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Microstructure of a Triton X-100–xylene–water microemulsion studied using 1.5th-order derivative electroanalysis

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The 1.5th-order derivative electroanalysis was used as an effective method for investigating the microstructure and structural transition in the title system.

Electrochemical techniques, such as polarography, rotation disk voltammetry, chronocoulometry, cyclic voltammetry, as popular tools for colloid and surface chemists, have been successfully applied to study the physicochemical properties of aqueous surfactant solutions.[1–4] Previously[5,6] we used cyclic voltammetry for investigating the properties of aqueous surfactant solutions. Electrochemical measurements are useful for characterising organised surfactant solutions. However, the limitation of these methods lies in the fact that the concentration of an electroactive probe and/or the supporting electrolyte in solution should be reasonably high because the internal resistance of solution is high in the presence of surfactants and hydrocarbons. In this work, the Triton X-100–xylene–water system was examined by 1.5th-order derivative electroanalysis using an electroactive probe for determining the diffusion coefficients of microemulsion droplets and for detecting microstructure inversion in the microemulsion region.

Triton X-100 (Aldrich) was used as an emulsifier, and the hydrocarbon was *o*-xylene (Aldrich). Ferrocene (Fc) was used as the electroactive probe. Doubly distilled and deionised water was used. Potassium chloride (A. R. grade) was used as the supporting electrolyte.

The 1.5th-order derivative electroanalysis and cyclic voltammetric measurements were performed using an electrochemical analyzer model XJP-821(B) (Jiangsu Electrochemical Instruments Inc.) equipped with a 3036 X-Y recorder. The working electrode was a highly polished glassy carbon disk electrode (surface area of 3.3×10^{-6} m^2). An Ag/AgCl reference electrode and a platinum counter electrode were used. The electrochemical cell was thermostatted at 13.5±1.0 °C.

The single-phase microemulsion was obtained by a simple titration technique. A small amount of the electroactive probe (Fc, 0.0005 g) was dissolved in 1 g of xylene; then, 4 g of Triton X-100 was added, and this mixture was titrated with a dilute aqueous KCl solution (0.02 mol dm^{-3}). We found that a continuous stable single-phase microemulsion can always be observed over the range of water content from >0 to ≤100 wt%. This single-phase microemulsion region is ideally suitable for studying the structure and structural inversion of microemulsions. The samples were stored at least for 48 h in order to attain a solubilization equilibrium of ferrocene between microemulsion droplets. The 1.5th-order derivative electroanalysis was performed in this microemulsion region at different water contents. IR compensating has made the correction for the ohmic drop due to the solution resistance between the Luggin capillary and the electrode.

The semiderivative electroanalytical method was first introduced in 1975 by Goto and Ishii[7] based on the semiintegral electroanalysis method. It measures the semiderivative of current against the electrode potential. In the case of a reversible electrode reaction, the following relationship between the electrode potential E and the semiderivative of current $e(t)$ applies for a planar electrode and a ramp signal:

$$e(t) = \frac{d^{1/2}}{dt^{1/2}} i(t) = (n^2F^2AvD^{1/2}c/4RT)\,\mathrm{sech}^2[(nF/2RT)(E - E_{1/2})], \qquad (1)$$

