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Examination of Surface Adsorption of Cetyltrimethylammonium Bromide and Sodium Dodecyl Sulfate

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ⓢ *Supporting Information*

ABSTRACT: Several pieces of experimental evidence of condensation of soluble surfactant molecules, cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS), into the air/water surface region from the bulk solution are presented at different added salt concentrations in order to substantiate that the concentrated molecules do not locate just at the air/solution interface. The insoluble monolayer just at the air/subphase interface for the two surfactants could be studied by surface pressure (π) versus molecular surface area (A), surface potential (ΔV) versus the area (A), infrared absorption of the surface region, and BAM (Brewster angle microscope) image. From surface tension versus concentration curves for the two surfactant solutions, the apparent molecular surface area and the cmc values were determined at different added salt concentrations, and the degree of counterion binding to micelle was found to be 0.70 and 0.73 for CTAB and SDS, respectively. Further examination was made on infrared absorption from the surface region of the surfactant solutions and on BAM images of the surface planes in order to examine the difference between the insoluble monolayer and the condensation in the surface region. Finally, the new concept of bilayer or bilamellar aggregate for soluble surfactant solutions is presented together with the former experimental evidence, which is consistent with several interfacial phenomena of the surfactant solutions.
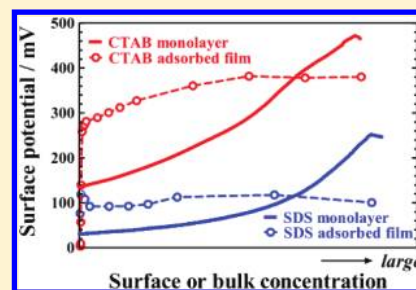
1. INTRODUCTION

The surface tension of water (γ_0) is 72.0 mN m^{-1} at 298.2 K, which is a physical quantity and, at the same time, a thermodynamical variable determined by water molecules of the order of Avogadro's number. On the other hand, the surface tension of aqueous surfactant solution (γ) is a thermodynamical variable which is specified by the steric structure made of surfactant and water molecules over many molecular layers beneath the air/solution interface. In other words, surface tension obtained by several methods is not a surface property in a strict sense but a macro property including a number of molecular layers in a bulk subphase, an interface layer above them, and a gaseous phase.

On the other hand, an insoluble monolayer or an insoluble monomolecular film just at the air/water interface can decrease the above surface tension (γ_0) of water down to ca. 20 mN m^{-1},[1] depending on the chemical species of insoluble materials, where almost all molecules placed on the air/water interface must be present just on the interface because of their insolubility into the water subphase. However, common molecules forming an insoluble monolayer are an amphiphile with one hydrophilic group or more groups and, therefore, have a strong interaction with water molecules in the subphase. If a monolayer material does not have any hydrophilic group, the material would escape into air with time. At the same time, the whole of the molecule cannot escape into the aqueous subphase due to its insolubility into the subphase, but a certain part of hydrophobic group goes in and out from the subphase quite frequently together with the hydrophilic group, which results in demolition of steric structure

of water molecules in the interfacial layer. As is known, *n*-propanol (C3) and *tert*-butanol (C4) can mix with water at any molar ratio, and therefore, a part of the insoluble molecule with three and four carbon atoms next to a hydrophilic group can freely move into the inner surface layer. When a molecular surface area of insoluble molecules is several nm^2, the molecules are in gaseous state and the surface pressure ($\pi = \gamma_0 - \gamma$) is less than a few mN m^{-1}. The surface pressure for liquid-expanded state increases rather slowly with decreasing molecular surface area over an area less than a few times of the cross-sectional area of the hydrocarbon chain, while the surface pressure for a solid condensed state is forced to steeply increase up to a collapse pressure of ca. 50 mN m^{-1} with little decrease in molecular surface area. This is quite an important characteristic of the insoluble monomolecular film. Such great decrease of surface tension down to less than 20 mN m^{-1} is due to destruction of the steric structure of water molecules over many molecular layers induced by high dipole moments due to collaboration of concentrated hydrophilic groups of insoluble molecules together with the demolition mentioned above. In other words, the decrease in surface tension by the insoluble monolayer must result from destruction of the steric structure over many layers of water molecules beneath the air/subphase interface or from collaboration between an insoluble monolayer and the many

water layers beneath it. In addition, ions in the subphase also have somewhat influence on the interfacial tension.[2]

As for an adsorbed film of soluble amphiphiles, on the other hand, the Gibbs surface excess has always been employed to evaluate the corresponding molecular surface area at the air/solution interface which is derived from a change of surface tension against surfactant concentration. However, the Gibbs adsorption isotherm is factitious as for the mathematical derivation,[3] and therefore, other adsorption isotherms have been presented.[4] The point is that a molecular surface area thus obtained remains almost constant above a half critical micelle concentration (cmc) of soluble amphiphile solutions. This is a big difference between an insoluble monolayer and an adsorbed film. Indeed, the surface excess amount of soluble amphiphiles has been determined experimentally,[5−7] but the location of adsorbed film could not be definitely and experimentally made clear, yet.

As mentioned above, the surface pressure of an insoluble monolayer is very much dependent upon actual molecular surface area, while a molecular surface area of adsorbed film is almost the same at concentrations above a half cmc regardless of surface tension. In addition, a molecular surface area (A) of 0.11 nm^2 was obtained for octaoxyethylene glycol mono-n-octadecyl ether (C18E8) by the surface tension study of the solution,[8] when the Gibbs surface excess was evaluated from the change of surface tension with the concentration. The molecular area is nearly a half of cross-sectional area of alkyl chain; i.e., the molecular surface area of adsorbed film is an apparent one. On the other hand, the surface adsorption amount by neutron scattering has been standardized by the Gibbs surface excess,[9] which means that the adsorbed amount cannot be verified by the neutron scattering.

The above results strongly indicate that an adsorbed film is quite different from an insoluble monolayer or is not localized just at the air/solution interface. If surface excess locates just at the interface, the interfacial tension should be less than a few mN m^{-1}, judging from the fact that an interfacial tension of double layer film is 0.2−6 mN m^{-1}, where both sides of the interface are aqueous bulk.[10] This is quite contrary to the fact that the surface tension of surfactant solution is ca. 40 mN m^{-1} around cmc. The above-mentioned can be substantiated by the following fact too. A black film of soap bubble is made of a double layer of soap molecules, where both sides of the film are air gaseous phase, and the duration of the film could be made as long as 95 days by J. Dewer in 1917.[11] Molecules in the air can easily transfer across the double layer film, and therefore, pressure difference between inside and outside of the black film must be almost zero after 95 days. In other words, surface tension of the film is also very much close to zero according to the equation of the Laplace pressure, where each soap molecule would have a few water molecules around the head group as hydrated water. Judging from the above facts too, it seems quite fallacious to reach the conventional conclusion that the surface excess is concentrated just at the air/solution interface.

The new concept of the surface excess presented later will be questioned by many surface chemists, but the correct new concept is to be established only when all interfacial phenomena on interfacial region can be reasonably elucidated among themselves without any contradiction. Fortunately, the authors have succeeded in examining the surface properties of insoluble monolayer of quite common soluble surfactants, cationic surfactant (cetyltrimethylammonium chloride) and anionic one (sodium dodecyl sulfate), which is the first invaluable heroic deed, as far as the authors know. The results thus obtained can lead to a clear difference between an insoluble monolayer and a condensation of soluble surfactant in the surface region. The reasonable elucidation on several interfacial phenomena will be presented below so that many readers may accept the new concept on the surface excess as much more reliable one than before.

