

# Analysis of Polydispersity of Mixed Micelles of TX-100/SDS and C<sub>12</sub>E<sub>8</sub>/SDS by Capillary Electrophoresis

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Capillary electrophoresis (CE) was used to study the polydispersity of TX-100/SDS and C<sub>12</sub>E<sub>8</sub>/SDS micelle systems. Compared with other techniques, CE provides more specific and graphically detailed information on the compositional polydispersity of such micellar systems. Clear evidence of the coexistence of micelles rich in either nonionic or anionic component has been obtained. This coexistence is explained by considering that the stability of mixed micelles is affected by several factors, including counterion binding, and steric shielding of the electrostatic repulsive interaction among the headgroups of SDS by the bulky EO groups of TX-100. Due to these two factors, micelles with different compositions may be energetically equivalent, leading to a broad distribution of micelle size and composition. In this study, we observe how the pattern of the distribution changes with the mole fraction of SDS. Electrophoretographic patterns also showed that broader compositional distribution of the original components produces a wider distribution of mobilities. © 1997 Academic Press

**Key Words:** micelle heterogeneity; CE of micelles; mixed micelles; micelle composition.

## INTRODUCTION

All micellar systems exhibit some degree of polydispersity with respect to micelle size and aggregation number. In mixed micelles, this distribution is accompanied by compositional heterogeneity, which, for ionic systems, goes hand in hand with a distribution of micelle charge. The polydispersity of micelle size and aggregation number has been the subject of several theoretical studies (1–5). Mukerjee (1, 2) for example described polydispersity in terms of weight and number average degrees of aggregation. However, experimental evidence of polydispersity so far is rare and largely qualitative (6–8). Hence, the existence of polydispersity has often been inferred from either theory or indirect interpretation of results (9, 10) rather than by direct observation.

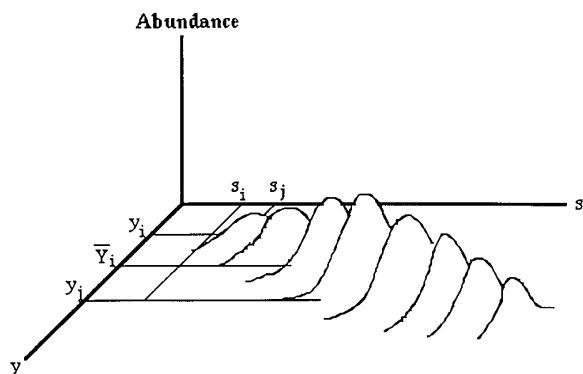
Different methods may be used to reveal the aggregation number polydispersity of chemically homogeneous micelle systems. Corti and Degiorgio (11, 12) used quasi-elastic light scat-

tering (QELS) to determine for SDS micelles the polydispersity, defined as  $v = \frac{\sum (N_i M_i^2) [\sum N_i M_i^2 (D_i - D)^2] / \sum (N_i M_i^2 D_i)^2}{\sum (N_i M_i^2) [\sum N_i M_i^2 (D_i - D)^2] / \sum (N_i M_i^2 D_i)^2}$ , where  $N_i$  is the number of particles with diffusion coefficient  $D_i$  and molecular weight  $M_i$ , and  $D$  is the average diffusion coefficient. The polydispersity decreases with temperature but increases with concentration and ionic strength. Using the same method, Benedek *et al.* (13) described the polydispersity of SDS in NaCl solutions by means of the variance ( $V$ ), defined as  $N_z/N_w \cong 1 + 4V^2$  ( $N_z$  and  $N_w$  are the  $z$ -average and weight-average aggregation numbers, respectively). Several workers used a fluorescence quenching method (14–16) in which the fluorescence decay curve of the probe was analyzed to obtain surfactant aggregation numbers. Using this method, Reekmans *et al.* (16) concluded for hexadecyltrimethylammonium chloride systems that “the system exhibits a rather broad polydispersity in micellar aggregation numbers at low surfactant concentration. Increasing the surfactant concentration leads to a growth of the smaller micelles and, thus, to a more narrow size distribution.” Gel chromatography may also be applied to evaluate micelle size distributions. Using this method, Funasaki *et al.* (17) observed that at intermediate concentrations, C<sub>12</sub>E<sub>6</sub> micelle peaks exhibited some broadening and they concluded that two micellar species with different sizes coexist at such concentrations.

