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Effect of different hydrocarbons on phase behavior of dihydrogenated tallowalkyl dimethyl ammonium chloride, hydrocarbon and water

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ABSTRACT

The phase behaviors of dihydrogenated tallowalkyl dimethyl ammonium chloride (DHTDMAC), water and different hydrocarbons were studied. Addition of different hydrocarbons to DHTDMAC and water system formed rich aggregates, including two liquid crystal aggregates and water in oil microemulsion. The polarity of hydrocarbon affects stability and phase behavior of hydrocarbon–DHTDMAC–water. The polar hydrocarbons, cyclohexane and benzene stabilize the phase structure. Interaction of different hydrocarbon molecules with liquid crystal phase was studied by the small angle X-ray diffraction. The results indicate that the variable hydrocarbon and water fraction penetrate into surfactant association structure with the different hydrocarbons, which affects the stability and Kraft point of surfactant aggregates. Less water penetrates into lamellar liquid crystal where more oil penetrates into the same area, which stabilizes the aggregate's phase structure.

1. Introduction

Dialkyldimethylammonium surfactant is an important class of amphiphiles used in industries as fabric softeners, corrosion inhibitors and antistatic agents. Dialkyl surfactant molecules are also model compounds to form bilayer lipid structures [1,2], lamellar liquid—crystalline and vesicles [3–7].

The binary phase behavior of dioctadecyl dimethylamonium chloride (DODMAC)-water system has been systemically studied [8–10]. The results indicated that a large area of lamellar structure existed from 31.5% to 95% DODMAC at elevated temperature. The hydration and dehydration rate of DODMAC is depended on the number of hydrate bonding on crystal below the Kafft temperature. Gel and coagel colloid structures existed in dilute aqueous region of DODMAC. The studies showed that Krafft point is well above the room temperature. The microemulsion and associate phase behavior has been studied in dialkyl dimethylamonium amphilies with alkyl chain length below twelve [11].

The long chain dialkyl dimethylamonium amphilies have super lubrication, antistatic and corrosion-inhibited effect in textile, hair care and oilfield applications. Research has been focused on aggregate structure with dioctadecyl dimethylamonium bromide [12,13]. Much research has been done on their interaction with other surfactants [14–16] or alcohol [17]. The similar long chain dihydrogenated tallowalkyl dimethyl ammonium chloride (DHTDMAC) is a natural derivative product. The ternary phase behavior of DHTDMAC–water–oil has been studied with hexane as oil phase [18]. The results showed that a kinetic stable phase including temporary microemulsion and liquid crystal structure existed. The phase diagram showed unusual metastable phase behavior. The association structures are stable for a short time with the input of mixing energy initially, and the crystals were formed within microemulsion and liquid crystal area after a few hours. The mechanism of such unstable liquid crystal system with crystal formation is proposed as multiple step of dehydration of lamellar liquid crystal. The interaction of aliphatic and aromatic hydrocarbons with nonionic surfactant, polyethylene glycol alkyl ether, has been studied [19]. However, there are no reports on stable system containing three components DHTDMAC, water and different hydrocarbons. The stable systems containing hydrocarbons are useful in industrial applications. It would be meaningful to study the effect of different hydrocarbon molecules on the phase behavior of the system containing cationic surfactant, DHTDMAC. We hereby study the phase behavior of the three components system containing DHTDMAC, water and different hydrocarbon molecules. The mechanism of the stabilization and interaction of DHTDMAC with polar hydrocarbon molecule was proposed. The results provide guidance for developing stable colloidal system in industrial applications.

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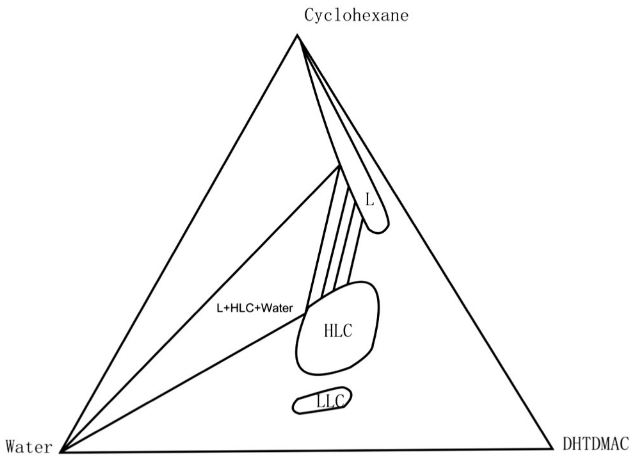


Fig. 1. Phase diagram of DHTDMAC, cyclohexane and water.

2. Experimental

2.1. Materials

Dihydrogenated tallowalkyl dimethyl ammonium chloride was supplied by Rhodia Feixiang Co., China. The compound was further purified by repeated crystallization from acetone.

Cyclohexane and benzene were >99% in purity, and received from Sinopharm Chemical Co., China. Water was twice distilled.

