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Sodium-23 NMR in the Lyomesophases of Disodiumcromoglycate

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^{23}Na NMR spectra are reported for the various lyomesophases of disodiumcromoglycate (DSCG). The spectra were studied as function of DSCG concentration, temperature, and added NaCl as well as some other electrolytes. In the isotropic liquid phase there is a steep increase in the ^{23}Na MNR linewidth upon cooling, in a range of 10 to 15 ° C above the clearing point. This is interpreted in terms of the formation of DSCG micelles before the onset of the mesomorphic phases. Within all mesophases distinct splittings due to quadrupolar interaction were observed. These splittings were found to decrease upon addition of NaCl and appear to change sign above a certain salt concentration. As function of DSCG concentration, the splitting first increases and then decreases. The results are qualitatively interpreted in terms of two distinct solvation sites in which the sodium ions experience quadrupole interaction of opposite signs. Possible assignment for the two sites are discussed.

INTRODUCTION

The lyotropic liquid crystalline mesophases formed in aqueous solutions of disodiumcromoglycate (DSCG) were studied by a variety of physical methods including X-ray diffractions, optical microscopy, calorimetry and more recently also by NMR.[1-11] The phase diagram of the water-DSCG system based on NMR measurements[9] is shown in Figure 1. Depending on the DSCG concentration and the temperature, the following three mesophases were identified:

(i) A nematic N phase consisting of columns of stacked molecules distributed randomly in the aqueous solutions but retaining a degree of orientational order. It was suggested[6,7] that the columns consist of

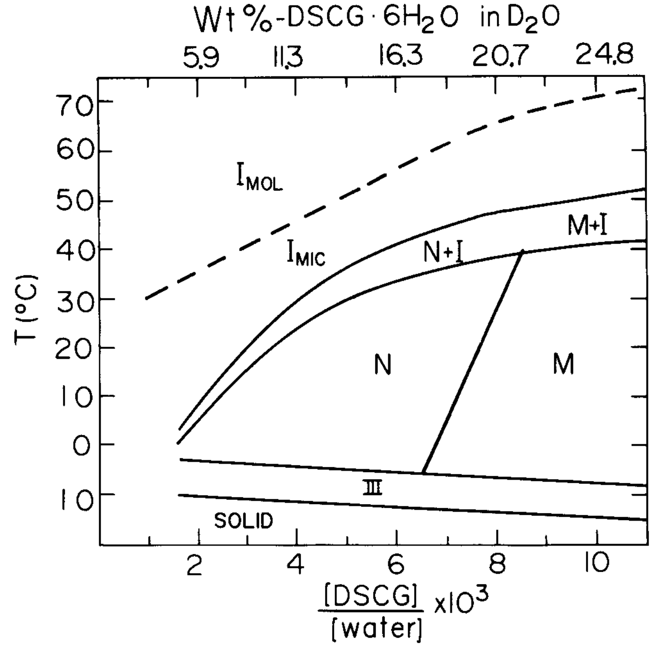


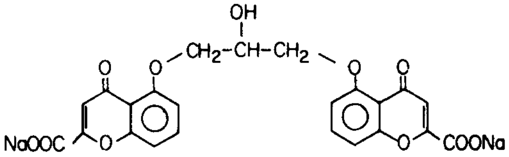
FIGURE 1 Phase diagram of the DSCG-water system taken from ref. 9. The full lines are phase boundaries determined by deuterium NMR. The dashed line is a suggested boundary line between isotropic-micellar and isotropic-molecular phases as determined from ^{23}Na NMR (see text).

square hollow rods in which the stacking units are made of four co-planar DSCG molecules held together by salt bridges via sodium ions. The anisotropic magnetic susceptibility, $\Delta\chi$, of this phase is negative.[8,9] This is consistant with the assumption that the DSCG molecules are oriented preferentially with their aromatic planes perpendicular to the rod axis. This phase is quite fluid and in polarizing microscopy it exhibits curving dark lines, characteristic of nematic phases.[3] It exists in the concentration range 3 to 16 wt% DSCG between about $-4\,°C$ and, depending on the concentration, up to between 5 and 35 °C.

(ii) A smectic M mesophase resembling the soap middle phase in which the columns of stacked molecules form an hexagonal array separated by a water continuum. Like the N phase this mesophase is of type II ($\Delta\chi < 0$), and in a polarizing microscope it shows a herringbone texture frequently observed in soap middle phases.[3] It is more viscous than the N phase and exists above about 16 wt% DSCG in the temperature range $-4\,°C$ to ~ 40 °C.

(iii) Below about −4 °C another smectic phase is formed which is labeled III.[9] As yet no structural studies on this phase have been reported but it appears to be more highly ordered than the N or M phases described above.

