Molecular Crystals and Liquid Crystals

Mesomorphic Behaviour of Dodecyl Benzene Sulfonic Acid and Its Sodium Salt

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X-ray and optical studies in the paper show that dodecyl benzene sulfonic acid and the mixtures of its sodium salt with (i) water and (ii) methane sulfonic acid exhibit the smectic A phase. Interference studies are described in the paper to establish the molecular orientation in the droplets and batonnets.

INTRODUCTION

The mesomorphic behaviour of soaps, synthetic detergents and esters of organic acids had been studied earlier by many investigators.[1-11] However, it is found that detailed studies have not been carried out so far on the mesomorphic behaviour of dodecyl benzene sulfonic acid and its sodium salt. Dodecyl benzene sulfonic acid (DBS), produced by the sulfonation of dodecyl benzene, is used in the large scale manufacture of sodium dodecyl benzene sulfonate (NaDBS), the latter being a principal component in detergent formulations. Dodecyl benzene sulfonic acid is a thick highly viscous compound with a brown honey-like colour. The structural formula of DBS is shown in Figure 1. In view of the presence of the benzene ring and the long
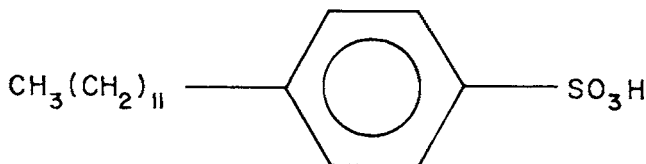

FIGURE 1   Structural formula of dodecyl benzene sulfonic acid.

chain of methylene groups, it was felt by us that DBS might exhibit meso-
morphism. In fact, it is found that DBS is liquid crystalline and belongs to
the smectic type of liquid crystals.

Sodium dodecyl benzene sulfonate has surface active properties and
forms micellar solutions[12] and it is found to be lyotropic, as is to be expected.
In parts A and B of the following are presented the results of our investiga-
tions on these two compounds. The substances studied here are found to
exhibit striking optical textures. In view of the importance of the optical
textures with regard to the identification of mesophases, we have selected
some of the most striking photographs for reproduction in this paper.

Part A

DODECYL BENZENE SULFONIC ACID

A(1)   Preliminary observations

The substances used in these investigations were obtained from M/s Tata
Oil Mills Co., Ltd., Bombay, who produce them on a large scale. The sample
of DBS had the following approximate composition: 95 percent of active
DBS, 2 percent of free sulfuric acid, 2 percent of unsulfonatables and 1 per-
cent of traces of other impurities. In order to minimize the content of water
in DBS, the sample was kept in a desiccator for several days. The density of
this sample of DBS was determined at different temperatures using the
capillary tube method described in an earlier paper.[13] The variation of the
density with temperature is shown graphically in Figure 2. The experimental
determinations are accurate to within ± 0.001 gm/cm^3. In Figure 2, there
is a point at 115°C showing the value of the density in the isotropic phase at
that temperature. This value is distinct and discontinuous from all other
values at lower temperatures owing to the discontinuous change in density
which occurs during the transition from mesomorphic to isotropic phase.

When a thin film of the sample of DBS 25°C, kept between a microscope
slide and cover glass, was observed through the polarizing microscope
(between crossed polars), almost the entire field of view was found to remain
dark when the stage containing the specimen was rotated. However, at
the edges of the sample, over small areas, restoration of light was observed,
indicating the birefringent nature of the substance. When the cover glass
was slightly displaced, it was found that in some of those regions which were
originally dark, there appeared restoration of light as a consequence of the
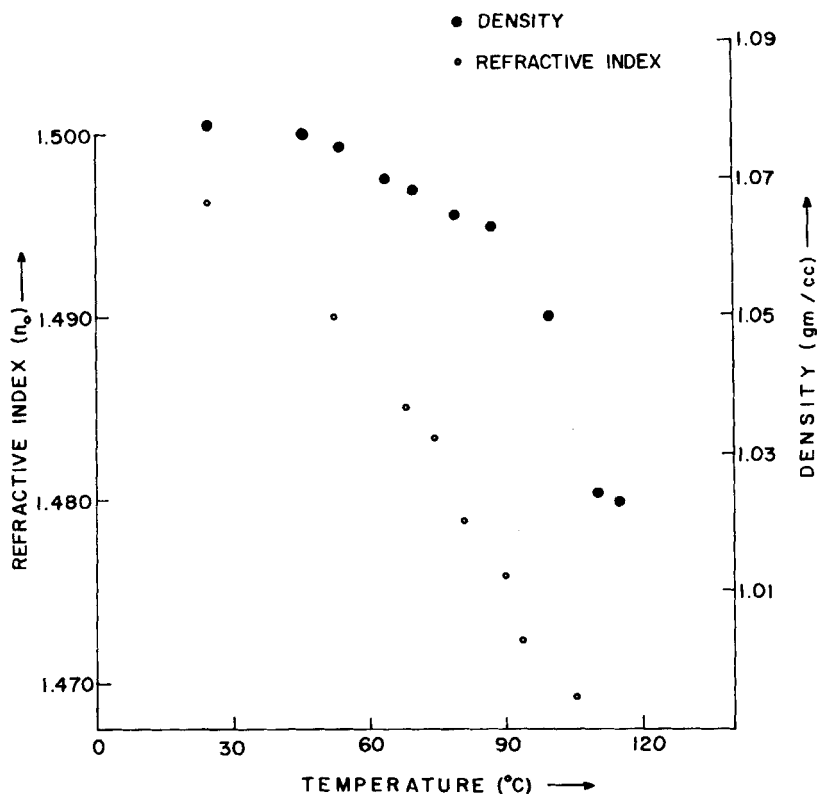
FIGURE 2   Variation of density and the ordinary refractive index of DBS with temperature.

disturbance of the molecular arrangement. The areas which were originally dark were readily inferred to correspond to the well-known homeotropic regions, wherein the molecules are arranged with their long axes normal to the surface of the microscope slide and cover glass. In fact, it was found that characteristic textures exhibiting birefringence developed in the course of several hours, when the homeotropic specimen was left at room temperature. The birefringence persists over a wide range of temperature and the transition point from the birefringent to the isotropic phase was determined by observing the specimen kept in a hot stage. The temperature at which the birefringence disappeared was determined to be $110 \pm 0.5°C$, this temperature being the clearing point of the sample.

