

## **The correlation between the surface free energy of the anionic surfactant and its free energy of adsorption and micellization**

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Measurements of the surface tension of aqueous solution of sodium hexadecyl sulphonate (SDHS), the interfacial tension of SDHS solution-dodecane and the contact angle for water, glycerol and diiodomethane on polyvinyl chloride surface covered with SDHS film were made at 293 K. On the basis of these measurements the adsorption isotherms, the solubility, the standard free energies of adsorption and dissolution were determined. Also, the standard free energies of adsorption and dissolution were determined from the free energy of the tail and head of SDHS and interfacial free energy of the tail-water and head-water systems. From the data of the tail-water and head-water interfacial free energy and electrostatic free energy of interactions the critical micelle concentration for the sodium n-alkanesulphonate was determined and compared with the literature data of CMC. It was found that the standard free energy of adsorption does not depend on the type of the phase in contact with the solution of the surfactant and it can be predicted from the surface free energy of the tail and head of the surfactant and interfacial free energy of the water-tail and water-head systems. It was also found that the adsorption data of n-paraffins on graphitized carbons used for calculations of the contactable area of sodium n-alkanesulphonates tail confirmed the usefulness of the phase separation model for determination of standard free energy of micellization for AB type of ionic surfactants.

### **1. INTRODUCTION**

Ionic and nonionic surfactants have a wide applicability from biological and technological points of view. The fundamental properties of the surfactants are their tendency to adsorb at interfaces and ability to form micelles in solution.

The processes of adsorption and micellization have been studied intensively [1-3] to determine, among other things, the surfactant concentration at the interface, the orientation of the surfactant at interface, the critical micelle concentration (CMC), and the energy changes (thermodynamic parameters) in the system resulting from adsorption and micellization.

One of the most useful tools for the study of surface and bulk phenomena in liquid systems involving surfactants is evaluation of the interfacial tension [1,2,4,5]. On the basis of the interfacial tension data measured in the range of surfactant concentrations exceeding CMC it is possible to calculate the standard free energy of adsorption and micellization of the surfactants. This is a good measure of their tendency to adsorb at interfaces and ability to form micelles.

Recent studies [6-12] have proven that there is a relationship between the free energy of adsorption at water/air and water/hydrocarbon interfaces as well as free energy of micellization of surfactants in aqueous media and the free energy of interactions between the tails and heads of surfactants in water, calculated on the basis of the surface free energy components and parameters of surfactants resulting from Lifshitz-van der Waals and Lewis acid-base intermolecular interactions. However, there is a problem to calculate the total free energy of interactions between the tails and heads of surfactants through the water phase because of difficulties in determination of credible values of the Lifshitz-van der Waals component and electron-acceptor and electron-donor parameters of the acid-base components of the head surface free energy of the surfactants as well as the so-called contactable area of the molecule of the surfactants.

In this paper we try to show a different possibility to calculate the contactable area of sodium hexadecylsulphonate (SDHS) and determine the components and parameters of the surface free energy of its head. Another aim of our paper is to establish the correlation between the free energy of the adsorption as well as micellization and free energy of interaction between the tails and heads of anionic surfactant through water.

## 2. THEORY

**Adsorption.** One of the characteristic features of surfactants is their tendency to adsorb at interfaces in an oriented fashion. This adsorption has been studied to determine the concentration of surfactant at interface, the orientation of surfactant at interface and the energy changes in the system, resulting from the adsorption.

Direct determination of the amount of surfactant adsorbed per unit area of liquid-gas or liquid-liquid interface, although possible, is not generally under-



taken because of the difficulty of isolating the interfacial region from the bulk phase for purposes of analysis when the interfacial region is small, and of measuring the interfacial area when it is large, instead, the amount of material adsorbed per unit area of interface is calculated indirectly from surface or interfacial tension measurements. As a result, a plot of surface (or interfacial) tension as a function of (equilibrium) concentration of surfactant in one of the liquid phase, rather than an adsorption isotherm, is generally used to describe adsorption at interface. From such a plot the amount of surfactant adsorbed per unit area of interface can readily be calculated by using the Gibbs adsorption equation.

During the last 25 years, application of the Gibbs equation of adsorption to aqueous solutions of ionic surfactants has been discussed by many researchers [1-3,13], but for such surfactants the form of the Gibbs equation is less certain than for nonionic surfactants. If we consider a surfactant of AB type as a strong electrolyte, it dissociates in water solution into  $A^+$  and  $B^-$  ions, and the appropriate form of the Gibbs equation is

$$d\gamma = -RT(\Gamma_{A^+} d \ln a_{A^+} + \Gamma_{B^-} d \ln a_{B^-}) \quad (1)$$

Since  $\Gamma_{A^+} = \Gamma_{B^-} = \Gamma$  to maintain electroneutrality and  $a_{A^+} = a_{B^-} = C \times f_{AB}$  without a significant error, then

$$d\gamma = -4.606RT\Gamma d \log(C \cdot f_{AB}) \quad (2)$$

where  $f_{AB}$  is the mean activity coefficient of the surfactant,  $\log f_{AB}$  can be assumed to equal  $(\log f_A + \log f_B)/2$  and calculated on the basis of the Debye-Hückel equation [13].