2. EXPERIMENTAL METHODS

2.1. Materials. Cetyltrimethylammonium bromide (CTAB) from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) was purified by repeated recrystallizations from acetone. Sodium dodecyl sulfate (SDS) from EMD Biosciences, Inc. (Calbiochem, NJ) was purified by repeated recrystallizations from aqueous solution and by ether extraction. The purity of CTAB and SDS was checked by elemental analysis and the high purity was also confirmed by surface tension measurements.[12,13] In addition, there was no minimum along the surface tension versus concentration curve up to twice the cmc. Sodium chloride (NaCl) and sodium bromide (NaBr) from Nacalai Tesque were respectively roasted at 1023 and 973 K for 24 h to remove all surface-active organic impurities. Chloroform (99.7%) and methanol (99.8%) used as the spreading solvent for Langmuir monolayer study were obtained from Kanto Chemical Co., Inc. (Tokyo, Japan) and nacalai tesque (Kyoto, Japan), respectively. Water used here was triply distilled (surface tension of 71.9 mN m^{-1} and resistivity of 18 MΩ cm at 298.2 K).

2.2. Surface Tension Measurement. The surface tension (γ) of the surfactant solutions was determined at 298.2 K by using a drop volume tensiometer (DVS-2000 and DVS-2010, YTS, Japan).[14] This tensiometer measures the volume of a drop detaching from a capillary with known diameter. The temperature was kept constant within ±0.03 K by means of a thermostat. The experimental error for estimating the surface tension was ±0.05 mN m^{-1}.

2.3. Surface Potential Measurement. Surface potential (ΔV) was measured at 298.2 K by using an ionizing ^{241}Am electrode positioned at a certain level (1−2 mm) above the air/solution interface, while a reference electrode was immersed in the identical solution of 50 mL. The standard deviation for the potential values was ca. 5 mV. The surface potential was standardized to be zero for just the air/subphase-solution interface.[12,13] An aliquot of the concentrated solution for the two kinds of surfactants was added stepwise into 50 mL of water or into the electrolyte solutions to increase their overall concentration, where each addition of the mother solution was made once the potential became stable. The surface potential value depends on the distance between the ionizing electrode surface and the air/liquid interface, and therefore, the calibration for the potential was made first for the distance by changing the total volume of subphase solution after fixing the electrode position.[12,13]

2.4. Compression Isotherm Measurement. The surface pressure (π) of the monolayers was measured using an automated homemade Wilhelmy balance.[15] The surface pressure balance (Mettler Toledo, AG-245) had a resolution of 0.01 mN m^{-1}. The pressure-measuring system was equipped with a Pt plate (periphery = 39.24 mm). The trough was made from Teflon-coated brass (area = 750 cm^2), and Teflon-made barriers (both hydrophobic and lipophobic) were used in this study. Surface pressure (π)−molecular area (A) isotherms were recorded at 298.2 K within ±0.1 K. Stock solutions of CTAB (1.0 mM) and SDS (0.5 mM) were prepared in chloroform/methanol (2/1, v/v). The aqueous solution of 5 M NaBr for CTAB and that of 5 M NaCl for SDS were respectively selected as the subphase to prevent the surfactants from dissolving into the subphase. The spreading solvents were allowed to evaporate for 30 min prior to compression. The monolayer was compressed at a speed of ∼0.10 nm^2 molecule^{-1} min^{-1}.

The standard deviations (SD) for molecular surface area and surface pressure were ~0.01 nm^2 and ~0.1 mN m^{-1}, respectively. The $\Delta V - A$ isotherm was simultaneously recorded with the $\pi - A$ isotherm.

2.5. Brewster Angle Microscopy. A Brewster angle microscope, KSV Optrel BAM 300 (KSV, Finland), was used for microscopic observation of the surface of the CTAB and SDS solutions including 100 mM NaBr and 1 M NaCl, respectively. It is equipped with a 20 mW laser emitting p-polarized light of 632.8 nm wavelength, which is not reflected off from the air—water interface at ca. 53.1° (Brewster angle).[16] The lateral resolution of the microscope was 2 μm. The images were digitized and processed to obtain the best quality of BAM (Brewster angle microscope) pictures. Each image corresponds to the area of 400 μm × 300 μm. The data shown here are representative of three experiments at least. It took less than 30 min to take a stable BAM image. All measurements were performed at 298.2 K.

2.6. PM-IRRAS Measurement. In situ polarization modulation infrared reflection absorption spectrum (PM-IRRAS) measurements at the air—solution interface were performed using a KSV PMI 550 instrument (KSV Instruments Ltd., Helsinki, Finland) coupled with a commercially available film balance system (KSV Minitrough, KSV Instruments Ltd.). The PMI 550 instrument contains a Fourier transform IR spectrometer equipped with a PM unit on one arm of a goniometer and a HgCdTe (MCT) detector on the other arm. The IR beam was conducted out of the spectrometer and was directly steered into the interface by using no mirrors or external reflection accessory. The incident beam angle at 80° relative to the normal of the air—solution interface was selected in the present study. More information on the apparatus was reported in the previous paper.[17] The bare water and electrolyte solution surfaces containing no surfactants were used as the background, and the surface of surfactant solutions was used as the sample. The total acquisition time for each spectrum was 5 min, resulting in 3000 interferograms per spectrum. The spectral range of the PMI 550 device is 800—4000 cm^{-1}, and the resolution is 8 cm^{-1}. The spectra displayed in the figures were the representatives of five runs at least. Spectra were subjected to second-derivative and curve-fitting procedures in order to fit the methylene stretching vibration bands of aliphatic chains in a molecule (2800—3000 cm^{-1}) with a Gaussian band shape, PeakFit software (ver. 4.12, SeaSolve Software Inc., CA, USA) being used.[17] The standard deviation of RA value is 0.000 75.

3. RESULTS AND DISCUSSION

3.1. Interfacial Energy. In the present study, the following statements are quite important to discuss the present experimental results and to reach the conclusions. The origin of energy or an energy zero of a system is the state that both kinetic energy and potential energy are zero, where the whole molecules are infinitely separated and stay there without any movement. Molecules in liquid state are small in their kinetic energy but negatively large in their potential energy due to their closer interaction. The larger in negative value the potential energy of the liquid molecules becomes, the more stabilized the steric structure of the molecules is, or the more energy is required to destroy their steric structure; i.e., the interfacial tension of the system increases. Liquid molecules in the air/liquid interfacial layer have smaller numbers of nearest-neighboring molecules

than those in a bulk, and therefore, they have higher energy than those in the inner bulk. As for water molecules in particular, each molecule is strongly bound to surrounding ones by hydrogen bonds, and they are in the energy state of relatively large negative value. This is the reason why liquid water has higher surface tension than other liquid molecules. For instance, common organic liquids have 30—40 mN m^{-1} for their surface tension at room temperature (293.2—298.2 K), while that of water is twice as much as the above value, 72—73 mN m^{-1}.