For mixed surfactant systems, polydispersity in both size (or aggregation number) and composition of micelles may co-exist. As shown in Fig. 1, for a two-component system with a bulk mole fraction of component 1 ( $Y$ ), a compositional distribution may appear in addition to a size distribution; namely, the mole fraction of component 1 in the micelles ( $y$ ) may be distributed around the mean value,  $Y$ , which corresponds to the bulk, or stoichiometric mole fraction of component 1. Micelles of the same microcomposition ( $y$ ) may vary in aggregation number (size); micelles of the same size(s) may differ in microcomposition. When  $Y$  is changed, distributions of both size and composition may change. Differences in the structure of the hydrophobic moieties of the two surfactants and interactions among their hydrophilic groups are among the factors that may influence the polydispersity of size or composition.

Experimental evidence for compositional heterogeneity in mixed micelles is not abundant. Abe *et al.* (18–20) found

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**FIG. 1.** Schematic description of polydispersity of mixed micelles.  $\bar{Y}$  represents bulk mole fraction of one of components,  $y$  stands for microcomposition of micelles;  $s$  represents size of micelles.

two break points in the surface tension vs concentration curve for 3,6,9-trioxaicosanoate (TOI)/C<sub>12</sub>E<sub>20</sub>, corresponding to the CMC's (critical micellization concentration) of TOI and C<sub>12</sub>E<sub>20</sub>, respectively. This phenomenon, under the assumption of additivity of surface tensions, was interpreted in terms of co-existing micelles, one rich in TOI and the other in C<sub>12</sub>E<sub>20</sub>. On the other hand, both Akasu *et al.* (21) and Kameyama and Takagi (22) carried out electrophoretic light scattering measurements of C<sub>12</sub>E<sub>8</sub>/SDS mixed systems and reported electrophoretically monodisperse mixed micelles. Nakagawa and Inoue (23), who measured the mobilities of C<sub>12</sub>E<sub>5</sub>/SDS mixed micelles using a Tiselius device, concluded that the system was quite monodisperse, but this observation might have resulted from the limited separating ability of the device. Lastly, Tokiwa and Aigami (24) studied C<sub>8</sub>φE<sub>9</sub> (isooctylphenyl nonaoxyethylene ether)/SDS and C<sub>12</sub>E<sub>9</sub>/SDS systems using both light scattering and the Tiselius device. In both systems, one or more minor peaks were observed in the electrophoretic patterns, although these were sometimes irreproducible.

The development of suitable and convenient methods for studying the polydispersity in such mixed micelle systems, especially for charged micelles, has thus been a continuing objective, but few studies have been reported. Size measurements using quasi-elastic light scattering (QELS) are complicated by intermicellar interactions, especially for charged micelles; furthermore, the size resolution of QELS is poor. The results of fluorescence quenching measurement can be probe-dependent, and the effect of the probe on micelle polydispersity is not clear. Surface tension measurements can only reflect the overall contribution from all species in the system, so that conclusions about polydispersity based on this method can only be indirect.

In this study, we employed capillary electrophoresis (CE) to observe the compositional polydispersity of mixed micelles of SDS/TX-100 and SDS/C<sub>12</sub>E<sub>8</sub>. As a chromatographic method, CE enables different species to be manifested as different peaks, in contrast to the other techniques described

above. Our results provide a detailed description of the polydispersity of mixed anionic/nonionic micelles, and strongly suggest that pure nonionic surfactant micelles co-exist with mixed anionic/nonionic surfactant micelles.

## EXPERIMENTAL

**Materials.** Monodisperse hexaoxyethylene dodecyl ether (C<sub>12</sub>E<sub>8</sub>) was from Nikkol Chemicals Co. (Tokyo, Japan). SDS (purity > 99%) was from Fluka (Buchs, Switzerland). Triton X-100 (TX-100) was from Sigma (St. Louis, MO, USA). Milli-Q water was used throughout this work.

