イオン性と非イオン性界面活性剤の吸着膜とミセルでの混和性

安部, 浩司
九州大学理学研究科化学専攻

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MISCIBILITY OF IONIC AND NONIONIC SURFACTANTS
IN THE ADSORBED FILM AND MICELLE
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IN THE ADSORBED FILM AND MICELLE

Koji Abe
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Chapter I

Introduction

The quantification and subtle transitions of both fluid and electric activity in tissues have been characteristics of the subject for many centuries, because they are often different from those of the uncleared biological systems. Which are supposed to best identify the role of host to host. It has been observed that a variety of short to medium term exposures have led to similar concentrations (CMC) or higher hemodynamic activity in the CMC than the pure water (2,13). This phenomenon may be attributed to the tissue, because short and medium term exposure works for the interface film next to the medium. Most of researchers minimal time absorption and initial location of ions of the regular biochemistry theory (1,13). Therefore, it is necessary to look at the chromatic properties that the regular solute exposure is not appropriate for the absorbed film and interface (1,11,14,16). The other theories proposed (2,13) also seem to be based on inappropriate models.

We have developed the chromodynamic network, which then are used in our model, to estimate the axial surface density and composition of adsorbed bond on atomic substrate in the exposed film and medically (14,20). The axon of microalgal and algae formation of the axon can be divided by taking an arm of the energetics involved. It has been demonstrated that the axon is started in a manner for the excitability of conduction in the absorbed film and distally.
The adsorption and micelle formation of ionic and nonionic surfactant mixtures have been one of the subjects of many studies, because they are quite different from those of the mixtures of homologous surfactants, which are supposed to mix ideally. It was observed that a certain mixture of ionic and nonionic surfactants bears a lower critical micelle concentration (CMC) or a higher interfacial tension at the CMC than the pure surfactants (1-15). This phenomenon must be attributed to the interaction between ionic and nonionic surfactant molecules in the interfacial film and micelle. Most of researchers analyzed the adsorption and micelle formation by use of the regular solution theory (1-11). However, it is clear from the theoretical standpoint that the regular solution approximation is not appropriate for the adsorbed film and micelle (11,13,14,16). The other theories presented (12,13) also seem to be based on inadequate models.

We have developed the thermodynamic treatment, which does not rely on any model, to estimate the total surface density and compositions of surfactant based on excess quantities in the adsorbed film and micelle (14-20). The diagrams of adsorption and micelle formation of the mixture are depicted by making use of the compositions evaluated. It has been demonstrated that the diagrams are useful to account for the miscibility of surfactants in the adsorbed film and micelle.
The object of this study is to elucidate the cause of nonideal mixing of ionic and nonionic surfactants. For this purpose, it is necessary to consider systematically the behavior of the mixture of surfactants having simple chemical structure. In this study, alkylammonium chloride and decyldimethylphosphine oxide (DePO) are chosen as ionic and nonionic surfactants, respectively, since they have been studied well in our laboratory. In order to clarify the effects of charge and alkyl chain length of the ionic surfactant on its miscibility with DePO, we examine the mixtures of DePO with dodecylammonium chloride (DAC), hexylammonium chloride (HAC), and sodium chloride (NaCl). Usually, sodium chloride is regarded as a mere additive. However, it is treated like a surfactant in this study. As seen in Fig. 1, the surface activity of DePO, DAC, and HAC decreases in this order and NaCl is inactive. Furthermore, it is clear that DePO and DAC form micelles. The surface tension of surfactant mixtures is measured as a function of the total molality and composition of surfactants. The results are analyzed by applying the thermodynamic equations derived in Chap. II to experimental data and discussed in Chap. IV.
Fig. 1  Surface tension vs. molality curves at 298.15 K: (1) DePO; (2) DAC; (3) HAC; (4) NaCl.
Chapter II

Theoretical
Let us consider a system composed of air and the aqueous solution, which consists of water, uni-univalent strong electrolyte (component 1), and nonionic surfactant (component 2), separated by a plane interface. When the surface excess quantities are defined with respect to the two dividing surfaces chosen so as to make the surface excess numbers of moles of air and water zero simultaneously (21), the total differential of surface tension is expressed as a function of temperature $T$, pressure $p$, electrochemical potential of ion $i \tilde{\mu}_i$, and chemical potential of nonionic surfactant $\mu_2$ in the form

$$d\gamma = -s^HdT + v^Hdp - \Gamma^H_{1+}d\tilde{\mu}_{1+} - \Gamma^H_{1-}d\tilde{\mu}_{1-} - \Gamma^H_2d\mu_2,$$  \[1\]

where $s^H$, $v^H$, and $\Gamma^H_i$ are the surface excess entropy, volume, and number of moles of species $i$ per unit area, respectively, and subscripts $1+$ and $1-$ indicate the cation and anion of component 1. Here, because the conditions of electroneutrality in the bulk phases and whole system under consideration hold, we have

$$\Gamma^H_{1+} = \Gamma^H_{1-} = \Gamma^H_1$$  \[2\]

and thus $d\tilde{\mu}_i$ in Eq. 1 can be replaced by $d\mu_i$.

First, we restrict our discussion to the system which is free from the micelle. Since the chemical potential is not a convenient variable from the experimental viewpoint, Eq. 1 should be
transformed into an equation expressed as a function of the variables based on the concentrations of surfactants. Assuming an ideal solution, the total differential of the chemical potential of species $i$ is written by

$$d\mu_i = - s_i dT + v_i dp + (RT/m_i) dm_i, \quad i = 1+, 1-, and 2,$$  \[3\]

where $s_i$, $v_i$, and $m_i$ are the partial molar entropy, partial molar volume, and molality of species $i$ in the aqueous solution, respectively. Then, substituting Eq. 3 into Eq. 1 and introducing the total molality of components 1 and 2, $\hat{m}$, and mole fraction of component 2 in the total surfactant, $\hat{X}_2$ (14-17):

$$\hat{m} = m_{1+} + m_{1-} + m_2 = 2m_{1} + m_2$$  \[4\]

and

$$\hat{X}_2 = m_2/(m_{1+} + m_{1-} + m_2)$$  \[5\]

as the independent variables, the total differential of surface tension turns out to be

$$d\gamma = - \Delta s(1) dT + \Delta v(1) dp - (RT^H/\hat{m}) d\hat{m}$$

$$- (RT^H/\hat{X}_2) (\hat{X}_2^H - \hat{X}_2) d\hat{X}_2, \quad [6]$$
where $\Delta s(1)$ and $\Delta v(1)$ are the entropy and volume changes associated with adsorption defined by