DSCG is an unusual amphiphilic compound. Unlike the conventional amphiphiles, characterized by a well defined hydrophilic end and a hydrophobic part, the molecules of DSCG consist of two unsaturated hydrocarbon units, bonded via a short chain and possessing at various sites several hydrophilic groups including —C=O, —COH and —COONa. The sodium and carboxylate groups are most probably responsible for the stability of the columnar structure of the DSCG mesophases by forming salt bonds between neighboring molecules and perhaps also between columns. Indeed, it was found that addition of NaCl increases the temperature range of stability of the DSCG mesophases[8,11] and that in the presence of NaCl the N phase can be formed even at concentrations of DSCG lower than 3 wt%.



To learn more about the role played by sodium ions in stabilizing the DSCG mesophases we have studied the ^{23}Na NMR signals in the water-DSCG system and its dependence on a number of experimental parameters, including the DSCG concentration, temperature, and addition of NaCl and other electrolytes. Some preliminary results and a short discussion of the ^{23}Na spectrum in DSCG solutions were presented in a previous publication.[9]

EXPERIMENTAL

The experimental procedure was similar to that described in ref. 9. DSCG was kindly provided by Fisons Ltd as a crystalline solid. It contained some tightly bound water estimated at 6 water molecules per DSCG molecule. Solutions in D_2O were prepared in water containing 99.7 at .% deuterium. Solutions in normal water were made in doubly distilled H_2O (pH 6.8 to 7.2). Addition of electrolytes was made gravimetrically using analytical grade salts.

Unless otherwise indicated all ^{23}Na NMR measurements were made on a Bruker WH 90 spectrometer operating at 23.6 MHz. Some measurements were also performed on a Bruker CXP 300 spectrometer operating at 79.4 MHz. Ten milimeter sample tubes were used and the signals were obtained as Fourier transform of the FID signals following short rf pulses. Some ^{2}D NMR measurements were also carried out as described in ref. 9. In all experiments the sample temperature was first raised to above the clearing point and then allowed to cool within the magnetic field to the mesophase region. Once the mesophase region was reached the measurements were made both on heating and cooling. The temperature was controlled with a BST 100/700 unit and its absolute value was calibrated with a Fluke 2190 digital thermometer (estimated accuracy ±1°C). Since $\Delta\chi$ is negative for all phases a planar distribution of domains is obtained[9] with the magnetic field normal to all directors.

RESULTS

A. ^{23}Na NMR in DSCG solutions

In this section we describe the ^{23}Na NMR spectra in the various DSCG mesophases and their dependence on the temperature and concentration of the solution. In Figure 2 (left column) are shown ^{23}Na NMR spectra of a 10 wt% solution DSCG in the temperature range −12°C to about 60°C. In this solution the N → I transition falls at around 20°C and the III → N at ~ −4°C. In the isotropic region and just below the N → I transition the ^{23}Na spectrum consists of a single line. However, on further cooling the line splits into a triplet due to quadrupolar interaction as expected for a $I = \frac{3}{2}$ nucleus in an ordered phase. The quadrupole interaction parameter, ν_Q, measured as the spacing between neighboring components in the triplet, increases gradually with decreasing temperature until the N to III transition, where a sharp decrease in ν_Q occurs. At this point there is also an abrupt change in the linewidth of the triplet components. In Figure 3 the observed quadrupole splitting for this solution is plotted (see open circles) vers. temperature in the N and III phases. In drawing this plot it was assumed that the sign of ν_Q in both phases is the same and arbitrarily taken to be positive. We shall return to this point shortly. In the region close to the N → I transition the splitting is small compared to the linewidth of the triplet components and thus not observed. The exact transition temperature therefore cannot be determined from the ^{23}Na spectrum. This is best determined from the ^{2}D NMR of solutions containing D_2O, as was indeed done[9] for the construction of the phase diagram in Figure 1.

The sodium spectrum above the N → I transition temperature consists of a singlet, but its width in the isotropic region is strongly temperature dependent. The full linewidth, Δ, at half maximum height, of this signal in the isotropic phase (and just below the I to N transition temperature) is plotted vers. the temperature in Figure 4 for several DSCG concentrations ranging from 5 to over 20 wt% DSCG.

