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The Mechanism of Hydrotrope Action of a Dicarboxylic Acid

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The mechanism of the hydrotrope action of a dicarboxylic acid monosoap was investigated by determination of the change in order parameter of the amphiphile in a lamellar liquid crystal. The results showed addition of the hydrotrope considerably to reduce the order while addition of a surfactant had no effect. © 1986 Academic Press, Inc.

INTRODUCTION

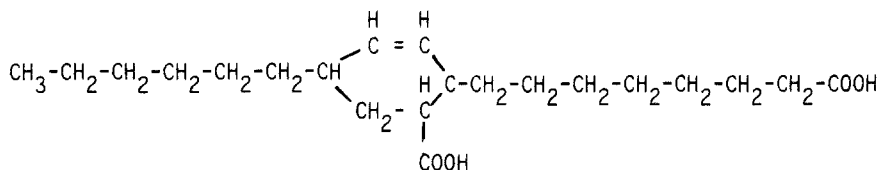
The mechanism of hydrotrope action has attracted interest all the time since the first article by Neuberg (1). During the evaluations of the hydrotropic effect three main directions have been followed. The initial investigations (2) emphasized the molecular structure of the hydrotrope relating the solubilization capacity to individual features in the molecular structure of the hydrotrope molecule (3). An assumption of pairwise association was made and the thermodynamics of such association has been investigated (4). The second approach (5) involved experimental investigation of the primary association structure and the hydrotropes were compared to surfactant. The third approach (6) focused its attention on the fact that in an aqueous solution of a typical hydrotrope, a sodium xylene sulfonate, the huge solubilization of amphiphilic substances with predominantly hydrophobic properties such as a long chain carboxylic acid is obtained due to the fact that the hydrotrope molecule does not form a liquid crystalline phase with the long chain hydrophobic amphiphile.

In fact, the formation of a lamellar liquid crystalline phase is the factor that limits the

solubilization of long chain carboxylic acids or alcohols in an aqueous micellar solution of a surfactant (7). A combination of surfactant and a long chain amphiphile such as an alcohol always shows a lamellar liquid crystalline phase separating the aqueous micellar solution and the alcohol inverse micellar solution. It is intuitively evident that the difference in structure of a typical hydrotrope such as the sodium xylene sulphonates and a long chain amphiphile should not facilitate the regular structure of a liquid crystalline phase. A mixture of short and long chain amphiphiles in a lamellar liquid crystal leads to enhanced disorder of the excess hydrocarbon chain part of the long chain variety. This enhanced disorder leads to destabilization of the lamellar structure. A good example is the combination of sodium octanoate with octanol and with butanol (7). The former combination displays a huge lamellar liquid crystalline region with water while the latter, instead, shows a continuous isotropic liquid solubility region from the aqueous micellar structure to the butanol corner. The similarity between butanol and a short chain hydrotrope such as a sodium xylene sulfonate is immediately evident.

The hydrotrope dicarboxylic acid, 5- (and

6-) carboxy-4-hexyl-2-cyclohexene-1-yl octanoic acid (8), on the other hand, has a different structure with two long hydrocarbon chains in tandem:



In spite of this fact, hydrotropic effect of its monosodium salt has been demonstrated to arise from a destabilization of the liquid crystalline structures involved (9).

In these contributions it was assumed that the bulky conformation of this monosoap at an interface led to enhanced disorder of the lamellar liquid crystalline phase and subsequent destabilization. However, no proof has been given that the presence of the monosodium soap of the dicarboxylic acid leads to enhanced disorder of a lamellar liquid crystalline structure.

The hydrotropes are, at present, heavily investigated (10) and we found a proof of the disordering action of dicarboxylic acid to be of both scientific and technical value.

EXPERIMENTAL

Chemicals

Sodium caprylate was prepared by neutralization of octanoic acid (Aldrich Gold Label, 99.5%) with sodium ethoxide in ethanol. The salt so obtained was recrystallized twice from ethanol. Octanol-d17 was obtained from MSD Isotopes and was used without further purification. Pure dicarboxylic acid (99%, fractionally distilled) was a gift from the Westvaco Corporation. The monosodium salt was prepared as described previously (11).

Sample Preparation

Three samples of lamellar liquid crystals (A, B, C) containing a fixed weight ratio of sur-

factant to cosurfactant, were prepared through an addition of water to a stock liquid crystalline sample of octanol, sodium caprylate, and water. From each of the three samples two series of samples were prepared as follows. In one series varying amounts of monosodium salt of dicarboxylic acid were added while in the other series equal weight percentages of sodium caprylate were added. The latter series provided a convenient standard to compare the perturbing effect of the monosodium salt of the dicarboxylic acid. Samples were then mixed by forcing the matrix back and forth, in constricted glass tubes sealed at both ends, using a high speed centrifuge. The homogeneity of the lamellar liquid crystalline phases was confirmed using optical microscopy. The mixed samples were then allowed to equilibrate at room temperature (25°C) over a period of 2 months. The composition of the samples is presented in Table I wherein the last column always represents the amount of the dicarboxylic acid salt or surfactant added to the stock liquid crystal to prepare the sample.

