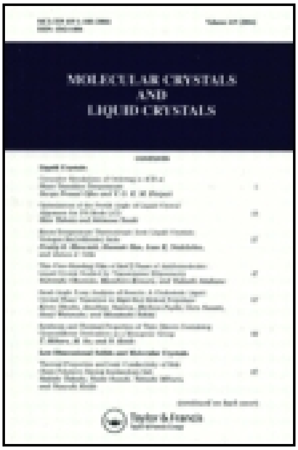

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L J. Yu [a] & A. Saupe [a]
[a] Liquid Crystal Institute, Kent State University, Kent, Ohio, 44242

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Deuteron Resonance of D_2O of Nematic Disodium Cromoglycate-Water Systems

L. J. YU and A. SAUPE

Liquid Crystal Institute, Kent State University, Kent Ohio 44242

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Disodium cromoglycate (DSCG) in mixtures with water forms a nematic state of high water concentration with cylindrical aggregates. Samples prepared with D_2O were studied by deuteron magnetic resonance. The splitting of the D_2O signal in the nematic range is reported for mixtures of D_2O and DSCG varying in the molar ratio D_2O/DSCG from 120 to 260 and for mixtures containing NaCl with molar ratios D_2O/DSCG of 167 and 207 and NaCl/DSCG of 0.5 and 2. The splitting in the nematic range increases with decreasing temperature. At corresponding temperatures and for a given NaCl concentration the splitting is approximately inversely proportional to the D_2O concentration. The addition of NaCl increases the temperature stability of the nematic range and reduces the temperature dependence of the splitting. It indicates that the addition of salt leads to stiffer aggregates.

I INTRODUCTION

The liquid crystalline phases of disodium cromoglycate (DSCG)-water have been studied by Hartshorne and Woodard[1] using microscopy and x-ray diffraction. According to the microscopic textures[1] the system forms a nematic phase in a water concentration range of about 84 to 94 wt% and over temperature ranges from below −20°C to an upper limit that varies with the concentration from about 0° at the high water concentration limit to about 40°C at the low concentration limit. At water concentrations between 80 and 40% a smectic liquid crystal is formed that resembles middle soap.

The x-ray studies indicate that DSCG forms cylindrical aggregates. In the smectic phase the aggregates are packed in a hexagonal array.[1] In the nematic phase the cylinders retain some degree of parallel orientation but the regular hexagonal packing is lost.[1] The existence of nematic textures with splay deformation also indicates that the aggregates break up into cylinders of finite lengths. The detailed structure of the aggregates is still under discussion.[1-3] According to a proposal by Lydon[2] the aggregates consist of hollow square-shaped cylinders with a molecular arrangement similar to that in the solid crystalline state as found by x-ray studies.[4] The actual structure in the liquid crystalline state may be different but there is good indication that the aggregates incorporate a significant amount of water.[3]

The associated water is partially oriented. In samples prepared with D_2O the orientation leads to a splitting of the deuteron resonance signal. The signals were found to be sharp which indicates that there is a relatively rapid exchange between associated and non-associated water. The splitting is a measure for the average orientation of the D—O bond axis and gives some information on the degree of association and order in the liquid crystalline state.

We report in this paper deuteron resonance studies of nematic DSCG/D_2O mixtures as a function of temperature and water concentration. Some measurements were also made on solutions containing NaCl.

II EXPERIMENTAL

DSCG obtained from the Fisons Corporation was used as received. Appropriate amounts of DSCG and D_2O were weighed into a test tube and sealed immediately. The components were mixed by centrifuging through a constricted neck in the middle of the tube. The samples were kept in the nematic phase for several days before transferring to the NMR tube for the measurements. The measurements were made with a Varian XL-100 spectrometer.† The sample compositions are given in Table I.

Difficulties arose with the two samples of the highest salt concentrations, molar ratio of NaCl to DSCG about 2:1. Small amounts of a white solid precipited. Only the solutions were withdrawn and the composition of these samples are therefore somewhat uncertain.

