

Examination of Surface Adsorption of Soluble Surfactants by Surface Potential Measurement at the Air/Solution Interface

Hiromichi Nakahara,^{†,‡} Osamu Shibata,^{*,†,‡} Muhammad Rusdi,[§] and Yoshikiyo Moroi^{*,‡}

Division of Biointerfacial Science, Graduate School of Pharmaceutical Sciences, Kyushu University, 3-1-1 Maidashi, Higashi-ku, Fukuoka 812-8582, Japan, Department of Biophysical Chemistry, Faculty of Pharmaceutical Sciences, Nagasaki International University, 2825-7 Huis Ten Bosch, Sasebo, Nagasaki 859-3298, Japan, and Faculty of Education (FKIP), Jambi University, Campus Mendalo Darat, Jalan Jambi-Muara Bulian KM 12, Jambi 36122, Indonesia

Received: November 12, 2007

Surface potential (ΔV) of the air/surfactant-solution interface was measured by using an ionizing ^{241}Am electrode method at 298.2 K, where the effect of the head groups on ΔV was also examined. Hexadecyltrimethylammonium bromide (CTAB) and its homologous head group tetramethylammonium bromide (TAB) were used for examination of a cationic surfactant, sodium dodecyl sulfate (SDS), sodium methylsulfate ($\text{CH}_3\text{-SO}_4\text{Na}$), and sodium hydrogensulfate (NaHSO_4) for an anionic surfactant, and octaethylene glycol mono-*n*-tetradecyl ether (C14E8) and octaethylene glycol (E8) for a nonionic surfactant. For the cationic and nonionic systems, the surface potential of the homologous solutions gradually changed with concentration, whereas that of the corresponding surfactant solutions steeply increased up to 420 mV for CTAB at a concentration far below the critical micelle concentration (CMC), CMC/9, and up to 480 mV for C14E8 at CMC/18. For the anionic system, the surface potential traced a more complex variation with concentration. The above results indicate that the molecular arrangement of CTAB and C14E8 near the interfacial region becomes established at a concentration far below the CMC. The molecular dipole moment at the surface, derived from the surface potential, was also discussed. Change of surface tension with concentration was discussed with change in the surface potential and with preceding observations depending upon the concentrations. Finally, the Brewster angle microscopy (BAM) images of the surfactant solutions below and above the CMC and that of pure water are quite the same in darkness, which strongly indicates no adsorption of the surfactants at the air/solution interface contrary to an insoluble monolayer at the interface. This fact is substantiated by the distinct change of the BAM images in darkness for a small change in refractive index increment of the substrate.

1. Introduction

According to the conventional Gibbs adsorption model, which is a common assumption about the molecular concentration at surfaces, the adsorbed film of soluble amphiphiles is located at the air/solution interface just like an insoluble monolayer, which is illustrated in many textbooks on "Colloid and Interface Science".¹ However, recently, one of the authors has questioned the conventional concept of the above adsorbed film on the basis of the water evaporation rate data from aqueous surfactant solutions.² Since then, additional experimental evidence that differentiates an insoluble monomolecular film at the air/water interface from a surface excess of soluble amphiphile solution has been presented. These observations suggest that the surface excess does not locate at the air/solution interface but at a certain distance below the interface as a bilayer aggregate.² Consequently, a new concept for the surface excess has been presented. This new concept is supported by Brewster angle microscopy (BAM) images,² surface tensions,³ evaporation rates from a liquid mixture,⁴ and surface potentials.⁵ Furthermore, pyrene

fluorescence spectra from SDS solution strongly suggested the presence of organized SDS molecules in the surface region.⁶

The surface tension of an aqueous solution of a simple salt like NaCl increases with increasing the salt concentration due to the negative adsorption according to the Gibbs adsorption equation.⁷ On the other hand, the surface tension of a surfactant solution like sodium dodecyl sulfate (SDS) decreases with an increase in the concentration due to the positive adsorption up to the critical micelle concentration (CMC) and then stays almost constant above it. The point here is that the surface excess remains almost constant over the concentration range from about half CMC to CMC for almost all surfactants that are able to form micelles, although the surface tension steadily decreases with increasing concentration up to the CMC.

The surface potential results from an unequal shift of electric charges in the surface region above the bulk region where the electroneutrality is held. This potential results from the different distributions of positive and negative electric charges in the air/solution interfacial region above the bulk. The value of the surface potential has a high possibility of yielding a measure of the spatial distribution of ionic charges about this air/solution interface.^{8,9} Unfortunately, there are few papers on the surface potential of soluble surfactant solutions,^{5,10} as far as the authors know.