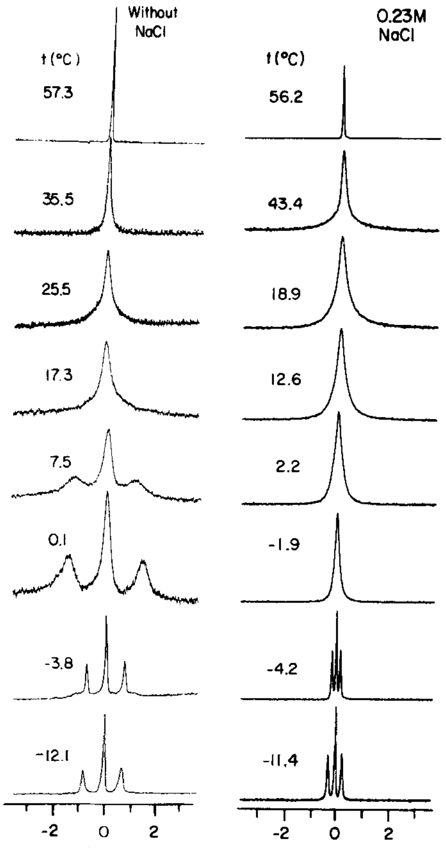


FIGURE 2 ^{23}Na NMR spectra at 23.6 MHz of a solution containing 10 wt% DSCG at the indicated temperatures. The spectra on the left correspond to solutions without added NaCl, while those on the right to solutions to which 0.23 M NaCl was added. The phase transition III → N in these solutions is about −4 °C while N → I is ~ 20 °C without NaCl, and ~ 25 °C in the 0.23 M NaCl solution.

It may be seen that in all solutions over a range of 15 to 20 °C there is a very steep decrease in Δ, dropping from 400 to 600 Hz down to about 30 Hz. We believe that this effect is due to formation of micelles in the isotropic phase. As the temperature is decreased their number and size increases causing enhanced relaxation of the sodium signal. We have indicated in Figure 4 by arrow heads the estimated points at which the isotropic–molecular (I_{mol}) solutions begin to transform into the isotropic–micellar (I_{mic}) phase. These points were taken to correspond to the temperatures at which the ^{23}Na lines begin to broaden

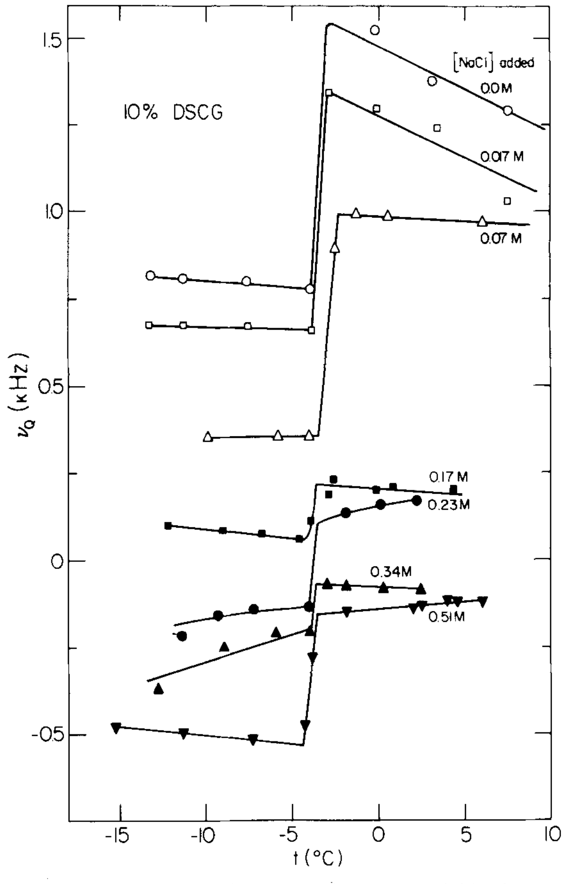


FIGURE 3 The quadrupole splitting, ν_Q, (between neighboring peaks) of the ^{23}Na NMR spectrum of solutions containing 10 wt% DSCG and various amounts of added NaCl as function of temperature. The sign of ν_Q was arbitrarily assumed to be positive for the solution free of excess sodium. The sign in the other plots was determined by assuming a continuous change in ν_Q with added salt concentration (see text). The phase transition III → N in these solutions is around −4 °C.

excessively upon further cooling. Also indicated in this figure are the N → I transition temperatures as determined from the deuterium spectra in solutions containing about 1 wt% D_2O. It may be seen that both the transition temperatures N to I, and I_{mic} to I_{mol} increase with DSCG concentration. The boundary line between the latter two phases derived from the results in Figure 4 is indicated by a dashed line in Figure 1.

It should be noted that the effect of micellar formation in the isotropic phase was also observed in the deuterium NMR linewidth, however the effect was much less pronounced than in the ^{23}Na case. This is most likely due to the fact that for sodium most of the ions are associated with the micelles and thus the full effect of their formation is manifested in its NMR spectrum. In the case of the deuterium signal only the contribution due to the small fraction of water mole-

