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SHORT COMMUNICATION

Surface active inverse micelles

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Abstract Surface tension of solutions of a commercial non-ionic surfactant, Laureth 4, and two hydrocarbons, decane and hexadecane, with added water, was determined using a de Nouy ring. The results showed a reduction of surface tension with added water, confirming an earlier suggestion of surface activity of inverse micelles. The surface activity is ascribed to the orientation of the hydrocarbon chains in the inverse micelle, giving a preferential location of the low surface free-energy methyl groups at the surface of the micelle. The location of the micelle at the surface was estimated from calculations of the minimum in the free energy when a solid particle was transferred across the liquid–air interface. This energy showed a distinct minimum indicating the location of the particle. However, the conditions for that minimum to occur were such that no balance of surface tension forces along the liquid surface to air could occur. The reason for that apparent discrepancy is discussed.

Keywords Microemulsions · Pickering emulsions · Surface tension · Emulsion stabilization

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Introduction

The surface activity in water of traditional surfactants is based on the difference in intermolecular interaction between the water molecules and the hydrophobic part of the surfactant, a hydrocarbon or fluorocarbon chain. The chains, hence, bring low solubility to the surfactant, and the dual nature of the molecular interaction causes the molecules to adsorb at the interface, reducing the interfacial free energy. The water/oil (W/O) or water/air systems are of such tremendous technical importance that the phenomenon of surface activity has become almost solely connected with the conditions in such systems.

However, there are several instances, for which non-traditional compounds show similar activity. Among these, should be mentioned semifluorinated alkanes in multi-phase hydrocarbon–fluorocarbon systems. In such systems, low-molecular-weight di-block molecules give surface activity that is not based on hydrophilic–hydrophobic forces [1, 2].

Another example is alkyl-aromatic di-blocks in diiodomethane, a high cohesive energy density solvent [3]. Finally, an interesting surface activity is shown by molecules combining nonspecific hydrophobic forces with specific, programmable DNA hybridization forces.

In a different case, a separate phase with low surface free-energy served as a "surfactant" to stabilize foams from hydrocarbons [4–6]. This phenomenon was not amenable to explanations by traditional molecular surface activity because molecular adsorption of a hydrocarbon-based surfactant in such systems does not take place.

With the present contribution, we present a case of surface activity by an association structure of a surfactant, which per se lacks surface activity in the system. The present results confirm a recently reported case [7] using a different system and, more essentially, introduce some difficult fundamental problems related with the phenomenon.

Experimental

Materials

The following chemicals were used: polyoxythylene-4-lauryl ether, Laureth 4 (Brij® 30), was from Sigma-Aldrich, USA; Hexadecane, C16, and *n*-decane, C10, were from Fluka, Germany (both hydrocarbons were filtered through a micro-filter, 0.45-μm pore size and 25-mm diameter from Advanced Microdevices, Pvt, India). Water was deionized and doubly distilled.

Instruments

A Precise 410AM-FR Balance was used to determine the weight. Vibrofix VF1Electronic (shaker) was used to mix the samples with a Labtech hotplate stirrer (magnetic stirrer) as a complementary device. JAC Ultrasonic 1002 was used to ensure fast dissolution of the water. A Kruss tensiometer was used to determine surface tension.

Determination of the W/O microemulsion region

The hydrocarbon was dissolved into the surfactant and water was added to this solution at 2% increments and the point of turbidity noted. Preparation of samples for surface tension measurements: Four series of samples were prepared in the tensiometer vessel in the one-phase region along the decane/Laureth 4 axis with 20, 40, 60, and 80% of decane. For each series, water was added stepwise with increments at the level of 1% and mixed by magnetic stirrer for each addition, placed in ultrasonic for 10 min for defoaming and to enhance the mixing. The samples were set to relax for 15 min before measuring the surface tension at 20 °C. Three series of hexadecane samples were prepared with 10, 20, and 30% of hexadecane and measured in the same manner.

Surface tension measurements

The surface tension was measured at 20 °C using the Kruss tensiometer. The ring was cleaned between each series samples with a Bunsen burner flame followed by a rinse with distilled water and absolute alcohol before the actual measurements. The scale on the instrument was calibrated against freshly distilled water.