$$\Delta y(1) = y^H - (\Gamma^H_{1+} y_{1+} + \Gamma^H_{1-} y_{1-} + \Gamma^H_{2} y_{2}), \quad y = s \text{ and } v, \quad [7]$$

and $\hat{\Gamma}^H$ and $\hat{X}^H_2$ are the total surface density and mole fraction of nonionic surfactant in the adsorbed film defined by

$$\hat{\Gamma}^H = \Gamma^H_{1+} + \Gamma^H_{1-} + \Gamma^H_{2} \quad [8]$$

and

$$\hat{X}^H_2 = \Gamma^H_2 / (\Gamma^H_{1+} + \Gamma^H_{1-} + \Gamma^H_{2}) \quad [9]$$

which are the analogs of Eqs. 4 and 5, respectively. These quantities are useful to understand the adsorption behavior of the systems under consideration. Therefore, if the surface tension is measured as a function of $\hat{m}$ and $\hat{X}_2$ at a concentration below the critical micelle concentration (CMC), $\hat{\Gamma}^H$ can be easily obtained from the dependence of $\gamma$ on $\hat{m}$;

$$\hat{\Gamma}^H = - (\hat{m}/RT)(\partial \gamma / \partial \hat{m})_{T,p,\hat{X}_2} \quad [10]$$

and $\hat{X}^H_2$ can be evaluated by two ways;
\[ \hat{X}_2 = \hat{X}_2 - (\hat{X}_1 \hat{X}_2/R T \hat{X}_2^H) (\partial \gamma/\partial \hat{X}_2)_{T,p,m} \]  \hspace{1cm} [11]

and

\[ \hat{X}_2^H = \hat{X}_2 - (\hat{X}_1 \hat{X}_2^H) (\hat{m} (\partial \hat{m}/\partial \hat{X}_2))_{T,p,T} \]  \hspace{1cm} [12]

Here, it is important to note that the values of \( \hat{X}_2 \) and \( \hat{X}_2^H \) are identical at the extremum point on the \( \hat{m} \) vs. \( \hat{X}_2 \) curve.

Next, we focus our attention on the mixed micelles at the CMC. It has been proved that the micelle formation can be treated thermodynamically like an appearance of a macroscopic phase when the behavior of micelles is described by excess quantities with reference to the dividing surface which makes the excess number of moles of water zero \((14,22)\). Therefore, taking into account that the total concentration and composition of surfactants in monomer state are equal to those in all states at the CMC, the fundamental equation for the mixed micelle formation, which is analogous to Eq. 6, is derived in the form

\[ 0 = - \Delta_{w,s}^M dT + \Delta_{w,v}^M dp - (RT/\hat{C}) d\hat{C} - (RT/\hat{X}_1 \hat{X}_2) (\hat{X}_2^M - \hat{X}_2) d\hat{X}_2, \]  \hspace{1cm} [13]

where \( \hat{C} \) is the total molality defined by Eq. 4 at the CMC, \( \Delta_{w,s}^M \) and \( \Delta_{w,v}^M \) are the entropy and volume of micelle formation, and \( \hat{X}_2^M \) is the mole fraction of component 2 in the micelle. Here, \( \Delta_{w,s}^M, \Delta_{w,v}^M, \) and \( \hat{X}_2^M \) are defined by the excess molar thermodynamic quantity.
of micelle $y^M$ and excess number of molecules of species $i$ in one micelle particle $N^M_i$;

$$\Delta^M_{y^M} = \{y^M - (N^M_{1,y^M} + N^M_{1,y^M} + N^M_{2,y^M})\}/(N^M_{1,y^M} + N^M_{1,y^M} + N^M_{2,y^M}),$$

$$y = s \text{ and } v,$$  \[14\]

and

$$\tilde{X}^M_2 = N^M_2/(N^M_1 + N^M_1 + N^M_2),$$  \[15\]

which are similar to Eqs. 7 and 9, respectively, and

$$N^M_{1+} = N^M_{1-} = N^M_1.$$  \[16\]

The use of Eq. 13 enables us to evaluate immediately the composition in the micelle $\tilde{X}^M_2$ which provides the information about the miscibility of surfactants in the micelle;

$$\tilde{X}^M_2 = \tilde{X}_2 - (\tilde{X}_1 \tilde{X}_2 / \tilde{C})(\partial \tilde{C} / \partial \tilde{X}_2)|_{T_P}.$$  \[17\]

It can be found from Eq. 17 that, when $\partial \tilde{C} / \partial \tilde{X}_2 = 0$, $\tilde{X}^M_2$ has the same value as $\tilde{X}_2$. Moreover, Eq. 6 is still valid at the CMC;

$$d\gamma^C = -\Delta s^C(1)dT + \Delta v^C(1)dp - (RT\tilde{T}^{H,C} / \tilde{C})d\tilde{C}$$

$$- (RT\tilde{T}^{H,C} / \tilde{X}_1 \tilde{X}_2)(\tilde{X}^{H,C}_2 - \tilde{X}_2)d\tilde{X}_2,$$  \[18\]
where the superscript C designates the CMC. Combination of Eqs. 13 and 18 yields the relation between the compositions in the adsorbed film and micelle at the CMC;

\[ \tilde{X}_2^{HC} = \tilde{X}_2^M - \frac{\tilde{X}_2}{RT \tilde{\Gamma}_{HC}} (\partial \gamma_C / \partial \tilde{X}_2)_{T_\phi}. \] \[ 19 \]

In a similar manner as Eqs. 12 and 17, this equation indicates that \( \tilde{X}_2^M \) and \( \tilde{X}_2^{HC} \) agree with each other at the point where \( \partial \gamma_C / \partial \tilde{X}_2 = 0 \). It is worth noting that the above equations resemble the ones for a nonionic-nonionic surfactant system (18,20).

