

## Air/Solution Interface and Adsorption – Solution for the Gibbs Paradox\*

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Several experimental evidences differentiating an insoluble monomolecular film just on the air/water interface from an adsorbed film of soluble amphiphile solution are presented in order to suggest that the adsorbed film is not located at the air/solution interface. The difference between the two films can be observed by evaporation rates of water across the air/solution interface of three kinds of surfactant solutions and across an insoluble film or monolayer, by the corresponding activation energies, and by the kinetic theory of evaporation across the air/solution interface. The difference was further substantiated by the Brewster angle microscopy, BAM, image of the air/water interface. Surface tension *vs.* concentration curve for soluble surfactant solution was divided into three regions to solve the Gibbs paradox, and then the adsorbed film turned out to be concentrated as aggregates at some distance beneath the air/solution interface. The new concept of adsorbed film is consistent with several interfacial phenomena of surfactant solutions.

### Keywords

interface  
adsorption at the air/solution interface  
interfacial tension  
evaporation rate of water  
BAM image

## INTRODUCTION

The present title is not the main research subject pursued for many years by the present author *et al.* Although the subject is quite important to the author who has been studying micellar colloids in surfactant solutions, the knowledge of the subject was mainly gained through hearing. Recently, however, attention has been paid to the subject due to the recent study of evaporation from the gas/liquid interface. No one would throw any doubt on the fact that evaporation is a physical phenomenon taking place just at the gas/liquid interface. The evaporation study from surfactant solutions for several years has made the author draw up a new concept of the surfactant

adsorption at the air/solution interface, which is quite different from the conventional Gibbs adsorption. The author supposes that the new concept introduced here could become a trigger for other surface scientists to examine again whether the conventional concept is correct or not.

One mole of water is only 18 cm<sup>3</sup> in volume at room temperature, in which Avogadro's number of molecules are present. If a water molecule is replaced by a rice grain whose size is 5 mm long, 3 mm wide, and 2 mm high, the rice grains of Avogadro's number pile up to 47.8 km in height over the whole area of Japan (3.78 × 10<sup>5</sup> km<sup>2</sup>) or *ca.* 40 meters high all over the earth. Avogadro's number is such a tremendous number and, in other words, chemistry deals with very small molecular particles. From

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\* Dedicated to Professor Nikola Kallay on the occasion of his 65<sup>th</sup> birthday.

this simple calculation, it seems hard to accept that any change of one or two molecular layers just at the gas/liquid interface would give rise to a big change in the interfacial tension.

The surface tension of water is  $72.0 \text{ mN m}^{-1}$  at  $298.2 \text{ K}$ , which is a physical quantity and, at the same time, a thermodynamic variable determined by water molecules of the order of Avogadro's number. 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 mono-molecular film at the air/water interface can decrease the above surface tension ( $\gamma_0$ ) of water down to  $15 \text{ mN m}^{-1}$  at most, 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 in the water subphase. However, common molecules forming an insoluble monolayer are amphiphilic molecules having a hydrophilic group or groups in them 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, but a certain part of hydrophobic group goes in and out from the aqueous phase quite frequently along with the hydrophilic group, which results in demolition of the steric structure of water molecules in the interfacial layer. By the way, *n*-propanol (C3) and *tert*-butanol (C4) can mix with water at any molar ratio. In other words, a part of 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  $\text{nm}^2$ , the molecules are in the gaseous state and the surface pressure is less than a few  $\text{mN m}^{-1}$ . In that case, surface tension ( $\gamma$ ) or surface pressure ( $\pi = \gamma_0 - \gamma$ ) result from collaboration between an insoluble monolayer and many water layers beneath the insoluble monolayer. As it is well known, surface pressure for the liquid expanded state increases rather slowly with decreasing molecular surface area over the area less than a few times of the cross-sectional area of the hydrocarbon chain of the molecule, while the surface pressure for a solid condensed state steeply increases up to a collapse pressure of *ca.*  $50 \text{ mN m}^{-1}$  with a slight decrease in molecular surface area. This is quite an important characteristic of the insoluble monomolecular film. Such great decrease of surface tension down to  $20 \text{ mN m}^{-1}$  is due to destruction of the steric structure of water molecules over many molecular layers, induced by high dipole moments enforced by collaboration of concentrated hydrophilic groups of insoluble molecules along with the demolition mentioned above.

In other words, the decrease in surface tension by the insoluble monolayer must result from the destruction of steric structure over many layers of water molecules beneath the interface.

As for an adsorbed film of soluble amphiphiles or surfactants, 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 the change of surface tension against concentration for a soluble surfactant. However, the Gibbs adsorption isotherm is factitious for mathematical derivation,<sup>1</sup> and therefore, other adsorption isotherms have been presented.<sup>2</sup> The point is that the molecular surface area thus obtained remains almost constant above *ca.* half of the critical micellization concentration (c.m.c.) of soluble amphiphile solutions. This is the big difference between an insoluble monolayer and an adsorbed film. Indeed, the surface excess amount of soluble amphiphiles has been determined experimentally,<sup>3-5</sup> but the location of adsorbed film could not be definitely and experimentally clarified so far. As for Ref. 5, it is quite clear from the initial statement of this section that taking a few molecular layers out of a solution surface by a microtome technique seems impossible. If possible, the amount of the volume taken out is too small to determine the adsorbed amount of amphiphiles.

As mentioned above, the surface pressure of an insoluble monolayer is very much dependent upon the molecular surface area, while the molecular surface area of adsorbed film is almost the same at concentrations above *ca.* half c.m.c. regardless of surface tension. In addition, a molecular surface area of  $11 \text{ \AA}^2$  was obtained for octaoxylethylene glycol mono-octadecyl ether (C18E8) in our recent surface tension study of the solution,<sup>6</sup> when the Gibbs surface excess was evaluated from the change of surface tension with the concentration. The molecular area is nearly half that of the cross-sectional area of the alkyl chain. On the other hand, the surface adsorption amount in neutron scattering has been standardized by the Gibbs surface excess,<sup>7</sup> which means that the adsorbed amount cannot be verified by neutron scattering.

The above results strongly indicate that an adsorbed film is quite different from an insoluble monolayer or is not localized at the air/solution interface. If surface excess is located just at the interface, the interfacial tension should be less than a few  $\text{mN m}^{-1}$ , judging from the fact that the interfacial tension of a double layer film is  $0.2\text{--}6 \text{ mN m}^{-1}$ , where both sides of the interface are aqueous bulk.<sup>8</sup> This is contrary to the fact that the surface tension of surfactant solution is *ca.*  $40 \text{ mN m}^{-1}$  around c.m.c. The above said can be substantiated by the following fact, too. Black film of a soap bubble is made of a double layer of soap molecules, where both sides of the film are the air gaseous phase, and the duration of the film could be made as long as 95 days by J. Dewar in 1917.<sup>9</sup>

Molecules in air can easily pass through the double layer film, and therefore, the 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 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 at the air/solution interface.

On the other hand, no one can throw any doubt on the fact that evaporation of water molecules takes place at the air/water interface. If the interface is covered by an adsorbed film or by an insoluble monolayer, the water evaporation rate should be retarded and the activation energy of the evaporation should be different from that of water itself at the same time. In fact, the water evaporation rate and the activation energy across an insoluble monolayer are different from those of purified water.<sup>10,11</sup> In contrast, there was no difference in either the rate or the energy between passing through an adsorbed film and just from water surface.<sup>11</sup> This article aims to clarify the difference between the insoluble monolayer and the film adsorbed by water evaporation and activation energy and by other experimental evidences. At the same time, it is important to present the new concept of the surface excess that is quite different from the conventional one.

