

## Electrochemistry in Middle Phase Microemulsion Composed of Saline and Toluene with Sodium Dodecylsulfate and n-Butanol

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A "middle phase" microemulsion, which bicontinuously composed of saline and toluene microphases, with sodium dodecylsulfate (SDS) and n-butanol was electrochemically characterized. When electrochemistry was performed in the "middle phase" microemulsion, reversible redox peaks of the  $\text{Fe}(\text{CN})_6$  ion in the micro water phase and the ferrocene in the micro toluene phase could be observed simultaneously, although the electrolyte was present only in the water phase.

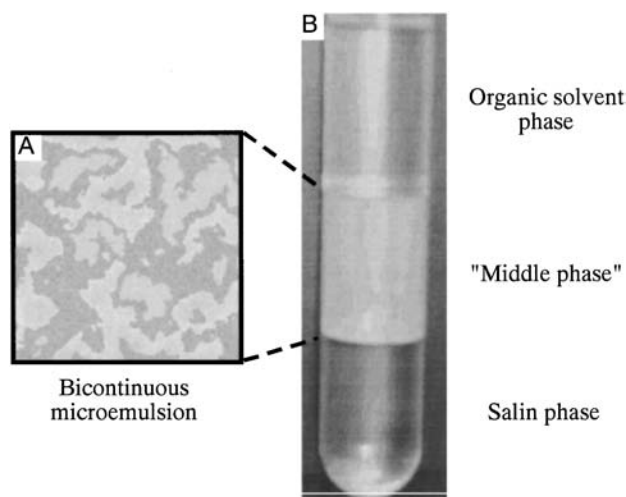
The solution chemistry of organized systems with surfactants is a field of much interest.<sup>1</sup> A microemulsion is a low-viscosity, isotropic, thermodynamically-stable, spontaneously-formed solution phase composed of water, organic solvent and surfactants. The dynamic morphology of microemulsion is determined by the characteristics of surfactant in the emulsion system. When a surfactant is strongly hydrophilic, an O/W microemulsion is formed. On the other hand, a W/O microemulsion is formed by an lipophilic surfactants. Although the hydrophilicity and lipophilicity of the surfactants are balanced in the system, the microemulsion reveals a bicontinuous structure, a so-called "middle phase" microemulsion.<sup>2-4</sup> In the middle phase, the microscopic water phase and the microscopic oil phase alternately coexisted as shown in Figure 1A.

Figure 1B shows a photograph of the three typical phases of microemulsion solutions in the saline/sodium dodecylsulfate

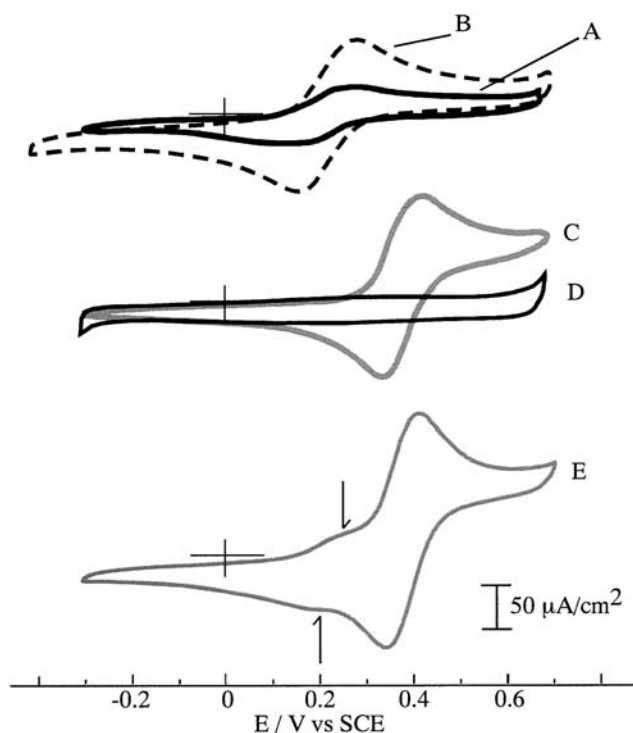
(SDS) and n-butanol/toluene system. The typical content of the three phase microemulsion solution, including a "middle phase", were water (19.3 ml), NaCl (1.10 mol/l), SDS ( $2.76 \times 10^{-3}$  mol), n-butanol ( $2.16 \times 10^{-2}$  mol) and toluene (21.3 ml). In the system, the balance between hydrophilicity and lipophilicity can be adjusted by the appropriate additions of NaCl and n-butanol in order to form the middle phase. The solution was separated into three phases: a "toluene phase", a "middle phase" and a "saline phase" in the order from the upper phase to the lower. The details of this emulsion system have been examined by NMR.<sup>1,5,6</sup> They proved that the diffusion coefficients of both water and toluene species were kept in high level in the "middle phase" microemulsion. Their report directed our attention toward electrochemical research in middle phase microemulsions, because it is possible that water-soluble species and water-insoluble (lipophilic) species can be detected in the middle phase simultaneously. Assuming that the occupied area of SDS in the surfactant layer is  $0.2 \text{ nm}^2/\text{molecule}$ , the thicknesses of saline and toluene microphases in the microemulsion are estimated roughly at 50 nm.

