properties. The results obtained are in good agreement with chemical experience and simple theory. In particular, they show that the relaxation effect increases in the order $H \approx F < CH_3 \lesssim Cl < Br$. For alkyl groups the contribution increases with the size of the group. The relaxation energy decreases with distance between the substituent and the site at which the charge is being changed. For the initial state, the effect depends on whether the substituent is attached directly to the atom of interest or is more remote in the molecule. In the first case, the order is $CH_3 < H < Cl < Br < F$; in the second, $CH_3 < H < Cl \approx Br \approx F$. The striking results here are that hydrogen produces a more positive environment than does methyl and that halogens in remote positions affect the ground-state potential about equally.

The influence of an alkyl group on the initial-state charge distribution is, by definition,[6] essentially neutral. The effect of alkyl groups arises from their polarizability, or, equivalently, their ability to disperse charge. Comparison of the results obtained here with those from studies of carboxylic acid shows that an alkyl group can act either as an electron acceptor or as an electron donor, depending on the sign of the charge that must be dispersed.

Acknowledgments. This work was supported in part by the National Science Foundation. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the Americal Chemical Society, for partial support of this research. We are indebted to Leon Ungier for valuable comments.

Liquid Crystalline Phases of the Sodium Decyl Sulfate/Decanol/Water System. Nematic–Nematic and Cholesteric–Cholesteric Phase Transitions

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Contribution from the Liquid Crystal Institute, Kent State University, Kent, Ohio 44242.
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Abstract: The existence of a thermally induced phase transiton between two nematic phases in the ternary mixture of sodium decyl sulfate, decanol, and water is verified by microscopic studies and deuteron resonance of D_2O. The phase diagram over the range that gives two nematic phases is reported as a function of temperature and water to sodium decyl sulfate ratio keeping the weight percent of decanol constant. The lower temperature nematic (N_L) possesses a negative diamagnetic and a positive optical anisotropy, the higher temperature nematic (N_C) a positive diamagnetic and a negative optical anisotropy. Our results indicate that the N_L phase has micelles of a bilayer structure and the N_C phase micelles of a cylindrical structure. Two cholesteric phases are obtained by adding a chiral compound into the mixture exhibiting the aforementioned nematic phases. The responses of the cholesterics to a magnetic field and the thermally induced phase transition between them are observed. The twist induced in the bilayer micelle phase is twice that of the cylindrical micelle phase at equal concentration of added chiral compound.

I. Introduction

A nematic phase in aqueous solutions of sodium decyl sulfate (NaDS) and decanol was first reported by Lawson and Flautt,[1] who used it as a solvent for NMR spectroscopy. Radley and Reeves[2] found that the system forms two different nematic phases. They showed by NMR studies that a direct, thermally induced transition between the two phases can be observed. The diamagnetic anisotropy changes its sign at the transition. It is negative for the lower temperature phase and positive for the higher temperature phase.

The two phases are perhaps best described as anisotropic micellar solutions which differ in the structures of the micelles.[3] Our studies indicate that the high-temperature nematic phase has rod-like micelles of a structure similar to the surfactant aggregates in the normal hexagonal smectic phase or middle soap. The low-temperature phase, on the other hand, has disk-like micelles of a structure similar to the bilayers in the lamellar smectic phase or neat soap.

Table I. Concentrations of the Components of the Ternary Mixture

	concn, wt %		
sample no.	D_2O	decanol	NaDS
1	58.54	6.99	34.47
2	58.0	7.0	35.0
3	57.53	7.0	35.47
4	57.05	7.0	35.95
5	56.5	7.0	36.5
6	56.0	7.0	37.0
7	57.52	7.19	35.29
8	58.02	6.80	35.18
9	55.97	7.21	36.82
10	56.51	6.79	36.70
11	54.97	7.07	36.96

We will refer to these two nematic phases as N_C and N_L phase, respectively. They correspond for the given system to type I and type II nematic, respectively, as defined by Reeves and coworkers,[2,4–6] but the assignment may have to be changed for other systems.[3] An N_L phase is transformed to a cholesteric phase by addition of a chiral compound.[7] It twists about as readily as a thermotropic nematic phase. The response of an N_C phase to chiral compounds has not been studied earlier.

It is the purpose of this paper to provide more evidence on the nematic phases in the NaDS/decanol system. A section of the phase diagram of the D_2O/NaDS/decanol system focused on the range of the nematic phases along with the various surrounding phases is given. It is demonstrated that the addition of a chiral compound induces in both cases the formation of cholesteric phases and that a thermally induced transition between the two cho-

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(2) Radley, K.; Reeves, L. W. *Can. J. Chem.* **1975**, *80*, 174.

