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# Critical micelle concentration of mixed surfactant SDS/NP(EO)$_{40}$ and its role in emulsion polymerization

Li-Jen Chen [b], Shi-Yow Lin [a], Chorng-Shyan Chern [a,]*, Shuo-Cheng Wu [b]

[a] *Department of Chemical Engineering, National Taiwan Institute of Technology, Taipei, Taiwan 106, China*
[b] *Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan 106, China*

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**Abstract**

In emulsion polymerization of styrene, nearly all of the polymer particle nuclei are formed in micelles. Therefore, it is of fundamental importance to understand the relations involved in micelle formation. In this study, the critical micelle concentrations (CMC) of the mixed surfactant, sodium dodecyl sulfate (SDS)/nonylphenol tetracontylethoxylate (NP(EO)$_{40}$), were determined for various compositions at 25°C and at 80°C by performing the surface tension measurements. The CMC data were well described by the regular solution model for mixed micelles. The system of mixed micelles exhibits a quite non-ideal behavior, especially at lower temperature (25°C). The effect of the mixed surfactant SDS/NP(EO)$_{40}$ on the formation of latex particles was demonstrated by a series of styrene emulsion polymerization. Adding only a small amount of the anionic surfactant SDS into the polymerization system can dramatically increase the concentration of latex particles and also reduce the particle size of the latex product. Furthermore, emulsion polymerization of styrene stabilized by the mixed surfactant system does not follow the conventional Smith-Ewart theory when the level of NP(EO)$_{40}$ is relatively high.

*Keywords:* Critical micelle concentration; Emulsion polymerization; Latex; Mixed surfactants; Surface tension

## 1. Introduction

A latex product is a dispersion of a large number of tiny polymer particles (ca. 50–1000 nm) in water, which has been widely used in coatings, adhesives, plastics, and rubber industry. These latex particles are thermodynamically unstable in nature and they are often stabilized by a mixture of anionic surfactants (e.g. sodium dodecyl sulfate, abbreviated by SDS) and non-ionic surfactants (e.g. nonylphenol polyethoxylate with an average of 40 ethylene oxides per molecule $C_9H_{19}$–$C_6H_4$–O–$(CH_2CH_2O)_{40}H$, abbreviated by NP(EO)$_{40}$) [1–5]. Anionic surfactants can provide repulsive force between similarly charged electric double layers to the particles, whereas non-ionic surfactants can impart the interactive particles with the steric stabilization mechanism. In addition, non-ionic surfactants can improve the chemical and freeze–thaw stability of the latex products.

The process of particle formation for batch emulsion polymerization of a relatively water-insoluble monomer (e.g. styrene) using an anionic surfactant can be described by the conventional micellar nucleation mechanism [6]. According to the micellar nucleation mechanism, micelles, formed by aggregation of surfactant molecules when the surfactant concentration is above the

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* Corresponding author.

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critical micelle concentration (CMC), are the principal locus of particle nucleation. The CMC of a surfactant solution can be determined by any physical property (e.g. surface tension used in this work) that shows a distinct transition around the CMC. Based on this particle nucleation mechanism, the well-known Smith-Ewart theory predicts that the number of particles nucleated is proportional to the surfactant concentration to the 0.6 power [7]. This is reasonable because for a given surfactant the number of micelles formed generally increases with an increase in the surfactant concentration. Thus, the number of micelles that can be transformed into latex particles increases as the surfactant concentration is increased. There is no doubt that the CMC of a surfactant solution and the number of micelles present in the reaction system play an important role in the particle nucleation process.