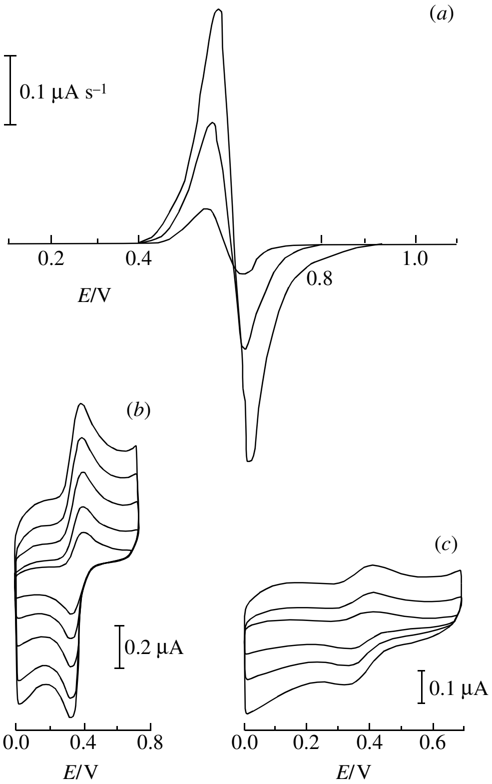

Figure 1 The electrochemical behaviour of ferrocene in microemulsions at 13.5 °C. (*a*) 1.5th-order derivative of current *vs* electrode potential. Scan rates: 20, 40 and 60 mV s^{-1}. Sample solution: 0.0005 g of Fc, 1 g of $C_6H_4Me_2$, 4 g of Triton X-100 and 22 g of H_2O (0.02 M KCl). (*b*) Cyclic voltammograms. Scan rates: 10, 30, 50, 90 and 120 mV s^{-1}. Sample solution: 0.0005 g of Fc, 1 g of $C_6H_4Me_2$, 4 g of Triton X-100 and 4 g of H_2O (0.02 M KCl). (*c*) Cyclic voltammograms. Scan rates: 10, 30 and 50 mV s^{-1}. Sample solution was the same as in (*a*).

where $E_{1/2}$ is the half-wave potential, n is the number of electrons involved in oxidation or reduction, F is the Faraday constant, A is the area of the electrode, c is the concentration of the electroactive probe, R is the gas constant, T is the absolute temperature, D is the diffusion coefficient of the electroactive probe, and v is the scan rate.

Differentiating the semiderivative of current $e(t)$ with respect to time t, we obtain e', the 1.5th-order derivation of current, as a function of the electrode potential E[8]

$$e'(t) = \frac{d^{3/2}}{dt^{3/2}} i(t) = (n^3F^3Av^2D^{1/2}c/4R^2T^2)\,\mathrm{sech}^2(x)\tanh(x), \qquad (2)$$

where $x = (nF/2RT)(E - E_{1/2})$. The curve of e' *vs* E is comprised of a maximum peak and a minimum peak of current, they are exact inversion symmetry about the half-wave potential in the case of the reversible electrode reaction. Two important parameters for the 1.5th-order derivative electroanalysis, E'_{np}, the peak potential, and e'_p, the peak height at E'_{np}, were derived by Wang[9] as follows:

$$E'_{np} = E_{1/2} - 1.32(RT/nF); \quad (3)$$

$$e'_p = (0.77n^3F^3Av^2D^{1/2}c/4R^2T^2). \quad (4)$$

Note that equations (1)–(4) were derived from a model which assumes linear diffusion to a planar electrode, concentration variations can only occur perpendicular to the electrode surface. One of its important applications is to estimate the diffusion coefficient.

In microemulsion systems with an electroactive probe completely solubilised in microemulsion droplets, the diffusion coefficient D in equation (4) corresponds to the diffusion coefficient of microemulsion droplets because the probe diffuses with the droplet. In order to examine the microstructure of microemulsion droplets, we use oil-soluble ferrocene as the electroactive probe in 1.5th-order derivative electroanalysis. Figure 1 illustrates the electrochemical behaviour of Fc for microemulsions of a typical composition. Figure 1(*b*) is a cyclic voltammogram of 0.0005 g of Fc, 1 g of $C_6H_4Me_2$, 4 g of Triton X-100 and 4 g of H_2O (0.02 M KCl). The difference between the anodic and cathodic peak potentials ΔE_p is found to be constant and equal to ~61 mV, it is independent of the scan rate v. The anodic peak current plotted versus the square root of the scan rate is linear passing through the origin, as shown in Figure 2(*b*). Thus, the electron transport properties of the Fc^+/Fc electrode reaction in the microemulsion medium are reversible under our experimental conditions. In principle, we can determine the diffusion coefficient of ferrocene in the microemulsion from the slope of the line in Figure 2(*b*) according to the Randles–Sevcik equation.[5] However, we experimentally found that it is difficult to exactly measure the peak height from the cyclic voltammogram at high water contents [see Figure 1(*c*)]. The corresponding 1.5th-order derivative voltammogram is shown in Figure 1(*a*) at same water content as Figure 1(*c*). It is clear that the e'_p *vs* E curve has the analytical advantage over the ordinary i *vs* E curve under the same experimental conditions. A plot of equation (4) yields a straight line [Figure 2(*a*)], the slope of which was used to determine the diffusion coefficient (D in m^2 s^{-1}).

