutes in HCl (1:1), washed many times with doubly distilled water, and placed in an ultrasonic bath for 15 min. Then the SDSs film was prepared in the same manner as on the glass surface. The TX-100 film was built from the immersion of the Teflon plates in pure TX-100, air-dried for 48 h in a vertical position, and further dried in a desiccator as for the formation of the SDSs film.

Contact Angle Measurements

The Teflon plates used for the contact angle measurements of water and TX-100 were polished and washed as for the formation of the surfactant film, but after cleaning, they were dried at 50°C and kept in the desiccator over a dehydrating agent. Similarly, the glass slides were cleaned, dried at 100°C, and cooled in the desiccator. On the glass slides the contact angle for water, glycerol, diiodomethane, and TX-100 were measured. In the cases where the Teflon plates were covered with TX-100 and SDSs films and the glass slides with SDSs film, the contact angles were measured for water, glycerol, formamide, and diiodomethane.

The advancing contact angle measurements were made at $20 \pm 1^\circ\text{C}$ by the sessile drop method using a goniometer–camera–computer system made in the Physics Department of Extremadura University, Spain (15). For each solid–liquid–air system at least 10 plates were used and the mean value of not less than 30 contact angle determinations was taken for calculations.

The standard deviations of the contact angles for water, glycerol, formamide, diiodomethane, and TX-100 were ± 1.2 , ± 0.9 , ± 1.0 , ± 0.7 , and $\pm 0.8^\circ$, respectively.

Interfacial Tension Measurements

The surface tension of TX-100 was measured at $20 \pm 1^\circ\text{C}$ under atmospheric pressure with the ring method. The apparatus used was controlled by a computer which analyzed the results obtained. The surface tension of TX-100 was also measured by the pendant drop method using the camera–computer system. These two methods were also employed for the determination of the interfacial TX-100–*n*-dodecane and TX-100–diiodomethane tensions.

In the case of the TX-100–*n*-dodecane system, the interfacial tensions were measured by the ring method relative to the interfacial tension of the water–ethyl acetate system, which has a similar value.

The standard deviation of surface tension measurements is below ± 0.05 mN/m.

RESULTS AND DISCUSSION

Free Energy of Interaction between TX-100 Molecules through Water

Recently it was shown that it is possible to calculate the total free energy of interaction between two molecules of surfactant through water (8, 9). To solve this problem, the (Lewis) acid–base (AB) and the Lifshitz–van der Waals (LW) interfacial interactions through water for both the apolar chain and the polar head of the surfactant molecules and the electrostatic (EL) interaction between the polar heads should be taken into account. However, as a first approximation, for TX-100 the electrostatic free energy of repulsion may be neglected. Thus for the evaluation of the free energy of interaction between TX-100 molecules through water, the LW and AB components of the TX-100 surface tension must be determined.

According to van Oss and co-workers (16, 17) the surface tension of a liquid and a solid can be expressed as

$$\gamma = \gamma^{\text{LW}} + \gamma^{\text{AB}}, \quad [1]$$

where γ is the surface tension of the solid or liquid and $\gamma^{\text{AB}} = 2(\gamma^+ \gamma^-)^{1/2}$ (γ^+ and γ^- are the electron-acceptor and electron-donor parameters of the acid–base component of the surface tension, respectively).

The interfacial liquid–liquid and solid–liquid tension can be described by the equation (16, 17)

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^{\text{LW}} \gamma_2^{\text{LW}})^{1/2} - 2(\gamma_1^+ \gamma_2^-)^{1/2} - 2(\gamma_1^- \gamma_2^+)^{1/2}. \quad [2]$$

By the measurements of the interfacial tension of a liquid–liquid system where only Lifshitz–van der Waals forces are acting at the liquid–liquid interface, it is possible to determine the Lifshitz–van der Waals components of the TX-100 surface tension, γ_2^{LW} , if γ_1^{LW} is known, from the equation

$$\gamma_2^{\text{LW}} = \frac{\gamma_1 + \gamma_2 - \gamma_{12}}{2(\gamma_1^{\text{LW}})^{1/2}}. \quad [3]$$

By introducing into Eq. [3] the measured value of the surface tension of TX-100, the value taken from literature (18) of the surface tension of *n*-dodecane, γ_1 , assuming also that $\gamma_1^{\text{LW}} = \gamma_1$, and the interfacial tension TX-100–*n*-dodecane listed in Table 1, the γ_2^{LW} values were calculated and are presented in Table 1. For the calculation both values of the surface and interfacial tensions measured by the ring and the pendant drop methods were taken into account, showing slight differences between both γ_2^{LW} values.