Chu and Piirma [2] studied batch emulsion polymerization of styrene stabilized by a mixed surfactant system. They found that the latex particles stabilized by a non-ionic surfactant alone were less stable and showed a tendency to flocculate with one another during the reaction, as compared to those particles stabilized by an anionic surfactant. Recently, Unzueta and Forcada [3] investigated semibatch seeded emulsion polymerization of acrylic monomers using a mixed surfactant system and came to a similar conclusion to that of Chu and Piirma [2]. Chern et al. [4,5] carried out semibatch emulsion polymerization of acrylic monomers stabilized by the mixed surfactant SDS/NP(EO)$_{40}$. They showed that the concentration of SDS in the initial reactor charge is the most important parameter in determining the particle size of the latex product. On the other hand, NP(EO)$_{40}$ is less effective for nucleating and stabilizing the particles and it only acts as an auxiliary surfactant. It is apparent that the non-ionic surfactant exhibits different behavior in particle nucleation and growth from the anionic counterpart. Nevertheless, the general validity of Smith-Ewart theory has not been established in the literature when applied to the styrene emulsion polymerization system stabilized by a surfactant mixture such as SDS/NP(EO)$_{40}$.

The objective of this work was therefore to determine the CMCs of the mixed surfactant SDS/NP(EO)$_{40}$ with various compositions at room temperature and at the polymerization temperature (80°C in this work). Furthermore, thermodynamic analysis on the CMC data of the mixed surfactant system, based on the mixed micelle model [8] shown in the following section, will be presented in this report. Such information should be useful for examining the generality of Smith-Ewart theory in future research. Preliminary data dealing with the role of the mixed surfactant in styrene emulsion polymerization will also be discussed in this report.

## 2. Mixed micelle model of rubingh [8]

The observed CMC of mixed surfactants is often significantly lower than would be expected based on the CMCs of the pure surfactants. This phenomenon is simply due to the fact that there exist some interactions between different surfactant molecules in the formation of mixed micelles. Rubingh [8] has developed a non-ideal mixed micelle model to describe this behavior, based on a phase separation model and a regular solution approximation.

A phase separation model is applied to the micellization. That is, the micelles are treated as a separate phase. At equilibrium, the chemical potential of the mono-dispersed surfactants in solution must be exactly the same as that of the surfactants in micelles. Based on these assumptions, one can derive the following relationship:

$$\alpha_i C_M^* = f_i x_i C_i^* \tag{1}$$

where $C_i^*$ and $C_M^*$ are the CMC of the pure surfactant $i$ and the mixed surfactants, respectively, $x_i$ is the mole fraction of surfactant $i$ in mixed micelles, $\alpha_i$ is the mole fraction of surfactant $i$ in the total mixed surfactants, and $f_i$ is the activity coefficient of surfactant $i$ in mixed micelles.

The activity coefficient in binary mixed micelles $f_i$ is approximated by the regular solution theory,

$$f_1 = e^{\beta x_2^2} \tag{2a}$$

$$f_2 = e^{\beta x_1^2} \tag{2b}$$

where the interaction parameter $\beta$ is formally defined as an excess heat of mixing. However, the calorimetric result showed that the regular solution approximation fails to account for the observed heat of mixing [9]. The interaction parameter $\beta$ of the non-ideal mixed micelle model is then more generally interpreted as an excess free energy of mixing parameter.

This mixed micelle model has been successfully applied to a considerable variety of binary nonideal surfactant mixtures, including anionic–non-ionic surfactants of the kind used in this study [9]. Note that in this model the ionic surfactant is not explicitly treated. That is, the effect of counterions is implicitly included in the activity coefficient of the ionic surfactant, SDS, in our case.

## 3. Experimental

### 3.1. Materials

The non-ionic surfactant nonylphenol polyethoxylate with an average of 40 ethylene oxides per molecule, $C_9H_{19}$–$C_6H_4$–O–$(CH_2CH_2O)_{40}H$, was purchased from Union Carbide. The anionic surfactant sodium dodecyl sulfate (technical grade) was purchased from Henkel, while the reagent grade one from Fluka with purity >99%. The monomer used in this work was styrene (Taiwan Styrene Monomer Co.). Sodium persulfate (Riedel-de-Haen) was used as the polymerization initiator. To mimic the industrial operation, all the chemicals were used as supplied without further purification, except the monomer styrene, which was distilled under reduced pressure before use. Water was purified via a Barnstead NANOpure II system with the resistance around 18 MΩ·cm.

### 3.2. Determination of CMC

The surface tension measurements were made by a Surface Tensiometer (CBVP-A3, Face) and a Dynamic Contact Angle Analyzer (DCA322, Cahn). A sandblasted platinum plate of dimensions 1.95 × 1.00 × 0.02 cm was used.