Certainly, the evaporation rate measurement of water molecules across the air/solution interface covered by amphiphilic molecules is valuable for the basic study of molecular transport across an interface. This can be done by using the remodeled apparatus for thermal gravitational analysis. The activation energy of water evaporation is very useful to see the process through which evaporation takes place. This can be investigated by the temperature dependence of the evaporation rate. The soluble surfactants examined were cationic, anionic, and nonionic to see if there is any difference in the rate between the surfactant species used. The rate was also examined from the viewpoint of molecular surface area of the surfactants derived from the Gibbs adsorption isotherm. The effect of the insoluble monolayer on water evaporation was also examined by using 1-heptadecanol as an insoluble amphiphile. Indeed, these results are quite useful to investigate where the surface excess material is concentrated or what type of a reasonable model should be designed for the surface excess of a surfactant solution. Retardation of water evaporation due to the concentration of surfactant molecules could be evaluated by a change in the activation energy of evaporation. The evaporation rate of liquid molecules should provide useful information on the gas/liquid interface, because evaporation takes place just from the interface. On the other hand, from the viewpoint of the dynamic surface tension study which considers the mechanism of the adsorption process, there

is still uncertainty about the transport of a surfactant molecule from the sub-interface to the interface.<sup>12-15</sup> The several experimental results mentioned below will give a new insight into the conventional amphiphile adsorption 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 in the interfacial region can be reasonably elucidated without any contradiction. Reasonable elucidation of several interfacial phenomena will be presented below so that many readers may accept the new concept of surface excess as much more reliable than before.

### *Interfacial Energy*

The origin of energy or energy zero of a system is the state where both kinetic energy and potential energy are zero, where the whole molecules are infinitely separated and stay there without any movement. Molecules in the 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 liquid molecules becomes, the more stabilized the steric structure of the molecules is or the more energy is required to destruct 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 compared to those in the inner bulk. As for water molecules in particular, each molecule is strongly bound to the surrounding ones by hydrogen bonds, and they are in the energy state of a relatively high negative value. This is the reason why liquid water has higher surface tension than other liquid molecules. For instance, common organic liquids have surface tension of 30–40 mN m<sup>-1</sup> at room temperature, while that of water is twice as much as the above value, 70 mN m<sup>-1</sup>.

As for aqueous surfactant solutions, surfactant molecules are supposed to concentrate in the surface region, to destruct 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 for decreasing surface tension or interfacial tension are called »surface active agents«. 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 an aqueous solution of a simple salt like sodium chloride increases linearly with the salt concentration. The dielectric constant of water is 78.3 at 25 °C, while that of air is one. When an ion in a medium of a higher dielectric constant comes closer to another

medium of a lower one, a charge of the same sign and the same magnitude as the ion is formed in the latter medium at the symmetrical position to 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«. Contrary to that, 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 negative adsorption. It is often said that 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 rather stupid. 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 to say that the negative adsorption must lead to an increase in surface tension with concentration. An increase in surface tension results from the following: 1) the dissociated ions form hydrated ions with several water molecules, 2) the positive and negative hydrated ions form a 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 the area of the air/solution interface.

#### Evaporation Rate of Water and Its Activation Energy

*Evaporation Rate Measurement.* – The apparatus was modified from the usual thermogravimetric balance (Rigaku

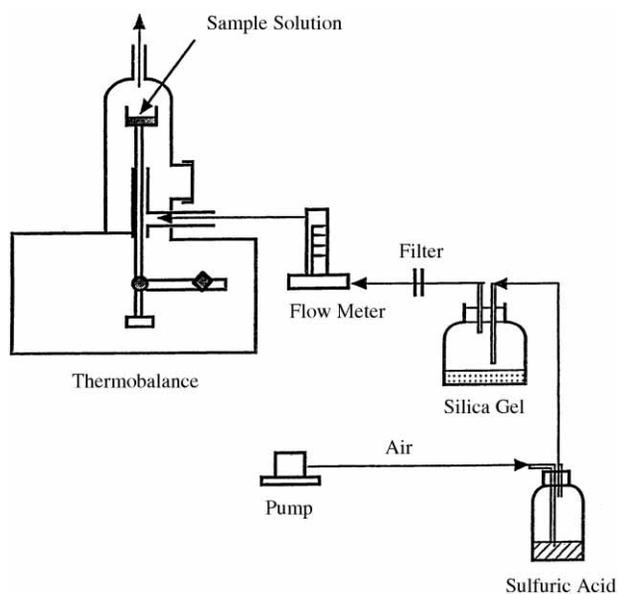


Figure 1. The apparatus used for evaporation rate measurement.

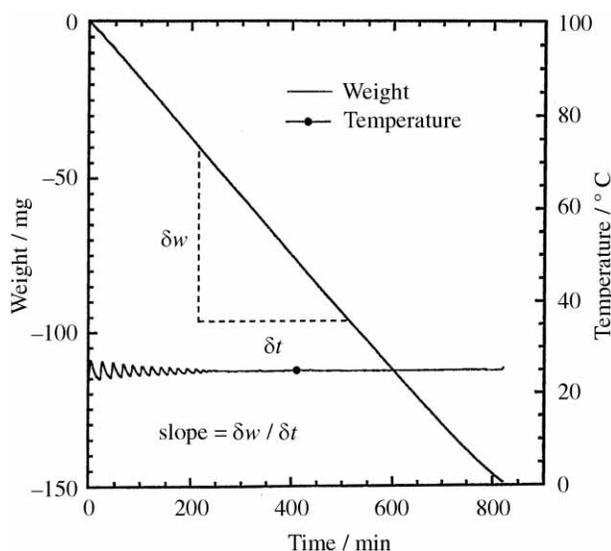


Figure 2. Typical change of weight with time for evaporation across C17-OH monolayer.

Thermo Plus 2), where the sample pan had a large area of 0.739 cm<sup>2</sup> to reduce the edge effects as much as possible.<sup>16</sup> A constant volume (150  $\mu$ L) of liquid sample was pipetted into a shallow platinum pan for thermogravimetric measurement, where the height from the surface of the liquid to the top of the pan was 0.480 cm (Figure 1). Air moisture was completely removed by passing it through concentrated sulfuric acid and then storing over dried silica gel. Then, the dry air was passed two times through a filter of pore size 0.22  $\mu$ m (Millipore, SLGV025LS) to remove dust, and the flow rate was controlled by a flow meter with a needle bulb.<sup>10</sup> The apparatus monitors the change in weight as a function of the temperature with time (Figure 2). The temperature was controlled within  $\pm 0.1$  °C throughout the run except for the initial stabilization period of less than 3 h at 25 °C. This stabilization period became shorter with increasing temperature, less than 30 minutes at 60 °C. The experimental reproducibility was such that the weight loss with time could trace a line for the same sample. Such high reproducibility is sufficient to estimate the activation energy of evaporation by the rate change with temperature.

The run was started without allowing for thermal equilibrium with the furnace temperature because of the small thermal mass of the sample. For the 1-heptadecanol sample (C17-OH), purified water with a tiny solid particle of C17-OH placed on the surface was kept at 100 % relative humidity for 1 day in the pan. This procedure served to allow the spreading monolayer of C17-OH to be in equilibrium with the solid phase prior to starting the run.