In this study, the surface potential was determined and analyzed for three different kinds of surfactants, having chemi-

* Corresponding author. Phone/fax: +81-956(20)5686. Website: <http://www.niu.ac.jp/~pharm1/lab/physchem/index.html>. E-mail: wosamu@niu.ac.jp (O.S.); yoshimoroi@ybb.ne.jp (Y.M.).

[†] Kyushu University.

[‡] Nagasaki International University.

[§] Jambi University.

cally different head groups, as a function of their concentration, with change in surface tension with concentration, and with the BAM images. The results were compared with that of SDS from a previous study.⁵ The newer ideas for the surface adsorption are shown to be confirmed again, which is quite different from the conventional Gibbs surface excess model at the air/solution interface.

2. Experimental Methods

2.1. Materials. CTAB from Tokyo Chemical Industry Co., Ltd was purified by repeated recrystallizations from acetone. TAB (>99%) and NaHSO₄ of specially prepared reagent grade from nacalai tesque (Japan) were used without further purification. CH₃SO₄Na of analytical reagent grade from Tokyo Chemical Industry, Co., Ltd was used after drying at 333.2 K for 48 h. The purity was confirmed by elemental analysis: C 8.98 (8.96), H 2.23 (2.26), where the values in parentheses (in %) are the calculated ones. Sodium dodecyl sulfate (SDS) from nacalai tesque was purified by repeated recrystallizations from aqueous solution and by ether extraction. The observed and calculated values (numbers in parentheses in %) for the elemental analysis were in satisfactory agreement by weight percentage: C 49.88 (49.98), H 8.69 (8.74). In addition, there was no minimum along surface tension vs concentration curve up to twice CMC. The surface tension at 8.0 mmol dm⁻³ just below the CMC was 39.3 ± 0.1 mN m⁻¹ at 298.2 K. C14E8 with a purity of more than 99% from Nikko chemicals was used without further purification, because the gas chromatograph, attached for purity certification, showed only one sharp peak. The purity was further checked by an elemental analysis: C 63.60 (63.42), H 10.95 (11.01). E8 from Fluka (oligomer purity >95%) was used without further purification. Water used here was triply distilled (surface tension of 71.9 mN m⁻¹ and resistivity of 18 MΩ cm at 298.2 K). The high purity of CTAB, SDS, and C14E8 was also confirmed by surface tension measurements.

2.2. Surface Potential Measurement. Surface potential was measured at 298.2 K by using an ionizing ²⁴¹Am electrode positioned at a certain level 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/water interface.⁵ An aliquot of the concentrated solution for the three kinds of surfactants and the four chemicals representing their corresponding hydrophilic head groups was added stepwise into 50 mL of water 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 a 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 water after fixing the electrode position.⁵ It took about 10 h for one run, 5 h below the CMC and another 5 h above the CMC. The points in the figures are an average of the potential values of 9–15 runs. For SDS, the results were those reported from the previous paper.⁵

2.3. 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, YTS, Japan). 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.¹¹ The experimental error for estimating the surface tension was ±0.05 mN m⁻¹.

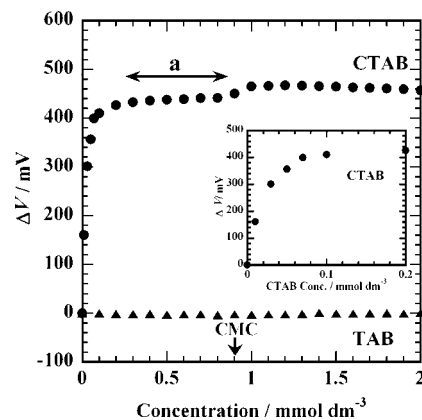


Figure 1. Change of the surface potential (ΔV) with concentration of CTAB and TAB at 298.2 K, where the insert is the potential change for the expanded dilute CTAB region.

2.4. Brewster Angle Microscopy. A Brewster angle microscope, KSV Optrel BAM 300 (KSV, Finland), was used for microscopic observation of the surface. 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). The lateral resolution of the microscope was 2 μ m. The images were digitized and processed to obtain the best quality of BAM pictures. Each image corresponds to the area of 400 μ m × 300 μ m, but a part of the image is presented. 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.