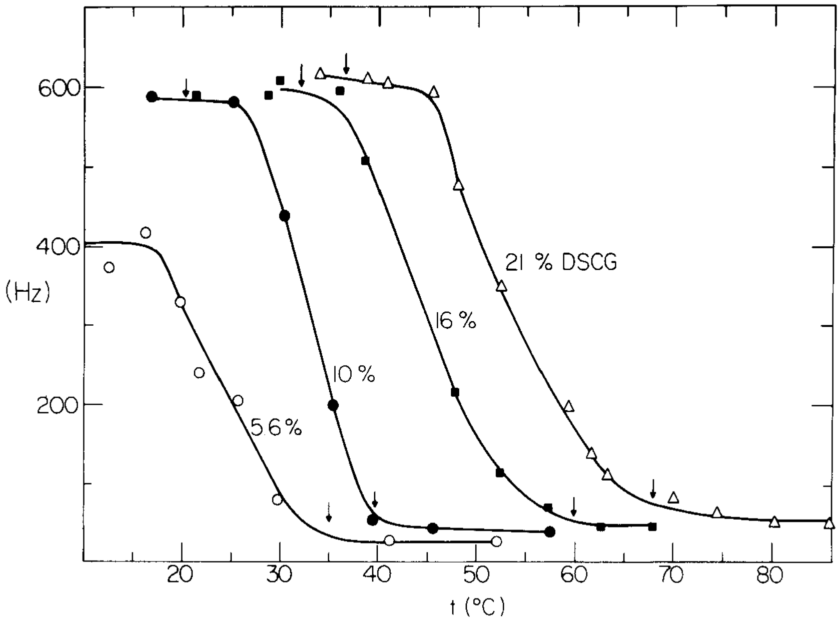


FIGURE 4 The full linewidth at half maximum height Δ, of the ^{23}Na signal in solutions containing various concentrations of DSCG, as indicated in the figure, as function of temperature near the N/M to Isotropic transition region. The arrow heads at the low temperature range indicate the N/M → I transition temperatures in corresponding solutions containing 1 wt% D_2O as determined by deuterium NMR. (For the 5.6% solution this transition occurs at about 5°C). The arrow heads at the high temperature range represent the estimated $I_{mic} \rightarrow I_{mol}$ transition temperatures based on these results.

cules associated with the micelles will affect the linewidth of the observed signal.

Next we consider the dependence of the ^{23}Na quadrupole splitting on the DSCG concentration. The results, together with other data to be discussed below, are summarized in Figure 5. In part (a) of this figure ν_Q in the N or M phases is plotted at temperatures just above the transition from III to N/M, while in part (b) the corresponding results are shown for phase III just below this transition. Note that in both phases with increasing DSCG concentration, ν_Q first increases and then, above about 10 wt% DSCG, it decreases again.

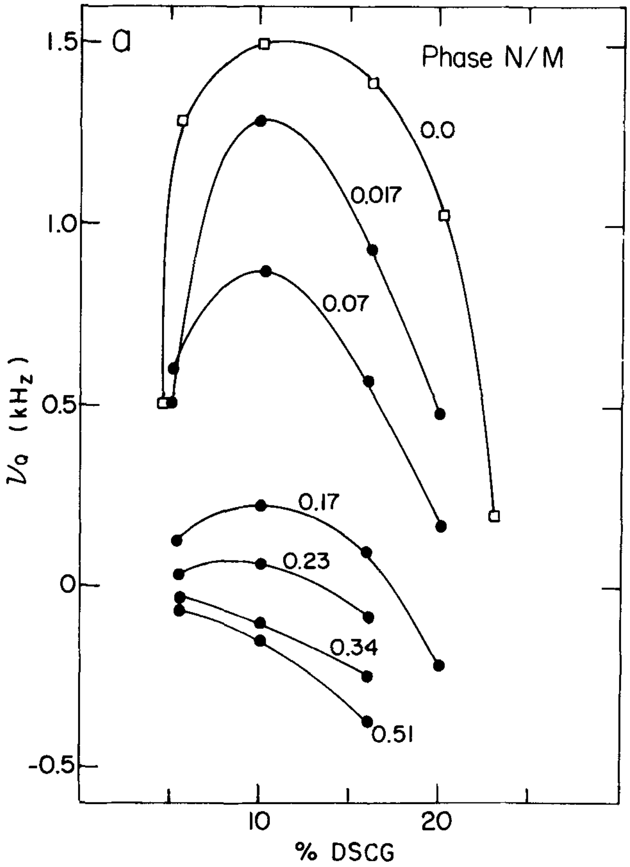


FIGURE 5a ^{23}Na quadrupole splitting for DSCG solutions without, and with added NaCl as indicated in the figure as function of DSCG concentration in the N/M phases just above the III → N/M transition.

