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STUDIES ON THE PHASE DIAGRAM OF THE SURFACTANT/1-PENTANOL / WATER TERNARY SYSTEM II: THE LIQUID CRYSTALLINE PHASE

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STUDIES ON THE PHASE DIAGRAM OF THE SURFACTANT/1-PENTANOL /WATER TERNARY SYSTEM II: THE LIQUID CRYSTALLINE PHASE

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ABSTRACT

The phase behavior of liquid crystalline in the ternary system of dodecyl dimethyl ammonium hydroxyl propyl sulfonate(DDAHPS)/1-pentanol(C₅H₁₁OH) /water deuteron(D₂O) has been investigated by polarizing optical microscopy, ²H NMR spectroscopy methods. The results indicate that two kinds of liquid crystals (the lamellar, and the hexagonal) exist in the liquid crystalline phase region. In this paper, we also use the polarized Raman spectroscopy method to measure the values of the order/ disorder parameters and the values of the environment polarity parameters for the samples selected from the liquid crystalline phase region, and compare these two parameters of the samples with those of solid state DDAHPS and liquid state pentan-1-ol.

INTRODUCTION

In general, when a considerable amount of amphiphlic materials is mixed with water or other polar solvent, the lyotropic liquid crystal is formed. Adding some oils

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to these systems, cosurfactants (mainly moderate length carbon chain alcohols, from three to eight carbon atoms) are needed in order to form microemulsions and lyotropic liquid crystal simultaneously. Both for scientific interest and for technological importance, microemulsion and liquid crystal (L.C.) cause scientists much interest in recent years.

Alcohol has been used as oil substitute to investigate the phase behavior of amphiphiles/alcohol/water systems^[1-4]. When the chain length of the alcohols increase From three to eight carbon atoms, the continuous isotropic solution phase region from the water to the alcoholic corner (L phase) is divided into two subregions, an aqueous phase (L₁) and an alcoholic phase (L₂). The hexagonal region reduces in size, simultaneously, while the lamellar phase area increases considerably, appearing at the lower surfactant and the higher water contents region of the phase diagrams. Likewise, small regions with more complicated cubic and reverted structures, appear in the middle of the diagrams^[1].

In this paper, polarized optical microscopy, and deuterium NMR spectroscopy methods are used to investigate the phase behavior of the L.C. phase in the DDAHPS/ $C_{3}H_{11}OH/D_{2}O$ system.

Raman spectra in the C-H stretching region around 2800-2970 cm⁻¹ are sensitive to the structure and environment of hydrocarbon chain of molecules, probably because of a change of Fermi resonance conditions. Raman spectra have been used to investigate surfactant micellar properties^[5,6] and liquid crystalline system^[7]. Here we also use polarizing Raman spectroscopy method to investigate the physicochemical properties of the L.C. phase in DDAHPS/ $C_5H_{11}OH/D_2O$ system.

MATERIALS AND METHODS

D₂O (99.9%)(Beijing Chem. Co.), 1-pentanol (A. P.) and DDAHPS (Nanjing Chem. Co.) were used as supplied.

The phase diagram was constructed using macroscopic samples prepared by weighing the components in screw cap glass test tubes. Samples were mixed and homogenized by shaking and storing in WMK-10 vibrator (Shandong Uni. Apparatus Co.), thermostated at 30 ± 0.1 °C for at least one week. The samples were checked by visual inspection through crossed polarizers in order to determine the boundary of phase regions.

The L.C. phase was investigated by using polarized optical microscopy (Guizuo Optical Apparatus Co.) with a camera for photography of the samples. Each sample was identified by comparing its textures with photomicrographs from the references [8.9].

The nuclear magnetic resonance (NMR) spectrum of deuterated water was measured with FX-90Q (90MHZ) spectrometer (JEOL, Japan). A detailed theoretical treatment of ²H quadrupole splitting in lyotropic liquid crystalline phases has been reported by Khan et al ¹¹⁰.

The Raman spectroscopy was measured with a SPEX1403 Raman spectrophotometer(SPEX,USA). An argon-ion laser(200-500mW, 5145Å green line) was used for excitation. In the present paper, we measure the Raman spectral intensities and frequencies of the hydrocarbon (C-H) stretching modes (2800-2970 cm⁻¹) for each sample. A theoretical treatment of C-H stretching vibration has been reported by T. Kitagawa et al^[11,12]. All the experiments are operated at 30 \pm 0.1°C.

RESULTS AND DISCUSSION

Ternary phase diagram

The isothermal ternary phase diagram obtained at 30 ± 0.1 °C for the system DDAHPS/C₅H₁₁OH/D₂O is given in Figure 1. It contains two isotropic solution phases, one rich in water (L₁) and the other rich in pentanol (L₂), and one liquid crystalline phase. Both the aqueous and pentanolic solutions are transparent low-viscosity flowing Newtonion liquids with no shear birefringence. But the samples (a, b, c, d, e and f) labeled in Fig.1 are sticky and transparent.