A sample of DBS of about one millilitre in volume was taken in a double walled glass container and allowed to cool from a temperature of 140°C. The space between the two walls of the container was kept continuously evacuated during the cooling. A graphical plot of the temperature versus

time exhibited a plateau at 110°C, in confirmation of the occurrence of the phase transition here. The details of the experimental technique are described in an earlier study.[3]

A(2)   X-ray studies

An X-ray diffraction photograph of DBS, in the forward direction was obtained at room temperature, using a flat film camera. The sample of DBS was taken in the form of a thin film on a loop of platinum wire. $Cu-K_\alpha$ radiation was used. Figure 3 exhibits the diffraction pattern obtained with the sample. The diffraction pattern consists of two low angle rings with effective spacings of 26.5 and 13.3 Å indicating that they correspond to the first and second order of diffraction from the same set of planes. There is also a very diffuse outer ring at a larger angle and corresponding to a spacing "d" of about 4.6 Å, calculated using the formula $2d \sin \theta = \lambda$. The homeotropic textures as well as the presence of a diffuse outer ring and the sharp rings at the lower angles clearly confirm that here DBS is in the smectic A phase.[14,15] The outer ring is diffuse owing to the fact that within each smectic layer there is no exact regularity in the arrangement of the molecules in the lateral directions lying in the plane of each layer. The effective spacing of 26.5 Å mentioned above is the smectic layer spacing and corresponds approximately to the estimated molecular length of DBS which is about 25 Å. There is a small difference and such differences have been reported in several cases.[15,16] The origin of the difference here is not quite clear and more detailed investigations are required with regard to the structure of the substance.
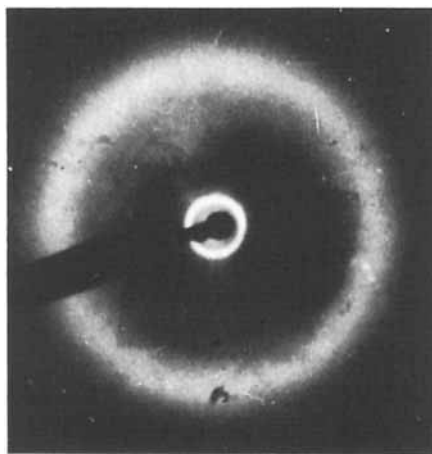

FIGURE 3   X-ray diffraction photograph of DBS at 25°C.

A(3) Optical textures in DBS

In order to observe the textures, the following experimental procedure was adopted. A thin film of the substance was taken between a microscope slide and cover glass. No spacer was used. The specimen was kept inside a hot stage, the temperature of which was initially slightly higher than the clearing point of DBS, i.e., slightly greater than 110°C. The temperature of the hot stage was slowly reduced at the rate of about 2°C per hour and the textures that were growing were observed through the polarizing microscope. At a temperature immediately below the melting point of DBS, when the sample was observed between crossed polars, the entire field of view was dark, corresponding to the entire region being homeotropic. When the temperature had fallen to about 50°C, "batonnets" with characteristic cylindrical symmetry, grew out of the homeotropic regions and with efflux of time they coalesced and formed the fan-shaped textures. Figure 4(a) is an enlargement of a batonnet. In Figure 4(b) may be seen the different stages of the growth viz., (i) the dark homeotropic region on the left, (ii) the batonnets at the centre and (iii) the fan-shaped texture on the right. These features are characteristic of the smectic mesophase. When the sample was left for a day at room temperature, fan-shaped textures and focal conic textures with typically identifiable polygons were found to have developed over the different areas of the specimen. An enlargement of the focal conic texture is reproduced in Figure 4(c). Often, birefringent "droplets" were found within homeotropic regions. When observed between crossed polars these droplets exhibit the typical cross as shown in Figure 5(a). Some other features characteristic of the smectic mesophase have also been observed by us. In particular, with a thick specimen (prepared by using a spacer of thickness of about 100 μ) a characteristic texture with the ellipses and the typical brushes was observed as in Figure 5(b). This photograph was obtained by focusing the upper surface of the specimen. Another texture which was frequently observed was the so-called "oily streaks" appearing as striated bands as shown in Figure 5(c). This texture appeared only when the cover glass over a specimen (exhibiting the focal conic texture) was disturbed by slightly pressing or displacing it.[2] Quantitative optical interference studies were carried out in order to establish the nature of the molecular ordering in batonnets and "droplets" and these aspects are discussed in detail in the following section.