Results

The solubility areas for the inverse micellar regions in the water/Laureth 4 diagrams with decane and hexadecane are similar (Fig. 1). The solubilization of water increases with the surfactant content, and there are no marked maxima in either case. The values of surface tensions of surface tensions are given in Fig. 2 for the hexadecane system. The spread in the values is significant, but was considered acceptable because of their small range and because the trend is the feature of importance. As an example, the values for the series starting with 20% decane is described by a straight line with an R^2 value of 0.95. Without the obvious outlier the R^2 value becomes 0.99, and the values were judged as adequate as long as trends are the only feature of interest. Hence, two tendencies may be concluded from the results. At first, addition of water to samples with high amounts of surfactant leads to a reduction of the surface tension, and secondly, there is no reduction for the highest level of hydrocarbon. These trends are also fond in the decane system (Fig. 3). In this case, series with significantly higher levels of hydrocarbon were used, and the trend towards less reduction of surface tension with increased hydrocarbon content is now extrapolated to a case, in which the addition of water leads to increased surface tension.

In summary, the results confirmed earlier results [7] for a system with a surfactant of uniform molecular weight and support the hypothesis that addition of water to form inverse micelles causes the surface tension to be reduced in a hydrocarbon system.

Discussion

The results confirm the relation between the formation of inverse micelles in a hydrocarbon system stabilized by a molecularly defined non-ionic surfactant and a reduction in surface tension [7]. Even in the present case with a commercial surfactant, the results show a small but statistically significant reduction in the surface tension with added water. Furthermore, the initial increase in surface tension found in the earlier system is present in the current set of results, albeit only for the decane series with the lowest surfactant content.

This deviation serves as an additional confirmation of the central tenet of these investigations. The reduction of surface tension is presumed specifically due to the presence of inverse micelles; the pre-micellar aggregates found in the W/O microemulsion systems actually appear to have the opposite effect, increasing the surface tension [7].

This variance is related to the influence of the hydrocarbon structure on inverse micellization as early investigated

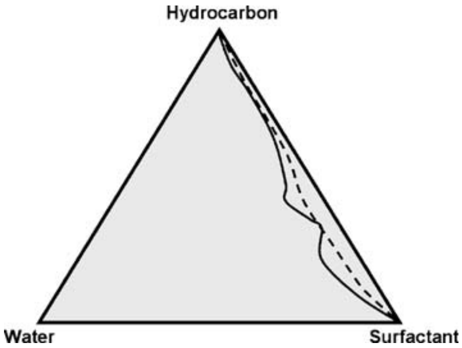

Fig. 1 The hydrocarbon/Laureth 4 isotropic liquid region with solubilized water (*solid line* decane, *hatched line* hexadecane)

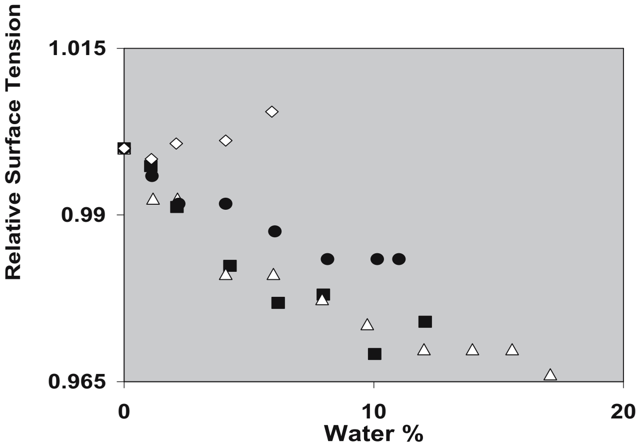

Fig. 3 The surface tension vs the water content for inverse micellar solutions. Laureth 4/decane: 8/2 (*filled square*), 6/4 (*open triangle*), 4/6 (*filled circle*), 2/8 (*open diamond*)

by Christenson et al. [8] using NMR and by Nakamura et al. [9] using calorimetric measurements. The results of the two methods agreed, indicating that the comparatively strong interaction between an aromatic hydrocarbon and the polar group of a non-ionic surfactant delayed the formation of inverse micelles, when water was added. For aliphatic hydrocarbons, there was no delay; the micellization commenced with the initial addition of water. This result serves to explain the difference between the earlier results and the present ones. In the former investigation, the hydrocarbon was aromatic, while in the current investigation, the hydrocarbon is aliphatic. Hence, the primary increase of surface tension in the former case is well explained by the fact that the initial addition of water did not cause micelles to form.