**Capillary electrophoresis.** Capillary electrophoresis measurements were made on a Beckman P/ACE 2000 Instruments, USA, with UV detector and a voltage of 30 kV. A 50 μm (ID) × 50 cm (effective length) capillary was kept at 25 ± 0.1°C. The mobile phase was pH = 9.1, 0.05 M Na borate. Methanol was used as the reference material and assumed not to undergo electrophoresis. The electrophoretic mobility was calculated by

$$\mu = (lL(t_0 - t_s)/t_0 t_s)E^{-1} \quad [\text{cm}^2/\text{V} \cdot \text{s}] \quad [1]$$

where  $l$  is the effective length of the capillary and  $L$  the total length of the capillary (both in cm), and  $t_s$  and  $t_0$  are retention time(s) of a sample and a reference material, respectively, and  $E$  is the electric field (volts). The total concentration of surfactants was 50 mM, far above the mixed CMC (ca. 0.1 mM), so that nearly all of the surfactants were in micellar form. TX-100, having a strong chromophore, was detected at 254 nm. Although SDS and C<sub>12</sub>E<sub>8</sub> do not have chromophores at  $\lambda = 200\text{--}300$  nm, negative "absorption" peaks still could be obtained at  $\lambda = 200$  nm since the absorbance of the buffer (background) was relatively stronger. The mobilities of two reference compounds, SDS micelles and BSA, were measured in 0.01 M, pH = 6.94 sodium phosphate buffer + 0.03 M NaCl, giving  $-3.0 \times 10^{-4}$  and  $-1.3 \times 10^{-4}$  cm<sup>2</sup>/V · s, respectively, in good agreement with the values reported by Nakagawa and Inoue (23) and Sasa and Takeda (25) under similar conditions.

**Quasi-elastic light scattering.** Micellar sizes were determined by quasi-elastic light scattering with a DynaPro-801 (Protein Solutions Inc., Charlottesville, VA), which employs a 30 mW solid-state 780-nm laser and an avalanche photodiode detector. Samples prepared in pH 9.1, 0.05 M Na borate buffer were introduced into the 7-μl cell via 0.1 μm Anotec filters. The 90° scattering data were analyzed via the method of cumulants. The measured diffusion constant was used to obtain the apparent hydrodynamic radius of the micelles,  $R_h$ . This analysis is based on the assumption that the mutual diffusion coefficient can be equated to the translational diffusion coefficient, which presupposes that contributions from intermicellar interactions are small. In support of this are