If we adopt another total molality and mole fraction defined as

\[ m = m_1 + m_2 \] \[ 20 \]

and

\[ X_2 = m_2 / m, \] \[ 21 \]

the following equations are derived instead of Eqs. 12 and 17;

\[ X_2^H = \frac{(2X_2 - 2(X_1X_2/m)(\partial m/\partial X_2)_{T_\phi,\gamma})}{\{1 + X_2 - (X_1X_2/m)(\partial m/\partial X_2)_{T_\phi,\gamma}\}} \] \[ 22 \]

and
where \( C \) is the CMC expressed by the total molality defined by Eq. 20, and \( X^H_2 \) and \( X^M_2 \) are defined by

\[
X^M_2 = \frac{2X_2 - 2(X_1X_2/C)(\partial C/\partial X_2)_{T,p}}{1 + X_2 - (X_1X_2/C)(\partial C/\partial X_2)_{T,p}},
\]

[23]

Comparing the two sets of the equations which give the compositions of the adsorbed film and micelle, Eqs. 12 and 17 have simpler forms than Eqs. 22 and 23, respectively. Furthermore, looking at Eq. 22, \( X^H_2 \) is found to have a different value from \( X_2 \) at the point where \( \partial m/\partial X_2 = 0 \) in contrast to Eq. 12 (16). There exists a similar situation between Eqs. 23 and 17 (14,16). In Sec. IV-1, we will briefly discuss which set of variables is preferred to discuss the miscibility of surfactants in the adsorbed film and micelle.
Chapter III

Experimental
1. Materials

Decyldimethylphosphine oxide (DePO) was synthesized from decyl bromide and bromomagnesium dimethylphosphinite, which is prepared by mixing diethyl phosphonate and tetrahydrofuran (THF) solution of methylmagnesium bromide (23). The unreacted Grignard reagents were hydrolyzed by pouring into hydrochloric acid. THF was removed from the reaction product solution in a rotary evaporator. By adding chloroform, DePO was extracted from the product mixture. Then the chloroform solution of DePO was washed four times with distilled water. After the removal of chloroform, DePO was recrystallized six times from hexane and twice from octane.

Dodecylammonium chloride (DAC) and hexylammonium chloride (HAC), which were previously synthesized and purified in our laboratory, were recrystallized twice from ethanol. The purities of these three surfactants were checked by elementary analysis and those of DePO and DAC were further confirmed by checking the absence of minimum on the respective surface tension vs. concentration curves. Sodium chloride (Manac standard reagent 99.99%) were used without further purification.

Water used in this study was triply distilled and second and third stages were carried out from dilute alkaline permanganate solution.
2. Surface tension measurement

Drop volume technique (24) was employed for determination of the equilibrium surface tension. The originally designed apparatus is illustrated in Fig. 2. The volume per length in the syringe was corrected by use of mercury. The measurement was carried out at 298.15 ± 0.01 K under atmospheric pressure by immersing the cell in thermostated water for 30 minutes. The filter paper was set in the cell to facilitate the establishment of vapor-liquid equilibrium. The drop of aqueous solution made on the tip of capillary was allowed to stand for 10 minutes in order to achieve the equilibrium of surface adsorption.

The value of surface tension $\gamma$ is calculated by use of the following equation

$$\gamma = V \Delta \rho g \Phi / 2 \pi r,$$

where $V$ is the volume of drop, $\Delta \rho$ the density difference between aqueous solution and humid air, $g$ the acceleration of gravity, $r$ the capillary radius, and $\Phi$ the correction factor. In the estimation of $\Delta \rho$, we neglected influences of DAC and DePO upon the density of the aqueous solution of surfactant mixture, because of low concentrations of DAC and DePO in this study. The densities of humid air, water, and aqueous solution of NaCl and HAC were
Fig. 2  Schematic diagram of the drop volume apparatus: (1) micrometer; (2) syringe; (3) glass cell; (4) aqueous solution; (5) filter paper.
taken from the literatures (25-28). The correction table of Lando and Oakley was employed for estimating the value of $\Phi/2\pi$ (29). The radius of capillary was evaluated by use of the surface tension value of water in the literature (30). The equilibrium surface tension values measured by this procedure were reproducible within 0.05 mN m$^{-1}$. 
Chapter IV

Results and discussion
1. Dodecylammonium chloride - decyldimethylphosphine oxide system

First, we consider the miscibility of the cationic surfactant dodecylammonium chloride (DAC) and nonionic surfactant decyldimethylphosphine oxide (DePO) in the adsorbed film and micelle. Both the surfactants are surface active and can form micelles in the aqueous solution.

The experimental data is given in the form of surface tension $\gamma$ vs. total molality $\hat{m}$ curve at constant composition $\hat{x}_2$ in Fig. 3. Here, the $\hat{m}$ and $\hat{x}_2$ are respectively defined by Eqs. 4 and 5 and DePO is chosen as the component 2. These notations are also applied to the sodium chloride - DePO and the hexylammonium chloride - DePO systems. The surface tension values of the aqueous solutions of DAC, DePO, and their mixtures decrease as $\hat{m}$ increases. All of their $\gamma$ vs. $\hat{m}$ curves break at lower surface tension. The concentration at the break point is referred to as the critical micelle concentration (CMC). The other break point on the $\gamma$ vs. $\hat{m}$ curve of DAC is observed at higher surface tension and assigned to the first order phase transition between gaseous and expanded adsorbed films (24). Here, it is worthwhile to mention the shape of the surface tension vs. total molality curve at a concentration above the CMC. The surface tension of micellar solution slightly decreases as $\hat{m}$ increases at all the compositions,
Fig. 3  Surface tension vs. total molality curves of DAC-DePO system at constant composition: \( \hat{X}_2 = (1) 0; (2) 0.040; (3) 0.111; (4) 0.200; (5) 0.333; (6) 0.500; (7) 0.667; (8) 0.818; (9) 1. \)
but the slope of curve of the mixture is steeper than those of pure DAC and DePO at a composition below \( \tilde{x}_2 = 0.3 \) and is gentler at a composition above \( \tilde{x}_2 = 0.3 \).

The composition dependence of the surface tension at constant total molality is demonstrated together with that at the CMC in Fig. 4. It is seen that the surface tension at constant \( \hat{m} \) diminishes as the value of \( \tilde{x}_2 \) rises. Considering the \( \gamma \) vs. \( \hat{m} \) curve at a composition between \( \tilde{x}_2 = 0 \) and 0.04, there must be a break point attributable to the phase transition of adsorbed film on the \( \gamma \) vs. \( \tilde{x}_2 \) curves at \( \hat{m} = 1, 2, \) and 3 mmol kg\(^{-1} \). As is distinct from the \( \gamma \) vs. \( \tilde{x}_2 \) curve, the surface tension at the CMC \( \gamma^C \) vs. \( \tilde{x}_2 \) curve has the apparent maximum at the composition around \( \tilde{x}_2 = 0.3 \). Such a behavior of the \( \gamma^C \) vs. \( \tilde{x}_2 \) curve is observed also for the DAC - 2-(octylsulfanyl)ethanol (OSE) system (15). The common characteristic of these ionic-nonionic surfactant systems may result from the fact that the \( \gamma^C \) values of pure surfactants, of which the system consists, are close to each other (DAC, 29.40; DePO, 30.95; OSE, 28.10 mN m\(^{-1} \)). Figure 5 shows the \( \hat{m} \) vs. \( \tilde{x}_2 \) curves at constant \( \gamma \) together with the total molality at the CMC \( \hat{C} \) vs. \( \tilde{x}_2 \) curve. It is found that the increase in the composition of DePO reduces the \( \hat{m} \) and \( \hat{C} \) values.

