1198 Bull. Chem. Soc. Jpn. Vol. 83, No. 10, 1198–1202 (2010)

First-Order Wetting Transition and Line Tension of Hexadecane Lens at Air/Water Interface Assisted by Surfactant Adsorption

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A first-order transition from partial wetting to pseudo-partial wetting of hexadecane droplets on aqueous solutions of surfactant, hexadecyltrimethylammonium bromide, has been investigated by using interfacial tensiometry and ellipsometry. A regular solution model was applied to calculate the surface free energy of the wetting film as a function of thickness and then the connection between calculated surface free energy profiles and line tension measured at the wetting transition was discussed based on the interface displacement model. The reversal of the sign of the line tension associated with the wetting transition was confirmed from both the experiment and the interface displacement model.

We have previously demonstrated that hexadecane on aqueous solutions of dodecyltrimethylammonium bromide (DTAB) exhibits a first-order wetting transition from partial wetting to pseudo-partial wetting as the surfactant concentration is increased.[1,2] The air–water interface is almost completely covered by a mixed monolayer of oil and surfactant molecules in the pseudo-partial wetting state. We modified the theory of the spreading of nonvolatile liquids developed by Brochard-Wyart and co-workers to calculate the surface free energy of the wetting film in the presence of surfactant molecules and revealed that the surfactant adsorption induces the first-order wetting transition by decreasing required enthalpies for oil molecules to be transferred from a lens to the film due to the lateral van der Waals interaction between hydrocarbon chains and increasing the mixing entropy in the film.[3,4] Furthermore, we could measure the tension at the three phase contact line of air–hexadecane–DTAB solutions (we call this the line tension of hexadecane lenses) and discovered that the line tension changes sign from positive to negative when the surfactant concentration passes through the wetting transition concentration.[5,6]

Line tension is considered to be a crucial factor to control interfacial phenomena occurring in microscopic systems such as closing of the hole on bilayer membranes, and adsorption of fine particles at fluid interfaces[7–9] and thus attracts a great deal of attention these days. However, the line tension values measured by different research groups are still quite different and its significance is controversial.[10–18] Therefore, exploring the general relation between wetting transition and line tension is an important comprehensive research in colloid and surface sciences. For this purpose, interfacial tensiometry and ellipsometry were applied to hexadecane lens on aqueous solutions of hexadecyltrimethylammonium bromide (HTAB) in this paper. The relation between calculated surface free energy profiles and measured line tension will be discussed.

Experimental

Materials. HTAB (Nacalai tesque, >99%) was recrystallized from mixture of acetone and ethanol (4:1 volume ratio) five times and dried in vacuum. TTAB (Aldrich Chemical Co., Ltd., ca. 99%) was purified seven times by recrystallization from a mixture of acetone and ethanol. Oil-soluble impurities were removed by extraction from hexane. The purification of DTAB is described in Ref. 5. These purities were confirmed by the absence of a minimum on the surface tension vs. molality curves around the critical micelle concentrations (cmc). Water for measurements was distilled three times from dilute alkaline permanganate solution. *n*-Hexadecane (Kanto Chemical Co., Inc., >98%) was distilled fractionally under reduced pressure (bp 133–134 °C at 3.0 mmHg). The purity of oil was estimated to be >99.5% by GC.

Interfacial Tensiometry. Interfacial tension at the air/aqueous solution interface in the absence of oil (AW-0) and those at the air/aqueous solution (AW), air/hexadecane (AO), and hexadecane/water (OW) interfaces were measured as a function of the molality, m, of aqueous surfactant solutions at 298.15 K by the analysis of the shape of a pendant drop hanging on a glass capillary tip.[19–22] For the AW interfacial tension measurement, a water drop was formed in the hexadecane-saturated air phase in a closed glass measurement cell. The equilibration time for the interfacial tension measurements was within 60 min.

