Surface Tension Study on Aqueous Solution of Nonionic Surfactant with Unsaturated Hydrocarbon Chain

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Abstract: Surface tension measurements were carried out for aqueous solutions of polyoxyethylene oleyl and stearyl ethers with average number of oxyethylene units of 20 (abbreviated as POEOl and POESt, respectively) in order to examine the effect of introducing a double bond into hydrocarbon chain on the surface activity of the surfactants. The overall features of surface chemical properties of these two surfactant solutions are similar to each other, although the surface tension and the critical micelle concentration (CMC) are slightly higher while the amount of surface adsorption is slightly smaller for POEOl compared with those for POESt. Thermodynamic parameters of micelle formation derived from the temperature dependence of the CMC are also close to each other for the two surfactant species. These results demonstrate that the effect of double bond in the surfactant hydrocarbon chain on the surface activity is rather small at least for nonionic surfactant species with relatively long polyoxyethylene chain.

Key words: polyoxyethylene oleyl ether, unsaturated hydrocarbon surfactant, surface chemical property, micelle formation

1 Introduction

The surface chemical properties of aqueous surfactant solutions have so far been extensively studied in view of both the academic interest and practical importance. Most of these studies have been concerned with the surfactants with saturated hydrocarbon chains as a hydrophobic part. The soaps and detergents derived from unsaturated fatty acids, in particular oleic acid, are expected to be suitable for sensitive skin, because their irritation for skin is weak (1). In this respect, polyoxyethylene (POE)-type nonionic surfactants with oleyl chain are interesting for practical use as a skin care material.

As for polyoxyethylene oleyl ethers, the aqueous phase behavior has been reported in the wide ranges of concentration and temperature for species with different POE chain lengths (2, 3). However, no surface chemical study in dilute aqueous solution has been reported for these surfactant systems. For the practical application as a detergent, it is desirable to clarify the surface chemical properties of dilute aqueous solution. Thus, in the present work, we investigated the surface chemical properties of aqueous solution of a POE-type nonionic surfactant with oleyl chain by means of surface tension measurements, and compared the results with those of saturated hydrocarbon surfactant with stearyl chain. The purpose of this study is to examine how the surface chemical properties are affected by introducing the unsaturated hydrocarbon chain as a hydrophobic
part of the surfactants.

2 Experimental

The surfactants used are polyoxyethylene oleyl and stearyl ethers with average number of oxyethylene units of 20, which are abbreviated as POEOl and POESt, respectively. The number of carbon atoms in hydrocarbon chain is 18 for both the two surfactants; the difference between the two surfactant species is that POEOl has a cis-double bond in the center of its hydrocarbon chain, whereas POESt has a saturated hydrocarbon chain. These surfactant samples were obtained from Research Institute of Biological Materials, and used without further purification. The surface tension was measured for aqueous solutions of these surfactants with various concentrations in the temperature range 15-40°C. For surface tension measurements, the pendant drop method was used with a Yamashita Giken Model DVS2000 automatic surface tensiometer. Quasi-elastic light-scattering measurements were carried out to estimate the micellar size using a Nicomp Model 370 particle sizing system.

3 Results and Discussion

3.1 Time Dependence of Surface Tension

According to the pendant drop method used in the present study, the surface tension is determined by applying the relation between gravimetric force and surface tension at the moment that a drop of sample solution formed at the capillary tip falls down. We checked the dependence of the surface tension on the time during which the drop was held at the capillary tip just before falling down. Figure 1 shows the plot of surface tension against the time for both POEOl and POESt of different concentrations and different temperatures. As can be seen in this figure, the surface tension reaches constant value rather quickly for the case of surfactant solutions with high concentration (6 × 10⁻⁵ M), whereas it takes long time to reach the equilibrium value for dilute solutions (6 × 10⁻⁶ M). The possible reason for the decrease in the surface tension with time may be the problem of adsorption equilibrium; the attainment of the adsorption equilibrium of surfactant molecules at the air-water interface needs certain time which would become longer with the decrease in the

Fig. 1 Time Dependence of Surface Tension, γ, for (a) POEOl and (b) POESt. The surfactant concentration and temperature are (a) 6.04 × 10⁻⁶ M, 20°C (○); 6.04 × 10⁻⁶ M, 35°C (●); 6.04 × 10⁻⁵ M, 20°C (□); 6.04 × 10⁻⁵ M, 30°C (▲); 6.04 × 10⁻⁵ M, 40°C (△) and (b) 6.24 × 10⁻⁶ M, 20°C (○); 6.24 × 10⁻⁶ M, 30°C (●); 6.10 × 10⁻⁵ M, 20°C (□); 6.10 × 10⁻⁵ M, 35°C (■).
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surfactant concentration. We checked the time needed for the equilibration for several concentrations, and decided to adopt the equilibration time for surface tension measurements of 20 min for sample solutions with the concentration higher than $1 \times 10^{-5}$ M and of 60 min for those of lower concentrations.

