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Phase behaviors of Gemini cationic surfactants/*n*-butanol/water systems

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ABSTRACT

Phase diagrams for ternary system of the Gemini cationic surfactants, N,N-long chain alkyl-2-hydroxyl-N,N,N,N-tetramethyl diammonium dichloride (G_nCl_2) with butanol and water have been drawn based on experimental data at 25 °C. The phase diagrams show that L phase and different liquid crystalline phases are existent in the ternary system at different components. Electric conductivity of the L phase has been studied. Small-angle X-ray scattering (SAXS), ^{2}H (deuterium) quadrupolar splitting (^{2}H NMR) and the polarizing-light microscope were employed to confirm the characteristic texture structures and the microstructure of three different liquid crystalline phases.

1. Introduction

A Gemini surfactant can be regarded as the dimer formed from two normal surfactants connected by a group. In comparison to normal surfactants, Gemini surfactants have some unique properties, for instance, the lower surface tension, the lower critical micelle concentration, the rheological properties, etc., which may be helpful to diversified use of them for manifold applications such as detergent, germicide, emulsion, diffusion, antisepsis, cosmetic, printing and dyeing, thrice oil extraction, and the synthesis of mesoporous materials [1–11]. However, there are only limited investigations on the property of liquid crystals for such Gemini cationic surfactants [12–14], though this type of surfactants was synthesized 10 years ago [15].

Lyotropic liquid crystals, as important supramolecular assemblies of amphiphilic surfactants, have attracted increasing interest in a wide range of applications, including materials science, household products, chemical reaction media, gene therapy, and pharmaceutical vehicles. In the previous work, we have investigated some physicochemical properties of G_nCl_2 in aqueous solution. In this presentation we report sequentially their phase behaviors in the mixed *n*-butanol/water system.

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2. Experimental

2.1. Reagents

The Gemini cationic surfactant N,N,-long chain alkyl-2-hydroxyl-N,N,N,N,-tetramethyl diammonium dichloride [$(C_nH_{2n+1}(CH_3)_2N)CH_2CH(HO)CH_2(N(CH_3)_2C_nH_{2n+1}]Cl_2$, simply written as G_nCl_2, n = 12, 14, 16) were synthesized and purified in our laboratory with the method described in the literature [15]. The surfactant met the criterion for purity, *i.e.*, there was no minimum point in the curve of surface tension versus the logarithm of surfactant concentration in aqueous solution. *n*-Butanol is chemical pure reagent obtained from Shanghai Reagents Company (Shanghai, China), and was purified by distillation under reduced pressure; heavy water (deuterium oxide) was a product of Aldrich with the isotopic purity better than 99.96 (atom D)%. Water used in the experiment was doubly distilled in the presence of basic potassium permanganate and its conductance was less than 3 μS cm^{-1}.

2.2. Methods and instruments

2.2.1. Phase diagram determination

Pre-weighed mixtures of G_nCl_2 and *n*-butanol, with weight ratios varying from 0:1 to 1:0 were well stirred at a temperature of 25 °C to be homogenized; then the water was added sequentially and the samples were mixed using a vortex mixer. Phase equilibrium were determined by visual observation of the samples in normal light, boundary lines of microemulsion regions and liquid crystal regions were determined by use of turbidity titration and polarizing light microscope (XP-201, Nanjing Optician Factory, the maximum magnification is 1000 and the thermal controller was made by ourselves). The optical texture of lyotropic liquid crystals has been checked by polarizing light microscopy at 25.0 ± 0.1 °C and effective texture identification of the lyotropic liquid crystals was recorded with a super camera. The types of liquid crystals were identified by small-angle X-ray scattering (SAXS) and nuclear magnetic resonance (^{2}H NMR).

2.2.2. Small-angle X-ray scattering (SAXS)

A sample containing liquid crystal phase was enclosed in a special capillary tube in nitrogen gas. The temperature in the camera was regulated by a Peltier element at 25.0 ± 0.1 °C and the chamber was kept under vacuum to minimize air scattering. Measurement of the interlayer spacing of different liquid crystals was performed on a PW-1700 small-angle scattering goniometer (SAXS, Philips Company, Holland), with Ni-filtered Cu Kα radiation (0.154 nm) operating at 50 kV and 40 mA. The sample-to-detector distance was 277 mm.

2.2.3. Nuclear magnetic resonance (^{2}H NMR)

A mixture, the composition of which was in liquid crystal region of a ternary phase diagram, was prepared using heavy water and stored at 25.0 ± 0.1 °C for a week. Then the quadrupole splitting spectrum of deuterons (^{2}H NMR) in the sample was obtained with an MP-400 nuclear magnetic resonance spectrometer (Varian Company, USA). TMS is used as an exterior reference.