Ellipsometry. Ellipsometric measurements were performed on a Picometer Ellisometer (Beaglehole Instruments, Wellington, NZ). The coefficient of ellipticity, $\bar{\rho}$, defined as the imaginary part of r_p/r_s at the Brewster angle (r_p and r_s are the complex Fresnel reflection coefficients for p- and s-polarized light, respectively) is measured.

Line Tension Measurement. For sufficiently small contact angles θ, a balance of forces acting on the contact line is

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Published on the web October 5, 2010; doi:10.1246/bcsj.20100158

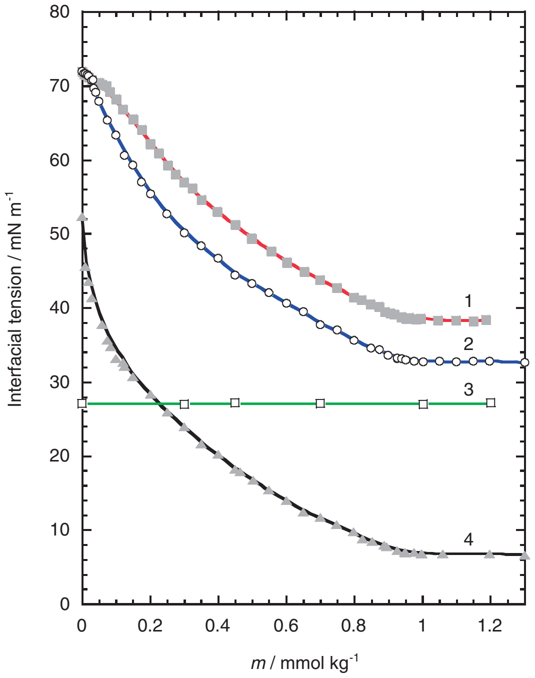

Figure 1. Interfacial tension versus surfactant concentration curves for hexadecane lens on HTAB aqueous solutions: 1) $\gamma^{\mathrm{AW\text{-}0}}$, 2) γ^{AW}, 3) γ^{AO}, and 4) γ^{OW}. The solid lines are the guides to the eye.

described by[23]

$$\gamma^{\mathrm{AO}}\cos\left(\frac{\gamma^{\mathrm{OW}}\theta}{\gamma^{\mathrm{OW}}+\gamma^{\mathrm{AO}}}\right)+\gamma^{\mathrm{OW}}\cos\left(\frac{\gamma^{\mathrm{OW}}\theta}{\gamma^{\mathrm{OW}}+\gamma^{\mathrm{AO}}}\right) = \gamma^{\mathrm{AW}}-\frac{\tau}{r} \tag{1}$$

where $\gamma^{\alpha\beta}$ represents the interfacial tension between the α and β phases, and r and τ the radius and line tension of the lens. Therefore, the slope of a straight line fitted to the plots of the value of the left-hand-side against r^{-1} yields a line tension. The θ and r values were estimated by the interferometric measurement which has been already applied to dodecane lenses on a water surface by Aveyard et al. with satisfactory precision.[23] Around 30–40 sets of θ and r were employed to calculate the line tension at each surfactant concentrations. The (θ, r) values measured for hexadecane lenses on HTAB solutions are given in the Supporting Information.

Results and Discussion

The results of surface tension measurements and ellipsometry are summarized in Figures 1 and 2. The wetting behavior of hexadecane on HTAB solutions is essentially similar to that on DTAB solutions. $\gamma^{\mathrm{AW\text{-}0}}$ and γ^{AW} take almost the same values at very low concentrations then have a break point corresponding to the phase transition of the surfactant adsorbed film from the gaseous to the expanded states but γ^{AW} is appreciably lower than $\gamma^{\mathrm{AW\text{-}0}}$ in the latter and the transition concentration (0.08 mmol kg^{-1}) is also diminished by the presence of hexadecane (0.03 mmol kg^{-1}). From ellipsometric measurements, it was found that the coefficient of ellipticity abruptly changes when the initial spreading coefficient