TABLE 1
Values of the Lifshitz–van der Waals Component (γ^{LW}) and the Electron-Acceptor (γ^+) and Electron-Donor (γ^-) Parameters of the Acid–Base Component (γ^{AB}) of the Surface Tension (Surface Free Energy), in mJ/m²

Solid/liquid	γ^{LW}	γ^+	γ^-	γ^{AB}	γ	Ref.
Water	21.8	25.5	25.5	51.0	72.8	(17)
Glycerol	34	3.92	57.4	30	64	(17)
Formamide	39	2.28	39.6	19	58	(17)
Diiodomethane	50.8	0.72	0	0	50.8	(19)
<i>n</i> -Dodecane	25.08	0	0	0	25.08	(18)
1,1,3,3-Tetramethyl butylene	18.41	0	0	0	18.41	^a
Benzene	28.88	0	3.04	0	28.88	(22)
TX-100– <i>n</i> -Dodecane					6.47	^a
TX-100–diiodomethane					5.28	^b
TX-100					0.0	^b
	28.58	—	—	6.36	34.94	^a
	29.24	0.24	33.84	5.70	34.94	^c
	29.97	0.30	21.08	5.06	35.03	^b
Teflon/TX-100 Film	WDG 29.27	0.96	33.68	11.35	40.62	^c
	WFD 29.18	0.84	34.48	10.76	39.95	^c
	GFD 27.86	0.62	47.75	10.92	38.78	^c
Teflon/SDSs	WDG 27.28	0.70	52.20	12.05	39.33	^c
	WFD 27.31	0.73	51.86	12.31	39.63	^c
	GFD 27.76	0.81	46.83	12.30	40.06	^c
Glass/SDSs	WDG 27.20	0.75	51.54	12.40	39.60	^c
	WFD 27.17	0.70	51.95	12.08	39.25	^c
	GFD 26.63	0.62	58.40	12.00	38.63	^c

^a Measured by the ring method.

^b Measured by the pendant drop method.

^c Calculated from contact angle measurements.

The AB component of the surface tension of TX-100 was determined from the difference $\gamma_2^{AB} = \gamma_2 - \gamma_2^{LW}$. The γ_2^+ and γ_2^- values have been calculated from Eq. [2] using the interfacial tension data for the TX-100–diiodomethane system measured by the pendant drop method. All the calculated values are shown in Table 1. It appears from this table that the γ_2^+ parameter is very small and many times lower than γ_2^- . This means that TX-100 has a strong basic character.

The LW and AB components of the TX-100 surface tension and the γ_2^+ and γ_2^- parameters of γ_2^{AB} can be determined also by contact angle (θ) measurements in the proper systems.

Introducing Eq. [2] into Young's equation gives (16, 17)

$$(1 + \cos \theta) \gamma_L + \Pi e = 2[(\gamma_L^{LW} \gamma_S^{LW})^{1/2} + (\gamma_L^+ \gamma_S^-)^{1/2} + (\gamma_L^- \gamma_S^+)^{1/2}], \quad [4]$$

where L stands for the liquid and S for the solid, and Πe is the surface pressure.

By measurements of the contact angle for a liquid onto an apolar solid, it is possible to calculate the Lifshitz–van der Waals component of the surface tension of the liquid. Thus, by introducing into Eq. [4] the value of the contact angle of TX-100 on the Teflon surface (Table 1), the γ_L^{LW} value for TX-100 was evaluated. For this calculation the

γ_S^{LW} value for Teflon was determined from the contact angle measured in the system Teflon–water drop–air, and Πe was assumed to be equal to 0.

