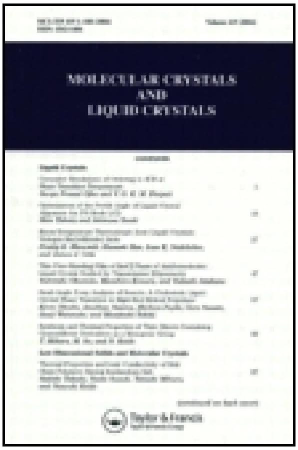

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EFFECT OF THE HYDROCARBON CHAIN LENGTH ON THE INTERFACIAL TENSION IN n-ALKANE-WATER-SODIUM DODECYL SULFATE SYSTEMS

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Abstract The interfacial tension in some normal alkane-water-sodium dodecyl sulfate systems has been measured with the spinning drop technique. The alkane scan of the data shows a deep minimum in the interfacial tension at dodecane as an oil phase. Simple explanation of this phenomenon based on the entropy of random mixing in the interfacial layer is proposed.

INTRODUCTION

The interfacial tension lowering in oil-water-surfactant systems is of great interest, both fundamental and practical, because it is of importance in many phenomena such as microemulsion stability, wetting and cleaning action etc. Systematic investigations of a number of hydrocarbon homologous series and their mixtures and commercial surfactants with a potential use in the tertiary oil recovery have been performed by Schechter, Wade and collab[1-4]. At the same concentration of given surfactant they have observed a deep minimum in the interfacial tension as a function of the carbon atoms number in the oils studied. For the homologous series of n-alkanes this plot yielding a pronounced minimum was termed "alkane scan"[4].

The interfacial tension in the minimum is ultralow (between 10^{-3} and 10^{-4} dyn/cm). The minimum is very sensitive to additions and changes its position and magnitude in the presence of salt, alcohol and a second surfactant. This behaviour is observed both with commercial petroleum sulfonates [1-3] and with pure alkyl benzene sulfonates[4].

The former are complex mixtures but there is a surfactant equivalent molecular weight[2] with a particular hydrocarbon (or hydrocarbon mixture with an average carbon number[3]): the greater the surfactant equivalent weight, the greater must be the molecular weight of the prefered hydrocarbon.

The pure alkyl benzene sulfonates are surfactants with the benzene ring attached at different positions on the alkyl chain. In this case the minimum in the interfacial tension is shiffted toward a higher carbon number when the total number of carbon atoms in the alkyl tail is increased[4].

Here we test the possibility for the existence of a similar minimum in the classical system normal alkane-water-surfactant with a linear alkyl chain. A comprehensive study of such systems with sodium dodecyl sulfate (SDS) as a surfactant has been performed by Rehfeld[5]. The interfacial tensions observed (between 5 and 50 dyn/cm) are of a rather higher magnitude compared with the systems of interest in tertiary oil recovery. At a given surfactant concentration the interfacial tension shows a tendency to increase with increasing hydrocarbon length. But unfortunately, in his extensive study, Rehfeld has not published data about the interfacial tension of n-dodecane as an oil phase. From a qualitative consideration of the entropy of mixing in the surface layer one would expect the minimum in the alkane scan to occur at alkane with the same carbon number as the surfactant tail.

The purpose of this paper is to produce an alkane scan of the interfacial tension in the n-alkane-water-SDS systems using both Rehfeld's and new data.

The interfacial tension measurements were carried out with the spinning drop method.

EXPERIMENTAL

SPINNING DROP METHOD

The spinning drop technique was developped by Vonnegut[6], Princen, Zia and Mason[7], Cayias, Schechter, and Wade[1] and Slattery and Chen[8]. In the general case (sufficiently high interfacial tension) the rotating drop acquires the shape of a rotational ellipsoid on Figure 1.

Slattery and Chen by a simple numerical procedure (through elliptic integrals) obtained the following expressions for the interfacial tension γ:

$$\gamma = \frac{\Delta\rho\omega^2}{2} \left(\frac{R}{r^*}\right)^3 \qquad (1)$$

where $\Delta\rho = \rho_w - \rho_{hc}$ is the difference between the water density (for dilute surfactant solutions)and the hydrocarbon density, ω is the velocity of rotation, r^* is a quantity tabulated as a function of the ratio R/L (see table 1 from Ref.8), R and L are the lengths of the drop semiaxes.