$$S_i = \gamma^{\mathrm{AW\text{-}0}} - \gamma^{\mathrm{OW}} - \gamma^{\mathrm{AO}} \tag{2}$$

becomes positive in the presence of oil (0.05 mmol kg^{-1}). On the basis of a simple model in which the hydrocarbon chains of surfactant and hexadecane molecules at the interface are treated as a single thin layer with a density equal to that of bulk liquid hexadecane, the thickness of the hydrocarbon layer calculated is about 0.8 nm just after the wetting transition,[24] where the contribution from head groups, counter ions, and capillary waves were separately calculated and subtracted.[2] From these findings, it is concluded that oil does not spread on the air–water interface in the lower concentration region but the adsorption of surfactant induces the wetting transition of hexadecane lens and, after that, a hexadecane lens coexists with molecularly thin film.

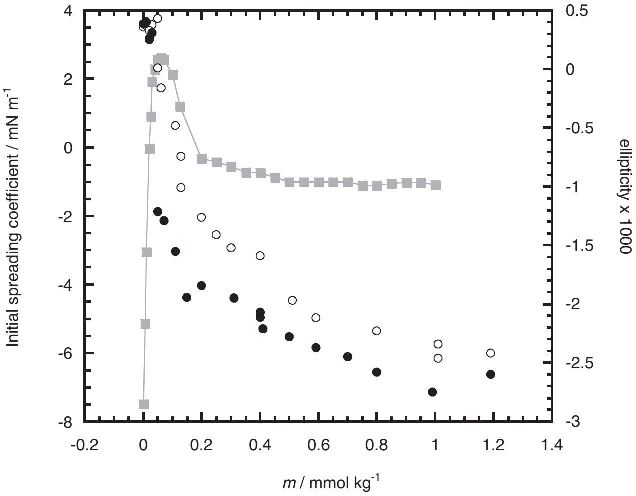

Figure 2. Initial spreading coefficient versus surfactant concentration (■) for hexadecane lens on HTAB aqueous solutions. The right hand axis shows the coefficient of ellipticity for air–water interface without oil (○) and with oil (●).

The existence of the pseudo-partial wetting state with a positive initial spreading coefficient can be explained by the long-range van der Waals interaction through the oil film;[4]

$$V(l) = -\frac{A}{12\pi l^2} \tag{3}$$

where A is the Hamaker constant and l the thickness of the film.[25] For all liquid alkanes on the water surface, $A > 0$, therefore, the surface free energy $V(l)$ favors the thinner film in equilibrium with lens than the uniformly spread film when the initial spreading coefficient is positive. Although this picture decidedly gives intuitive framework for understanding the wetting behavior of oil for given initial spreading coefficient and Hamaker constant, it does not explain the order of the wetting transition which is probably clarified by exploring more detail shape of the surface free energy profile in the short-range region. From this point of view we previously proposed the model to calculate the surface free energy of surfactant–oil monolayers based on the regular solution assumptions and then construct the free energy profile for not only a thinner but also a thicker film by connecting them with the van der Waals interaction given by eq 3.[3]