*Evaporation Rate and Its Activation Energy.* – Two surfactant groups were used in this research, *i.e.*, water-soluble surfactants and an insoluble surfactant. Soluble sur-

Table I: Evaporation rate of water across air/surfactant solution interface

System	Initial concentration	MSA <sup>(a)</sup> / nm <sup>2</sup>	Evaporation rate / 10 <sup>-7</sup> mol s <sup>-1</sup> cm <sup>-2</sup>							
			298.2 K	303.2 K	308.2 K	313.2 K	318.2 K	323.2 K	328.2 K	333.2 K
H <sub>2</sub> O	–	–	3.26	4.25	5.70	7.71	10.1	13.1	17.0	21.8
SDS / H <sub>2</sub> O	0.5 c.m.c.	–	3.18	–	5.85	–	10.0	–	17.1	–
	1.0 c.m.c.	0.41	3.13	–	5.86	–	10.2	–	17.1	–
C8-TAC / H <sub>2</sub> O	0.5 c.m.c.	–	3.13	–	5.60	–	10.1	–	16.8	–
	1.0 c.m.c.	0.41	3.09	–	5.86	–	10.1	–	17.0	–
MEGA-10 / H <sub>2</sub> O	0.5 c.m.c.	–	3.27	–	5.75	–	10.1	–	16.7	–
	1.0 c.m.c.	0.34	3.21	–	5.70	–	9.90	–	16.8	–
C17OH / H <sub>2</sub> O	–	0.22	2.39	3.47	4.76	6.67	9.07	11.9	15.6	20.1

(a) Molecular surface area at 298.2 K

factants were *N*-(1,1-dihydroperfluoro-octyl)-*N,N,N*-trimethylammonium chloride (C8-TAC),<sup>17</sup> sodium dodecyl sulfate (SDS), and *n*-decanoyl-*N*-methylglucamide (MEGA-10) for cationic, anionic, and nonionic surfactants, respectively. The insoluble surfactant was 1-heptadecanol (C17-OH). Their high purity was confirmed by elemental analysis. The solutions were examined at two initial concentrations, a half of and just below the c.m.c. The molecular surface area at the interface was derived from the surface excess by the surface tension – concentration curve using the Gibbs equation. As given in Table I, the molecular surface area occupies more than 80 % of the surface, even when molecules stand vertically against the surface (C8-TAC). As for another nonionic surfactant (octaethylene glycol mono-octadecyl ether, C18E8), the molecular surface area becomes 0.11 nm<sup>2</sup> from surface excess that corresponds to half the cross-sectional area of the alkyl-chain, which suggests the surfactant condensation as a bi-molecular lamellar layer.<sup>6</sup> The Gibbs surface excess is an excess amount obtained by integration over the range from inner bulk to the surface and, therefore, is not confined to the interface. Hence, there is no necessity to place the surface excess just at the air/solution interface. In most surface chemistry textbooks, however, the surface excess is said to be located just at the interface. If the surface excess or the adsorbed film is really located just at the air/solution interface, the evaporation rate of water from the surfactant solutions and the corresponding activation energy should be different from those of purified water itself. Fortunately or unfortunately, however, both the rate and the energy are the same within the experimental error for the surfactant solutions and purified water (Table I). A more detailed description will be given below.

An example of the changes of weight and temperature with time is given in Figure 2. The evaporation rate ( $k$  in mol s<sup>-1</sup> cm<sup>-2</sup>) was determined by the slope for the weight against time after the initial shift of temperature. The temperature dependence of the evaporation rate is shown in Figure 3. Logarithm of the  $k$  values against the

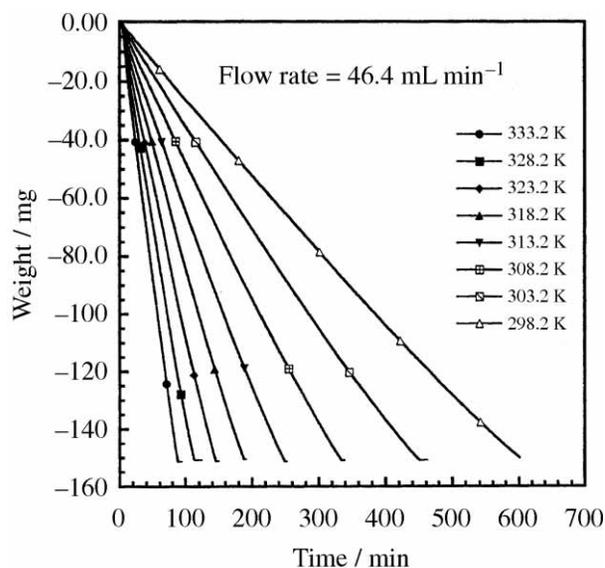
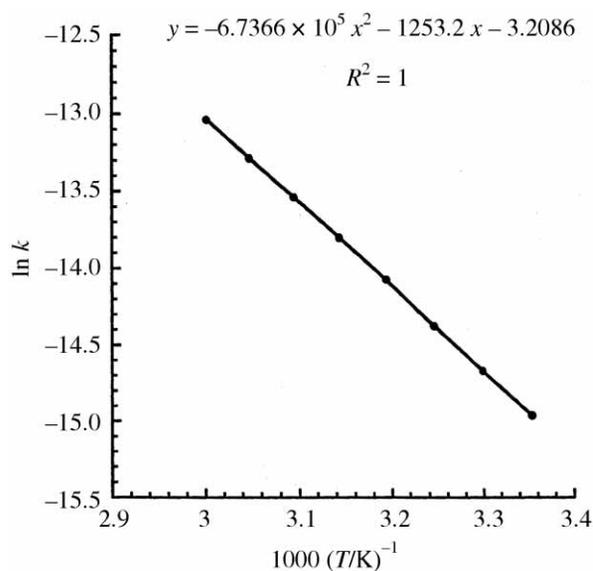


Figure 3. Evaporation rate of water across air/water interfaces at different temperatures.

Figure 4. Plots of  $\ln k$  vs.  $T^{-1}$  for water evaporation just from purified water:  $y = \ln k$  and  $x = T^{-1}$ .

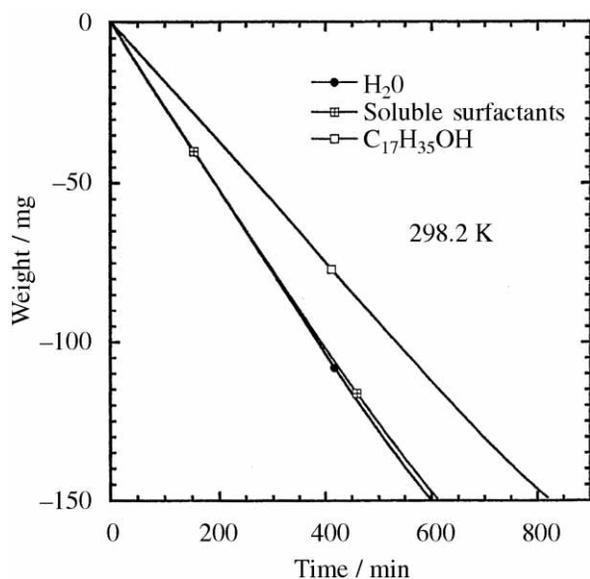


Figure 5. Evaporation rate of water across the air/water interface for three types of interfaces.

