The Structural Conversion in Microemulsion Systems of $C_{12}H_{25}SO_3Na-C_4H_9OH-C_7H_{16}-H_2O$

Chun Sheng MO

Department of Chemistry, Jiangxi Normal University, Nanchang 330027

Abstract: An investigation of the structural conversion in microemulsion system of sodium dodecylsulfonate-butanol-heptane-water was carried out by cyclic voltammetry and conductivity techniques.

Keywords: Microemulsion, sodium dodecylsulfonate, cyclic voltammetry, conductivity.

Diffusion measurements have become a widely used technique for characterizing surfactant aqueous solutions. The most common tools have been quasi-elastic light scattering(QELS)[1,2], pulsed field gradient NMR(PFG NMR)[3,4], small angle X-ray scattering(SAXS)[5,6], neutron scattering[7], Taylor dispersion[8] and polarography[9]. In this work, cyclic voltammetric(CV) measurements were made on microemulsion systems of sodium dodecylsulfonate-butanol-heptane-water using ferrocene(Fc) and potassium ferricyanide [$K_3Fe(CN)_6$] as the electroactive probes for the determination of the diffusion coefficients of microemulsion microdroplet and thus an identification of structure and structural conversion in one-phase microemulsion region. The electric conductivity measurements were also designed to justify the results of cyclic voltammetric measurements.

Sodium dodecyl sulfonate (C.P. grade) was washed repeatedly with ether and then recrystallized several times with an acetone : methanol : water=90 : 5 : 5 (v/v) mixture and dried *in vacuo* for 24 hr at room temperature. The cosurfactant was n-butanol (A.R. grade) and the hydrocarbon n-heptane (A.R. grade). Ferrocene(Fc) and potassium ferricyanide[$K_3Fe(CN)_6$] were used as the electroactive probes. Water used was double distilled and deionized. Cyclic voltammetric measurements were performed using an electrochemical analyzer(model HPD−1A) equipped with a TYPE 3036 X−Y recorder. A glassy carbon working electrode, a saturated calomel reference electrode (SCE) (all experimental potentials are referred to this electrode), and a platinum counter electrode were used. The potential was scanned between −0.3 and +0.6 V, and the sweep rate range used was 10 to 90 mV/s in this work. The microemulsion conductivity, κ, was measured by means of DDS−11A conductivity meter equipped with a DJS−1 or DJS−10 platinum conductance electrode coated platinum black. The experimental temperature was thermostated at 30 ± 0.1^0C.

Results and Discussion

In cyclic voltammetry the peak current for a reversible system is described by the Randles−Sevcik equation[10]

$$i_p = 4.463 \times 10^{-4} nFAC_0 (nF/RT)^{1/2} D^{1/2} \upsilon^{1/2} \qquad (1)$$

Where n is the number of electrons involved in oxidation or reduction, F is the Faraday constant, A is the area of the electrode, C_0 is the concentration of electroactive probe, R is the gas constant, T is the absolute temperature, D is the diffusion coefficient of the electroactive probe, υ is the scan rate and i_p is the peak current. If it follows from Eq.(1) i_p will increase linearly with $\upsilon^{1/2}$ for a given electrode area and a constant probe concentration, a plot of i_p *vs* $\upsilon^{1/2}$ should give a straight line,   the diffusion coefficient D can be calculated from the slope of this line.

With microemulsion system involving an electroactive probe completely solubilized in the microemulsion droplet, the diffusion coefficient D in Eq.(1) would correspond to the microemulsion droplet diffusion coefficient since the probe diffuses with the microemulsion droplet. In order to detect the microstructure of microemulsion droplets, in CV experiments we used an oil−soluble ferrocene(Fc) and a water−soluble potassium ferricyanide $K_3Fe(CN)_6$ as the electroactive probes, respectively. The test sample, at first, is a mixture of emulsifier(surfactant+cosurfactant) and heptane in which the initial oil content is 21%, the water is then added drop by drop, the composition of the system moves towards 100% water corner. A continuous one−phase optical transparent microemulsion was formed when the water content falls within 20% to 83% range. Cyclic voltammetric measurements were made in this microemulsion region at different water content.The changes in the diffusion coefficient of the probes with water content in microemulsions are illustrated in **Figure 1**.