$\text{K}_3\text{Fe}(\text{CN})_6$  and ferrocene were selected because they are some of the most popular hydrophilic and lipophilic redox monitor compounds, respectively. The "middle phase" microemulsions with redox compounds were prepared using a 1 mM  $\text{K}_3\text{Fe}(\text{CN})_6$  aqueous solution and/or a 1 mM ferrocene toluene solution. The color of the solution phases clearly demonstrated the distribution of the redox molecules in the microemulsion systems.  $\text{K}_3\text{Fe}(\text{CN})_6$  was distributed to the saline phase and the microscopic saline phase in the "middle phase" microemulsion. Conversely, ferrocene was present in toluene phase and microscopic toluene phase in the "middle phase" microemulsion. No effects were observed following the addition of  $\text{K}_3\text{Fe}(\text{CN})_6$  and/or ferrocene in terms of the phase diagram. The fact that the volumes of both macroscopic "saline" and "toluene" phases in whole solution system (Figure 1B) were almost equal, suggests that the volume ratio between saline and toluene in "middle phase" were almost equal, and that the concentrations of  $\text{Fe}(\text{CN})_6$  ion and ferrocene in the "middle phase" were approximately 0.5 mM. In order to conduct electrochemistry in the "middle phase" microemulsion, a polished Au disc electrode (diameter 1.6 mm), a Pt wire and a saturated calomel electrode (SCE) were set into the "middle phase" in the solution as working, counter and reference electrodes, respectively.

Figure 2A shows cyclic voltammograms (CVs) of the "middle phase" microemulsion in the presence of  $\text{K}_3\text{Fe}(\text{CN})_6$ . Reversible redox peaks of  $\text{Fe}(\text{CN})_6$  ion (Figure 2A) were clearly observed in the "middle phase" at  $E_{pa} = 0.27$  and  $E_{pc} = 0.19$  V



**Figure 1.** Schematic representation (A) of a middle phase microemulsion and a picture (B) of a typical three phase microemulsion consisting of the saline/sodium dodecylsulfate (SDS) and n-butanol/toluene system.



**Figure 2.** Cyclic voltammograms observed in the middle phase microemulsion in the absence (D) or presence of  $K_3Fe(CN)_6$  (A, E) and ferrocene (C, E), and in a 0.1 M NaCl aqueous solution in the presence of 0.5 mM  $K_3Fe(CN)_6$  (B). The scan rate was 0.1 V/s.