To determine the γ_L^+ and γ_L^- parameters of γ_L^{AB} of TX-100, the measurements of the contact angle of water, glycerol, diiodomethane, and TX-100 on the surface of a glass slide were made. First, introducing into Eq. [4] the values of the measured contact angle for water, glycerol, and diiodomethane (Table 2) on the glass slide, and the γ_L^{LW} , γ_L^+ , and γ_L^- values for these liquids (Table 1), the γ_S^{LW} , γ_S^+ , and γ_S^- values of the glass surface tension were evaluated. Next the γ_L^+ and γ_L^- parameters of the TX-100 surface tension were calculated using the data included in Tables 1 and

TABLE 2
Measured Values of the Contact Angles for Water (θ_w), Glycerol (θ_G), Formamide (θ_F), Diiodomethane (θ_D), and TX-100 (θ_{TX}) in Different Systems, in Degrees

Solid	θ_w	θ_G	θ_F	θ_D	θ_{TX}
Teflon	112.0				59.4
Glass	57.3	65.0		47.4	20.0
Teflon/TX-100 film	50.6	54.8	48.1		44.6
Teflon/SDSs film	38.0	53.4	46.7		45.0
Glass/SDSs film	38.3	53.2	47.2		45.3

2 (17, 19). In this case it was also assumed that $\Pi_e = 0$ (16, 17).

The determined values of the TX-100 surface tension components are presented in Table 1. It is seen from this table that the values of the Lifshitz-van der Waals and acid-base components are close to those determined from interfacial tension measurements; however, there are differences between γ_L^+ and γ_2^+ or γ_L^- and γ_2^- .

It is also possible to determine the γ_L^{LW} , γ_L^{AB} , γ_L^+ , and γ_L^- values for TX-100 from the contact angle data obtained on the Teflon/TX-100 film surface, using Eq. [4] for $\Pi_e = 0$ (16, 17). For this evaluation the measured values of the contact angle for water, glycerol, formamide, and diiodomethane on the Teflon/TX-100 system (Table 2) and the values of γ_L^{LW} , γ_L^+ , and γ_L^- for these liquids taken from literature (Table 1) (17, 19) were used. The resulting values of γ_S^{LW} , γ_S^{AB} , γ_S^+ , and γ_S^- for TX-100 are presented in Table 1.

In Table 1 there are three sets of γ_S^{LW} , γ_S^+ , and γ_S^- values, because it is known that in order to solve Eq. [4] against γ_S^{LW} , γ_S^+ , and γ_S^- , the measured contact angle for three liquids is needed, but as the contact angle has been determined for four different liquids there are four possible solutions of Eq. [4]. The values of γ_S^{LW} , γ_S^+ , and γ_S^- obtained from contact angles of the systems of three liquids, WGD, WFD, and GFD (denoted with the first letter of each of the liquids used), are presented in Table 1. The system WGF was not included because it is saddled with the largest error (20). There is good agreement between the values of γ_S^{LW} , γ_S^+ , and γ_S^- obtained from contact angles for the WGD, WFD, and GFD systems.

For the Teflon/TX-100 film surface the γ_S^+ parameter is small and many times lower than γ_S^- . This fact confirms that TX-100 has a strong basic character.

From Table 1 it appears that the γ_S^{LW} component is close to γ_L^{LW} and γ_2^{LW} for TX-100; however, the γ_S^{AB} component is almost two times higher than γ_L^{AB} and γ_2^{AB} .

To obtain the values of the surface tension of TX-100 and its components it has been taken into account that, according to van Oss *et al.* (8, 9), the surfactant can be treated as consisting of "hydrophobic" and "hydrophilic" parts which can be treated separately if its surface tension is considered. This is based on the assumption that each part of the surfactant has "its own surface tension."

TX-100 consists of a 1,1,3,3-tetramethylbutyl (hydrocarbon, HC) group, a phenyl (PH) group, and, grafted at PH, an $-(O-CH_2-CH_2)_{9,10}OH$ chain (POE).

The dimensions of the contactable area of the TX-100 molecule can be estimated as the sum $S_{HC} + S_{PH} + S_{POE}$. The surface area of the 1,1,3,3-tetramethyl group (S_{HC}) can be roughly evaluated assuming that the length of HC is equal to the length of the butyl group and its width is equal to the width of the propane group. For the calculation of the length and width of HC the bond distances given by Pauling were

used, namely, C-C (tetrahedral angle), 1.27 Å, and C-H, 1.1 Å. Thus, the length is $4 \times 1.27 + 1.1 = 6.18$ Å and the width is $2 \times 1.27 + 2.2 = 4.74$ Å. Thus, $S_{HC} \cong 6.18 \times 4.74 = 29.29$ Å².

