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Electrochemical investigation of microemulsions in the $C_{12}H_{25}SO_3Na$–BuOH–C_7H_{16}–H_2O system at different water contents

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The phase inversion from water-in-oil to oil-in-water microemulsions in the title system was examined by cyclic voltammetry and conductivity measurements.

Diffusion measurements are widely used for characterising aqueous surfactant solutions. Quasi-elastic light scattering,[1] pulsed field gradient NMR,[2] small angle X-ray scattering,[3] neutron scattering,[4] Taylor dispersion[5] and electrochemical measurements[6] are also among the most commonly used techniques. In this work, the sodium dodecyl sulfonate–butanol–heptane–water system was examined by cyclic voltammetry using electroactive probes for determining the diffusion coefficients of microemulsion droplets and for detecting phase inversion in the microemulsion region. Electric conductivity measurements were also carried out to support the results obtained by cyclic voltammetry.

In cyclic voltammetry, the peak current for a reversible system is described by the Randles–Sevcik equation[7]

$$i_p = 4.463\times10^{-4}\, nFAC_0(nF/RT)^{1/2}D^{1/2}v^{1/2}, \qquad (1)$$

where n is the number of electrons involved in the oxidation or reduction, F is the Faraday constant, A is the electrode surface area, C_0 is the concentration of an electroactive probe, R is the gas constant, T is the absolute temperature, D is the diffusion coefficient of the electroactive probe, v is the scan rate, and i_p is the peak current. It follows from equation (1) that i_p linearly increases with $v^{1/2}$ at a given electrode surface area and a constant probe concentration, a plot of i_p against $v^{1/2}$ is linear, and the diffusion coefficient D can be calculated from the slope of this straight line.

In microemulsion systems with an electroactive probe completely solubilised in the microemulsion droplets, the diffusion coefficient D in equation (1) corresponds to the diffusion coefficient of microemulsion droplets because the probe diffuses with the droplets. In order to examine the microstructure of microemulsion droplets, we used oil-soluble ferrocene (Fc) and water-soluble potassium ferricyanide [$K_3Fe(CN)_6$] as the electroactive probes in cyclic voltammetry. The initial test sample was a mixture of an emulsifier (a surfactant and a cosurfactant) and heptane, in which the initial oil content was 21 wt% (3 g of $C_{12}H_{25}SO_3Na$, 6 g of BuOH and 2.4076 g of C_7H_{16}). Next, water was added drop by drop to the mixture. A continuous single-phase optically transparent microemulsion was formed when the water content was within the range 20–83 %. Figure 1 demonstrates the plots of i_p against $v^{1/2}$ for the two electroactive probes at different water contents. Figure 2 shows the diffusion coefficients of the probes as functions of the water content of microemulsions.

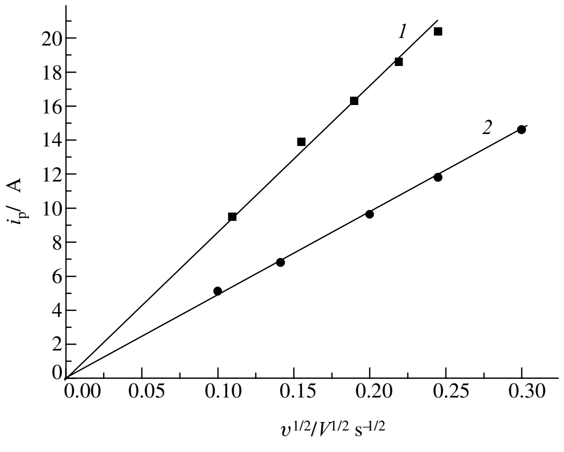

Figure 1 Peak current i_p *vs.* $v^{1/2}$ for the $C_{12}H_{25}SO_3Na$–BuOH–C_7H_{16}–H_2O system in the presence of ferrocene or $K_3Fe(CN)_6\cdot3H_2O$: (*1*) 0.0055 g of ferrocene and 34.20 g (75%) of H_2O, (*2*) 0.0364 g of $K_3Fe(CN)_6\cdot3H_2O$ and 3.80 g (25%) of H_2O.

The plots in Figure 1 are straight lines passing through the origin. This fact indicates that the electron transport properties of Fc^+/Fc and $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ electrode reactions in the microemulsions are diffusion controlled. The measurement error in the peak current i_p was evaluated as ±0.02 A. Thus, diffusion coefficients D found from these lines are reliable. As can be seen in Figure 2, the diffusion coefficient of ferrocene decreases with increasing water content over the entire single-phase microemulsion region. At water contents lower than 45%, this decrease is gradual; an abrupt decrease in the diffusion coefficient is observed in the range from 45 to 65%, and a gently sloping curve is also observed at water contents above 65%. Similar inflection points are also observed in Figure 2 for potassium ferricyanide used as the electroactive probe; however, the diffusion coefficient of $K_3Fe(CN)_6$ in microemulsions increases with increasing water content.

