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Study on lyotropic liquid crystals of the 3-octyloxy-2-hydroxypropyl trimethyl ammonium bromide-*n*-hexanol-water system

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Phase diagram of ternary system for 3-octyloxy-2-hydroxypropyl trimethyl ammonium bromide (R_8TAB)-*n*-hexanol-water has been investigated using turbidity titration method at 25°C. Typical lyotropic liquid crystals (LLCs) of lamellar, hexagonal and cubic phases have been found in the system. The structure and the structure conversion have been determined using polarizing-light microscope, ^{2}H nuclear magnetic resonance (^{2}H NMR) and differential scanning calorimetry (DSC). Experimental results show that with the enhancement of relative amount of water in a mixture maintaining mass ratio of R_8TAB to $C_6H_{13}OH$ at 3:2, the phase transition is as follows: from mixed lamellar and hexagonal liquid crystals to mixed lamellar, hexagonal and cubic ones, then to single cubic one and finally to mixed hexagonal one and isotropic liquid phase.

Lyotropic liquid crystals (LLCs) can often be formed in binary solution of surfactant in polar solvent such as water or in ternary system in which assistant surfactant or other polar organic component is present. Characteristics, structures and forming conditions of LLCs have drawn great attention around the world[1-6]. Earlier researches[7, 8] reported that symmetric structure of crystals might be lamellar hexagonal and cubic *etc*. In recent years, LLCs formed in ternary system of water-normal alcohol-anionic/cationic/zwitterionic/non-ionic[9] surfactant have been studied by various methods. In the present work, LLCs formed in the system of 3-octyloxy-2-hydroxypropyl trimethyl ammonium bromide (R_8TAB)-*n*-hexanol-water have been investigated with ternary phase diagram, ^{2}H nuclear magnetic resonance (^{2}H NMR) and differential scanning calorimeter (DSC). Nice photographs showing texture structure of LLCs were obtained using a polarizing light microscope.

Experimental

3-Octyloxy-2-hydroxypropyl trimethyl ammonium bromide (R_8TAB) was synthesized by us[10]. *n*-Hexanol was chemical reagent obtained from Shanghai Reagents Company (Shanghai, China), and was purified by distillation under reduced pressure; heavy water was a product of Aldrich. Water used in the experiment was doubly distilled.

The ternary phase diagram of the R_8TAB-*n*-hexanol-water system was drawn using the method reported by Li *et al.*[11] Boundary lines of emulsion regions and liquid crystal regions were determined by means of turbidity titration and polarizing light microscopy. Some experimental samples were prepared using heavy water and stored at 25.0±0.1°C for a week, and then quadrupole splitting spectrum (^{2}H NMR) of deuterons was got with an FX-90Q NMR spectrometer (JEOL Company, Japan). About 5 mg sample containing LLC was sealed in aluminum crucible, and heating scan was performed on a Pyris Diamond DSC calorimeter (Perkin-Elmer, USA), with the temperature rising rate at 2° per minute.

Results and discussion

Ternary phase diagram of the R_8TAB-*n*-hexanol-water system

The ternary phase diagram of the R_8TAB-*n*-hexanol-water system is shown in Fig.1. Structure for every type of LLC has been further confirmed with ^{2}H NMR.

Texture photographs and ^{2}H NMR spectra of lyotropic liquid crystals

Excellent photographs (Fig. 2) have been obtained with a polarizing-light microscope for some R_8TAB-*n*-hexanol-water mixtures, whose compositional representing points are indicated by Arabic numerals in Fig. 1. ^{2}H NMR spectra of these mixtures were shown in Fig. 3. Because our main destination is to find out how the structure of LLC changes with the relative amount of water, the mass ratio of R_8TAB to *n*-hexanol has been kept about 3:2 in the hetero-

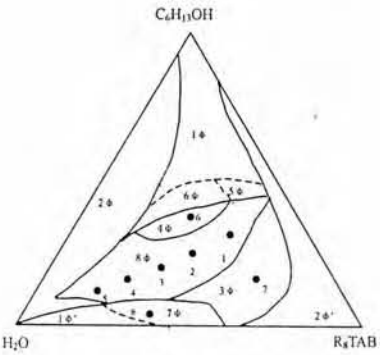

Fig. 1—Ternary phase diagram of the R_8TAB-*n*-hexanol-water system (25°C). 1φ.w/o microemulsion; 1φ'. o/w microemulsion; 2φ. Water-hexanol partially mutual soluble region; 2φ'. turbid region; 3φ. lamellar liquid crystal(L); 4φ. hexagonal liquid crystal(H); 5φ. lamellar liquid crystal/microemulsion(L+w/o); 6φ. hexagonal liquid crystal/microemulsion(H+w/o); 7φ. cubic liquid crystal/microemulsion(C+o/w); 8φ. mixed liquid crystals

geneous samples whose composition points are in Region 8φ of Fig. 1.

