REVIEW

New Adsorption Model — Theory, Phenomena and New Concept —

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Abstract: 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 Langmuir monolayer which is illustrated in many physical chemistry text books on "Colloid and Interface Science". According to many proofs of the experimental results here, the newer idea for the surface adsorption is confirmed and explained, which is quite different from the conventional Gibbs surface excess model at the air/solution interface.

Key words: Gibbs adsorption, Langmuir monolayer; surface tension, surface potential, PM-IRRAS

1 Introduction

On the basis of the traditional 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 a Langmuir 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 solutions²⁾. 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 aggregate²⁾. Consequently, a new concept for the surface excess has been presented. This new concept is supported by Brewster angle microscopy (BAM) images²⁾, surface tensions³⁾, evaporation rates from a liquid mixture⁴⁾, and surface potentials⁵⁾. Furthermore, pyrene fluorescence spectra from SDS solution strongly suggested the presence of organized SDS molecules in the surface region⁶⁾. 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 equation⁷⁾. 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.

In this review, additional experimental evidence that differentiates an insoluble Langmuir monomolecular film at the air/water interface from a surface excess of soluble amphiphile solution has been presented. For example, the surface potential was determined and analyzed for three different kinds of surfactants (CTAB, SDS, and C14E8) having chemically different head groups as a function of their concentration^{5, 8)}, with change in surface tension with concentration, and with the BAM images^{8, 9)}. The newer idea for the surface adsorption is shown to be confirmed, which is quite different from the conventional Gibbs surface excess model at the air/solution interface.

2 Evidence of contradiction for Gibbs adsorption model

2.1 Surface properties

The surface tension (γ) is a function of temperature (T), pressure (P), and chemical potential (μ_i) of component i (the Gibbs–Duhem equation for interface). However, as for

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a system of two phases (air and solution) and three components (surfactant, water, and air), it becomes trivariant under equilibrium according to the phase rule. Then, we have the following Gibbs equation for the surface tension^{10,11}:

$$d\gamma = -s^s dT + \tau^d dP - \Gamma d\mu \quad (1)$$

where s^s , τ^d , and Γ are the excess entropy per unit area at the interfacial layer, the thickness between the two dividing surfaces, and the surface excess of surfactant per unit area, respectively. At constant temperature and pressure, the surface excess of the surfactant (Γ) becomes a function of the surfactant concentration,

$$\Gamma = -\frac{1}{RT} \left(\frac{\partial \gamma}{\partial \ln C} \right)_{T, P} \quad (2)$$

where R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the absolute temperature, and C is the surfactant concentration. The surface tension versus the logarithm of the concentration below the CMC was analyzed by dividing the plot into two parts.

The surface tensions at higher concentrations were analyzed by a linear equation, while those at lower concentrations were done by the second-order equation against the concentration; the slope of the equations was used to determine the surface excess by Eq. 2.

From the surface excess, the molecular surface area (A) at the surface layer can be calculated by

$$A = 1/N_A \Gamma \quad (3)$$

where N_A is Avogadro's number. The temperature dependence of molecular surface area (A) are shown in Fig. 1. The molecular surface area increased with increasing temperature and with decreasing carbon number of C_nE_8 , as

Fig. 1 Temperature dependence of molecular surface area of C_nE_8 just below the CMC.

is usually observed. This result indicates that a longer alkyl chain becomes more closely packed than a shorter one by a stronger attractive interaction between the hydrophobic chains. The important finding is that the molecular surface area is less than the cross-sectional area of the alkyl chain for C16E8 and C18E8. Such small molecular surface areas strongly suggest that the Gibbs adsorption model just at air/water interface is inadequate. This is one of contradictions for the Gibbs adsorption.

2.2 Evaporation from water-ethylene glycol liquid mixture by a thermogravimetric balance

Evaporation rates were determined for water-ethylene glycol (non-volatile) liquid mixtures with different mole fractions by a thermogravimetric balance, where the evaporation rate expressed as $\text{mg min}^{-1}/\text{area}$ was used because of the presence of two kinds of molecular species. The decrease in the mole fraction of water in the liquid with time can be evaluated by the initial weight and the weight loss by evaporation, where the loss at higher mole fractions of water was assumed to be due only to the water molecules evaporated. The rate increased with increasing temperature and decreased with increasing mole fraction of ethylene glycol, almost obeying ideal mixing of the two components, although a small positive deviation was observed over the mole fraction from 0 to 0.5 of ethylene glycol at higher temperatures (Fig. 2)⁵. The positive deviation of evaporation rate suggests (1) a decrease in interaction among water molecules and between water and ethylene glycol molecules or destruction of steric structure of water molecules by intervening ethylene glycol and (2) a higher mole fraction of water molecules in the surface layer than