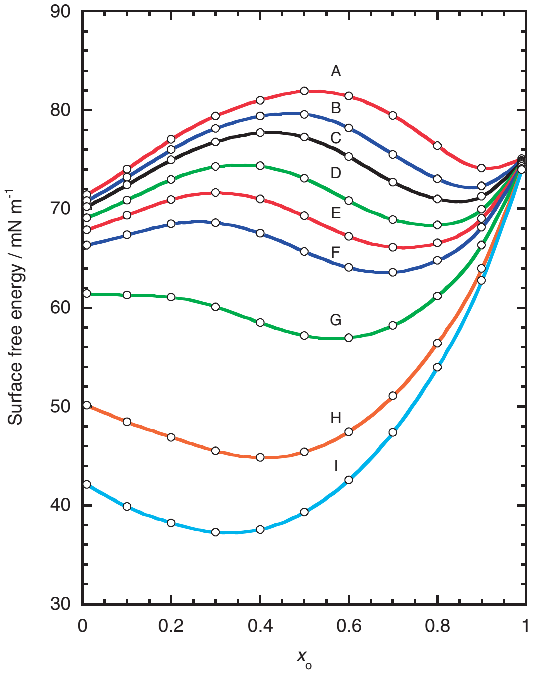

Figure 3. Surface free energy against mole fraction of oil in the mixed monolayer for a bulk surfactant concentration of (A) 0.01, (B) 0.02, (C) 0.03, (D) 0.05, (E) 0.07, (F) 0.1, (G) 0.2, (H) 0.5, and (I) 0.8 mmol kg^{-1} from top to bottom. Constants used for the calculation are $K_L = 0.47$ mmol kg^{-1}, $\Gamma_m = 4.0$ µmol m^{-2}, $\beta_{ss} = -2.6kT$, $\beta_{oo} = -10.2kT$, and $\beta_{so} = -10.2kT$. For calculation details, see Ref. 3.

Figure 3 shows the surface free energy thus calculated by the two-dimensional regular solution model against the mole fraction of oil in the mixed monolayer, x_o, for various bulk surfactant concentrations. At the low surfactant concentrations (curves A to C), the free energy profile has a double minima corresponding to a dilute gaseous monolayer of hexadecane molecules ($x_o \approx 0$, partial wetting) and a nearly complete monolayer ($x_o \approx 0.7$–0.9, pseudo-partial wetting), respectively. Clearly, the global minimum is the partial wetting state in this concentration region. Increasing surfactant concentration reduces the surface free energy of both minimum but the reduction in energy is more pronounced in the minimum of the pseudo-partial wetting. As a result, the first-order transition from the dilute gas of oil to the complete monolayer occurred at $m = 0.03$–0.05 mmol kg^{-1}. This concentration is very close to the transition concentration between partial wetting and pseudo-partial wetting determined by the tensiometry and ellipsometry (0.03–0.05 mmol kg^{-1}). At higher concentrations, there is only a single minimum and the equilibrium state is now the pseudo-partial wetting. The x_o of the complete monolayer was calculated from theory and proved to change from 0.8 to 0.3 with increasing concentration up to the cmc. On the other hand, the interfacial tensiometry and ellipsometry give the surface density of surfactant molecules and the total amount of hydrocarbon chain, respectively. The x_o value of the complete monolayer calculated from the combination of these two methods is 0.75 just after the transition and 0.2 at the cmc, which is in good agreement with our theoretical estimations.

