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Electrophoretic Light Scattering of Alkyl- and Oleyldimethylamine Oxide Micelles

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Electrophoretic light scattering measurements were performed for aqueous NaCl solutions of dodecyl-, tetradecyl-, and oleyldimethylamine oxides (C_{12}DAO, C_{14}DAO, and ODAO). Electrophoretic mobility for 0.1 M NaCl solutions of C_{14}DAO changed from negative to positive, as degree of protonation was increased. NaCl solutions (0.03 M) of ODAO displayed similar behavior, and their positive mobility increased with degree of protonation. On the other hand, 0.05 M NaCl solutions of C_{14}DAO presented three kinds of electrophoretic mobility at $\sim -2.5 \times 10^{-4}$, ~ 0, and $\sim 2 \times 10^{-4}$ $cm^2 V^{-1} s^{-1}$ depending on degree of protonation, and there were transitions from negative to zero and from zero to positive at narrow degrees of protonation. A similar result was also obtained for 0.05 M NaCl solutions of C_{12}DAO. The electrophoretic mobility is related to the electrostatic potential of a micelle which is affected by degree of protonation of a micelle and counterion binding. Experimental results are qualitatively explained in relation to the variation of such parameters.

Introduction

The electrostatic potential is one of the important factors for the stabilization of dispersed colloidal particles in aqueous medium. The electrokinetic phenomenon such as electrophoresis, which may be evaluated by mobility, is in close connection with the electrostatic potential.

The development of an electrophoretic light scattering instrument simplified the measurement of the electrophoretic mobility of small colloidal particles such as surfactant micelles.[1,2] However, the electrophoretic mobility of micelles was reported only for a few cases by using such an instrument.[3–6]

The mobility of sodium dodecyl sulfate (SDS) estimated from the electrophoretic light scattering was in good agreement with that from the moving boundary in a Tiselius-type electrophoretic apparatus.[7] Moreover, it was reported that the mobility of mixed micelles of SDS and octaethylene glycol dodecyl ether increased in proportion to molar ratio of SDS less than 0.3.[5] The electrophoretic mobility of tetradecyl- and hexadecyltrimethylammonium salicylate micelles changed from positive to negative with addition of 0–0.5 M sodium salicylate, indicating specific adsorption and penetration of salicylate ions.[4,6]

The electrophoretic mobility of protonated C_{12}DAO micelles in 0.1 M NaCl was investigated with the moving boundary method.[8,9] The mobility was affected by pH. The surface potential of micelles was evaluated from the potentiometric titration and compared with the zeta potential of the electric double layer which was calculated from the electrophoretic mobility.

In this work, the electrophoretic light scattering is measured for aqueous NaCl solutions of dodecyl-, tetradecyl-, and oleyldimethylamine oxides (C_{12}DAO, C_{14}DAO, ODAO). The effect of degree of protonation on electrophoretic mobility is discussed in relation to the electrostatic potential of a micelle.

C_nDAO and ODAO molecules are protonated and converted into *N*-hydroxyammonium ions, if HCl is added into aqueous surfactant solutions. The potentiometric titration for aqueous solutions of C_nDAO and ODAO was investigated, and the electrostatic potential on micellar surface was discussed.[8–12] It was also reported that the critical micelle concentration and the aggregation number of C_nDAO and ODAO micelles varied with the degree of protonation.[13–15] The degree of protonation also affected the liquid–liquid phase separation of aqueous solutions of C_nDAO and ODAO.[11,12,16] Therefore, the conditions where homogeneous micellar solutions of C_nDAO and ODAO without liquid–liquid phase separation were obtained were chosen in this work.

Experimental Section

Samples of C_{12}DAO, C_{14}DAO, and ODAO are the same as previously prepared and used.[12,14] NaCl was heated for an hour to remove organic contaminations. Redistilled water was prepared by a routine method. The pH of aqueous NaCl solutions of surfactants was adjusted by adding a small amount of standardized HCl solution. The degree of protonation α was calculated by dividing the difference between total and free molar concentrations of hydrogen ion by the molar concentration of surfactant.[12] The solutions were purified from dust by circulating them through a 0.2-μm membrane filter.

