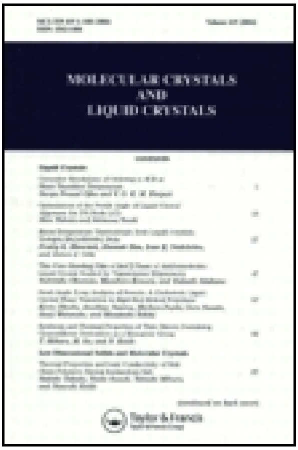

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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To cite this article: Tom Haven, Keith Radley & Alfred Saupe (1981): Refractive Index and Deuterium Resonance Measurements on Nematic Decylammoniumchloride, Ammoniumchloride, Water Mixtures, Molecular Crystals and Liquid Crystals, 75:1, 87-94

To link to this article: http://dx.doi.org/10.1080/00268948108073605

Mol. Cryst. Liq. Cryst., 1981, Vol. 75, pp. 87–94
0026-8941/81/7504-0087 $06.50/0

Printed in the United States of America

Refractive Index and Deuterium Resonance Measurements on Nematic Decylammoniumchloride, Ammoniumchloride, Water Mixtures

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(*Received January 28, 1981*)

Mixtures of decylammoniumchloride and NH_4Cl in a molar ratio of 2.76:1 with H_2O or D_2O were studied. The water concentration varied between 89 and 91 mole %. Refractive index and deuteron resonance measurements were made as a function of temperature covering the nematic range. The transition temperatures for samples with D_2O were about 8°C higher than those with H_2O at the same molar composition. The birefringence and the deuteron resonance splittings of D_2O are a relative measure for the orientational order in the nematic phase. The two methods give results which are in good agreement. On a reduced scale the temperature dependence of the order follows for all studied mixtures approximately the same curve. The curve is similar to that found with typical thermotropic nematics.

1 INTRODUCTION

Mixtures of decylammoniumchloride (DACl), NH_4Cl and water are known to form a nematic liquid crystalline phase. Such mixtures have been used in NMR studies,[1-3] curvature elastic and viscous properties have been studied on thin films[4,5] and electric conductivity measurements have been reported.[6]

It is well established that the nematic phase in this system is formed by amphiphilic aggregates that have a bilayer structure[3] as is directly evident from the apparently continuous transition to the lamellar smectic phase (neat soap) upon cooling. We denote this nematic phase accordingly as N_L.[7] Its diamagnetic anisotropy is negative and it may be classified as type II when we follow the notations of Radley and Reeves[8] who classify phases by the sign of their diamagnetic anisotropy. In the nematic phase the bilayer micelles show some degree of parallel orientation which is responsible for the macroscopic aniso-

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tropy of the phase. Birefringence measurements are useful to obtain some information on the degree of alignment of the micelles.

We report in this paper refractive index measurements as a function of temperature for samples of various water concentration and deuteron resonance measurements on similar mixtures with deuterated water. The data are analyzed in terms of the degree of parallel orientation of DA. The two methods give consistent results.

2 EXPERIMENTAL PROCEDURES

DACl was prepared and purified as previously described.[3] All mixtures that were studied contain the same weight ratio 10:1 of DACl to NH_4Cl. It corresponds to molar ratio of 2.76:1. The amount of water varied between 50 and 56 wt %, which corresponds to 89 and 91 mole %. The sample for the deuteron resonance studies were made with D_2O while normal water was used in the refractive index measurements.

The deuteron resonance spectra were observed with a Varian XL-100 spectrometer.† Measurements of the indices of refraction were done using an Abbe refractometer. The values reported correspond to a wavelength of 589.3 mμ. Some points connected with these measurements need a detailed discussion.

The sample is introduced between the two prisms of the refractometer and forms a film about 0.1 mm thick. The sides of the prisms are not sealed and water can evaporate during the measurements. The amount that evaporated during our measurement series was, however, relatively small and did not affect the results significantly. Before the measurements the prisms were cleaned with a surfactant (RBS-11, Norell Chemical Company). The cleaned glass surfaces produce a uniformly aligned homeotropic nematic film i.e. the optical axis of the nematic film is vertical. A complete alignment of the film by surface action may take hours but already after a few minutes two sharp boundaries of total reflection can be observed in the refractometer, since the alignment of a relatively thin boundary region is sufficient for this experiment.