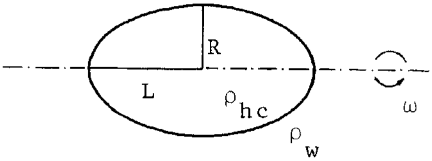

FIGURE 1. Sketch of the rotating drop.

In Refs.1 and 7 an alternative procedure has been used. A set of equations were derived which allowed the computation of the interfacial tension. From them after some algebra we obtained the following simple equation:

$$\gamma = \frac{\Delta\rho\omega^2}{2\alpha}\left(\frac{L}{1+\beta}\right)^3 \tag{2}$$

where α and β are quantities tabulated as functions of the ratio L/R (see table 1 from Ref.7); β denotes the parametric group cr^3 used in Ref.7. Comparing Eqs.(1) and (2) we found the following relation between tabulated quantities in the two approaches

$$\left(\frac{R}{L}\right)^3 = \frac{1}{\alpha}\left(\frac{r^*}{1+\beta}\right)^3 \tag{3}$$

The limiting values of the parameters[7,8] for approximately cylindrical drops with hemispherical caps (L>4R) are

$$r^* = 2^{1/3} \tag{4a}$$

$$\alpha=16/27 \tag{4b}$$

$$\frac{L}{R}=\frac{2}{3}(1+\beta) \tag{4c}$$

Then Eqs.(1) and (2) lead to the well known Vonnegut's formula[6]

$$\gamma=\frac{1}{4}\Delta\rho\omega^2R^3 \tag{5}$$

and Eq.(3) is an identity.

MATERIALS

The SDS came from Touzart & Matignon (pur.). The following normal alkanes were used: hexane and heptane from Reachim (USSR) and dodecane from BDH (England).

INTERFACIAL TENSION MEASUREMENTS

The interfacial tension was measured with the Krüss-GMBH (Site 04) spinning drop aparatus. The temperature was maintained at $25^0\pm0.1^0$C. The frequency of rotation was varied between 4000 and 5000±10 rpm. The density difference was known within 10^{-3} g/cm^3. The geometrical dimensions of the oil drops were approximately $R\sim0.05-0.08$ cm and $L\sim0.08-0.15$ cm. measured with an accuracy of 4.10^{-4} cm. Thus for the systems studied the limiting condition $L>4R$ was never reached and hence the simplest formula (5) could not be applied.

We calculated the interfacial tension using the full profiles described by Eqs. (1) and (2). The numerical values needed were extracted from the tables in Refs.7 and 8 with an interpolation.

We calculated a relative error for one individual measurement of 1.5% assuming that the tabulated values are exact at the quoted experimental conditions and accuracies.

We performed two independent measurement series for the whole concentration range: at least two drops at each system and at least five readings for each drop after the initial period of equilibration which usualy was greater than an hour.

The interfacial tensions calculated by the two approaches differ no more than 0.2 dyn/cm for all alkanes and the respective dispersion is 0.1-0.5 dyn/cm.

RESULTS

In Figure 2 we have plotted the interfacial tension γ at the solution/alkanes interface as a function of the SDS concentration. As seen the steady tendency of increasing γ with the addition of one CH_2 group to the hydrocarbon molecule breaks down at dodecane: the interfacial tension of the systems hexane/SDS water solution and dodecane/SDS water solution practically coincide within the experimental accuracy (see Table I). Our data for hexane are in good coincidance with the data of Rehfeld[5] obtained using the drop-volume method.

The data presented in Figure 2 allow to produce alkane scans of γ at different surfactant concentrations. Two such plots at $c=5.10^{-3}$ mol/l and