Solutions were contained by a double-walled Pyrex vessel thermostatted at 25.0±0.2°C or at 80.0±0.5°C. To prevent the contamination of solution from dust in air during the operation, the vessel had a cover with a hole only allowing a thin wire hanging the platinum plate to go through, and the whole vessel was placed inside a closed sample chamber of the surface tensiometer or the dynamic contact-angle analyzer.

Solutions were allowed to equilibrate until the surface tension stabilized. Therefore, the surface tension was measured as a function of time. It was found that the surface tension decreases as time evolves. It is believed that this dynamic behavior of surface tension is simply due to the rearrangement of surfactant molecular configuration at the interface. For certain systems, this phenomenon is very pronounced and it even took more than 20 h to reach equilibrium. The equilibrium surface tension was then determined whenever the tension leveled off to ensure the system reached fully equilibrium.

### 3.3. Batch emulsion polymerization

Batch emulsion polymerization experiment was performed in a 250 ml glass reactor equipped with a four-bladed fan turbine agitator, a thermometer, and a reflux condenser. A typical recipe is given in Table 1. The total solid content was designed at 15%. First, the reactor was charged by water, the mixed surfactant SDS/NP$(EO)_{40}$, and the monomer styrene and then purged with nitrogen for 10 min to remove dissolved oxygen while heated to 80°C, followed by adding the initiator solution to trigger the reaction. The polymerization was carried out at 80°C over 4 h. The finished latex product was filtered through a 40-mesh (0.42 mm)

Table 1
A typical recipe for the batch emulsion polymerization of styrene: $[S]=6\times10^{-3}$ M, $[\mathrm{NP(EO)_{40}}]=50\%$, $[I]=6.43\times10^{-3}$ M

| | Reagent | Weight (g) |
|---|---|---|
| Reactor charge | $H_2O$ | 80 |
| | SDS | 0.128 |
| | NP$(EO)_{40}$ | 0.128 |
| | Styrene | 15 |
| Initiator solution | $H_2O$ | 5 |
| | $Na_2S_2O_8$ | 0.130 |

and a 200-mesh (0.074 mm) screen in series to collect the filterable solids. Scrap adhering to the agitator, thermometer, and reactor wall were also collected. Most of the finished batches showed relatively low levels of coagulum. Total solid content was determined by the gravimetric method. The dynamic light scattering method (Otsuka, Photal LPA-3000/3100) was applied to measure the latex particle size.

## 4. Results and discussion

### *4.1. Determination of CMC*

The surface tension was measured as a function of surfactant concentrations at two different temperatures 25°C and 80°C. The results of the surface tension measurements for both pure surfactants are given in Fig. 1. A perceptible minimum appears in each curve, except the curve for the $NP(EO)_{40}$ at 80°C. It is believed that occurrence of this minimum is simply due to the more surface-active impurities in the surfactants, since the technical grade surfactants were used [10, 11]. The impurities in SDS may be dodecyl alcohol, a homolog of different chain length or inorganic salts due to the synthesis process. Note that this minimum behavior is less pronounced at higher temperatures. It is believed that at 80°C the amount of impurities adsorbed onto the air-liquid interface is reduced and mainly all the impurities dissolve in bulk aqueous phase.