3. Results and Discussion

3.1. Surface Potential of Surfactant Solutions. Figure 1 shows the net surface potential changes of CTAB and TAB as a function of concentration, where the term “net” means that a correction for the distance between the electrode and the surface due to the volume change of the solution is made.⁵ It is quite surprising that the surface potential for TAB remains constant at 0 mV over the whole concentration range examined from 0 up to 2 mmol dm⁻³, which means that the electroneutrality is maintained up to just the air/solution interface or that there is no specific concentration of tetramethylammonium cation or bromide anion in the surface region. On the other hand, the surface potential of CTAB solution steeply increased from 0 up to 420 mV within quite a narrow concentration range from 0 to 0.1 mmol dm⁻³, CMC/9 of CTAB, and then remained almost constant up to the CMC, 0.92 mmol dm⁻³ at 298.2 K determined by surface tension.¹² The large positive potential value results from a larger excess concentration of the cationic group over the bromide ion just at the surface region, which results from the long hydrophobic alkyl-chain attached to the cationic head. In other words, the average center of the positive charges is located closer to the surface than the center of the negative charges. It is quite surprising that such high surface potential in the surface region becomes established at such a dilute surfactant concentration far below the CMC and that the concentration of ammonium cation is brought about by the hexadecyl chain. In addition, the potential suddenly jumped up by ca. 30 mV at the CMC with further increase in the concentration. This increase can be elucidated by disappearance of the bimolecular layer formed below the air/solution interface due to molecular transfer from the bilayer to stable micelles in the bulk.^{2,5,6} In other words, the molecular aggregates below the air/solution interface must depress the surface potential due

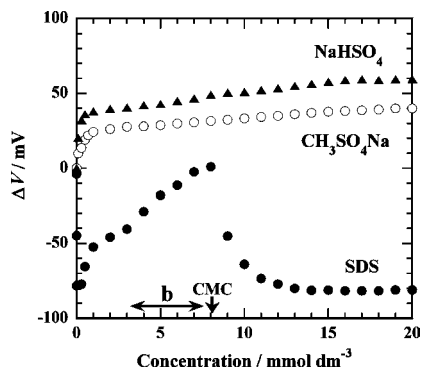


Figure 2. Change in the surface potential (ΔV) with concentration of SDS, $\text{CH}_3\text{SO}_4\text{Na}$, and NaHSO_4 at 298.2 K.

to concentration of counterions in the surface region of the bimolecular layer by electrostatic attraction of the bimolecular aggregates of large opposite charge. When the aggregates start to disappear due to transfer of cationic surfactant molecules from the aggregates to stable micelles in the bulk above the CMC, the surface potential for CTAB must increase. This positive jump was truly observed as was expected. The form of this bimolecular layer or molecular aggregate, whose size and shape are uncertain, is ill-defined but the bilayer is the most promising description according to a previous study.³ Judging from the linear decrease in surface tension up to the CMC (see the section for surface tension), the rearrangement among water and CTAB molecules is taking place in the bulk region where electroneutrality is held, leading to a decrease in surface tension due to decreasing total attractive interaction among these molecules. This is the reason why the surface tension decreases with surfactant concentration, the surface potential being kept constant.

Figure 2 illustrates the changes of the surface potential with concentration of NaHSO_4 , $\text{CH}_3\text{SO}_4\text{Na}$, and SDS, where the potential change for SDS is from the previous publication.⁵ Two analogous chemicals were used to model the corresponding head group to gain further experimental confidence. An important result is the fact that the potential change for SDS could be traced irrespective of the starting concentration, which means that the potential is the equilibrium one and that the decomposition of SDS and the subsequent adsorption of dodecanol are unnecessary to consider here.⁵ The surface potential for $\text{CH}_3\text{SO}_4\text{Na}$ rapidly increased from 0 up to 27 mV within a quite narrow concentration range from 0 to 1 mmol dm^{-3} and then gradually increased up to 40 mV with increasing concentration up to 20 mmol dm^{-3} . A similar change was also observed for NaHSO_4 . This sharp positive change in such a narrow concentration range is quite different from that of TAB, which results from an increased concentration of Na^+ cations in the region just near the interface rather than CH_3SO_4^- . The increase can be explained as follows: an air/water interface is negatively charged, and therefore, Na^+ cations concentrate at the surface more than anions. This change is different from that of NaCl , too, which showed the highest potential value of 20 mV at 20 mmol dm^{-3} .⁵

The surface potential of SDS steeply decreased from 0 down to -80 mV within a very narrow concentration range from 0 to 0.01 mmol dm^{-3} contrary to the positive increase for $\text{CH}_3\text{SO}_4\text{Na}$, which clearly indicates the preferential adsorption of DS^- at the interface resulting in a higher concentration of DS^- anion than Na^+ cation due to the hydrophobic dodecyl-chain analogous to the concentration of hydrophobic CTA^+ ion. Here, the Na^+ ion is completely dissociated from DS^- and stays far away from the concentrated DS^- due to the extremely dilute