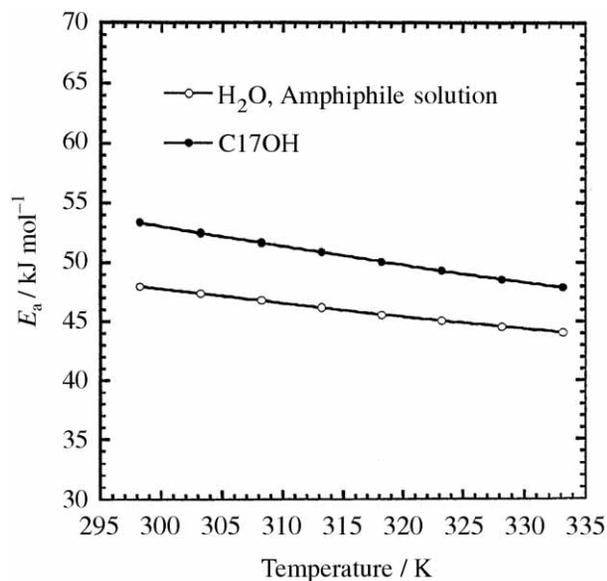


Figure 6. Dependence of the activation energy of water evaporation on temperature for purified water, amphiphile solutions, and water covered by the insoluble monolayer of C17-OH.

inverse of temperature (Figure 4) leads to the activation energy of water evaporation from the slope at the corresponding temperature.

Dependencies of the evaporation rate on temperature and concentration are given in Table I and it becomes quite evident that there is no clear difference in the  $k$  value between the three surfactant solutions and just water. On the other hand, 1-heptadecanol formed an insoluble monolayer, a solid condensed film at the air/water interface in equilibrium with the solid, which was confirmed by the pressure-area curve at 30 °C. The evaporation rate across the insoluble monolayer is clearly slower than those

of the four other liquids (Figure 5) and, at the same time, the activation energy is higher than those of the other liquids (Figure 6). These results clearly indicate that the monomolecular film is really present at the air/water interface and that the free surface available to water evaporation diminishes and more energy is required to cross the film. Judging from the molecular surface area of 0.22 nm<sup>2</sup> for C17-OH and from the results in Figures 5 and 6, almost all activation energy must be consumed to break hydrogen bonds between water molecules. The decrease in the activation energy with temperature for the monolayer is similar to that of water, but the slope is steeper for the former than for the latter. These facts suggest that the hydrogen bonding becomes weaker with increasing temperature and that, at the same time, the transport across the insoluble monolayer becomes more feasible due to increased movement of insoluble molecules at the interface.

*Theory of Evaporation Rate Across the Air/Solution Interface.* – Evaporation is a material flow or a flux ( $J$ ) across a gas/liquid interface and is closely connected with the following three processes. First, molecular diffusion through a stagnant layer above a liquid is rate-determining in an experimental geometry. Second, there is a significant energy barrier for molecules to leave a vapor/liquid interface. Third, evaporation of a volatile species from a multi-component liquid mixture may generate a concentration gradient within the liquid, and therefore, the gradient may be another rate-determining factor for mass transfer within the liquid.<sup>18</sup>

The material flow rate ( $J$ ) at the gas/liquid interface is definitely determined by the concentration profile of the material in the interfacial region. Namely, this is given by Fick's first law:<sup>19</sup>

$$J = -D^l \left( \frac{\partial c^l}{\partial x} \right)_{x=0} = -D^g \left( \frac{\partial c^g}{\partial x} \right)_{x=0} \quad (1)$$

where  $D^l$  and  $D^g$  are the diffusion coefficients of material in the liquid phase and in the gas phase, respectively, and  $\partial c / \partial x$  is the concentration gradient. Eq. (1) represents the continuity of material flow and, at the same time, the flow rate is equal to the evaporation rate ( $k$ ). Based on the kinetic theory of diffusion,<sup>20</sup> the self-diffusion coefficient  $D^g$  of gas molecules is given by:

$$D^g = \frac{1}{3} \lambda \bar{v} \quad (2)$$

where  $\lambda$  is the mean free path of molecules ( $1/(\sqrt{2}\pi N d^2)$ ) and  $\bar{v}$  is the average speed of molecules ( $\sqrt{8RT/\pi M}$ ). Then,  $D^g$  is given by the following equation:

$$D^g = \frac{2}{3\pi^{3/2}N} \sqrt{\frac{RT}{Md^4}} \quad (3)$$

where  $N$  is the number of molecules per unit volume,  $d$  is molecular diameter, and  $R$ ,  $T$ , and  $M$  are the gas con-

stant, absolute temperature, and molecular mass, respectively. Eq. (3) cannot be applied to evaporation as it stands, although it is reasonable. However, it is quite possible to rewrite Eq. (3) as  $D^g = K\alpha(T)\sqrt{T}$ , where  $\alpha(T)$  is a function of temperature. On the other hand, an average concentration gradient in a stationary state for the gaseous phase is supposed to be given by:

$$\left(\frac{\partial c^g}{\partial x}\right)_{x=0} = \frac{c_v - c_{eq}}{l} \quad (4)$$

where  $c_{eq}$  is the concentration just above the interface, which is proportional to the saturated equilibrium vapor pressure ( $P^{eq}$ ) and  $c_v$  is the concentration at a distance  $l$  above the interface. If  $l$  is the distance at which  $c_v$  can be set zero, the flow rate or the evaporation rate ( $k$ ) becomes the following equation:

$$k = K\alpha(T)\sqrt{T} \frac{P^{eq}}{l} \quad (5)$$

with

$$K = 2R^{1/2} / (3\pi^{3/2} M^{1/2}) \quad (6)$$

$$\alpha(T) = \frac{1}{Nd^2} \quad (7)$$

where  $K$  is the constant irrespective of experimental conditions, while the rest of the right hand side of Eq. (5) depends on experimental conditions. The  $l$  value obtained from the reference  $D^g$  value ( $0.242 \text{ cm}^2 \text{ s}^{-1}$  at  $25^\circ \text{C}$  for water molecule)<sup>21</sup> and from the water evaporation rate was calculated to be  $0.99 \text{ cm}$ , which is quite reasonable judging from the size of the evaporation pan. If the logarithm of Eq. (5) is differentiated with respect to inverse temperature, one obtains the following equation:

$$\frac{d \ln k}{d(1/T)} = \frac{d \ln P^{eq}}{d(1/T)} + \frac{1}{2} \frac{d \ln T}{d(1/T)} + \frac{d \ln \frac{\alpha(T)}{l}}{d(1/T)} \quad (8)$$

Finally, the equation for the activation energy ( $E_a$ ) results:<sup>11</sup>

$$E_a = \Delta H_{vap} + \frac{RT}{2} - R \left\{ \frac{d \ln \beta(T)}{d(1/T)} \right\} \quad (9)$$

with

$$\beta(T) = \frac{1}{Nd^2 l} \quad (10)$$

$$\frac{d(\ln P^{eq})}{d(1/T)} = - \frac{\Delta H_{vap}}{R} \quad (11)$$

where  $\Delta H_{vap}$  is the enthalpy change for vaporization and  $\beta(T)$  is a function of temperature. According to Eq. (9),  $E_a$  value becomes larger than  $\Delta H_{vap}$  just by  $RT/2$ , when  $\beta(T)$  is independent of temperature.<sup>10</sup>

In the present study, it is quite instructive to know the concentration profile of water molecules in the inter-

facial region. Fick's differential equation for the water phase and for the gaseous phase is given by the following relations (12) and (13), respectively:<sup>22</sup>

$$\frac{\partial c}{\partial t} = D^l \frac{\partial^2 c}{\partial x^2} \quad \text{for liquid phase } (x < 0) \quad (12)$$

$$\frac{\partial c}{\partial t} = D^g \frac{\partial^2 c}{\partial x^2} \quad \text{for gas phase } (x > 0) \quad (13)$$

where  $D^l$  and  $D^g$  are the diffusion coefficients for a liquid phase and a gaseous phase, respectively, as mentioned above.