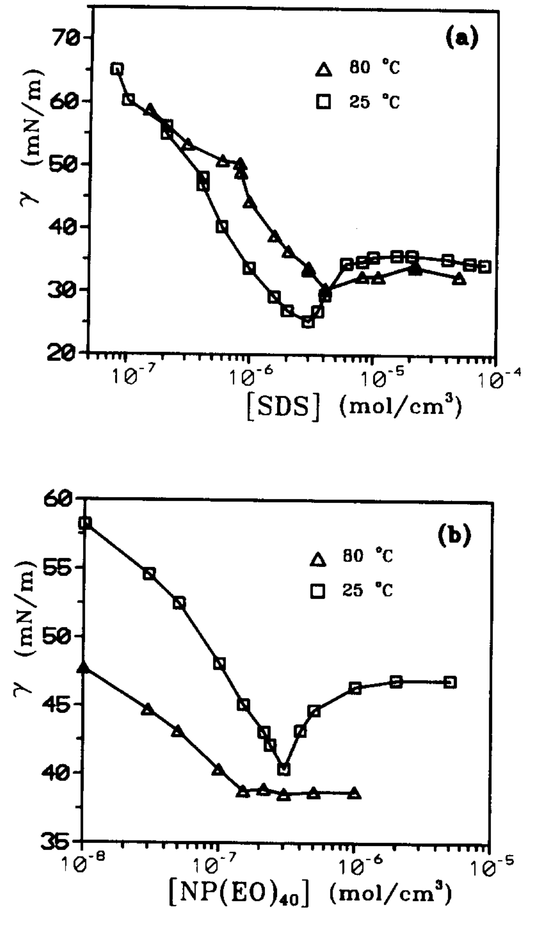

Fig. 1. Surface tension measurements as a function of surfactant concentration at 25°C (□) and 80°C (▲): (a) SDS and (b) $NP(EO)_{40}$.

In addition, this minimum can be removed if a high purity surfactant is used [10]. For example, Fig. 2 demonstrates the results of the surface tension measurements for both technical and reagent grade SDSs. Obviously, the minimum disappears in the curve of reagent grade SDS. The critical micelle concentration (CMC) of reagent grade SDS was then determined as the concentration at a sharp break in the plot of the surface tension vs. the logarithm of the SDS concentration, and found to be $6 \times 10^{-6}$ mol cm$^{-3}$, consistent with previous studies of Nakagaki and Yokoyama [12] and Fan et al. [13] within the experimental uncertainty. On the other hand, the CMC for the technical grade surfactants was then determined to be right at the minimum tension [11]. The CMC of the technical grade SDS (Henkel) is $3 \times 10^{-6}$ mol cm$^{-3}$, that is plausibly smaller than that of the reagent grade one.

For the CMC of the mixed surfactant $SDS/NP(EO)_{40}$, the surface tension measurements were also carried out as a function of total surfactant concentration while the ratio of the two surfactant $SDS/NP(EO)_{40}$ was held constant. Note that the technical grade SDS was used for these mixed surfactant systems. Our results showed that at 25°C the minimum tension still exists in every curve of the surface tension vs. the logarithm of total surfactant concentration over all the mixed surfactant ratios. Therefore, the CMC was deter-

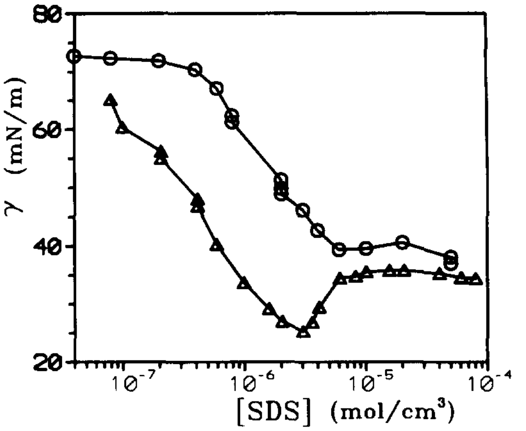

Fig. 2. Effect of impurities upon the surface tension of solutions of SDS at 25°C: reagent grade (○) and technical grade (▲).

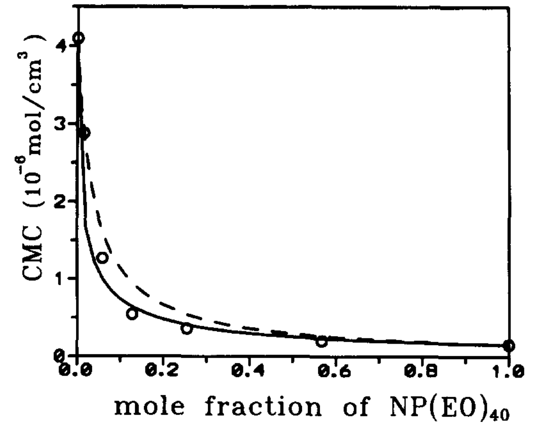

Fig. 3. CMCs of mixed surfactant SDS/NP(EO)$_{40}$ at 25°C: Points are experimental data, the solid line is the result for the non-ideal mixed micelle model with $\beta = -5.1$, and the dashed line is the result for the ideal solution ($\beta = 0$).