The electrophoretic mobility was measured at 25 °C on an Otsuka Electronics electrophoretic light scattering spectrophotometer, ELS-800. The experimental procedure is described in

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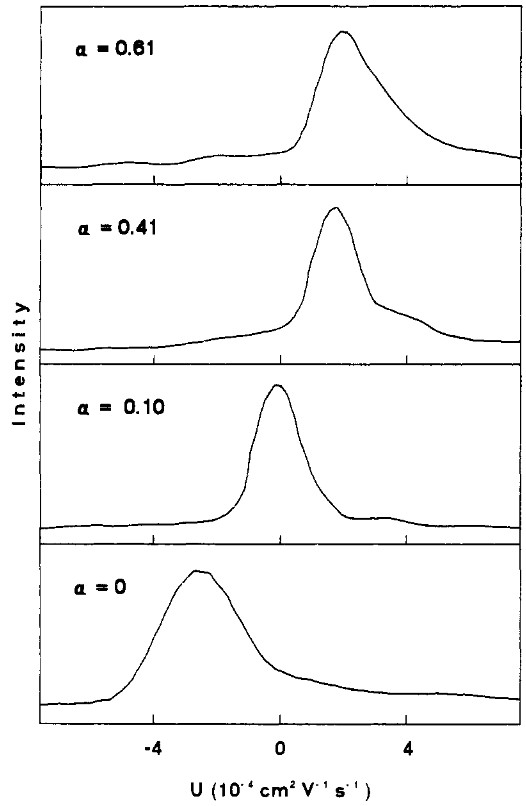

Figure 1. Electrophoretic light scattering power spectra for 0.1 M NaCl solutions of C_{14}DAO at surfactant concentration of 0.5 × 10^{-2} g cm^{-3} with various degrees of protonation.

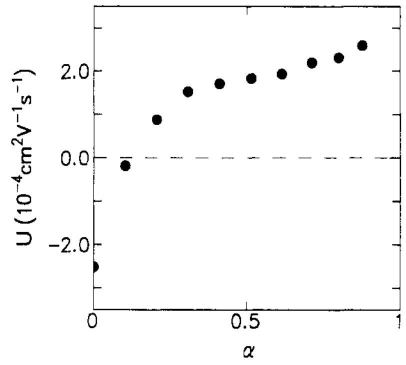

Figure 2. Electrophoretic mobility as a function of degree of protonation for 0.1 M NaCl solutions of C_{14}DAO at surfactant concentration of 0.5 × 10^{-2} g cm^{-3}.

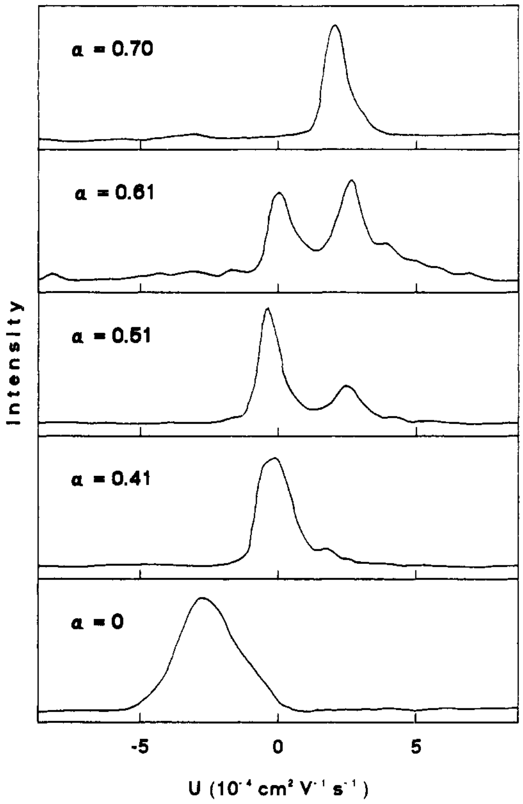

Figure 3. Electrophoretic light scattering power spectra for 0.05 M NaCl solutions of C_{14}DAO at surfactant concentration of 0.5 × 10^{-2} g cm^{-3} with various degrees of protonation.

detail in a separate paper.[17] The apparatus was operated at 10–20° scattering angle with a He–Ne laser of 633 nm wavelength. The electric field perpendicular to the incident radiation was applied in 1-s pulses which were reversed on each successive application. The electrophoretic drift velocity v at an applied electric field strength E was evaluated from a Doppler shift frequency on the electrophoretic light scattering power spectrum. The electric field strength was changed between 5 and 25 V cm^{-1}, and the drift velocity at different electric fields was averaged.