A(4) Optical interference studies

When a birefringent material held between crossed polars, is observed through a spectroscope, the spectrum of white light transmitted through the system consists of a series of dark bands. When the polarizer and analyzer
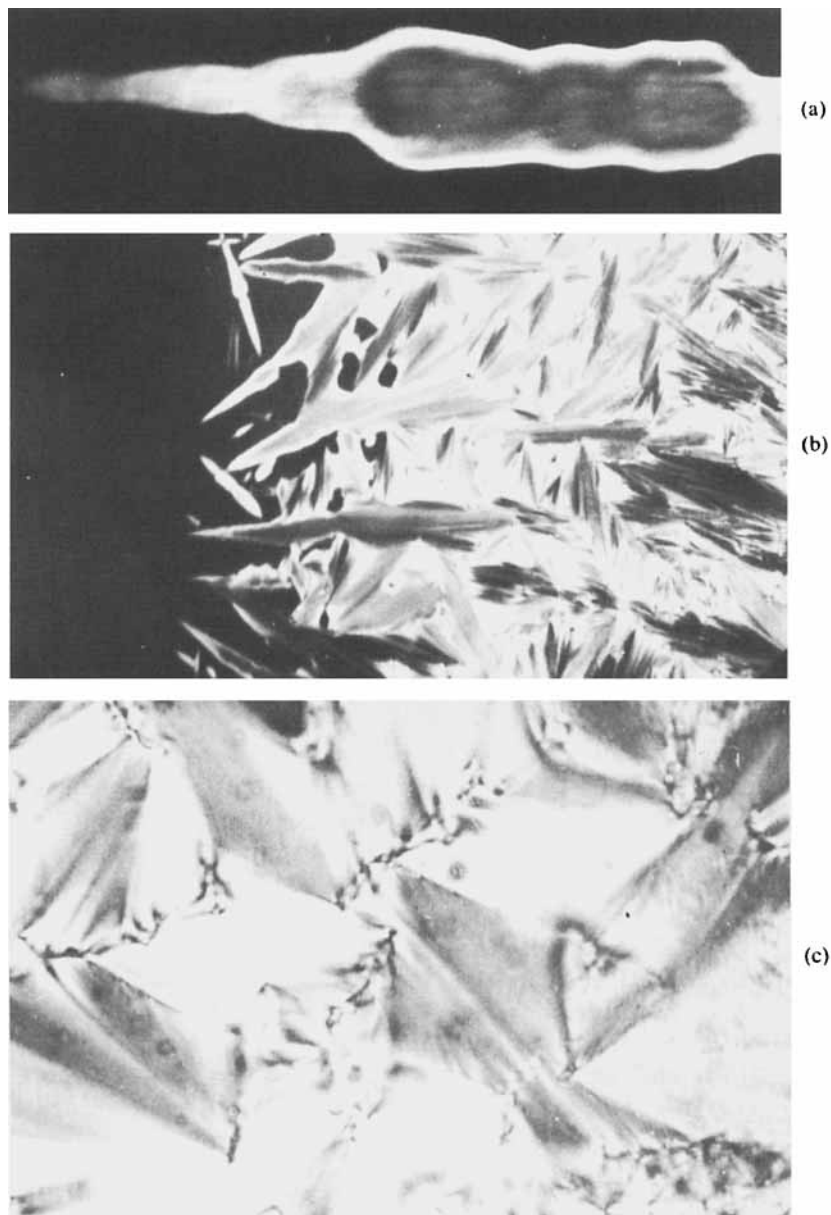
FIGURE 4   Microphotographs of (a) batonnet (360x), (b) fan shaped texture and batonnets (60x) and (c) focal conics (240x), obtained with DBS (between crossed polars) at 25°C.
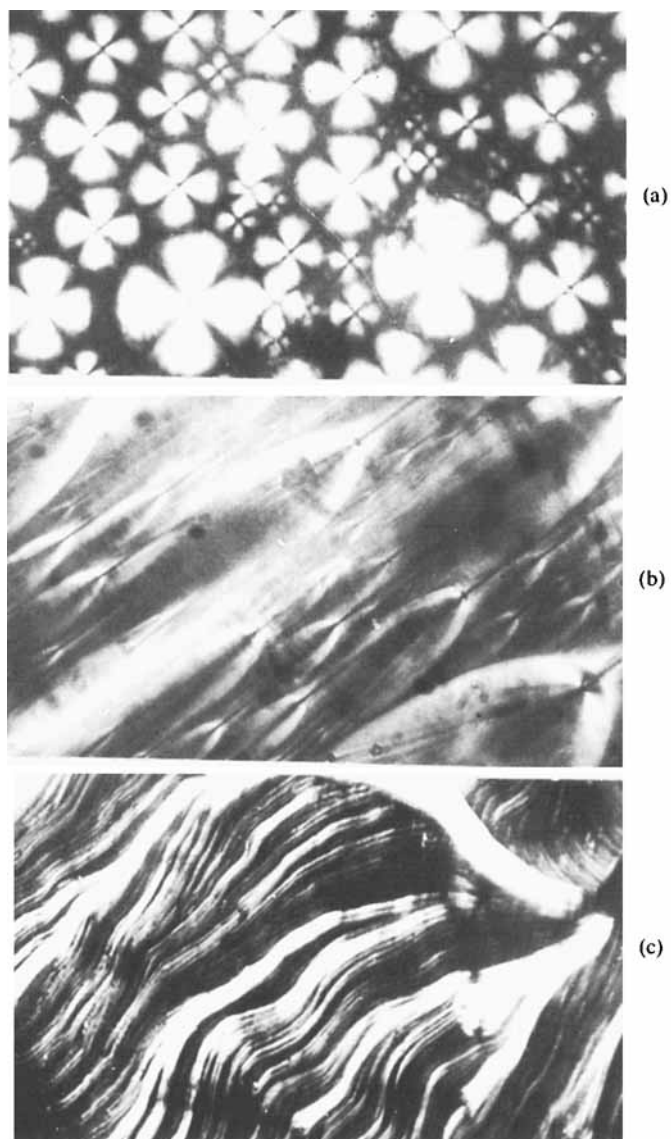
FIGURE 5 Microphotographs of (a) birefringent droplets (540x), (b) focal conic domains exhibiting the ellipses (180x) and (c) oily streaks (60x), obtained with DBS (between crossed polars) at 25°C.

make angles of 45 and 135° with the principal vibration directions of the birefringent material, the wavelengths (λ) of the extinctions observed, satisfy the equation[17,18]

$$m\lambda = t_1\Delta n_1 \tag{1}$$

where m is an integer, t_1 is the thickness of the birefringent material and Δn_1 is the birefringence. In fact, if two birefringent samples are there, with their principal directions making 45 and 135° to the polarizer and analyzer, the wavelengths of the extinctions are given by

$$m\lambda = t_1\Delta n_1 \pm t_2\Delta n_2. \tag{2}$$

Here, the subscript 2 refers to the second birefringent material. The positive sign is applicable when the fast directions of the two birefringent materials are along the same direction. The negative sign is used when the fast direction of one material is parallel to the slow direction of the other material (and vice versa).

The interference studies were carried out using the experimental arrangement which consisted of the following elements set up in sequence: (i) A source of white light (sunlight or filament lamp), (ii) condensing lens, (iii) polarizer at 45° to the vertical, (iv) a birefringent specimen of a cleavage plate of $BaSO_4$ with its slow direction along the horizontal, (v) aperture, (vi) second birefringent specimen, i.e., the optical texture to be studied, (vii) travelling microscope used to focus the enlarged image of the texture on the slit of the spectrograph, (viii) analyzer crossed with the polarizer and (ix) spectrograph. An identical experimental arrangement may be found to be described in detail in two earlier papers from this laboratory.[18,19]