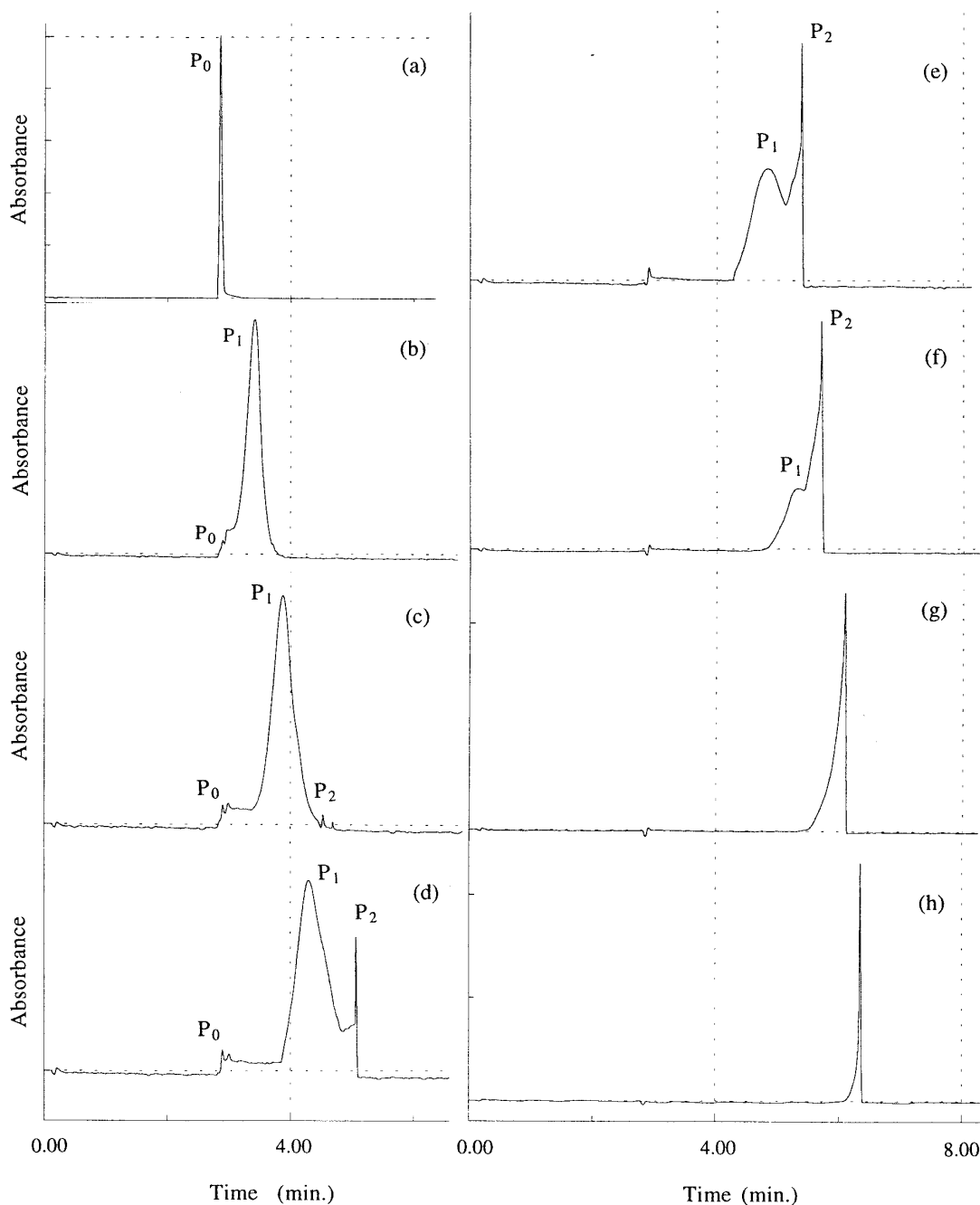


FIG. 2. Capillary electrophoretograms of TX-100/SDS systems in Ph 9.1, 0.05 *M* Na Borate at different mole fractions of SDS, *Y*: (a) 0, (b) 0.10, (c) 0.20, (d) 0.30, (e) 0.40, (f) 0.50, (g) 0.60, (h) 0.80.

the good agreement between  $R_h$  obtained by QELS and size-exclusion chromatography for SDS/TX-100 under similar solution conditions (26).

## RESULTS AND DISCUSSION

*TX-100/SDS systems.* Figure 2 shows the dependence of the mobility and the pattern of the electrophoretogram on the

mole fraction of SDS, *Y*, for TX-100/SDS mixed micelles. At  $Y = 0$  (Figure 2(a)), all nonionic species move at the same speed as the bulk flow, and only one narrow peak is observed. When  $Y \geq 0.10$ , several peaks occur and the total width of the peaks is widened dramatically. For  $0.1 \leq Y < 0.6$ , more than one peak is observed. A peak with virtually the same mobility as the pure nonionic micelles is seen, denoted as " $P_0$ ." Thus, this experiment serves as direct

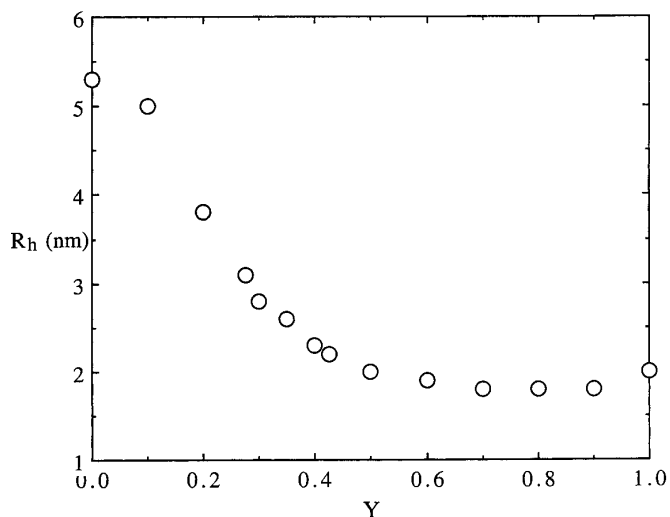


FIG. 3. Size dependence of mixed TX-100/SDS micelles on mole fraction of SDS.