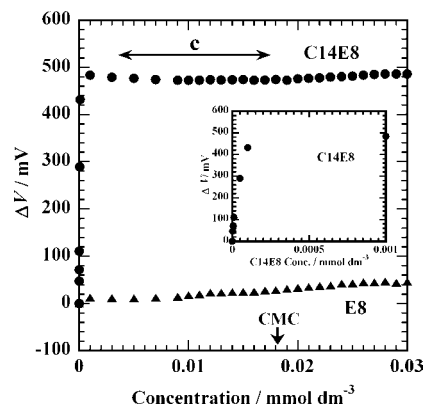


Figure 3. Change of the surface potential (ΔV) with concentration of C14E8 and E8 at 298.2 K, where the insert shows the potential change for the expanded concentration range (0–1 mmol dm^{-3}).

solution. The subsequent increase to -50 mV between 0.1 and 2 mmol dm^{-3} and the following increase to 0 mV over the concentration range from 2 mmol dm^{-3} to the CMC, 8.2 mmol dm^{-3} at 298.2 K,¹² were brought about by the increased population of Na^+ driven by the electrostatic interaction with the negatively charged head groups of the bimolecular layer of DS^- .⁵ The following steep decrease in potential down to -82 mV from the CMC to 10 mmol dm^{-3} can be rationalized from the destruction or disappearance of the bimolecular layer beneath the air/solution interface due to transfer of DS^- anion from the bilayer to stable micelles in the bulk.⁵ With a further increase in concentration, the potential stayed almost constant at -82 mV up to a concentration of 20 mmol dm^{-3} . The potential value is very close to the one at 0.01 mmol dm^{-3} just after the initial steep decrease (-80 mV), which means that the surface is nearly the same at 0.01 mmol dm^{-3} and at the concentrations above the CMC. This similarity was attained after the decomposition of the aggregates beneath the air/solution interface.

The change in the surface potential for SDS is much more complicated than and quite different from that for CTAB. This is because the head group $-\text{SO}_4\text{Na}$ of SDS has a pretty large positive potential, while the head group $-\text{N}(\text{CH}_3)_3\text{Br}$ of CTAB has no contribution to surface potential. In other words, the change in surface potential for CTAB reflects the change in concentration of the surfactant cation, CTA^+ , in the surface region with the concentration.

Figure 3 illustrates the surface potential against concentration for C14E8 and E8. For the E8 solution, the surface potential steadily but quite slowly increased from 0 to 40 mV with increasing concentration up to 0.03 mmol dm^{-3} . The E8 molecule is electrically neutral but forms a structure with the water molecules due to hydrogen bonding. This results in a positive surface potential mainly with the oxygen atoms of the water molecules sitting with the dipole orientated from the bulk to the surface at such dilute E8 solution. In addition, such structure gradually increases in magnitude with E8 concentration. This is opposite to an air bubble in water that is negatively charged due to oxygen atoms of the water molecules located at the air/water interface. On the other hand, the surface potential of C14E8 showed a rapid increase from 0 up to 480 mV within quite a narrow concentration range from 0 to 0.001 mmol dm^{-3} , CMC/18 for C14E8, and then remained nearly constant up to 0.03 mmol dm^{-3} without any jump at the CMC, 1.8×10^{-2} mmol dm^{-3} at 298.2 K.³ It is quite interesting, in this case too, that the surface potential rapidly increased within a very narrow concentration range and stayed constant at ca. 500 mV over a wide concentration range above CMC/18. Indeed, it is quite

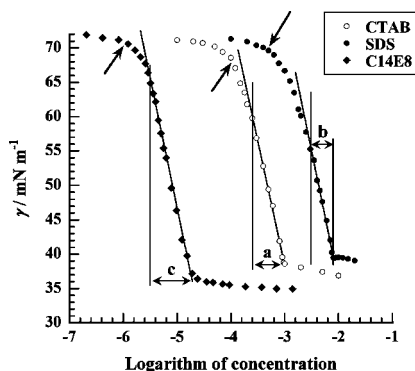


Figure 4. Plots of surface tension against logarithm of concentration for CTAB, SDS, and C14E8, where a, b, and c are the concentration ranges over a constant slope for the plots.

hard to understand the reason behind such a high surface potential, but this fact clearly indicates a certain molecular arrangement in the surface region and its stability irrespective of an increase in C14E8 concentration in the bulk up to the concentration far above the CMC. Namely, the amount of surface adsorption just at the air/solution interface remains constant over the wide concentration range. Contrary to the two previous cases, there exists no change in the surface potential at the CMC for this nonionic surfactant. No change suggests that the bilayer aggregates with no charge disappear without any relation to the surface potential.