Accepting the relation between the presence of inverse micelles and a reduction of surface tension in a hydrocarbon, the actual mechanism for the action at the interface remains to be explained. Unfortunately, attempts to analysis meet with what appears to be serious impediments. The following discussion serves to characterize these.

In fact, there are three phenomena to be discussed; all based on a surface free energy of the methyl group (≈21 mJ/m^2), significantly less than that of the methylene group (≈28 mJ/m^2) [10].

The first phenomenon is the insufficiency of one methyl group on a molecularly dispersed surfactant to cause a reduction of the surface tension in an aliphatic hydrocarbon. This feature is explained by the change in free energy between the molecule in the bulk of the solution and at the surface. The free energy gain by the methyl group reaching the hydrocarbon surface to air is maximally 3.510^{-21} J if the area at the interface is estimated at 50 Å^2, a reduction in free energy by 0.85 kT. This gain is compensated by an increase in free energy of approximately 0.75 kT due to restricted rotation at the interface and 0.5 kT due to restricted translational movement. The net change in free energy is positive, and no adsorption takes place.

In the second circumstance, the initially added water is bound to the polar groups of the surfactant adding to the intermolecular interaction, causing an increase in cohesive

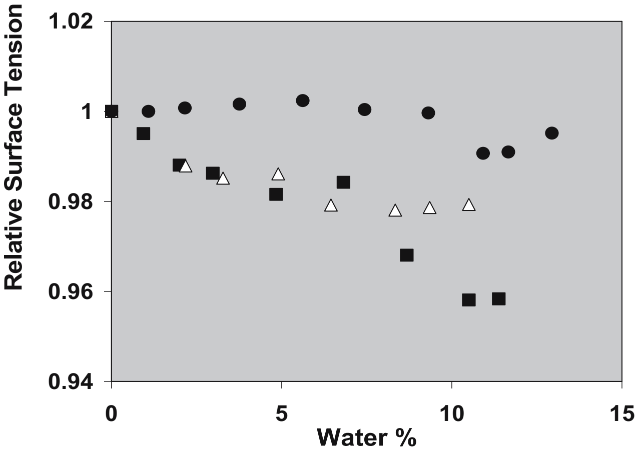

Fig. 2 The surface tension vs the water content for inverse micellar solutions. Laureth 4/hexadecane: 9/1 (*filled square*), 8/2 (*open triangle*), 7/3 (*filled circle*)

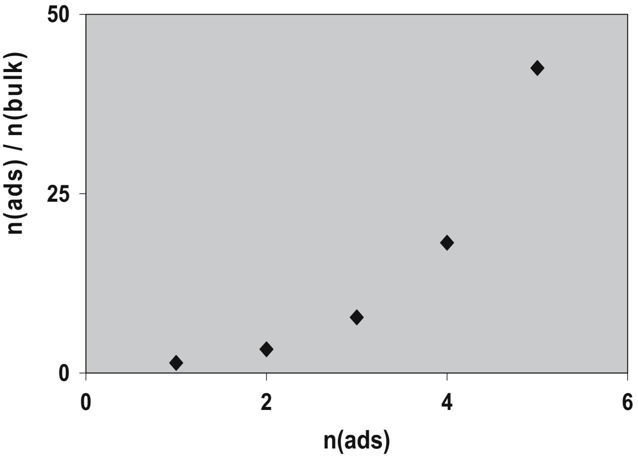

Fig. 4 The ratio between the number of molecules at the interface and in bulk according to a Boltzmann distribution