B. Effect of added salt

The effect of added salt on the DSCG mesophases was studied by Lee and Labes[11] and by Yu and Saupe.[8] Both studies indicate that addition of electrolytes increase the range of stability of the mesomorphic phases. It is interesting to note in this connection that dilute solutions of DSCG which normally do not form a mesophase (i.e. below 3 wt% DSCG) will become liquid crystalline when sufficient amounts of NaCl is added. For example, a 2.3 wt% DSCG solution will become liquid crystalline at around −4°C when 0.14M NaCl is added. It appears therefore that excess sodium ions will stabilize the formation of micellar columns by strengthening the intermolecular ion bonds. To learn more about the direct involvement of the sodium ions

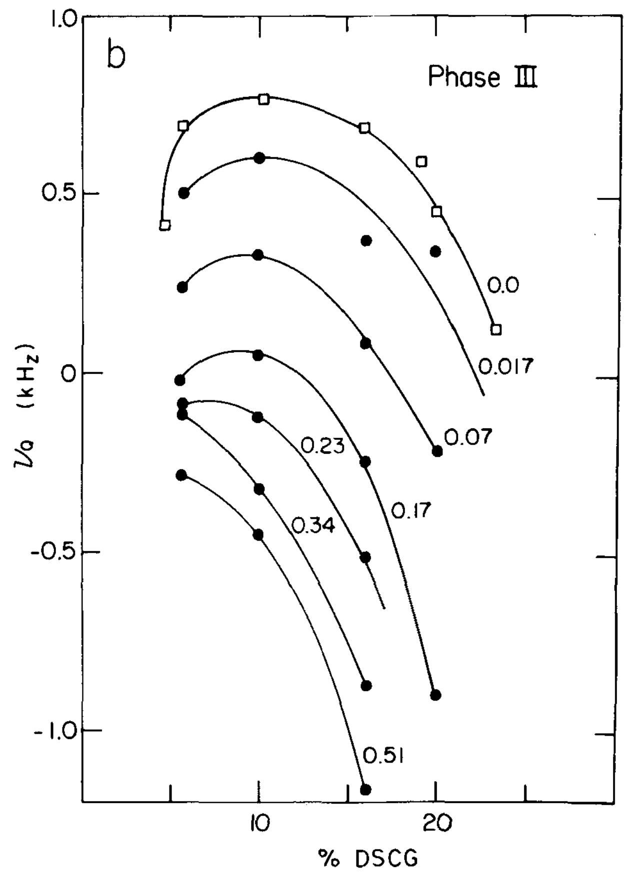


FIGURE 5b Same as Figure 5a but for phase III just below the III → N/M transition.

in this effect we have studied the ^{23}Na NMR spectrum in DSCG solutions to which successive amounts of NaCl were added. Measurements were made for several different DSCG concentrations and over the whole temperature range of the mesophase stability.

We first discuss the ^{23}Na resonance in the isotropic region: The measured linewidths as function of temperature in this region for 10 wt% DSCG solutions containing various amounts of added NaCl are shown in Figure 6, and the corresponding phase diagram is depicted in Figure 7. In the latter figure the N to I transition was determined from the deuterium signal in a D_2O solution while the $I_{mic} \rightarrow I_{mol}$ transition from the ^{23}Na resonance. It may be seen that the addition of NaCl not only increases the N → I transition temperature, but it also increases quite considerably the stability range of the isotropic micellar phase. The transition from N/M to III is however essentially unaffected by added NaCl. Similar results were obtained for other DSCG solutions.

Addition of NaCl also affects the ^{23}Na quadrupole splittings in both the N/M and III phases. The effect is best seen at temperatures near the transition from III to N or M, since the magnitude of the splittings at this region is largest. In Figure 8 are shown two series of

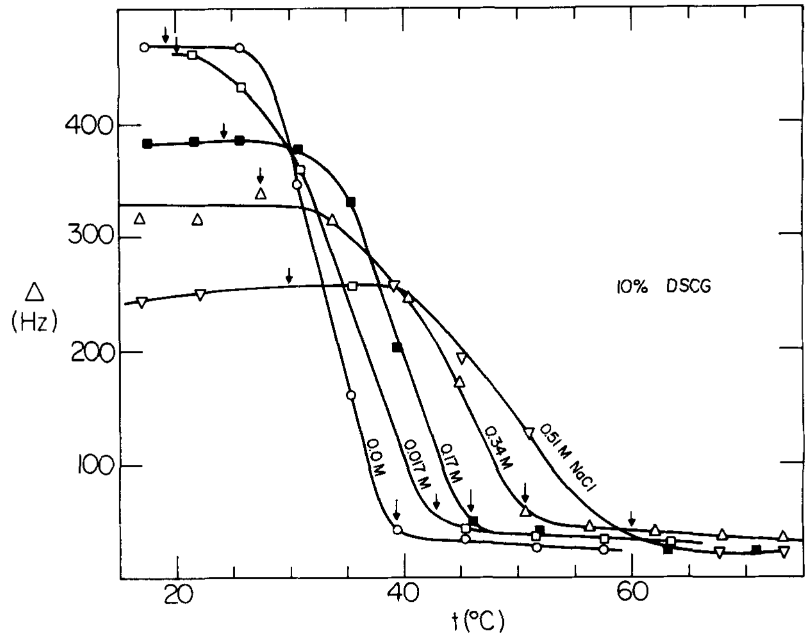


FIGURE 6 As in Figure 4 for solutions containing 10 wt% DSCG and various amounts of added NaCl.