The initial conditions are  $c = c_0$  for  $x < 0$  and  $c = 0$  for  $x > 0$  at  $t = 0$ .

Continuity of flow must satisfy the following relation:

$$D^l \left(\frac{\partial c}{\partial x}\right)_{x=0}^l = D^g \left(\frac{\partial c}{\partial x}\right)_{x=0}^g \quad (1')$$

The solutions to the above relations are:

$$c = c_0 \left\{ 1 - \frac{\kappa \sqrt{D^g}}{\kappa \sqrt{D^g} + \sqrt{D^l}} \left[ 1 + \operatorname{erf} \left( \frac{x}{2\sqrt{D^l t}} \right) \right] \right\} \quad \text{for } x < 0 \quad (14)$$

$$c = c_0 \frac{\kappa \sqrt{D^l}}{\kappa \sqrt{D^g} + \sqrt{D^l}} \left[ 1 - \operatorname{erf} \left( \frac{x}{2\sqrt{D^g t}} \right) \right] \quad \text{for } x > 0 \quad (15)$$

where

$$\frac{(c^g)_{x=0}}{(c^l)_{x=0}} = k$$

Flux at interface:

$$J = -D^g \left(\frac{\partial c}{\partial x}\right)_{x=0}^g = \frac{c_0 \kappa \sqrt{D^l} \sqrt{D^g}}{\kappa \sqrt{D^g} + \sqrt{D^l}} \times \frac{1}{2\sqrt{t}} \quad (16)$$

The concentration profile of water derived from the above relations is shown in Figure 7.

As can be seen from the figure, the concentration change can be observed within the range of a few times the root-mean-square (*rms*) displacements. If the concentration profile was disturbed by the presence of surfactant molecules, the evaporation rate of water would change. In other words, the concentration profile of water molecules should be the same if the water evaporation rate remains the same even for an aqueous surfactant solution.

On the other hand, the concentration profile of water molecules in the aqueous subphase below an insoluble monolayer at the air/water interface is quite the same as that in the bulk water phase, when no evaporation of water takes place or vapor is under the saturation pressure. This is because amphiphiles in the monolayer are insoluble in the aqueous bulk and because the chemical

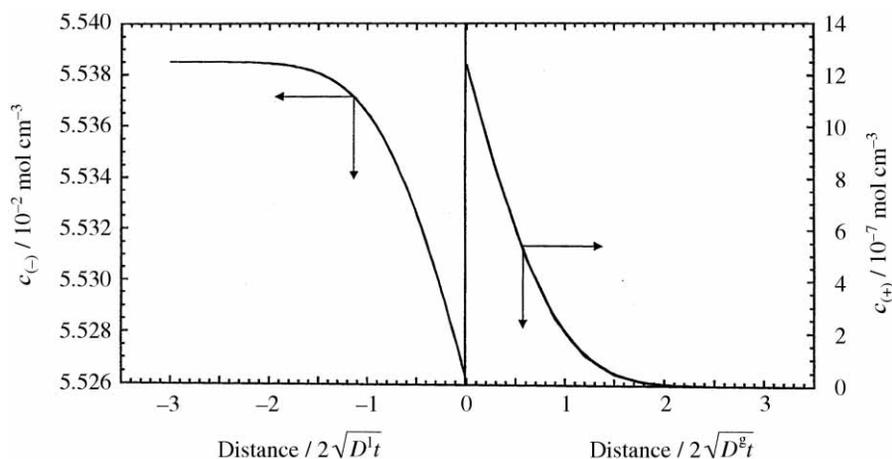


Figure 7. Concentration profile of water molecules in the interfacial region;  $D^l = 2.28 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ,  $D^g = 2.19 \times 10^{-1} \text{ cm}^2 \text{ s}^{-1}$ .

potentials are the same throughout the phases under equilibrium. This is quite different from the concentration profile of water molecules in the soluble surfactant solution around the interface, because the soluble surfactant molecules are concentrated around the interface and, in addition, the concentrated surfactant molecules below the interface are in dynamic equilibrium with those in the bulk subphase during the life time of a micro-second. When the evaporation of water molecules starts, the concentration profile of water molecules becomes different from that of no vaporization or under the saturated vapor pressure. If the presence of the insoluble monolayer at the interface does not retard the evaporation rate of water, as is the case of n-tridecanol monolayer,<sup>10</sup> the concentration profile of water molecules should be almost the same as that of just bulk water itself. At the same time, the activation energy also remains almost the same. This means that the energy to break hydrogen bonds between water molecules for their evaporation is so large that the presence of the monolayer of shorter molecules has little effect on both the evaporation rate and the activation energy. However, the molecules in the monolayer become longer, water molecules have to pass through a longer hydrophobic region for their evaporation and, therefore, the evaporation rate becomes slower and the activation energy becomes larger, as is the case of n-alkanols longer than n-tridecanol.<sup>10</sup> In this case, of course, the concentration profile of the water molecules becomes different from that of just water.

### BAM Image

As said above, the concentration profile of water molecules is illustrated for the steady state of evaporation in Figure 7. The concentration gradient determines the material flux and, therefore, surfactant molecules do not disturb the gradient according to the observations mentioned above. In other words, the surfactant molecules are not supposed to be present just near the air/solution inter-

face. In addition, evaporation in the steady state is very close to the thermodynamic equilibrium state, because it takes almost ten hours for 150  $\mu\text{L}$  water to evaporate (Figure 5). In order to verify this fact, the Brewster angle microscopy (BAM) image of the air/solution interface was examined. BAM image reflects the difference in the refractive index between air and interfacial aqueous layer using polarized light perpendicular to the interface.<sup>23</sup> The Brewster angle is  $53.1^\circ$  at  $25^\circ \text{C}$  just for the air/water interface, where the BAM image is only black due to no reflection from the interface.

A Brewster angle microscope (Nippon Laser Electronics Labo., NL-EMM633) was placed above the surfactant solutions whose concentration was just below c.m.c. and above the insoluble monolayer under the equilibrium spreading pressure. Initially, the angle of illumination was adjusted to the Brewster angle to minimize the light reflected from the water surface. The dark image means that most of the light illuminated onto the water surface does not reflect from the surface. If there is a condensed layer of amphiphiles, more light is reflected from the surface and bright images can be observed. The images were taken with a CCD camera and recorded on videotape by using a video system (video recorder, video monitor and video printer). The recorded BAM images were transferred to a computer using analysis software and processed. These procedures were conducted at room temperature.

