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Semidifferential Electroanalysis of Aqueous Triton X-100/Toluene/H_2O Microemulsion

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Abstract: Semidifferential electroanalysis is used as an effective method for investigating microstructure and structural transition of Triton X-100 microemulsions.

Keywords: Semidifferential electroanalysis, Triton X-100, microemulsion.

Electrochemical techniques, such as polarography, rotation disk voltammetry (RDV), chronocoulometry (CC), cyclic voltammetry (CV), as the popular tools for colloid and surface chemists, have been successfully applied in the study of physicochemical properties of aqueous surfactant solutions [1-2]. In our recent articles[3-5], we employed the cyclic voltammetric method to investigate properties of aqueous surfactant micelle solutions. Being less sophisticated and generally less time-consuming, electrochemical measurements are useful for characterizing organized surfactant solutions. But, the limitation of these methods lies in the fact that the concentration of an electroactive probe and/or the supporting electrolyte in solutions should be moderately high because the internal resistance of solution is high in the presence of surfactant and/or hydrocarbon. Adding sufficient electroactive probe into a surfactant solution must cause some changes in properties of the dispersion, which makes the parameters obtained from electrochemical measurements not true to the original in a sense. In order to overcome these shortcomings, we attempt to use a novel technique–semidifferential electroanalysis–for characterizing surfactant solutions. In this work, we demonstrate that semidifferential electroanalysis, which can be used to investigate physicochemical properties of organized surfactant solutions at very low electroactive probe concentrations and low supporting electrolyte concentrations.

Semidifferential electroanalytical method was first introduced in 1975 by Goto and Ishii[6] based on the semiintegral electroanalysis method. It measures the semidifferential of current against the electrode potential. In the case of the reversible electrode reaction the following relationship between the electrode potential, *E*, and the semiintegral of current, m, applies for a planar electrode and a ramp signal[7]:

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$$m(t) = (m_c/2)\{1\text{–}\tanh[(nF/2RT)(E - E_{1/2})]\} \qquad (1)$$

Differentiating equation (1) with respect to time, t, we obtain an expression for the semidifferential of current, $e(t)$:

$$e(t) = (n^2F^2A\,\upsilon D^{1/2}c/4RT)[\text{sech}^2[(nF/2RT)(E - E_{1/2})] \qquad (2)$$

where $E_{1/2}$ is the half-step potential. Equation (2) represents a symmetrical peak, the peak height is:

$$e_p = (n^2F^2A\upsilon D^{1/2}c/4RT) \qquad (3)$$

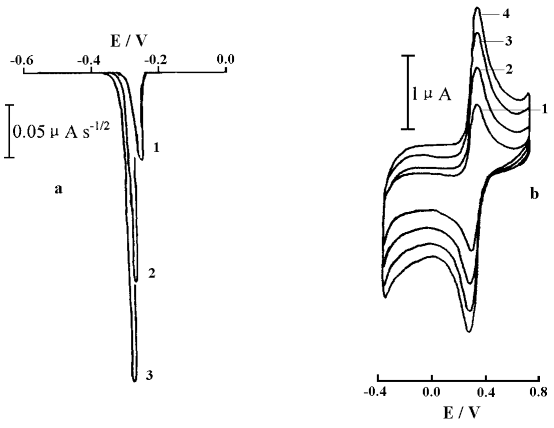
Following the equation (3) that the peak height e_p is directly proportional to the concentration c, the area of the electrode A, and the scan rate υ, which is the theoretical basis of quantitative analysis. A plot of e_p against υ should give a straight line, the diffusion coefficient D can be calculated from the slope of this line.