3.2. Surface Dipole Moment Analysis. From the surface potential values, a molecular dipole moment perpendicular to the surface (μ_{\perp}) of the surfactant can be evaluated by the following procedure. The surface charge density (σ) can be calculated by using eq 1:¹³

$$\Delta V = \frac{2kT}{e} \ln \frac{\sigma}{\sqrt{2\epsilon\epsilon_v n_0 kT}} \quad (1)$$

where k is the Boltzmann constant, T the absolute temperature, e an elementary charge, ϵ_v the dielectric constant of a vacuum, ϵ the specific dielectric constant, and n_0 the concentration of the electrolyte, and the ionic surfactants are assumed to be completely dissociated. From the molecular surface area ($A = e/\sigma$), the dipole moment can be obtained by the following relationship:¹⁴

$$\mu_{\perp} = \Delta V \epsilon \epsilon_v A \quad (2)$$

A concentration specific to each surfactant is the one at which a stable and constant surface potential is reached (see Figures 1, 2, and 3): 0.10 mmol dm⁻³ for CTAB, 0.25 mmol dm⁻³ for SDS, and 0.0010 mmol dm⁻³ for C14E8, where the concentration at the first minimum surface potential was selected for SDS due to the absence of the constancy. The above three concentrations are indicated by the arrows in Figure 4 for the surface tension of the surfactant solutions. These concentrations are far less than the corresponding CMC, and in addition, the surface tension at these concentrations is close to that of water as is mentioned below. In other words, ionic concentrations in the surface region are significantly different from those in the bulk, whereas the steric structure of water molecules in the bulk remains almost the same at such dilute concentration. The molecular dipole moment thus obtained at the above specific concentration becomes 7.8 Debye (D) for CTAB and -6.3×10^2 D for SDS. As for C14E8, the dipole moment is evaluated by eq 2 as a function of the molecular surface area (A), because the surfactant is nonionic. From the dipole, the distance between

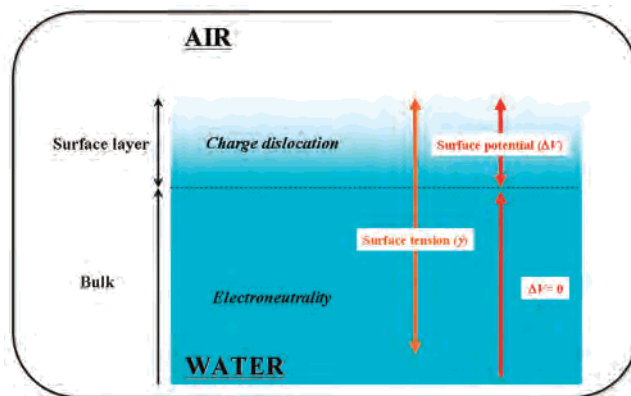


Figure 5. Schematic illustration of domains for surface tension and surface potential.

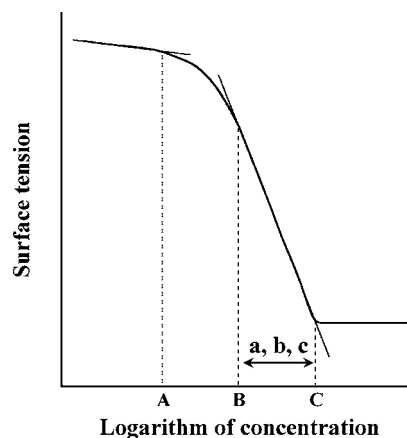


Figure 6. Schematic illustration of surface tension against concentration; A, B, and C are characteristic concentrations for each surfactant (A is the concentration for maximum adsorption of surfactant just at the air/solution interface, B is the maximum surfactant concentration in the bulk at some distance below the surface, and C is the CMC).

+ and - charges becomes 0.17 nm for CTAB, 13 nm for SDS, and 0.42 (0.2 nm²/A) to 2.1 nm (1.0 nm²/A) for C14E8 depending upon the molecular surface area (A). Such a small distance for CTAB is consistent with a surface potential of 0 for TAB. On the other hand, the longer distance for SDS suggests that the affinity of DS⁻ ion for the interface is stronger than that for the Na⁺ ion. The distance 13 nm is plausible, judging from the fact that an average distance between two ions at the concentration of 0.25 mmol dm⁻³ is 14.9 nm for the 1-1 electrolyte. From the values above, a surface region above the bulk of electroneutrality was found to depend very strongly upon the type of chemical species in the bulk.