As can be seen from **Figure 1** that the diffusion coefficients of ferrocene decreases with increasing water content in the whole one−phase microemulsion region. At the water content of less than about 45%, this decrease was gradual, an abrupt decrease in the diffusion coefficient was observed in the range of water content about 45% to 65%, and then at water content above 65%, the decrease becomes again relatively slow. The similar abrupt turn points were also observed in **Figure 1** when potassium ferricyanide was used as the electroactive probe, merely, the diffusion coefficients of $K_3Fe(CN)_6$ in microemulsion medium increases with increasing water content.

The difference in diffusion behavior between ferrocene and potassium ferricyanide in the same microemulsion regions can be understood with their different soluble nature in water and oil. Ferrocene was expected to preferentially probe the oil environment because of its limited water solubility. At low water content, the microemulsion of water−in−oil type can be formed, and the oil is the continuous phase. The values of diffusion coefficient of ferrocene, in this case, were found to be relatively large. As contrasted with ferrocene, the diffusion coefficients of $K_3Fe(CN)_6$ in oil continuous phase, therefore, would correspond to the diffusion coefficients of w/o microemulsion droplets since the $K_3Fe(CN)_6$ diffuses with aqueous phase. The diffusion coefficients of both Fc and $K_3Fe(CN)_6$ in the range of water content about 20% to 45% changes slowly,

which indicates that the microenvironment of microemulsoin is unchanged. A similar trend has been observed for this microemulsion with high water contents (above 65%). In the latter case, the oil microdroplets were dispersed in water medium, and the diffusion coefficient of ferrocene can be considered as that of o/w microemulsion droplet. However, a relatively large change in diffusion coefficients of both Fc and $K_3Fe(CN)_6$ with water content has been observed in **Figure 1** when the content of water is in the range from about 45% to 65%, which signifies that the microenvironment of microemulsions has undergone a continuously change. In other words, neither w/o type nor o/w type microemulsion existes in this region. According to Lindman[11], we can suggest that a bicontinuous microstructure in which aqueous and oil solutions are both local continuous phase was formed.

We have also measured the electrical conductivity of microemulsions for which the composition of system changes the same as that of the CV measurements. **Figure 2** shows that the electrical conductivity κ *vs* the water content plot exhibits features characteristic of percolative conduction. The water content dependence of the conductivity in w/o type microemulsion region takes the form[12,13]

$$\kappa = \kappa_0(\Phi_c–\Phi)^\alpha \quad \Phi<\Phi_{c;} \qquad \kappa = \kappa_0(\Phi–\Phi_c)^\alpha \quad \Phi>\Phi_c \qquad (2)$$

Where Φ is the water content, Φ_c is the percolation threshold or the critical water content, κ_0 and α are constants. With $\Phi<\Phi_c$, $\alpha\neq1$, the microemulsion displys a vary small conductivity and the κ values increase slowly with increasing Φ. In the case of $\Phi>\Phi_c$, however, $\alpha=1$, and the κ increases linearly and steeply up to $\Phi=\Phi_b$, $\kappa=\kappa_b$. Various mechanisms have been proposed to explain the percolative conduction observed with some w/o microemulsions, one of the most accepted mechanisms is the model of "sticky droplet collisions" suggested by Fletcher[14]. According to this model, the frequent "sticky" collisions between spherical microdroplets of w/o type microemulsion above the percolation threshold Φ_c, may occur due to their attractive interactions. This sticky collisions may lead to the formation of the narrow water tubes or channels in an oil continuous phase, and counterions can move through these narrow channels, which results in an abrupt and steep increase of the conductivity. Evidently, a water in oil type microemulsion was formed in this low water content region. At high water contents, for example, $\Phi>\Phi_m$, the electrical conductivity, after arriving at a maximum κ_m, decreases with increasing water content. This obvious decrease in κ values is brought about by dilution of added water, which decreased concentration of dispersing phase. Accordingly, o/w type microemulsion was formed in this high water content region. But, in a moderate water content region, $\Phi_b<\Phi<\Phi_m$, the curve of conductivity shows an abnormal behavior, the κ increases deviated from former line up to achieving a maximum. This feature of conductivity curve was often used to identify the existence of a bicontinuous microemulsion.