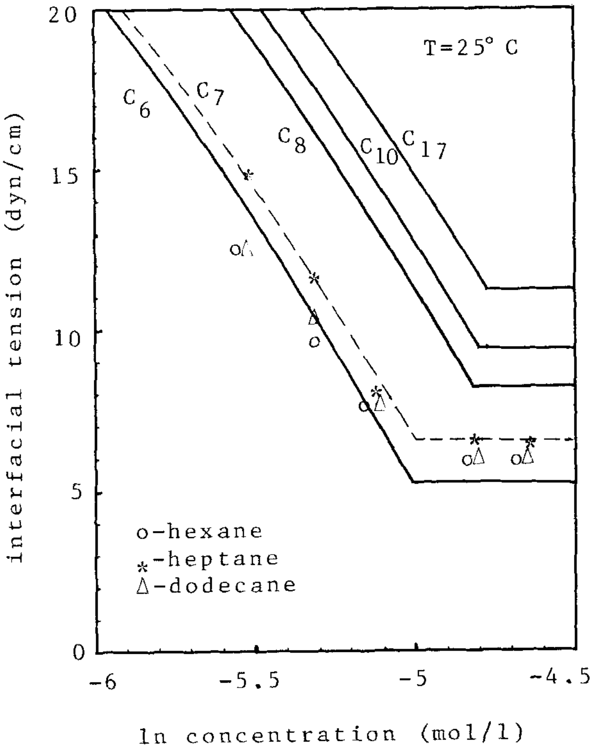

FIGURE 2. Interfacial tension vs. concentration for water-alkane-SDS systems. The full lines represent Rehfeld's fit[5].

$c=8.10^{-3}$ mol/l are presented on Figure 3 revealing a pronounced interfacial tension minimum at dodecane. Similar minima (but less pronounced) are obtained at constant surfactant excess (calculated from Gibbs' adsorption isotherm).

TABLE I Interfacial tensions of hexane and dodecane in SDS solution

concentration $x10^3$ (mol/l)	interfacial tension hexane		(dyn/cm) dodecane
4	12.4±0.5	12.5*	12.4±0.5
5	9.6±0.5	9.5*	10.2±0.3
6	7.7±0.1	7.5*	7.7±0.3
8	6.2±0.2	5*	6.2±0.1
10	6.3±0.1	5*	6.3±0.1

*Data of Rehfeld[5]

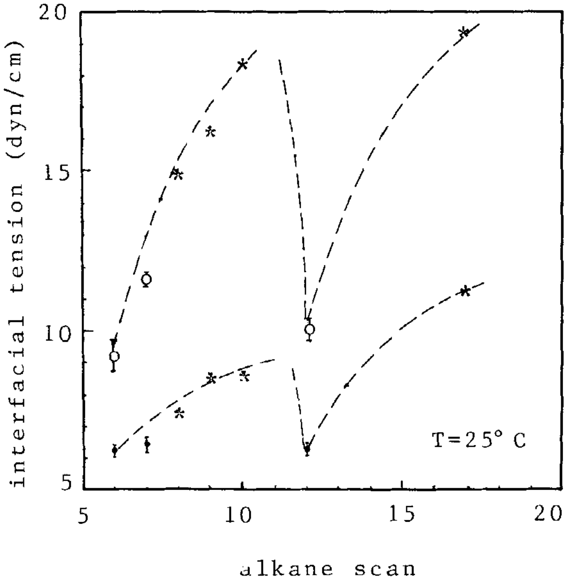

FIGURE 3. Alkane scan of the interfacial tension at various SDS concentrations: (o) 5.10^{-3} mol/l, (.) 8.10^{-3}mol/l with (*) are denoted the Rehfeld's data[5].

DISCUSSION

Qualitatively the existence of an interfacial tension minimum in the alkane scan at dodecane may be understood considering the entropy of mixing in the interfacial layer. The free energy of mixing in the interfacial layer can be defined as

$$\Delta F=\Delta E-T\Delta S \tag{6}$$

where ΔE is the energy and ΔS is the entropy of mixing (T is the absolute temperature). The nature of the interfacial layer suggests that the quantities in Eq.(6) have to contain contributions from both hydrocarbon and water parts of the layer. It is difficult to obtain explicit forms of these terms in the general case. A very simple model is proposed by Vassilieff, Denkov and Ivanov[10].

Here we shall not consider the energy contribution to ΔF, because there is no indication to expect a peculiarity in this term with respect to the length of the hydrocarbon molecule (see e.g. Adamson[11] and references there in): We shall focus on the term ΔS which for random mixing of differently sized molecules in a bulk phase can be written as[12-14]

$$-\frac{\Delta S}{k}=\sum_i N_i \ln\phi_i \tag{7}$$

where ϕ_i is the volume fraction and N_i - number of molecules of component i. Generally speaking the validity of Eq.(7) is not restricted to space dimensions: bulk, surface or line lattices, but ϕ_i changes its meaning from volume to surface or line fractions respectively.