The electrophoretic mobility U is the velocity per unit electric field and calculated by $U = v/E$. The effect of electroosmosis was corrected on the basis of the theoretical equation by Mori and Okamoto,[18] and the true mobility at the stationary level was evaluated. The sign of the mobility was determined by modulating the frequency of reference light.

Results

Figure 1 shows electrophoretic light scattering power spectra for 0.1 M NaCl solutions of C_{14}DAO at a surfactant concentration of 0.5 × 10^{-2} g cm^{-3} with various degrees of protonation. Each spectrum displays a strong peak. The electrophoretic mobilities at the peak position are plotted as a function of degree of protonation in Figure 2. The mobilities shift from −2.5 × 10^{-4} to 2.6 × 10^{-4} cm^2 V^{-1} s^{-1} with increasing degree of protonation from 0 to 0.88. Those change drastically between $\alpha = 0$ and 0.3 and gradually above $\alpha = 0.3$.

The power spectra for 0.05 M NaCl solutions of C_{14}DAO at 0.5 × 10^{-2} g cm^{-3} are given in Figure 3. The dependence of spectra on degree of protonation is fundamentally different from that for 0.1 M NaCl solutions. The spectra at $\alpha = 0$ and 0.41 exhibit a strong peak with negative and zero mobilities, respectively, and the third peak with positive mobility appears above $\alpha = 0.51$. The magnitude of the peak with zero mobility is almost equivalent at $\alpha = 0.61$ to that with positive mobility, and the peak disappears at $\alpha = 0.70$.

The electrophoretic mobilities as a function of degree of protonation for 0.05 M NaCl solutions of C_{14}DAO are shown in Figure 4 for surfactant concentration at 0.5 × 10^{-2} g cm^{-3} and in Figure 5 for concentrations at 0.3 × 10^{-2} and 1.0 × 10^{-2} g cm^{-3}. Figure 4 includes the fraction of the third peak f_3 as a function of degree of protonation. The f_3 values were evaluated from the intensity of peaks. Remarkable concentration dependence is not observed. Commonly, the mobilities at $\alpha = 0$ are ~−2.5 × 10^{-4} cm^2 V^{-1} s^{-1}, and those at high α values are ~2 × 10^{-4} cm^2 V^{-1} s^{-1}. Negative, zero, and positive mobilities transferred at α = 0–0.1 and 0.5–0.7.

The behavior of power spectra at various degrees of protonation for 0.03 M NaCl solutions of ODAO at 0.1 × 10^{-2} g cm^{-3} is similar to that for 0.1 M NaCl solutions of C_{14}DAO at 0.5 × 10^{-2} g cm^{-3}. The mobility of the strong

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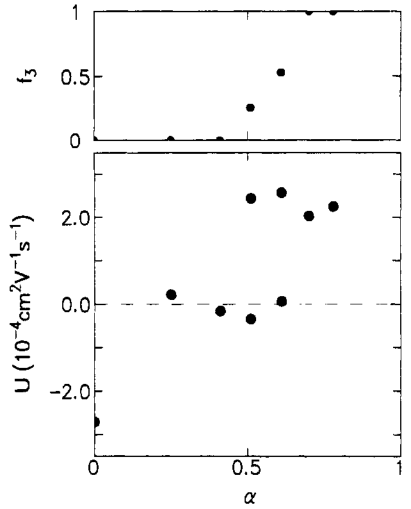

Figure 4. Electrophoretic mobility and f_3 value as a function of degree of protonation for 0.05 M NaCl solutions of $C_{14}DAO$ at surfactant concentration of 0.5×10^{-2} g cm^{-3}.

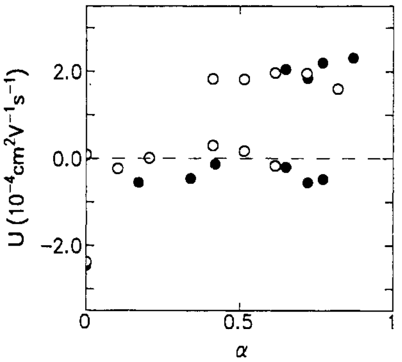

Figure 5. Electrophoretic mobility as a function of degree of protonation for 0.05 M NaCl solutions of $C_{14}DAO$ at surfactant concentrations of 0.3×10^{-2} (●) and 1.0×10^{-2} (○) g cm^{-3}.