The two boundaries of total reflection correspond to the two principle refractive indices of the nematic film. The ordinary ray is polarized parallel to the plane of the film while, at the angle of total reflection, the extraordinary is polarized perpendicular to the film. It is, therefore, possible to assign the boundaries to ordinary and extraordinary rays using a polarization filter.

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†Funds for the equipment were obtained partly from the National Science Foundation under Grant No. GP-10481.

3 RESULTS AND DISCUSSION

The transition temperatures as a function of water concentration are given in Figure 1. They have been determined by microscopic observations. The transition to the isotropic phase is first order and there exists a two phase range of about 2° C. The temperatures given in the figure correspond to the lower temperature limit of this two phase range. The N_L-neat soap transition appears to be continuous and is relatively difficult to recognize. The nematic range shifts to higher temperatures nearly linear with decreasing water concentration but the width of the range remains constant. The transition temperatures of the mixture containing D_2O are about 8° C higher than mixtures of the same molar composition but containing H_2O. The results of the refractive index measurements and of the DMR measurements are summarized in Tables I and II.

We use a somewhat modified Lorentz-Lorenz formula and obtain for the extraordinary and ordinary refractive index n_1 and n_2.

$$\frac{n_1^2 - 1}{n_1^2 + 2} = \frac{4\pi}{3} N(X_{H_2O}\alpha_0(H_2O) + X_{NH_4^+}\,\alpha_0(NH_4^+) + X_{Cl^-}\alpha_0(Cl^-) + X_{DA^+}\left[\alpha_0(DA^+) + \frac{2}{3}\,\alpha_a(DA^+)S\right] \qquad (1)$$

$$\frac{n_2^2 - 1}{n_2^2 + 2} = \frac{4\pi}{3} N(X_{H_2O}\alpha_0(H_2O) + X_{NH_4^+}\,\alpha_0(NH_4^+) + X_{Cl^-}\alpha_0(Cl^-) + X_{DA^+}\left[\alpha_0(DA^+) - \frac{1}{3}\,\alpha_a(DA^+)S\right] \qquad (2)$$

Here N is the number of molecules per unit volume and X_{H_2O} etc. denote the mole fraction of the indicated compound or ion, $\alpha_0(H_2O)$ etc. their mean polarizabilities. Furthermore, we assume that the birefringence is in its significant part due to the alignment of DA^+ only and that the polarizability tensor of DA^+ can be approximated by a tensor of rotational symmetry with the principle polarizability α_1 parallel to the long axis and α_2 perpendicular to it. $\alpha_a(DA^+) = \alpha_1 - \alpha_2$ and $S = 1/2\ (3_{\cos^2\theta} - 1)$ is the degree of order of DA^+, where θ is the angle between the long molecular axis and the optical axis of the nematic liquid crystal. $_{\cos^2\theta}$ is the average over the molecular motion.

Subtracting Eq. (2) from (1) and using $n_a = n_1 - n_2 \ll 1$ we obtain

$$n_a = \frac{2\pi}{9}\frac{(n_2^2 + 2)^2}{n_2} N\alpha_a(DA^+)\ X_{DA^+}S. \qquad (3)$$

TABLE I

Refractive indices, dashed lines indicate nematic-neat soap and nematic-isotropic transitions.

	H_2O Concentration (mole %)					
	91.1		90.5		89.7	
Temp. (°C)	n_1	n_2	n_1	n_2	n_1	n_2
22	1.4065	1.4025	1.4098	1.4054		
24	1.4060	1.4020	1.4095	1.4051		
26	1.4054	1.4016	1.4089	1.4046		
28	1.4050	1.4012	1.4085	1.4042		
30	1.4044	1.4008	1.4080	1.4038		
32	1.4039	1.4005	1.4076	1.4034	1.4114	1.4065
34	1.4034	1.4009	1.4071	1.4030	1.4110	1.4061
36	1.4028	1.3996	1.4065	1.4025	1.4103	1.4055
38	1.4024	1.3994	1.4061	1.4021	1.4098	1.4051
40	1.4018	1.3990	1.4056	1.4017	1.4092	1.4046
42	1.4013	1.3987	1.4050	1.4014	1.4088	1.4041
44	1.4008	1.3985	1.4045	1.4010	1.4083	1.4038
46		1.3982	1.4040	1.4006	1.4078	1.4034
48		1.3979	1.4036	1.4002	1.4074	1.4030
50			1.4028	1.3996	1.4067	1.4024
52			1.4023	1.3993	1.4063	1.4020
54			1.4017	1.3989	1.4057	1.4015
56			1.4012	1.3985	1.4050	1.4011
58				1.3982	1.4045	1.4008
60				1.3980	1.4038	1.4003
62				1.3978	1.4032	1.3999
64				1.3975	1.4025	1.3995
66					1.4019	1.3992
68						1.3987
70						1.3985
72						1.3983
74						1.3980