3.3. Surface Tension of Surfactant Solutions. The change in surface tension with concentration for the three kinds of surfactants was measured to examine whether any relationship between surface potential and surface tension exists or not. The results are shown in Figure 4. The CMC value was found to be 0.92 mmol dm⁻³ for CTAB, 8.2 mmol dm⁻³ for SDS, and 1.8×10^{-2} mmol dm⁻³ for C14E8 at 298.2 K. The CMC values are very close to the reference ones.¹² The concentration region which gives a linear relationship between surface tension and logarithm of concentration is shown by a, b, and c for CTAB, SDS, and C14E8, respectively. These concentration ranges are those for saturation of surface adsorption according to the conventional Gibbs surface excess. These ranges (a, b, and c) are also illustrated in Figures 1, 2, and 3, respectively. Now, it becomes quite clear that surface potential becomes definite far below the concentration for the surface saturation above. In other

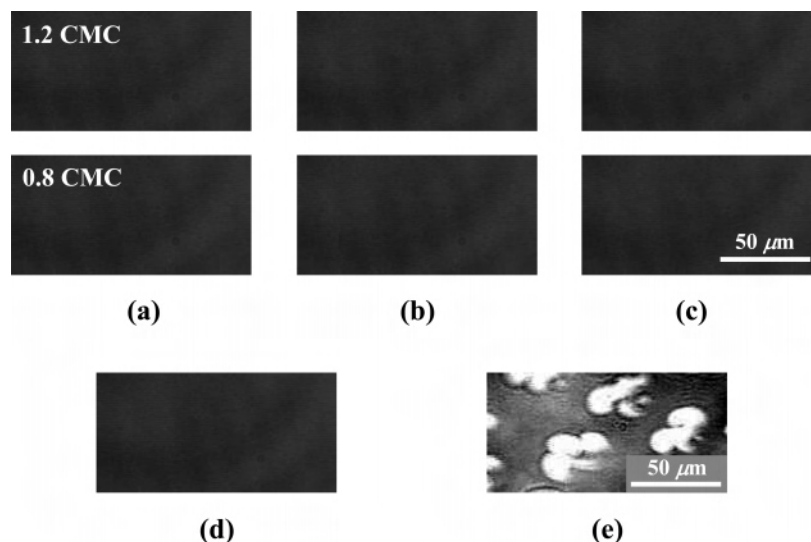


Figure 7. BAM images of CTAB (a), SDS (b), and C14E8 (c) solutions at 0.8 CMC and 1.2 CMC at 298.2 K. (d and e) BAM images respectively for just water and an insoluble monolayer of dipalmitoylphosphatidylcholine (DPPC) at a surface pressure of 13 mN m^{-1} on 0.15 mol dm^{-3} NaCl solution.

words, the decrease in surface tension does not correlate with true surface adsorption just at the air/solution interface. That is, the surface tension is determined not by adsorption of the surfactant molecules at the air/solution interface but mainly by a steric molecular arrangement formed by water and surfactant molecules in many multimolecular layers extending into the bulk of electroneutrality (Figure 5). In other words, a decrease in surface tension results from destruction of this three-dimensional network of water molecules by surfactant molecules over multimolecular layers near the surface region in the bulk. All the while, the adsorbed amount at the air/water interface for the surface potential remains constant. The above results for the surface potential cannot be elucidated by the conventional Gibbs surface excess of a soluble surfactant.

Summarizing the above experimental evidence together with the preceding observations,^{2–6} a change of surface tension with logarithm of concentration for soluble surfactant can be schematically illustrated as the one in Figure 6. The concentration region up to the concentration *A* is the range for adsorption of surfactant molecules just at the air/solution interface, where the adsorption increases with the concentration. At the concentration *A*, a surface potential becomes definite and the surface adsorption is saturated. The above statement is substantiated by the arrows in Figure 4. The concentration range between *A* and *B* is the one for growth of certain aggregates in the bulk at some distance apart below the interface,⁶ where *A* is the concentration for a commencement of the aggregates and *B* is the one for completion, and the aggregates destruct the molecular structure in a bulk much more than the adsorbed surfactants at the surface, resulting in a decrease of the surface tension. Above *B*, the surface tension decreases with increasing concentration due to the above destruction by further increase in surfactant molecules, while the conventional surface excess remains almost constant because of the presence of large aggregates beneath the interface. Above *C*, new aggregates called “micelle” start to form in a bulk and the molecules in the surface aggregates are transferred to the micelles, because the micelles are energetically more stable. This transfer can be seen in a sharp and reasonable change in surface potential at the CMC. Hence, the surface potential stays constant above the CMC as is clear from the results in Figures 1 and 2. For consistency with the above, the bilayer or large aggregates must locate in the electroneutral bulk in Figure 5.