III RESULTS

The measurements on the DSCG/D_2O mixtures are represented in Figure 1. All but one set of data were taken on heating with freshly mixed samples. Only for sample 3 are data also given on cooling. The nematic phase aligns perpendicular to the magnetic field. Its diamagnetic anisotropy is negative as expected on the basis of the structure of the aggregates.[1] The aromatic parts are

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TABLE I

Sample Compositions in Molar Ratios

Sample	D_2O/DSCG	NaCl/DSCG
1	121	0
2	141	0
3	167	0
3-1	167	0.54
3-2	167	1.9
4	187	0
5	207	0
5-1	207	0.50
5-2	207	2.0
6	233	0
7	262	0

preferably perpendicular to the cylinder axis so that the diamagnetic polarization is lowest when the magnetic field lies perpendicular to the axis.

In the nematic phase a simple doublet with sharp lines is observed. The transition to the smectic phase is difficult to recognize. There is no sudden change observable. Upon heating the splitting decreases with temperature until the two phase range is entered where nematic and isotropic phase coexist. In addition to the doublet a single line appears that is due to the isotropic solution. In the two phase region the doublet splitting increases with increasing temperature. It follows a common curve since the compositions of the two phases in equilibrium depends only on the temperature. For a given sample the intensity of the doublet decreases, of course, rapidly with increasing temperature because the nematic fraction diminishes.

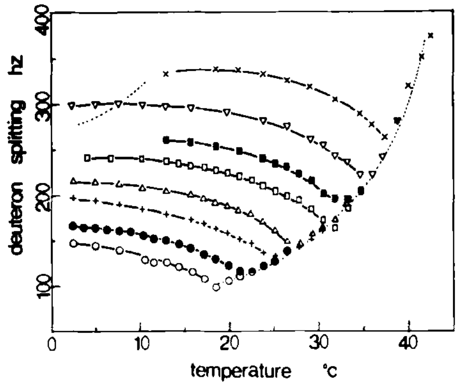

FIGURE 1 The deuteron quadrupole splitting of D_2O in different mixtures as a function of temperature. Sample 1, x: 2, ∇; 3, □; 3, ■ (on cooling); 4, Δ; 5, +; 6, ●; and 7, O. The dashed line at the upper left corner indicates the transition to the hexagonal smectic phase.

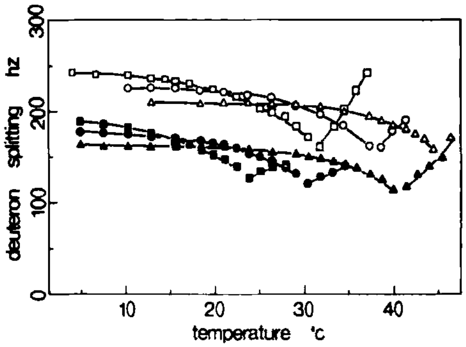

FIGURE 2 The deuteron quadrupole splitting of D_2O as a function of temperature for samples containing various amounts of NaCl. Sample 3, □; 3-1, ○; 3-2, △; 5, ■; 5-1, ●; and 5-2, ▲.

Due to gravity a separation takes place in the two phase range. The anisotropic fraction has a higher density and begins to aggregate in the lower part of the sample. The curves are therefore not reproducible on cooling once the two phase range has been entered. An example are the two curves for sample 3 in Figure 1. The data obtained on cooling indicate a significantly higher DSCG concentration in the part of the sample volume probed by the spectrometer.

In Figure 2 measurements are represented for two sets of samples containing various amounts of NaCl. The molar ratios of D_2O to DSCG are 167 for the first set and 207 for the second set. The approximate molar ratios of NaCl to DSCG are 0, 0.5 and 2. The qualitative features of the curves are the same for both sets. Remarkable is the decrease of the temperature dependence with increasing salt concentration. The beginning of the nematic isotropic two phase ranges is again clearly recognizable by the sudden change in slope.