Polarizing optical microscopy

Figure 2 shows microphotographs of samples containing liquid crystal (shown in Fig.1). All the samples are different strongly in birefringent texture under the optical microscope. Fig.2a shows the texture of nongeometric striation indicating the existence of hexagonal liquid crystal. The phase should be built up by cylindrical surfactant aggregates in a hexagonal array. Meanwhile Fig.2b shows the typical fanlike texture of hexagonal liquid crystal. The very stiff feature of this sample implies that it may be the mixture of a large amount of hexagonal crystal and a little amount of cubic crystal; and the results obtained in the L.C. phase region of dodecyl carboxylic diehanol amine /paraffin oil/butan-1-ol/D₂O system^[13] can prove this idea.



FIG.1 Phase diagram for the system DDAHPS/C₅H₁₁OH/D₂0 at 30 \pm 0.1°C. The L₁ and L₂ represent the isotropic aqueous and pentanolic solutions respectively; the L.C., lyotropic liquid crystalline; the sample points (a, b, c, d, e, f) labeled are selected for investigation.

The liquid crystalline phase in the range from 30 to 64wt% of DDAHPS, and from 16 and 41wt% of pentan-1-ol, microphotographs of Fig.2c, 2d, 2e, and 2f show different textures of the lamellar liquid crystalline phase. These samples are not as stick as the hexagonal ones and some of them have semicloudy appearance. The phase is built up from flexible bimolecular sheets of infinite area but arranged parallel to each other. Fig.2c displays polygonal texture; Fig.2d, mosaic texture with some crossing flowers; Fig.2e, typical mosaic texture of. lamellar liquid crystalline phase. Sample of Fig.2f has lower viscosity, separated into one isotropic solution phase (a large amount) and one birefringence phase(a little amount) a week later, so the composition of sample f is in the two phase region in Fig.1. The polarizing image of Fig.2f is of little polygonal patterns scattering in black background because of photographed immediately after it was prepared.



FIG.2 Polarizing optical photographs of liquid crystalline samples (a, b, c, d, e, and f, shown in Fig.1), ca.100×, 30 ± 0.1 °C.

a: 54%DDAHPS/10%C₅H₁₁OH/36%D₂O, b: 40%DDAHPS/32%C₅H₁₁OH/20%D₂O c: 4%DDAHPS/30%C₅H₁₁OH/30%D₂O, d: 43%DDAHPS/29%C₅H₁₁OH/28%D₂O e: 60%DDAHPS/20%C₅H₁₁OH/20%D₂O, f: 36%DDAHPS/40%C₅H₁₁OH/24%D₂O

(continued)

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FIG. 2. Continued



FIG. 2. Continued

²H NMR spectroscopy

The ²H NMR spectra for samples of a, b, c, d, e and f (shown in Fig.1 , and their compositions, shown in the caption of Fig.2) are recorded and illustrated in Figure 3.

For the hexagonal liquid crystals, proved by polarizing microscopy method, sample a generates two equally intense peaks, with splitting magnitude, \triangle , 650Hz (shown in Fig.3a) and sample b, one singlet and one doublet with 2000Hz splitting magnitude (shown in Fig.3b). Fig.3a shows the existence of one anisotropic phase, and Fig.3b, the coexistence of one isotropic phase and one anisotropic phase.

Samples c, d, e and f are proved to be the lamellar liquid crystal by polarizing optical microscopy, and their ²H NMR spectra are shown in Figure 3c, 3d, 3e and 3f respectively. Fig.3c, Fig.3d and Fig.3e all give one double of equally intense peaks which have magnitudes ranging from 1450 to 1700 Hz. In ternary system, the \triangle value of lamellar liquid crystal with different compositions depends primarily on the water content. Samples with high water content give small values irrespective of the ratios of surfactant to amphiphilic additive^[1]. As far as the splitting magnitude in ²H NMR spectra is concerned, sample a is the half value of sample c, this may be used to prove that the former is hexagonal phase and the latter, lamellar phase. Sample f gives a singlet in ²H NMR spectrum showing the present of isotropic solution, but the presence of liquid crystal is easily recognized under the polarizing microscope.

The polarized Raman spectroscopy

Some samples were selected from the L.C. phase region to measure their Raman spectra. Samples a and c are proved to be typical hexagonal and lamellar phase structure respectively by using polarizing optical microscopy and ²H NMR spectroscopy, and their polarized Raman spectra are illustrated in Figure 4.

The polarized Raman spectrum of sample a (shown in Fig.4a) is only composed of parallel bands (2842-, 2855-,2870-,2880-, 2900-, 2928-, 2960cm⁻¹), and the maximum peak appears at 2928cm⁻¹ . According to T. Kitagawa opinions ^[11], the 2842- and 2855 cm⁻¹ lines are assigned to the CH₂ groups' symmetric stretching vibration . The 2842cm⁻¹ peak comes from DDAHPS molecules and the 2855 cm⁻¹ line, the higher, comes from pentanol molecules. The 2870- and 2880cm⁻¹ lines are assigned to asymmetric stretching vibration of the CH₂ groups. The 2870 cm⁻¹ peak comes from pentan-1-ol molecules, and the 2880cm⁻¹ line, the higher, from DDAHPS molecules. The 2928- and 2960cm⁻¹ lines are assigned to the CH₃ symmetric and asymmetric stretching vibration respectively. The value of the order/disorder



FIG.3 ²H NMR spectra for various samples(a, b, c, d, e and f, same composition as these in Fig. 2)

parameter, the ratio of the 2880-/ 2842cm⁻¹ peak intensities, is 0.94. The environment polarity parameter, the ratio of the 2928-/2842cm⁻¹ peak intensities, has the value of 1.08. The two parameters can be used to estimate the disorder and polar character of hydrocarbon chains respectively.