Our conductivity curve in **Figure 2** illustrates excellently three microemulsion regions: a water in oil region with $\Phi_c=16\%$ and water content range from 20% to 43%, an oil in water region with water content range from 64% to 83%, and a bicontinuous region with water content range from 43% to 64%. Evidently, the results obtained by the two methods are in satisfactory agreement.

Figure 1. Diffusion coefficients of probes as a function the water content Φ for initial composition of system (30°C): [3 g $C_{12}H_{25}SO_3Na$ + 6 g C_4H_9OH + 2.4076 g C_7H_{16}]. 1: with 0.005 g Fc 2: 2.50×10^{-2} mol/L $K_3Fe(CN)_6$
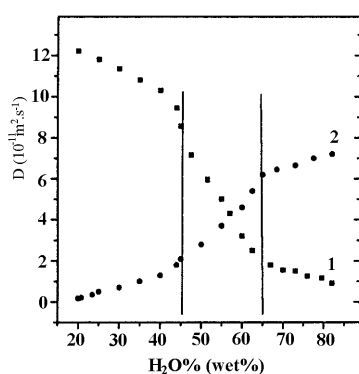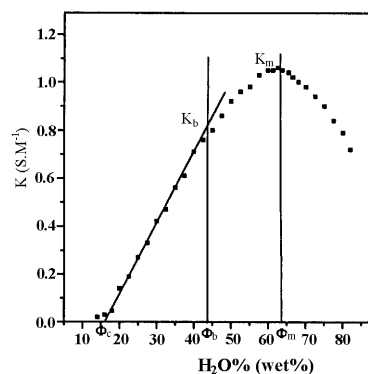
Figure 2. Variations of the electrical conductivity κ with the water content Φ for initial composition of system (30°C): [3 g $C_{12}H_{25}SO_3Na$ + 6 g C_4H_9OH + 2.4076 g C_7H_{16}].

In summary, the information about the structural conversion of microemulsion obtained from diffusion measurements using cylic voltammetric technique is in agreement with the results of conductivity measurements. A novel electrochemical technique-cyclic voltammetry was presented in this work, and its utility was also demonstrated here. It is possible to use alone this technique to identify structures and structural transition in others macro- and microemulsions.

Acknowledgment

References

1. E. Dayalan, S. Qutubuddin, J. Texter *J. Colloid Interface sci.*, **1993**, *158*, 249.
2. N. A. Mazer, G. B. Benedek, M. C. Carey, *J. Phys. Chem.*, **1976**, *80,*1075.
3. M. H. Blees, J. C. Leyte, *J. Colloid Interface Sci.*, **1993**, *157*, 355.
4. G. Fleischer, F. Stieber, U. Hofmeier, H.-F. Eicke, *Langmuir,* **1994**, *10*, 1780.
5. H. H. Paradies, *J. Phys. Chem.*, **1980**, *84*, 599.
6. J. Marignan, J. Appell, P. Bassereau, G. Porte, R. P. May, *J. Phys.(Paris)* **1989**, *50*, 3553.
7. J. B. Hayter, T. Zemb, *Chem. Phys. Lett.*, **1982**, *93*, 91.
8. D. G. Leaist, H. Ling, *J. Phys. Chem.*, **1993**, *97*, 7763.
9. R. Zana, R. A. Mackay, *Langmuir,* **1986**, *2*,109.
10. P. T. Kissinger, W. R. Heineman, *J. Chem. Educ.*, **1983**, *60*, 702.
11. P. Guering, B. Lindman, *Langmuir,* **1985**, *1,* 464.
12. M. Lagues, C. Sauterey., *J. Phys. Chem.*, **1980**, *84,* 3503.
13. B. Lagourette, J. Peyrelasse, C. Boned, M. Clausse, *Nature,* **1979**, *281,* 61.
14. P. D. I. Fletcher, B. H. Robinson, *Ber Bunsen-Ges Phys. Chem.,* **1981**, *85,* 863.