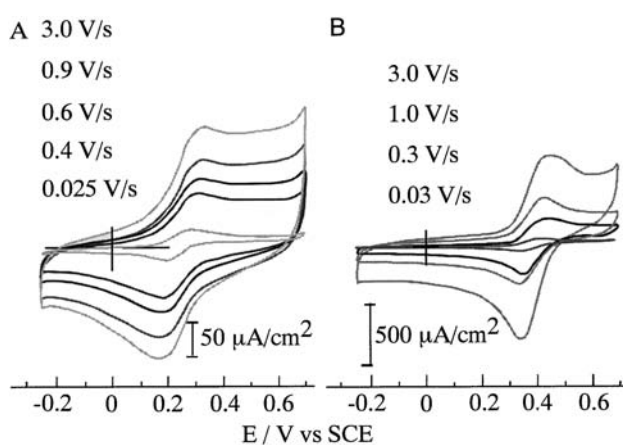
vs SCE, which is essentially the same as the response in the aqueous solution shown in Figure 2B (dotted line). The same cyclic voltammograms were observed for both systems, even if the reference and counter electrodes were moved from the “middle phase” into the saline phase.

On the other hand, the redox peaks of lipophilic ferrocene were also clearly observed at  $E_{pa} = 0.43$  and  $E_{pc} = 0.36$  V vs SCE as shown in Figure 2C. In spite of the lack of electrolyte in the toluene phase, it is clear that the electrochemical reactions of the organic solvent species were also possible in the “middle phase” microemulsion. Figure 2D shows a feature-less CV when absence of redox species. It is important to emphasize that there was no electrolyte in the microscopic toluene phase in the “middle phase”; this was supported by the high electrochemical resistance in the macroscopic toluene phase, which completely inhibits the electrochemical reaction. In fact, the electrochemistry in toluene was not conducted because of the low dissociation constant of electrolyte such as tetrabutylammonium perchlorate (TBAP). The observed redox potential of ferrocene in the “middle phase” was negatively shifted by 0.17 V with respect to the redox potential ( $E_{1/2} = 0.57$  V vs SCE) found in THF with TBAP. This indicates that the more hydrophilic ferrocenium cation in the “middle phase” is more stable than in toluene phase.

Figure 2E shows the CV of the “middle phase” emulsion system in the presence of both  $Fe(CN)_6$  ion and ferrocene. Both redox peaks from  $Fe(CN)_6$  ion (marked by arrows) and from ferrocene were observed simultaneously, and the peak potentials and peak currents were essentially the same as those observed in the “middle phase” solution in the presence of  $K_3Fe(CN)_6$  only or ferrocene only.

The peak currents of the  $Fe(CN)_6$  ion was approximately 26% smaller than that observed in the aqueous electrolyte solution in the presence of 0.5 mM  $K_3Fe(CN)_6$ . Furthermore, the peak currents of ferrocene were significantly larger than those of  $K_3Fe(CN)_6$  in aqueous solution. This was probably due to the effects of the surfactant adlayer on the electrode and/or the surface characteristics of the electrodes, such as their hydrophilicity and lipophilicity, rather than a difference in the concentrations or diffusion coefficients of the redox molecules in the “middle phase” microemulsion.

Figures 3A and 3B show the CV's obtained in the “middle phase” microemulsion in the presence of  $K_3Fe(CN)_6$  and ferrocene, measured at various scan rates. The cathodic and anodic peak currents of  $K_3Fe(CN)_6$  and ferrocene in the “middle phase” were also found to increase linearly with the square root of the scan rate. This clearly indicates the electrochemical responses in the “middle phase” are regulated by diffusion control.



**Figure 3.** Cyclic voltammograms observed in the middle phase microemulsion in the presence of  $K_3Fe(CN)_6$  (A) and ferrocene (B) at various scan rates.

In conclusion, the electrochemical responses of both the  $Fe(CN)_6$  ion in the micro aqueous phase and ferrocene in the micro organic phase in the “middle phase” microemulsion were observed simultaneously. This proves that the water phase and toluene phase coexisted microscopically, and that both phases can be contacted electrochemically in the “middle phase” microemulsion. The electrochemistry of “middle phase” microemulsions provides a unique approach to the study of the solution chemistry of organized systems with surfactants. Further investigation into the electrochemistry of “middle phase” microemulsions, including the effects of the electrodes are now in progress.

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