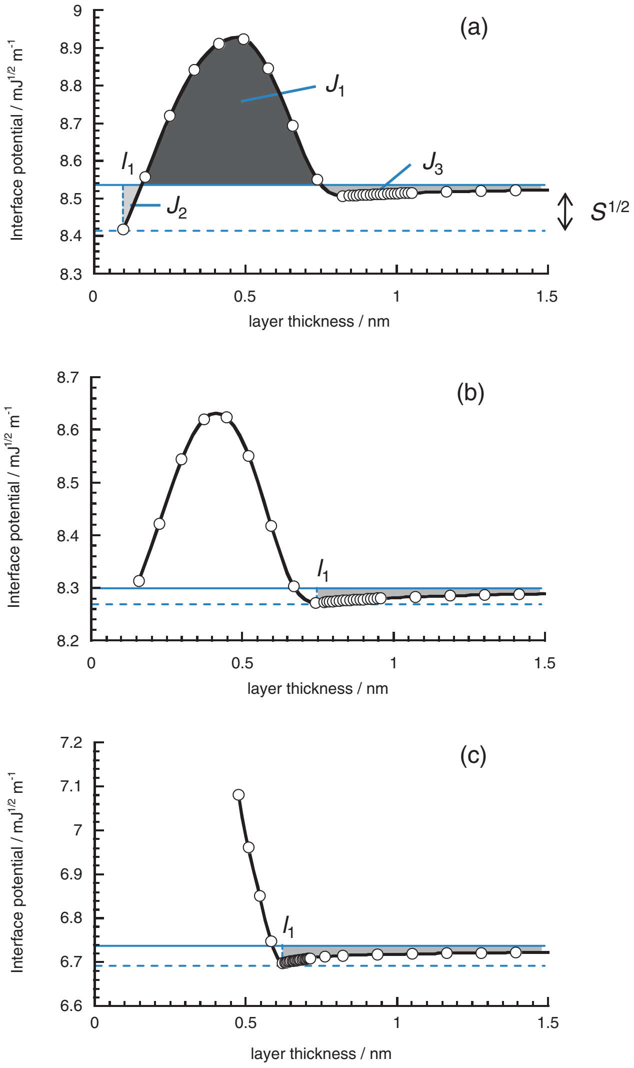

Figure 4. Surface free energy diagrams for HTAB + hexadecane (a) 0.02, (b) 0.05, and (c) 0.5 mmol kg^{-1}. We used the non-retarded van der Waals potential for the long-range interaction and deduced the Hamaker constant for air/hexadecane/water as 1.0×10^{-20} J from the Ref. 25.

These calculations confirm that the lateral van der Waals interaction between surfactant and oil molecules and mixing entropy is the cause of the first-order wetting transition between the partial wetting and the pseudo-partial wetting.

The theoretical connection between wetting transition and line tension is provided by the interface displacement model proposed by Indekeu et al.,[26–28] where the line tension τ is expressed as an integral of the square root of the surface free energy $V(l)$ from the film thickness in equilibrium with a lens l_1 to infinity by taking $\gamma^{AO} + \gamma^{OW}$ as the origin of free energy by[11,13,29]

$$\tau = (2\gamma^{AW})^{1/2}\xi \int_{l_1}^{\infty} [V(l)^{1/2} - S^{1/2}]\mathrm{d}l \qquad (4)$$

where ξ is the bulk correlation length and S the spreading coefficient defined by γ^{AW} instead of $\gamma^{AW\text{-}0}$ in eq 2. Some examples of the free energy profiles calculated for the HTAB–hexadecane system are demonstrated in Figure 4. All these

Table 1. Results of Line Tension Measurement for Hexadecane Lens at Aqueous Solution Surface of (a) DTAB, (b) TTAB, and (c) HTAB[a)]

(a)		(a)′		(b)		(c)	
m/mmol kg^{-1}	τ/pN	m/mmol kg^{-1}	τ/pN	m/mmol kg^{-1}	τ/pN	m/mmol kg^{-1}	τ/pN
0.371	12 ± 9	0.505	31	0.099	123 ± 47	0.015	416 ± 182
0.438	22 ± 15	0.677	14	0.123	79 ± 14	0.020	382 ± 59
0.480	11 ± 10	0.699	13	0.148	90 ± 44	0.025	530 ± 149
0.545	4 ± 5	0.734	3	0.198	51 ± 19	0.030	415 ± 60
0.598	2 ± 6	0.797	-3	0.209	64 ± 50	0.038	449 ± 128
0.619	-27 ± 10	0.912	-55	0.222	19 ± 35	0.040	-557 ± 59
0.648	-21 ± 45	1.013	-17	0.230	12 ± 60	0.043	-306 ± 97
0.678	-17 ± 11	1.037	-35	0.247	-33 ± 63	0.045	-688 ± 119
0.700	-62 ± 6	1.106	-117	0.273	-33 ± 54	0.050	-590 ± 274
0.709	-37 ± 16			0.297	-58 ± 33	0.060	-539 ± 75
0.793	-39 ± 8			0.325	-17 ± 19		
0.798	-19 ± 13			0.337	-79 ± 16		

a) For estimate the reproducibility of the line tension measurement, the line tension previously measured for hexadecane on DTAB solutions was also listed as (a)′.[5,6]