As for aqueous surfactant solution, surfactant molecules are supposed to concentrate in the surface region, to destroy the steric structure of water molecules, to weaken their molecular interaction, and to increase the energy of whole molecules in the surface region. This is the surface activity and, at the same time, the reason why the materials to decrease a surface tension or an interfacial tension are called "surface-active agent". Surface-active agents or surfactants are concentrated in the surface region, and therefore, this concentration is said to be "positive adsorption". On the other hand, the surface tension of the air/solution interface for aqueous solution of a simple salt like sodium chloride increases linearly with the salt concentration. The dielectric constant of water is 78.3 at 298.2 K, while that of the air is 1. When an ion in a medium of higher dielectric constant comes closer to another medium of lower one, a charge of the same sign and same magnitude as the ion is formed in the latter medium at the symmetrical position against the interface between the two media. Then, an electrostatic repulsive force works for the two ions with the same charge, which is called "image force". On the contrary, when an ion in a medium of lower dielectric constant comes closer to another medium of higher dielectric constant, a charge of the opposite sign is formed in the latter medium, and therefore, an electrostatic attractive force works between the two charges. As a result, ions in a simple salt aqueous solution cannot come closer to the air/solution interface, which results in a negative adsorption. It is often said that the negative adsorption gives rise to an increase in surface tension with increasing salt concentration due to the requirement of the Gibbs adsorption isotherm. However, the above statement is quite unreasonable. An interfacial tension should be fixed by the energy automatically determined by the steric structure of the whole molecules of the interfacial region. It is not correct, therefore, to say that the negative adsorption must lead to an increase in surface tension with concentration. The increase in surface tension results from the following three: (1) the dissociated ions form hydrated ions with several water molecules, (2) the positive and the negative hydrated ions form more stable steric structure with water molecules by their electrostatic attraction, and (3) as a result, an energy more than that without salt is required to break their steric structure or to increase an area of the air/solution interface.

3.2. Insoluble Monolayer of CTAB and SDS. Both the surfactants are soluble in water, and therefore, an extraordinary subphase condition is required to have their stable insoluble monolayers. Their stability was examined finally on 5 M NaBr and 5 M NaCl aqueous subphases for CTAB and SDS at 298.2 K, respectively. Their monolayers were compressed first up to 30 mN m^{-1} by moving a Teflon barrier, and then the Teflon barrier was stopped, after which relaxation of surface pressure was traced against time. The pressures steeply decreased during the first 10 min, and then gradually decreased down to 20 mN m^{-1} after 120 min (see Figure S1 in the Supporting Information). These variations are durable for a $\pi - A$ (molecular surface area)
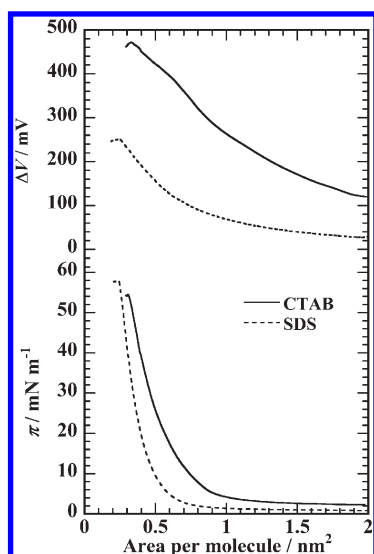
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Figure 1. Surface pressure (π)− and surface potential (ΔV)−molecular surface area (A) isotherms of CTAB and SDS on 5 M NaBr and 5 M NaCl at 298.2 K, respectively.

Figure 2. (a) RA intensity of $\nu_{as}(CH_2)$ mode at ∼2920 cm^{-1} for CTAB and SDS monolayers on 5 M NaBr and 5 M NaCl at 298.2 K, respectively, as a function of molecular surface area (A) during compression and (b) wavenumber at the maximum intensity of $\nu_{as}(CH_2)$ mode for CTAB and SDS monolayers under the same condition as (a).

isotherm according to the previous studies,[15] and therefore the above subphases were employed to examine their insoluble monolayers. The π−A and ΔV−A isotherms of CTAB and SDS monolayers spread on the subphase are shown in Figure 1. The π−A isotherms show that both monolayers are an entirely liquid-expanded film and are compressed down to collapse without any phase change over wide change of the molecular area. The molecular surface areas at the monolayer collapse are 0.32 and 0.24 nm^2 for CTAB and SDS, respectively, which indicates that the subphases are enough to support the insoluble monolayer without loss of the molecules from the surface, because the value of 0.32 nm^2 is an area of the cationic head group of CTAB and the value of 0.24 nm^2 is a cross-sectional area of alkyl chain of SDS.[18] In other words, the insoluble monolayers have collapsed after the closest packing of the molecules. The surface tension of the subphases with the added salts were 80.9 and 81.5 mN m^{-1}, respectively, and therefore the final surface tension decreased down to 23.2 and 27.3 mN m^{-1}, respectively. These final small values are much less than the value of surface tension at cmc of usual soluble surfactants, which clearly indicates that strong dipoles gathered just at the air/subphase interface have destroyed the hydrogen-bond network of water molecules beneath the interface. This is also substantiated by quite high surface potentials, 470 and 250 mV for CTAB and SDS, respectively. The former value of 470 mV is almost the same as that at the cmc of CTAB just in water,[13] whereas the value for SDS changed from a negative value of −80 mV at the cmc just in water to the high positive value of 250 mV at the monolayer. This positive value results from the location of Na$^+$ ions nearer to the interface than −SO$_4^-$ ions. This is because the anions are dragged more into inner bulk by concentrated Na$^+$ ions in the inner bulk.

Infrared measurements were made together with the above π−A and ΔV−A isotherms, where changes in RA absorption intensity and wavenumber at the absorption maximum for methylene antisymmetric vibration mode, $\nu_{as}(CH_2)$, were obtained against molecular surface area of insoluble molecules (Figure 2). The RA intensity for SDS is almost inversely proportional to the molecular surface area (panel a), which suggests that methylene groups under a certain molecular arrangement for SDS is quite sensitive to an
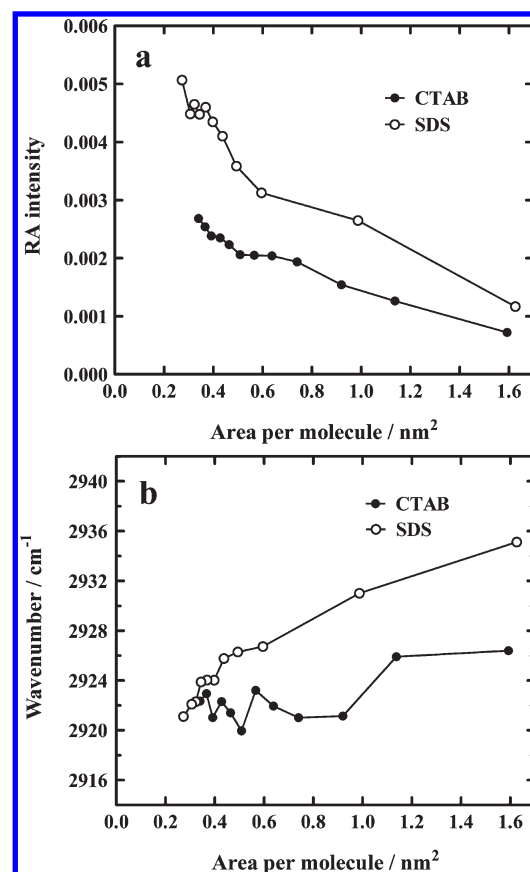
incident beam. On the contrary, that for CTAB is not the case. This difference between CTAB and SDS can be observed also for change in the wavenumber (panel b). The decrease in wavenumber with decreasing molecular area means increasing difficulty of movement for CH$_2$ groups with decreasing the area. At the closest packing, however, the difference disappears between CTAB and SDS. Further discussion on the matter will be made in the later sections.