Dark BAM images of surfaces for just water and three surfactant solutions at the c.m.c. are illustrated in Figure 8a, where nothing is observed on the surfaces. In addition, there are no differences between the four samples in image darkness, either. This fact strongly suggests no condensation of soluble surfactants just near the surface. However, for MEGA-10 solution only, when it was left for one hour or longer under an aerobic atmosphere, some structures were observed on small areas of the surface (Figure 8b). On the other hand, distinct structures of mo-

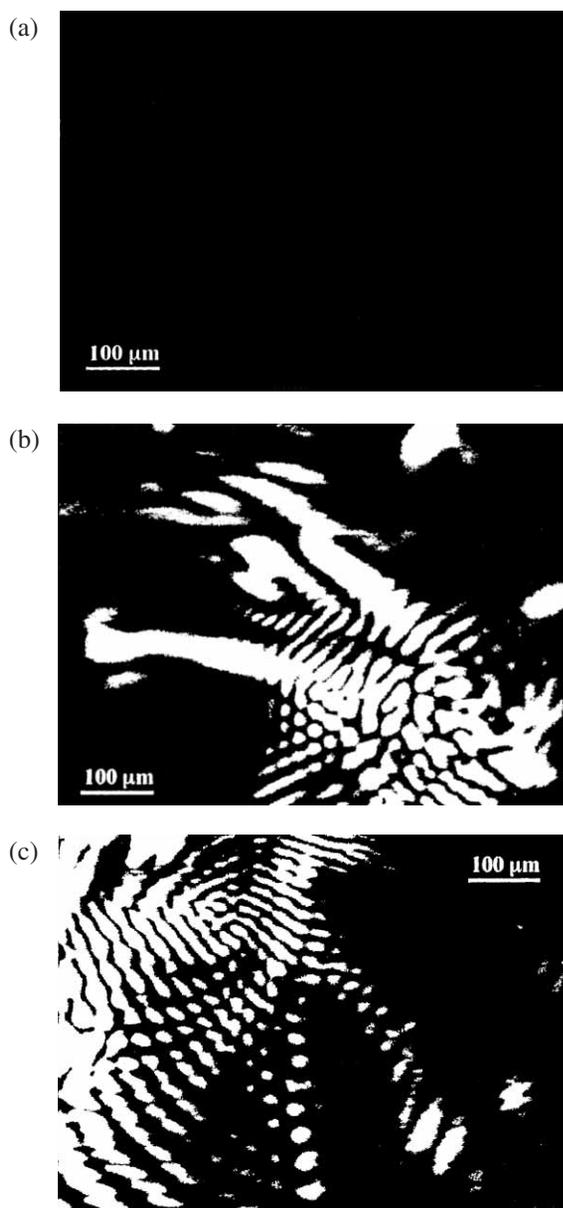


Figure 8. BAM images for just water and surfactant solutions of C8-TAC, SDS, and MEGA-10 at the c.m.c. (a), BAM image of some parts of MEGA-10 solution (b), and BAM image of the insoluble monolayer of C17-OH (c).

lecular assemblies were observed over the whole surface of the insoluble monolayer. The C17-OH monolayer was spread either from a chloroform solution or from the solid placed on water surface. For the latter case, the BAM image was taken one day later, which means that the monolayer was under an equilibrium spreading pressure ( $\pi$ );  $\pi = 41 \text{ mN m}^{-1}$  at 298.2 K.<sup>24</sup> The images of C17-OH monolayer spread by both methods were quite similar (Figure 8c). The bright images and their structure indicate an organized assembly of islands of C17-OH molecules at the surface, which are quite different from those for the surfactant solutions. The structure indicates that the molecules are not homogeneously dispersed at the surface.

The apparent absence of amphiphiles at the air/solution interface based on the water evaporation rate was also substantiated by the absence of BAM images. A BAM image catches the light reflected from the focal plain. A BAM image over several nanometers depth can be taken clearly, only when there is a difference in the refractive index around the focal plain. In fact, a BAM image can be observed for an insoluble monolayer also in the liquid expanded state, although it is not as clear as that in the solid condensed state. The surface excess corresponding to a molecular surface area of *ca.*  $0.40 \text{ nm}^2$  is representative of the liquid expanded state of the insoluble monolayer. However, no BAM image for the ionic amphiphiles was observed for a similar molecular surface area from the surface excess,  $0.34\text{--}0.41 \text{ nm}^2/\text{molecule}$ .<sup>6</sup> This difference can be elucidated by the aggregate formation of the surfactants at a certain distance beneath the air/solution interface, which is mentioned in more detail later.

The aggregates are 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 of negative adsorption for ionic salts. Electrostatic force is a long-range force. Thus, a water layer of 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. On the contrary, the non-ionic aggregates are electrically neutral. Therefore, no repulsive image force acts onto 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.

#### Other Interfacial Phenomena

A small air bubble in purified water moves to the positive pole when electric voltage is applied to water, which means that the air/water interface is negatively charged. The negative charge is due to the orientated arrangement of oxygen atoms of water molecules toward air. The same movement is also the case of a cationic surfactant (*N*-alkylammonium chloride) solution. This fact clearly indicates that the water molecules keep their original structure at the interface and that the cationic surfactant molecules are not concentrated at the air/solution interface at the same time.<sup>25</sup>

Another interesting experimental fact can be seen for polyelectrolyte solution.<sup>26</sup> Figure 9 illustrates the changes of surface tension and electromotive force (emf) with SDS concentration added to the cationic polyelectrolyte solution, where a homopolymer of diallyldimethylammonium chloride was used as the polyelectrolyte. As for emf, the emf values steeply decrease when the SDS concentration comes closer to saturation and never increase again, because  $\text{DS}^-$  concentration increases with increas-

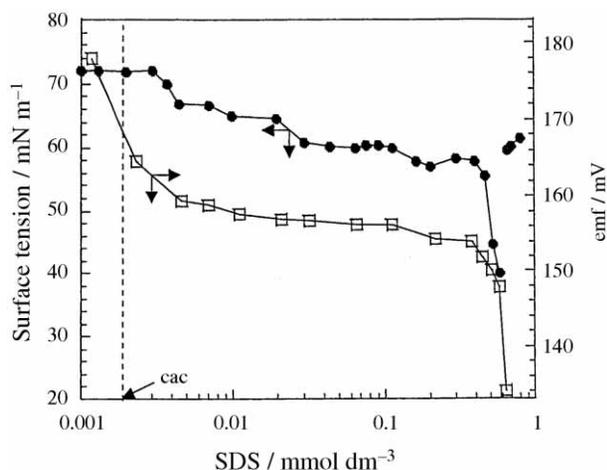


Figure 9. Changes of emf and surface tension with SDS concentration of the cationic polyelectrolyte solution at 303.2 K; [polyelectrolyte] = 100 ppm in 1.0 mmol dm<sup>-3</sup> NaCl solution at 298.2 K.

ing concentration. On the other hand, surface tension steeply increases up to more than 60 mN m<sup>-1</sup> after the rapid decrease with increasing concentration. The decrease takes place at very dilute concentrations of less than 1/10 of the original c.m.c. (*ca.* 8 mmol L<sup>-1</sup>) and, in addition, the slope of the decrease is 3.44 times larger in magnitude than that just below the original c.m.c.<sup>27</sup> The former decrease originates from the movement of semi-neutralized polymers towards the surface layer by buoyancy and from the subsequent destruction of molecular structure made up of many molecular layers beneath the interface. When the polymers are completely neutralized, they get located and float just at the air/solution interface as precipitates, and then the surface tension goes up to more than 60 mN m<sup>-1</sup>. The presence of the polymers as precipitates just at the interface does not contribute much to the destruction of water structures in the surface layer and, therefore, the surface tension increases up to the value close to that of just pure water. In other words, the large decrease in the surface tension is not a result of the change just at the air/solution interface but is due to the destruction of water molecules at some distance from the air/solution interface.