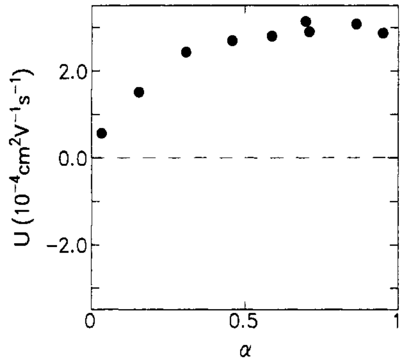

Figure 6. Electrophoretic mobility as a function of degree of protonation for 0.03 M NaCl solutions of ODAO at surfactant concentration of 0.1×10^{-2} g cm^{-3}.

peak varies from 0 to ~3×10^{-4} cm^2 V^{-1} s^{-1} with the change of $\alpha = 0$–1. The variation is abrupt at low α values, as seen in Figure 6.

Figure 7 gives electrophoretic mobilities for 0.05 M NaCl solutions of $C_{12}DAO$ at 1.0×10^{-2} g cm^{-3}. The behavior is very similar to that for 0.05 M NaCl solutions of $C_{14}DAO$. There are three kinds of mobilities, and they transfer at α = ~0.05 and ~0.65. The data for 0.1 M NaCl solutions of $C_{12}DAO$, which were measured with the moving boundary method,[8,9] are plotted in Figure 7. The behavior of mobility is consistent with that for $C_{14}DAO$ micelles in 0.1 M NaCl rather than that for $C_{12}DAO$ micelles in 0.05 M NaCl in this work.

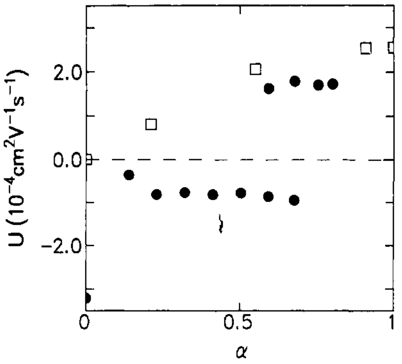

Figure 7. Electrophoretic mobility as a function of degree of protonation for 0.05 M NaCl solutions of $C_{12}DAO$ at surfactant concentration of 10^{-2} g cm^{-3}. Square signs are data for 0.1 M NaCl solutions of $C_{12}DAO$ which were taken from refs 8 and 9.

Discussion

Alkyldimethylamine oxide is protonated by the equilibrium

$$C_nH_{2n+1}N(CH_3)_2O + H^+ \rightleftarrows C_nH_{2n+1}N^+(CH_3)_2OH \qquad (1)$$

Then the apparent dissociation constant for a micellar solution is written by

$$pK_{app} = pH + \log[\alpha/(1-\alpha)] \qquad (2)$$

Since micelles coexist with monomeric molecules in a solution, the dissociation constant must be described for each species. For micellar species, expressing the intrinsic dissociation constant of micelles by K_m and the electrostatic potential at micellar surface by Ψ_0,

$$pK_{m,app} = pH + \log\frac{\alpha_m}{1-\alpha_m} = pK_m - \frac{0.434}{k_BT}e\Psi_0 \qquad (3)$$

and

$$\alpha_m = \frac{c\alpha - c_1\alpha_1}{c - c_1} \qquad (4)$$

where e is the elementary electric charge, k_B is the Boltzmann constant, and T is the absolute temperature. c and c_1 are total and monomeric surfactant concentrations (g cm^{-3}), respectively. α_1 and α_m are degrees of protonation of monomer and micelle, respectively.

The micellar surface is usually surrounded by small ions, which form immobile and mobile parts of the electric double layer, that is, the Stern layer and the diffuse double layer. Therefore, the electrostatic potential Ψ_s at the boundary between two parts (at the Stern layer) is different from the potential Ψ_0 at the micellar surface.

Under the electric field, colloidal particles move together with hydrated small ions which are adsorbed or bound on particles. Then the electrophoretic mobility U is written by

$$U = f(\kappa a)\frac{\epsilon}{\pi\eta}\zeta \qquad (5)$$

where $f(\kappa a)$ is a function of the Debye–Hückel shielding parameter κ, radius of particle a, and particle shape. ϵ is the dielectric constant and η is the viscosity of solvent. ζ is the zeta potential at the slipping plane and can be approximated to the potential Ψ_s.