3.3. Gibbs Surface Excess of CTAB and SDS. The change in surface tension with surfactant concentration for CTAB and SDS was measured to examine whether the Gibbs surface excess (Γ) obtained from the surface tension has any relationship with their insoluble monolayer or not. The results are shown in Figure 3, where the surface tensions are plotted against logarithm of the surfactant concentrations at different added salt concentrations. From the plots, the surface excess is found to reach at lower surfactant concentration with higher added salt concentration. The surface excess can be obtained from the slope[4,7]

$$\Gamma = -\frac{1}{nRT}\left(\frac{\partial \gamma}{\partial \ln C}\right)_{T,P} \qquad (1)$$

where n = 1 and 2 are for large amount of added salt and for no added salt, respectively, and the concentration can replace the activity because of the constancy of activity coefficient due to definite excess amount of added salt for n = 1 and of quite dilute surfactant concentration for n = 2. The former means no
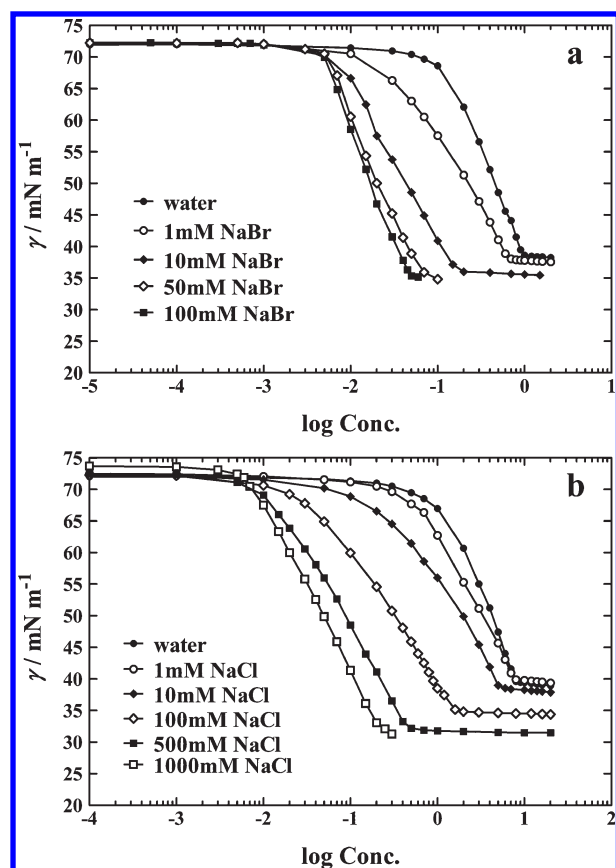
Figure 3. (a) Plots of surface tension against logarithm of CTAB concentration at different NaBr subphase concentrations at 298.2 K and (b) plots of surface tension against logarithm of SDS concentration at different NaCl subphase concentrations at 298.2 K.

Figure 4. (a) Plots of logarithm of cmc against logarithm of Br^- concentration at the cmc for CTAB and (b) plots of logarithm of cmc against logarithm of Na^+ concentration at the cmc for SDS.

Table 1. Values of cmc and Molecular Surface Area Derived from Change of Surface Tension with Surfactant Concentration at Different Added Salt Concentrations

	CTAB		SDS	
salt concn, mM	cmc, mM	A_a, nm^2/ molecule	cmc, mM	A_a, nm^2/ molecule
0	0.98	0.55	8.21	0.54
1	0.71		7.80	
10	0.15	0.38	5.84	
50	0.06	0.29		
100	0.04	0.25	1.51	0.42
500			0.52	0.38
1000			0.21	0.36

contribution of the counterion from the ionic surfactants to the surface tension in the presence of large amount of the counterion from the added salt. The apparent molecular surface area (A_a) can be available from Γ: $A_a = 1/N_A\Gamma$, where N_A is Avogadro's number. The critical micelle concentrations (cmc) are also obtained as the concentration at which the above plots come to remain almost constant. The values of cmc and the molecular surface area thus obtained for the two ionic surfactants are summarized in Table 1, in which the molecular areas (A_a) except for no added salt are those from $n = 1$
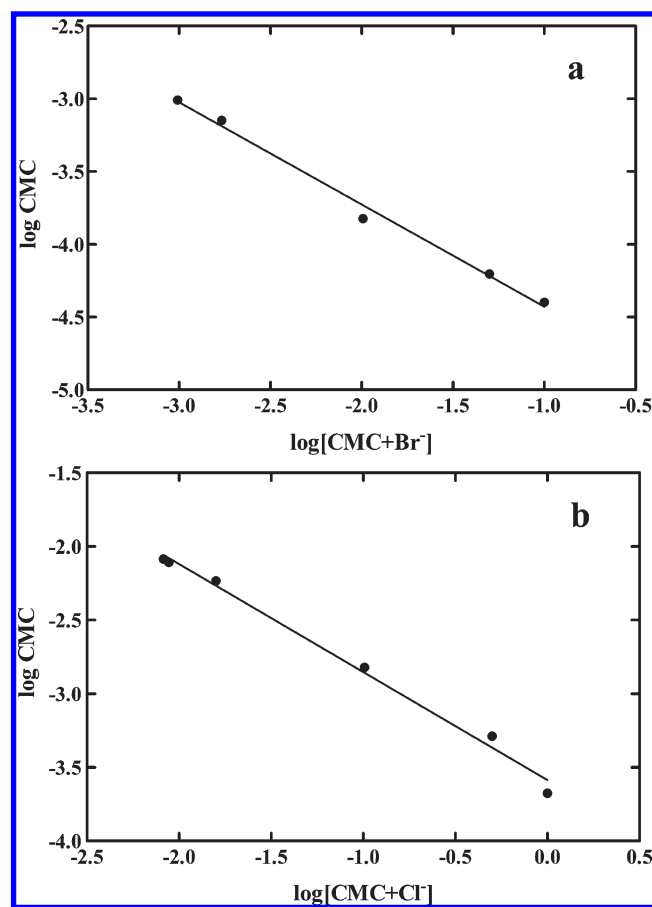
because of the presence of more than 70 times excess counterions at the cmc. The molecular area decreased with increasing added salt concentration, which results from decreasing electrostatic repulsion between ionic head groups. The point is, however, that the area of 0.25 nm^2 for CTAB is less than the head-group area of 0.32 nm^2, which clearly means that the area is an apparent one and that the surface excess cannot locate just at the air/solution interface, whereas the excess location has been shown just at the air/solution interface in many text books.[19,20] In other words, bimolecular layer formation or bilamellar micellization at some distance below the interface is more preferable to an adsorption at the air/solution interface, where the hydrophobic tails contact one another intruding inward from the upper and lower sides instead of intruding into the air by placing the head groups at the surface, just like a bimolecular layer arrangement in a cell membrane. Then, the lamellar surface is positively charged for a cationic surfactant, while negatively charged for an anionic surfactant. Highly charged aggregates cannot come closer to the air/water interface due to the repulsive image force, which give rise to a certain width of water layer. This model is much easier and more reasonable to elucidate evaporation rate of water and the activation energy.[21,22]