The area of the phenyl group can be taken as 21.5 Å² (9). In the case of the polyoxyethylene chain, it can be roughly assumed that $S_{POE} = 2.6 \times (3.75 \times 10) = 97.5$ Å², where 2.6 Å is the width of the $-O-CH_2-CH_2$ group, 3.75 Å is its length (9), and 10 is the number of $-O-CH_2-CH_2$ groups (the average number of the $-O-CH_2-CH_2$ groups in the TX-100 molecule is 9.5) (21) but the $-OH$ group must be also counted. Therefore, by taking into account 10 oxyethylene groups, an approximation good enough for the S_{POE} calculation can be made. Thus, taking into account the dimensions of the three groups existing in the TX-100 molecule, its contactable surface is equal to 148.29 Å².

If we assume that the surface tension of TX-100 is the average value resulting from the groups CH, PH, and POE and that it is additive, then γ for TX-100 should be equal to $[(29.29/148.29) \times 18.41] + [(21.5/148.29) \times 28.88] + [(97.5/148.29) \times 40.62] = 34.53$ mN/m, where 18.41 mN/m is the surface tension of 1,1,3,3-tetramethylbutylene (for the HC group) (Table 1), 28.88 mN/m is the surface tension of benzene (22) (for the PH group), and 40.62 mN/m (Table 1) is the surface tension of the POE group (it was assumed that the value of the Teflon/TX-100 film surface tension corresponds to the surface tension of the polar head of the TX-100 molecules).

From the above calculations it appears that the value of 34.53 mN/m is close to those measured by the ring and pendant drop methods (34.94 and 35.03 mN/m, respectively—Table 1).

Knowing the size of the contactable area of the TX-100 molecule and the γ_L^{LW} , γ_L^+ , and γ_L^- components of the surface tension of TX-100 (particular parts) and water, it is possible to calculate the free energy of interaction (ΔG^{tot}) between TX-100 molecules through water. ΔG^{tot} is the free energy change when two unity areas of the surfactant-water interface are eliminated to form a continuum of surfactant (9). For TX-100 the ΔG^{tot} can be expressed as

$$\Delta G^{tot} = \Delta G_{141} + \Delta G_{242} + \Delta G_{343}, \quad [5a]$$

where ΔG_{141} is the free energy of the interactions between CH groups through water, ΔG_{242} is the free energy of interactions between PH groups through water, and ΔG_{343} is the free energy of interactions between POE groups through water. It can be written that

$$\Delta G_{141} = -2\gamma_{14} \quad [5b]$$

$$\Delta G_{242} = -2\gamma_{24} \quad [5c]$$

$$\Delta G_{343} = -2\gamma_{34} \quad [5d]$$

Thus,

$$\Delta G^{\text{tot}} = -2(\gamma_{14} + \gamma_{24} + \gamma_{34}). \quad [6]$$

(It was mentioned above that in the case of TX-100 the electrostatic energy of repulsion may, as a first approximation, be neglected.)

For aliphatic hydrocarbons, ΔG_{141} is almost constant and equal to ca. -102 mJ/m^2 . For benzene γ_{24} is equal to 33.9 mJ/m^2 (22) and then $\Delta G_{242} = -67.8 \text{ mJ/m}^2$. The value of γ_{34} can be determined from Eq. [2] using the values of γ^{LW} , γ^+ , and γ^- for the Teflon/TX-100 film and water (Table 1); the obtained value of γ_{34} is equal to -5.61 mJ/m^2 and then $\Delta G_{343} = 11.22 \text{ mJ/m}^2$. Thus, ΔG^{tot} is equal to -158.58 mJ/m^2 . As the free energy of interaction between molecules of TX-100 is negative, they tend to aggregate and form micelles.