In the case of interest (mixed interfacial layer), however, Eq.(7) cannot be applied in a straightforward manner, because the surfactant (biphilic) molecule penetrates both the hydrocarbon and water parts of the interfacial layer. Hence the interfacial layer has a third dimension (a thickness) which for simplicity will be assumed to be length of the surfactant molecule (considered to be rigid and always perpendicular with respect to a plane interface). We place the plane of the interface between the surfactant heads and tails and allow water molecules to fill up the remaining space on the water side of the layer and hydrocarbon molecules - the remaining space on the hydrocarbon part. No empty sites in the two quasilattices are allowed.

With the experimental data from the previous section in mind (one surfactant, different alkanes) we shall consider further only the hydrocarbon part of the interfacial layer. Generally both surfactant tail and alkanes possess some flexibility, which will be neglected and both will be considered as rigid bars. We simplify further the treatment assuming that alkane chains can be either perpendicular or parallel to the interface.

In the case of dodecane and SDS (equal carbon number of surfactant tail and alkane) Eq.(7) yields

$$-\frac{\Delta S_{hc}}{kM} = \frac{\phi_{(12)}}{r_{(12)}} \ln\phi_{(12)} + \frac{\phi_s}{r_s} \ln\phi_s \qquad (8)$$

where $\phi_i=N_i r_i/M$ are area fractions: (12) - dodecane, s - surfactant, M is the total number of sites in the surface lattice and r_i - the number of surface sites occupied by one molecule of component i. According to the assumptions outlined above always $r_s=1$ (perpendicular rigid surfactant tail) and $r_{(12)}=1$ for perpendicular arrangement and $r_{(12)}=12$ for parallel arrangement.

In the latter case there are 12 layers of parallel dodecane molecules filling up the hydrocarbon part of the interfacial layer with thickness determined by the perpendicular straight surfactant tail with 12 carbon atoms. Since the different segments of the perpendicular surfactant tail cannot move independently just one of the twelve layers determines the entropy of mixing. The two different arrangements would hardly affect the energy of interaction of the interfacial layer and, hence, in order to minimize its free energy (to maximize its entropy) the system would prefer the perpendicular arrangement of the dodecane molecules yielding the maximum entropy of mixing of equally sized molecules in the surface ($r_s=r_{(12)}=1$).

Now using similar arguments we can rewrite Eq.(7) for ΔS_{hc} of SDS and alkanes with different carbon numbers.

$$-\frac{S_{hc}}{kM} = \frac{\phi_n}{r_n} \ln\phi_n + \phi_s \ln\phi_s \qquad (9)$$

where ϕ_n is the surface fraction of alkanes with carbon atoms number n, $M=N_n r_n+N_s$ $(\phi_n+\phi_s=1)$ and the number of surface sites occupied by one alkane molecule r_n is given in Table II. This approximate relation between n and r_n implies the fact that except for the cases of n=6 and 12 at least in one layer alkane molecules must lie parallel to the interface in order to fill up the hydrocarbon part of the interfacial layer.

TABLE II Number of surface sites r_n occupied by one alkane molecule as a function of the carbon atoms number n in the alkane chain.

n	6	7	8	9	10	11	12	... 17
r_n	1 (6)	7	8	9	10	11	1 (12)	... 17

As in the case of n=12, considered in more details above, in order to maximize the entropy of the interface hexane molecules (n=6) would arrange perpendiculary to the surface ($r_s=r_{(6)}=1$). The hydrocarbon part of the interface is filled up by two layers of perpendicular hexane molecules.

Eq.(9) with the relation between n and r_n given in Table II predicts a general decrease of the entropy of mixing with n (independently of the values of ϕ which are not exactly known) with a sharp break at n=12. Since changes in the energy of interaction with n are small this would lead (see Eq.(7)) to an increase in the surface free energy with n with a sharp minimum at n=12. This qualitative physical picture coincides with experimental findings (see Figures 1 and 2).

A better theoretical description of the interface /hydrocarbon/ water in the presence of surfactant would involve many more assumptions and introduction of sets of adjustable parameters. For example Antoniewicz and Rodriguez [15] have fitted the data of Wade et al. with a lattice model involving at least three adjustable parameters. Their treatment does not reveal the physical cause for observed minima in alkane scans, which are most probably due to entropic effects.

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