For the dilute solutions ( $10^{-2}$  or less), Eq. (2) assumes the form

$$\Gamma = -\frac{1}{2RT} \frac{d\gamma}{d \ln C} = -\frac{Cd\gamma}{2RTdC} \quad (3)$$

or

$$\Gamma = -\frac{1}{4.606RT} \frac{d\gamma}{d \log C} \quad (4)$$

Determining the  $\Gamma$  from Eq. (4) for saturated surface concentration,  $\Gamma_m$ , we can calculate the minimal area per surfactant molecule ( $A_m$ ) at interface from the following equation

$$A_m = \frac{10^{16}}{N\Gamma_m} \quad (5)$$

where  $N$  is Avogadro's number.

On the basis of  $A_m$  value, equilibrium concentration of surfactant in the bulk phase corresponding to the saturation of the interface and the value of interfacial tension, it is possible to calculate the standard free energy of adsorption of surfactant,  $\Delta G^o$ , at interface.

According to Rosen and Aronson [14] the standard free energy of adsorption at interface for an ionic surfactant of the AB type from aqueous solution at a concentration less than  $10^{-2}$  can be calculated from the relation

$$\Delta G^o = 2.303RT \left( \log \frac{C_{A^+}}{\omega} + \log \frac{C_{B^-}}{\omega} \right) - 6.023\pi A_m \quad (6)$$

where  $\omega$  is the number of water moles in 1 l.

Because in the absence of the neutral salt  $C_{A^+} = C_{B^-} = C$ , the Eq. (6) assumes the form

$$\Delta G^o = 4.606RT \log C - 6.023\pi A_m \quad (7)$$

If we assume that after adsorption at the solution-air interface the hydrophobic tail of the surfactant is present in the air phase and the hydrophilic head is in the water phase, then the transfer of surfactant molecules from the bulk aqueous phase to the interface is associated with changes in the interfacial free energy of the water-tail ( $\gamma_{WT}$ ) to the surface free energy of the tail ( $\gamma_T$ ), and the interfacial free energy water-head ( $\gamma_{WH}$ ) from  $\gamma_{WH}$  to  $\gamma_{WH1}$  because of dehydration of the head during the adsorption process.

Thus, the standard free energy of adsorption should fulfill the condition [6]

$$\Delta G^o = (\gamma_T - \gamma_{WT}) A_T + (\gamma_{WH1} - \gamma_{WH}) A_H \quad (8)$$

where  $A_T$  is the contactable area of the surfactant tail, and  $A_H$  is the contactable area of the surfactant head.

The analogous expression for solution-oil interface is

$$\Delta G^o = (\gamma_{TO} - \gamma_{WT}) A_T + (\gamma_{WH1} - \gamma_{WH}) A_H \quad (9)$$

where  $\gamma_{TO}$  is the interfacial free energy of tail-oil. Of course, if we assumed that after adsorption at the aqueous solution-oil interface the tail of the surfactant is present in the oil phase and the head in the water phase.

Assuming that there is not a considerable difference between  $\gamma_{WH1}$  and  $\gamma_{WH}$  values, the Eqs (8) and (9) give

$$\Delta G^o = (\gamma_T - \gamma_{WT}) A_T \quad (10)$$

and

$$\Delta G^o = (\gamma_{TO} - \gamma_{WT}) A_T \quad (11)$$

respectively.



The values of tail-oil interfacial tension can be determined from the relation [6,10]

$$\gamma_{TO} = \gamma_T + \gamma_o - 2\sqrt{\gamma_T^{LW} \cdot \gamma_o^{LW}} \quad (12)$$

where the subscript *LW* refers to the Lifshitz-van der Waals component of the surface free energy of the liquid (in this case  $\gamma_T = \gamma_T^{LW}$  and  $\gamma_o = \gamma_o^{LW}$  [10,11])

**Micellization.** Almost from the very beginning of the study of the properties of surfactant solutions it was recognized that their bulk properties were unusual and indicated the presence of colloidal particles - so-called micelles in the solution. Micelle formation, or micellization is an important phenomenon not only because a number of important interfacial phenomena, such as detergency and solubilization, depend on the existence of micelles in solution, but because it affects other interfacial phenomena, such as surface or interfacial tension reduction, that do not directly involve micelles.

If the surfactants are dissolved in water then their hydrophobic groups distort the structure of water and thus increase the free energy of the system [2]. The distortion of the solvent structure can be decreased, among other things, by aggregation of the surface-active compound into clusters (micelles) with their hydrophobic groups directed toward the interior of the cluster and their hydrophilic groups directed toward the solvent. Decrease of the distortion of the solvent structure is joined with decrease of the free energy of the system, which corresponds to free energy of micellization [1,10,15].

For a surfactant of AB type which in water solution dissociates into A<sup>+</sup> and B<sup>-</sup> ions the phase separation model (PS) is used by some authors [16-19] for determination of the free energy of micellization. This model treats the micelle together with its counterions as a phase separate from that of the monomers. According to the phase separation model the standard free energy of micellization is given by

$$\Delta G_{cmc}^o = 2RT \ln CMC \quad (13)$$

where *R* is the gas constant.