evidence of the existence of purely nonionic surfactant micelles in such mixed micellar systems. Such interpretation had been suggested 20 years ago by Meguro *et al.* (27) based on the studies of interaction between 7,7,8,8-tetracyanoquinodimethane (TCQN) and C<sub>12</sub>E<sub>8</sub>/SDS (9:1), via absorbance band shifts due to charge transfer between TCQN and the surfactants. The magnitude of  $P_0$  becomes smaller with increasing  $Y$ , vanishing when  $Y \geq 0.50$ , while the position and intensity of other peaks also vary with  $Y$ . Since other peaks occur after  $P_0$ , the mobilities of the micelles associated with these peaks have negative sign; therefore, these micelles must contain anionic component, namely SDS. Since SDS does not have any chromophore at 254 nm, and the absorbance only comes from TX-100, all peaks except  $P_0$  must represent mixed TX-100/SDS micelles.

Peaks appearing at different positions in the range  $0.1 \leq Y \leq 0.50$  (Figure 2(b–f)) must correspond to micellar species of different electrophoretic mobilities. The mobility is given by

$$\mu = q/6\pi\eta r \quad [2]$$

where  $\eta$  is the viscosity of the solvent, and  $q$  and  $r$  the charge and radius of the particle, respectively. When the solvent and the temperature are fixed, the electrophoretic mobility  $\mu$  will depend on  $q$  and  $r$  only. The charge  $q$  is the product of the aggregation number  $N$  and the mole fraction of the ionic component ( $y$ ) in the mixed micelle. If  $N$  were constant, the mobility of a mixed anionic/nonionic micelle would increase linearly with  $y$ . Although the size polydispersity in such systems is not known, the average size of the micelles decreases as  $Y$  increases, as shown in Fig. 3, in which we plot the  $Y$ -dependence of the apparent hydrody-

dynamic radius by QELS. Since the mobility depends on  $Ny/r$ , with  $r$  and  $N$  both decreasing with increasing  $y$ , the analysis is complicated, but we nevertheless expect that micelles with large  $y$  will move migrate rapidly in the direction opposite to electro-osmotic flow. The first main peak in Fig. 2(c),  $P_1$ , which represents the majority of TX-100, should be identified as micelles rich in TX-100, whereas the second peak,  $P_2$ , corresponding to the micelle with largest absolute mobility, can be identified with micelles rich in SDS. Here, the subscripts 1 and 2 only represent, respectively, the two different categories of mixed micelles. Thus, Fig. 2(d–f) shows that all systems have two different types of mixed micelles: those rich in TX-100, denoted by  $P_1$ , and those rich in SDS, denoted by  $P_2$ . The amplitudes of  $P_0$ ,  $P_1$ , and  $P_2$  depend on  $Y$ . In contrast to  $P_1$ , the intensity of  $P_2$  increases with  $Y$ , becoming dominant at  $Y \geq 0.50$ , while  $P_1$  gradually becomes smaller, finally merging into  $P_2$ .

Manifold forces may be responsible for maintaining the coexistence of compositionally different micelles. Among the factors that determine micelle stability are hydrophobic interactions, hydrogen bonding among hydrophilic groups, and electrostatic interactions, which in turn depend on the degree of counterion binding ( $\beta$ ). For a mixed ionic/nonionic surfactant system, there may be additional factors. TX-100, with a bulky EO chain, can separate the charged groups of an ionic surfactant, such as SDS, reducing the electrostatic repulsive interaction among them. When the mole fraction of the nonionic surfactant is sufficiently high, SDS can be fully separated and shielded by the EO chains. Using an ion-selective electrode, Treiner *et al.* (28) found that binding of Na<sup>+</sup> to mixed SDS/C<sub>12</sub>E<sub>23</sub> micelles did not occur when  $Y \leq 0.15$ , indicating sufficient separation and shielding of  $-\text{SO}_3^-$  groups, so that the micelle is stable without counterion binding. The major peak in Fig. 2(b) may correspond to such micelles. When  $Y$  increases, an increase in repulsive interaction among  $-\text{SO}_3^-$  groups results in decreased micelle stability. Higher counterion binding is necessary to reduce the increasing repulsive electrostatic interactions. Treiner *et al.* showed that  $\beta$  increases from 0.24 to 0.74 when  $Y$  increases from 0.40 to 1. The interaction among the headgroups of SDS is also affected by the microenvironment of the  $-\text{SO}_3^-$  groups. The palisade layer, composed of the EO chains, has a dielectric constant of  $\epsilon = 40-50$  (29), much smaller than that of water (80), which brings about an increased repulsion between ionic headgroups and destabilizes the micelle.