Fig. 2 Change of evaporation rate from a water-ethylene glycol liquid mixture with the mole fraction of ethylene glycol at different temperatures, where the lines represent the ideal mixing.

in the bulk. The important experimental fact is that the evaporation of water is roughly proportional to the mole fraction of water in the liquid mixture. The deviation from the ideality becomes smaller with decreasing temperature. At any rate, the mole fraction just in the interfacial layer mainly determines the evaporation rate. The decrease in the interaction among the molecules in the system corresponds to higher energy of the system, which results in smaller surface tension of the system.

This can be verified by the negative deviation in the surface tension of a water-ethylene glycol mixture from the ideal line (Fig. 3)¹²⁾. The activation energy of evaporation was determined from the temperature dependence of the evaporation rate, where the energy was an apparent one because the composition of evaporated species was not determined. The activation energy increased with decreasing temperature and with increasing mole fraction of ethylene glycol, where the energy obeyed the ideal mixing at lower temperatures while it positively deviated at higher temperatures. The evaporation rates were examined by surface tension of the liquid mixture (Fig. 3)¹²⁾, but any definite relation between them was not found. Both the evaporation rate and the activation energy were found to be determined mainly by the mole fraction in the surface layer from which the evaporation takes place.

2.3 Pyrene fluorescence spectra

One of the contradictions for the Gibbs adsorption model is clear by pyrene fluorescence spectra. The dependence of pyrene fluorescence spectra on the concentration of sodium dodecyl sulfate (SDS) was observed, where the solution was prepared from water saturated with pyrene. Pyrene fluorescence spectrum has five monomer fluorescence spectral peaks and excimer peak (480 nm : excimer, I_{ex})⁶⁾. The I_1/I_3 values of pyrene fluorescence spectra for

Fig. 3 Change of surface tension (γ) of a water-ethylene glycol liquid mixture with the mole fraction of ethylene glycol at different temperatures¹²⁾.

the bulk solution and the upper meniscus region is the same within experimental error (Fig. 4). It indicates that the fluorescence is from pyrene molecules mainly in the bulk. The I_1/I_3 values remain almost constant at around 1.7 in the aqueous bulk up to the surfactant CMC, although a very small decrease in this value can be seen.

The values of the I_1/I_3 ratio from the bulk solution and from the upper meniscus region in an optical cell were similar but decreased rapidly around the CMC of SDS, indicating that pyrene molecules preferred to be solubilized in the micelles having a lower dielectric constant (Table 1). The fluorescence intensity of the excimer indicated the concentration of pyrene molecules at the air/solution interface or the surface activity of pyrene molecules. In addition, the intensity from the meniscus region is much larger than that from the bulk at the concentrations below the CMC, whereas there was no difference in the intensity between the bulk and the meniscus above 8 mmol dm⁻³ of SDS. The analysis of the fluorescence intensity from the excimer strongly suggests the presence of molecular aggregates that are favorable to the pyrene molecules just like the micelles in the bulk, making them less movable. The extent of pyrene excimer was evaluated by the fluorescence intensity ratio of the spectral peaks at 373 (I_1) and 480 nm (excimer, I_{ex}), I_{ex}/I_1 . The changes of this ratio with SDS concentration are plotted in Fig. 5. The ratios from the meniscus are larger than those from the bulk at SDS concentrations up to the CMC, which means that the chance for pyrene molecules to collide with each other is higher in the surface region than that in the bulk. In addition, the fluorescence intensity from the excimer is more sensitive than that from the monomer, because there is no difference in the I_1/I_3 ratio between the bulk and the meniscus

Fig. 4 An optical cuvette to observe the fluorescence spectra of pyrene molecules in the upper meniscus region (a) and in the bulk (b).

Table 1 Change in the Value of the I_1/I_3 Ratio with SDS Concentration.