The nonionic surfactant Triton X-100 (abbreviated as TX 100) was obtained from Shanghai Chemical Reagent Company and used without further purification. Toluene (A. R. grade) was purchased from Serva Chemicals. Ferrocene (Fc) was used as the electroactive probe. 0.02 mol/L KCl solution was used as the supporting electrolyte. Semidifferential electroanalysis and cyclic voltammetric measurements were performed using an electrochemical analyzer (model XJP–821 (B), Jiangsu Electrochemical Instruments Factory) equipped with a 3036 X–Y recorder (Sichuan Instruments Factory). A glassy carbon working electrode, a saturated calomel reference electrode (SCE), and a platinum counter electrode were used. The working electrode area was $A = 3.3 \times 10^{-6}$ m^2. The experimental temperature was thermostated at 25 ± 0.1°C.

Results and Discussion

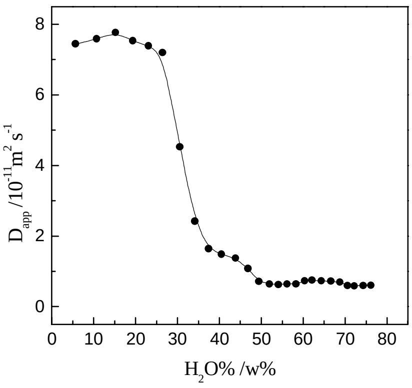
Microemulsion samples were prepared by adopting a simple titration technique: a mixture of TX100 and toluene was first prepared by combining the required mass of the surfactant and hydrocarbon. Next, water was added drop by drop to the mixture, the composition of the system moves towards 100% water corner. Our experiment found that a continuous single-phase optical transparent microemulsion could always be obtained across the entire water content range (from 0% to 100%) when the initial toluene content in the mixture is lower than about 25%. Semidifferential electroanalysis measurements were made in this microemulsion region at different water contents. **Figure 1** shows typical *e vs. E* curves (a) for given systems, the corresponding cyclic voltammogram, *i.e.*, *i vs. E* curves (b), being given for comparison. It is clear that the *e vs. E* curves have the analytical advantage over the ordinary *i vs. E*

Figure 1 The electrochemical behavior of ferrocene in o/w microemulsion at 25°C



Sample solution: 0.015 g Fc + 1 g $C_6H_5CH_3$ + 4 g TX100 + 7 g H_2O (in 0.02 mol/L KCl).
Scan rate: a: 1. 20, 2. 40, 3. 60 mV s^{-1}. b: 1. 20, 2. 40, 3. 60, 4. 80 mV s^{-1}.

Figure 2 The apparent diffusion coefficient of ferrocene as a function of water content (0.02 mol/L KCl) in a single-phase microemulsion region



The initial composition of system is: 0.0021 g ferrocene (Fc) +1 g $C_6H_5CH_3$ +4 g TX 100.

curves. At a relative low supporting electrolyte concentration (0.02 mol/L KCl) and at low probe concentrations, the values of semidifferential of the current, *e*, are more sensitive than those of cyclic voltammetric measurements. The changes in the apparent diffusion coefficient D_{app} of the probe with water content are illustrated in **Figure 2**. As shown in **Figure 2**, D_{app} decreases with increasing water content over the entire single-phase microemulsion region. At water contents lower than 27%, this decrease is gradual; an abrupt decrease in the apparent diffusion coefficient is observed in the range from 27 to 50%, and a gently sloping curve is observed at water contents above 50%. 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_{app} was found to be relatively high. The apparent diffusion coefficient of ferrocene in the water content range from 5 to 27% changed slowly. This fact indicates that the microenvironment of microemulsions remains unchanged. A similar behavior was observed in this microemulsion at high water contents (above 50%). In the latter case, the oil microdroplets were dispersed in a water medium, and the D_{app} 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 from 27 to 50%. 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, in which both aqueous and oil solutions are local continuous phases [8].

In summary, our preliminary results show that semidifferential electroanalysis can be used to investigate the diffusion of particles in organized surfactant solutions at very low electroactive species concentrations and low supporting electrolyte concentrations. Compared with other electroanalytical methods, the semidifferential electroanalytical technique has the merits of high sensitivity and high resolution. It is reasonable to expect that the method can also be extended to many microheterogeneous systems, including micelles, macro and microemulsions, vesicles, and polymer films,*etc*..

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