The free energy of micellization is joined with the free energy of interaction between surfactant molecules through the water phase resulting from Lifshitz-van der Waals, acid-base and electrostatic forces.

According to the extended DLVO theory [13,20] the total free energy of interaction through water between two identical particles or moieties,  $\Delta G_{1W1}^{Tot}$ , is

$$\Delta G_{1W1}^{Tot} = \Delta G_{1W1}^{LW} + \Delta G_{1W1}^{AB} + \Delta G_{1W1}^{EL} \quad (14)$$

where the superscripts *LW*, *AB*, and *EL* refer to the contribution in the free energy coming from interactions which result from Lifshitz-van der Waals, acid-

base, and electrostatic forces, and the subscripts 1 and W refer to particles or moieties and water, respectively. In the case of a surfactant in water Eq. (14) can be rewritten in the form

$$\Delta G_{1W1}^{Tot} = \Delta G_{1W1}^{LW}(T) + \Delta G_{1W1}^{AB}(T) + \Delta G_{1W1}^{LW}(H) + \Delta G_{1W1}^{AB}(H) + \Delta G_{1W1}^{EL}(H) \quad (15)$$

where  $T$  and  $H$  are for the tail and head of surfactants, correspondingly.

The free energy of interfacial interaction between the surfactant tails or heads through water should be expressed by the equations

$$\Delta G_{1W1}^{LW}(T) + \Delta G_{1W1}^{AB}(T) = -2\gamma_{1W}(T) \quad (16)$$

$$\Delta G_{1W1}^{LW}(H) + \Delta G_{1W1}^{AB}(H) = -2\gamma_{1W}(H) \quad (17)$$

where  $\gamma_{1W}(T)$  and  $\gamma_{1W}(H)$  are the interfacial free energy of the water-surfactant tail and water-surfactant head systems, respectively.

The water-aliphatic hydrocarbons interfacial tension is independent of the number of carbon atoms in the molecule and nearly constant, equal to ca. 51.1 mN/m [21,22]. This value should correspond to the value of  $\gamma_{1W}(T)$  for alkyl tail of the surfactant-water system.

The  $\gamma_{1W}(H)$  value can be calculated, among other things, on the basis of the van Oss et al. [10,11,20] approach to the interfacial tension. Thus, expressing  $\gamma_{1W}(H)$  by  $\gamma_{HW}$  the van Oss et al. [10,11,20] equation assumes the form

$$\gamma_{HW} = \gamma_H + \gamma_W - 2\sqrt{\gamma_H^{LW} \cdot \gamma_W^{LW}} - 2\sqrt{\gamma_H^+ \cdot \gamma_W^-} - 2\sqrt{\gamma_H^- \cdot \gamma_W^+} \quad (18)$$

where  $\gamma^{LW}$ ,  $\gamma^+$  and  $\gamma^-$  are the Lifshitz-van der Waals components, and electron-acceptor and electron-donor parameters of the surface free energy of the head of surfactant and water, respectively.

Knowing the size of the contactable area of tails,  $A_T$ , and heads,  $A_H$ , of the surfactant it is possible to calculate the free energy of interaction between two molecules (ions) of surfactant in water,  $\Delta G$ . Then, from Eqs (15), (16) and (17) it results that

$$\Delta G = -2\gamma_{1W}(T) \times A_T - 2\gamma_{1W}(H) \times A_H + \Delta G_{1W1}^{EL}(H) \times A_H \quad (19)$$

### 3. EXPERIMENTAL

**Interfacial tension measurements.** Sodium hexadecyl sulphonate (SDHS) (Sigma Chemical CO.) aqueous solutions were prepared with doubly distilled and deionized water from a Milli-Q system, whose surface tension was always checked before preparing the solutions. SDHS used for solution preparation was purified by using the method described in the literature [23].



Surface and interfacial tension measurements were made at 293 K under atmospheric pressure by the weight-volume method [13,24]. Measurements of the surface tension of aqueous solutions of SDHS and the interfacial tension of solution-dodecane system were repeated many times, and the standard deviation depending on the region of surfactant concentration did not exceed  $\pm 0.2$  mN/m.

For measurements of the surface and interfacial tension, capillaries of different diameters were used, depending on the concentration of the surfactant and the system studied, to enable the drop to detach exactly from the total surface of the capillary top.

**Contact angle measurements.** The advancing contact angle for water (doubly distilled and deionized from Milli-Q system), anhydrous glycerol (Fluka, pure > 99.5%) and diiodomethane (Fluka, pure > 98%) were measured on polyvinyl chloride surface covered with SDHS monolayer formed from aqueous solution. The type of polyvinyl chloride and the way of its surface preparation were described earlier [25]. The solution used for formation of SDHS layer was prepared by mixing  $10^{-3}$  mole of SDHS with  $1 \text{ dm}^3$  of water and heating up to dissolving the whole SDHS in water and then cooling to 293 K. The SDHS layer was formed by immersing the PVC plate to saturated solution of SDHS for 24 h. After taking out the plate it was dried by a stream of dry air and then kept in a dessicator.