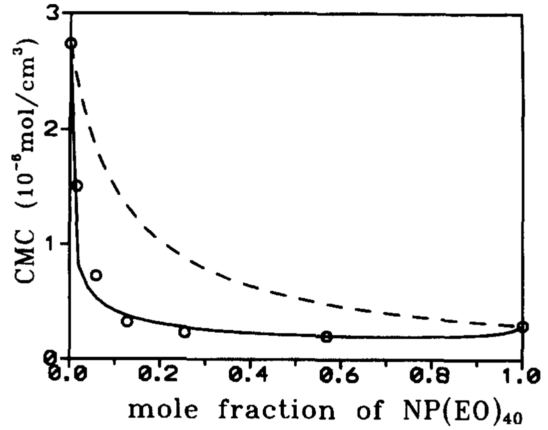

Fig. 4. CMCs of mixed surfactant SDS/NP(EO)$_{40}$ at 80°C: Points are experimental data, the solid line is the result for the non-ideal mixed micelle model with $\beta = -2.0$, and the dashed line is the result for the ideal solution ($\beta = 0$).

mined to be the concentration where the minimum tension occurred. While at 80°C none of the surface tension curves had a detectable minimum, and the CMC then corresponds to the break point in the surface tension curve. Note that the anionic surfactant SDS would be hydrolyzed and transformed into dodecyl alcohol. For simplicity, we neglect the existence of this alcohol in the thermodynamic analysis of the CMC of the mixed surfactant solution.

The CMC values of the mixed surfactant SDS/NP(EO)$_{40}$ at different ratios in aqueous solutions at 25°C and 80°C are listed in Table 2. Figs. 3 and 4 exhibit quite a large negative degree of non-ideality of mixed micelle formation at 25°C and 80°C, respectively, as seen from the mixed CMC values. The temperature effect on the strength of the parameter $\beta$ is fairly strong. The parameter $\beta$ increases from $-5.1$ to $-2.0$ as the temperature increases from 25°C to 80°C. In other words, the system of mixed micelles becomes more non-ideal at lower temperatures. This tendency is in accord with the result of mixed surfactant sodium dodecyl benzene sulfonate/NP(EO)$_{10}$ [14].

Table 2
The CMC data of mixed surfactant SDS/NP(EO)$_{40}$ at different ratios at 25°C and 80°C. (mol cm$^{-3}$)

| [NP(EO)$_{40}$] (wt.%) | 25°C | 80°C |
|---|---|---|
| 0 | $2.74 \times 10^{-6}$ | $4.10 \times 10^{-6}$ |
| 10 | $1.51 \times 10^{-6}$ | $2.88 \times 10^{-6}$ |
| 30 | $7.21 \times 10^{-7}$ | $1.27 \times 10^{-6}$ |
| 50 | $3.21 \times 10^{-7}$ | $5.42 \times 10^{-7}$ |
| 70 | $2.30 \times 10^{-7}$ | $3.60 \times 10^{-7}$ |
| 90 | $2.00 \times 10^{-7}$ | $2.00 \times 10^{-7}$ |
| 100 | $2.94 \times 10^{-7}$ | $1.52 \times 10^{-7}$ |

### 4.2. Batch emulsion polymerization

First, a series of styrene emulsion polymerization stabilized by SDS/NP(EO)$_{40}$ was carried out to demonstrate the effect of the surfactant mixture on the number of latex particles ($N_p$) formed. The initiator concentration $[I]$ was kept constant ($6.43 \times 10^{-3}$ M) in this series of experiments. The total surfactant concentration, denoted by $[S]$, was also fixed at $6 \times 10^{-3}$ M, whereas the weight percentage of $NP(EO)_{40}$ in the surfactant mixture, abbreviated by $[NP(EO)_{40}]$, was set at four different concentrations: 0%, 40%, 70% and 100%. The value of [S] was about 1.5 times the CMC of the pure SDS solution at the reaction temperature (80°C). In this manner, the difference between the parameters $[S]$ and CMC is the greatest for the polymerization system containing pure $NP(EO)_{40}$ since the non-ionic surfactant has the lowest value of CMC, as given in Table 2. The number of latex particles $N_p$ can be calculated according to the following equations:

