LETTERS

Influence of the Alkyl Surfactant Tail on the Adhesion between Emulsion Drops

P. Poulin,* W. Essafi, and J. Bibette

Centre de Recherche Paul Pascal/CNRS, Avenue du Dr. Schweitzer, 33600 Pessac, France

Received: February 8, 1999

Foam or emulsion films stabilized by ionic surfactants can exhibit strong adhesion in the presence of salts. We study, in this letter, the influence of the alkyl surfactant tail on the adhesion. We show that the chain length does not play an important role, whereas the presence of alkyl groups bound near the polar head greatly modifies the energy of adhesion. Our results suggest that the adhesion is mainly driven by the polar heads and the molecular structure in their vicinity rather than by van der Waals interactions between the alkyl tails.

The forces between the interfaces of surfactant liquid films control the stability and the properties of important dispersions such as foams[1] or emulsion systems.[2] As shown on Figure 1, these films are composed of an aqueous core delimited by two air/water or oil/water interfaces covered by surfactant molecules. When stabilized by ionic surfactants, the interfaces can strongly adhere to each other in the presence of salts.[3,4] The adhesion leads to the formation of very thin films known as Newton black soap films (NBF). NBF are usually modeled as hydrated surfactant bilayers since no free water is present between the interfaces.[4,5] As sketched on Figure 1, the counterions are condensed onto the ionic polar heads of the surfactants to ensure electrostatic neutrality of the film.

Experimental studies of NBF clarified the role of some contributions in the adhesive behavior. For example, the similarity between foam and emulsion films stabilized by the same surfactant ruled out the contribution of van der Waals forces between the macroscopic air or oil media as a driving mechanism of adhesion.[4] By contrast, the counterions and their affinity to the ionic surfactant heads were shown to play a critical role.[6,7] This behavior mainly reflects the contribution of the ionic condensation that is necessary to ensure the film neutrality as the interfaces adhere to each other. Despite this experimental information, the driving mechanism of adhesion remains unclear

and the knowledge of the important molecular parameters is still far from being completed.

We study, in this letter, the influence of an additional molecular parameter: the structure of the surfactant tail. To carry out this study, we use emulsion drops that are stabilized in water by various surfactants which both have the same polar head but different alkyl tails. We find that the length of the alkyl tail does not affect the adhesive behavior. By contrast, the presence of alkyl groups bound near the polar head greatly modifies the adhesion. This behavior indicates that the attraction is driven mainly by the molecular structure in the vicinity of the polar heads rather than by the length of the hydrophobic tails. We briefly discuss this finding in the framework of theoretical models related to attractive interactions between charged interfaces. Indeed, we believe that the present experimental observations provide support to electrostatic attractions between the interfaces rather than to van der Waals interactions between the surfactant tails.

The experimental systems consist of hexadecane drops stabilized in salted water by six ionic surfactants listed in Table 1. The polar head of both surfactants is a sulfate group. Drops of a few tens of microns are produced by gently shaking 5 wt % of hexadecane in an aqueous solution (95 wt %) that contains 5×10^{-3} mol/L of surfactant and 0.7 mol/L of NaCl. The presence of NaCl induces adhesion between the drops. As
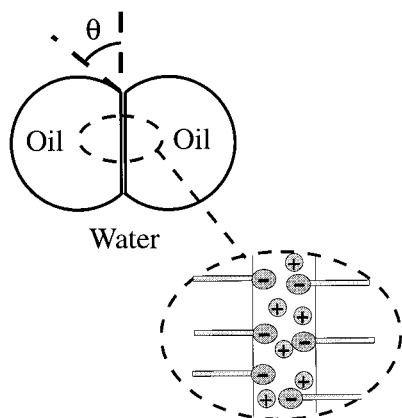
Figure 1. Schematic representation of two oil adhesive droplets separated by a thin surfactant film. For soap films the oil is replaced by air. The adhesion is reflected by the formation of a contact angle, θ, between the drops. The structure of the thin film is schematically zoomed to sketch the ionic charges of the surfactants and the condensed counterions.

TABLE 1: Surfactant Molecules Used in the Present Study

surfactant structure	designation in the text
$CH_3(CH_2)_9SO_4Na$	$C_{10}H_{21}SO_4Na$
$CH_3(CH_2)_{11}SO_4Na$	$C_{12}H_{25}SO_4Na$ or SDS
$CH_3(CH_2)_{12}SO_4Na$	$C_{13}H_{27}SO_4Na$
$CH_3(CH_2)_{13}SO_4Na$	$C_{14}H_{29}SO_4Na$
$CH_3(CH_2)_{10}CH(CH_2CH_3)SO_4Na$	EDS
$CH_3(CH_2)_{10}CH(CH(CH_3)_2)SO_4Na$	IPrDS