For contact angle measurements the Krüss G 10 apparatus was used.

The standard deviation of contact angle depending on the kind of liquid did not exceed  $\pm 0.9^\circ$ .

#### 4. RESULTS AND DISCUSSION

**Adsorption isotherms.** The results obtained for the surface tension ( $\gamma$ ) of SDHS aqueous solutions and the interfacial ( $\gamma$ ) of solution-dodecane system as a function of the concentration ( $C$ ) of SDHS are presented in Figure 1. The shape of the  $\gamma$ -versus- $\log C$  curves is the same for solution-air (curve 1) and solution-dodecane (curve 2) systems, but the values of  $\gamma$  at a given concentration depend on the kind of the phase being in contact with aqueous surfactant solution. A small decrease of the  $\gamma$  as a function of  $\log C$  is observed in the range of SDHS concentration from  $10^{-8}$  to  $10^{-5}$  M. It is clear that a linear dependence exists between  $\gamma$  and  $\log C$  near the concentration, which corresponds to the saturated aqueous solution of SDHS. It should be mentioned that the Kraftt point for SDHS [23] is higher than the temperature of the measurements and therefore, the break points in the surface and interfacial tension versus- $\log$

$C$  curves cannot be treated as CMC. However, the break points are close to the CMC of SDHS at 323 K [2].

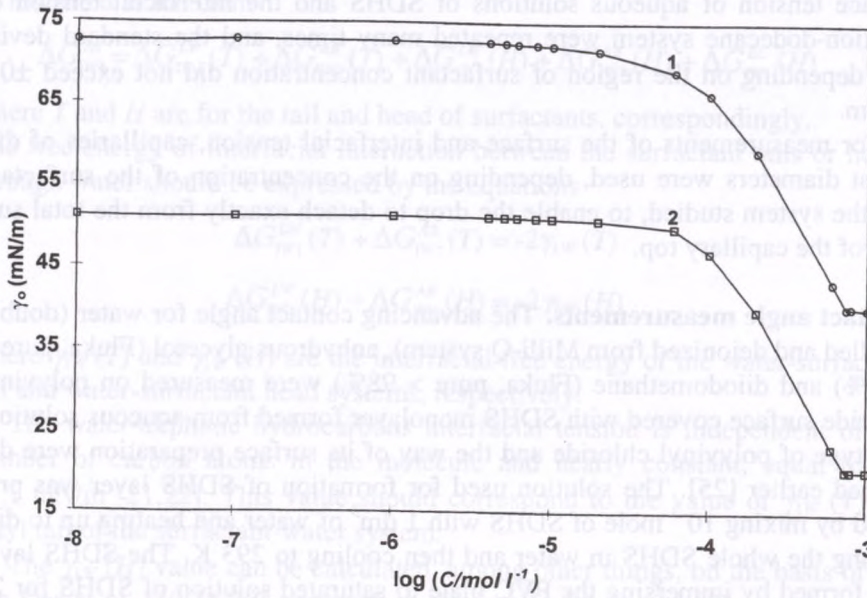


Figure 1. Relationship between surface (interfacial) tension ( $\gamma_0$ ) and  $\log C$  for SDHS at 293 K. Curve 1 - solution-air system and curve 2 - solution-dodecane system

Table 1. Values of  $C$  correspond to the break points on the  $\gamma$  versus  $\log C$  curves, maximal excess of SDHS concentration at interface ( $\Gamma_m$ ) and minimal area occupied by SDHS molecule at interface ( $A_m$ ) determined on the basis of Figure 1 and Gibbs equation of adsorption, as well as the values of the standard free energy of adsorption ( $\Delta G_{ads}^0$ ), the standard free energy of dissolution ( $\Delta G_{dis}^0$ ) and free energy of interaction between SDHS ions ( $\Delta G^0$ ) calculated from Eqs (7), (10), (11), (13) and (15), respectively

| System | $C$<br>[mol dm <sup>-3</sup> ] | $\Gamma_m$<br>[mol m <sup>-2</sup> ] | $A_m$<br>[nm <sup>2</sup> ] | $\Delta G_{ads}^0$<br>[kJ mol <sup>-1</sup> ]<br>Eq. (7) | $\Delta G^0$<br>[kJ mol <sup>-1</sup> ] | $\Delta G_{dis}^0$<br>[kJ mol <sup>-1</sup> ] | $\Delta G^0$<br>[kJ mol <sup>-1</sup> ]    |
|--------|--------------------------------|--------------------------------------|-----------------------------|--|---|---|--|
| S/A    | $7.4 \times 10^{-4}$           | $2.95 \times 10^{-6}$                | 0.563                       | -65.73   | -62.75 <sup>a</sup>                     | 35.12 <sup>c</sup>                            | -15.57 <sup>d</sup><br>-35.02 <sup>e</sup> |
| S/D    | $7.2 \times 10^{-4}$           | $3.1 \times 10^{-6}$                 | 0.536                       | -64.77   | -65.96 <sup>b</sup>                     | 35.26 <sup>c</sup>                            | -15.57 <sup>d</sup><br>-35.02 <sup>e</sup> |

S - aqueous solution of surfactant; A - air; D - dodecane; a - calculated from Eq. (10); b - calculated from Eq. (11); c - calculated from Eq. (24); d - calculated from Eq. (19) on assumption that  $A_T$  is equal the geometric contactable area and e - calculated from Eq. (19) on assumption that the contactable area is equal to  $A_T$  value resulting from adsorption data [28]



On the basis of the adsorption isotherms the amount of surfactant per unit area ( $\Gamma$ ) at solution-air and solution-dodecane interfaces was calculated by using the Gibbs equation of adsorption (Eq. (4)), and then for  $\Gamma = \Gamma_m$ , the minimal area per SDHS molecule at the interfaces was determined from equation [5]. The values of  $\Gamma_m$  and  $A_m$  are listed in Table 1.