2.2.4. Conductance measurements

The samples whose component fell in the micelle region of the ternary diagram were prepared with doubly distilled water. Electric conductivity of the microemulsions was measured using a Conductometer (Model DDS-308A, Shanghai Instrument Ltd., China) fitted with a platinum electrode, and the conductance cell was calibrated with 10.00 mmol/L KCl solution. To guarantee homogeneity of the solution, it was stirred for 10 min and then equilibrated at 25.0 ± 0.1 °C in water bath before the measurements of electrical conductivity. Conductivity measurements were carried out during the titration of starting mixtures of the surfactant and *n*-butanol with water through a different dilution line. The electrode was dipped in the microemulsion sample until equilibrium was reached. Reproducibility was checked for certain samples and no significant differences were observed.

3. Results and discussion

3.1. Ternary phase diagrams of G_nCl_2–butanol–water system

The ternary phase diagrams of the G_nCl_2–butanol–water systems at 25 °C are presented in Fig. 1(A)–(C). All the three systems exhibit a large isotropic liquid region or L phase, two 2-phase regions (the coexist region of the unsolvable surfactant and liquid 2φ, and 2φ*) in the diagrams. The L phase is a transparent, isotropic, and low viscosity solution, whose phase regions extends from the water corner to the alcohol corner of the ternary phase diagram. In the L phase, there are three different micelle structures in existence, corresponding to the alcoholic solution containing G_nCl_2 reverse micelles (I), bicontinuous structure micelles (B.C. II) and aqueous solution of mixed G_nCl_2–C_4H_9OH micelles (III), respectively. Of course, in order to study these changes, character of L phase will be discussed in more detail based on electric conductivity in the following sections. In the phase diagrams (A) and (B) of Fig. 1, there are four different anisotropic regions, *i.e.* Region IV (hexagonal liquid

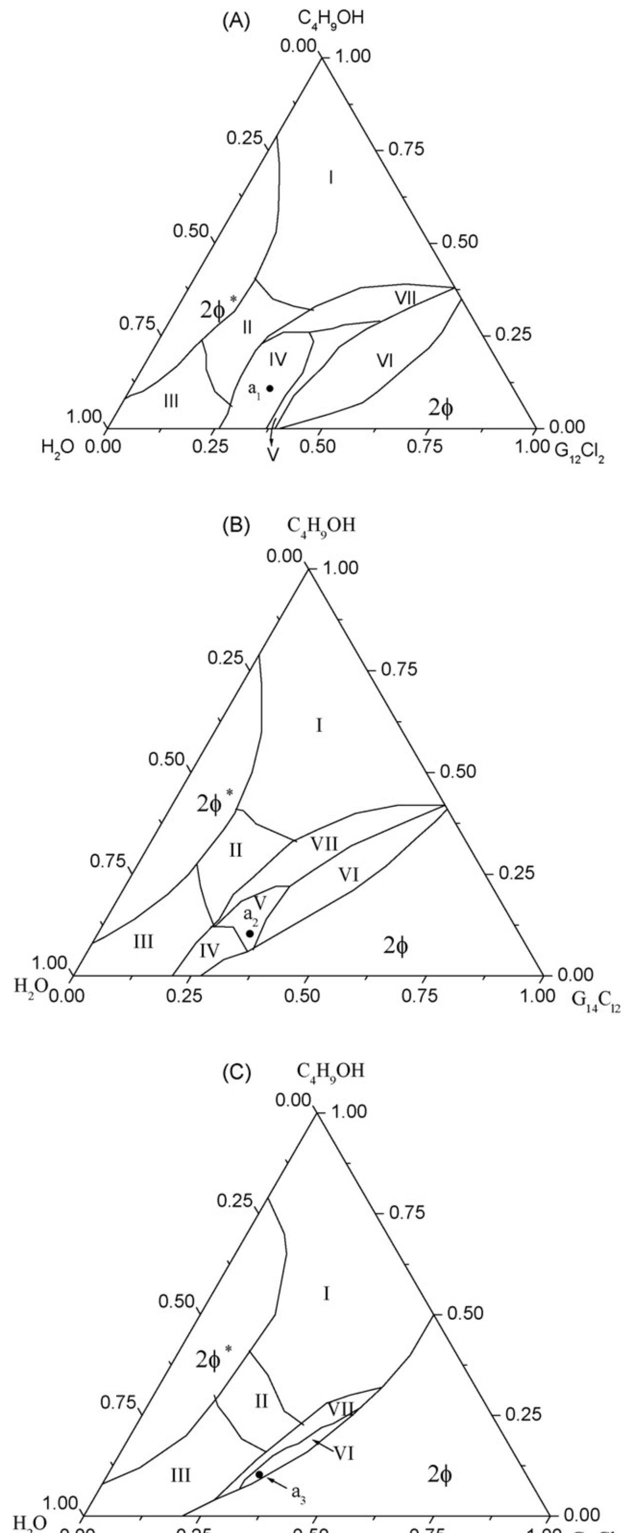

Fig. 1. The phase diagram of the ternary systems G_nCl_2–butanol–water at 25.0 ± 0.1 °C. I, reverse micelles region; II, bi-continuous micelles region (B.C.); III, micelles in aqueous solution of butanol; IV, hexagonal liquid crystal phase; V, coexist region of hexagonal/lamellar liquid crystal; VI, lamellar liquid crystal; VII, a littler liquid crystal/micelle coexist region.