#### Interpretation of Surface Tension vs. Concentration Curve

The number of surfactant molecules, which are able to go up to an interfacial region, should increase with increasing surfactant concentration below the c.m.c., according to the Gibbs adsorption isotherm.<sup>1</sup> This condensation of the surfactant is called »adsorption at gas/liquid interface«. In other words, an apparent molecular surface area is supposed to decrease with increasing surfactant concentration below the c.m.c. If, therefore, surfactant molecules are really able to go up to the air/solution interface, a reduction in the water evaporation rate should be

observed. In reality, however, the water evaporation rate from surfactant solutions and its activation energy are quite the same as those for just purified water within experimental error. For a reasonable explanation of the above experimental facts, the surfactants are concentrated not just at the air/solution interface but at some distance beneath the interface so that the presence of the surfactants may not disturb the concentration profile of water molecules around the interface. Namely, a certain length of layer just beneath the air/surfactant solution interface should be occupied only by water molecules over »the root-mean-square displacement« of the molecules. In addition, when the evaporation is under stationary state, (1) the surfactant molecules move downwards, or (2) water molecules move upward in order for water molecules to evaporate at the same rate as purified water molecules. If neither (1) nor (2) took place, surfactant molecules would concentrate at the interface and the water evaporation rate would decrease.

The above issue is a requirement of the evaporation study. Now, the following supposition seems quite possible according to the requirement. The critical concentration A (a quite narrow concentration range) for some aggregate formation can be observed at a very low concentration as a sudden decrease in the slope of surface tension *vs.* concentration curve (Figure 10).<sup>28</sup> The corresponding sudden increase in the surface excess at this critical concentration suggests the onset of aggregate formation and the subsequent concentration of the aggregates at some distance below the air/water interface. At concentrations above the critical concentration for the aggregate formation, adsorption and aggregation continue to take place in the interfacial region simultaneously with increasing concentration up to *ca.* half c.m.c. (concentration B in Figure 10) until completion of the aggregation. The aggregation is governed by the mass action model

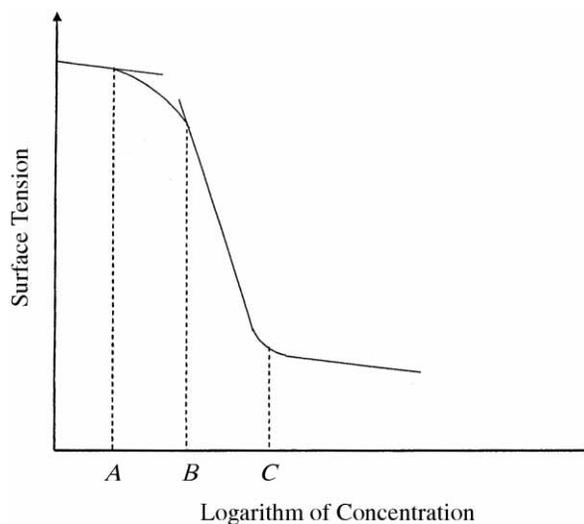


Figure 10. Schematic change in surface tension against surfactant concentration on logarithmic scale.

and, therefore, both monomer and aggregate concentrations simultaneously increase with increasing concentration, resulting in a continuous decrease of surface tension with the concentration. At the same time, the monomeric molecules are under dynamic equilibrium between the interfacial region and the aggregates through aqueous bulk. After completion of aggregation (*B* in Figure 10), where a constant slope for the surface tension *vs.* logarithm of concentration curve or a constant surface excess starts, almost all the amphiphile molecules work as a monomer up to the conventional c.m.c., which leads to a steeper decrease in slope for the surface tension *vs.* concentration curve. Monomer molecules work to destruct the steric structure of water molecules beneath the interface. The contribution of monomeric concentration to the surface excess should be very small at concentrations between *ca.* half c.m.c. and the c.m.c. due to the presence of a large amount of surface excess as large aggregates near the interfacial region, which leads to constancy of the surface excess.

From the above consideration, it is highly possible that the surface tension lowering by a soluble surfactant really results from an increase in monomeric surfactant as expressed by the Gibbs adsorption isotherm,<sup>3,4</sup> where the aggregates should be quite large in order to keep the constancy of the surface excess. In other words, the surface tension lowering automatically results from condensation of soluble amphiphiles as bi-lamellar aggregates and from demolition of the steric structure of water molecules over many molecular layers below the air/water interface. The above bi-lamellar aggregates can be suggested by the molecular surface area of 0.11 nm<sup>2</sup> from the surface excess or a half cross-sectional area of alkyl chain for aqueous C18E8 solution.<sup>6</sup>

### The New Concept of Adsorbed Film of Soluble Surfactants

About 50 years ago, the effect of the insoluble monolayer on retardation of water evaporation was intensively studied<sup>29</sup> and the theories were reported in relevant papers.<sup>30–32</sup> On the other hand, quite a number of papers on both the insoluble monolayer and the Gibbs adsorbed film have been published. Unfortunately, however, both of the above have been independently discussed in fundamental textbooks.<sup>19,33–35</sup> Nevertheless, schematic illustrations of the monolayer and the adsorbed film are quite similar, as shown in Figure 11, which is quite strange. If the illustration in Figure 11a correctly represents the adsorbed film, the film should retard the evaporation rate of water like monolayers do.<sup>10</sup> However, there is no retardation at all for three kinds of surfactant solutions, as mentioned above. For another example, no effect was found for aqueous solution of C18E8, whose molecular surface area is 0.11 nm<sup>2</sup> of the surface excess according to the Gibbs surface excess. These experimental facts give rise

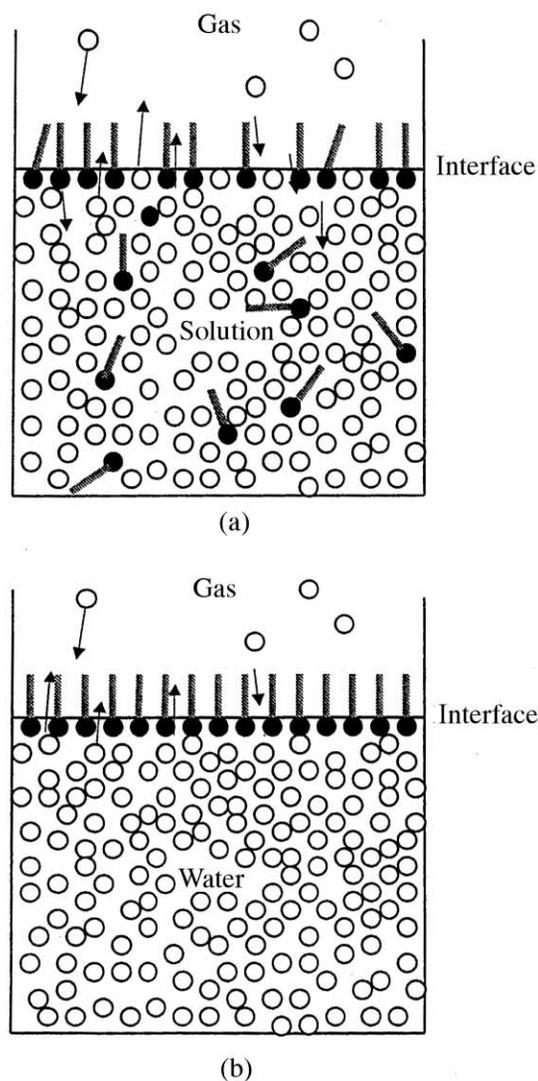


Figure 11. Conventional model of surfactant solution (a) and insoluble monolayer model (b).

to the following two questions: 1) why does the adsorbed film have no effect on water evaporation?, and 2) where do surfactant molecules concentrate? The answers to the above two questions will be given below.