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(7) Radley, K.; Saupe, A. *Mol. Phys.* **1978**, *35*, 1405.

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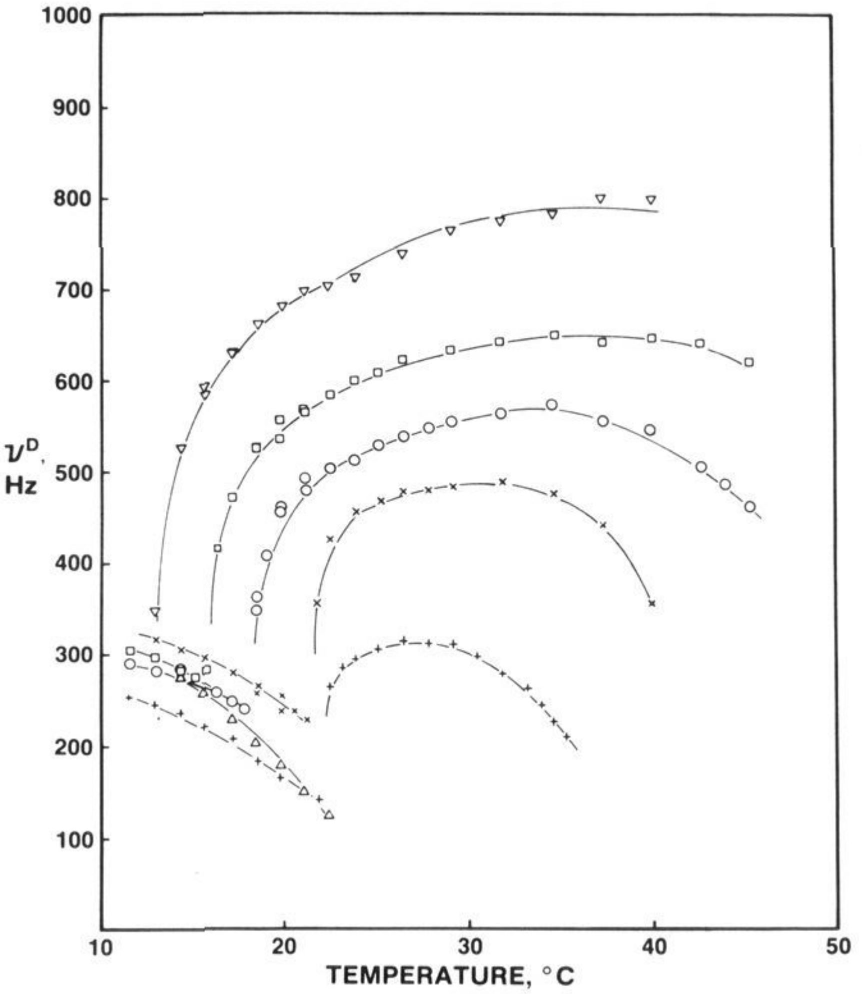

Figure 1. The deuteron resonance splittings as a function of temperature: Δ, sample (1); +, (2); x, (3); ○, (4); □, (5); ∇, (6) (see Table I for composition).

lesterics occurs with a discontinuous change of the pitch.

II. Experimental Section

Deuterium water (D_2O, 99.8% atom D, from Aldrich and Stohler Isotope Chemicals) is used without futher treatment. 1-Decanol (Aldrich) is vacuum distilled. NaDS is made according to ref 2 and purified by recrystallization from 95 and 100% ethanol several times and from isobutyl alcohol (Aldrich) twice, then dried in a vacuum desiccator for several days. NaDS contains no observable impurity when checked with a Varian XL-100 spectrometer.[8] Brucine sulfate heptahydrate (Matheson Coleman and Bell) is used without further purification.

Appropriate amounts of the components are weighed into a test tube with a constricted neck in the middle. The test tube is sealed immediately and centrifuged back and forth through the neck for mixing. Usually the mixture is chilled with cold water duing the mixing process because the solution is nematic at lower temperatures and can be mixed easier; heating is therefore avoided. After a homogeneous solution is obtained, the sample is left at room temperature, and occasionally centrifuged, for over 24 h before use.