### 3·2 Critical Micelle Concentrations Determined by Surface Tension Measurements

Typical examples of the plot of surface tension, $\gamma$, against logarithmic concentration are shown in Fig. 2 for POEOl and POESt at different temperatures. With the increase in logarithmic concentration the surface tension decreases almost linearly and the slope changes drastically at certain concentrations. Two straight lines were drawn in low and high concentration regions using a linear least-squares analysis, and the concentration corresponding to the intersection of the two straight lines was determined as a critical micelle concentration (CMC). As shown in Fig. 2, both the surface tension value and the CMC are slightly higher for POEOl than for POESt. This means that the surface activity of POEOl is somewhat poorer compared with POESt. However, the difference is quite small, and hence, cleansing power judged from the surface activity would be practically comparable for these two surfactants.

Figure 3 depicts the temperature dependence of the CMC for the two surfactant species. In both cases there appears a minimum in the CMC vs. temperature curve. This behavior is general for the micelle formation in surfactant solutions (4-6). For the case of the POE-type nonionic surfactants, the initial decrease of the CMC with the temperature rise is caused by the reduced hydrophilicity of the surfactant molecules due to the decrease in hydration of the POE chain with the temperature increase, which is in favor of the formation of micelles. The increase in temperature also causes the destruction of structured water molecules around the hydrocarbon chains, or in other words, causes the reduction of the hydrophobic hydration, which is in disfavor of the formation of micelles. With the increase in temperature, this effect of the reduction of hydrophobicity begins to exert its influence, and then becomes to overcome the effect of the reduction of hydrophilicity. Thus, with the increase in temperature, the CMC begins to increase after reaching minimum value.

It has been reported that the temperatures of minimum CMC, $T_{\text{min}}$, depend on the lengths of both the POE and hydrocarbon chains of the POE-type nonionic

![Fig. 2](image)

**Fig. 2** Plot of Surface Tension, $\gamma$, against Logarithmic Concentration at (a) $25^\circ\text{C}$ and (b) $40^\circ\text{C}$. The surfactant species are POEOl (○) and POESt (□).
surfactants (5, 6). For example, the $T_{\text{min}}$s are 46, 49, and 52°C for C$\text{_{12}}$E$\text{_{4}}$, C$\text{_{12}}$E$\text{_{6}}$, and C$\text{_{12}}$E$\text{_{8}}$, respectively, and are 61, 52, and 46°C for C$\text{_{10}}$E$\text{_{8}}$, C$\text{_{12}}$E$\text{_{8}}$, and C$\text{_{14}}$E$\text{_{8}}$, respectively (6). These results demonstrate that $T_{\text{min}}$ increases with the increase in the POE chain length, or in other words, with the increase in hydrophilicity of the surfactant molecules, while it decreases with the increase in the hydrocarbon chain length, or hydrophobicity; this trend is in accordance with the above interpretation for the existence of a minimum in the CMC vs. temperature curve. The surfactant species used in the present work have rather long POE chains which act to elevate $T_{\text{min}}$, but the hydrocarbon chains are also long; the balance of the lengths of the two chains would lead to the $T_{\text{min}}$ values around 30°C.

3·3 Micellar Size Estimated by Quasi-elastic Light-scattering Measurements

Hydrodynamic diameters were measured for micelles of both surfactant species by means of a quasi-elastic light-scattering technique. The surfactant concentrations were approximately $1 \times 10^{-2}$ M being far above the CMC. Figure 4 shows the plot of the mean hydrodynamic diameter $<D>$ against temperature. Although the data points are somewhat scattered, it can be seen in this figure that the values of $<D>$ exhibit no temperature dependence in the measured temperature range and that the $<D>$ values for POESt are somewhat larger than those for POEOl. The length of fully extended chain of POESt with all-trans conformation is estimated to be approximately 20 nm, and hence, the maximum diameter is expected to be 40 nm if POESt with the extended chain form a spherical micelle. The actually obtained $<D>$ value is 9.3 nm. This value looks reasonable since both the hydrocarbon chain and the POE chain may take a folded structure containing many gauche conformers due to their flexible nature, and the surfactant molecules could be closely packed to form spherical micelles only when they have folded chains. The somewhat smaller values of $<D>$ for POEOl compared with POESt may reflect its hydrocarbon chain shortened by the existence of cis-double bond.

3·4 Surface Adsorption Estimated from the Gibbs Adsorption Isotherm

The amounts of surfactant molecules adsorbed at the surface, $\Gamma$, were estimated from the slopes of straight lines in the plot of surface tension vs. logarithmic concentration drawn in the concentration region below the CMC according to the Gibbs adsorption isotherm (7),

$$\Gamma = -\frac{1}{RT} \frac{d\gamma}{d\ln c}$$  \[1\]
The results are shown in Fig. 5(a) as a function of temperature. In addition, the values of area occupied by a surfactant molecule at the surface, $a$, were calculated from the $\Gamma$ values, and are plotted in Fig. 5(b) against temperature.