From this table it is seen that at solution-air interface the maximal surface excess is higher and the minimal area per molecule is lower than at solution-dodecane interface. The values of  $\Gamma_m$  and  $A_m$  for SDHS shown in the table are close to those for other surfactants having sulphonate heads [2,26].

### Standard free energy of adsorption and surface free energy of surfactant.

Substituting into Eq. (7) the values of  $C$  corresponding to the concentration region in the bulk phase that produces saturated adsorption at interface (minimal area per molecule), the  $A_m$  values and the values of  $\pi = \gamma_0 - \gamma$  (where  $\gamma_0$  is the surface tension of water or interfacial water-dodecane tension at 293 K and  $\gamma$  is the surface tension of aqueous solution of SDHS or interfacial solution-dodecane tension corresponding to the concentration range producing saturated adsorption at interface), the  $\Delta G^o$  values were calculated and listed in Table 1. The value of  $\Delta G^o$  for solution-air system is a little lower than for solution-dodecane system.

Thus, the change of the air for dodecane as a apolar phase does not influence the free energy of adsorption. It is in good agreement with the conclusions drawn for other anionic surfactants [2,6].

As mentioned above, the standard free energy of the adsorption in the studied systems can be calculated on the basis of Eq. (10) or (11) if it is possible to determine the contactable area of the surfactant tail,  $A_T$ .

In the case of the hydrocarbon tail of surfactant there are five contactable areas, for example with water phase, one with the surfactant head, and four of them correspond to the proper contactable areas of the alkyl groups. Thus, the total contactable area of the surfactant tail is found by the expression [6]

$$A_T = 4(l + d/2)(w + d) + (w + d)^2 \quad (20)$$

where  $l$  is the length of alkyl chain,  $w$  is the width of the alkyl chain and  $d$  is the constant value for a given temperature corresponding to the intermolecular distance.

Taking into account the fact that for hydrocarbon at 293 K the  $d$  values can be assumed to equal 0.2 nm, which results from the least-squares analysis of the hydrocarbon molecule volume,  $w = 0.26$  nm [10,11] and the length of alkyl chain  $l = 0.0932 + (n - 1) + 0.127/2$  (where  $n$  is the number of carbon atoms in the alkyl groups, 0.127 nm is the C-C distance in the chain [27], and 0.0932 nm is the C-H distance in the terminal  $\text{CH}_3$ - group), the contactable area for hexa-



decyl group is calculated from Eq. (20). Thus calculated  $A_T$  value for the hexadecyl group is equal  $4.189 \text{ nm}^2$ .

Introducing into Eq. [10] this value of  $A_T$ , the value of  $\gamma_T$  equal to the surface tension of hexadecane ( $26.35 \text{ mN/m}$ ) [22] and the value of  $\gamma_{WT}$  equal to hexadecane-water interfacial tension ( $51.22 \text{ mN/m}$ ) [22], the value of the free energy of adsorption of one molecule of SDHS was calculated. Next, taking into account Avogadro's number, the free energy of adsorption per mol of SDHS was determined and shown in Table 1. From this table it appears that the free energy of adsorption determined on the basis of Eq. (10) is somewhat higher than the standard free energy of adsorption calculated from Eq. (7). It suggests that on the basis of the contactable area of the surfactant tail and its surface free energy, as well as water-tail interfacial free energy it is possible to predict the standard free energy of adsorption at water-air interface, and that at this interface perpendicular orientation of hexadecyl group in the saturated monolayer can be expected. However, the contactable area of hexadecyl group in the monolayer can be different from that in the bulk phase. The influence of the dehydration of  $\text{SO}_3^-$  group on the standard free energy of adsorption should also be taken into account.

Perhaps the small difference between the values of the standard free energy of adsorption calculated from Eq. (7) and (10) results from these reasons.

It was stated that in the case of solution-alkane systems parallel orientation of the alkyl groups is more probable than perpendicular one at solution-alkane interface [6].

Thus the total contactable area of the hydrophobic chain at the solution-dodecane interface can be expressed by the equation [6]

$$A_T = 3(l + d/2)(w + d) + (w + d)^2 \quad (21)$$

It can be shown on the basis of Eqs (21), (11) and (7) that the standard free energy of SHDS adsorption at solution-dodecane interface corresponds to the free energy of decyl group adsorption at this interface (Table 1).