The difference between the diffusion behaviour of ferrocene and potassium ferricyanide over the same microemulsion region can be explained by the solubility in water and oil. 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, the diffusion coefficient of ferrocene was found to be relatively high. In contrast to ferrocene, the diffusion coefficient of $K_3Fe(CN)_6$ in an oil medium corresponds to the diffusion coefficient of water-in-oil microemulsion droplets because $K_3Fe(CN)_6$ diffuses

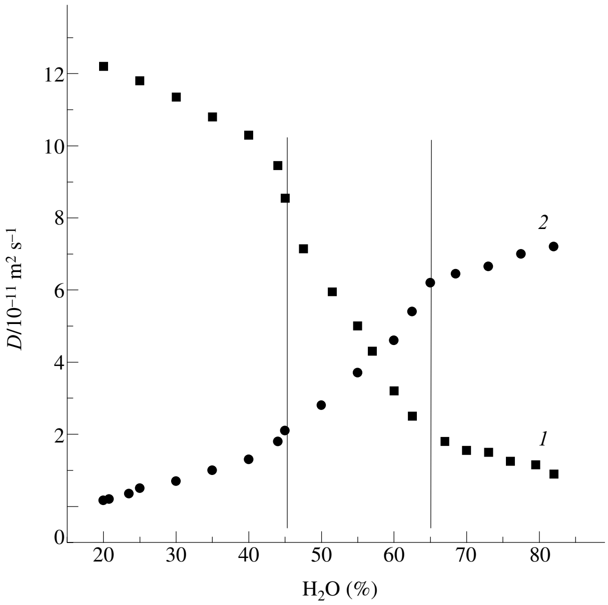

Figure 2 Diffusion coefficients of probes as functions of water content *Φ* of the system (30 °C) in the presence of (*1*) 0.005 g of ferrocene or (*2*) 2.50×10^{-2} mol dm^{-3} $K_3Fe(CN)_6$.

with the aqueous phase. The diffusion coefficients of both ferrocene and $K_3Fe(CN)_6$ in the water content range from 20 to 45% change slowly. This fact indicates that the microenvironment of microemulsions remains unchanged. A similar behaviour was observed in this microemulsion at a high water content (above 65%). In the latter case, the oil microdroplets were dispersed in a water medium, and the diffusion coefficient of ferrocene can be considered as that of oil-in-water microemulsion droplets. However, a dramatic change in the diffusion coefficients of both ferrocene and $K_3Fe(CN)_6$ was observed at water contents in the range from 45 to 65% (Figure 2). 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]

We also measured the electric conductivity of the above microemulsions, and Figure 3 demonstrates typical experimental results. The electric conductivity κ plotted against water content exhibits features characteristic of percolate conduction. The relationship between the conductivity and the water content in the water-in-oil microemulsion region takes the form[9,10]

$$\kappa = \kappa_0(\Phi_c - \Phi)_\alpha \Phi < \Phi_c, \kappa = \kappa_0(\Phi - \Phi_c) \;\; \Phi > \Phi_c, \qquad (2)$$

where Φ is the water content, Φ_c is the percolation threshold or the critical water content, κ_0 and α are constants. At $\Phi < \Phi_c$, $\alpha \neq 1$, the conductivity of microemulsions is very low, and the electric conductivity κ slowly increases with Φ. However, in the case of $\Phi > \Phi_c$, $\alpha = 1$, and the electric conductivity κ linearly and steeply increases up to $\Phi = \Phi_b$, $\kappa = \kappa_b$. Various mechanisms have been proposed to explain the percolate conduction observed in some water-in-oil microemulsions. One of the commonly accepted mechanisms is the model of ‘sticky droplet collisions’ suggested by Fletcher and Robinson.[11] According to this model, frequent sticky collisions between spherical microdroplets of water-in-oil microemulsions above the percolation threshold Φ_c can occur due to the attractive interactions. These sticky collisions may lead to the formation of narrow water tubes or channels in an oil medium, and counter-ions can migrate through these narrow channels to result in an abrupt and steep increase in the electric conductivity. Evidently, a water-in-oil microemulsion is formed in this region of low water contents. At high water contents, for example, at $\Phi > \Phi_m$, the value of κ, after arriving the maximum value κ_m, decreases with increasing water content. This obvious decrease in the electric conductivity κ results from dilution with the added water, which decreased the concentration of the dispersion phase. Accordingly, an oil-in-water microemulsion was formed in this region of high water contents. However, in the region of moderate water contents at $\Phi_b < \Phi < \Phi_m$, the conductivity curve exhibits an abnormal behaviour: the electric conductivity κ nonlinearly increases up to a maximum. This feature of conductivity curves was often used to identify the occurrence of a bicontinuous microemulsion.

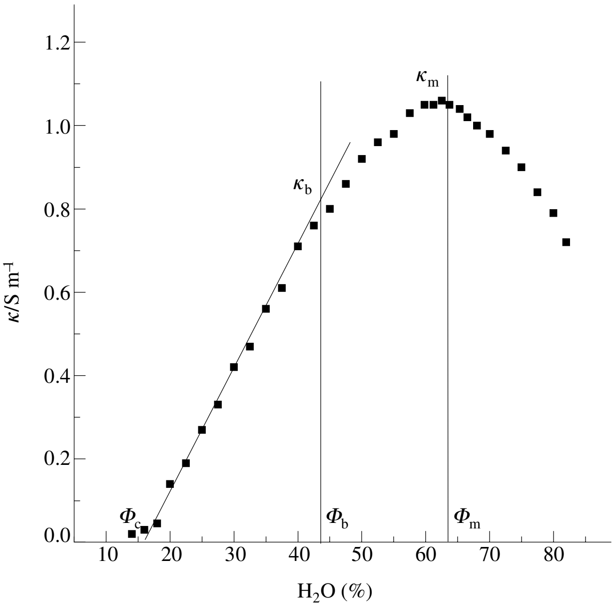

Figure 3 Electric conductivity κ as a function of water content Φ of the system (30 °C).

The conductivity curve in Figure 3 clearly illustrates the occurrence of the three regions: water-in-oil (20–43% water), oil-in-water (64–83%) and bicontinuous (43–64%) microemulsions. Thus, the results obtained by the two electrochemical methods are in agreement.

In summary, cyclic voltammetry was found to be a promising technique for examining structural transformations in macro- and microemulsion systems.

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