Samples for microscopic and NMR studies are made at the same time. The compositions of the samples studied are listed in Table I. Microscope samples are prepared in flat capillaries (Microslides, obtained from Vitro Dynamics, Inc., N.J.) of various thicknesses (0.2, 0.3, and 0.4 mm) and sealed with a torch right after the solution is introduced. The transition temperatures observed with the polarizing microscope (Leitz, Mettler hot stage (FP2)) and by ^{2}H NMR (Varian XL-100) on bulk samples are in good agreement (±1 °C). If a large discrepancy occurs (>2 °C), a new microslide sample is made.

Some of the samples for microscopic studies are aligned in magnetic field before the observation. A field of 23 000 G is used for the alignment.

III. Deuteron Resonance Studies

The deuteron splittings of D_2O as a function of temperature are shown in Figure 1 for six different mixtures (samples 1–6 of Table I). The concentration of decanol is 7.0 wt % in all mixtures. The concentration of D_2O is varied from 56.0 to 58.54 wt % and the NaDS concentration accordingly 37.0 to 34.46 wt %. In the N_L phase the signal is not affected by spinning the sample around an axis vertical to the field. It confirms the negative sign of the diamagnetic anisotropy. On cooling, the splitting increases until the sample finally solidifies. The optical studies show that before solidification the sample transforms at least partially into a middle soap. The liquid crystalline states are only metastable at temperatures below about 20 °C. Once the material has crystallized it has to be heated to above 20 °C before it returns into a nematic state.

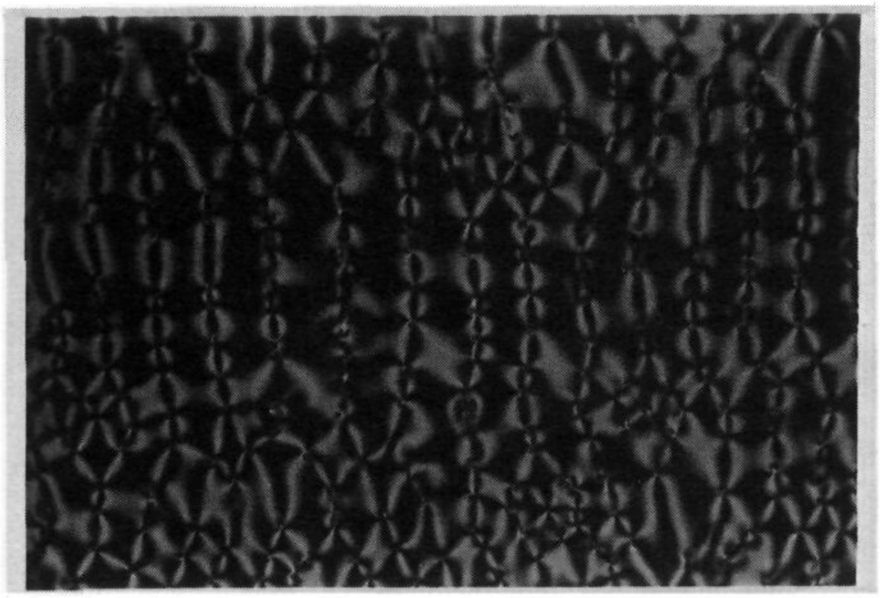

Figure 2. N_L phase texture, obtained after applying a magnetic field normal to a pseudoisotropic texture for 20 min, 0.3 mm thick, 60×, crossed polarizers.

Upon heating the N_L phase a second doublet appears when the transition to the N_C phase is reached. The second doublet belongs to the N_C phase. It has a larger splitting. The diamagnetic anisotropy of the N_C phase is positive as can be easily verified by rotation of the sample. When the water concentration reaches 58.5 wt %, sample 1 of Figure 1, only an N_L phase exists. Upon heating it turns isotropic at 24 °C. The quadrupole splitting in the N_C phase shows in all cases a very steep increase with temperature right after the N_L–N_C transition. On further heating the splitting of samples 2–4 reaches a maximum and then decreases again. A central peak appears which indicates the formation of an isotropic phase. Samples 5 and 6 do not make a transition from the N_C phase to the isotropic phase but transform to middle soap on heating. The signals at this transition change to doublets with a considerably larger splitting. It is worthy of note that the middle soap obtained in this way preserves to a good extent the alignment of the N_C phase but it cannot be reoriented with the magnetic field. Our observations on the deuteron splittings in the nematic phases are in good agreement with the results of Reeves and co-workers.[4]

IV. Microscopic Textures

Birefringent textures with more or less aligned large domains were observed with both nematic phases right after the sample preparation. These textures show the effect of flow alignment since centrifugation was used for the preparation. The N_L phase relaxes slowly to a pseudoisotropic texture. It is optically uniaxial positive. Occasionally there are schlieren domains that take a longer time to relax. When a strong magnetic field is applied normal to the pseudoisotropic sample, a schlieren texture forms with convergence points having four dark brushes (Figure 2). A more uniform schlieren texture is obtained when the sample is left in the field for several hours.