SDS concn. mmol dm^{-3}	I_1/I_3 ratio	
	bulk	meniscus
0	1.77	1.74
0.80	1.74	1.70
1.00	1.71	1.69
1.33	1.66	1.60
2.00	1.69	1.56
4.00	1.62	1.62
8.00	1.21	1.28
16.0	1.15	1.14

Fig. 5 Changes in the I_{480}/I_1 value with SDS concentration: (a) for the meniscus and (b) for the bulk.

cus. The I_{ex}/I_1 ratios from the bulk gradually increase to the CMC, although there is one exception at $1.33 \text{ mmol dm}^{-3}$, approximately $\text{CMC}/6$ (Fig. 5). This increase suggests an increase in the probability for pyrene molecules to associate, which is mediated by an increasing concentration of DS^- ions. At concentration of twice the CMC, however, the micellar concentration is much larger than the pyrene concentration and, therefore, the low occupation number of micelles by pyrene results in a low probability of an encounter with another pyrene, leading to a small ratio of 0.06.

2.4 Examination of surface adsorption of soluble surfactants by surface potential measurement at the air/solution interface

The surface potential results from an unequal shift of electric charges in the surface region above the bulk region where the electroneutrality is held; 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 special distribution of ionic charges about

Fig. 6 Apparatus of surface potential measurement. **Fig. 7** 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.

this air/solution interface^{13, 14}. Unfortunately, there are few papers on the surface potential of soluble surfactant solutions^{5, 15}, as far as the authors know.

To elucidate above phenomena more clearly, surface potential (ΔV) measurement of the air/surfactant-solution interface was measured by using an ionizing ^{241}Am electrode method at 298.2 K (Fig. 6), 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 (Fig. 7), sodium dodecyl sulfate (SDS), sodium methylsulfate ($\text{CH}_3\text{SO}_4\text{Na}$), and sodium hydrogensulfate (NaHSO_4) for an anionic surfactant (Fig. 8), and octaethylene glycol mono-*n*-tetradecyl ether

Fig. 8 Change of the surface potential (ΔV) with concentration of SDS, $\text{CH}_3\text{SO}_4\text{Na}$, and NaHSO_4 at 298.2 K.

Fig. 9 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}).

(C14E8) and octaethylene glycol (E8) for a nonionic surfactant (Fig. 9)⁸⁾. For the cationic and nonionic systems (Figs. 7 and 9), 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 CMC, CMC/9 and up to 480 mV for C14E8 at CMC/18. For the anionic system, the surface potential traced a more

Fig. 10 Surface tension (γ) and surface potential ΔV vs concentration of C14E8.

Fig. 11 Schematic illustration of domains for surface tension and surface potential.

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.

2.4.1 Difference between surface tension and surface potential

It becomes quite clear that surface potential becomes definite far below the concentration for the surface saturation above (Fig. 10)⁸⁾. In other words, the decrease in surface tension does not correlate with true surface adsorption just at the air/solution interface (Fig. 11). 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. 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 (Fig. 10). The above results for the surface potential cannot be elucidated by the conventional Gibbs surface excess of a soluble surfactant.

2.5 BAM image

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 just at the air/solution interface contrary to an insoluble monolayer at the interface (Fig. 12)⁸⁾. 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. 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.

2.6 Examination of surface adsorption of cetyltrimethylammonium bromide and sodium dodecyl sulfate

Several pieces of experimental evidence of condensation

of soluble surfactant molecules, CTAB and 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 under high salt concentration 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) image⁹⁾.

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 (Fig. 13).

To establish a new scientific concept, many experimental observations and data are required to support it. When any

Fig. 12 BAM images of CTAB (a), SDS(b), and C14E8(c) solutions at 0.8CMC and 1.2CMC at 298.2K. (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.

Fig. 13 Schematic illustration of the new concept on the surface excess for soluble surfactants in aqueous solution.

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 NaCl^{16, 17)} and for the positive adsorption of surfactant molecules at the air/solution interface need to be reevaluated from many aspects¹⁸⁾. The five kinds of observations (evaporation rate, pyrene fluorescence spectrum, the surface potential, the surface tension, and the BAM images) and their concentration changes are very interrelated¹⁹⁾.

3 Conclusions

The surface tension lowering by Langmuir 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 bulk⁸⁾. 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 Langmuir 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 curve²⁰⁾, and by pyrene excimer formation⁶⁾. The corresponding sudden increases in the surface excess and in excimer formation suggest the commencement of the ag-

gregate formation below the air/water interface. The above large bilamellar aggregate formation can explain a 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 bulk⁸⁾.

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