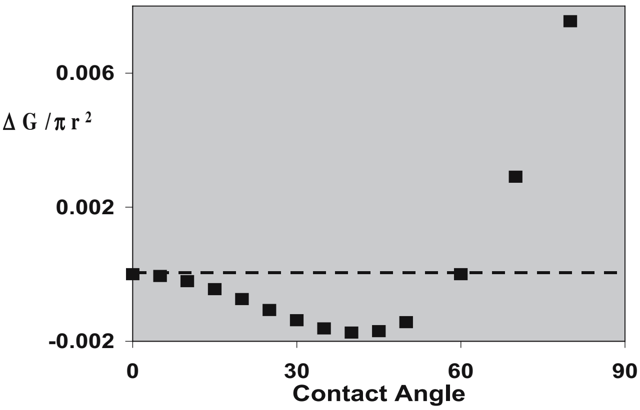

Fig. 5 The free energy change ($\Delta G/\pi r^2$) vs contact angle for a solid particle (*P*) at the liquid/air (L/A) interface. $\gamma_{L/A}$=28 mN/m, ($\gamma_{P/A}-\gamma_{L/P}$)= 21 mN/m

energy density. The initial increase in surface tension when water is added is expected and has been found [7].

The third phenomenon, the reduction in surface tension after the inverse micelles are formed, has been suggested to be due to a preferential orientation of methyl groups at the surface of the inverse micelle [7]. For a micelle at the interface, the orientation of the molecules in the association structure causes *several* methyl groups to reach the interface, each contributing approximately 0.85 kT to the reduction of surface free energy. The adsorption of the micelle is additionally furthered by the fact that the restriction of the rotational freedom of the molecules in the micelle is less influenced by the surface location than is the case for a single surfactant. In addition, the free energy loss due to the restriction of the translational movement is approximately 0.5 kT *per micelle*. The total free energy reduction becomes approximately (0.85n−0.5) kT, and a Boltzmann estimation of the number of micelles adsorbed becomes very favorable (Fig. 4). In fact, one molecule in the micelle at the interface now already gives a tendency to adsorption due to fact that there is little or no difference in rotational energy at the surface and in bulk. This approximate evaluation disregards any contribution from the internal dynamics of the micelle, as well as from the exchange of molecules between the micelle and the monomers in the solution.

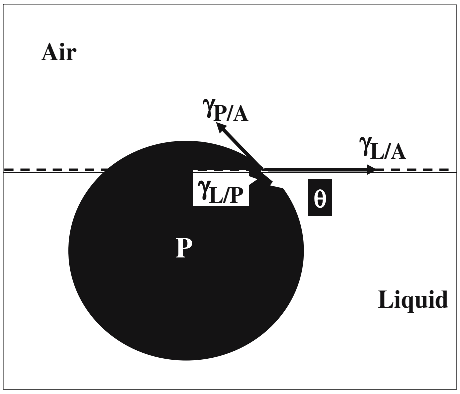

Fig. 6 Particle and surface forces at an interface. *P* Solid particle, θ contact angle into the liquid, $\gamma_{L/A}$ surface tension between air and liquid, $\gamma_{P/A}$ surface tension between air and particle, $\gamma_{L/P}$ surface tension between liquid and particle

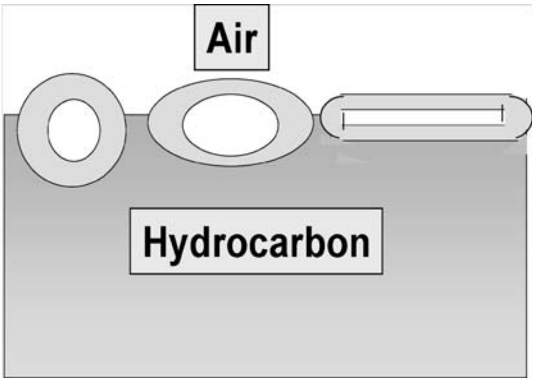

Fig. 7 Shapes of inverse micelles at the interface between oil and air. *Left* Spherical micelle, *middle* elongated micelle, *right* micelle spread along the interface

The results of these evaluations provide a strong support of the earlier conclusion [7] of an interaction between the inverse micelle and the liquid/air surface. However, the conclusion leads to what appears to be an insurmountable encumbrance, the deficient surface force balance at the interface.