a)   Molecular orientation in the batonnets

It is well known that the batonnets are classified as G batonnets, and M batonnets.[1] In the G batonnets, the smectic layers are normal to the central long axis of the batonnet, so that here the optic sign is positive. On the other hand, in the M batonnets, the long axes of the molecules are transverse to the central axis and the molecules are so arranged that their long axes encircle the central axis. Figure 6(a) reproduces the spectrogram obtained when a batonnet (which had its long axis perpendicular to the length of the slit) was focused on the slit of the spectrograph. The regions outside the batonnet were homeotropic regions. It may be noticed from the figure that at the centre of the spectrum, the dark bands have shifted towards the red end of the spectrum (on the left). This indicates that the batonnet has introduced a positive contribution associated with the second term of Eq. (2) and hence the long axis of the batonnet should correspond to the
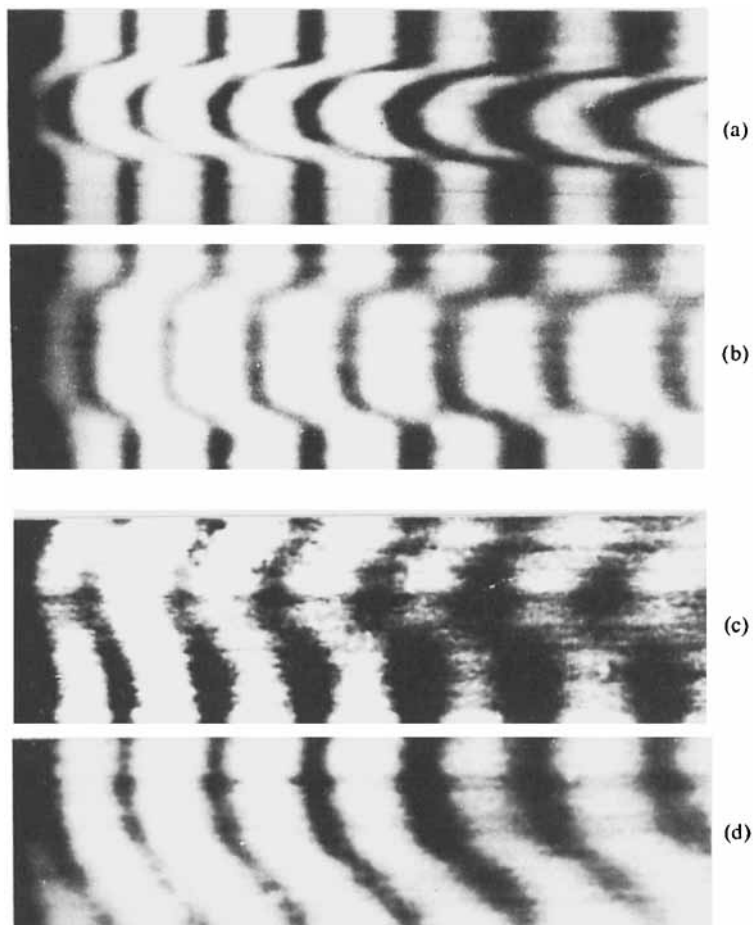
FIGURE 6   (a) and (b). Banded spectrum obtained with a crystal of $BaSO_4$ and a batonnet of DBS kept across the slit, showing respectively the gradual and abrupt shift of the bands towards the red. (c) and (d). Banded spectrum obtained with a crystal of $BaSO_4$ and a droplet of DBS, showing the shifts towards the red and blue respectively.

direction of the higher refractive index or the slow direction. On the other hand, if the batonnet was focused on the slit of the spectrograph, with its long axis parallel to the length of the slit, the dark bands are found to shift towards the short wavelength side. The batonnets here are identified as "G" batonnets because only in this case the molecules have their long axes parallel to the length of the batonnet which is the direction of the higher refractive index. Since the batonnets are usually cylindrical in shape, for the

beam passing through the center of a batonnet, the optical thickness is a maximum and for beams passing on either side of the centre, the optical thickness decreases progressively and becomes zero at the edge. From Figure 6(a), it may be seen that in each band the shift towards the red increases smoothly, reaches a maximum and beyond that the shift smoothly decreases to zero. This feature is observed only in the cases, where the diameters of the batonnets are less than the thickness of the layer of the specimen between the slide and cover glass. As the batonnets grow bigger, they ultimately become flattened and acquire an approximately oval cross section. Therefore, in such cases each interference band exhibits an almost abrupt shift at the points corresponding to the edge of the batonnet. The shift of each band is practically constant over the entire batonnet. This feature is shown in Figure 6(b) which was obtained with another batonnet of different thickness.

In the case of those batonnets for which the shift is maximum at the centre and decreases smoothly on either side, it is reasonable to assume that the maximum thickness of the batonnet corresponds to its diameter. Hence, from measurements of the diameters and the maximum shifts, the birefringence of the substance was calculated. If one assumes that the dispersion of the birefringence may be neglected, it follows that

$$m\Delta\lambda = t_2\Delta n_2, \tag{3}$$

where $\Delta\lambda$ is the shift and m is the order of interference. Here, t_2 corresponds to the diameter of the batonnet. At first, the wavelengths (λ) of the straight bands of extinction (observed when only $BaSO_4$ was used) were determined. Next, the wavelengths of the maximum shift ($\Delta\lambda$) were determined. The order m may be determined by plotting on two strips of graph sheets, $\log_e(1/\lambda)$ and $\log_e m$ respectively, and by matching these two strips to get the best coincidences of the plotted values on the two strips. The values of $\Delta\lambda$ for any chosen m are found to be proportional to the diameters of the batonnets, as may be seen from the graph in Figure 7. Using the known values of the diameters of the batonnets, it is calculated that the birefringence Δn_2 for 5780 Å (at 25°C) is equal to 0.015.

The temperature variation of the ordinary refractive index in the case of the same specimen of DBS was determined using the hollow prism method[13] and the values are represented graphically in Figure 2. It was not possible to measure the extraordinary refractive indices (n_e) directly by the same method, because of the fact that we could not obtain any other homogeneously oriented textures other than the homeotropic textures. If we assume the value of Δn_2 given above and the value of n_0 (1.496) at 25°C, the value of n_e at 25°C for 5780 Å turns out to be 1.511. It is well-known that the mean polarizability ($\bar{\alpha}$) of the molecule may be calculated by using the Born
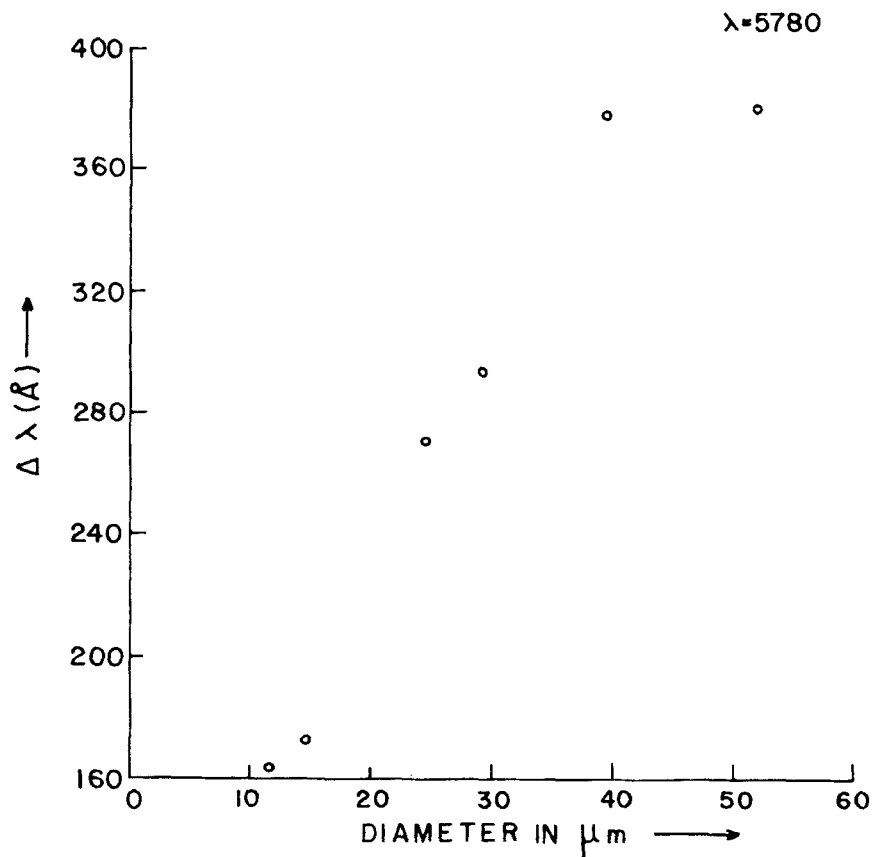
FIGURE 7   Variation of the wavelength shifts of the bands with the diameter of the batonnets of DBS.