To explore the state of adsorbed film, first, let us examine the total surface density by use of Eq. 10. The \( \hat{\Gamma}^H \) value evaluated is plotted against \( \hat{m} \) and \( \tilde{x}_2 \) in Figs. 6 and 7, respectively. The value
Fig. 4 Surface tension vs. composition curves of DAC-DePO system at constant total molality: $\tilde{m}$ (mmol kg$^{-1}$) = (1) 1; (2) 2; (3) 3; (4) 4; (5) 5; (6) 7; (7) 9; (8) 12; (9) $\gamma^C$ vs. $\tilde{x}_2$. 

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Fig. 5  Total molality vs. composition curves of DAC-DePO system at constant surface tension: $\gamma$ (mN m$^{-1}$) = (1) 55; (2) 50; (3) 45; (4) 40; (5) 35; (6) 33; (7) $\hat{C}$ vs. $\hat{x}_2$. 

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Fig. 6  Total surface density vs. total molality curves of DAC-DePO system at constant composition: \( \hat{X}_2 = (1) \ 0; (2) \ 0.040; (3) \ 0.111; (4) \ 0.200; (5) \ 0.333; (6) \ 0.500; (7) \ 0.667; (8) \ 0.818; (9) \ 1. \)
Fig. 7  Total surface density vs. composition curves of DAC-DePO system at constant surface tension: $\gamma$ (mN m$^{-1}$) = (1) 55; (2) 50; (3) 45; (4) 40; (5) 35; (6) $\hat{\Gamma}^H_C$ vs. $\hat{X}_2$. 
of \( \hat{\mathcal{I}}^H \) at constant \( \hat{X}_2 \) rises with increasing \( \hat{m} \) and approaches to a saturated value at a concentration near the CMC. The total surface density at the CMC \( \hat{\mathcal{I}}^{H,C} \) is determined by extrapolation of the \( \hat{\mathcal{I}}^H \) vs. \( \hat{m} \) curve to the CMC and represented by the solid circle in Fig. 6. At a glance of Fig. 6, one may notice that the \( \hat{\mathcal{I}}^H \) vs. \( \hat{m} \) curve changes its shape regularly from that of DAC to that of DePO. This result suggests that DAC and DePO molecules are miscible with each other in the adsorbed film.

Next, in order to elucidate the miscibility of DAC and DePO at the water/air interface in further detail, we examined the composition of adsorbed film \( \hat{X}_2^H \) defined in terms of the surface excess numbers of moles. Application of Eq. 11 to the \( \gamma \) vs. \( \hat{X}_2 \) plot given in Fig. 4 yields the \( \hat{X}_2^H \) value which is demonstrated in the form of the \( \gamma \) vs. \( \hat{X}_2^H \) curve together with the \( \gamma \) vs. \( \hat{X}_2 \) curve in Fig. 8. The use of Eq. 12 enables us to obtain the \( \hat{X}_2^H \) value at constant \( \gamma \) and the result is given in Fig. 9. Looking at these two figures, we notice that the mixed adsorbed film abounds with more surface active DePO in all proportions. As can be seen from Fig. 9, the \( \hat{m} \) vs. \( \hat{X}_2^H \) curves deviate negatively from the line which connects the corresponding \( \hat{m} \) values of pure DAC and DePO. Such results are also obtained in the cases of decylammonium chloride (DeAC) - OSE and tetradecyltrimethylammonium chloride (TTAC) - DePO systems (17,31).
Fig. 8  Surface tension vs. composition curves of DAC-DePO system at constant total molality: $\hat{m}$ (mmol kg\(^{-1}\)) = (1) 1; (2) 2; (3) 4; (•) $\gamma^C$; (---) $\hat{x}_2$; (-----) $\hat{x}_2^H$. 
Fig. 9  Total molality vs. composition curves of DAC-DePO system at constant surface tension: $\gamma$ (mN m$^{-1}$) = (1) 55; (2) 45; (3) 35; (---) $\tilde{x}_2$; (-----) $\tilde{x}_2^H$. 
On the other hand, the relation between the compositions in the micelle $\hat{X}_2^M$ and the bulk phase $\hat{X}_2$ at the CMC is illustrated in Fig. 10. This diagram appears to convey some information about the mixing of surfactants in the micelle. It is manifest from Fig. 10 that the DAC and DePO molecules are completely miscible in the micelle and the micelle is rich in DePO which has a lower $\hat{C}$ value than DAC. Moreover, It is of great importance to note that the $\hat{C}$ vs. $\hat{X}_2^M$ curve is explicitly convex downward over the whole composition range and its deviation from straight line joining the $\hat{C}$ values of pure DAC and DePO is larger than the corresponding ones of the $\hat{m}$ vs. $\hat{X}_2^H$ curves shown in Fig. 9, especially at a composition near $\hat{X}_2 = 1$.

Here, we show the superiority of the analysis using $\hat{m}$ and $\hat{X}_2$ over that using $m$ and $X_2$. In Fig. 11, the variation of $C$ with $X_2^M$ estimated by applying Eq. 23 is displayed together with that with $X_2$. Although there are minimum points on both the $C$ vs. $X_2^M$ and $C$ vs. $X_2$ curves in Fig. 11, they do not agree with each other; therefore, we cannot say that this figure is the phase diagram representing an azeotrope. Even in the case of the system which exhibits azeotropic transformation, e.g. DAC-OSE and TTAC-DePO systems (Figs. 12-14), if we adopt $m$, $C$, and $X_2$ as the variables, neither minimum point is identical with the point where the compositions in the two states have the same value. This is not compatible with the thermodynamic demand on the three-
Fig. 10  Critical micelle concentration vs. composition curves of DAC-DePO system: (—) \( \hat{C} \) vs. \( \hat{x}_2 \); (-----) \( \hat{C} \) vs. \( \hat{x}_2^M \).
Fig. 11  Critical micelle concentration vs. composition curves of DAC-DePO system: (—) $C$ vs. $X_2$; (——) $C$ vs. $X_2^M$. 

