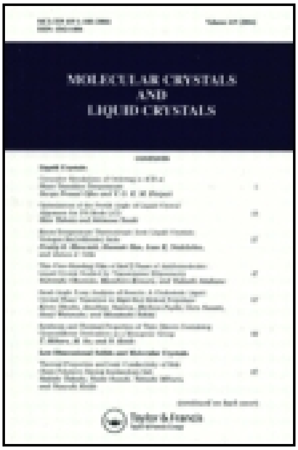

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Effects of Salt on the Orientational Order in Decylammonium Chloride/Ammonium Chloride/Water Systems

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Effects of Salt on the Orientational Order in Decylammonium Chloride/Ammonium Chloride/Water Systems

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The effect of NH_4Cl on the temperature dependence of deuterium oxide splitting (water order) and proton line width (surfactant order) in decylammonium chloride (DACl), D_2O systems is reported. The molar ratio of DACl to D_2O was held constant at .085 and the molar ratio of NH_4Cl to D_2O was varied from .012 to .029. We find for the above concentration ranges that in the nematic range the relative temperature dependence of the D_2O splitting is little affected by changes on salt concentration. The slopes of the proton line widths as a function of temperature decrease with increasing salt concentration. The results are compared with earlier data on salt effects on order obtained with the disodium cromoglycate system.

I. INTRODUCTION

In recent studies on ternary systems of disodium cromoglycate (DSCG), sodium chloride and water[1,2] it has been found that salt has a significant effect on the temperature dependence of the order in the nematic state. It may be expected that similar effects occur also in a nematic surfactant water system. An extensively studied nematic system suitable for the observation of these effects is decylammonium chloride (DACl), ammonium chloride and water. It forms a nematic phase with discoidal micelles[3] (N_L phase). The nematic state is due to a partial parallel orientation of the micelles.

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The orientational order has been investigated by nmr[3,4,5] and by birefringence measurements. Specifically its dependence on salt and D_2O concentration has been studied at constant temperature and the temperature dependence at various D_2O concentrations. In this paper we investigate the effect of the NH_4Cl concentration on the temperature dependence of the order. Two methods are used to study orientational order: deuteron resonance measurements on D_2O, and proton resonance measurements.

The dmr signal shows a doublet splitting due to the orientation of D_2O by association to the micelles. There is an exchange between associated and non-associated D_2O. The exchange is fast so that only one doublet of D_2O is observed in the dmr spectrum. In samples with pure D_2O the signals are broadened and difficult to observe because of an exchange with the ammonium protons of DA. The samples were therefore prepared with acidified D_2O (0.1N DCl). Due to the slower exchange with the ammonium protons the dmr lines sharpen to a width of only a few Hz.[3] The results of the earlier studies[4,5] indicate that the doublet splitting is a relative measure for the order in the nematic range. It has been found that it is nearly proportional to the doublet splittings of the deuterons in alkyl chains and in the ammonium group of DA.[4] It is also proportional to the birefringence.[5]

The pmr signals of the alkyl protons appear as a very broad line with an indication of a triplet structure, and a superimposed sharp signal, due to ammonium protons of the salt and the proton impurities of D_2O. Its width is proportional to the degree of order of the alkyl chain and therefore more directly a measure for the degree of order than the dmr signal of D_2O. In order to relate it to the orientational order of the micellar aggregates we assume that the temperature dependence of the effective conformational structure of the alkyl chains is negligible, secondly, that the average alignment of the chain axis is a direct measure for the micellar order.

The ratio of the dmr splitting to the width of the pmr signal must therefore be temperature independent. The results show that this is approximately true in the nematic phase. Larger deviations occur in the smectic phase where the temperature dependencies have opposite signs.

II. EXPERIMENTAL

The DACl used was prepared by Radley.[1] The concentration of NH_4Cl was varied between 1.18 and 2.63 mole %, and the ratio of DACl to D_2O in each sample was held approximately constant (see Table I).