Photograph A is taken for sample containing 44% R_8TAB, 34% *n*-hexanol and 22% water by weight (point 1 in Fig. 1), which is a transparently colloidal liquid. Many cross–shaped textures and some fan–shaped ones are observed from it. Two doublets are observed on its ^2H NMR spectrum (spectrum 1 in Fig. 3), which means existence of two non-isotropic phases in the system[1]. The splitting width of the external doublet is about 1200Hz, twice that of the internal one, and the former is much higher than the latter. By comparing this photograph with those in the literature[12], it can be known that this mixture contains large amount of lamellar LLCs and some hexagonal ones.

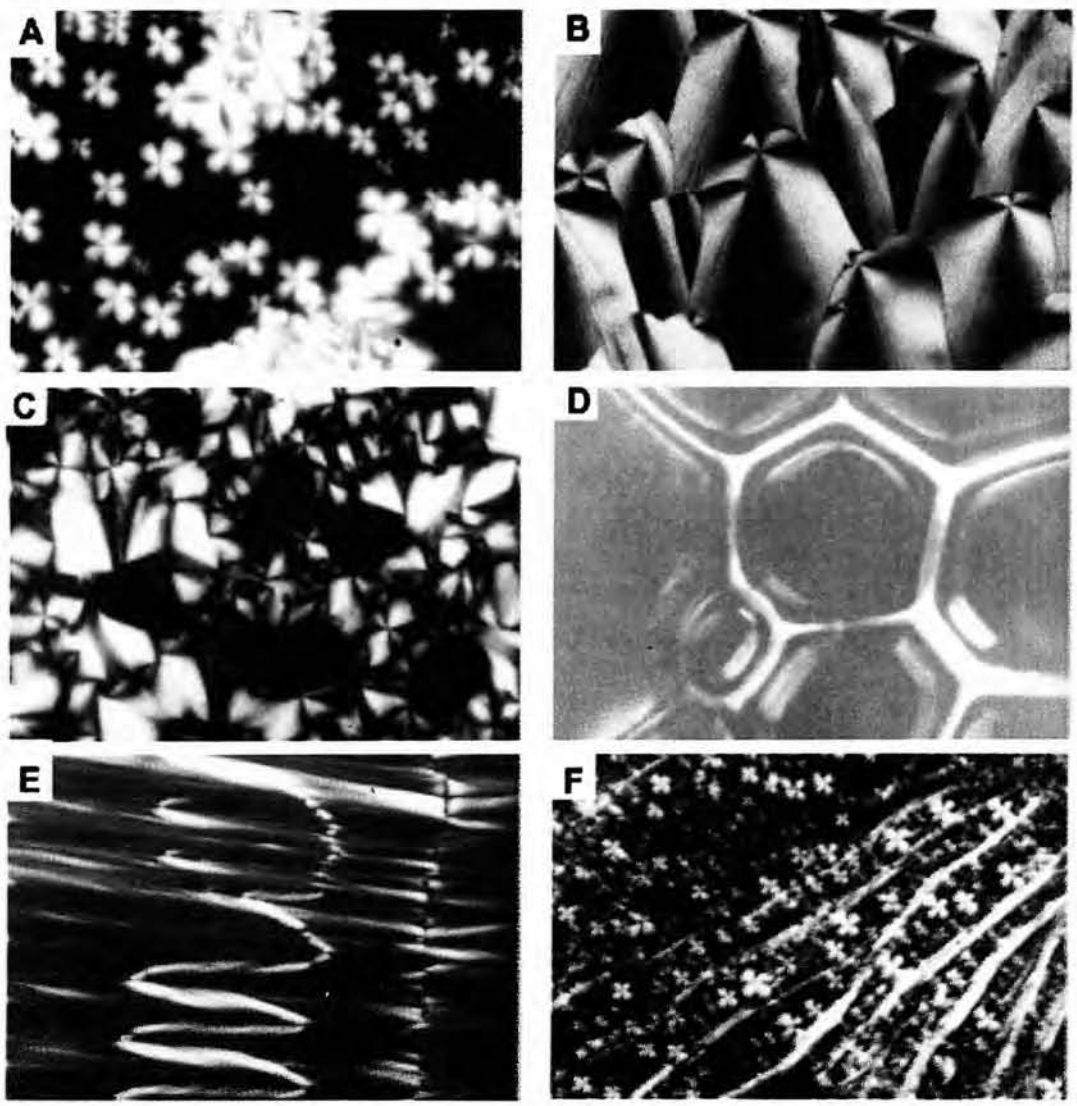

Fig. 2—Liquid crystal texture photographs of various samples

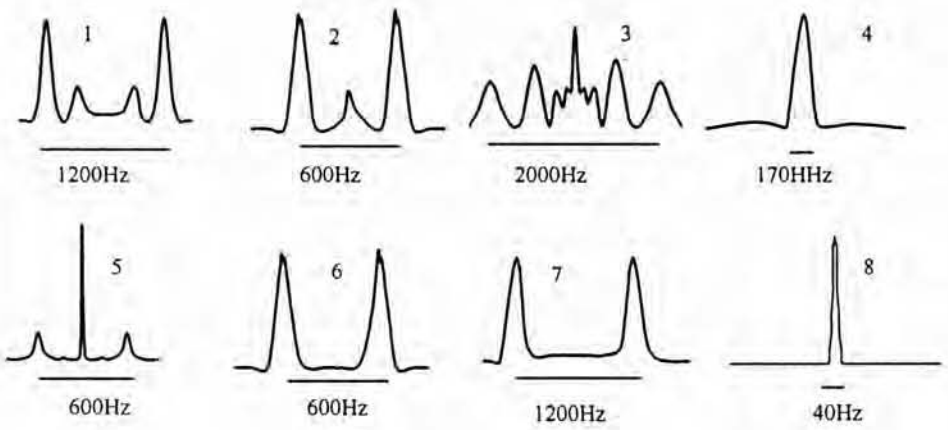

Fig. 3—^{2}H NMR spectra for various samples

^{2}H NMR spectrum 2 is obtained from the sample containing 39% R_8TAB, 24% *n*-hexanol and 37% water (point 2 of Fig. 1), a higher doublet and a lower singlet are observed in it, which means that there are one non-isotropic and one isotropic phases in the mixture. The distance between two peaks of the doublet is 600 Hz, and correspondingly, fan–shaped textures are shown clearly in the photograph (B of Fig. 2). It can be judged that the non-isotropic phase is hexagonal LLC and the isotropic phase is probably W/O microemulsion[4,5,12] or cubic LLC.

If the relative amount of water is raised still further to 49%, three pairs of doublets appear along with a central singlet on the ^{2}H NMR spectrum (spectrum 3), with the splitting width of the most external doublet is about 2000Hz. It indicates that the lamellar and hexagonal LLCs are still in existence in addition to another non-isotropic phase. Photograph C shows that the cross-shaped, fan-shaped, mosaic-shaped textures and black holes are appearing simultaneously. By combining ^{2}H NMR spectrum with the corresponding photograph and consulting literatures[4,12], the existence of cubic LLC can be ascertained.