sketched on Figure 1, the adhesion is reflected by the formation of large contact angles between the drops. The energy of adhesion, ϵ, can be determined by measuring the contact angle, θ, and the hexadecane/water interfacial tension, γ. According to the Young−Dupré equation, one has $\epsilon = 2\gamma(1 - \cos(\theta))$. We measure θ from optical microscopy pictures using a technique already described in the literature.[8] γ is measured by using the spinning drop technique. The energy of adhesion between the oil drops depends strongly on the temperature.[3,4] Above a given temperature taken as T^* the contact angle is zero and the droplets are not adhesive. Below T^* a non-zero contact angle is formed and the energy of adhesion increases with lowering the temperature. We found the same features for each system we used. However, T^* and the temperature dependency of the energy of adhesion can depend on the surfactant tail. To make quantitative comparisons we take $C_{12}H_{25}SO_4Na$ as reference. On Figure 2, we plot the energy of adhesion between drops stabilized by linear surfactants: $C_{10}H_{21}$-SO_4Na, $C_{12}H_{25}SO_4Na$, $C_{13}H_{27}SO_4Na$, and $C_{14}H_{29}SO_4Na$. The latter surfactants have longer tails and precipitate in the presence of salt at temperatures above the room temperature. Below the precipitation temperature, surfactant crystals tend to be stuck to the droplets and make it difficult to measure the contact angle and interfacial tension. However, the shorter the surfactant the slower the precipitation. Consequently, we were able, for $C_{12}H_{25}$-SO_4Na and $C_{13}H_{27}SO_4Na$, to obtain reproducible results, even at temperatures slightly below the precipitation temperature, before most of the surfactant precipitates. The precipitation of $C_{14}H_{29}SO_4Na$ is too fast to permit accurate measurements below the precipitation temperature. $C_{10}H_{21}SO_4Na$ is soluble in the whole temperature range of the present study. The precipitation temperatures of the surfactants are indicated on Figure 2 by black arrows. The onset-of-adhesion T^* was found to be similar for both surfactants, of about 57 °C. Moreover, we clearly see from the data that the energy of adhesion is essentially the same for these four linear surfactants, meaning that the thickness of
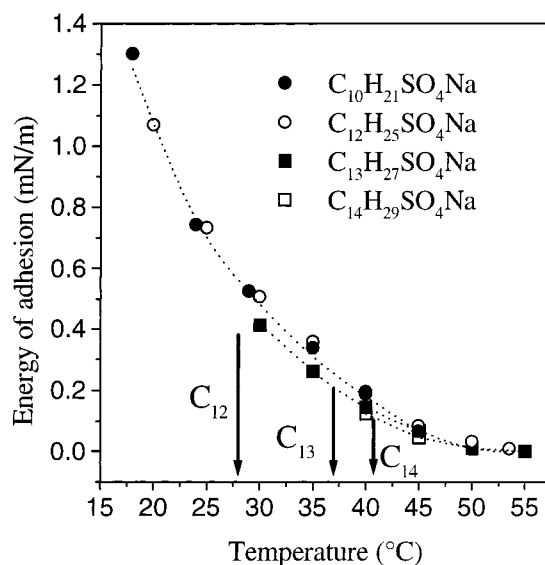

Figure 2. Energy of adhesion between hexadecane drops in salted water as a function of the temperature. The four surfactant molecules have linear tails of different length. The energy of adhesion is similar for both systems. The dark arrows indicate the precipitation temperatures of $C_{12}H_{27}SO_4Na$, $C_{13}H_{27}SO_4Na$, and $C_{14}H_{29}SO_4Na$ (arrows C_{12}, C_{13}, C_{14}).
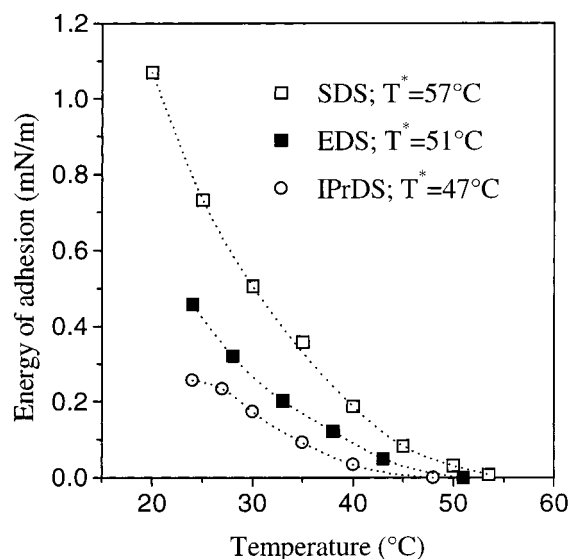

Figure 3. Energy of adhesion between hexadecane drops in salted water as a function of the temperature. Two surfactants with different alkyl groups are compared to the linear surfactant $C_{12}H_{25}SO_4Na$. The surfactants exhibit different T^* and different energies of adhesion. The larger the alkyl group, the weaker the adhesion.

the hydrophobic surfactant layer does not play an important role in the adhesion.