The distribution of mobilities observed in Fig. 2 corresponds to a distribution of compositions. If the energy of micellization were unfavorable for micelles with high SDS content ( $y$ ), a rather narrow distribution might prevail so as to minimize the content of micelles with large  $y$ . However, counterion binding could be expected to preferentially reduce the electrostatic repulsive energy of such micelles, thus permitting a broader distribution to exist. These micelles

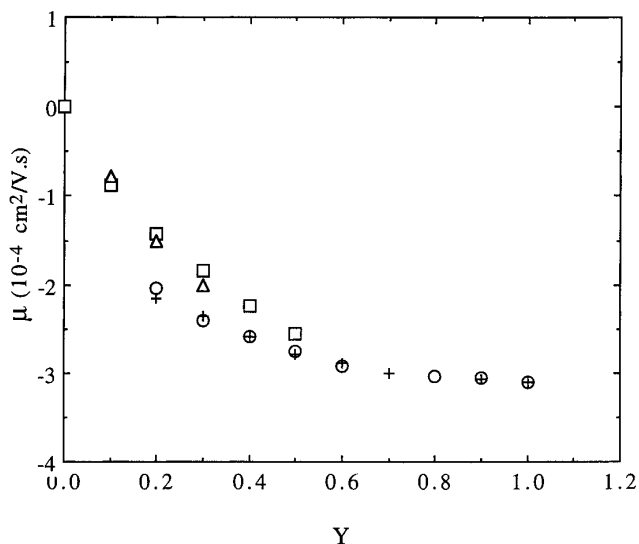


FIG. 4. Effect of mole fraction of SDS on micellar compositional polydispersity: TX-100/SDS, peak 1 (○), peak 2 (□); C<sub>12</sub>E<sub>8</sub>/SDS, peak 1 (△), peak 3 (+).

with a low mole fraction of nonionic could also be stabilized by steric separation of some of the numerous SDS headgroups, if the nonionic headgroups are large; while the electrostatic energy of micelles with small  $y$ , in which SDS headgroups are necessarily well-separated, is not expected to be affected very much by nonionic headgroup size. However, a third effect which would alter the mobility of low- $y$  micelles could result from an increase in the distance between the shear plane and the sulfonate groups arising from the congested state of bulky nonionic headgroups. Consequently, micelles with low  $y$  would have even lower mobilities than expected on the basis of the mole fraction of SDS. All three effects can lead to a large distribution of mobilities in the electrophoretograms.

The dependence of peak positions (mobilities) on  $Y$  is shown in Fig. 4. For  $0 < Y \leq 0.2$ , the effect of  $Y$  on the mobility of micelle,  $|d\mu/dY|$ , is large, whereas, for  $0.7 < Y < 1$ , the mobilities of the micelles are almost independent of  $Y$ . The rapid increase in the absolute value of the mobility at low  $Y$  should be considered together with the similarly dramatic fall in  $R_h$  over the same range in  $Y$ . This might correspond to a decrease in the thickness of the nonionic headgroup layer, due to an alleviation of steric congestion, and the corresponding increase in the absolute value of the  $\zeta$ -potential. These phenomena may also be related to the effect of  $Y$  on the degree of counterion binding. At low  $Y$ , the addition of charged SDS molecules results in a dramatic change of the mobility; this large  $|d\mu/dY|$  is in part due to the small  $\beta$ ; reduced counterion binding is possible since anionic surfactant molecules can be fully isolated by bulky nonionic surfactant molecules. For  $0.25 < Y < 0.6$ , the

change of mobility with  $Y$  is smaller. The higher counterion binding could be responsible for this result. For a similar reason, the mobility becomes less sensitive to  $Y$  for  $0.7 < Y < 1$ .