IV DISCUSSION AND CONCLUSION

The concentration dependence of the deuteron splitting (Figure 1) is mainly due to the change in ratio of free to associated water. Let n_a be the number of D_2O molecules associated with one DSCG molecule, θ the angle between the OD axis and the symmetry axis of the liquid crystal, and $S_{OD} = < 3\cos^2\theta - 1 >_{AV}/2$ the degree of order of the OD-bond axes where the average is taken over the associated (and integrated) water molecules and, because of exchange, the OD-bond of DSCG. Taking into account that the nematic phase aligns perpendicular to the field we can write for the splitting

$$(x + \tfrac{1}{2})\nu = \tfrac{3}{4}(n_a + \tfrac{1}{2})\, Q\, S_{OD}. \tag{1}$$

Here x is the molar ratio of D_2O to DSCG and Q an average quadrupole coupling constant for the OD axis. Q is essentially a temperature independ-

TABLE II

Deuteron resonance splitting at $T_R = 0.96$ as a function of the molar ratio x of D_2O to DSCG.

x	ν[Hz]	$\nu(x + \frac{1}{2})$ [kHz]
121.2	330	40.0
140.5	284	39.9
166.7	230	38.3
187.0	201	37.6
206.6	180	37.2
232.8	157	37.5
262.2	141	37.0

ent bond property. We assume that n_a in the considered ranges is independent of temperature and concentration. We assume further that S_{OD} is in first approximation only dependent on the reduced temperature $T_R = T/T_c$ where T_c is the transition temperature to the two phase range. Under these assumptions the product $(x + \frac{1}{2})\nu$ is independent of the concentration at a given reduced temperature. Table II demonstrates that this is approximately true but there is some deviation. It could be due to a temperature and concentration dependence of n_a or due to the fact that S_{OD} depends not only on T_R but also on the concentration.

It is apparent from Figure 2 that the addition of NaCl increases the temperature stability of the nematic range and there is also a reduction in the temperature dependence of the splitting. An increase of the temperature stability by the addition of salt is also commonly observed for nematic phases formed in aqueous solutions of ionic surfactants. It can be explained by a reduction of the repulsive electric interaction between the surfactant ions which may lead to stiffer and longer aggregates. A similar explanation may be valid also for the DSCG water system since the DSCG molecules will be ionized to a considerable extent in the nematic mixture where the water concentration is relatively high. A second effect of the salt is the reduction of the range of the interactions between the cylindrical aggregate. The interaction is dominated by electrostatic repulsion and its range is shortened because of enhanced screening. The total effect of the addition of salt is a change towards a system of rigid hard rods as is indeed experimentally indicated by the reduction of the temperature dependence of the order. For ideal hard rod systems S depends only on the volume but is independent of the temperature.

Finally, it may be noticed that the magnitude of the D_2O splitting in typical nematic surfactant solutions is of the same order as for the DSCG-water system. It is surprising at first sight since the molar ratio of D_2O to DSCG is about 10 times higher than a typical D_2O to surfactant ratio. Obviously the association number is much larger for DSCG molecules. It agrees well with the estimation of Hartshorne and Woodard[1] that about 10 to 20 water molecules per DSCG molecule are integrated into the aggregates. The amount of integrated water will depend on the addition of NaCl. We can expect that the amount decreases by the addition since the higher Na^+ concentration reduces the ionization of DSCG. In agreement with this consideration there is in fact some decrease of the splitting at corrsponding temperatures. Our measurements do not give direct support to the model proposed by Lydon[2] since we do not observe two separate D_2O doublets, one corresponding to included and second to the interstitial water. It should be kept in mind, however, that a moderate exchange rate between included and interstitial water is sufficient to average out the difference so that only one doublet appears in the nmr spectrum.

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