The degree of counterion binding to micelle can be obtained from change of cmc with counterion concentration. Linear relationships for logarithm of cmc plotted against logarithm of counterion concentration are shown in Figure 4, where their linearities are quite good and the slope value becomes the degree
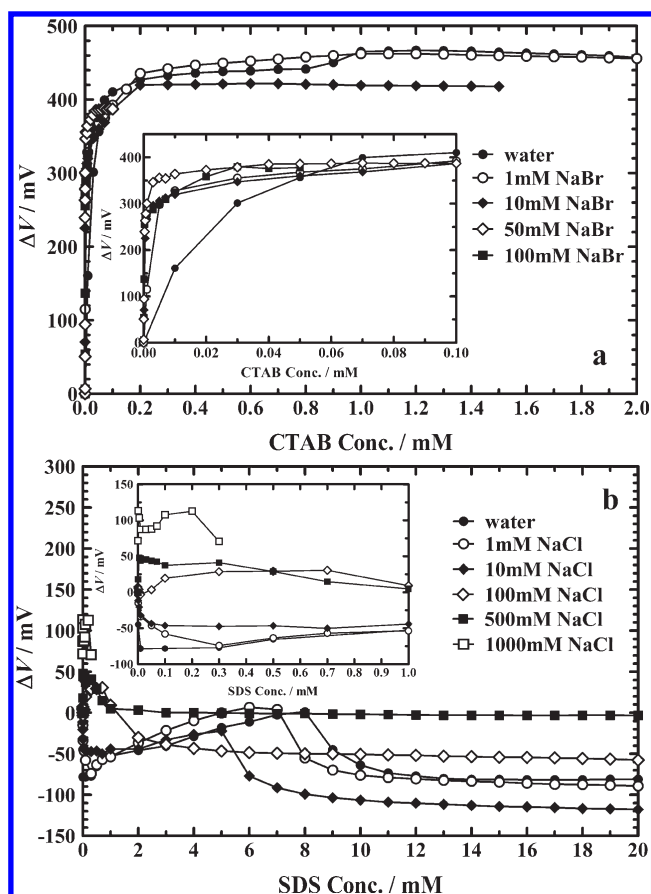
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Figure 5. (a) Change of the surface potential (ΔV) with CTAB concentration at different NaBr subphase concentrations at 298.2 K and (b) change of the surface potential (ΔV) with SDS concentration at different NaCl subphase concentrations at 298.2 K.

of counterion binding to micelle:[23] 0.70 and 0.73 for CTAB and SDS, respectively. The latter value is quite the same as the previous one.[24] Smaller degree of counterion binding to the micelle for CTAB is due to larger surface area of the cationic headgroup at the micellar surface.

The plausible explanations for the change of surface tension with surfactant concentration are made in relation with evaporation rate of water from soluble surfactant solution in the previous papers,[21,22] where the presence of the bilayer aggregates beneath the air/subphase interface is strongly supported.

3.4. Surface Potentials of CTAB and SDS Solutions. Figure 5 shows the net surface potential changes of CTAB and SDS as a function of concentration, where the term "net" means that a correction for the distance between the electrode and the surface of the subphase solution is made.[12] As for CTAB (Figure 5a), the small jump of surface potential (ΔV) around the cmc found for water subphase became unclear even for 1 mM NaBr subphase solution. This fact suggests easy neutralization of the subphase under added NaBr condition, where the neutralization has no electrostatic effect on the positive surface potential. The important point is that the surface potentials remain almost constant over wide concentration range irrespective of the steep decrease in surface tension up to cmc, which strongly indicates that the total attractive interactions among water molecules, surfactant ions, and ions of added salts in the bulk phase beneath the air/subphase interface steeply decrease with increasing surfactant concentration. This decrease takes place at

lower surfactant concentration under higher added salt concentration (Figure 3). In addition, the high surface potential becomes established at very dilute surfactant concentration far below the cmc. The above relationships between the molecular surface area and the surface potential are quite different from that for insoluble monolayer (see Figure 1).

On the other hand, the potential changes for SDS with the concentration are more complicated than those for CTAB, where the potential steeply decreases from 0 mV down to -80 mV at lower NaCl concentrations, then gradually increases up to almost 0 mV, then suddenly decreases again down to -80 mV around cmc, and finally remains almost constant. The final decrease can be elucidated by the disappearance of the bimolecular aggregates below the air/subphase interface due to molecular transfer from the bilayer to stable micelles in the bulk.[12,13,25] Under higher added NaCl concentrations, on the contrary, the potential starts to increase without any decrease with increasing SDS concentration. This change results from more concentration of Na^+ ions closer to the interface than DS^- ions, as was observed for NaCl, NaHSO$_4$, and CH$_3$SO$_4$Na.[13] The important fact is the presence of the potential decrease around the cmc even under higher NaCl concentrations, which is quite contrary to the case for CTAB. This is because excess Na^+ ions locate in the subphase near the interface due to the presence of negatively charged bilayer aggregates beneath the interface. However, the excess Na^+ ions move into inner bulk once more stable micelles are formed in the bulk. In other words, the neutralization of the subphase near the interface for SDS is not so easy as the case for CTAB, which is reflected in the potential 0 mV for tetramethylammonium bromide solution over the wide concentration range.[13]

3.5. Infrared Spectrum from CTAB and SDS Solutions. The changes in RA intensity with surfactant concentration are shown in Figure 6, a and b, for CTAB and SDS, respectively, under different added salt concentrations, where the change is larger for SDS than for CTAB similar to that of insoluble monolayer. The intensities steeply increase with the surfactant concentration at lower concentrations and then remain almost constant at higher concentrations, which clearly indicates an increase in the molecular amounts in the interfacial region at lower concentrations. The point here is that the changes might be divided in two groups: one is for lower added salt concentrations and the other is for higher ones. That is, the first is more expanded bilayer, while the second is more condensed bilayer. This might be a morphological alteration of the bilayer similar to a sphere-to-rod shape change of micelle with increasing added salt concentration.[26] The higher value of 0.0027−0.0030 for CTAB corresponds to 0.3 nm^2 of molecular surface area at the insoluble monolayer state or of the closest packed molecular state, while the lower value of 0.0015−0.0020 corresponds to 0.5−0.9 nm^2 of the molecular area or loosely packed molecular state (see Figures 1 and 2). The former packed state nicely represents the molecular area from the Gibbs surface excess (see Table 1), while the latter loosely packed state fairly does. As for SDS, on the other hand, the higher value of 0.0048−0.0055 corresponds to 0.25 nm^2 of molecular surface area at insoluble monolayer state or of closest packed molecular state, while the lower value of 0.0030−0.0038 corresponds to 0.45−0.6 nm^2 of the molecular area or loosely packed molecular state (see Figures 1 and 2). The former packed state hardly represents the molecular area from the Gibbs surface excess (see Table 1), while the latter loosely packed state nicely does. These contradictions strongly indicate that the Gibbs surface excess does not locate just at the air/subphase interface, too.
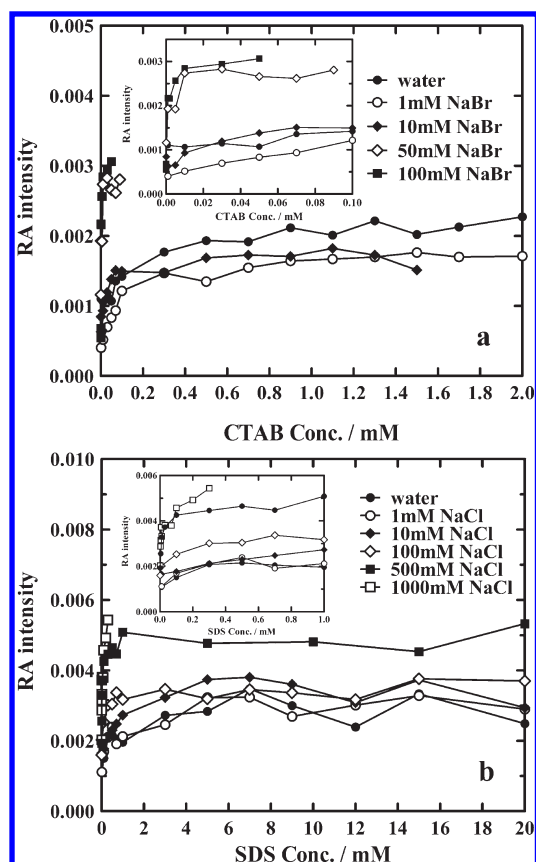
Figure 6. (a) Change of the RA intensity of $\nu_{as}(CH_2)$ mode with CTAB concentration at different NaBr subphase concentrations at 298.2 K and (b) change of the RA intensity of $\nu_{as}(CH_2)$ mode with SDS concentration at different NaCl subphase concentrations at 298.2 K.

