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Polarization Microscopy of Short Chain Sodium Carboxylate Mesophases

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Polarization microscopy has been used to study the ionic mesophases of melts of short chain sodium alkyl carboxylates. The smectic A or neat structure is confirmed for all the sodium carboxylates studied: isovalerate, *n*-butyrate, *n*-valerate, *n*-hexanoate and *n*-heptanoate. The domain sizes and transition temperatures are reported and an empirical correlation between birefringence and the order parameter is observed. The birefringence is predicted to be negative for all the compounds studied. It is interesting to note that sodium isovalerate exhibits quite different properties from those found for the other *n*-alkyl carboxylates. Both the birefringence temperature coefficient and the average domain size (500 μm) are unusually large for sodium isovalerate.

I. INTRODUCTION

Short chain carboxylic acid salts have been the subject of recent investigation because of the unusual ability to form a liquid crystalline mesophase in their molten form despite their small length-to-width ratios. Not only do these ionic mesophases possess many unusual macroscopic properties,[1-7] but they are also interesting on the molecular level.[8-11] Furthermore, this class of materials can serve as model systems for inproving our understanding of membranes and one can foresee as well their potential technological applications in the area of high energy batteries.

In connection with our NMR study[10,11] of the dynamic structure of the liquid crystalline ionic mesophase of molten sodium carboxylates, we needed to confirm the type of liquid crystalline mesophase and, more importantly, to determine the domain size for individual compounds. In addition, we had to establish whether the mesophase is homogeneous. Therefore, we have used optical microscopy to obtain information about the domain size, and to monitor birefringence change with temperature in the following sodium carboxylates: *n*-butyrate isovalerate, *n*-valerate, *n*-hexonoate and *n*-heptonoate. Michels and Ubbelohde[12] have previously employed differential scanning calorimetry (DSC) to determine the transition temperatures in these materials. Their transition temperatures were in good agreement with our NMR results, but our data for several compounds disagreed with the results obtained by Baum *et al.*[13] using polarization microscopy (PM). One may add that the latter PM study gave neither domain sizes nor reported the changes of birefringence with temperature. Duruz and Ubbelohde[3] only roughly estimated the domain size of sodium isovalerate to be more than an order of magnitude larger than the domain size for sodium *n*-butyrate. They reported that the domain size of sodium *n*-butyrate was smaller than 100 μm.

Our measurements show that the liquid crystalline mesophase has a homogeneous smectic A or neat structure. A strong variation of the domain size among the individual compounds is found. An interesting correlation between the retardation factor, R, in sodium isovalerate and the order parameter, S, is proposed. The measurements indicate that due to the layered structure of the ionic mesophase and the short chain length of the anion, the observed birefringence is negative.

II. EXPERIMENTAL

The carboxylate salts were synthesized with 2% excess acid in a manner previously described[14] for high temperature studies. The resulting pastes were then dried under vacuum (<.01 torr) at 180°C for more than 24 hr. The dried compounds were subsequently handled in an inert atmosphere. Microanalysis of samples prepared in this fashion showed better than 99% purity.

The compounds were melted between a glass slide and cover slip. Both the pyrex glass microscope slides (Erie Scientific Sybron Corp.) and the pyrex cover slips (Gold Seal) were cleaned with acetone prior to their use. It was desirable to prepare melts which were thin enough to insure only one interference color would result, enabling an unambiguous observation of color change with temperature. With the exception of sodium isovalerate, this proved to be quite difficult due to spontaneous homeotropic[15] formation. It was found that heating to the isotropic phase followed by immediate cooling to the neat phase would produce the desired nonhomeotropic condition. If the sample was heated from the solid phase or cooled slowly from the isotropic phase, the homeotropic condition invariably resulted. With sodium isovalerate, spontaneous formation of the homeotropic condition usually did not occur, although it could easily be produced by rubbing of the cover slip. If thicker samples were prepared, spontaneous formation of the homeotropic condition also was not a problem for the *n*-alkyl carboxylates, but many interference colors were observed due to randomly overlapping domains.