The polarized Raman spectra of sample c (shown in Fig.4c) are composed of parallel components (2855-, 2870-, 2908-, 2924-, 2934-and 2956cm⁻¹) and perpendicular bands (2852-, 2868-, 2898-, 2925-, 2952cm⁻¹). The 2855cm⁻¹ peak is the highest one in the parallel component, and the 2898 cm⁻¹, the highest in the



FIG.4 C-H stretching Raman spectra of two samples (a and c). the right curves, the perpendicular components; the left curves, the parallel components. The I and II, the symmetric and asymmetric stretching vibrations of the CH₂ groups; the III and IV, the CH₃ groups' symmetric and asymmetric vibrations.

perpendicular component. The 2855- and 2870 cm⁻¹ lines are assigned to the symmetric and asymmetric stretching vibration of the CH₂ groups respectively. The 2934- and 2956 cm⁻¹ peaks are assigned to the CH₃ groups' symmetric and asymmetric stretching vibrations respectively. The values of I_{2870}/I_{2855} ratio and I_{2934}/I_{2855} ratio are 0.95 and 0.92 respectively.

In the polarized Raman spectrum of solid state DDAHPS, only parallel bands appear, and the highest peak appears at 2940cm⁻¹. The symmetric and asymmetric stretching vibration of the CH₂ groups appear at 2840- and 2880 cm⁻¹ respectively. The CH₃ stretching vibration lines are overlapped by the background line of Raman spectrum. The value of I_{2880}/I_{2840} ratio is 0.86.

In the polarized Raman spectra of liquid state pentan-1-ol, 2870- and 2890 cm⁻¹ peaks are the highest peaks in the parallel and perpendicular components respectively. The symmetric and asymmetric stretching vibration of the CH₂ groups appear at 2850- and 2870cm⁻¹ respectively. The 2930- and 2952cm⁻¹ lines are the symmetric and asymmetric stretching vibration of the CH₃ groups. The value of I_{2870}/I_{2850} ratio is 1.15 and the value of I_{2930}/I_{2850} ratio , 0.84.

Comparing the spectrum of sample a with that of sample c, it can be seen that sample a (the hexagonal L.C.) has no perpendicular peaks, but sample c (the lamellar L.C.) has ; and the features of DDAHPS molecules and pentan-1-ol molecules dominate in the spectra of sample a and sample c respectively. Comparing the spectra of the two samples with those of the others, we also can see that the spectrum of sample b has the same features as that of sample a , and the spectra of the samples with lamellar texture have the same features as those of sample c. The reason for the emergence of the spectra with different characteristics for sample a and c is that the hexagonal phase structure is two-dimensional structure, and the lamellar phase , one-dimensional structure. It must be pointed out that the results have no correlation with the contents of DDAHPS and pentan-1-ol.

Concerning the value of the order/disorder parameters, the four samples (list above) are in order: liquid state pentan-1-ol, (1.15), > the liquid crystalline , (0.95 for the sample c , 0.94 for the sample a), > solid state DDAHPS, (0.86) . Because of the increasing mobility of methylene groups, more gauche rotational isomers are present ^[11], and the asymmetric peak of the CH₂ groups becomes bigger. For the other samples selected form the L.C. phase region, their order/disorder parameters have values ranging from 0.92 to 1.08, and all values are in the range of 0.86 and 1.15 .

The value of the environment polarity parameters increases greatly from liquid state pentan-1-ol (0.84) to the liquid crystalline phase (1.08 for sample a , 0.92 for sample c). The reason is that the water molecules penetrate into the methylene layer of hydrocarbon chains. For the other samples, selected from the L.C. phase region, their environment polarity parameters have values in the range of [0.87, 1.00], and all the values are bigger than that of pentan-1-ol.

CONCLUSION

Although there are hydrocarbon chains in both DDAHPS and pentan-1-ol molecules, we tentatively used the Raman spectroscopy method to investigate the C-H stretching vibration of the lyotropic liquid crystals in the ternary system of

DDAHPS/C₅H₁₁OH/D₂O, and compared the results with those obtained using simple methods, the polarizing optical microscopy and the ²H NMR spectroscopy. The Raman spectra of the lamellar have the same characteristics as those of alcohol, and the Raman spectra of the hexagonal are almost the same as that of DDAHPS. The order/disorder parameters of the samples selected from the L.C. phase region are larger than that of DDAHPS, and smaller than that of 1-pentanol. The environment polarity parameters are larger than that of 1-pentanol.

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