The range of compositions of micellar species (including but not limited to  $P_1$  and  $P_2$ ) can be described by a mobility range ( $\Delta\mu$ ) encompassing all the peaks (including the plateau before the main peaks). Since plateaus only occur before  $P_1$ , they should correspond to those micelles rich in nonionic surfactant. The dependence of  $\Delta\mu$  on  $Y$ , plotted in Fig. 5, reflects the effect of the mole fraction of SDS on the compositional polydispersity of the system. One interesting feature of the curves is the maximum at  $Y = 0.30$  for SDS/TX-100 systems. The increase of  $\Delta\mu$  with  $Y$  up to  $Y = 0.30$  indicates a greater compositional polydispersity range.

*C<sub>12</sub>E<sub>8</sub>/SDS.* The electrophoretograms of C<sub>12</sub>E<sub>8</sub>/SDS in Fig. 6 are similar to those of TX-100/SDS. The dependence of mobilities and their polydispersity on the mole fraction of SDS are also included in Figs. 4 and 5, respectively. However, there are two significant differences between the two sets of data. First, the plateau observed for TX-100/SDS is absent, resulting in smaller  $\Delta\mu$ , as seen in Fig. 5. We suggest that the plateau corresponds to micelles rich in longer EO chain length surfactants. According to Ogino and Abe (14, 15), longer-EO chain nonionic surfactants form mixed micelles less readily than shorter-EO chain surfactants, so that micelles rich in longer EO chain species might be relatively poor in SDS. Our previous work (30) shows that at constant  $Y$ , the absolute value of the mobility of mixed C<sub>12</sub>E<sub>*n*</sub>/SDS micelles decreases with increase of EO chain length. For these reasons, the greater range of mobilities  $\Delta\mu$  for TX-100/SDS compared with C<sub>12</sub>E<sub>8</sub>/SDS may be attributed to the broader distribution of EO chains in TX-100. A