Figure 7. (a) Change of wavenumber of $\nu_{as}(CH_2)$ mode with CTAB concentration at different NaBr subphase concentrations at 298.2 K and (b) change of wavenumber of $\nu_{as}(CH_2)$ mode with SDS concentration at different NaCl subphase concentrations at 298.2 K.

The changes in the wavenumber with surfactant concentration are shown in Figure 7, a and b, for CTAB and SDS, respectively, under different added salt concentrations. The wavenumbers steeply decrease with the surfactant concentration at lower concentrations and then remain almost constant at higher concentrations, where the decrease becomes more slow at lower added salt concentration. The changes are quite hard to divide into two groups, contrary to those for RA intensity. As for the insoluble monolayer, on the other hand, the decrease is more sensitive to molecular surface area for SDS than for CTAB in the monomolecular state, although the wavenumber becomes 2921–2922 cm^{-1} at the closest packed state for both surfactants (see Figure 2b). In the bulk solutions, however, the total changes in the wavenumber are almost the same for the two surfactants. These observations also suggest that the Gibbs surface excess does not locate just at the air/subphase interface. The decrease in the wavenumber results from an increase in difficulty of motion of CH$_2$ group. In other words, when the molecules are more apart one another, the molecular motion is easier and then the wavenumber becomes larger. On the contrary, when the molecules are more closely packed, the motion is harder and therefore the wavenumber becomes smaller. The difficulty in the motion even at low concentrations for both CTAB and SDS strongly suggests a commencement of a bilayer aggregation at the very low concentrations.

3.6. BAM Observation. Dark BAM image of the surface for just water is illustrated in Figure S2 in the Supporting Information, where nothing is observed on the surfaces. In addition, there
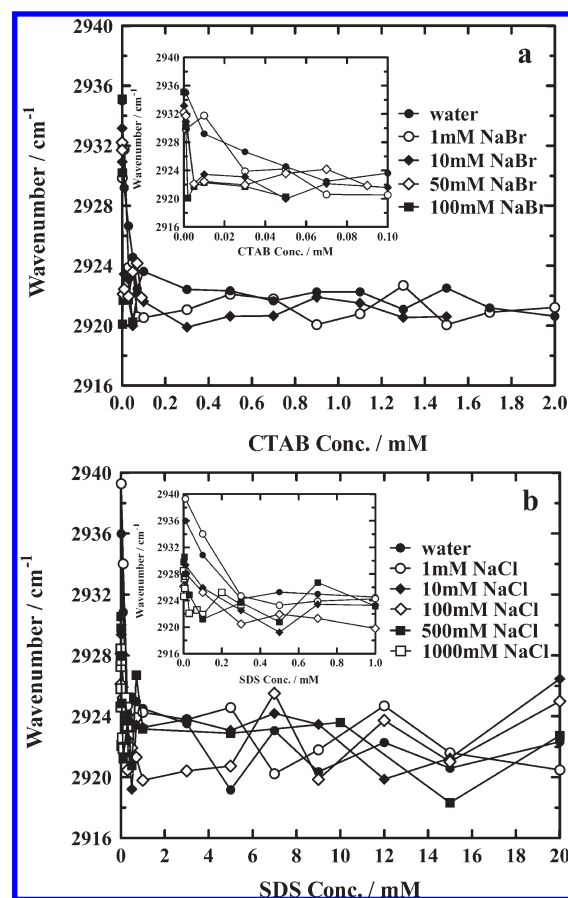
was no difference among the four systems (just water and surfactant solutions of SDS, MEGA-10, and N-(1,1-dihydroperfluorooctyl)-N,N,N-trimethylammonium chloride at the cmc) in image darkness either.[21] This fact strongly suggests no condensation of soluble surfactants just near the surface. On the other hand, distinct structures of molecular assemblies were observed over the whole surface for the insoluble monolayer at a condensed state.[13,21] A BAM image catches the light reflected from the focal plane. A BAM image over several nanometers depth can be taken clearly only when there exists a difference in refractive index around the focal plane. In fact, a BAM image can be observed for an insoluble monolayer in the liquid expanded state, too, although it is not so clear as that in the solid condensed state.