The N_C phase remains in the schlieren texture. Its surface alignment is accordingly parallel in contrast to the N_L phase, which has perpendicular surface alignment. By applying a magnetic field parallel to the sample plane a uniformly aligned sample is obtained with the optical axis parallel to the field direction. When the magnetic field is applied perpendicular to a uniformly aligned sample, the texture changes first to a regularly spaced stripe pattern with the stripes perpendicular to the original alignment axis (Figure 3). Gradually dark areas develop which are separated by inversion walls. Eventually, the whole sample assumes a quasi-pseudo-isotropic texture. The experiment shows that the N_C phase is also uniaxial. It is optically negative while its diamagnetic anisotropy is positive. The pseudoisotropic texture of

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[8] Funds for the equipment were obtained in part through the National Science Foundation, Grant GP-10481.

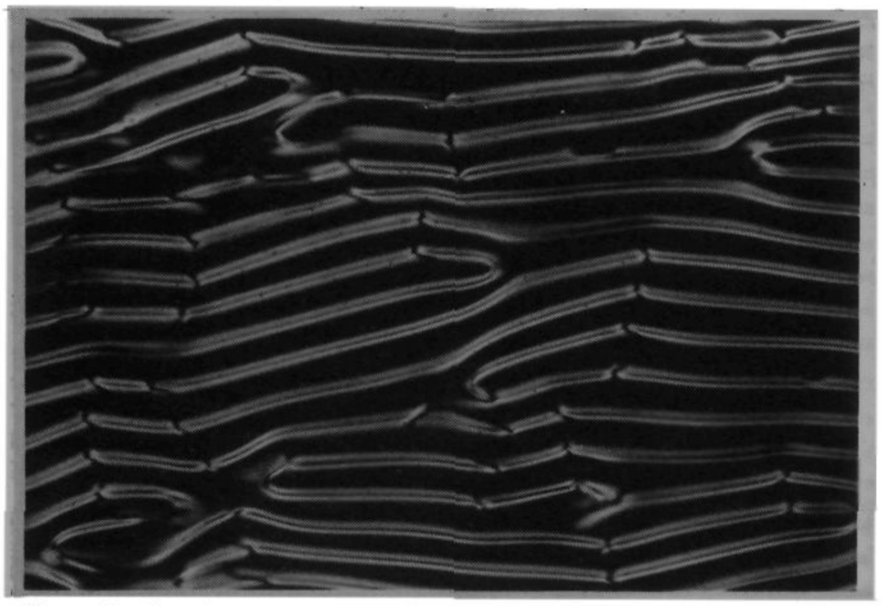

Figure 3. N_C phase texture, obtained after applying a magnetic field for 5 min normal to the plane of a planarly aligned sample, 0.3 mm thick, 60×, crossed polarizers.

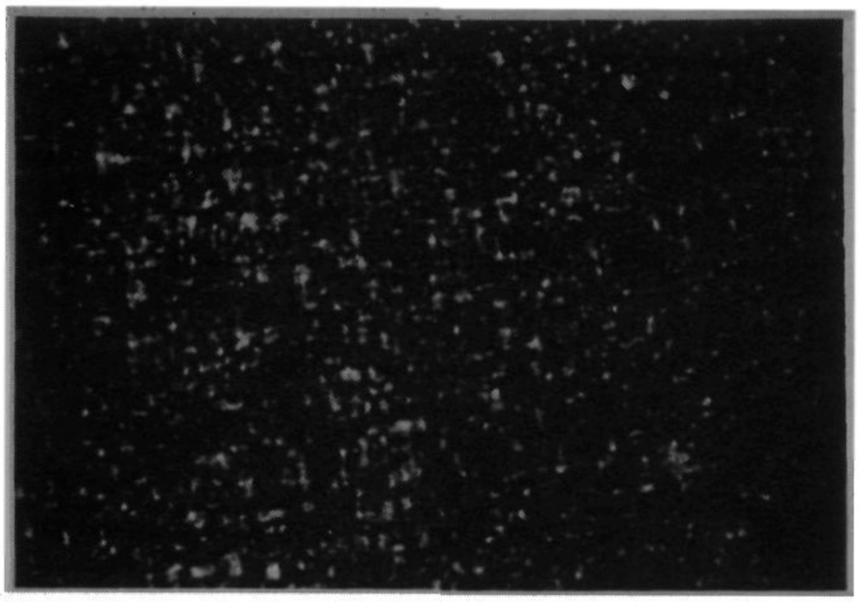

Figure 4. $N_L \rightarrow N_C$ phase transition. Birefringent areas of N_C phase in pseudoisotropic N_L phase, 0.3 mm thick, 60×, crossed polarizers.