relation[20] viz.,

$$\frac{\overline{n^2} - 1}{\overline{n^2} + 2} = \frac{4\pi N \bar{\alpha}}{3}, \tag{4}$$

where $\overline{n^2} = (n_e^2 + 2n_o^2)/3$ and N is the number of molecules per unit volume. The value of the mean polarizability of the molecule was calculated using the values of the density at $25°C$ and the refractive indices $n_e(= 1.511)$ and $n_o(= 1.496)$ at $25°C$. This value turns out to be 35.4×10^{-24} cm^3. The value of $\bar{\alpha}$ calculated from the refractive index $n_1(= 1.468)$ and the density $(= 1.022)$ at $113°C$ in the liquid (isotropic) phase, using the Lorenz-Lorentz relation, is found to be 35.20×10^{-24} cm^3, in good agreement with the value calculated using the Born relation. From the values of the extra-ordinary and ordinary refractive indices (n_e and n_o) in the case of DBS at

room temperature, it is possible to estimate the value of the polarizability anisotropy ($\Delta\alpha$) of the molecule of DBS, using the Vuks formulae.[21] Here, $\Delta\alpha$ is found to be positive and has a value equal to 1.3×10^{-24} cm^3.

b)   Molecular orientation in droplets

The molecular orientation in the droplets mentioned earlier, was also studied using the interference technique described above. It is well known that in G droplets the smectic layers form concentric shells like the layers of an onion.[1] Here, the long axes are parallel to the radial direction of the sphere. When the edge of the droplet (on the right or on the left-hand side) corresponding to the azimuthal angle 0 or 180° is brought to focus on the slit of the spectrograph, the straight bands should shift towards the red. For different points of the slit, the shift should be different owing to the varying thickness of the material at the edge of the sphere. The shift towards the red increases progressively, reaches a maximum and decreases to zero, as shown in Figure 6(c). The top and bottom regions of the spectrum correspond to the homeotropic regions outside the droplet and there is no shift associated with the homeotropic region owing to Δn_2 being equal to zero here. On the other hand, when the edge of a droplet (near the top or bottom) corresponding to the azimuthal angle 90 or 270° is brought into focus on the slit of the spectrograph, the straight bands corresponding to the homeotropic region may be expected to shift towards the blue and Figure 6(d) exhibits this shift.

Light scattering patterns also provide information regarding the molecular orientation. Scattering patterns arising from spherical droplets were photographed using the same technique as was adopted by Rhodes et al.[4] When the polarizer and the analyzer are vertical, the pattern obtained is referred to as the V_v pattern. When the polarizer is vertical and the analyzer is horizontal, the pattern obtained is referred to as the H_v pattern. From the theory of Clough et al.,[22,23] it is known that when the optic axial directions (long axes) make an angle of nearly 0 or 90° to the radial direction of the droplet, the scattering pattern H_v should exhibit maxima around the azimuth $\pm45°$ and the V_v pattern should appear as a vertical cross. The typical cross (V_v) and four leaf clover pattern (H_v) observed by us are shown in Figures 8(a) and 8(b). The scattering patterns shown in Figures 8(a) and 8(b) have an angular diameter of about 7° of arc approximately.

c)   'Oily streaks'

When observed between crossed polarizers, using a high power objective the oily streaks appear as tapes shown in Figure 9(a). The tapes show extinction transverse to their length giving the appearance of striated bands. Such
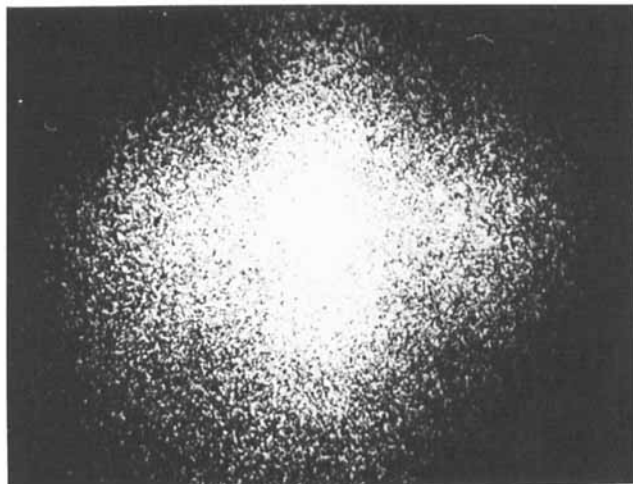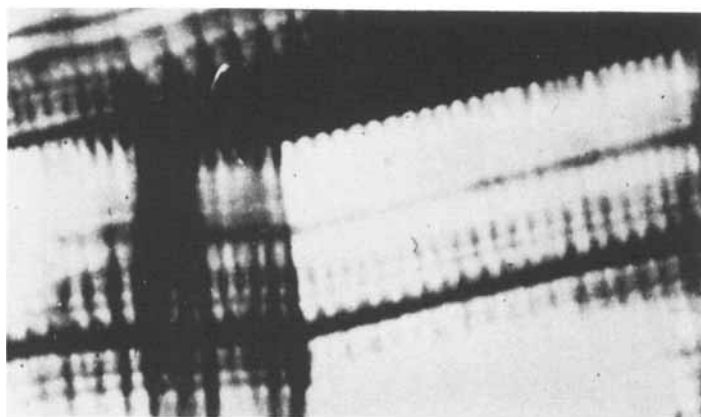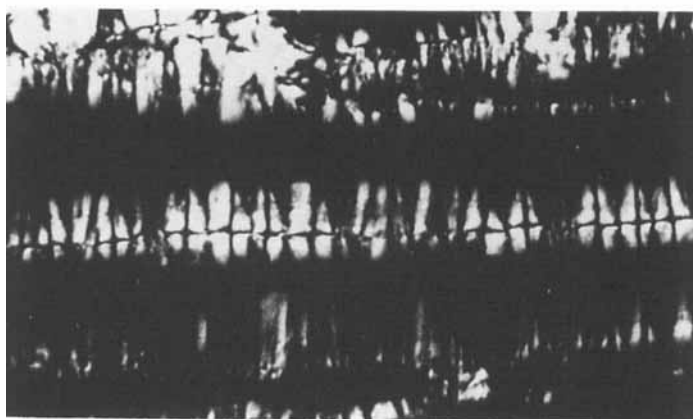
(a)
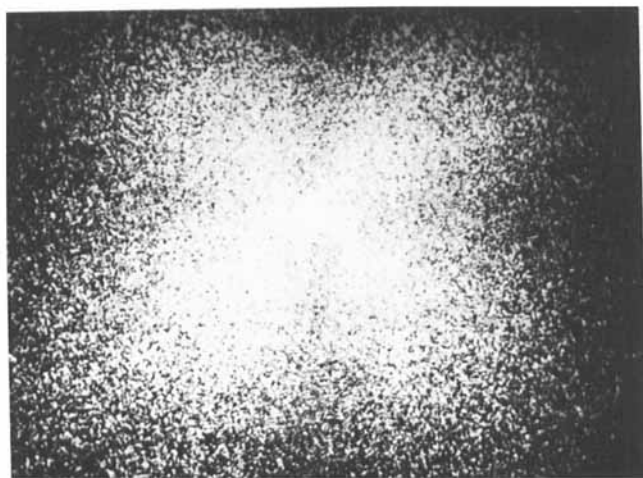
(b)