3.4. BAM Observation. Finally, a mention is made of the BAM images for the three kinds of surfactant solutions whose concentrations are 0.8 CMC (below the CMC) and 1.2 CMC (above the CMC) (Figure 7). As is clear from the images, there is no difference among the above six solutions and, in addition, the images are identical with that of pure water. This means that the effective refractive index of the surface of all the surfactant solutions is the same and equal to that of water and that the surface property also remains the same above the CMC. This observation is contrary to that of an insoluble monolayer of DPPC just above the transition pressure whose BAM image indicates the presence of organized molecular arrangement at the air/water interface.² If the soluble surfactant molecules truly locate just at the air/solution interface as the conventional model suggests, the refractive index of the surface region must be different from that of water. To justify our new adsorption model as a bilayer aggregate below the interface, BAM images of a water–ethylene glycol mixture were taken (Figure 8). The gradual changes in brightness or darkness of the BAM images for the solution surface as a function of the ethylene glycol concentration are shown together with the change in refractive index of the mixture and in the ethylene glycol concentration up to 36% in volume. Quite clear differences in the image darkness or brightness can be observed between water and the ethylene glycol solution (a and c in Figure 8), although the change in refractive index between them is only 1.3%. In other words, the theory for the Brewster angle is truly valid. This experimental observation that there is no difference in the darkness in the BAM images between pure water and surfactant solutions at concentrations of 0.8 and 1.2 CMC (Figure 7) clearly indicates that the soluble surfactants are not concentrated just at the air/solution interface like the conventional adsorbed model. This observation also strongly suggests that the adsorbed film of soluble surfactant molecules is quite different from an insoluble molecule at the air/water interface, although many textbooks schematically show an idealized molecular arrangement at the air/water interface for both adsorbed film and insoluble monolayer. It is worth mentioning that some nonionic soluble surfactants present clear BAM images at very dilute concentrations.^{2,15}

In the previous studies,^{2–6} it was found highly possible for ionic surfactants to form a bimolecular layer just like a cell-membrane at a certain distance below the air/solution interface,

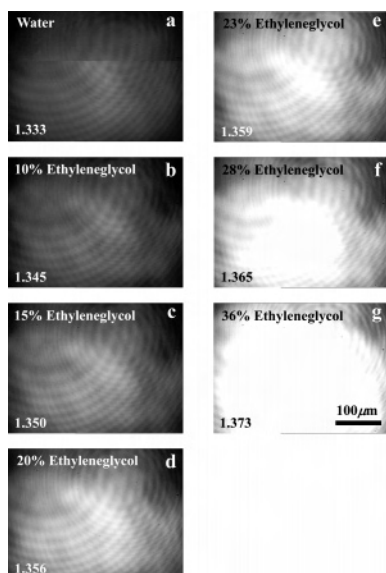


Figure 8. BAM images of a water–ethylene glycol mixture with different ethylene glycol contents (vol %): the value in the lower left corner is the refractive index of the mixture.¹⁸

as judged from the surface excess measurements from the dependence of surface tension on the concentration. In this case, the head groups stay at the bilayer surface with the tail groups intruding inward to the bilayer.² Then, the redistribution of counterions at the large aggregate surface takes place by long-range electrostatic attractive forces between the counterions and the large aggregate, which results in the complicated change in the surface potential up to the CMC for SDS. Above the CMC, however, micelle formation starts in the bulk far below the interface, where the conventional micellar aggregates are energetically more stable than the bilayer aggregates. The large aggregates near the interface will now disintegrate with increasing micellar concentration above the CMC. In other words, the disintegration starts from the CMC and onward, above which only adsorbed surfactant ions and concentrated counterions near the interface determine the surface potential, as is evidenced by the same surface potential as that at 0.01 mmol dm⁻¹.⁵ Further increase in the surfactant concentration only increases the number of micelles in the bulk and does not change the distribution of the ions in the interfacial region. This would be an explanation as to why the surface potential remains constant above the CMC. This change in the surface potential with the surfactant concentration is consistent with experimental data for the evaporation rate of water from surfactant solutions and activation energies.² That is, the evaporation rate of water has no relation with the conventional concept of surface excess² and, at the same time, is truly proportional to the mole fraction of water at the air/solution interface.⁴