the N_C phase changes slowly back to the schlieren texture when the sample is left outside the magnetic field. Figure 4 shows a typical texture formed at the N_L–N_C transition on heating. Birefringent areas of N_C phase appear when the pseudoisotropic texture of the N_L phase is brought to the transition temperature.

The opposite optical signs and the opposite diamagnetic anisotropies confirm the proposed structures. In the N_L phase with micelles of bilayer structure the surfactant molecules are aligned preferably parallel to the optical axis but in the N_C phase with micelles of a cylindrical structure they are preferably perpendicular to it. For NaDS the optical polarizability will be somewhat larger along the molecular axis than perpendicular to it. The same can be expected for the absolute value of the diamagnetic susceptibility. The optical sign of N_L is as expected the same as that of the lamellar neat soap while that of N_C is the same as that of middle soap.

The observed surface alignment can also be explained readily. The glass surfaces are coated by a surfactant layer so that the polar head groups are pointing outward. The interaction is repulsive. Neighboring micellar aggregates will accordingly tend to align so that their long axes, in case of cylinders, or their planes, in case of disks, are parallel to the interphase. This reduces for a given distance the electrostatic repulsion from the surface. An aggregate that is not aligned this way will in fact experience a torque that tends to turn it parallel to the interphase.

V. Phase Diagram

Figure 5 shows the temperature and concentration ranges of the various phases. The data were obtained with samples 1–6 and 11 for which the concentration of decanol is 7.0 wt %. Table II gives the transitions for a few mixtures with different decanol concentrations. The classification of the smectic phases has been made by textures.

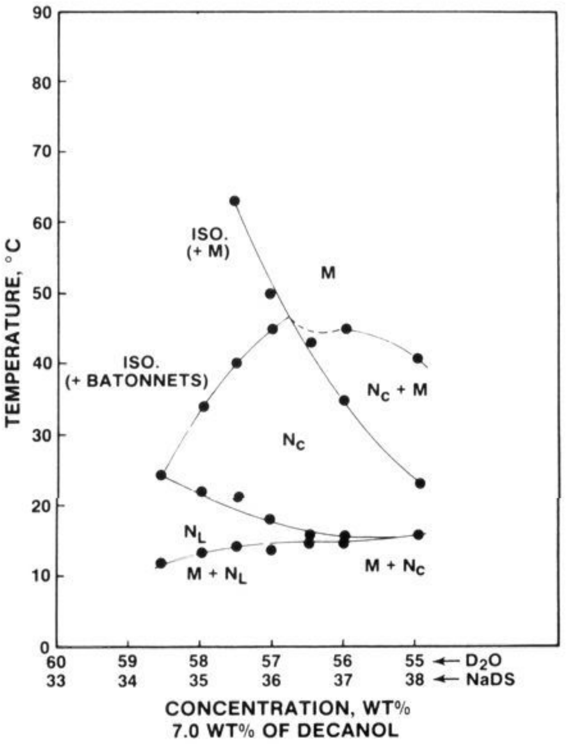

Figure 5. Phase diagram of the mixtures containing 7.0 wt % of decanol. M: middle soap. N_L and N_C: nematic. Iso: isotropic solution.

Table II. Phase Transitions of Ternary Mixtures Containing Other Than 7.0 wt % of Decanol[a]

sample no.	transition temp, °C
7	$M + N_L \overset{13}{\text{—}} N_L \overset{23.5}{\text{—}} N_C \overset{33.6}{\text{—}} N_C + B \overset{39}{\text{—}} \text{Iso}$
8	$M + N_L \overset{14.5}{\text{—}} N_L \overset{18}{\text{—}} N_C \overset{34.5}{\text{—}} \text{Iso} \overset{60}{\text{—}} \text{Iso} + M$
9	$M + N_L \overset{15}{\text{—}} N_L \overset{16}{\text{—}} N_C \overset{26}{\text{—}} N_C + M \overset{46.8}{\text{—}} M$
10	$M + N_L \overset{15}{\text{—}} N_L \overset{16}{\text{—}} N_C \overset{40}{\text{—}} N_C + M \overset{46.5}{\text{—}} M$

[a] M: middle soap. B: neat soap batonnets. Iso: isotropic.