NMR Spectroscopy

Deuterium NMR spectroscopy was carried out on a high power CXP 200 (Bruker) spectrometer operating at 30.709 MHz for deuterium. Due to the large quadrupolar splittings of the hydrocarbon chain deuterons in the octanol, it was essential to use a high power multinuclear probe to circumvent the baseline problems. Typically, 5000–25,000 scans were

TABLE I
Composition of Samples

Host			Addition NaDA (%)
NaC ₈ (%)	Water (%)	C ₈ OH (%)	
A. Series 1			
18.00	47.04	34.96	0.00
17.55	45.85	34.07	2.53
17.25	45.06	33.50	4.19
16.90	44.16	32.82	6.12
16.18	42.26	31.42	10.14
A. Series 2			
18.00	47.04	34.96	0.00
17.55	45.86	34.09	2.50
17.10	44.69	33.22	4.99
16.90	44.18	32.83	6.09
16.12	42.14	31.32	10.42
B. Series 1			
14.96	55.98	29.06	0.00
14.72	55.06	28.58	1.64
14.52	54.37	28.22	2.89
14.19	53.10	27.57	5.14
13.58	50.80	26.38	9.24
B. Series 2			
14.96	55.98	34.96	0.00
14.71	55.03	34.09	1.70
14.49	54.23	33.22	3.13
14.05	52.59	32.83	6.06
C. Series 1			
8.84	73.98	17.18	0.00
8.67	72.56	16.85	1.92
8.43	70.59	16.39	4.59
8.16	68.27	15.86	7.71
C. Series 2			
8.85	73.98	17.18	0.00
8.66	55.03	16.84	2.00
8.43	54.23	16.39	4.59

collected using a delay time of 0.4 s (sweepwidth = 100 kHz). Though the spectrometer could be tuned to yield a 90-degree pulse width of the order of 5–7 μ s, typically less than 90-degree pulse widths were used in order to pre-

vent the NMR lineshape saturation. The probe temperature was maintained by a flow of N₂ gas at 22°C.

RESULTS

The expected spectrum for the perdeuterated octanol is a composite pattern of eight overlapping Pake doublets. However, the order parameters of the methylene deuterons of the octanol exhibit the plateau typically observed in a lamellar liquid crystalline phase (12). Thus, typically three to four patterns are easily resolved. We assign the splittings as follows. The distinct smallest quadrupolar splitting is associated with the methyl group and the greatest splitting with the methylene group carrying the OH group. As C₄ through C₈ methylene deuterons have similar quadrupolar splitting, we chose the one marked in Fig. 1 as typical of this group. In Fig. 1 we present two typical spectra where approximately equal amounts of dicarboxylic acid monosoap and sodium caprylate are present in samples prepared from the same stock liquid crystal. The reduction in quadrupolar splitting clearly demonstrates the reduced splitting at addition of the hydrotrope in the appropriate sample.

In all the spectra of samples without addition, the ratio of the methyl group quadrupolar splitting to the next higher splitting is 0.233, independent of water content on added compound. This is expected from the free rotation of the methyl group around its threefold symmetry axis. The corresponding ratio for the methylene group adjacent to the hydroxyl group varied with water content as expected, with smaller splits for the methylene group at higher water content.

For all cases, addition of the dicarboxylic acid monosoap caused a reduction of the split while addition of the sodium octanoate left it virtually unchanged (Figs. 2A–C). The reduction of the split was most pronounced for the methylene group adjacent to the hydroxyl group; the terminal methyl group showed only insignificant changes.