If the dimensions of the TX-100 molecule are known, the free energy of interaction between two molecules of the TX-100 through water can be calculated by

$$\begin{aligned} \Delta G_0^{\text{tot}} &= \Delta G_{141} \times S_{\text{HC}} + \Delta G_{242} \times S_{\text{PH}} + \Delta G_{343} \times S_{\text{POE}} \\ &= (-102 \times 29.29) + (-67.8 \times 21.5) \\ &\quad + (11.22 \times 97.5) = -33.51 \times 10^{-21} \text{ J.} \end{aligned}$$

A result of the interactions between TX-100 molecules through water is the formation of micelles. The free energy of micellization can be expressed by the relation (2, 23)

$$\Delta G_m^{\circ} = kT \ln \text{cmc}. \quad [7]$$

As the cmc for TX-100 at 293 K is $2.754 \times 10^{-4} \text{ M}$ (24), ΔG_m° was calculated from Eq. [7]. The value of ΔG_m° obtained is $-33.17 \times 10^{-21} \text{ J}$.

From comparison of the values obtained of ΔG_m° and ΔG_0^{tot} it is clear that there is good agreement between the value of the free energy of interaction between TX-100 molecules through the water phase and the free energy of micellization per molecule.

Free Energy of Interaction between SDSs Molecules through Water

In contrast to TX-100 the free energy of interaction between SDSs molecules through water, apart from the Lifshitz–van der Waals and acid–base interfacial interactions, results also from electrostatic interactions. Thus,

$$\Delta G^{\text{tot}} = \Delta G_{131} + \Delta G_{232} + \Delta G_{232}^{\text{EL}} \quad [8a]$$

or

$$\Delta G^{\text{tot}} = -2(\gamma_{13} + \gamma_{23}) + \Delta G_{232}^{\text{EL}}, \quad [8b]$$

where γ_{13} is the interfacial tension hydrocarbon chain of DSs⁻ ion–water, γ_{23} is the interfacial tension polar head of DSs⁻ ion–water, and $\Delta G_{232}^{\text{EL}}$ is the electrostatic free energy of interaction between DSs⁻ ions through water.

The value of γ_{13} can be assumed, as for TX-100, to be equal to 51 mN/m . Then the free energy of interfacial interactions between the chains of DSs⁻ ions through water, ΔG_{13} , is equal to -102 mJ/m^2 .

The γ_{23} value can be calculated from Eq. [2] if the γ^{LW} , γ^+ , and γ^- values for the polar head of DSs⁻ and for water are known. These parameters for the polar head of DSs⁻ have been determined from the measurements of the contact angle for water, glycerol, formamide, and diiodomethane on Teflon/SDSs film and glass/SDSs film surfaces (Table 2). Introducing into Eq. [4] these measured values of the contact angles and γ^{LW} , γ^+ , and γ^- for water, glycerol, formamide, and diiodomethane taken from the literature (17, 19) (Table 1), the γ_s^{LW} , γ_s^+ , and γ_s^- values have been evaluated and are presented in Table 1 for the WDG, WDF, and FGD systems, as for TX-100. From Table 1 it appears that there are only slight differences between the γ_s^{LW} , γ_s^+ , and γ_s^- values evaluated from contact angles for different groups of three liquids, both on Teflon/SDSs film and on glass/SDSs film surfaces. The γ_s^+ values are small and many times lower than those for γ_s^- . Thus, the polar heads of DSs⁻ ions have a strong base character.

Similarly to the case of TX-100, evaluations of γ_{23} from Eq. [2] were made using the values of γ_s^{LW} , γ_s^+ , and γ_s^- determined from the contact angles of the group of liquids WGD (on the glass/SDSs surface). The γ_{23} value obtained is equal to -17.55 mN/m , and then $\Delta G_{232} = 35.11 \text{ mJ/m}^2$.

The contribution from electrostatic forces to the free energy of interaction between DSs⁻ ions through water, $\Delta G_{232}^{\text{EL}}$, can be determined on the basis of the DLVO theory (25).