By contrast, the presence of an alkyl group bound near the polar head leads to large differences. We compare, on Figure 3, the energy of adhesion as a function of temperature for $C_{12}H_{25}SO_4Na$ and surfactants with an ethyl group or an isopropyl group (refered to as EDS or IPrDS in Table 1). The salt and surfactant concentrations are similar for both systems. However, the temperature T^* and the energy of adhesion decrease with increasing size of the alkyl group. This well-defined behavior demonstrates the importance of the molecular structure in the vicinity of the polar head.

According to the comparison between the surfactant tails with different length, we believe that the adhesion is not driven by van der Waals interactions between the surfactant tails. As proposed in the literature,[9] the adhesion may instead arise from

Letters

J. Phys. Chem. B, Vol. 103, No. 25, 1999 **5159**

spatial organization of the ionic species confined within the film. Indeed, two charged interfaces may attract each other when the separation between the interfaces is on the order of or smaller than the distance between neighboring surfactants.[10,11] The charges are expected to be spatially correlated so that the electrostatic energy is minimized, resulting in a short-range attraction between the interfaces. Since the aqueous core of NBF, including the hydrated polar heads, is about 1.6 nm,[4] the average separation between the centers of facing sulfate groups is typically smaller than 1 nm. The area per polar head has been determined from Gibbs adsorption isotherms[12] for $C_{12}H_{25}SO_4$-Na in the present experimental conditions. It is of about 0.42 nm^2, meaning that the average separation between neighboring surfactant molecules is about 0.6 nm. Similar orders of magnitude were found for soap films.[13] In these conditions, electrostatic attraction arising from the discrete nature of the charges may play an important role. For IPrDS, the surfactant with the larger group, the area per polar head was found to be of about 0.48 nm^2 in the present experimental conditions.[12] Even though this area is close to the $C_{12}H_{25}SO_4Na$ area, the observed difference may lead to distinct energies of adhesion. Moreover, the presence of the alkyl group is expected to strongly interfere with any form of molecular organization of the polar heads. This again should be reflected in differences in the adhesive behavior as observed experimentally. We believe therefore that the present study provides support to a driving mechanism which involves ionic correlations between the charged species confined within the film.

Studying the adhesive behavior of emulsions drops in water, we have shown that the alkyl surfactant tails can play an important role on the adhesion between the interfaces. The tail length does not affect the interactions whereas the presence of an alkyl group bound near the polar head leads to weaker adhesion. By considering the present results and previous studies, an electrostatic attraction which involves the polar heads seems to be the more likely driving mechanism of adhesion. However, a complete model of the interactions in such adhesive films would require accounting for the delicate interplay between ionic condensation, van der Waals forces, and hydration forces, in addition to the purely electrostatic attraction. Any progress in this direction would be particularly useful in understanding the strong temperature dependencies in foam or emulsion systems as the behavior of a variety of other charged systems such as surfactant vesicles, lamellar phases, and mixtures of ionic polymers and surfactants.[14]

References and Notes

(1) Exerowa, D.; Kashiev, D.; Platikanov, D. *Adv. Colloid and Interface Sci.* **1992**, *40*, 201.

(2) Leal Calderon, F.; Stora, T.; Mondani Monval, O.; Poulin, P.; Bibette, J. *Phys. Rev. Lett.* **1994**, *72*, 2959.

(3) Aronson, M. P.; Princen, H. M. *Nature* **1980**, *286*, 370.

(4) Poulin, P.; Nallet, F.; Cabane, B.; Bibette, J. *Phys. Rev. Lett.* **1996**, *77*, 3248.

(5) Bélorgey, O.; Benattar, J. J. *Phys. Rev. Lett.* **1991**, *66*, 313.

(6) Aronson, M. P.; Princen, H. M. *Colloids Surf.* **1982**, *4*, 173.

(7) Jones, M. N.; Mysels, K. J.; Scholten, P. C. *Trans. Faraday Soc.* **1966**, *62*, 1336.

(8) Poulin, P.; Bibette, J.; *Langmuir* **1998**, *14*, 6341. Poulin, P.; Bibette, J.; Submitted.

(9) De Feijter, J. A.; Vrij, A. *J. Colloid Interface Sci.* **1979**, *70*, 456.

(10) Rouzina, I.; Bloomfield, V. A. *J. Phys. Chem.* **1996**, *100*, 9977.

(11) Kjellander, R.; Marcejla, S.; Pashley, R. M.; Quirk, J. P. *J. Chem. Phys.* **1990**, *92*, 4399. Kjellander, R.; Akesson, T.; Jonsson, B.; Marcelja, S. *J. Chem. Phys.* **1992**, *97*, 1424.

(12) Poulin, P. *Adhesion between fluid interfaces and colloidal aggregation in emulsions* (in French). Thesis, Université de Bordeaux I, 1995.

(13) De Feijter, J. A.; Rijnbout, B.; Vrij, A. *J. Colloid Interface Sci.* **1978**, *64*, 258. De Feijter, J. A.; Vrij, A. *J. Colloid Interface Sci.* **1978**, *64*, 269.

(14) Radler, J. O.; Koltover, I.; Salditt, T.; Safinya, C. R. *Science* **1997**, *275*, 810.