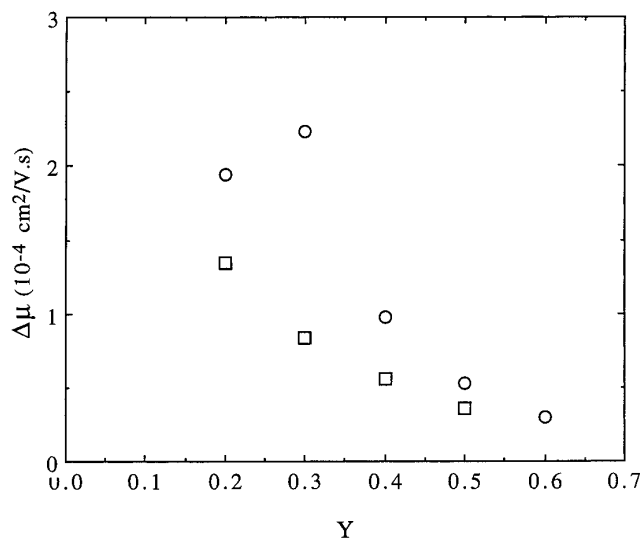
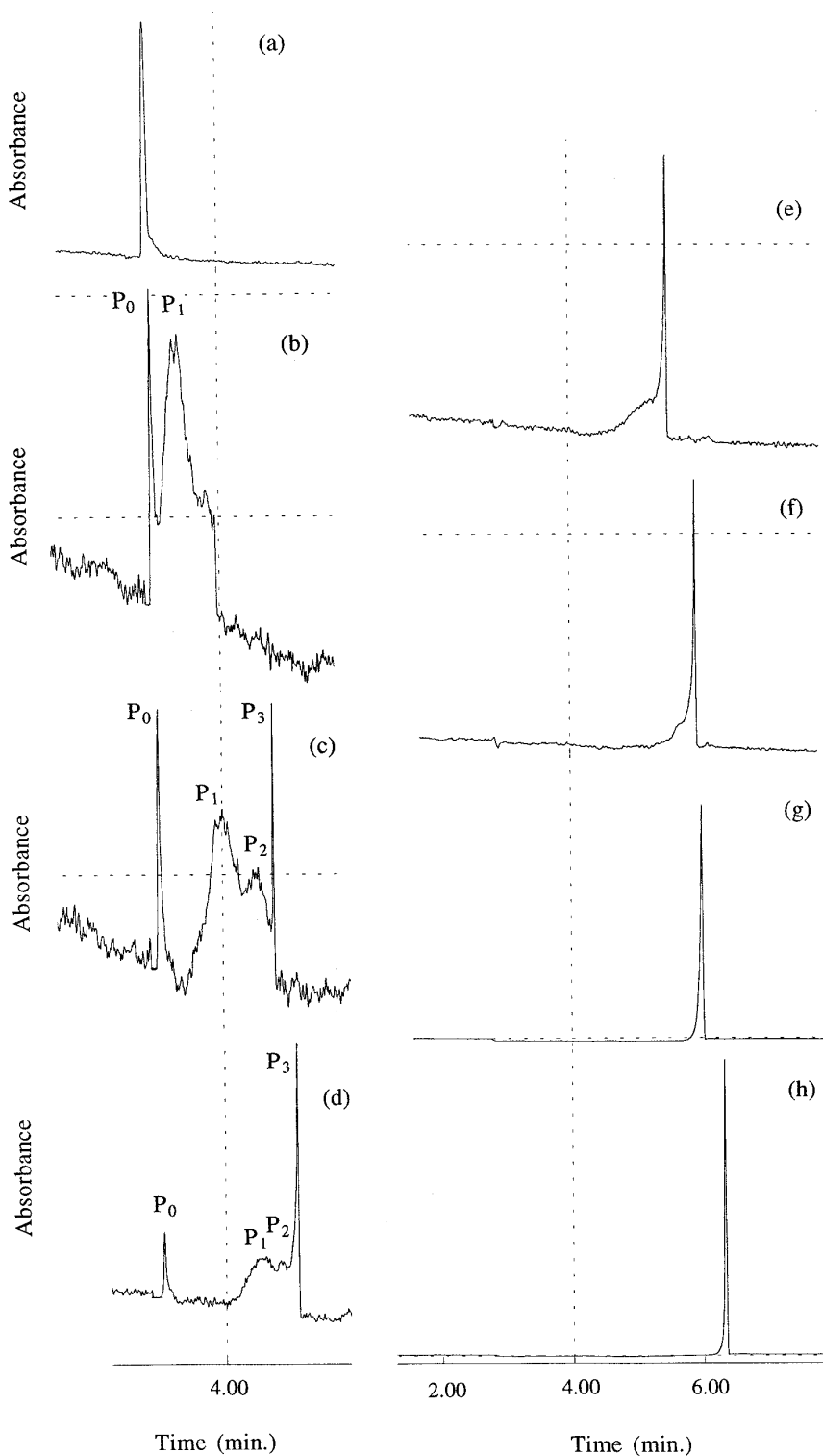


FIG. 5. Effect of mole fraction of SDS on the mobility polydispersity (in terms of  $\Delta\mu$ ) of mixed micelles: TX-100/SDS (○), C<sub>12</sub>E<sub>8</sub>/SDS (□).



**FIG. 6.** Capillary electrophoretograms of C<sub>12</sub>E<sub>8</sub>/SDS systems at different mole fractions of SDS,  $Y$ : (a) 0, (b) 0.10, (c) 0.20, (d) 0.30, (e) 0.40, (f) 0.50, (g) 0.60, (h) 0.70.

second observation is the presence of three major peaks besides  $P_0$  ( $P_1$ ,  $P_2$ , and  $P_3$ ) in the C<sub>12</sub>E<sub>8</sub>/SDS systems compared to two in TX-100/SDS, when  $0.20 \leq Y \leq 0.30$ . Al-

though the largest mobility peak must correspond to mixed micelles rich in SDS, the significance of the intermediate one is unknown.

## CONCLUSION

The current work shows that capillary electrophoresis is a powerful and convenient tool to study the polydispersity of anionic–nonionic mixed micelles. Through CE measurements, more specific and detailed information of distribution and the pattern of the distribution can be easily obtained than other techniques. The results prove the coexistence of micelles rich in nonionic surfactant and micelles rich in SDS. At present, the difficulty of identifying the microscopic mole fraction of SDS for each chromatographic species is an obstruction to the quantitative treatment of the data in terms of compositional polydispersity. This problem might be solved by elemental analysis of collected fractions.

## ACKNOWLEDGMENT

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