To establish a new scientific concept, many experimental observations and data are required to support it. When any new experimental evidence contradicts a conventional concept, the conventional wisdom must be re-examined. In this sense, the following conventional ideas for the negative adsorption for NaCl¹⁶ and the positive adsorption of surfactant molecules at the air/solution interface need to be reevaluated from many aspects.¹⁷

4. Conclusions

Surface potential (ΔV) of the air/surfactant–solution interface was measured by using an ionizing ²⁴¹Am electrode method at 298.2 K, where three types of surfactants, hexadecyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), and octaethylene glycol mono-*n*-tetradecyl ether (C14E8), and the compounds corresponding to hydrophilic head groups were used. Dependence of surface tension on concentration was well related with the surface potential changed with concentration. The BAM images were taken to further examine the surface properties. All the observed results are consistent with a newer concept of surface excess that surfactant molecules are concentrated not at the air/solution interface (the conventional surface excess) but at some distance below the interface as molecular aggregates like bilayer aggregates. The three kinds of observations (the surface potential, the surface tension, and the BAM images) and their concentration changes are very inter-related.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research 17310075 from the Japan Society for the Promotion of Science (JSPS), by Grant-in-Aid for Exploratory Research (17650139) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) Japan, and by Japan-Taiwan Joint Research, which are gratefully acknowledged. This work was also supported by Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists (18.9587) (H.N.).

References and Notes

- (1) Adamson, A. W.; Gast, A. P. *Physical Chemistry of Surfaces*, 6th ed.; Interscience: New York, 1997.
- (2) Hiemenz, P. C. *Principles of Colloid and Surface Chemistry*; Marcel Dekker: New York, 1986.
- (3) Moroi, Y.; Rusdi, M.; Kubo, I. *J. Phys. Chem. B* **2004**, *108*, 6351.
- (4) Rusdi, M.; Moroi, Y.; Hlaing, T.; Matsuoka, K. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 604.
- (5) Rusdi, M.; Moroi, Y.; Nakahara, H.; Shibata, O. *Langmuir* **2005**, *21*, 7308.
- (6) Nakahara, H.; Shibata, O.; Moroi, Y. *Langmuir* **2005**, *21*, 9020–9022.
- (7) Humphry-Baker, R.; Grätzel, M.; Moroi, Y. *Langmuir* **2006**, *22*, 11205.
- (8) Defay, R.; Prigogine, I.; Bellemans, A.; Everett, D. H. *Surface Tension and Adsorption*; Longmans Press: London, Great Britain, 1966; Chapter 7.
- (9) Shibata, O.; Krafft, M. P. *Langmuir* **2000**, *16*, 10281.
- (10) Nakahara, H.; Nakamura, S.; Kawasaki, H.; Shibata, O. *Colloids Surf. B* **2005**, *41*, 285.
- (11) Warszynski, P.; Barzyk, W. W.; Lunkenheimer, K.; Fruhner, H. J. *Phys. Chem. B* **1998**, *102*, 10948.
- (12) Masuda, J.; Nakahara, H.; Karasawa, S.; Moroi, Y.; Shibata, O. *Langmuir* **2007**, *23*, 8778.
- (13) Mukerjee, P.; Mysels, K. *Critical Micelle Concentrations of Aqueous Surfactant Systems*; NSRDS-NBS: Washington, DC, 1971; p 36.
- (14) Davis, J. T.; Rideal, E. K. *Interfacial Phenomena*; Academic Press: New York, 1963.
- (15) Schulman, J. H.; Rideal, E. K. *Proc. R. Soc. London, Ser. A* **1931**, *130*, 259.
- (16) Islam, M. N.; Kato, T. *Langmuir* **2004**, *20*, 6297.
- (17) Ikeda, N.; Aratono, M.; Motomura, K. *J. Colloid Interface Sci.* **1992**, *149*, 208.
- (18) Matsuki, H.; Ikeda, N.; Aratono, M.; Kaneshina, S.; Motomura, K. *J. Colloid Interface Sci.* **1994**, *162*, 203.
- (19) An, S. W.; Lu, J. R.; Thomas, R. K.; Penfold, J. *Langmuir* **1996**, *12*, 2446.
- (20) Landolt-Börnstein *Physikalisch-Chemische Tabellen*, 5th ed.; Springer-Verlag: Berlin, Germany, 1923.