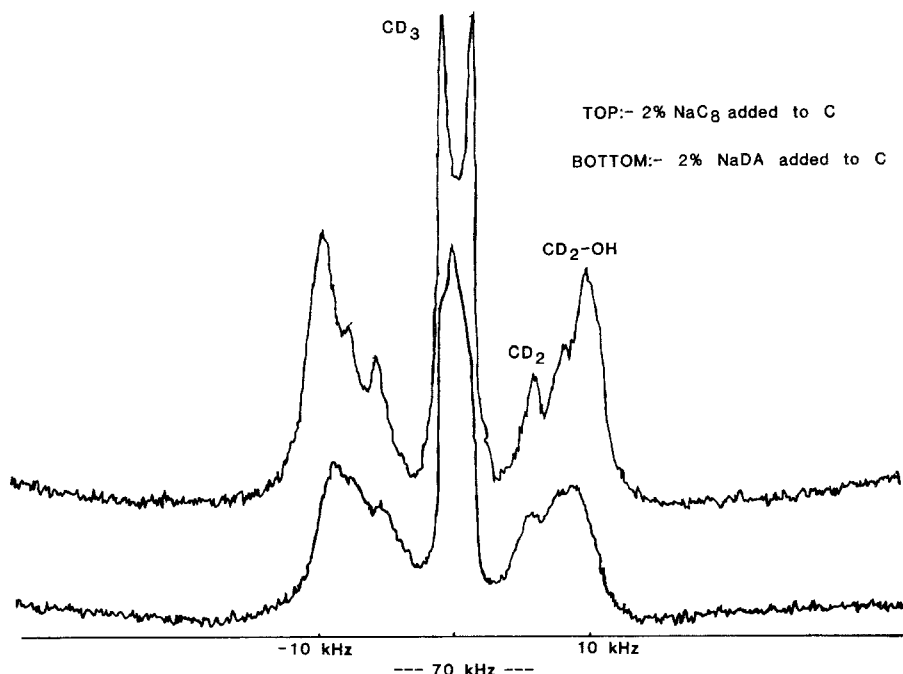


FIG. 1. Typical spectra obtained from host with added monosodium salt of the dicarboxylic acid (bottom) or with added sodium octanoate (top).

DISCUSSION

The results confirm our earlier interpretation (9) of the role of the hydrotrope molecule

as causing enhanced disorder of the lamellar liquid crystalline structure with a reduction in stability as a consequence. In addition, the results provide specific information on the dis-

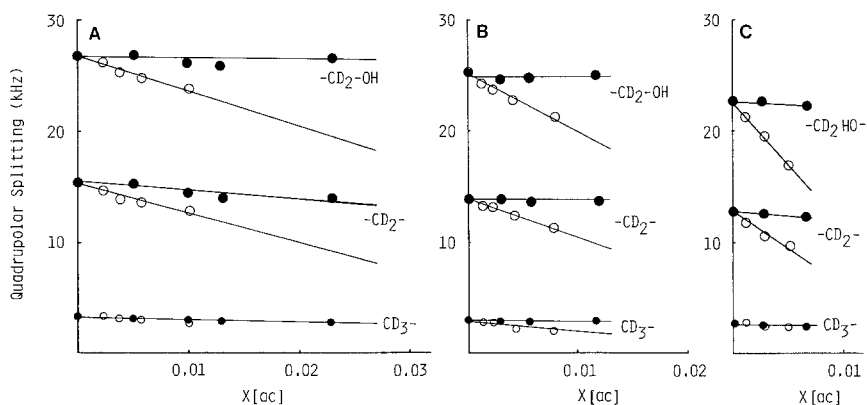


FIG. 2. The quadrupolar splitting of octanol in the host liquid crystal with added sodium octanoate (●) or the monosodium soap of the dicarboxylic acid (○). (a) Compositions according to Table Ia; (b) Compositions according to Table Ib; (c) Compositions according to Table Ic.

ordering on a molecular level. The addition of the monosodium salt of the dicarboxylic acid gave a strong reduction of the quadrupolar splitting while the addition of sodium octanoate caused no changes. Two features of the disordering are immediately evident.

The first one is the predominant influence exerted on the methylene groups adjacent to the polar group while the methyl group was not influenced. The difference in the shapes in all diagrams, Fig. 2A-C, makes this fact immediately evident and a semiquantitative measure of the effect may be given by the value of the slopes for the splitting with added monosoap versus mole fraction of the monosoap. The values (Table II) clearly demonstrate the more pronounced disordering effect on the methylene group adjacent to the polar group.

The second feature is the enhanced effect for samples with higher water content. An increase of the initial water content from 47 to 78% brought an almost fourfold increase of the value of the slope. This finding is important for the application of the monosoap in liquid cleaners. The enhanced cleaning action depends on the hydrotropic action (13) and it appears reasonable to assume that the large hydrophobic content of the monosoap is a key factor for this action.

These results are directly interpreted with the conformation of the monosoap taken into account. The extreme bulkiness of the head-group of the monosoap including both carboxylic groups and the hydrocarbon chain be-

tween them should be expected to cause enhanced disorder mostly close to the polar group of the amphiphiles (11). The terminal methyl group of the host amphiphile, on the other hand, with its free rotation should be less influenced in accordance with our results.

The broadening of the spectrum by the addition of the monosoap molecule as observed in Fig. 2 may be given the following tentative interpretation. The bulky head group of the monosoap is expected not only to give enhanced disorder to individual methylene groups of the alcohol but also to influence the dynamics of this molecule as a whole. The increased free space around the adjacent amphiphiles is sufficient to enable a slow wagging motion of the alcohol molecule as a whole. Such a motion leads to a reduction of the relaxation time T_2 , which, in turn, gives a broadening of the individual features of the spectrum (14).

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TABLE II

Slopes of Splitting versus Mole Fraction Added Dicarboxylic Acid (C, Figs. 1a, b, and c) in Megahertz per Mole Fraction

Group	A	B	C
CD ₂ -			
OH	0.31	0.52	1.11
Me-CD ₂	0.26	0.35	0.66
-CD ₃	0.04	0.11	0.05

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