The temperature and concentration dependence of N and n_2 is relatively small and we have, therefore, in good approximation $n_a = cX_{DA^+}\alpha_a(DA^+)S$ where c is a temperature and concentration independent constant.

We have neglected in Eqs. (1) to (3) that DA^+ assumes a number of different conformations to which different polarizabilities and order parameters should be assigned. Our experiments allow us to determine only one order parameter. We use, therefore, simply an effective polarizability with one effective order parameter. The approximation will be useful when the temperature dependence of the distribution over different conformations is small.

TABLE II

Deuterium resonance splittings of D_2O in Hz, dashed lines indicate nematic-neat soap transition.

	D_2O Concentration (mole %)			
Temp. (°C)	90.9	90.6	90.2	89.9

36.0	329	361		
38.0	324	361		

40.4	320	354	384	
42.8	313	347	382	

45.2	301	340	378	407
47.6	285	329	368	407

50.0	260	315	359	400
52.4	232	299	350	390
54.8	191	276	333	378
57.2		248	313	366
59.6		212	290	347
62.0			262	329
64.0			225	301
66.0				274
68.0				241

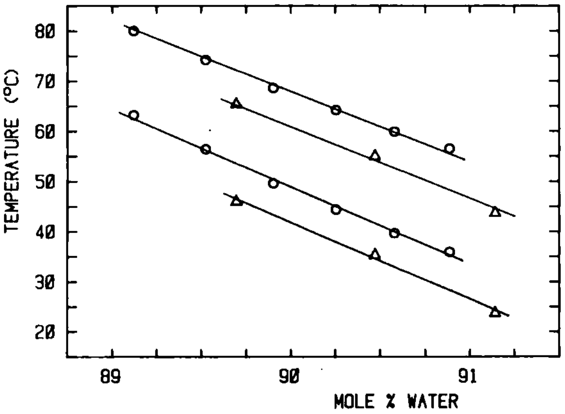

FIGURE 1 Temperatures for nematic-isotropic (higher values) and neat soap nematic transitions. Circles D_2O, triangles H_2O.

Figure 2 shows the temperature dependence of n_a. When we compare the n_a values for different concentrations at corresponding temperatures, i.e. at equal values of $T_{red} = (T - T_{NI})/T_{NI}$ where T_{NI} is the N_L – isotropic transition temperature, we see that within error limits n_a/X_{DA^+} is independent of the water concentration. It follows that the products $\alpha_a(DA^+)\ S$ are approximately equal and, since we expect that $\alpha_a(DA^+)$ remains constant, that the S values at corresponding temperatures are approximately equal.

The deuteron resonance splitting is proportional to the degree of order of the O-D axis. The water molecules are slightly oriented by association with the micelles. The exchange between associated and non-associated D_2O is fast so that only one sharp doublet is observed. We denote by Y_{ass} the mole fraction of associated D_2O and with S_{D_2O} the degree of order of the O-D bond axis. The splitting is then given by

$$\nu = \frac{Y_{ass}}{X_{D_2O}} \frac{3}{2} Q\, S_{OD} \tag{4}$$

where Q is the quadrupole coupling constant.[9] With $Y_{ass} = c_1 X_{DA^+}$ and $S_{OD} = c_2 S$ we obtain

$$\nu = \frac{X_{DA^+}}{X_{D_2O}} \frac{3}{2} Q\, c_1 c_2 S. \tag{5}$$

The factor c_1 is equal to the number of water molecules associated with one surfactant molecule. If the product $c_1 c_2$ has negligible concentration and temperature dependence than $\nu X_{D_2O}/X_{DA^+}$ should be the same for all samples at corresponding temperatures. The experimental results do not confirm this.

