

Phase Structures of Microemulsions Determined by the Steady-State Fluorescence Method

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Abstract: The steady-state fluorescence method has been tentatively used to determine the phase structures of microemulsion systems consisting of cetyltrimethylammonium bromide (CTAB), *n*-butanol (*n*-C₄H₉OH), octane (*n*-C₈H₁₈), and water. The excimer/monomer intensity ratio (I_e/I_m) of pyrene has demonstrated that the various structures in the microemulsion phase region can be distinguished. The results are consistent with electrical conductivity data already reported.

Keywords: Phase structure, fluorescence, microemulsion, CTAB, pyrene.

Experimental

The pyrene was purchased from Sigma Co., and the other chemicals were of A. R. grade. Water was deionized and distilled twice before use.

The microemulsions of required compositions were prepared in the following way. The stock microemulsions were made without water at first, corresponding to the A point (10wt% octane, 63wt% *n*-butanol, 27wt% CTAB) in the phase diagram of **Figure 1** and then a series of microemulsions were made along AW dilution line with adding water. Calculated amounts of pyrene were added to keep the concentration of 1.5×10^{-3} mol/L. Actually 1.0×10^{-2} mol/L *n*-butanol solution of pyrene was prior prepared, so the amount of *n*-butanol used in a microemulsion system should be appropriately subtracted.

Steady-state fluorescence spectra were recorded on RF-540 spectrophoto-fluorometer (Co., Japan) by using a narrow bandwidth of 1 nm. Pyrene was used as a fluorescence probe and its excitation was selected at wavelength of 335 nm. All the solutions were deoxygenated with 99.99% nitrogen before each measurement. The experiments were conducted at room temperature.

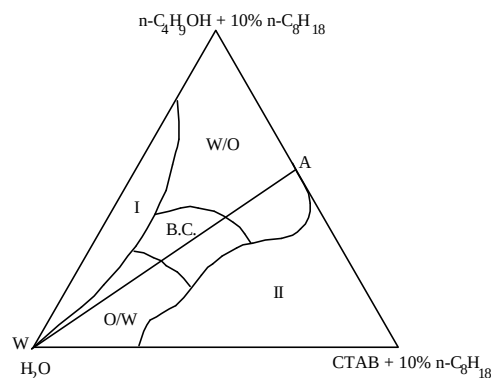
Results and Discussion

Figure 1 shows the pseudoternary phase diagram of the system, CTAB/*n*-butanol/octane/

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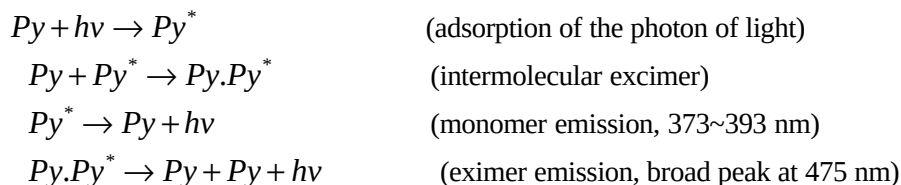
water. In our experiments we altered the water content of the microemulsion along the dilution line AW, and proceeded in the direction from A to W. This corresponds to constant weight ratios of $(\text{CTAB}/n\text{-C}_4\text{H}_9\text{OH}) = 0.43\%$ and $[\text{octane}/(\text{surfactant} + n\text{-butanol})] = 10\%$. From the electrical conductivity results in reference¹ the phase structures^{2,3} of isotropic microemulsions (exhibited by water content) along the AW line have been distinguished as water in oil (W/O) (0, 30), B.C. (30, 55), and O/W type (55, 100).

Figure 1 The pseudoternary phase diagram of CTAB/ $n\text{-C}_4\text{H}_9\text{OH}$ / $n\text{-C}_8\text{H}_{18}/\text{H}_2\text{O}$



I and II are two-phase regions, the other part of the triangle is single-phase region; AW is the dilution line along which experiments were performed.

Through the adsorption of a photon of light, the ground state of pyrene molecule is excited to a high energy state, and its reverse process is the generation of fluorescence, namely the monomer emission. But an excited species may return to ground state by collisional deactivation, which is the process for the formation of intermolecular excimer and is a radiationless process⁴. The intermolecular excimer formation is a function not only of diffusional motion of the probes, but also of the local probe concentration and distributions; hence the photophysical techniques can be a convenient method for the investigation of the structures of microemulsion systems⁵. The mechanism for monomer and excimer emission of pyrene can be given by the following scheme:



Although the triplet states of pyrene are generated in the photophysical process, there is no effect on our results.