FIGURE 8   Low angle scattering pattern obtained with droplets of DBS using λ 6328Å (a) V_v pattern and (b) H_v pattern.

(a)

(b)

FIGURE 9   (a) Micrograph of 'oily streaks' in DBS observed between crossed polars (350x), and (b) Micrograph of 'oily streaks' in DBS showing chains of focal conics (crossed polars, 310x).

tapes have been observed by Friedel.[24] Under favourable conditions the tapes appear as chains of focal conics shown in Figure 9(b). A similar texture had been reported in the G_1 phase of Sodium 3-undecyl sulphate-water system, (see for example Figure 2.21 in the treatise by G. W. Gray and P. A. Winsor).[1]

Part B

SODIUM DODECYL BENZENE SULFONATE (NaDBS)

B(1) Preliminary remarks

The sample of NaDBS obtained by us was in the form of a paste with about 38 percent of solid matter, 2% sodium sulfate and about 60% of water. However, prior to its use in our investigations we had minimized the content of water in the sample by keeping it in a desiccator for several days. The dehydrated sample was used to prepare mixtures of the substance with water. Mixtures of various concentrations were prepared with water and their optical textures were studied using the polarizing microscope. The sample was usually taken between slide and cover glass and no spacer was used. The thickness of the sample was about $25\,\mu$. Sodium dodecyl benzene sulfonate is lyotropic and forms birefringent textures. The textures are especially striking in the range of concentration of 20 to 40% of NaDBS by weight in the total weight of the mixture with water. At higher concentrations, the textures are not striking, owing to the opacity associated with the mixture.

Sodium doecyl benzene sulfonate is found to be completely soluble in methane sulfonic acid and with this mixture also, it was possible to observe birefringent textures. We must emphasize here that in this mixture there is no component of water. Here, the studies were carried out over a larger range of concentration (18 to 72%) of NaDBS in the total weight of the mixture. No significant variations could be found in the nature of the textures exhibited by mixtures of different concentrations, in the range of concentrations studied.

B(2) Optical textures

The optical textures exhibited by the mixtures discussed here are in many respects similar to those observed with DBS and consist of G droplets, tapes, oily streaks and focal conics, all of which are characteristic of the smectic A phase. Figures 10(a), 10(c) and 10(d) exhibit some typical focal conics[25] and spherulitic textures.[26] Figure 10(f) reproduces a birefringent texture observed between crossed polars. A similar texture is reported by Billard[27] in the case of polyethylene glycol monooleate. Figures 10(b) and 10(e) exhibit the droplets observed in the case of mixtures of NaDBS with water and methane sulfonic acid, respectively. Textures resembling the tapes observed in the case of DBS, as in Figure 9(b), were also obtainable with these mixtures. The shifts of the interference bands were recorded in the case
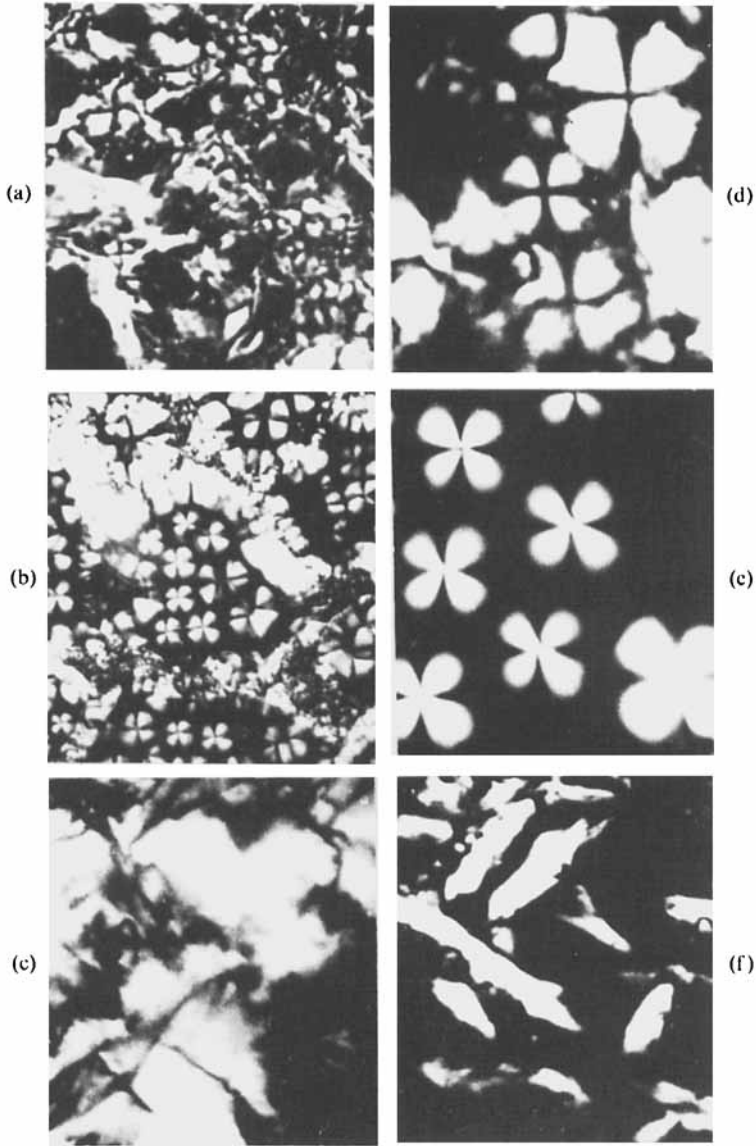
D. KRISHNAMURTI AND R. SOMASHEKAR