$C / \text{mmol kg}^{-1}$

$X_2, X_2^M$
Fig. 12  Total molality vs. composition curves of DAC-OSE system at constant surface tension: $\gamma$ (mN m$^{-1}$) = (1) 45; (2) 40; (3) 35; (4) 32; (A) $\bar{m}$ vs. composition (-----) $\hat{x}_2^H$; (B) $m$ vs. composition (-----) $X_2$, (-----) $X_2^H$. 
Fig. 13 Critical micelle concentration vs. composition curves of DAC-OSE system: (A) $\hat{C}$ vs. composition (-----) $\hat{X}_2$, (-----) $\hat{X}_2^M$; (B) $C$ vs. composition (-----) $X_2$, (-----) $X_2^M$. 
Fig. 14  Critical micelle concentration vs. composition curves of TTAC-DePO system: (A) $\hat{c}$ vs. composition $(\cdots\cdot)$ $\hat{x}^M_2$, $(\cdots)$ $\hat{x}^M_2$; (B) $C$ vs. composition $(\cdots\cdot)$ $x^M_2$, $(\cdots)$ $x^M_2$. 
dimensional phase diagram (32). As far as Eqs. 11, 12, 17, and 19 are adopted to examine the composition relationships among the bulk phase, adsorbed film, and micelle through the $\gamma$ vs. composition, $\hat{m}$ vs. composition, $\hat{C}$ vs. composition, and $\gamma^C$ vs. composition diagrams, the above problems are not the case. Consequently, we conclude that the employment of $\hat{m}$ and $\hat{x}_2$ is favorable for examining the miscibility in the adsorbed film and micelle compared with that of $m$ and $X_2$. In the remainder of this chapter, therefore, we confine our discussion to the consideration based on $\hat{m}$ and $\hat{x}_2$.

Now, we proceed to consider the interaction between DAC and DePO molecules in the adsorbed film and micelle. When the surfactant solution is dilute enough to assume the ideal solution, features of the $\hat{m}$ vs. composition and $\hat{C}$ vs. composition diagrams are closely related to the interaction of surfactants in the adsorbed film and micelle. Taking account of the fact that there seems to be variation in diagram from a distorted shape to an azeotropic one with a lowering of surface tension in the DAC-OSE system (Fig. 12(A)), Fig. 9 can be looked on as a precursor of the azeotropic diagram bearing an azeotropic point at a composition near $\hat{x}_2 = 1$. Therefore, this figure may indicate the slightly attractive interaction between DAC and DePO molecules in the adsorbed film. Further, when we observe the deformed diagram of DAC-DePO system in Fig. 10, we can conclude that the interaction between
DAC and DePO molecules is also attractive in the micelle. Comparison of the results with those of 2-(decylsulfinyl)ethanol (DeSE) - OSE and DAC-DeAC systems, which are supposed to behave ideally in the adsorbed film and micelle (Figs. 6 and 8 in Ref. 17), supports the above view concerning the interactions between DAC and DePO molecules.

Next, let us turn our attention to the $\gamma^C$ vs. composition diagram associated with the equilibrium between the adsorbed film and micelle. Here, the composition in the adsorbed film at the CMC $\hat{X}_2^{H.C}$ is evaluated by applying Eq. 19 to the dependence of $\gamma^C$ on $\hat{X}_2$ depicted in Fig. 4: the result is represented in the form of a diagram in Fig. 15. It is found that this exhibits the phase diagram of an azeotropic mixture, whereas those of DeSE-OSE and DAC-DeAC systems have a cigar-like shape (Fig. 11 in Ref. 17). This is undoubtedly related with a nonideal mixing of DAC and DePO molecules in the adsorbed film and micelle. Further, from the fact that the deformation of the diagram in Fig. 10 is more remarkable than those in Fig. 9, we infer that the interaction between DAC and DePO molecules in the micelle is more attractive than that in the adsorbed film.

The value of $\gamma^C$ is also plotted against $\hat{X}_2$ and $\hat{X}_2^M$ in Fig. 16. This figure is useful in explaining the dependence of $\gamma$ of the micellar solution on $\hat{m}$. It is clear from Fig. 10 that, as $\hat{m}$ and accordingly the concentration of micelle particles increases, the
Fig. 15  Surface tension at the CMC vs. composition curves of DAC-DePO system: (-----) $\chi^M_2$; (-----) $\chi^{H,C}_2$.
Fig. 16  Surface tension at the CMC vs. composition curves of DAC-DePO system: (—) $\tilde{\chi}_2$; (-----) $\tilde{\chi}_2^M$. 
composition of monomeric surfactant shifts to a lower one. Therefore, it can be expected that such a shift would make the surface tension fall at a lower composition than the maximum point on the \( \gamma^C \) vs. \( \tilde{X}_2 \) curve and rise at higher one. Taking into consideration that the \( \gamma \) vs. \( \tilde{m} \) curves of micellar solutions of pure DAC and DePO have small negative slopes, above prediction is consistent with the observation of Fig. 3.

2. Sodium chloride - decyldimethylphosphine oxide system

Now, in order to shed light on the role of the charge of ionic surfactant in its nonideal mixing with nonionic surfactant DePO in the adsorbed film and micelle, we investigated the combination of inorganic salt sodium chloride and DePO. There have been several investigations about salt effect on the micelle formation of nonionic surfactant at a relatively high salt concentration (33-42). Most of them have dealt the salt as a mere additive and usually observed the decrease in the CMC of surfactant with the salt concentration. Most of their observations were attributed to the "salting out" effect on nonionic surfactant, that is indirect influence to the activity of nonionic surfactant in the bulk phase or a change in the structure of water due to the addition of salt. However, in this study, NaCl was dealt primarily as if it is a surfactant.
component instead of an additive. We suppose NaCl as a limiting form of alkylammonium chloride, although it is not a surfactant. Therefore, we can apply the equation derived in Chap. II to this system.