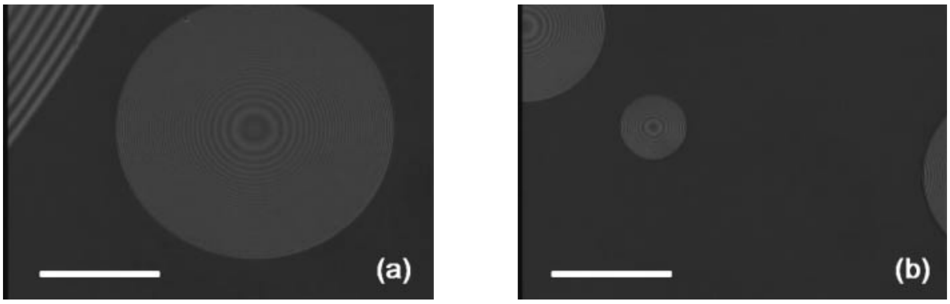

Figure 5. Microscopic images of hexadecane lenses on HTAB aqueous solutions of (a) 0.005 and (b) 0.040 mmol kg^{-1}. White bar shows 50 µm.

curves start from the thickness of the corresponding surfactant adsorbed film in the absence of oil calculated by $0.8x_S$ nm. The sign of the line tension is dependent on the difference between the positive (J_1) and negative (J_2 and J_3) contributions to the integral of eq 4. When oil lens is in equilibrium with a dilute gas of oil molecules in the partial wetting state, the line tension of oil lens is expected to be positive from the large potential barrier (J_1) in Figure 4a. When it is in equilibrium with a complete monolayer in the pseudo-partial wetting state on the other hand, the integral has to be taken from the thickness of the complete monolayer l_1, thus the line tension is expected to be negative (Figures 4b and 4c). In these cases, only the integral J_3 contributes to the value of the line tension. Therefore, it can be said that our surface free energy profile constructed by combining the two-dimensional regular solution theory and the long range van der Waals interaction using Hamaker constant satisfies the requirement for the reversal of the sign of the line tension deduced from the interface displacement model.

Table 1 summarizes our experimental results of line tension measured for hexadecane lens at the aqueous solutions of alkyltrimethylammonium bromides with different chain length. As shown in column (a) and (a)′, our line tension measurement is satisfactorily reproducible compared with the previous literature and gives precise order of line tension expected from the theory (10^{-9}–10^{-12} N).[30] Note that the line tension of the present system changes sign at the concentration around $m = 0.04$ mmol kg^{-1} which coincides well with the wetting transition concentration determined above. The reversal of the sign of the line tension was visually confirmed also by the observation that small oil lenses formed by stirring a large lens again merge into a large lens in the partial wetting regime but large lenses spontaneously break up into small lenses in the pseudo-partial wetting regime as shown in Figure 5.

Conclusion

The interfacial tension of the air–surfactant solution interface in the presence of hexadecane shows an abrupt change in slope at a concentration corresponding to a transition between the partial wetting and pseudo-partial wetting as the surfactant concentration changes. A discontinuity in the coefficient of ellipticity at this concentration confirms the first-order nature of this transition, which is in agreement with the prediction of the 2D regular solution theory. Our expectation that the wetting transition from partial wetting to pseudo-partial wetting leads to the change in the sign of line tension from positive to negative values was confirmed for hexadecane on three kinds of alkyltrimethylammonium bromide solutions and thus appears to be more universal. The transition concentrations of hexadecane determined by the tensiometry and ellipsometry were 0.75–1.00 mmol kg^{-1} for DTAB, 0.20–0.30 mmol kg^{-1} for TTAB, and 0.03–0.05 mmol kg^{-1} for HTAB, which respectively well coincide with the concentrations at which the line tension changes its sign. The increase of the absolute value of the line tension from the DTAB to HTAB systems may be followed by the strength of the lateral van der Waals interaction between surfactant and oil in the wetting film, however, this should be considered more carefully by comparing the line tension measured in different surfactant homologs in the future.

Supporting Information

Contact angles and radius of hexadecane lenses on HTAB solutions are also given. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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