This balance, in general, has attracted attention because of the stabilizing action of solid particles at the interface in Pickering emulsions. It has, hence, been analyzed by Denkov et al. [11], by the Hull group in a series of publications [12–14], including a detailed analysis of the components of the interfacial tension [15]. Professor Krachelsky et al. [16] has given a rigorous examination of the bending forces in a particle mono-layer on a liquid surface. Finally Professor Kaptay [17] has published a complete treatment on the influence of solid particles on the capillary pressure in their stabilization of emulsions and foams, and Friberg [18] has outlined the geometrical conditions for two layers. However, the inverse micelle is not a solid particle, nor is it a Newtonian liquid. For liquids at interfaces, Professor Kaptay [19] has recently given a thorough treatment.

However, the applicability of the relations for liquids for the case of inverse micelles in a hydrocarbon is limited due to the specific relations between the surface tensions involved. With $\gamma_{L/A}$ being the surface tension of the oil against the air, $\gamma_{P/A}$ the surface of the micelle against the air, and $\gamma_{P/L}$ the surface tension of the micelle against the oil, the reduction of surface tension by the presence of micelles leads to the relation $\gamma_{L/A} > \gamma_{P/A}$. Furthermore, because $\gamma_{L/A}$

and $\gamma_{P/A}$ are of similar magnitude and the energy origin of their mutual interaction is restricted to nonpolar interactions, the value of $\gamma_{P/L}$ may be estimated with accuracy from the well-known relation [20]:

$$\gamma_{P/L} = \left(\left(\gamma_{L/A}\right)^{1/2} - \left(\gamma_{P/A}\right)^{1/2}\right)^2 \tag{1}$$

The fact that the interfacial tension is rapidly reduced when the values of $\gamma_{L/A}$ and $\gamma_{P/A}$ approach each other is well demonstrated by putting $\gamma_{L/A} = \gamma_{P/A} + \varepsilon$, in which $\boldsymbol{\varepsilon}$ $<\gamma_{P/A}$. One obtains

$$\gamma_{P/L} = \left(\gamma_{P/A}\right)\left[\left(1 + \varepsilon/\gamma_{P/A}\right)^{1/2} - 1\right) \tag{2}$$

Furthermore, $(1+\varepsilon)^{1/2} \approx 1 + \varepsilon/2$ for $\boldsymbol{\varepsilon}<1$, which is surprisingly accurate. Even for values of $\boldsymbol{\varepsilon}$ of significant magnitude, such as $\boldsymbol{\varepsilon}=0.5$, the approximation gives a value within 2% of the exact one. In the present case with the approximation, one arrives at

$$\gamma_{P/L} \approx \varepsilon^2 / 4\gamma_{P/A} \tag{3}$$

Equation 3 illustrates the fact that $\gamma_{P/L} \ll \gamma_{P/A}$, and a conservative estimate from Eq. 1 leads to an interfacial tension of less than 2% of the tensions toward the air, which, actually, may be at the upper part of the range. This estimation is supported by the results from careful measurements by Allen et al. [21], which gave such interfacial tensions in the range of 0.15 to 0.005 mN/m.

Even for the realistically most conservative case of $\gamma_{L/A}=$ 28 mN/m and $\gamma_{P/A}=21$ mN/m, $\gamma_{P/L}$ is low and the conclusion is inevitable: $\gamma_{L/A} > \gamma_{P/A} + \gamma_{P/L}$. The micelle will spread along the liquid/air surface, unless prevented by forces from its elastic deformation. This spreading would certainly be influenced by a charge at the micellar surface, a phenomenon recently investigated [22, 23].