TABLE I

Sample	Mole Percent (D_2O, DACl, NH_4Cl)	Weight Ratio DACl/NH_4Cl	Transition Temperature °C N-I	N-Neat Soap
1	(89.70, 7.56, 2.74)	10:1	67	48
2	(90.55, 7.65, 1.80)	15:1	56	44
3	(90.95, 7.66, 1.39)	20:1	49	38
4	(91.25, 7.64, 1.11)	25:1	44	32

The appropriate components were weighed into glass tubes with airtight screw-top caps. The samples were immersed in water held at a temperature below the expected nematic-isotropic two-phase region and stirred magnetically for three to four hours. All samples were stored overnight and examined for homogeneity before use. The reproducibility of the transition temperatures was ±0.5°C. The transitions were determined microscopically and by nmr. The nmr spectra were recorded with a Varian XL-100 spectrometer.†

III. RESULTS AND DISCUSSION

The data summarized in Table I show the effect of salt on the phase transitions. It shifts the smectic–nematic and the nematic–isotropic transition to higher temperatures and widens the range of the nematic phase. We prepared also samples with higher salt concentration, $[DACl]/[NH_4Cl] \sim 1.7$. These mixtures do not give a uniform phase. Solid materials remain precipitated over the entire studied temperature range from 20 to 100°C.

The results of the dmr measurements are summarized in Figure 1. The splitting is due to the quadrupolar couplings in the OD bonds and result from the orientation of the associated water. The splittings in the nematic range when compared at corresponding temperatures increase with the salt concentration. The relative temperature dependence is nearly the same for all samples in the nematic range but there is a remarkable difference in the smectic range. The temperature dependence reverses its sign in the smectic range for the sample with the highest salt concentration. The reversal of the temperature dependence had already been observed by Fujiwara and Reeves[4] who studied a sample of similar salt concentration. The D_2O splitting of the other samples stud-

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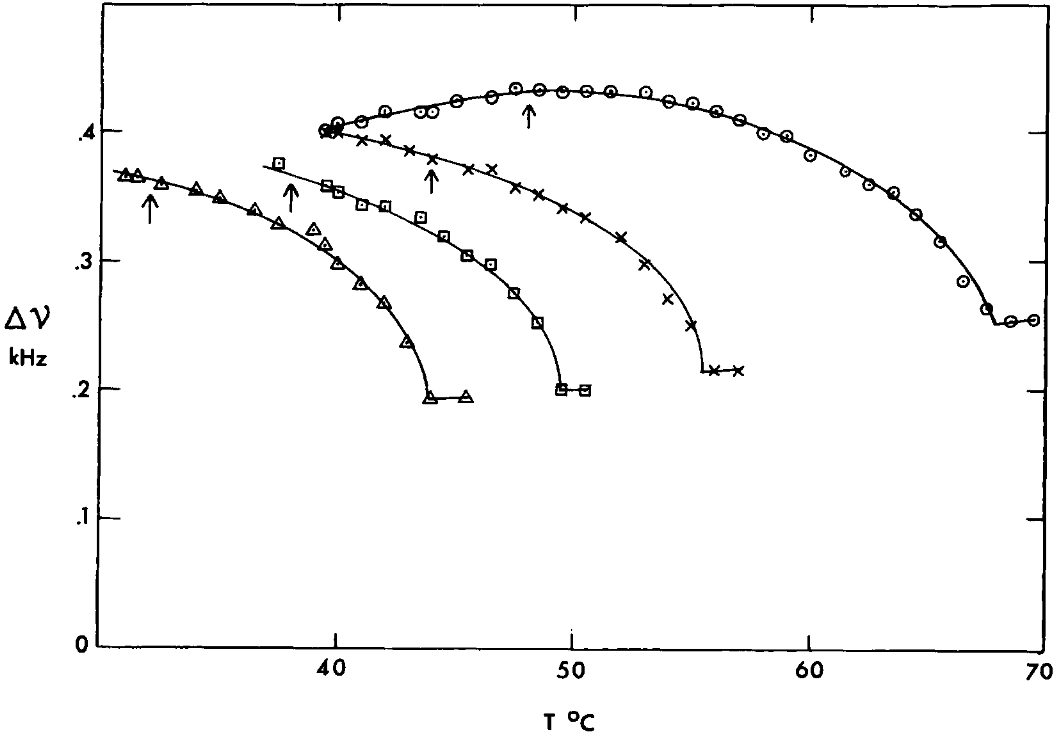

FIGURE 1 Deuterium splitting vs temperature. The symbols correspond to the samples of Table I. ⊙—1; x—2; ⊡—3; ◬—4. Points in the nematic–isotropic two phase region are connected by a straight line. The arrows denote the N_L-neat soap transition.

ied by us does not show any apparent changes at the nematic smectic transition. The micellar degree of order S can be related to the splitting by the equation[3]

$$\Delta\nu = \frac{[\mathrm{DACl}]}{[D_2\mathrm{O}]}\frac{3}{2}Q C_1 C_2 S. \tag{1}$$

The brackets indicate the molar concentrations, Q is the quadrupole coupling constant, and C_1 the (average) number of molecules associated with one surfactant molecule. The coefficient C_2 is defined so that C_2S is the effective degree of order of the OD bonds of associated water. The ratio $[\mathrm{DACl}]/[\mathrm{D_2O}]$ is practically the same for all samples and within the nematic range of a given sample C_1C_2 is approximately constant so that $\Delta\nu \approx \text{const}\ S$.