The surface tension $\gamma$ measured is plotted against the total molality at various compositions of DePO in Fig. 17. In the NaCl-DePO system, as well as the DAC-DePO system, the $\gamma$ value decreases with increasing $\hat{m}$ and also the $\gamma$ vs. $\hat{m}$ curve changes its slope abruptly at the CMC. But the shape of the curve is somewhat different from that of the DAC-DePO system. The difference can be seen clearly in the variations of $\gamma$ and $\hat{m}$ with $\hat{X}_2$ (Figs. 18 and 19). The remarkable distinction is the feature of the $\gamma^C$ vs. $\hat{X}_2$ curve: there seems to exist no dependence of $\gamma^C$ upon $\hat{X}_2$ within the accuracy of measurement for the NaCl-DePO system, while there exists a complicated dependence for the DAC-DePO system. Remembering Eq. 19, this constancy of $\gamma^C$ implies that the compositions of micelle and adsorbed film at the CMC have the same value over the composition range examined. It is also worth noting that the $\hat{m}$ vs. $\hat{X}_2$ curves in Fig. 19 seem to be a hyperbola of which the two asymptotic lines are $\hat{X}_2 = 0$ and $\hat{m} = 0$. If we regard NaCl as an additive, we can draw the surface tension vs. NaCl concentration $m_1$ curve at constant $m_2$ together with the $\gamma^C$ vs. $m_1$ curve as shown in Fig. 20. The $\gamma$ value at constant $m_2$ is found to have constant value irrespective of $m_1$. 41
Fig. 17  Surface tension vs. total molality curves of NaCl-DePO system at constant composition: \( \bar{X}_2 = (1) 0; (2) 0.053; (3) 0.081; (4) 0.111; (5) 0.176; (6) 0.250; (7) 0.333; (8) 0.500; (9) 0.667; (10) 1. \)
Fig. 18  Surface tension vs. composition curves of NaCl-DePO system at constant total molality: \( \tilde{m} \) (mmol kg\(^{-1}\)) = (1) 2; (2) 3; (3) 4; (4) 6; (5) 10; (6) 15; (7) 20; (8) 30; (9) \( \gamma^c \) vs. \( \tilde{X}_2 \).
Fig. 19  Total molality vs. composition curves of NaCl-DePO system at constant surface tension: $\gamma$ (mN m$^{-1}$) = (1) 55; (2) 50; (3) 45; (4) 40; (5) 35; (6) $\hat{C}$ vs. $\hat{X}_2$. 
Fig. 20  Surface tension vs. molality of NaCl curves at constant
molality of DePO: $m_2$ (mmol kg$^{-1}$) = (1) 0.5; (2) 1; (3) 2; (3) 3; (4) $\gamma^C$ vs. $m_1$. 

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Here, let us proceed to estimate the thermodynamic quantities of adsorbed film and micelle. It is confirmed by the data from literature (43) that the NaCl solution is assumed to be ideal in the concentration range up to 50 mmol kg\(^{-1}\): in the present study, there is little difference between the results estimated with and without the activity coefficient of NaCl. First, the total surface density is calculated numerically and illustrated in Figs. 21 and 22. It can be seen that pure NaCl is negatively adsorbed at the water/air interface. Except for the pure NaCl system, all \( \hat{\Gamma}^H \)'s bear positive values and increase as \( \hat{m} \) rises. It is also seen from Fig. 22 that all the \( \hat{\Gamma}^H \) values do not depend on \( \hat{X}_2 \) at constant \( \gamma \). This finding must be closely related to the miscibility of NaCl and DePO at the water/air interface. Now, we inquire the composition of the adsorbed film.

The mole fraction of DePO in the adsorbed film is calculated by means of Eqs. 11 and 12 and depicted diagrammatically in Figs. 23 and 24. It is seen that the value of \( \hat{X}^H_2 \) is almost unity at overall compositions except \( \hat{X}_2 = 0 \). These results indicate that the adsorbed film virtually consists of DePO molecules. If NaCl is taken as a mere additive, it may be said that there is no effect of NaCl on the adsorption of DePO in the concentration range examined as seen in Fig. 24. This view is supported by Figs. 20 and 22. However, by remembering the negative \( \hat{\Gamma}^H \) value of pure NaCl and the definition of \( \hat{X}^H_2 \) (Eq. 9), further insight is provided:
Fig. 21 Total surface density vs. total molality curves of NaCl-DePO system at constant composition: \( \tilde{X}_2 = (1) 0; (2) 0.053; (3) 0.081; (4) 0.111; (5) 0.176; (6) 0.250; (7) 0.333; (8) 0.500; (9) 0.667; (10) 1. \)
Fig. 22 Total surface density vs. composition curves of NaCl-DePO system at constant surface tension: $\gamma$ (mN m$^{-1}$) = (1) 55; (2) 50; (3) 45; (4) 40; (5) 35; (6) $\tilde{\Gamma}^{H,C}$ vs. $\tilde{x}_2$. 

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Fig. 23  Surface tension vs. composition curves of NaCl-DePO system at constant total molality: \( \hat{m} \) (mmol kg\(^{-1}\)) = (1) 2; (2) 4; (3) 6; (●) \( \gamma^C \); (——) \( \hat{X}_2 \); (-----) \( \hat{X}_2^H \).
Fig. 24 Total molality vs. composition curves of NaCl-DePO system at constant surface tension: $\gamma$ (mN m$^{-1}$) = (1) 55; (2) 45; (3) 35; (---) $\vec{x}_2^2$; (----) $\vec{x}_2^H$. 
we may state that there is somewhat attractive interaction between NaCl and DePO at the water/air interface. Since the hydrophilic group of nonionic surfactant molecule must bear electric dipole and lone pair, it is reasonable to anticipate a short range force between nonionic surfactant and ions. Actually, it is known that trialkylphosphine oxide forms adduct with salt and acid (44).

Similar estimation of the compositions in the micelle and adsorbed film at the CMC is made from Figs. 19 and 18 and visualized in Fig. 25. It should be noted that $x_2^M$ and $x_2^{H,C}$ are nearly equal to unity. Not only the adsorbed film but the micelle is found to be virtually made up of DePO molecules. However, it does not mean that there exist no sodium and chloride ions in the micelle. Again, we arrive at the conclusion similar to that of the adsorbed film. The attractive interaction between DePO and charged species may be one of the causes of the nonideal mixing of DePO and DAC in the surface and micellar states. If hydrogen chloride - DePO or multivalent electrolyte - DePO system is investigated and compared with the present system, the interaction between DePO and ions will further be clarified.