Sufficient information about the forces caused by a micellar deformation is not available, and the following discussion will be concerned with the conditions for solid particles with sufficiently low surface tension to be surface active in oils. Among the examples of these, the asphaltene particles in crude oil stand out because of their tremendous importance in the petroleum extraction and handling. Consequently, they have been thoroughly investigated [24]. Their critical association concentration (CNAC) has been determined to approximately 150 mg/l, and the compressibility of the solutions was constant after the association showing the particles to be solids [25]. These results agree with those from conductivity measurements [26] and have been confirmed by NMR determinations [27], which also revealed the size of the particles (approximately eight asphaltene units) and that the diffusion of the alkane chains on the particle becomes restricted during association. Because the many-fold of problems [28–30] caused by the asphaltene particles in the handling and treatment of crude oil are all related to surface properties, their interaction with air surface from the crude oil and from model hydrocarbons has been intensely investigated [24] and associated with the aggregation in the bulk phase. In the following, the conditions for equilibrium of solid particles with interfacial tensions at a level similar to those of inverse micelles will be examined.

The basic condition is $\gamma_{P/L} \ll \gamma_{P/A} < \gamma_{L/A}$; accordingly, $\gamma_{L/A} > \left(\gamma_{P/A} - \gamma_{P/L}\right)\cos\alpha$, in which $\boldsymbol{\alpha}$ is the contact angle and, as a result, non-equilibrium spreading along the liquid/air interface unless mechanical forces prevent such an event. Hence, the equilibrium position at the surface cannot be determined from a force balance along the liquid surface toward air. In this context, it is appropriate to remark that the traditional treatment in the form of equilibrium along a solid surface with the well-known Young equation is not applicable to a liquid surface.

In the present communication, the equilibrium position of the particle will instead be obtained from a calculation of the free energy change, when the it passes from the interior of the liquid through the surface to air. The free energy change is computed as function of an angle α between the (extended) liquid surface and the particle surface at the projection of the infinite liquid surface and the entropy contribution from the restriction of the translational movement of the particle is neglected.

With this qualification the negative contribution to the free energy change emanates from the reduction of the liquid/air interface ($\gamma_{L/A}\pi r^2 \sin^2\alpha$) and the reduction of particle/liquid interfacial free energy due to the removal of the top of the sphere $\left(\gamma_{P/L}\pi r^2 2(1-\cos\alpha)\right)$. The positive contribution comes from the interfacial free energy between the top and the air $\left(\gamma_{P/A}\pi r^2 2(1-\cos\alpha)\right)$. The two expressions are united to give the total free energy change

$$\left(\Delta G/\pi r^2\right) = 2\left(\gamma_{P/A} - \gamma_{P/L}\right)(1-\cos\alpha) - \gamma_{L/A}\sin^2\alpha \tag{4}$$

Using the surface tension of the oil system mentioned earlier, $\gamma_{L/A}=28$ mN/m and $(\gamma_{P/A}-\gamma_{P/L})=21$ mN/m, the free energy passes through a minimum (Fig. 5).

The exact value of the contact angle θ for this minimum is obtained from the first derivative of Eq. 4.

$$\left(\partial\left(\Delta G/\pi r^2\right)/\partial\alpha\right)_{\gamma,r} = \gamma_{P/A} - \gamma_{P/L} - \gamma_{L/A}\cos\alpha \tag{5}$$

$$\left(\partial\left(\Delta G/\pi r^2\right)/\alpha\right)_{\gamma,r} = 0 \tag{6}$$

gives a contact angle $\theta=41.4°$ as indicated by the values in Fig. 5.

This position of the free-energy minimum is obviously that of the particle at equilibrium at the surface and an examination about the relation with the non-equilibrium surface forces is of interest.

The relation is obvious from Fig. 6, illustrating the direction and size of the forces at the interface.

The final result is a surface balance along the tangent to the solid particle at the liquid/air surface

$$\gamma_{\mathrm{P/A}} = \gamma_{\mathrm{P/L}} + \gamma_{\mathrm{L/A}} \cos\theta\ , \tag{7}$$

the well-known Young's equation

The surface forces in the direction perpendicular to the tangent, on the other hand, are unbalanced. For a solid particle, they are compensated by forces from an elastic deformation of the particle, but the extent to which this balancing mechanism is available to an inverse micelle is not yet known. The potential structures of the modified micelle ranges from an elongated micelle to its complete spreading to a surface bi-molecular layer as represented without the magnitude nor direction of interfacial forces by the schematic structures in Fig. 7.

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