The bilayer or bilamellar aggregates are positively charged for a cationic amphiphile, while they are negatively charged for an anionic amphiphile. Highly charged aggregates cannot come closer to the air/water interface due to the repulsive image force, which is also the case for a negative adsorption for ionic salts. Electrostatic force is a long-range force. Thus, a water layer with a certain depth is formed between the air and the aggregates, which can give rise to the same evaporation rate of water, the same activation energy, and no BAM image just like bulk water.[21,27] On the contrary, the nonionic aggregates are electrically neutral. Therefore, no repulsive image force acts on the aggregates, and the aggregates can come closer to the air/water interface still keeping several layers of water molecules in between, which results in the appearance of the BAM image.[21]
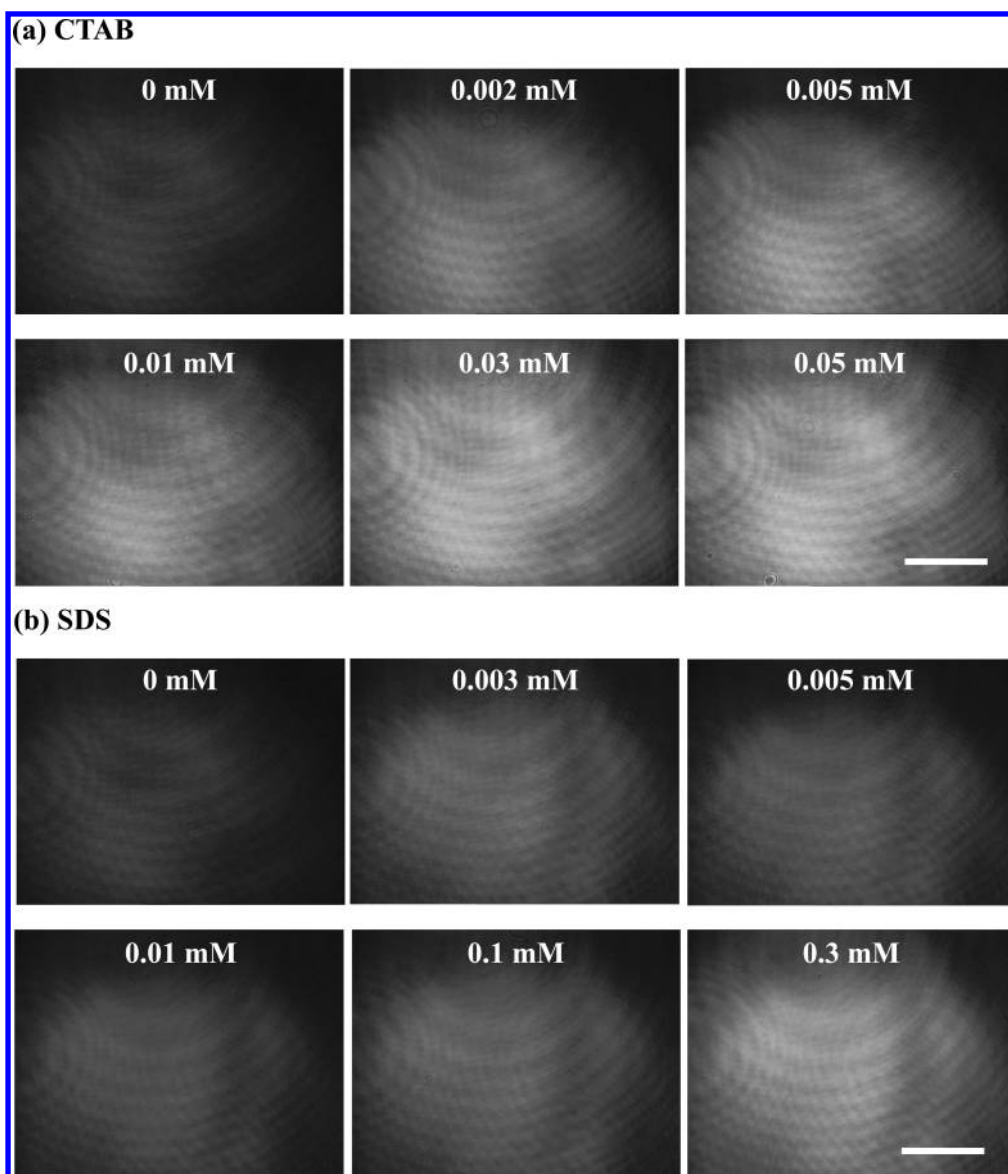
Figure 8. (a) BAM images at different CTAB concentrations under 100 mM NaBr subphase concentration at 298.2 K, where the cmc of CTAB is 0.04 mM, and (b) BAM images at different SDS concentrations under 1000 mM NaCl subphase concentration at 298.2 K, where the cmc of SDS is 0.21 mM. The scale bar represents 100 μm.

Now, the gradual changes in brightness of the BAM images for the solutions studied as a function of the surfactant concentration are shown in Figure 8, a and b, for CTAB and SDS, respectively, where the added salt concentrations are 100 mM NaBr for CTAB and 1000 mM NaCl for SDS. These concentrations are the highest ones used for the surfactant solutions, and therefore, the molecules in the surface layer are the most condensed state in the present study. The above gradual change is similar to that examined for water—ethylene glycol mixture with gradual change in glycol content.[13] The gradual brightness results from the increasing difference in refractive index from that of pure water, 1.333[28] at 298.2 K, due to increasing condensation of the surfactant in the surface layer. By the way, the refractive index of the mother subphase is 1.338[29] and 1.3450[30] for 100 mM NaBr solution and 1000 mM NaCl solution at 298.2 K, respectively.

The elucidation for the gradual increase in brightness can be also done as follows. The bilayer aggregates are positively charged for a cationic amphiphile, while they are negatively charged for an anionic amphiphile. Highly charged aggregates cannot come closer to the air/water interface due to the repulsive image force without added salt.[21] However, the repulsive force is diminished by the presence of added salt in the system, where the force becomes less with more added salt. This might be a strong reason for the increasing brightness with increasing concentration of added surfactant. The explanation can be applied to the case of nonionic surfactant as mentioned above.

3.7. The New Concept of Adsorbed Film of Soluble Surfactants. About 55 years ago, the effect of insoluble monolayer on retardation of water evaporation was intensively studied[31] and the theories were reported in the related papers.[32−34] On the other hand, quite many papers on both insoluble monolayer and the Gibbs adsorbed film have been published. Unfortunately, however, both the above have been independently discussed in fundamental textbooks.[35−38] Nevertheless, schematic illustrations for the monolayer and the adsorbed film have been quite similar. If an adsorbed

film truly locates just at the air/subphase interface, the film should retard the evaporation rate of water as the monolayers do.[39,40] However, there is no retardation at all for three kinds of surfactant solutions.[21]

Indeed, if the air is replaced by an organic liquid as an oil/water interface, soluble amphiphiles can readily concentrate at the oil/water interface, because the concentration at this interface is energetically favorable. However, is the condensation of surfactant at the air/solution interface energetically favorable? The answer should be given from the thermodynamic point of view. It is true that the concentration of amphiphiles really takes place in the interfacial region, judging from the simple fact that the surface tension increases immediately after cleaning the surface by suction of the interfacial region of surfactant solution through a pipet and from other experimental facts on radioactivity.[5−7] Considering the above matters, the molecular condensation as bilayer aggregate is much easier to accept from the free energy point of view. The free energy decrease per CH_2 group for transfer from aqueous bulk to inner micelle, $-(650$ to $720)$ cal mol^{-1} or $-(2.72$ to $3.01)$ kJ mol^{-1}, is larger in magnitude than that to the air/water interface, -625 cal mol^{-1} or -2.61 kJ mol^{-1}.[41] In other words, bimolecular layer formation or bilamellar micellization at some distance below the interface is more preferable to adsorption at the air/solution interface, where the hydrophobic tails contact one another intruding inward from the upper and lower sides instead of intruding into the air by placing the head groups at the surface on both sides, just as a molecular arrangement of phospholipids in a cell membrane. Then, the lamellar surface is positively charged for a cationic amphiphile, while negatively charged for an anionic amphiphile. Highly charged aggregates cannot come closer to the air/water interface due to the repulsive image force, which is also the case for a negative adsorption at the air/solution interface for simple ionic salts, although the surface tension decreases in the former case contrary to the increase in the latter case. Thus, a water layer with a certain depth is formed between the air and the aggregates, which can give rise to the same evaporation rate of water, the same activation energy, and the same BAM image as observed for purified bulk water. On the contrary, the lamellar surface of nonionic aggregates is electrically neutral. Therefore, no repulsive image force acts on the lamellar aggregates, and the aggregates can come closer to the air/water interface still keeping some layers of water molecules, which results in the appearance of the BAM image. The bilamellar aggregate formation can explain the saturation of the surface excess at ca. half cmc, although surface tension decreases with increasing concentration up to the cmc. That is, after completion of the aggregate formation around a half cmc, the concentration of monomeric surfactant keeps increasing above it with increasing corruption of intermolecular interaction among molecular species, where the large bilayer aggregates give rise to almost constant surface excess from a half cmc up to cmc in spite of decreasing surface tension.