It should be noted that the electrophoretic mobility at $\alpha = 0$ is negative for solutions of $C_{12}DAO$ and $C_{14}DAO$. This indicates the adsorption of chloride ions on micellar surfaces of nonionic C_nDAO, as illustrated in Figure 8(1). This may originate in the interaction between polarized

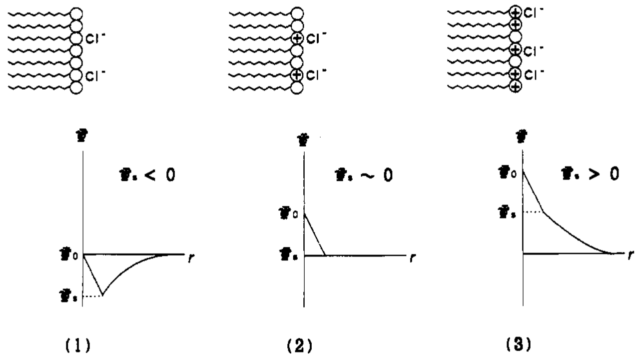

Figure 8. Schematic representation of counterion binding on C_nDAO micelles and electrostatic potential at the micellar surface.

amine oxide of surfactant and hydrated water on chloride ion. With increasing degree of protonation up to 0.1, the mobility increases to zero. Then protonated micelles are adsorbed by equivalent amounts of chloride ions owing to the electrostatic attraction force (see Figure 8(2)). At high degree of protonation, less amounts of chloride ions adsorb on charged micellar surfaces, since the electric double layer is formed (see Figure 8(3)). Therefore, the electrostatic potential Ψ_s changes from negative to positive with increasing degree of protonation.

When the electrostatic potential varies, there are two types of processes. The electrophoretic mobility for C_{12}DAO and C_{14}DAO micelles in 0.1 M NaCl as well as for ODAO micelles in 0.03 M NaCl increases abruptly with degree of protonation up to 0.3. This means that the electrostatic potential at the Stern layer of a micelle changes with degree of protonation, suggesting continuous variation of nonionic micelles to cationic ones and successive adsorption of chloride ions on micelles. At α = 0.3–1 where the mobility increases gradually, successive adsorption of chloride ions is restrained.

The situation is different for C_{12}DAO and C_{14}DAO micelles in 0.05 M NaCl. There is a transition from zero to positive mobilities at a narrow degree of protonation. Moreover, two species with different mobilities coexist at the transition region (α = 0.5–0.7).

Two kinds of interpretation are possible for the coexistence of two micelle species. The first possibility is the existence of nonionic-rich and cationic-rich micelles. The coexistence of two micelle species with different composition was reported for a mixed system of hydrocarbon and fluorocarbon surfactants.[19-21] Theoretical analysis proved that the fluorocarbon–fluorocarbon interaction was more desirable than the hydrocarbon–fluorocarbon interaction.[22,23] If the formation of separated micelles with different composition is possible for C_nDAO micelles at a moderate degree of protonation, the interaction between cationic head groups or between nonionic head groups must be superior to that between cationic and nonionic head groups. There is no theoretical support for this.

The second possibility is the existence of two micelle species with different degrees of counterion binding, while they have a same ratio of cationic and nonionic surfactant species. Then the difference between electrophoretic mobility of two micelle species is attributed to the difference of electrostatic potential at the Stern layer, as suggested by eq 5.

When shapes of two kinds of species are spherical and rodlike (or ellipsoidal), the contribution on electrophoretic mobility from two species is different. The effective degree of ionization of ionic micelles was investigated experimentally[24-29] and theoretically,[30] and it was reported that the effective degree of ionization of ionic spherical micelles differed from that of ionic rodlike micelles. Then the electrophoretic mobility for two species of micelles must be different from each other. The existence of two micelle species in aqueous NaCl solutions of C_nDAO was already suggested from results of the potentiometric titration.[12] However, different degrees of counterion binding for C_{12}DAO micelles in 0.05 M NaCl are not necessarily induced by micelles with different size or shape, since those micelles are always spherical at whole pH region.[10]

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