FIGURE 10   Microphotographs of (a) focal conics (280x) and (b) droplets (240x) exhibited by a mixture (34 percent in the total weight) of NaDBS in water. Microphotographs of (c) typical focal conics (270x, 27%) (d) spherulitic texture (230x, 38%), (e) droplets (380x, 18%) and (f) birefringent texture (300x, 68%) of a mixture NaDBS in methane sulfonic acid. The magnification and the weight concentration of NaDBS in the total weight of the mixture are given in brackets.

of the droplets of mixtures of (i) NaDBS in water and (ii) NaDBS in methane sulfonic acid, using exactly the same procedure as that adopted to record the shifts of the bands in Figure 6(c) in the case of the droplet of DBS. The shifts of the bands in all the three cases are towards the long wavelength side and it is confirmed that the molecular arrangement in all the droplets discussed here corresponds to that in G droplets.

Figures 11(a) and 11(b) exhibit the oily streaks observed with a mixture of NaDBS in methane sulfonic acid. Under low magnification they appear as tapes shown in Figure 11(a). Actually however, under high magnification it is found that individual tapes consist of chains of focal conics, with dark brushes within the series of ellipses as shown in Figure 11(b).

We have not recorded the X-ray diffraction in the case of the above mixtures because of the tendency of the solvent to evaporate. However, we find that X-ray diffraction studies have already been made in the case of solid
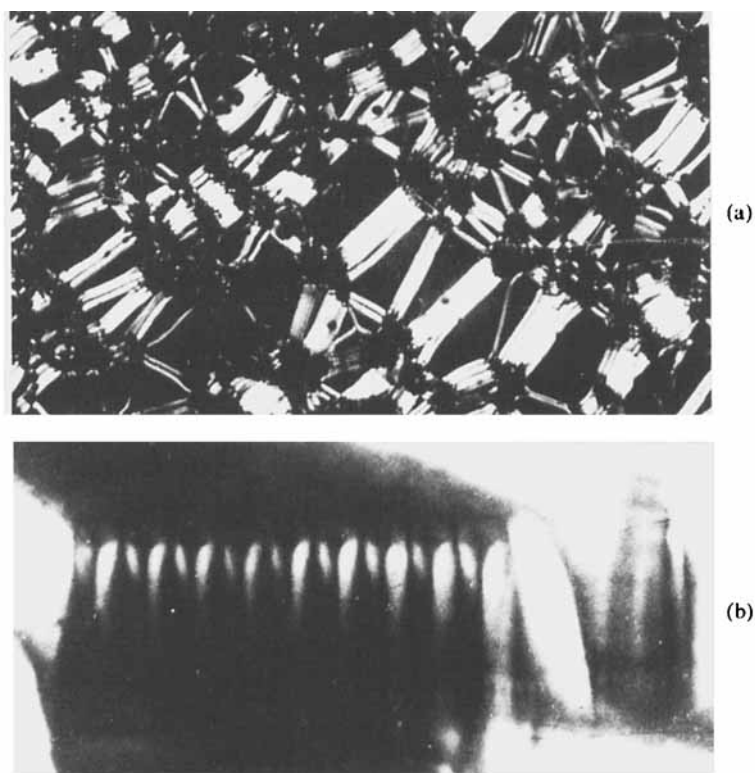

FIGURE 11   Microphotographs of 'oily streaks' in NaDBS in methane sulfonic acid. (a) 75x, with 27% and (b) 360x with 40% of NaDBS by weight in the total weight of the mixture.

NaDBS, wherein a low-angle diffraction ring corresponding to a spacing of 26.5A is reported.[28] This is in agreement with the value obtained by us in the case of DBS.

Infrared spectra

It was observed in an earlier investigation[3] with saturated aliphatic esters that the rocking, twisting and wagging vibrations of methylene groups show progressions of maxima which were found to be partially resolved in the ordered smectic phase. With a view to interpret and to check whether the methylenes associated with the dodecyl group here exhibit a similar feature, the infrared spectra of DBS, NaDBS and methane sulfonic acid were recorded and compared. The spectra were recorded with Perkin–Elmer model 580 spectrophotometer having a resolution of about 5 cm^{-1}. Although from a comparison of the spectra it was possible to broadly assign the different bands to different group-vibrations, it was not possible to discover any feature which may be attributed as strikingly characteristic of the mesophase. For the sake of completeness, the spectra are reproduced in Figure 12 and the assignments of the bands are given in Table I. In arriving at

TABLE I

Infrared absorption maxima observed at room temperature and assignment of the group vibrations. Band positions are in cm^{-1}

Dodecyl benzene sulfonic acid	Sodium dodecyl benzene sulfonate	Methane sulfonic acid	Assignment
—	—	3000 (broad)	OH and CH$_3$
2960(S)	2960(S)	—	CH$_2$ stretching
2940(Sh)	2945(Sh)	—	CH$_3$ stretching
2880(Sh)	2880(Sh)	—	CH ring stretching
1600(S)	1650(S), 1500(S),	—	Benzene ring
1495(m)	1470(m)		
1465(S), 1400(m)	—	—	Skeletal vibration + asymmetric bending of CH$_3$
—	—	1430(S)	Asymmetric bending of CH$_3$ or deformation
1362(S)	1385(S), 1340(m), 1320(m)	1320(S), 1340(S)	ω-CH$_3$ symmetric deformation
1200(m), 1180(S)	1210(Sh), 1185(S)	1050(S), 1240(S),	Characteristic of sulfonic
1140(S)	1140(S)	1070(Sh), 1170(S)	acid and sulfonates S=O stretching
1100(S)	—	—	Skeletal stretch
1040(S), 1005(S)	1010(S), 1005(S)	—	C—H in plane deformation
910(S), 835(S)	835(S), 765(S)	—	CH$_2$ rocking, twisting
860(S)			+ S—O—C vibration