^{23}Na spectra for a 10 wt% DSCG solution to which increasing amounts of NaCl was added. The spectra were taken in the N and III phases respectively, just above and just below the III → N transition point (i.e. at about −2°C and −5°C). It may be seen that in both phases the splitting first decreases to zero and then increases again. Since the concentration at which the splitting vanishes differs for both phases, and does not correspond to any phase transition, we must conclude that the quadrupole interaction changes sign as NaCl is added. Similar behavior of alkali metal ions in other lyotropic systems

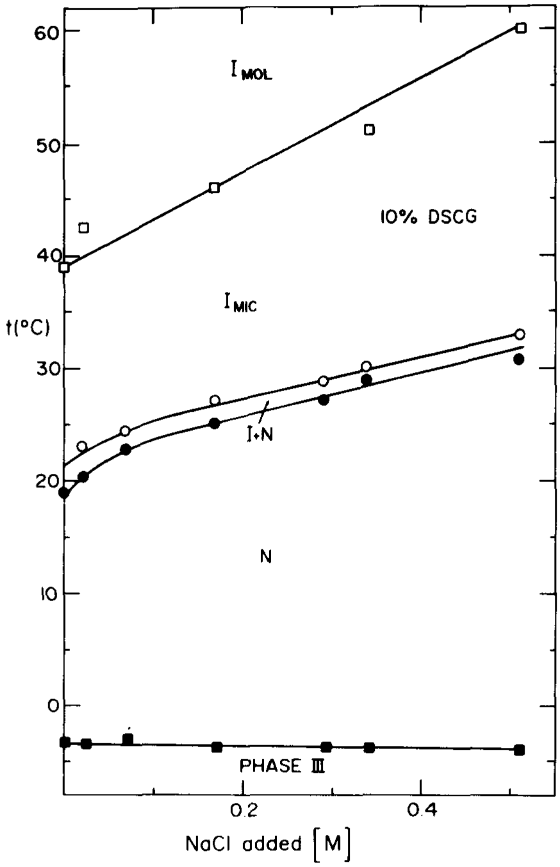


FIGURE 7 Phase diagram for a 10 wt% DSCG solution containing various amounts of added NaCl. The transitions N → N + I and N + I → I were determined from dueterium NMR in D_2O. The boundary line for I_{mic} → I_{mol} and the III → N transitions were determined from the ^{23}Na results as shown in Figures 3 and 6.

were observed previously and interpreted in a similar way.[12] In Figure 3 are plotted the observed ^{23}Na quadrupole splittings in a 10 wt% DSCG solution containing various amounts of NaCl as function of temperature. In plotting these results it was assumed, as mentioned before, that the sign of ν_Q for both the N and III phases in the solutions not containing NaCl is positive and that upon addition of salt the splitting decreases continuously and eventually becomes negative. Similar measurements were done on other solutions containing between 5 and 20 wt% DSCG. The results in the N/M phases, just

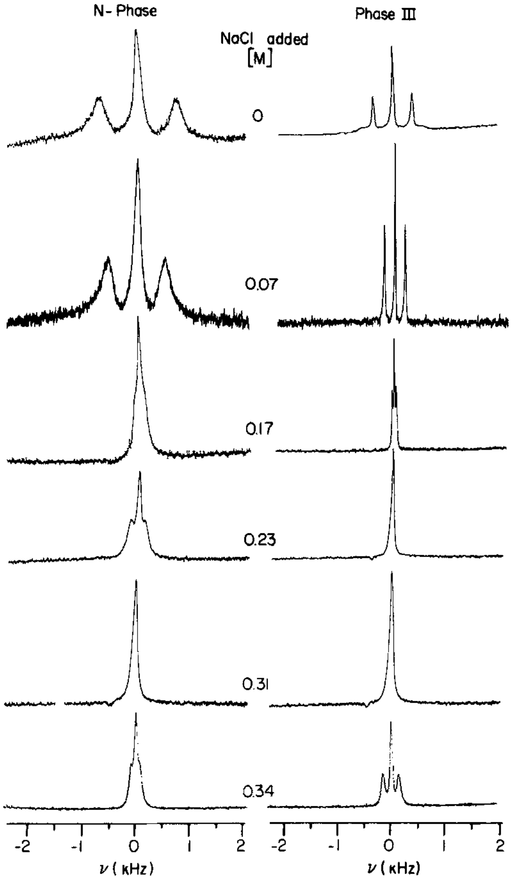


FIGURE 8 ^{23}Na NMR spectra at 23.6 MHz of a solution containing 10 wt% DSCG and various amounts of NaCl. The spectra on the left correspond to the N phase and were recorded at a temperature just above the N → III transition (~ −2 °C). The spectra on the right correspond to phase III and were recorded just below this transition (~ −5 °C).

above the transition to phase III and in phase III just below this transition are summarized in Figure 5. The general behaviour of ν_Q is similar to that described above for the solutions without added salt, i.e. ν_Q first increases and then decreases with DSCG concentration. However, the maximum in ν_Q shifts to lower DSCG content and its magnitude decreases upon addition of NaCl.