The value of  $\gamma_{OT}$  needed for determination of the free energy of decyl group adsorption was evaluated from [12], taking into account the literature data of surface tension of alkanes [22].

It should be emphasized that the so-called „excluded area” (the area of the interface unavailable to one molecule due to the presence of another) of the decyl group is equal  $0.546 \text{ nm}^2$  and it is close to the minimal area occupied by SDS molecule at solution-dodecane interface ( $0.536 \text{ nm}^2$ ) (Table 1). This fact confirms the reliability of the conclusion that the standard free energy of SHDS adsorption corresponds to the free energy of adsorption of the decyl group at solution-dodecane interface.



**Surface free energy of surfactant and standard free energy of dissolution and micellization.** To predict the free energy of micellization of an ionic surfactant on the basis of the Eq. (19), the tail of the surfactant-water and head of the surfactant-water interfacial tensions as well as the contactable area of the tail and head of the surfactant, and electrostatic interactions between the heads of surfactants must be known.

As mentioned above the n-alkane-water interfacial tension does not depend on the hydrocarbon chain length and is close to 51.1 mN/m [21,22]. Thus, the free energy of interfacial interaction between the tails of SDHS through the water phase is equal to  $-102.2 \text{ mJ/m}^2$ . The free energy of interactions between the heads of SDHS through water phase includes two components. The first component is joined with the head of surfactant-water interfacial tension, and second with electrostatic interactions.

Unfortunately, we have no direct methods to measure the head of surfactant-water interfacial tension. The head of surfactant-water interfacial tension is commonly calculated from Eq. (19) [9-12]. For this purpose the Lifshitz-van der Waals component and electron-acceptor and electron-donor parameters of the surface free energy of the head of surfactant must be known. It is possible to determine these magnitudes from contact angle measurements for the liquids on some solids covered with the surfactant layer [9-12]. However, it is assumed that for a thick surfactant layer formed on hydrophobic solid from aqueous solution of the surfactant at a high concentration the heads of the surfactant are oriented towards the air phase.

On the surfactant layer prepared in such a way it is very difficult to measure the reliable values of contact angles, particularly for water, because of high surfactant solubility in water and therefore, the components and parameters determined from contact angles measured on a thick surfactant layer are not quite certain. There is another problem dealing with a thick surfactant layer on hydrophobic solid surface from the point of view of contact angle. The surface of such a layer is not smooth enough for contact angle measurements. Therefore, we have tried to prepare SDHS monolayer on polyvinyl chloride surface. Some of the studies dealing with adsorption of ionic surfactant on monopolar polymeric solids indicate that by the adsorption of the surfactant from aqueous solution at a concentration close to that of CMC the monolayer is formed [2]. It is most probable that also from saturated solution of the SDHS the monolayer film is formed in which the SDHS molecules are oriented parallel to the polymer surface rather than perpendicular. Therefore, at the first approximation we assumed that in the case of the SDHS adsorption from the solution at a concentration close to that of CMC the monolayer is formed on PVC surface in which the SDHS molecules are oriented parallel to this surface and that the measured contact angle fulfils the expression



$$\theta_L = \theta_L(T) x_T + \theta_L(H) x_H \quad (22)$$

where the  $x_T$  and  $x_H$  are the ratio of the area occupied by the tails and heads of SDHS to the contact plane between the liquid drop and SDHS monolayer, respectively.

From the study of strong adsorption of long-chain n-paraffins on graphitized carbons, Groszek [28] proposed that the area occupied per  $-\text{CH}_2-$  group should be the area of one hexagon, equal to  $0.0524 \text{ nm}^2$ . At the first approximation it can be assumed that the area of  $-\text{CH}_3-$  group is equal to two hexagons. Taking this fact into account and that the area occupied by  $-(\text{CH}_2)_2\text{SO}_3^-$  group is equal to  $0.36 \text{ nm}^2$  [8], the  $x_T$  and  $x_H$  values were calculated amounting 0.686 and 0.314, respectively. Next, introducing these values and the measured values of contact angle for diiodomethane ( $50^\circ$ ), water ( $73.1^\circ$ ) and glycerol ( $76^\circ$ ) on PVC covered with SDHS monolayer, and contact angle ones for these liquids on paraffin taken from literature [29] as  $\theta_L(T)$  values into Eq. (22), the  $\theta_L(H)$  values for diiodomethane, water and glycerol were calculated.

Knowing the values of  $\theta_L(H)$  for water, glycerol and diiodomethane and the Lifshitz-van der Waals component and electron-acceptor and electron-donor parameters of the surface tension of these liquids, the  $\gamma_H^{LW}$ ,  $\gamma_H^+$  and  $\gamma_H^-$  were calculated from the following equation [10,11]

$$(\theta_L(H) + 1) = 2\sqrt{\gamma_L^{LW} \cdot \gamma_H^{LW}} + 2\sqrt{\gamma_L^+ \cdot \gamma_H^-} + 2\sqrt{\gamma_L^- \cdot \gamma_H^+} \quad (23)$$

The calculated values are:  $\gamma_H^{LW} = 33.7$ ,  $\gamma_H^+ = 0$  and  $\gamma_H^- = 60.94 \text{ mJ/m}^2$ . These values somewhat differ from those obtained for sodium dodecyl sulphonate obtained from contact angle measurements for the same liquids on a thick layer of the surfactant [6].