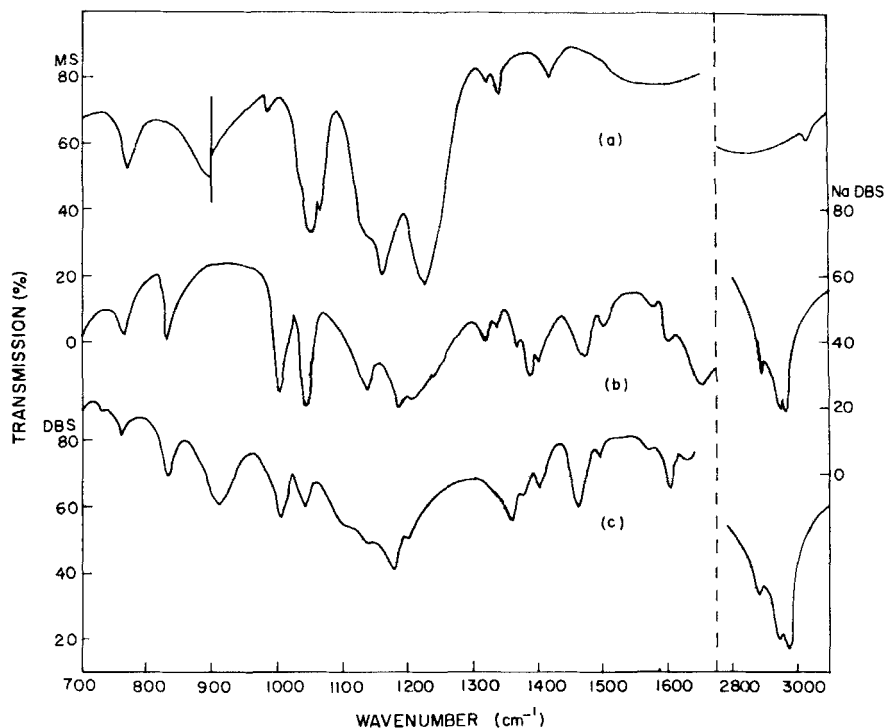Note: S, m and Sh denote strong, medium and shoulder respectively.

FIGURE 12   Infrared spectra of (a) methane sulfonic acid, (b) sodium dodecyl benzene sulfonate and (c) dodecyl benzene sulfonic acid. The spectra were recorded using a thin layer of the sample between KBr plates.

the assignments, the spectra of several compounds reproduced in the treatise, "Introduction to Infrared and Raman Spectroscopy" by Colthup, Daly and Wiberley,[29] were found to be useful.

Acknowledgements

References

1. G. W. Gray and P. A. Winsor, *Liquid Crystals and Plastic Crystals*, Ellis Horwood, Chichester, Vol. II (1974).
2. F. B. Rosevear, *J. Am. Oil Chem. Soc.*, **31**, 628 (1954).
3. D. Krishnamurti, K. S. Krishnamurthy, and R. Shashidhar, *Mol. Cryst. Liq. Cryst.*, **8**, 339 (1969).
4. a) M. B. Rhodes, R. S. Porter, W. Chu, and R. S. Stein, *Mol. Cryst. Liq. Cryst.*, **10**, 295 (1970). b) V. Luzzati, *Biological Membranes*, Chap. 3, p. 71, Academic Press, London (1968).

5. C. Eaborn and H. Norman, *J. Chem. Soc.*, **55**, 549 (1955).
6. M. Burgar, *Second Liquid Crystal Conference of Socialistic Countries*, Sunny Beach, Bulgaria 27–30, September (1977).
7. M. Sidorova, *Colloid and Polymer Science*, **254**, 45 (1976).
8. A. Forge, *J. Colloid and Interface Science*, **59**, 186 (1977).
9. D. B. Ludlum, *J. Phys. Chem.*, **60**, 1240 (1956).
10. T. Boyd, *J. Anal. Chem.*, **21**, 731 (1949).
11. K. D. Lawson and T. J. Flautt, *Mol. Cryst.*, **1**, 241 (1966).
12. J. R. Hansen and R. C. Mast, ACS Symposium series, *Magnetic resonance in Colloids and Interface* **35**, 440 (1976).
13. R. Somashekar, D. Revannasiddaiah, M. S. Madhava, H. S. Subramhanyam, and D. Krishnamurti, *Mol. Cryst. Liq. Cryst.*, **45**, 243 (1978).
14. A. de Vries, *Mol. Cryst. Liq. Cryst.*, **11**, 361 (1970).
15. S. Diele, P. Brand, and H. Sackmann, *Mol. Cryst. Liq. Cryst.*, **16**, 105 (1972).
16. A. Müller, *Proc. Roy. Soc.*, **A127**, 417 (1930).
17. M. Born and E. Wolf, *Principles of Optics* IV Edn. p. 696, Pergamon Press (1970).
18. D. Krishnamurti, M. S. Madhava, and D. Revannasiddaiah, *Mol. Cryst. Liq. Cryst.*, **47**, 153 (1978).
19. D. Krishnamurti and D. Revannasiddaiah, *Mol. Cryst. Liq. Cryst.*, **55**, 33 (1979).
20. M. Born, *Sitz. d. Phys.-Maths.*, **25**, 614 (1916).
21. M. F. Vuks, *Optics and Spectroscopy*, **20**, 361 (1966).
22. S. Clough, J. J. VanAartsen, and R. S. Stein, *J. Appl. Phys.*, **36**, 3072 (1965).
23. R. S. Stein and M. B. Rhodes, *J. Appl. Phys.*, **31**, 1873 (1960).
24. G. Friedel, *Annls. Phys.*, **18**, 273 (1922).
25. S. Chandrasekhar, S. Ramaseshan, A. S. Reshamwala, B. K. Sadashiva, R. Shashidhar, and V. Surendranath, *Liquid Crystals*, Proceed. of the International Conference held at the Raman Research Institute, Bangalore Dec (1973), *Pramana Suppl.* **1**, 117 (1975).
26. G. I. Stewart, *Mol. Cryst.*, **1**, 563 (1966).
27. J. Billard, *Mol. Cryst.*, **2**, 27 (1966).
28. Thomas F. Boyd, J. M. Macqueen, and I. Stacy, *Anal. Chem.*, **21**, 731 (1949).
29. N. B. Colthup, L. H. Daly, and S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, II Edn. Academic Press, Inc., New York (1975).