As mentioned above, there was no difference in either the evaporation rate of water or the activation energy between the air/water interface and the air/surfactant solution interface.<sup>11</sup> This means that the molecular surface area of the Gibbs surface excess has no relation with the evaporation rate and that the concentration profile of water molecules around the air/surfactant solution interfaces is the same as the profile of purified water. This is also the case of the nonionic surfactant solution, octaethyleneglycol mono-*n*-octadecyl ether (C18E8), whose molecular surface area is 0.11 nm<sup>2</sup>, a half of the cross-sectional area of alkylchain, which suggests a bi-molecular layer condensation below the interface. The surface excess was confirmed to be correct by two persons using different surface tensiometers. The evaporation

rate of water ( $3.18 \times 10^{-7} \text{ mol s}^{-1} \text{ cm}^{-2}$ ) and the activation energy of evaporation ( $48.2 \text{ kJ mol}^{-1}$ ) from the C18E8 solution just below the c.m.c. at 298.2 K were the same as those from purified water within experimental error; *i.e.*,  $3.26 \times 10^{-7} \text{ mol s}^{-1} \text{ cm}^{-2}$  and  $48.2 \text{ kJ mol}^{-1}$  for the evaporation rate and the activation energy, respectively.

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 surfactant condensation 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 pipette and from other experimental facts.<sup>3-5</sup> Considering the above matters, the molecular condensation depicted in Figure 12 is much easier to accept from the point of view of free energy. The free energy decrease per  $\text{CH}_2$  group for transfer from aqueous bulk to inner micelle,  $-(2720 \text{ to } 3013) \text{ J mol}^{-1}$ , is larger in magnitude than that to the air/water interface,  $-2615 \text{ J mol}^{-1}$ .<sup>36</sup> In other words, the bi-molecular layer formation or bi-lamellar micellization at some distance below the interface are 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 like 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 of negative adsorption at the air/solution interface for ionic salts. Electrostatic force is a long-range force. Thus, a water layer of 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 (Figure 8a). Contrary to that, the lamellar surface of non-ionic 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 resulted in the appearance of the BAM image (Figure 8b). The bi-lamellar aggregate formation can explain the saturation of the surface excess at *ca.* half c.m.c., although surface tension decreases with increasing concentration up to the c.m.c. Namely, after completion of the aggregate formation around half c.m.c., the monomeric surfactant concentration keeps increasing above it with increasing concentration.

Finally, some needs to be said to answer the question why large aggregates can be formed far below the conventional c.m.c. at a certain distance beneath the air/solution interface. As for this question, the following 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 bulk subphase and, therefore, the aggregate formation of surfactant molecules is more feasible in the surface region than in the bulk. Hence, the aggregate formation is more enthalpy-driven than micellization in the bulk above the conventional c.m.c.

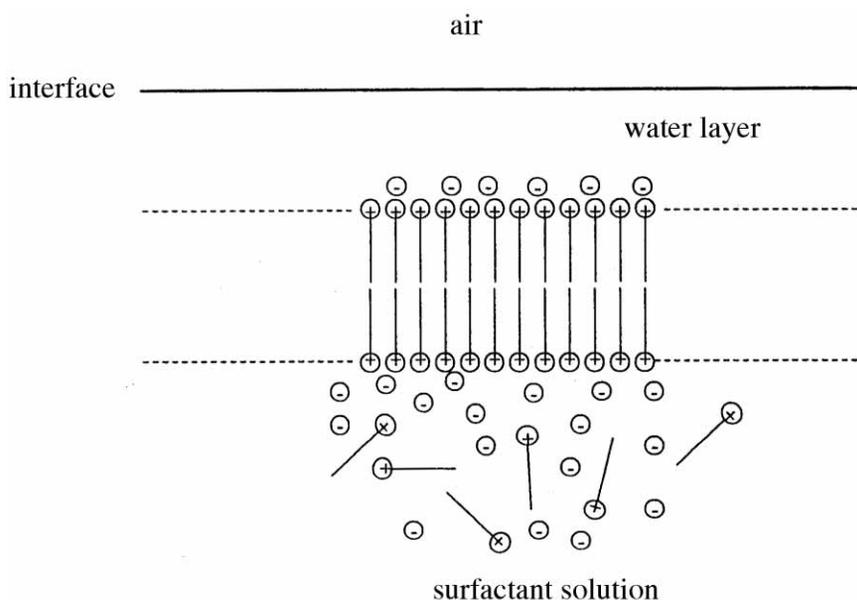


Figure 12. New model of soluble ionic surfactant solution for the interfacial region.

## CONCLUSIONS

From the above discussion, the surface tension lowering by a soluble amphiphile really results from the surface excess as expressed by the Gibbs adsorption isotherm.<sup>3,4</sup> In addition, the surface tension lowering automatically originates from condensation of soluble amphiphiles as large bi-lamellar aggregates at a certain distance below the air/water interface.

The critical concentration for bi-lamellar aggregate formation can be observed at very low concentrations by a sudden decrease in surface tension *vs.* concentration curve.<sup>28</sup> The corresponding sudden increase in the surface excess suggests commencement of the aggregate formation below the air/water interface. The above large bi-lamellar aggregate formation can explain saturation of the surface excess around half c.m.c., although surface tension decreases with increasing concentration up to the c.m.c. Namely, after completion of the aggregate formation around half c.m.c., the monomeric surfactant concentration keeps increasing above it with the concentration.

The surface tension lowering by an insoluble monolayer at the air/water interface is different in essence from the lowering by concentration of amphiphiles below the interface, where the latter lowering results from the surface excess as expressed by the Gibbs adsorption isotherm. The former lowering is confined to a few molecular layers just near the air/water interface by condensing insoluble molecules to a smaller area by an outside force, while the latter lowering automatically results from condensation of soluble amphiphiles over many molecular layers below the air/water interface (Figure 12).

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**SAŽETAK****Međupovršina zrak/voda i adsorpcija – Rješenje Gibbsovog paradoksa****Yoshikiyo Moroi**

Prikazani su raznovrsni eksperimentalni podatci koji ukazuju na to da se u otopinama amfifila netopljivi monomolekularni sloj na međupovršini zrak/voda razlikuje od adsorpcijskog sloja koji se ne nalazi na samoj međupovršini. Različitost tih dvaju slojeva utvrđena je proučavanjem brzine isparavanja vode kroz međupovršinu zrak/voda i kroz netopljivi monosloj za otopine triju vrsta površinski aktivnih tvari. Razmatranja su se temeljila na kinetičkoj teoriji isparavanja i odgovarajućoj aktivacijskoj energiji. Ta se različitost potvrdila i istraživanjem međupovršine zrak/voda pomoću BAM mikroskopije. Tako zvani Gibbsov paradoks riješen je razmatranjem ovisnosti međupovršinske napetosti o koncentraciji površinski aktivne tvari podjelom u tri koncentracijska područja. Ustanovljeno je, da se adsorpcijski sloj koncentriranih agregata nalazi na određenoj udaljenosti ispod međupovršine zrak/voda. Novi koncept adsorpcijskog sloja je u skladu s različitim međupovršinskim pojavama otopina površinski aktivnih tvari.