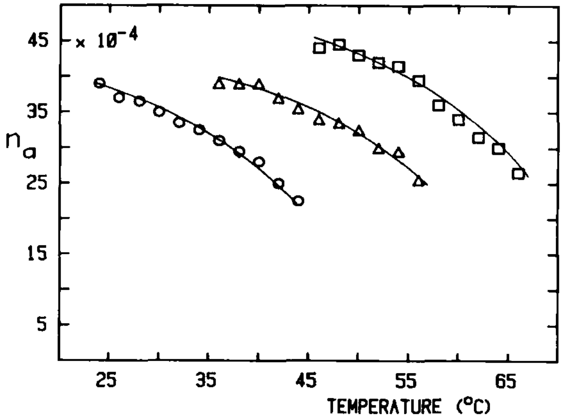

FIGURE 2 Birefringence in the nematic range for various H_2O concentrations. Circles 91.1, triangles 90.5, squares 89.7 mole %.

For instance from the splitting at the N_L-neat soap transition we obtain for the samples with 90.9, 90.6, 90.2 and 89.9 mole % D_2O $\nu X_{D_2O}/X_{DA^+} = 4.46 \cdot 10_3$, $4.63 \cdot 10^3$, $4.76 \cdot 10^3$ and $4.85 \cdot 10^3$ respectively. The result indicates that the product c_1c_2 in Eq. (4) is not independent of both the concentration and the temperature.

In Figure 3 the ratios $\nu(T)/\nu(T_{NS})$ are plotted for various water concentrations. The curves have similar shapes and it can be seen that the experimental points of all mixtures fit to the same curve within error limits when plotted against a reduced temperature scale. Furthermore, as can be seen from the birefringence curves in Figure 2 a plot of $n_a(T)/n(T_{NS})$ on a reduced temperature scale also gives the same curve. We can conclude, therefore, that c_1c_2 is fairly independent of the temperature but as we saw above, it seem to be affected by concentration changes. There may be several reasons for a concentration dependence. The thickness of the layer of associated water may be comparable to the distance between the micelles so that the layers of neighboring micelles interfere. In that case a concentration dependence will exist since the distance between micelles changes with the water concentration. A second reason may be the effect of the ion concentration on the degree of association and D_2O orientation. Experiments on mixtures of different salt concentration may help to decide this question.

In summary, we found that the deuteron resonance splitting of D_2O, as well as the birefringence, is proportional to the degree of order of the surfactant molecules with a proportionality factor that is practically independent of the temperature. Compared on a reduced temperature scale, all mixtures studied give approximately the same curve $S(T)$ provided that S-values at the N_L-neat soap transition are the same for all mixtures. It is likely that the internal mo-

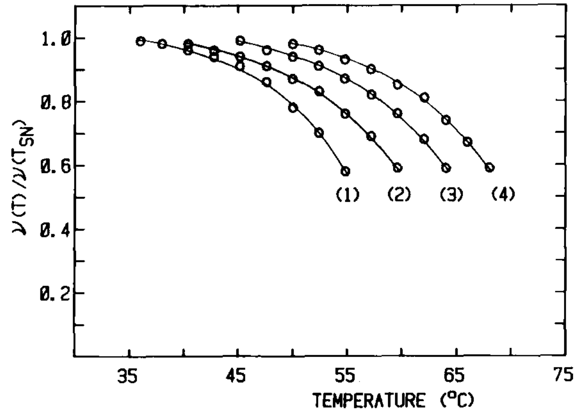

FIGURE 3 Deuterium resonance splittings of D_2O for various D_2O concentrations: (1) 90.9, (2) 90.6, (3) 90.2 and (4) 89.9 mole %.

lecular structure of the micelles shows only little temperature dependence. The temperature dependence of S is accordingly due to the temperature dependence of the parallel orientation of the micelles. It should be kept in mind that the micelles are flexible aggregates and that an increase in parallel orientation will also be connected with a reduction of the mean curvature. It should also be mentioned here that typical thermotropic nematics give very similar $S(T)$ curves.

Acknowledgments

This research was supported in part by grants from the National Science Foundation, DMR-76-21363 and DMR-79-07789.

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