Photograph D and ^{2}H NMR spectrum 4 are got from the mixture containing 23% R_8TAB, 17% *n*-hexanol and even larger amount in weight of (60%) water. The spectrum shows only one singlet with quite large width (170 Hz) in its base. The corresponding photograph also shows great growth of the hexagonal texture of cubic LLC[12], and the viscosity of the sample becomes even strong, which indicates that the major part of the system is cubic LLC.

Spectrum 5, got from sample 5 which contains 73% of water, is similar to spectrum 2, but the central single peak is much higher and narrow. Ripple-shaped textures can be found in corresponding photograph E. The viscosity of the sample is still stronger than that of sample 4. These facts show the sample contains large amount of microemulsion (o/w) and a small amount of hexagonal LLC.

Sample 6 is in the region of hexagonal LLC (region 4φ in Fig. 1), a doublet can be observed in ^{2}H NMR (spectrum 6 of Fig. 3), and its photograph is similar to photograph B.

On the ^{2}H NMR spectrum of the sample 7 (spectrum 7), the splitting width of a doublet is about 1200Hz. Cross-shaped textures of photograph F show the characteristic of lamellar LLC. Only this type of LLC can be found in the samples whose compositional points fall in region 3φ of Fig. 1.

Sample 8 contains 37% R_8TAB, 6% *n*-hexanol and 57% water. There is only a sharp singlet on its ^{2}H NMR spectrum, and the singlet bottom is much narrower than that in spectrum 4. No texture of LLC for the sample has been observed, while the sample is a very transparently colloidal liquid and possesses a very strong viscosity. There may be a little of cubic LLC and o/w type microemulsion in it. Similar ^{2}H NMR spectrum can be got for mixtures with compositional points in region 7φ of Fig. 1.

Tracings of differential scanning calorimetry

Through the DSC tracing and the texture observing of the selected sample with temperature changing, it has been known that the type of LLC changes from lamellar to cubic then to hexagonal, and all the transformation processes are endothermic.

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