At this stage, it is instructive to compare this mixture with the mixture of NaCl with nonionic surfactant having a similar structure to DePO. For the NaCl - octyl methyl sulfoxide (OMS) system, the compositions of OMS in the adsorbed film and micelle
Fig. 25 Critical micelle concentration vs. composition curves of NaCl-DePO system: (—) $\hat{C}$ vs. $\hat{x}_2$; (-----) $\hat{C}$ vs. $\hat{x}_2^M$, $\hat{x}_2^{H,C}$. 

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are observed to be less than unity (45). In the case of dimethyldodecylamine oxide, its surface tension and CMC are obviously depressed by an increase in the NaCl concentration, even at a concentration being as low as that of the system under consideration (41,42). These observations may also be attributed to the attractive interaction between hydrophilic group of nonionic surfactant and ions. Further, it is interesting to compare the present mixture with that of NaCl and DAC (46), which have a common anion. The corresponding diagrams to Figs. 23-25 show different shapes: i.e., the compositions of DAC in the adsorbed film and micelle are beyond unity. This fact is evidently attributable to the electrostatic repulsion between sodium ion and dodecylammonium ion in the adsorbed film and micelle.

The surface tension at a concentration above the CMC is understandable on the basis of the change in $\gamma^C$ with compositions: because the variations of micellar concentration and thus the composition of DePO in monomer state do not affect $\gamma^C$, the dependence of the surface tension of mixture at a concentration above the CMC upon $\tilde{m}$ are the same as that of pure DePO.

3. Hexylammonium chloride - decyltrimethylphosphine oxide system
In the last section of this chapter, let us consider the mixing of DePO with hexylammonium chloride (HAC). The character of HAC is intermediate between those of NaCl and DAC: HAC is slightly surface active but does not solely form the micelle. Comparison of the results obtained from the surface tension measurement of HAC-DePO system with those of DAC-DePO and NaCl-DePO systems gives the information about the influence of the hydrocarbon chain of alkylammonium chloride on its miscibility with DePO. There is few investigation of such a combination of surfactants as far as the author knows.

In a similar manner to the preceding sections, the interrelations among surface tension, total molality, and composition of DePO are shown in Figs. 26-28. It may be mentioned that these three figures resemble the corresponding ones of NaCl-DePO system (Figs. 17-19) rather than those of DAC-DePO system (Figs. 3-5). However, the composition dependence of the surface tension at the CMC of HAC-DePO system is somewhat different from that of NaCl-DePO system as seen in Fig. 29. At the low composition range, the $\gamma^C$ value seems to decrease slightly as $\hat{X}_2$ increases.

The total surface density of HAC-DePO mixture is plotted against $\hat{m}$ at constant $\hat{X}_2$ and against $\hat{X}_2$ at constant $\gamma$ in Figs. 30 and 31, respectively. The $\hat{\Gamma}^H$ value of pure HAC is observed to be positive and to increase with $\hat{m}$ in contrast to that of pure NaCl. On
Fig. 26  Surface tension vs. total molality curves of HAC-DePO system at constant composition: \( \tilde{x}_2 \) = (1) 0; (2) 0.053; (3) 0.081; (4) 0.111; (5) 0.176; (6) 0.250; (7) 0.333; (8) 0.500; (9) 0.667; (10) 1.
Fig. 27  Surface tension vs. composition curves of HAC-DePO system at constant total molality: $\tilde{m}$ (mmol kg$^{-1}$) = (1) 2; (2) 3; (3) 4; (4) 6; (5) 10; (6) 15; (7) 20; (8) 30; (9) $\gamma^C$ vs. $\tilde{X}_2$. 
Fig. 28   Total moiality vs. composition curves of HAC-DePO system at constant surface tension: $\gamma$ (mN m$^{-1}$) = (1) 55; (2) 50; (3) 45; (4) 40; (5) 35; (6) $\tilde{C}$ vs. $\tilde{x}_2$. 
Fig. 29 Surface tension at the CMC vs. composition curves: (A) NaCl-DePO system; (B) HAC-DePO system.
Fig. 30 Total surface density vs. total molality curves of HAC-DePO system at constant composition: $\tilde{x}_2 = (1)$ 0; (2) 0.053; (3) 0.081; (4) 0.111; (5) 0.176; (6) 0.250; (7) 0.333; (8) 0.500; (9) 0.667; (10) 1.
Fig. 31 Total surface density vs. composition curves of HAC-DePO system at constant surface tension: $\gamma$ (mN m$^{-1}$) = (1) 55; (2) 50; (3) 45; (4) 40; (5) 35; (6) $\tilde{\Gamma}_H^c$ vs. $\tilde{X}_2$. 
the other hand, the $\hat{I}^H$ vs. $\hat{m}$ curve of the mixture of HAC and DePO seems to be similar in shape to that of the mixture of NaCl and DePO given in Fig. 21. Moreover, it is seen that the $\hat{I}^H$ vs. $\hat{X}_2$ curve of HAC-DePO system is linear like that of NaCl-DePO system. These similarities may be associated with the miscibility of HAC and DePO molecules in the adsorbed film.

It is now required to see how HAC and DePO molecules mix in the adsorbed film. Given in Figs. 32 and 33 are the $\gamma$ vs. composition and $\hat{m}$ vs. composition diagrams corresponding to Figs. 23 and 24 of the NaCl-DePO mixture, respectively. At first glance, one may find a great resemblance of the HAC-DePO system to the NaCl-DePO system: the adsorbed film is practically made up only by more surface active DePO molecules. Taking notice of the positive adsorption of HAC in the absence of DePO, it may be said that the adsorption of DePO molecules at the water/air interface is so strong that the adsorbed film includes few HAC molecules. In Fig. 34, the value of $\hat{X}_2^H - \hat{X}_2$ at 45 mN m$^{-1}$ of the present system is compared with those of the DAC-DePO and NaCl-DePO systems. Judging from this figure, HAC is thought to be expelled more strongly by DePO than DAC especially at a low $\hat{X}_2$ value. This is inferable from the fact that HAC is much less surface active than DAC. In the cases of OSE - short chain alcohol systems, similar behavior was observed (19).
Fig. 32 Surface tension vs. composition curves of HAC-DePO system at constant total molality: \( \hat{m} \) (mmol kg\(^{-1}\)) = (1) 2; (2) 4; (3) 6; (●) \( \gamma^C \); (—) \( \hat{x}_2 \); (-----) \( \hat{x}_2^H \).
Fig. 33  Total molality vs. composition curves of HAC-DePO system at constant surface tension: $\gamma$ (mN m$^{-1}$) = (1) 55; (2) 45; (3) 35; (-----) $\tilde{X}_2^H$; (-----) $\tilde{X}_2^H$. 
Fig. 34 $\tilde{X}_2^H - \tilde{X}_2$ vs. composition curves at $\gamma = 45$ mN m$^{-1}$: (1) DAC-DePO system; (2) HAC-DePO system; (3) NaCl-DePO system.
In a similar manner, the equilibrium diagram of micelle formation is drawn in Fig. 35. It is remarkable that HAC, though does not form micelles by itself, takes part in the mixed micelle formation at low $\tilde{X}_2$. Such a mixing in micelle was also found for the 1-octanol - OSE system (20). This behavior of HAC seems essentially different from that of NaCl. The comparison of $\tilde{X}_2^M - \tilde{X}_2$ is carried out among the HAC-DePO, DAC-DePO, and NaCl-DePO systems in Fig. 36. It is seen that the difference of HAC-DePO system is much larger than that of DAC-DePO system and slightly smaller than that in NaCl-DePO system. Taking account of Fig. 35, we notice that the micelle is more abundant in HAC molecules than the adsorbed film. This difference in miscibility is thought to arise from the difference in the interaction of HAC and DePO molecules between the two states. The behavior HAC-DePO system forms an interesting contrast to that of NaCl-DePO system (Fig. 25).