In the temperature dependence of these quantities, $\Gamma$ exhibits a maximum, and hence, $a$ exhibits a minimum, around 30°C. The values of $\Gamma$ are larger, accordingly those of $a$ are smaller, for POESt than for POEOl. This behavior of surface adsorption is parallel to that of CMC; the lower the CMC, the higher the $\Gamma$ value. This correspondence suggests that the driving forces for the micelle formation and for the surface adsorption are essentially identical.

3.5 Thermodynamics of Micelle Formation

For nonionic surfactants, the free energy of micelle formation, $\Delta G_m$, is related to the CMC by the following equation (8).

$$\Delta G_m = RT \ln \text{CMC}$$  \[2\]

$\Delta G_m$ corresponds to the standard free energy change associated with the process that the micelles are formed from monomeric surfactant molecules in aqueous solution. The values of $\Delta G_m$ were determined for POEOl and POESt according to Eq. 2, and are plotted against absolute temperature in Figs. 6(a) and 6(b), respectively. The solid lines in these figures show the quadratic functions determined by the polynomial curve-fitting procedure.

From the temperature dependence of $\Delta G_m$, the entropy of micelle formation, $\Delta S_m$, was estimated on the basis of the following thermodynamic relation.

$$\Delta S_m = -\left(\frac{\partial \Delta G_m}{\partial T}\right)$$  \[3\]

Then, the enthalpy of micelle formation, $\Delta H_m$, was calculated according to the relation,

$$\Delta H_m = \Delta G_m + T \Delta S_m$$  \[4\]

Thermodynamic parameters thus obtained for micelle formation are plotted in Fig. 7 as a function of temperature.

It can be seen in Fig. 7 that with the increase in temperature, $\Delta H_m$ decreases from positive value and changes its sign at the temperature between 30 and 35°C, while $-T \Delta S_m$ exhibits an opposite behavior, i.e., it increases from negative value and becomes positive at high temperature. This temperature dependence indicates that $-T \Delta S_m$ contributes to negative $\Delta G_m$ at low temperature, while $\Delta H_m$ contributes to negative $\Delta G_m$ at high temperature. In other words, the micelle formation process is entropy-driven at low temperature but enthalpy-driven at high temperature. This is usual case for micelle formation of long-chained surfactant species. The overall feature of the temperature dependence of these thermodynamic parameters is quite similar for both POEOl and POESt, although the absolute values of $\Delta H_m$ and $-T \Delta S_m$ in low temperature region are somewhat larger for POEOl than for POESt. The dif-
ference in these parameter values may be attributed to the double bond included in the hydrocarbon chain of POEOI; it is likely that water molecules are more strongly hydrated around the double bond of the monomeric POEOI in aqueous solution due to less hydrophobic nature of the double bond, which would result in larger enthalpy change and entropy change associated with the release of hydrated water occurring in the course of micelle formation.

It has been frequently observed that a linear relationship between the enthalpy change and entropy change exists for processes occurring in aqueous solution such as protein unfolding (9). This phenomenon is known as enthalpy-entropy compensation. The micelle formation process in surfactant solution also exhibits such a compensation phenomenon (5, 6, 10-14). Figure 8 shows a plot of $\Delta H_m$ against $\Delta S_m$. A good linear relationship is seen, i.e., the enthalpy-entropy compensation relation holds well for the micelle formation of the present surfactant systems. The slope of the straight line of this plot has a dimension of temperature, and is called compensation temperature, $T_c$. It has been reported that $T_c$ values for nonionic surfactants are 322-328 K, while those for ionic surfactants are 304-308 K (6). The $T_c$ obtained for the present surfactant systems is 303 K, which is considerably smaller than the $T_c$ values reported for nonionic surfactants, instead, is rather close to those for ionic surfactants in spite of the fact that the present surfactants are nonionic. The above values for nonionic surfactants have been estimated from $T_c$ s obtained for polyoxyethylene alkyl ethers ($C_nE_m$) with n
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$= 10-15$ and $m = 4-8$, and polyoxyethylene $p$-tert-octylphenyl ethers (OPE$_m$) with $m = 5-10$ (6). Compared with these nonionic surfactant species, the present surfactants, POEOl and POESt, have much longer POE chain and slightly longer hydrocarbon chain. The difference in $T_c$ among these surfactant species suggests that the slope of the enthalpy-entropy compensation plot for micellization of nonionic surfactants depends on the chain length.

4 Conclusion

Surface chemical properties were investigated for aqueous solutions of POEOl and POESt by means of surface tension measurements in order to examine the effect of introducing a double bond into hydrocarbon chain on the surface activity of the surfactants. Overall feature of the surface chemical properties is similar to each other for these two surfactant species, although the surface tension and the CMC are slightly higher while the amount of surface adsorption is slightly lower for POEOl compared with those for POESt. Thermodynamic parameters of micelle formation derived from the temperature dependence of the CMC are also close to each other for the two surfactant species. These results demonstrate that the effect of introducing a double bond into surfactant hydrocarbon chain on the surface activity is rather small at least for the present surfactant species with relatively long POE chain. This suggests in turn that the cleansing ability of POE-type nonionic surfactants with unsaturated hydrocarbon chain is expected to be comparable to that of analogues with saturated hydrocarbon chain.

Acknowledgments

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References