On cooling the N_L phase makes a first-order transition to a middle soap. No batonnets are formed at this transition. The middle soap nucleates at the glass interface and forms the typical fan texture. The temperature range of the N_L phase narrows with decreasing D_2O concentration. The phase disappears at about 54 wt % of D_2O. The N_C phase transforms then directly to the middle soap on cooling.

The N_C phase of samples 2–4 (see Figure 5) transforms on heating to an isotropic phase with small batonnets that probably belong to neat soap. The batonnets disappear on further heating and a middle soap fan texture starts to grow. On heating still futher the material beomes isotropic before a complete transformation to middle soap has taken place. The phase boundaries for this partial transformations are not clearly defined and they are not shown in Figure 5. Sample 5 transforms on heating the middle soap at 43 °C. The transition is of first order. When the D_2O concentration is lowered further, batonnets form in the N_C phase at the transition to middle soap and there is an extended range over which the two phases coexist.

The results summarized in Table II show that the N_L–N_C transition occurs also with slightly different decanol concentrations. However, mixtures with more than 7.5 wt % decanol form two layer solutions at room temperature. The top layer is neat soap. The bottom layer changes at constant decanol concentration with decreasing D_2O concentration from an isotropic micellar solution to N_L and then to N_C. With decanol concentration below 6.5 wt % the mixture changes with decreasing D_2O concentrations from viscous isotropic to N_C and to middle soap. At lower temperatures the phase boundaries shift toward the side of lower D_2O concentration.

VI. Cholesteric Micellar Solutions

Cholesteric phases were obtained with both nematic phases by addition of brucine sulfate heptahydrate (BS). The addition of BS results in an elevation of the temperature for the bilayer micelle–cylindrical micelle transition and a descent of the tem-

Table III. Induced Twist ($1/P$) and Twisting Power ($1/PM_a$)[a]

	trans. temp, °C		$1/P$, cm^{-1}		$1/PM_a$, 10^3 cm^{-1}	
M_a	Ch_L-Ch_C	batonnet formation	Ch_L	Ch_C	Ch_L	Ch_C
0.412	22	36	244 (18.5)[b]	96.3 (26)[b]	59.2	23.2
0.547	26	33	293 (24)[b]	147 (28.5)[b]	53.6	27.8
0.615	28	33	337 (24)[b]	176 (32)[b]	54.8	28.6
1.116		30	732 (24)[b]		65.6	

[a] M_a = mol % of BS, based on the total amount of NaDS, decanol, and BS. [b] Temperature (°C) at which measurements were made.

Figure 6. Texture of coexistent cholesterics. Domains with smaller fingerprint texture, Ch_L, are separated by sharp boundaries from the large fingerprint pattern, Ch_C, 0.3 mm thick, 60×, crossed polarizers.

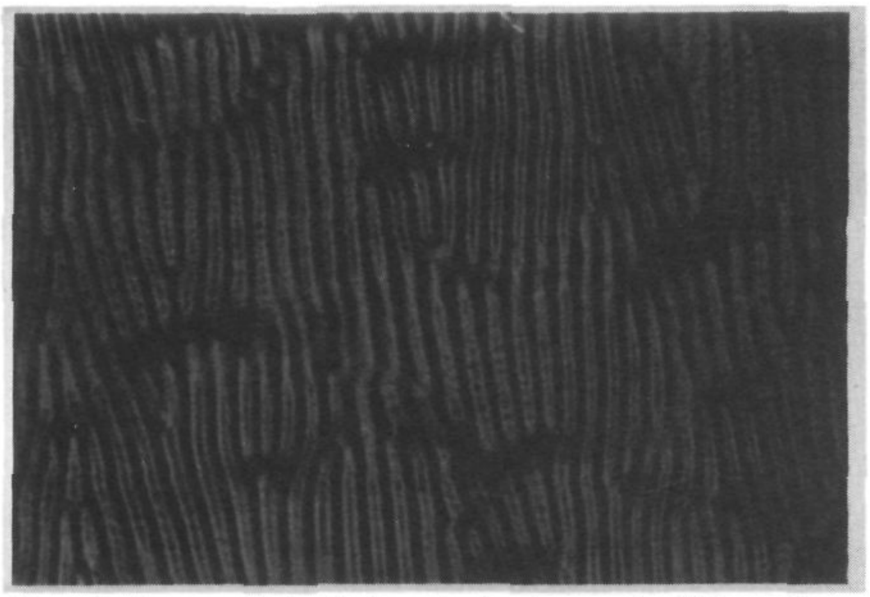

Figure 7. Texture obtained after spinning the sample of Figure 6 vertically to the magnetic field for 8 h. Spinning axis coincides with the long edge of the picture, 0.3 mm thick, 60×, crossed polarizers are slightly rotated.