$$N_p = 6\frac{V_m + V_p}{\pi d_p^3} \tag{3}$$

$$V_m = W_m(1-X)/\rho_m \tag{4}$$

$$V_p = W_m X/\rho_p \tag{5}$$

where $W_m$ is the total amount of monomer shown in the recipe (e.g. 15 g in this work), $d_p$ is the particle diameter, and $X$ is the monomer conversion at the end of polymerization. The parameters $V_m$ and $V_p$ are the total volumes of the unreacted monomer and polymer in the latex product, respectively. The parameters $\rho_m$ and $\rho_p$ are the densities of the monomer and polymer, respectively. The experimental data are compiled in Table 3.

It is shown in Table 3 that the parameter $N_p$ remains relatively constant, ca. $7.2 \times 10^{17}$ 1/$L$-$H_2O$, when $[NP(EO)_{40}]$ is increased from 0% to 70% and, thereafter, it drops rapidly to a value of only $4.6 \times 10^{16}$ 1/$L$-$H_2O$. It seems that only incorporation of a small amount of SDS into the polymerization system can greatly increase $N_p$ and also reduce $d_p$. According to the micellar nucleation mechanism [6], the latex particles are nucleated by penetration of the monomer-swollen micelles with oligomeric radicals produced in water. At constant $[S]$, the concentration of mixed micelles ($N_m$) formed immediately before the start of particle nucleation is a function of the CMC of the mixed surfactant solution and the number of surfactant molecules present in a mixed micelle (i.e., aggregation number, $m$). If the monomer effect is further neglected, the parameter $N_m$ for pure SDS or $NP(EO)_{40}$ can be estimated according to the following mass balance:

$$N_m = \{[S] - \mathrm{CMC}(80°\mathrm{C})\}/m \tag{6}$$

The values of $m$ are 71 and 7.88 for pure SDS [15,16] and $NP(EO)_{40}$ [17], respectively. The number of oligomeric radicals that can penetrate a micelle per second is then $2fK_d[I]/N_m$, where $f$ is the initiation efficiency factor ($f=1$, assumed in this work) and $K_d$ is the initiator decomposition rate constant ($K_d = 1.1 \times 10^{-4}$ s$^{-1}$ at 80°C [18]).

The estimated values of $N_m$ and $2fK_d[I]/N_m$ for pure SDS are $2.68 \times 10^{-5}$ M and 0.053, and those for pure $NP(EO)_{40}$ are $7.42 \times 10^{-4}$ M and 0.0019, respectively. This result shows that the parameter $N_m$ for the polymerization system stabilized by pure $NP(EO)_{40}$ is about 27 times greater than that for the system stabilized by pure SDS. The parameter $N_p$ produced in the former, however, is only 7% of that produced in the latter (see Table 3). One possible explanation for this interesting but contradictory result is that the term $2fK_d[I]/N_m$ for the $NP(EO)_{40}$ stabilized polymerization system is only 4% of that for the SDS stabilized system. Thus, for some reasons, a significant proportion of the $NP(EO)_{40}$ micelles cannot contribute to particle nucleation. One extra experiment (recipe: $[S] = 6 \times 10^{-3}$ M, $[NP(EO)_{40}] = 100\%$, and $[I] = 1.78 \times 10^{-1}$ M) was therefore carried out to verify this postulate. In this case, the $NP(EO)_{40}$ stabilized polymerization system should have the same level of $2fK_d[I]/N_m$ as the SDS stabilized system. The resulting $N_p$ for the $NP(EO)_{40}$ stabilized system is still only 24% of

Table 3

Experimental data of the designed series for demonstrating the effect of the mixed surfactant system at 80°C

| $[NP(EO)_{40}]$ (wt.%) | $d_p$ (nm) | $N_p$ (1/$L$-$H_2O$) |
|---|---|---|
| 0 | 78 | $6.6 \times 10^{17}$ |
| 40 | 70 | $8.6 \times 10^{17}$ |
| 70 | 73 | $6.5 \times 10^{17}$ |
| 100 | 182 | $4.6 \times 10^{16}$ |

that for the SDS stabilized system even though the former contains many more micelles than the latter. It is then postulated that not all the nucleated primary particles can survive flocculation during the particle formation stage when pure $NP(EO)_{40}$ is used in stabilizing the latex particles.