C. Effect of Other Ions

Several experiments were performed on solutions to which salts of cations other than Na^+ were added. The purpose of these experiments was to determine the relative binding tendency of other monovalent ions relative to sodium. Only a few preliminary experiments will be described.

Addition of LiCl to a DSCG solution usually results in a white precipitate but sometimes a metastable solution is formed that persists for several hours without precipitation. We have measured both the ^{23}Na and ^{7}Li spectra in such metastable solutions and examples are shown in Figure 9a. These spectra were obtained in the N phase of a solution containing 10 wt% DSCG to which 0.07 M LiCl was added. It may be seen that the quadrupole splitting of the ^{23}Na nuclei has decreased to below its linewidth (i.e. less than 300 Hz), and that the ^{7}Li resonance shows a finite splitting.

Likewise addition of KCl and $(CH_3)_4NCl$ also modifies the quadrupole splitting of the ^{23}Na. In Figure 9b are shown ^{23}Na spectra

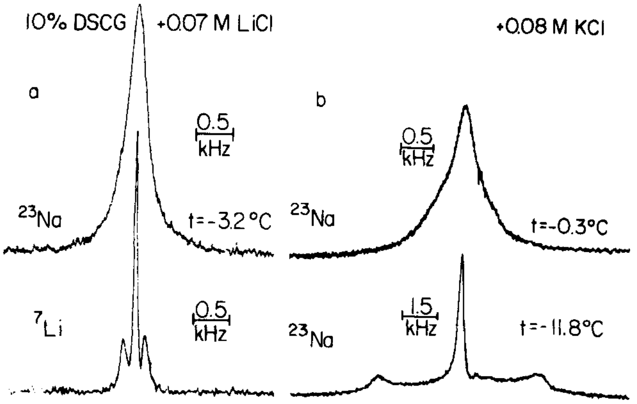


FIGURE 9 (a) NMR spectra of ^{7}Li (34.97 MHz) and ^{23}Na (23.6 MHz) in a solution containing 10 wt% DSCG and 0.07 M LiCl. (b) ^{23}Na spectra (at 79.4 MHz) in a 10 wt% solution of DSCG containing 0.08 M KCl in the N (−0.3°C) and III (−11.8°C) phases.

in a solution containing 10 wt% DSCG and 0.08M KCl at two different temperatures. (These spectra were taken at 79.4 MHz using a Bruker CXP 300 spectrometer). The −0.3°C and −11.8°C spectra correspond respectively to the N and III phases. It may be seen that in the N phase the splitting has been considerably reduced compared to its value in a solution not containing KCl, while in phase III it is much larger (cf. Figure. 2). We have studied the temperature dependence of the sodium splitting for solutions containing up to 0.35 M KCl and the results are summarized in Figure 10: There is a significant shift to low temperatures of the III to N (as well as the N to I) transitions and a gradual decrease and eventual change of sign of ν_Q upon the addition of KCl. The overall effect of added KCl on ν_Q is considerably larger than that of adding NaCl.

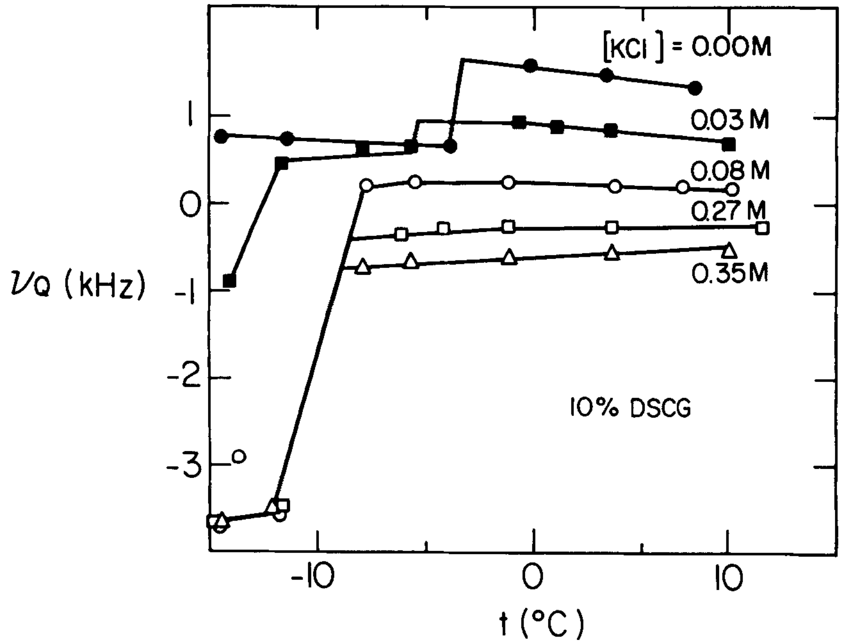


FIGURE 10 The ^{23}Na quadrupole splitting of a 10 wt% solution of DSCG containing various amounts of KCl as function of temperature. The discontinuity in the splitting corresponds to the III → N transition. The results were obtained at 79.4 MHz.