perature for neat soap batonnet formation. The shifts are roughly 3 °C per 0.2 mol % of BS (based on the toal amount of NaDS, decanol, and BS). The transition temperatures changed slowly with increasing age of the sample. We denote the two cholesteric phases as Ch_L and Ch_C corresponding to the nematic phases from which they result.

The Ch_L phase can be readily aligned with a magnetic field. The twist axis turns parallel to the field. A Grandjean texture or a fingerprint pattern with parallel stripes can be produced in this way depending on the direction of the field, being perpendicular or parallel to the plane of the film. The Ch_C phase is untwisted in sufficiently strong magnetic fields. Regularly aligned fingerprint patterns could, however, be obtained by the following procedure. A uniformly aligned nematic phase was first produced by applying the magnetic field in the plane of the sample. After removal of the field an irregular fingerprint pattern develops. The fingerprint pattern was then aligned by bringing the sample back into the magnetic field and spinning it around an axis that is in the sample plane and vertical to the magnetic field. The aligned fingerprint textures were used to determine the pitch, which is equal to twice the distance between the stripes.

Samples that show a Ch_L–Ch_C transition can be obtained with appropriate concentrations of BS. On heating the Ch_L phase a formation of droplets begins at the transition. The droplets gradually coalesce and form larger areas that usually show fingerprint patterns (Figure 6). Such samples with coexistent cholesteric phases can also be aligned with magnetic fields to a certain extent. An example is shown in Figure 7. The twist changes discontinuously at the transition. It is about twice as strong in the Ch_L phase as in the Ch_C phase under comparable conditions. This is also demonstrated by the data in Table III.

VII. Conclusion

The NaDS/decanol/water system is the first system in which a phase transition between two nematic phases has been observed. There is only a relatively narrow concentration range over which two nematic phases are formed. In the same range a reentrant middle soap can also be found. Both nematic phases are uniaxial but they have opposite signs of optical and diamagnetic anisotropies. The structure of the micelles changes at the transition from a bilayer structure to a cylindrical structure. It is in this respect similar to the transition between neat soap and middle soap. The bilayer structure of the micellar aggregates has been confirmed recently by X-ray scattering[9] on a similar system.[10] The transition is first order but there are pronounced pretransitional effects as the NMR studies show.

In contrast to the smectic phases the nematic phases have no periodicity in the molecular distribution. The surfactant aggregates in the N_L and N_C phases are micelles of a finite size. The latter conclusion is based on the curvature elastic and viscous properties. The curvature elastic properties of an N_L phase have been quantitatively studied.[11] No measurements have been made so far on an N_C phase but the textures indicate that splay and twist deformation constants are of the same magnitude. It excludes the possibility that the N_C phase is a "polymeric" nematic, as defined by de Gennes.[12] In that case it would differ from a middle soap by the absence of a hexagonal lattice but the aggregates would still form cylinders of a quasi-infinite length. Such a structure is not compatible with the readily observable splay deformations.

The periodic structure (Figure 3) that forms in the N_C phase when a strong magnetic field is applied vertically to a thin film is a transient effect that can be explained in terms of the Leslie–Ericksen theory of nematic systems. Because of the coupling between director reorientation and flow, periodic modes where the director tilts in opposite directions in adjacent domains can grow faster than a uniform tilt mode. It is necessary for the development of the periodic modes that the applied field is much higher than the threshold field.

The mechanism that induces the transition to a cholesteric phase in the presence of chiral compounds is not yet understood. Two

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(9) After submission of this paper an X-ray and optical study covering both nematic phases was published: Charvolin, J.; Levelut, A. M.; Samulski, E. T. *J. Phys.* (*Paris*) **1979**, *40*, L-587.

(10) Amaral, L. Q.; Pimentel, C. A.; Tavares, M. R.; Vanin, J. A. *J. Chem. Phys.* **1979**, *71*, 2940.

(11) Armitage, D.; Haven, T.; Radley, K.; Saupe, A., presented at the 7th International Liquid Crystal Conference, Bordeaux, France, 1978.