The excimer emission spectrum of pyrene in the microemulsion of point A the only could be observed at the pyrene concentration, $[Py]$, greater than 1.0×10^{-4} mol/L, hence experiments were carried out with a pyrene concentration of 1.5×10^{-3} mol/L (defined as molarity per liter of microemulsion). **Figure 2** shows the monomer and excimer emission spectrum of pyrene. The wavelength region 373~393 nm is the monomer emission spectrum of pyrene and the intensity at 393 nm is defined as I_m . The excimer emission spectrum of pyrene shows a broad peak with its maximum at 475 nm, and the maximum intensity is named I_e . Similarly the ratio of I_e/I_m is defined as the ratio between maximum monomer emission intensity and the maximum excimer emission intensity of pyrene.

Figure 2 Emission spectrum of pyrene in the microemulsion containing 30% water

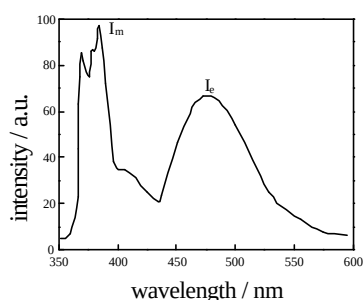
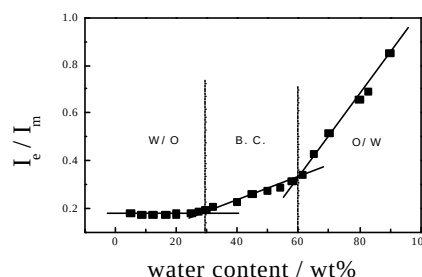


Figure 3 Dependence of I_e/I_m ratio on the water content along AW dilution line



For isotropic microemulsion systems along the AW line, the relationship between I_e/I_m value and water content is shown in **Figure 3**. Compared with the results determined by electrical conductivity method¹, the I_e/I_m values which varies with the water content as shown in **Figure 3**. These values could also be used to distinguish the phase structure of isotropic microemulsion systems. For W/O microemulsion systems along the AW line, the I_e/I_m values remain almost constant with water contents, but the I_e/I_m values for B.C. and O/W microemulsions increase linearly with the water contents and the line has a fixed slope for a certain phase structure of microemulsions.

Since the rate of excimer decay given earlier in the scheme is proportional to the rate of the formation of intermolecular excimer, the I_m and I_e values are proportional to the concentration of $[Py^*]$ and $[Py] \times [Py^*]$, respectively. Therefore the I_e/I_m values are proportional to the concentration of pyrene. Because the solubility of pyrene in water is very low ($2\sim 3 \mu\text{mol L}^{-1}$), the pyrene molecules should always stay in the hydrocarbon part of the microemulsion. In our experiments the $[Py]$ value was defined by the concentration of pyrene per unit volume of microemulsion and was kept constant at $1.5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$. In the B.C. and O/W regions, the increase of I_e/I_m implies that $[Py]$ denotes the local concentration, namely, pyrene molecules per unit volume of oil phase. However, the dependence of I_e/I_m does not show linearity in W/O region and the different slopes for the linear relationship between I_e/I_m and water content shows conclusively that merely redefining $[Py]$ would not account for the variation. It is imperative to assume

that the structure of microemulsion also affects the value of I_e/I_m .

There are two significant structure factors that could affect the pyrene excimer formation in the microemulsion. The first factor is the occupancy number of pyrene molecules in microemulsion droplets. In W/O type microemulsion systems, the water content is lower and the pyrene molecules are expected to be distributed in the continuous medium. The I_e/I_m value is small because the local concentration of pyrene is very low and the collision between pyrene molecules is less frequent. The increasing water content along the dilution line does not influence the I_e/I_m value until to the B.C. region.

The second factor which could influence I_e/I_m value is the microviscosity, because the ratio of excimer/monomer emission intensity can be used to determine the microemulsion microviscosity by comparing with the standards viscosity⁶. Since the pyrene molecules always stay in the hydrophobic parts of microemulsion, continuous oil media in B.C. region and oil poor in O/W region can have different rule of microviscosity, which accounts for different linear relationships between I_e/I_m values and water content along the AW dilution line in **Figure 1**.

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