Finally, some mention is necessary to answer the question why large aggregates are possible to be formed far below the conventional cmc at a certain distance beneath the air/solution interface. As for this question, the following answer is highly possible. The steric structure of water molecules in the surface layer is quite different from that in the inner bulk. In other words, the molecular structure is weaker than the one in the bulk subphase, and therefore, the aggregate formation of surfactant molecules is more feasible in the surface region than in the bulk at lower concentration than cmc. Therefore, the aggregate formation is more enthalpy driven than micellization in the bulk above the conventional cmc.

4. CONCLUSIONS

The surface tension lowering by an insoluble monolayer at the air/water interface is different in essence from the lowering by condensation of amphiphiles below the interface, where the latter lowering really results from the surface excess as expressed by the Gibbs adsorption isotherm. The former lowering is brought about by condensing insoluble molecules just at the air/subphase interface to a smaller area by an outside force together with a few molecular layers just near the interface, while the latter lowering automatically results from condensation of soluble amphiphiles over many molecular layers in the upper bulk.[13] In addition, it is highly possible that the surface tension lowering due to the surface excess automatically originates from condensation of soluble amphiphiles as large bilamellar aggregates at a certain distance below the air/water interface. This is quite contrary to the conventional concept that an adsorbed film is similar to an insoluble film. The above statements have been substantiated by the present experimental evidence.

The critical concentration for bilamellar aggregate formation can be observed at very low concentrations by a sudden decrease in surface tension versus concentration curve,[42] and by pyrene excimer formation.[25] The corresponding sudden increases in the surface excess and in excimer formation suggest the commencement of the aggregate formation below the air/water interface. The above large bilamellar aggregate formation can explain saturation of the surface excess around a half cmc, although surface tension decreases with increasing concentration up to the cmc. That is, after completion of the aggregate formation around a half cmc, the monomeric surfactant concentration keeps increasing above it with continuing destruction of molecular networks in the upper bulk.[13]

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■ REFERENCES

(1) Gaines, G. L., Jr. *Insoluble Monolayers at Liquid-Gas Interfaces*; Interscience Publishers: New York, 1966.
(2) Ralston, J.; Healy, T. W. *J. Colloid Interface Sci.* **1973**, *42*, 629–644.

(3) Gibbs, J. W. *The Collected Works of J.W. Gibbs*; Longmans: New York, 1928.

(4) Moroi, Y. *Micelles: Theoretical and Applied Aspects*; Springer: New York, 1992; Chapter 8.

(5) Muramatsu, M.; Tajima, K.; Sasaki, T. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1279–1284.

(6) Tajima, K.; Muramatsu, M.; Sasaki, T. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1991–1998.

(7) Defay, R.; Prigogine, I.; Bellemans, A.; Everett, D. H. *Surface Tension and Adsorption*; Longmans: London, 1966; Chapter 7, p 92.

(8) Rusdi, M.; Moroi, Y.; Hilain, T.; Matsuoka, K. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 604–610.

(9) Lu, J. R.; Thomas, R. K.; Penfold, J. *Adv. Colloid Interface Sci.* **2000**, *84*, 143–304.

(10) Tien, H. T. *Bilayer lipid mambrane (BLM): theory and practice*; M. Dekker: New York, 1974, Chapter 3.

(11) Dewar, J. *J. Franklin Inst.* **1919**, *188*, 713–749.

(12) Nakahara, H.; Shibata, O.; Moroi, Y. *Langmuir* **2005**, *21*, 9020–9022.

(13) Nakahara, H.; Shibata, O.; Rusdi, M.; Moroi, Y. *J. Phys. Chem. C* **2008**, *112*, 6398–6403.

(14) Masuda, J.; Nakahara, H.; Karasawa, S.; Moroi, Y.; Shibata, O. *Langmuir* **2007**, *23*, 8778–8783.

(15) Matsumoto, Y.; Nakahara, H.; Moroi, Y.; Shibata, O. *Langmuir* **2007**, *23*, 9629–9640.

(16) Hoenig, D.; Overbeck, G. A.; Möbius, D. *Adv. Mater.* **1992**, *4*, 419–424.

(17) Nakahara, H.; Lee, S.; Shibata, O. *Biochim. Biophys. Acta* **2010**, *1798*, 1263–1271.

(18) Kaganer, V. M.; Möhwald, H.; Dutta, P. *Rev. Mod. Phys.* **1999**, *71*, 779–819.

(19) Adamson, A. W. *Physical Chemistry of Surface*; Interscience: New York, 1967.

(20) Bikerman, J. J. *Physical Surfaces*; Academic Press: New York, 1970.

(21) Moroi, Y.; Rusdi, M.; Kubo, I. *J. Phys. Chem. B* **2004**, *108*, 6351–6358.

(22) Moroi, Y. *Croat. Chem. Acta* **2007**, *80*, 381–394.

(23) Moroi, Y. *Micelles: Theoretical and Applied Aspects*; Springer: New York, 1992; Chapter 4.

(24) Moroi, Y. *J. Colloid Interface Sci.* **1988**, *122*, 308–314.

(25) Humphry-Baker, R.; Grätzel, M.; Moroi, Y. *Langmuir* **2006**, *22*, 11205–11207.

(26) Ikeda, S.; Ozeki, S.; Tsunoda, M. *J. Colloid Interface Sci.* **1980**, *73*, 27–37.

(27) Moroi, Y.; Yamabe, T.; Shibata, O.; Abe, Y. *Langmuir* **2000**, *16*, 9697–9698.

(28) *Landolt-Börnstein Physikalisch-Chemische Tabellen*, 5th ed.; Springer-Verlag: Berlin, Germany, 1923.

(29) Fujio, K.; Ikeda, S. *Langmuir* **1991**, *7*, 2899–2903.

(30) Hosoda, H.; Mori, H.; Sogoshi, N.; Nagasawa, A.; Nakabayashi, S. *J. Phys. Chem. A* **2004**, *108*, 1461–1464.

(31) Archer, R. J.; La Mer, V. K. *J. Phys. Chem.* **1955**, *59*, 200–208.

(32) Barns, G. T. *Adv. Colloid Interface Sci.* **1986**, *25*, 89–200.

(33) Lunkenheimer, K.; Zembarak, M. *J. Colloid Interface Sci.* **1997**, *188*, 363–371.

(34) Clint, J. H.; Fletcher, P. D. I.; Todorov, I. T. *Phys. Chem. Chem. Phys.* **1999**, *1*, 5005–5009.

(35) Hiemenz, P. C. *Principles of Colloid and Surface Chemistry*; Marcel Dekker Inc.: New York, 1986; Chapter 2.

(36) Osipow, L. I. *Surface Chemistry*; Reinhold: New York, 1962.

(37) Adamson, A. W. *Physical Chemistry of Surface*; Interscience: New York, 1967.

(38) Bikerman, J. J. *Physical Surfaces*; Academic Press: New York, 1970.

(39) Rusdi, M.; Moroi, Y. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 919–926.

(40) Rusdi, M.; Moroi, Y. *J. Colloid Interface Sci.* **2004**, *272*, 472–479.

(41) Mukerjee, P. *Micellization, Solubilization, and Microemulsions*; Mittal, K. L., Ed.; Plenum Press: New York, 1977; Vol. 1, p 171.

(42) Motomura, K.; Iwanaga, S.; Hayami, H.; Uryu, S.; Matuura, R. *J. Colloid Interface Sci.* **1981**, *80*, 32–38.