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Studies on the Phase Behavior of Lyotropic Liquid Crystal in DAD/C_4OH/n-C_8H_{18}/D_2O System

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Abstract: The lytropic liquid crystals in dodecanic acid diethanolamine (DAD) /n-butanol (C_4OH) /octane (n-C_8H_{18}) /deuteron (D_2O) system were studied to determine the phase regions and were investigated by ^2H-NMR spectroscopy,optical polarizing microscope and small-angle X-ray diffraction (SAXD) methods.The results indicate that the lamellar,hexagonal and cubic liquid crystals all exist in the above system.Keeping the weight ratio of DAD and C_4OH constant,the microphase structure,^2H quadruple splitting and the interlayer spacing are all changed with the addition of deuteron.

Materials and Methods

The purity of deuteron is 99.9%,the others are analytical pure reagents.Sample preparation and ^2H-NMR measurements have been reported by several authors[1-3] .

Small-angle X-ray diffraction and the optical polarizing microscopy methods have been reported previously[4,5]. All the experiments are thermostated at 40℃.

Results and Discussion

The mixture of dodecanic acid and diethanolamine was used as amphiphilic substance. The isothermal (obtained at 40℃)phase diagram for the pesudoternary system DAD/C_4OH/n-C_8H_{18}/D_2O is presented in Figure1. It contains one isotropic solution phase region(I), one multiphase region(II)and a lytropic liguid crystal region(III). The boundaries of phase regions were drawn based on no macroscopic phase separation over a period of time and optical

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inspection.

The compositions of the specimens chosen from the liquid crystal region in the systems of DAD/C_4OH/n-C_8H_{18}/D_2O are shown in table 1. In all the samples,the weight ratio of DAD and C_4OH equals 4.00.To investigate the phase behavior and microphase structure of these samples,the ^2H-NMR spectrocopy and optical polarizing microscopy are employed by analyzing ^2H-NMR spectrum[1] and liquid crystal textures[6].

From Fig.2 and Fig.3, we can see that the second specimen exhibits a double of broad peaks in ^2H-NMR spectrum and mosaic texture under optical microscope,which are typical for the lamellar liquid crystal. The third specimen shows two doublets(in Fig.2) and a crisscross flower texture (in Fig.3),which indicate the presence of an anistropic phase,the lamellar liquid crystal phase.The fourth sample displays higher viscosity than the second sample and the third

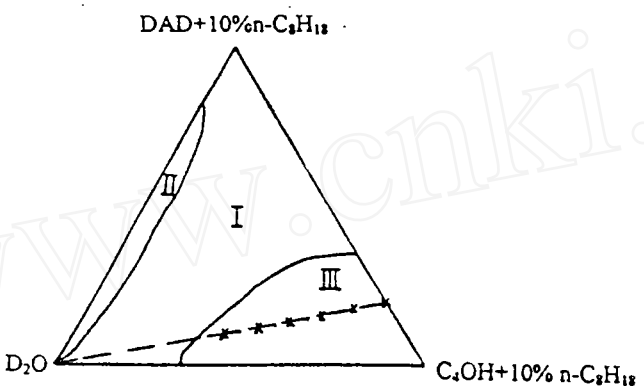

Fig.1 The phase diagram of DAD/C_4OH/n-C_8H_{18}/D_2O . Ⅰ,isotropic solution region; Ⅱ, multiphase region;Ⅲ,liquid crystal region.

sample, two doubles of ^2H equal quadruple splitting intense peaks and a singlet and a crisscross flower texture.These indicate the presence of the mixture of two liquid crystal phases: the lamellar and the cubic. A singlet and two doubles of equally intense peaks in Fig.2 and a fanlike angular texture in Fig.3 show that the fifth sample is the mixture of some isotropic solution,a hexagonal and a cubic liquid crystal phases.A double of broad peaks and a striated nongeometric texture of the sixth specimen show that it is a hexagonal liquid crystal phase.