The contribution to the free energy of the electrostatic forces between two planes separated by a distance d and with dissimilar double layers can be expressed as (25)

$$\begin{aligned} \Delta G^{\text{EL}} &= \frac{\epsilon\kappa}{8\pi} [2\psi_1\psi_2\text{csch } \kappa d + (\psi_1^2 + \psi_2^2)(1 - \coth \kappa d)] \quad [9a] \end{aligned}$$

or

$$\Delta G^{\text{EL}} = \frac{\epsilon\kappa}{4\pi} \psi_0^2 (\text{csch } \kappa d + 1 - \coth \kappa d), \quad [9b]$$

where ϵ is the dielectric constant of water (80, at 293 K), κ is the reciprocal Debye length, and ψ_1 and ψ_2 are the surface potentials for particles 1 and 2, respectively.

κ can be determined from (3)

$$\kappa = \left[\frac{4\pi e^2 E v_i n_i}{\epsilon kT} \right]^{1/2}, \quad [10]$$

where e is the electron charge, v_i is the valency of each ionic

species, and n_i is the number of ions of each species per unit volume in bulk.

Assuming that $\psi_1 = \psi_2 = \psi_0$ and, after Davies (26), that the ψ_0 for DSs⁻ ions is equal to ψ_G (the so-called Gouy potential), it can be written for $T = 293$ K (3) that

$$\psi_0 = 50.4 \sinh^{-1} \left(\frac{134}{AC^{1/2}} \right), \quad [11]$$

where A is the area occupied by the SDSs⁻ ion at water-air interface and C is the concentration of SDSs in the bulk phase in absence of neutral salt.

Introducing into Eq. [11] the values $A = 56.9$ and $C = 0.01$ M (27), the ψ_0 value has been calculated and is equal to 194 mV. Also the κ value estimated from Eq. [10] for $C = 0.01$ M is 0.33 nm^{-1} .

Using the values of $\psi_0 = 194$ mV and $\kappa = 0.33 \text{ nm}^{-1}$ in Eq. [9b], the $\Delta G_{232}^{\text{EL}}$ value corresponding to the minimum distance between DSs⁻ ions ($d = 0.158$ nm) (9) has been calculated. This value is equal to 8.51 mJ/m^2 .

Now, introducing into Eq. [8] the three parts of the free energy of interaction between the DSs⁻ ions through water, the ΔG^{tot} value can be determined, and it is equal to -58.38 mJ/m^2 . This value of ΔG^{tot} is almost three times higher than that for the nonionic TX-100 surfactant (-158.58 mJ/m^2), which is in accordance with the surface activity of these two surfactants and their cmc at 20°C .

Knowing the dimensions of the DSs⁻ ion, it is possible to determine the free energy of interactions between two DSs⁻ ions through water.

van Oss and Constanzo (8) assumed that for dodecyl sulfate ions the apolar chain dimension corresponds to the dimension of n -decane, but in our opinion it is more reasonable to assume that the chain of the DSs⁻ ion corresponds to the decyl group. Thus, the area of the DSs⁻ chain $S_{\text{CH}} = (1.1 + 9 \times 1.27 + 1.27/2) \times 2.6 = 34.23 \text{ \AA}^2$, where 2.6 is the width of the chain (8), 1.1 is the distance of the C-H bond, and 1.27 is that of the C-C bond (see above). In the case of the head of DSs⁻, $S_{\text{H}} \cong 36 \text{ \AA}^2$ (26).

Thus, $\Delta G^{\text{tot}} = \Delta G_{131} \times S_{\text{CH}} + \Delta G_{232} \times S_{\text{H}} + \Delta G_{232}^{\text{EL}} \times S_{\text{H}} = -102 \times 34.23 + 35.11 \times 36 + 8.51 \times 36 = -19.18 \times 10^{-21} \text{ J}$.

The result of the interaction between the DSs⁻ ions through water is the micellization process. The free energy of micellization can be calculated from Eq. [7]. Introducing into Eq. [7] the cmc of SDSs at 293 K ($1 \times 10^{-2} \text{ M}$, (27)), $\Delta G_{\text{m}}^{\circ}$ was evaluated, and the value obtained is $-18.63 \times 10^{-21} \text{ J}$. This value is slightly higher than that obtained from the free energy of interaction between DSs⁻ ions through water.

On the basis of the investigations presented above we can say that from the acid-base, or polar, as well as the Lifshitz-

van der Waals, or apolar, and the electrostatic interfacial interactions in aqueous media, it becomes possible to calculate the critical micelle concentration for both nonionic (TX-100) and ionic (SDSs) surfactants.

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