Introducing into Eq. (18) the components and parameters of the surface free energy of the head of SDHS and water [22], the head of SDHS-water interfacial free energy was calculated and then the first part of free energy of interactions between the heads of SDHS through the water phase was determined from Eq. (17), which is equal  $53.1 \text{ mJ/m}^2$ .

It is commonly known that in studies dealing with the micellization process the head of ionic surfactants is treated as a complex including one or two methylene groups [2].

Thus, the contactable area of tail and head of SDHS corresponds to tetradecyl and  $-(\text{CH}_2)_2\text{SO}_3^-$  groups, respectively.

The contactable area of  $-(\text{CH}_2)_2\text{SO}_3^-$  should not depend on the hydrocarbon chain length [2] and is equal  $0.36 \text{ nm}^2$  [8].

The contactable area of tetradecyl group in the process of micellization according to the literature data [8,10,11] should be fulfilled by the expression:  $A_T = (0.0932 + 13 \times 1.27 + 1.27/2) \times 2.6 = 0.47 \text{ nm}^2$ . In this case it is assumed



that the contactable area of the tails for two ions of surfactant in the water corresponds to the geometric area and the intermolecular distance between water and tails is constant in the contacting process.

Taking into account the  $A_T = 0.47 \text{ nm}^2$ ,  $A_H = 0.36 \text{ nm}^2$  and  $\Delta G^{EL} = 8.51 \text{ mJ/m}^2$  [8] it is possible to determine the free energy of interactions between SDHS ions through water on the basis of Eq. (19). Thus calculated value of the free energy of interaction is equal  $-15.57 \text{ kJ/mol}$  (Table 1). Of course, as mentioned above the surface and interfacial tension measurements were made below the Krafft point and therefore, the free energy of interaction cannot be compared directly to the standard free energy of SDHS micellization.

Below the Krafft point, a singly dispersed sodium hexadecyl sulphonate can be assumed to be in perfect dissociation and the standard free energy change in the process of its dissolution,  $\Delta G_{dis}^o$ , can be calculated by using equation [23]

$$\Delta G_{dis}^o = -2RT \ln S \quad (24)$$

where  $S$  is the solubility of surfactant.

Assuming that the break points on the  $\gamma$  versus  $\log C$  curves correspond to the solubility of SDHS, the  $\Delta G_{dis}^o$  values were calculated from Eq. (24) and they are listed in Table 1. From Table 1 it is seen that the absolute value of the free energy of interaction is about two times lower than that of the standard free energy of SDHS dissolution.

Table 2. The values of CMC taken from literature and calculated from Eq. (13)

| $C_nH_{n+1}SO_3Na$   | CMC<br>Eq. (13) | CMC      | Ref. |
|----------------------|-----------------|----------|------|
| $C_8H_{17}SO_3Na$    | 0.151           | 0.162    | 30   |
| $C_{10}H_{21}SO_3Na$ | 0.04            | 0.05     | 30   |
| $C_{11}H_{23}SO_3Na$ | 0.0207          | 0.0135*  | 31   |
| $C_{12}H_{25}SO_3Na$ | 0.0107          | 0.011    | 30   |
| $C_{13}H_{27}SO_3Na$ | 0.0055          | 0.00349* | 31   |
| $C_{14}H_{29}SO_3Na$ | 0.0028          | 0.0032   | 30   |

If we assume that the contactable area of SDHS tails can be calculated on the basis of the adsorption data of Groszek [28], then  $A_T = 0.0524 \times 15 = 0.786 \text{ nm}^2$ . Using this value of  $A_T$  for calculations of free energy of interactions between SDHS tails through the water phase we obtain that it is equal  $-35.02 \text{ kJ/mol}$  (Table 1). The absolute value calculated in this way is close to that of the standard free energy calculated from Eq. (24) on the basis of the  $S$  data determined from isotherms of SDHS adsorption at solution-air and solution-dodecane interfaces (Table 1). Thus, it is possible that on the basis of the

surface free energy of surfactant the standard free energy of dissolution of the surfactant can be determined, however, more studies dealing with this problem should be carried out.

Because on the basis of the available data in literature it is possible to calculate the free energy of interaction between ions of surfactants only at 293 K and the Krafft point for SDHS is higher than this temperature, therefore, to check the usefulness of our model for prediction of the standard free energy of micellization, the CMC values for some n-alkanesulphonates were determined from Eq. (13). For calculation the  $A_7$  values resulting from the adsorption data of Groszek and the value of head-head interaction through the water phase equal  $13.36 \text{ kJ m}^{-1}$  were used. It was assumed that the free energy of interaction between the head of  $\text{SO}_3^-$  does not depend on the length of the alkyl chain [2]. The values of CMC calculated in this way are listed in Table 2 together with the literature data [30,31]. There is excellent agreement between the calculated values of CMC and the obtained from measurements of the properties of surfactant solutions. It suggests that by using the Groszek adsorption data [28] for determination of the contactable area of alkyl sulphonate surfactant tail and then the free energy of interaction between the tails through water, the phase separation model for standard free energy of micellizations of surfactants of AB type of electrolyte is confirmed [16-19].