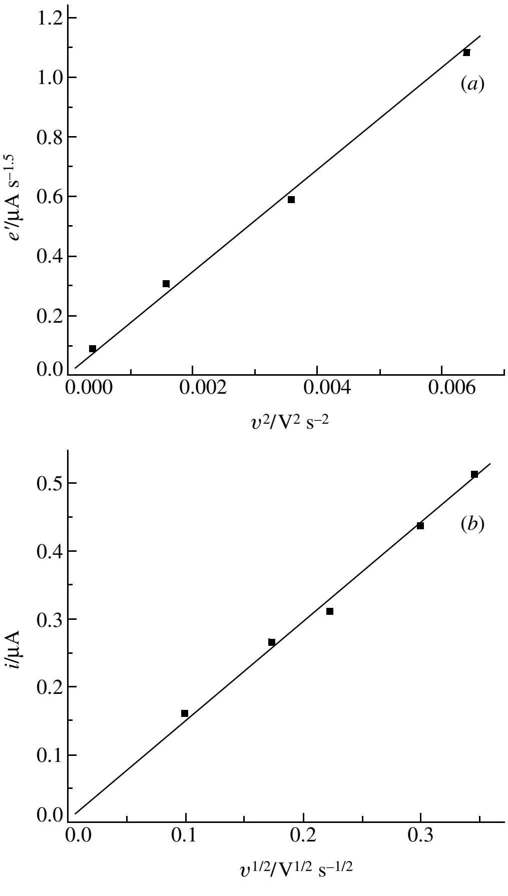

Figure 2 The plots of (*a*) e'_p *vs* v^2, and (*b*) i *vs* $v^{1/2}$. Sample solutions are specified in Figures 1(*a*) and (*b*), respectively.

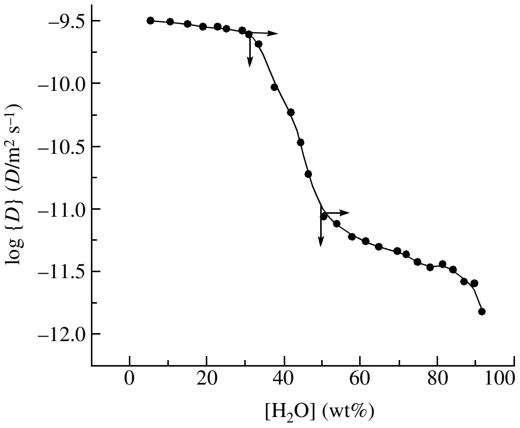

Figure 3 The diffusion coefficient of ferrocene as a function of water content (0.02 M KCl) in a single-phase microemulsion region. The initial composition of the system: 0.0005 g of Fc, 1 g of $C_6H_4Me_2$ and 4 g of Triton X-100.

Figure 3 demonstrates the diffusion coefficient of the probe (log $\{D\}$) as a function of the water content of the microemulsion. As shown in Figure 3, D decreases with water content over the entire single-phase microemulsion region. At water contents lower than 31.2%, this decrease is gradual; an abrupt decrease in the diffusion coefficient is observed in the range from 31.2 to 48.6%, and a gently sloping curve is observed at water contents above 48.6%. Ferrocene was expected to probe the oil environment because of its limited water solubility. At low water contents, a water-in-oil microemulsion is formed, and the oil is the medium. In this case, D was found to be relatively high. The diffusion coefficient of ferrocene at a water content lower than 31.2% changed slowly. This fact indicates that the microenvironment of microemulsions remains unchanged. A similar behaviour was observed in this microemulsion at high water contents (above 48.6%). In the latter case, the oil microdroplets were dispersed in a water medium, and the D of ferrocene can be considered as that of oil-in-water microemulsion droplets. However, a dramatic change in the diffusion coefficient of ferrocene was observed at water contents in the range 31.2–48.6%. This fact is indicative of a change in the microenvironment of microemulsions. In other words, neither water-in-oil nor oil-in-water microemulsions exist in this region. We can suggest that a bicontinuous microstructure was formed.[10] The bicontinuous microemulsion is a microstructure in which both aqueous and oil solutions are local continuous phases; the microemulsion as a whole may be considered as a coarse network composed from water tubes in a continuous oil medium.

In summary, our preliminary results show that 1.5th-order derivative electroanalysis can be used for investigating the diffusion of particles in organised surfactant solutions at very low concentrations of electroactive species and a supporting electrolyte. As compared with other electroanalytical methods, the derivative electroanalytical technique has the merits of high sensitivity and high resolution. It is reasonable to expect that this technique can be extended to many microheterogeneous systems including micelles, macro and micro emulsions, vesicles, and polymer films.

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