(12) de Gennes, P. *Mol. Cryst. Liq. Cryst. Lett.* **1977**, *34*, 177.

possibilities have been considered:[7] the twisting may be caused by the interaction between the micelles through dispersion forces or the primary effect of the chiral compound may be to distort the micelles so that they themselves assume a chiral structure. Theoretical considerations show that disk-shaped micelles are distorted in first order with the concentration of a chiral compound while cylindrical micelles do not have a first-order effect.[13] The observation that the twisting power of BS is indeed stronger in the N_L phase is in agreement with this conclusion. We intend to verify the importance of the second mechanism by a more extensive study of the concentration dependence of the induced twist in the N_C phase.

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(13) Allender, D.; Saupe, A., to be published.

Self-Inverse and Non-Self-Inverse Degenerate Isomerizations

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Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. *Received January 14, 1980*

Abstract: All possible degenerate isomerizations of any chemical structure can be rigorously separated into two classes on the basis of an intrinsic group-theoretical symmetry property of the structure and its $3N$-dimensional coordinate space. These classes are as follows: (1) self-inverse (SI) degenerate isomerizations for which there is a coordinate-space symmetry which exchanges reactants and products and (2) non-self-inverse (NSI) degenerate isomerizations for which there is no such coordinate-space symmetry. SI processes always have forward and reverse paths between reactant and product which "look alike". NSI processes do not generally have such "look alike" paths. Following others' earlier results on symmetry properties of saddle point transition states directly connecting reactant and product by paths of steepest descent, it is shown that SI processes can in principle proceed through such transition states with symmetries which exchange reactant and product. NSI processes can never proceed through such transition states with any more symmetry than that common to reactant and product. While NSI possibilities are statistically more abundant, SI processes tend to be favored for structures with any symmetry because of limitations on the kinds and orientations of symmetries possible in three-dimensional space, thus confirming empirical observations. The two classes could be conveniently differentiated experimentally in favorable cases by using two-dimensional NMR, and rules for predicting idealized spectra are given.

Degenerate isomerizations can be defined as those chemical reactions which lead to products differing from the reactants only by permutation of identical atoms and possible mirror-image reflection.[1] This definition encompasses cases in which both reactants and products include more than one molecule. While such reactions form a small subset of all possible reactions, they have been well studied in their own right.[1] It is the intention of the present work to show that degenerate isomerizations of structures with N atoms can be rigorously divided into two classes on the basis of an intrinsic symmetry property of the $3N$-dimensional coordinate space describing all possible arrangements of the N atoms. The symmetry group of this coordinate space includes all the possible permutations of identical atoms in the set of N atoms along with the operation of overall coordinate inversion. It is this subgroup of the overall symmetry group of the coordinate space (which also includes spatial rotations and translations) that will be explicitly considered here. Operations in this symmetry group will permute the possible products and reactants of degenerate isomerizations.

The present work is divided into five principal sections. The first section describes the representations of symmetry operations and isomerizations necessary to visualize the later results. The second section presents the intrinsic symmetry property of the coordinate surface which allows the classification of degenerate isomerizations into two types and discusses the effect of the coordinate surface symmetry operations on the possible paths connecting the reactants and products of degenerate isomerizations. The third section discusses properties of intermediates and transition states for the two possible types. Here the potential energy surface is considered in addition to the coordinate space. The fourth section addresses the question of whether either type of degenerate isomerization is likely to be preferred (either statistically or energetically). The final section discusses experimental differentiation of the two types, primarily by two-dimensional NMR.

Table I. Correlation of Group-Theoretical Concepts and Their Chemical Representations

group-theoretical concept	chem representation
cosets	isomers based on atom numbering
right multiplicatn based on ref numbering	degenerate isomerizatns
left multiplicatn based on atom nos.	coordinate-space sym

1. Representation

It is necessary to choose a representation of the coordinate-space symmetry operations and isomerizations to work with and to aid visualization of the results of this work. McIver and Stanton have noted a difficulty with this visualization of permutation operations in their work on the symmetry properties of transition states.[2] It should be noted that other representations are possible but that the key result is intrinsic to the underlying group-theoretical structure and does not depend on the particular representation chosen. Three features of this representation must be described along with their correspondence to chemical concepts. These are summarized in Table I.

In any given structure all the atoms are numbered to distinguish them. In addition, one of the possible isomers (based on the atom numbers) of the structure being considered is chosen as a reference

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(2) Stanton, R. E.; McIver, J. W., Jr. *J. Am. Chem. Soc.* **1975,** *97,* 3632.