## 5. REFERENCES

- [1] Chataraj D. K., and Birdi K. S., *Adsorption and Gibbs Surface Excess*, Plenum, New York, 1984.
- [2] Rosen M. J., *Surfactants and Interface Phenomena*, 2nd ed. Wiley, New York, 1989.
- [3] Jaycoch M. J., and Parffit G. G., *Chemistry of Interfaces*, Ellis Horwood, Chichester, 1981.
- [4] McLure I. A., Soares V. A. M., and Edmonds B., *J. Chem. Soc. Faraday Trans.*, 178, 2251 (1982).
- [5] Bowers J., and McLure I. A., *Langmuir*, 12, 3326 (1996).
- [6] Jańczuk B., Méndez-Sierra J. A., González-Martín M.L., Bruque J. M., and Wójcik W., *J. Colloid Interface Sci.*, 192, 408 (1997).
- [7] Jańczuk B., Zdziennicka A., Jurkiewicz K., and Wójcik W., *Tens, Surf. Deterg.*, 35, 213 (1998).
- [8] Jańczuk B., González-Martín M.L., Bruque J. M., Dorado Calasanz C., and Moreno del Pozo J., *J. Colloid Interface Sci.*, 176, 352 (1995).
- [9] Jańczuk B., Méndez-Sierra J. A., González-Martín M.L., Bruque J. M., and Wójcik W., *J. Colloid Interface Sci.*, 184, 607 (1996).

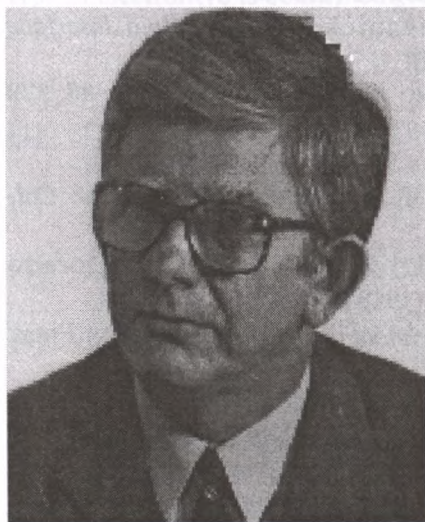


- [10] van Oss C. J., and Constanzo P. M., *J. Adhes. Sci. Technol.*, 6, 447 (1992).
- [11] van Oss C. J., and Good R. J., *J. Dispersion Sci. Technol.*, 12, 95 (1991).
- [12] Jańczuk B., Bruque J. M., González-Martín M.L., and Román Galán E., *Colloids Surf.*, 100, 93 (1995).
- [13] Adamson A. W., *Physical Chemistry of Surfaces*, 5th ed. Wiley-Interscience, New York, 1990.
- [14] Rosen M. J., and Aronson S., *Colloids Surf.*, 3, 201 (1981).
- [15] Murkejee P., *Adv. Colloid Interface Sci.*, 1, 241 (1967).
- [16] Stainsby G., and Alexander A. E., *Trans. Faraday Soc.*, 46, 587 (1950).
- [17] Matijevic E., and Pethica B. A., *Trans. Faraday Soc.*, 54, 587 (1958).
- [18] Barry B. W., and Russel G. F. J., *J. Colloid Interface Sci.*, 40, 174 (1972).
- [19] van Oss N. M., Daane G. J., and Bolsman T. A. B. M., *J. Colloid Interface Sci.*, 115, 402 (1987).
- [20] van Oss C. J., Giesse R. E., and Constanzo P. M., *Clays Clay Miner.*, 38, 151 (1990).
- [21] Fowkes F. M., *Ind. Eng. Chem.*, 56(12), 40 (1964).
- [22] Jańczuk B., Wójcik W., and Zdziennicka A., *J. Colloid Interface Sci.*, 157, 384 (1993).
- [23] Saito M., Moroi Y., and Matuura R., *J. Colloid Interface Sci.*, 88, 578 (1982).
- [24] Wilkinson M. C., *J. Colloid Interface Sci.*, 40, 14 (1972).
- [25] 27. Jańczuk B., Białopiotrowicz T., and Zdziennicka A., *J. Colloid Interface Sci.*, 211, 96 (1999).
- [26] Jańczuk B., González-Martín M.L., Bruque J. M., and Dorado Calasanz C., *Colloids Surf.*, 137, 15 (1988).
- [27] Pauling L., „*The Nature of the Chemical Bond*” Cornell Univ. Press, Ithaca, NY, 1945.
- [28] Groszek A. J., *Proc. R. Soc. London A* 473, 314 (1970).
- [29] Jańczuk B., and Białopiotrowicz T., *J. Colloid Interface Sci.*, 127, 189 (1989).
- [30] Kovtunencko L. I., Smirnov N. I., and Titova N. P., *Zh. Prikl. Chimii*, 48, 323 (1975).
- [31] Well J. K., Stirton A. J., Smith F. D., and Bistline R. G., US Pat. 32228980, 11.01.66.

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