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Table.1 Compositions and experimental results for some selected samples.

specimen	composition (g)				weight fraction of surfactant	weight fraction of deuteron	Bragg spacing	spacing thickness of deuteron	$\triangle^2H$
	DAD	C_4OH	n-C_8H_{18}	D_2O	Φ_{Saa}(%)	Φ_w(%)	d_l(A)	d_w(A)	H_Z
1	0.3600	0.0900	0.0500	0.0000	72.0	0.0	28.477	0.00	/
2	0.3241	0.0810	0.0450	0.0500	64.8	10.0	29.231	0.754	2200
3	0.2881	0.0720	0.0400	0.1000	57.6	20.0	30.868	2.389	1900
4	0.2521	0.0630	0.0350	0.1500	50.4	30.0	32.218	3.739	1300
5	0.2161	0.0540	0.0300	0.2000	43.2	40.0	32.939	4.460	620
6	0.1801	0.0450	0.0250	0.2500	36.0	50.0	33.693	5.214	570

The magnitude of deuteron quadruple splitting contains information on the hydration of the amphiphlic aggregates in terms of the fraction of water molecules appreciably orientated. The values of the ^2H quadruple splitting(shown in table 1),$\triangle(^2H)$,for the samples of 2,3,4 range from 1300to 2200 H_Z These values for samples of 5,6,are almost constant(about 600 H_Z),For the liquid crystals, the values of $\triangle(^2H)$ decrease with constant weight ratio between the surfactant and alcohol and constant weight of oil when the water content is increased, but a plot of $\triangle(^2H)$ vs.weight ratio of water to the other is not linear.This may be due to that the splitting does not follow the simple "two-site" model with constant hydration proposed for the water

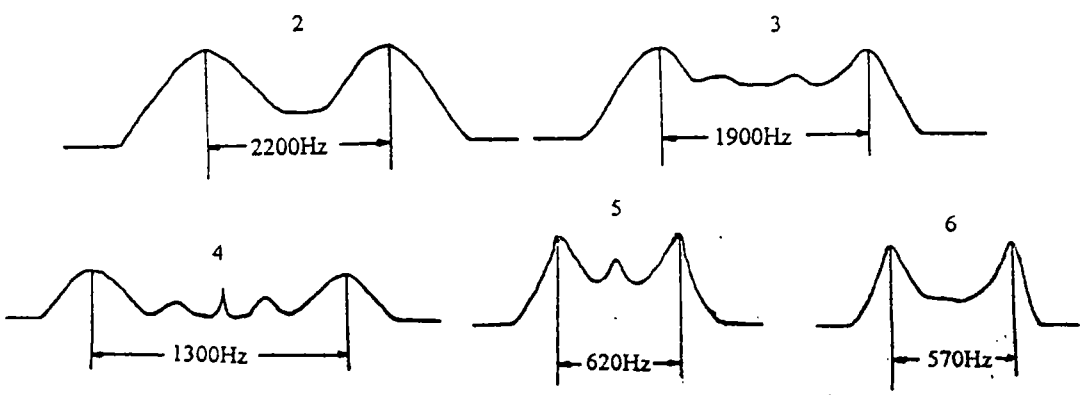

Fig.2 ^2H-NMR spectra for the four samples(2,3,4,5,6).

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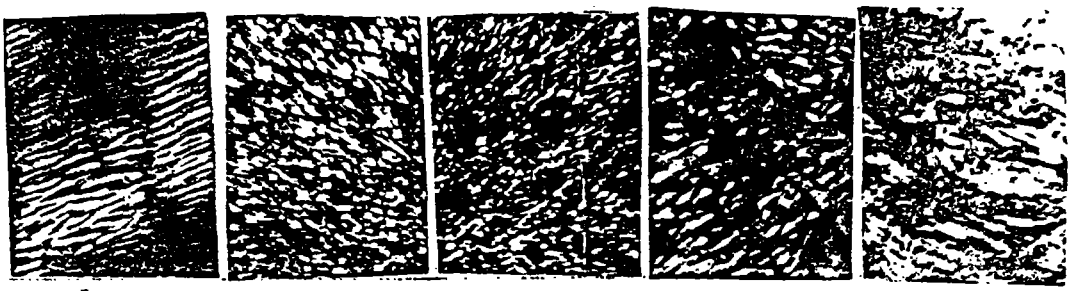

2 3 4 5 6

Fig.3 Optical microscope textures for various samples(2,3,4,5,6).

binding to amphiphile aggregates[8] ,or,it may be due to the existence of all the three kinds of liquid crystals.

The SAXD results in table 1 also show that the Bragg spacing d_1 of these samples increase as the weight fraction of deuteron is increasing. According to reference[4.7],spacing thickness of deuteron (d_w) is acquired by following equation:$d_w = d_1 - d_0$.

where d_0 is the Bragg spacing when the weight fraction of deuteron equals zero. The d_w values of these samples are also presented in table 1.A plot of d_w values vs. weight ratio of water to the other is not linear,this confirms the results of ^{2}H-NMR.

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