2.2. Methods

The phase diagram was determined by mixing of surfactant, solvent and water at different weight ratio. The water in oil (W/O) microemulsion region was determined by titration of water to various weight ratio of hydrocarbon to DHTDMAC with continuously mixing of the sample during titration. In order to increase dissolution rate, samples can be mixed by increasing temperature slightly. In viscous liquid crystal phase, the samples were centrifuged to move bubble. All samples were equilibrated at 25 °C for a week. The clarity or turbidity of solutions was observed visually. The formation of liquid crystal phase was detected by viewing the sample between crossed polarizer for birefringence. The borderline to the three-phase region, following the solution of hydrocarbon and water two phase area and the three phase area with liquid crystals, was also determined by observation of birefringence. The microstructure of liquid crystal was characterized by polarized optical microscope and small angle X-ray diffraction (Anton Par SAXSess).

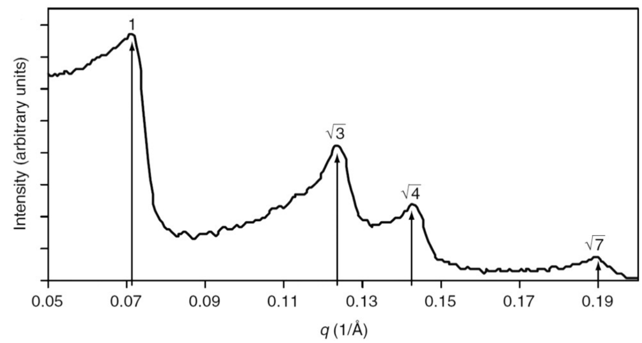


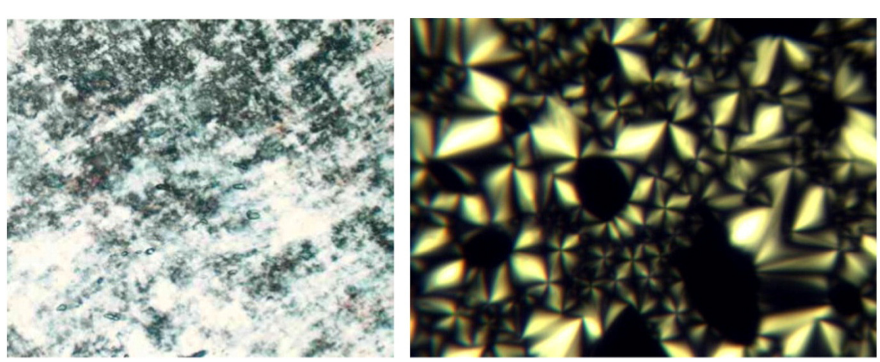
Fig. 3. Small angle X-ray diffraction patterns of the hexagonal phase.

3. Results and discussion

3.1. Phase behavior of DHTDMAC/hydrocarbon/water

The partial phase diagram of DHTDMAC/cyclohexane/water is shown in Fig. 1. DHTDMAC is not soluble in cyclohexane. Addition of water makes DHTDMAC soluble in cyclohexane and forms an isotropic area, L, which is inverted micelle or water in oil microemulsion with more water solubilized. There is a highly viscous hexagonal liquid crystal (HLC) phase from 15% to 40% water and 18% to 40% cyclohexane in the center region of phase diagram. HLC phase is an inverse hexagonal liquid crystal phase confirmed by their fan-shape texture as shown Fig. 2a under a polarized microscope [18,20]. The hexagonal structure is further confirmed for their long-range ordering in small angle X-ray scattering peaks in the ratio1:√3:√4 [18,20]. The typical X-ray diffraction patterns of a hexagonal phase are shown in Fig. 3. With these phases present, one finds a large three phase (L + HLC + Water) region on lower left side of L phase, and a two phase region. The tie-lines are also shown in the two phase area between L and HLC. The rigid gel phase HLC is transformed to a soft lamellar liquid crystal (LLC) phase from 10% to 15% cyclohexane and 40% to 55% water. LLC phase is characterized by matese-cross texture as shown in Fig. 2b under polarized microscope.[18,20] The lamellar structure is further confirmed for their long-range ordering in small angle X-ray scattering peaks in the ratio 1:2:3 [18,20]. The typical X-ray diffraction patterns of a lamellar phase are shown in Fig. 4.

The partial phase diagram of DHTDMAC/benzene/water is shown in Fig. 5. The phase diagram is similar to phase diagram of DHTDMAC/cyclohexane/water. DHTDMAC is not soluble in benzene. Addition of water makes DHTDMAC soluble in benzene and forms an isotropic area, L. A highly viscous inverse hexagonal liquid crystal, HLC, phase from 13% to 38% water and 16% to 38% cyclohexane exists in the center



(a) (b)

Fig. 2. The optical texture of (a) hexagonal liquid crystal (HLC) and (b) lamellar liquid crystal (LLC) under a polarized microscope.