The pmr measurements are summarized in Figure 2. The figure gives the width of the proton resonance signal, i.e., the frequency distance between the outermost inflection points.

The temperature dependence of the line width within the nematic phase is similar to that of the deuteron resonance splitting but it is somewhat stronger. The ratio of linewidth to splitting at a given reduced temperature is also dependent on the salt concentration. More pronounced differences occur in the lamellar smectic phase. Apparently the structure of associated water changes with the formation of the smectic state, in particular at high salt concentration. This change in the structure of water could contribute to the stabilization of the nematic state.

The effect of NH_4Cl on the temperature dependence of the D_2O splitting in the N_L phase of the DACl system is much smaller than the effect of NaCl in the DSCG, NaCl, D_2O system. The DSCG-system forms a nematic phase with rodlike micelles, N_C. The relative temperature dependence of the splitting in the nematic state decreases significantly in the DSCG system while it is nearly constant for DACl. The effect on the magnitude of the splittings is of opposite sign. At a given reduced temperature the magnitude increases for the DSCG system with increasing salt concentration, for the DACl system it decreases. The decrease in the DACl system is due to changes in the water association. The micellar order itself as indicated by the pmr linewidth increases in certain limits with the salt concentration.

The differences in the effects of salt on the two systems will in part be due to the fact that DSCG gives cylindrical micelles while DACl gives discoidal micelles. Additional studies on surfactant systems with cylindrical micelles will be needed to clarify this point.

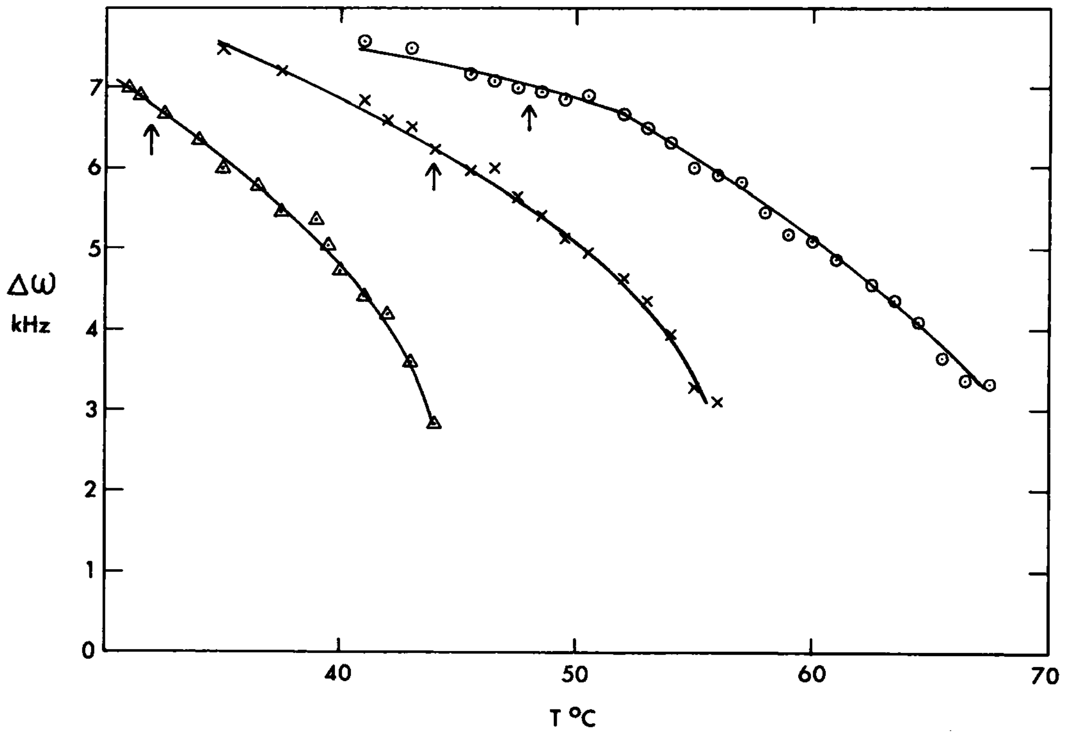

FIGURE 2 Proton linewidth vs temperature. The symbols correspond to the samples of Table I. ⊙—1; x—2; ◬—4. The arrows denote the N_L-neat soap transition.

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