DISCUSSION

The results of the ^{23}Na NMR presented above can be summarized as follows:

1. In the N and M phases the sodium quadrupole splitting increases slightly on cooling, followed by a sharp discontinuous drop upon transition to phase III. Within phase III ν_Q is fairly constant with temperature (Figure 3).

2. Addition of NaCl increases the stability range of the N and M phases, as well as of the isotropic micellar phase. However, it has almost no effect on the III → N/M transition (Figures 3 and 7). Other electrolytes seem to show a similar behavior.

3. For both the N/M phases and for phase III, upon addition of NaCl, ν_Q decreases in magnitude down to zero, and then changes sign and increases again (Figure 3).

4. With increasing DSCG concentration the sodium quadrupole splitting first increases and then decreases. The same general behavior of ν_Q is observed in solutions to which NaCl is added, however the point of maximum ν_Q shifts to lower DSCG concentration, and its magnitude decreases upon addition of NaCl (Figure 5).

We now attempt to explain these results in particular the change in sign of ν_Q upon addition of NaCl, and its inverse parabolic dependence on the DSCG concentration. A complete quantitative interpretation is however not possible because of the complexity of the system: There may be several solvation sites for the sodium ions at fast dynamic equilibrium, and the observed ν_Q is then a weighted average of the splittings in the various sites. To calculate ν_Q we would require to know the populations and the specific quadrupole splitting of each site. The situation is further complicated by the lack of a satisfactory theory of estimating the ^{23}Na quadrupole splitting even for a chemically well defined site. Nevertheless, because of the conspicuous concentration dependence of the ν_Q's, some qualitative conclusions regarding the nature of the solvation sites of the sodium ions in the DSCG mesophases may be drawn.

Perhaps the most striking result is that of the change in sign of ν_Q upon addition of NaCl (and KCL) to the DSCG mesophase (Figures 8 and 10). The simplest model that may explain this effect is to assume the presence of two solvation sites for the sodium ions having quadrupole interactions of opposite signs. The NMR results do not provide any clue about the identity of these sites and we can only speculate. One possibility would be to identify one site (say site I) with sodium ions which hold together the DSCG molecules within the columns, while the other site (site II) may be identified with sodium ions dissolved in the bulk water. Since this medium is ordered to some extent by the columns, sodium ions in it would experience a finite quadrupole splitting. It is not expected to be large, but it might be of the same order as the average intracolumnar site due to compensation effects in the latter. Whatever the identity of the sites, assuming fast exchange between them, the observed splitting is given by:

$$\nu_Q = P^{\mathrm{I}}\nu_Q^{\mathrm{I}} + P^{\mathrm{II}}\nu_Q^{\mathrm{II}}$$

where the P^i's and ν_Q^i's are the fractional populations and site-specific quadrupole interactions of the corresponding sites.

We now assume that in a DSCG mesophase not containing excess of NaCl, the sodium ions are mostly bonded in site I, so that the predominant contribution to ν_Q comes from ν_Q^{I}. Upon addition of the NaCl, most of the added ions enter site II, whose ν_Q^{II} was assumed to have an opposite sign to ν_Q^{I}, resulting in the decrease of ν_Q and eventual reversal of its sign. The effect of adding other ions may be explained by the same two-site model by assuming that they compete with Na^+ on site I.

The effect of DSCG concentration on ν_Q (Figure 5) is considerably more difficult to rationalize. To explain these results, either the ν_Q^i's and/or the ratio $P^{\mathrm{I}}/P^{\mathrm{II}}$ must be assumed to depend on the DSCG concentration. Since we have no definitive knowledge about the identity of the sites there is very little we can say to support one mechanism or the other.

It should be emphasized that in our discussion we did not distinguish between the N, M and III phases, because the general behaviour of the ^{23}Na spectra in all mesophases was quite similar. In fact as far as NMR is concerned all properties change continuously on going from the N to M phase, although the transition from both to phase III is discontinuous. As yet, no X-ray study of phase III was carried out and its structure is not known. The NMR results suggest that this is a more highly ordered phase, but whether the columnar structure of the N/M phases persists also in III or whether it has a completely different structure remains an open question. Nevertheless the two-site model for the sodium ions seems to apply to this phase as well although we are less specific concerning the nature of these sites.

Acknowledgments

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