As mentioned earlier, Smith-Ewart theory predicts that the parameter $N_p$ is proportional to $[S]$ to the 0.6 power [7]. Fig. 5 shows the log $N_p$-vs.-log $[S]$ data with $[NP(EO)_{40}]$ equal to 0%, 40%, 70%, and 100%, respectively. The slopes of the least-squares best-fitted straight lines in Fig. 5 are 0.60, 0.76, 1.3, and 1.1 for the experiment with $[NP(EO)_{40}]$ equal to 0%, 40%, 70%, and 100%, respectively. The data show that the polymerization system follows Smith-Ewart theory quite well when $[NP(EO)_{40}]$ is below 40%. On the other hand, the system starts to deviate significantly from Smith-Ewart theory when $[NP(EO)_{40}]$ is above 70%. The preliminary data presented in this section strongly suggest that styrene emulsion polymerization stabilized by a mixed surfactant mixture containing 70% $NP(EO)_{40}$ or more does not follow the conventional Smith-Ewart theory. The origin of this phenomenon is not clear, but it is most likely due to the very different stabilization mechanisms associated with SDS and $NP(EO)_{40}$ (i.e., electrostatic vs. steric stabilization). We are endeavouring to further verify this point in our laboratory.

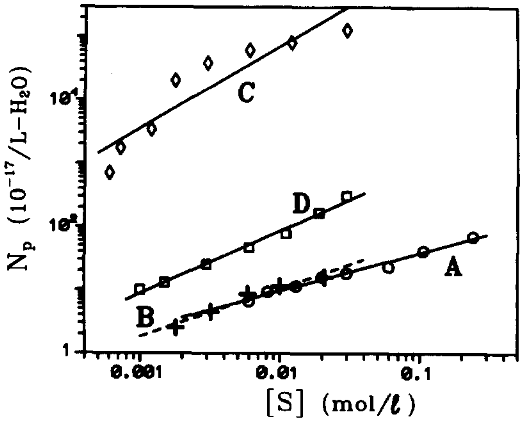

Fig. 5. Number of latex particles per liter water as a function of total surfactant concentration: $[NP(EO)_{40}]=0\%$ (A, ○), 40% (B, +), 70% (C, ◇), and 100% (D, □).

In conclusion, the surface tension measurements as a function of concentration of the mixed surfactant $SDS/NP(EO)_{40}$ were carried out at 25°C and at 80°C. Minima in these surface tension-concentration curves were observed. It is believed that the occurrence of minimum is simply caused by impurities. The CMC of the mixed surfactant $SDS/NP(EO)_{40}$ was further determined to be the concentration right at the minimum tension or at a break point in the surface tension curve. The regular solution model for mixed micelles of Rubingh [8] was applied to describe our CMC data. The interchange energy parameter $\beta$ is obtained by least square regression and found to be $-5.1$ and $-2.0$ for the system at 25°C and 80°C, respectively. That is, the system of mixed micelles (a pseudo-phase) exhibits more non-ideal behavior at low temperature. The effect of the mixed surfactant $SDS/NP(EO)_{40}$ on the formation of polystyrene particles is dramatic. It is found that adding only a small amount of the anionic surfactant SDS into the polymerization system can dramatically increase the number of latex particles and also reduce the particle size of the latex product. Furthermore, emulsion polymerization of styrene stabilized by the mixed surfactant $SDS/NP(EO)_{40}$ cannot be adequately described by the conventional Smith-Ewart theory when $[NP(EO)_{40}]$ is greater than 70%.

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