Hence, we may conclude that the miscibility of alkylammonium chloride and DePO is dominated by the balance of at least two effects: one is the attractive interaction between the hydrophilic portion of DePO and charged species of alkylammonium chloride in the adsorbed film and micelle and the other is the squeeze of the surfactant molecules bearing lower adsorptive activity and micelle formation ability from the adsorbed film and micelle. The investigations concerning the mixture of DePO with tetradecyl-,
Fig. 35 Critical micelle concentration vs. composition curves of HAC-DePO system: (—) \( \hat{C} \) vs. \( \hat{x}_2 \); (-----) \( \hat{C} \) vs. \( \hat{x}^M_2 \); (-----) \( \hat{C} \) vs. \( \hat{x}^{\text{H,C}}_2 \).
Fig. 36 $\hat{x}_2^M - \hat{x}_2$ vs. composition curves: (1) DAC-DePO system; (2) HAC-DePO system; (3) NaCl-DePO system.
decyl-, and octylammonium chlorides will provide more detailed information. Further, it is also important to study the mixture of nonionic surfactant with anionic surfactant in a similar way.

In Fig. 37, $\gamma^C$ is plotted against $\tilde{X}_2$ and $\tilde{X}_M$. This figure tells us that the $\gamma^C$ value does not change so much with the compositions and accordingly the $\gamma$ value of the mixture remains almost unchanged in the range of total concentration above the CMC. This result explains the feature of the $\gamma$ vs. $\tilde{m}$ curve above the CMC. The agreement between the expectation and observation suggests the utility of the diagrams.
Fig. 37  Surface tension at the CMC vs. composition curves of HAC-DePO system: (—) $\hat{X}_2$; (-----) $\hat{X}_2^M$. 
Chapter V

Summary

The main objective of this chapter was to study the interaction between the liquid-crystalline phase and the polymer backbone in the aggregation behavior of the liquid-crystalline polymer. The results showed that the aggregation behavior varied with the nature of the liquid-crystalline phase and the polymer backbone. The aggregation behavior was found to be affected by the interaction between the liquid-crystalline phase and the polymer backbone. The aggregation behavior was found to be influenced by the nature of the liquid-crystalline phase and the polymer backbone. The aggregation behavior was found to be affected by the interaction between the liquid-crystalline phase and the polymer backbone.

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In order to elucidate the nonideal mixing of ionic and nonionic surfactants in the adsorbed film and micelle, the miscibility of decyldimethylphosphine oxide (DePO) with dodecylammonium chloride (DAC), sodium chloride (NaCl), and hexylammonium chloride (HAC) were studied thermodynamically by evaluating the compositions defined on the basis of the excess numbers of moles of the surfactants. The surface tension of the aqueous solutions of mixtures was measured by drop volume method as a function of the total molality and composition of mixtures at 298.15 K under atmospheric pressure.

First, the case of DAC-DePO mixture has been considered. The diagrams of adsorption and micelle formation were drawn: the adsorbed film and micelle were observed to be abundant in DePO which has higher surface activity and lower CMC value than DAC. Further, the diagrams were found to have a distorted form, which is regarded as a precursor of the formation of azeotrope at a DePO rich composition. These observations may suggest that the interaction between DAC and DePO molecules in the adsorbed film and micelle is slightly attractive. Furthermore, it was found that the diagram representing the equilibrium between adsorbed film and micelle has an azeotropic point. Therefore, we concluded that the interaction between DAC and DePO molecules in the micelle may be more attractive than that in the adsorbed film.
Next, in order to clarify the effect of the charge of alkylammonium chloride on the miscibility of DAC and DePO, the adsorption and micelle formation of NaCl-DePO mixture were examined. Contrary to the case of DAC-DePO system, the adsorbed film and micelle of NaCl-DePO mixture were proved to be practically made up of DePO molecules. However, taking account of the negative adsorption of pure NaCl, it was probable to assume that the interaction between DePO and NaCl at the water/air interface is attractive. Similar conclusion was drawn for the micelle. This interaction between charged species and DePO was supposed to be one of the causes of the nonideal mixing of DAC and DePO in the adsorbed film and micelle.

Last, the HAC-DePO mixture was examined and its results were compared with the two mixtures mentioned above. It was found from the diagram of adsorption that the adsorbed film involves few HAC molecules although pure HAC molecule is adsorbed positively at water/air interface. On the other hand, the diagram of micelle formation indicates that the micelles of DePO include somewhat HAC molecules. This was attributed to the competitive adsorption and micelle formation of HAC and DePO molecules. Further, there was an appreciable difference in composition between the micelle and adsorbed film at the CMC. This suggests the difference between the interaction of surfactants in the adsorbed film and that in the micelle.
From these findings, we concluded that the miscibility of alkylammonium chloride and DePO is dominated by the balance of at least two effects: one is the attractive interaction between the hydrophilic portion of DePO and charged species of alkylammonium chloride in the adsorbed film and micelle and the other is the squeeze of the surfactant molecules bearing lower adsorptive activity and micelle formation ability from the adsorbed film and micelle.
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30. Reference 21, Part II, p. 81.