Samples were investigated using a polarizing microscope (Bausch and Lomb, Inc.) with a white light source and a hot stage designed in this laboratory. Temperature accuracy was verified using high purity standards of known melting points. The maximum estimated error in temperature was ±3°C. Changes in the interference colors for the salts were recorded on film at temperature intervals of 5 to 10°C.

III. RESULTS

For all samples studied a simple fan texture (see Figures 1 and 2) is observed in the mesophase which is formed by cooling from the isotropic phase. Upon slow cooling at the isotropic melt-mesophase transition, T_{CL}, batonnets typical of a smectic A phase are observed in all samples. Isolated spherulitic domains are occasionally observed for homeotropic preparations during the cooling runs. These above three observations, in addition to the occurence of a homeotropic condition for thin sample preparations, conclusively identify all of these mesophases as smectic A or neat phases.[15,16] A further observation is the paramorphic texture obtained upon heating from the solid for sodium isovalerate. All of these findings are consistent with previous results.[13] Importantly, the appearance of the textures remains constant with varying temperature for a particular heating or cooling cycle.

The solid phase generally consists of multi-colored paramorphic textures, although a definite softening and increased fuzziness in this texture is observed in sodium isovalerate during heating for a range of about 30°C before reaching the mesophase. Solid-solid transitions if present do not cause any significant change in the paramorphic tex-

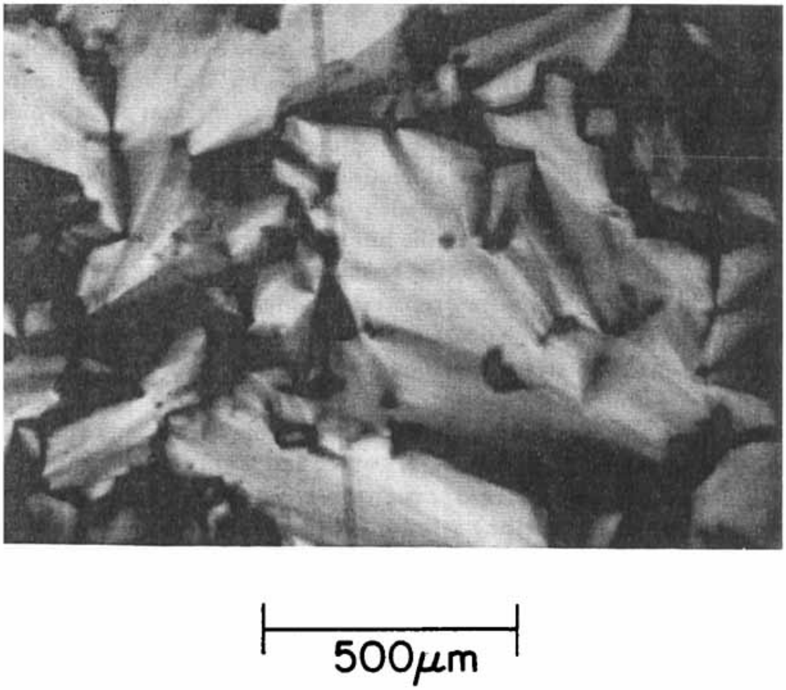

FIGURE 1 Simple fan textures observed under crossed polars for the mesophase of sodium isovalerate.

tures with one exception. In sodium *n*-butyrate there exists an intermediate multi-colored mosaic texture suggestive of a uniaxial smectic B liquid crystal corresponding to the solid I[2,3,10] phase. Both this texture and the texture for solid II are presented in Figure 3.

The estimated domain size is given in Table I. A definite decrease in domain size from an estimated average of 20 μm for sodium *n*-butyrate to about 7 μm for sodium heptanoate is observed with increasing chain length for the series of *n*-alkyl carboxylate salts as can be seen in Figure 2 and Table I. The domain size for sodium isovalerate (see Figure 1; Table I) is about 500 μm which is considerably larger than the sizes obtained for the *n*-alkyl carboxylate salts. No change in domain size is observed with temperature for any of the mesophases studied. It is a possibility that the absence of domain size temperature dependence may be due to surface effects. However, our results basically agree with Duruz and Ubbelohde[3] for a domain size disparity between sodium isovalerate and sodium *n*-butyrate. Yet for the latter study surface effects were negligible.

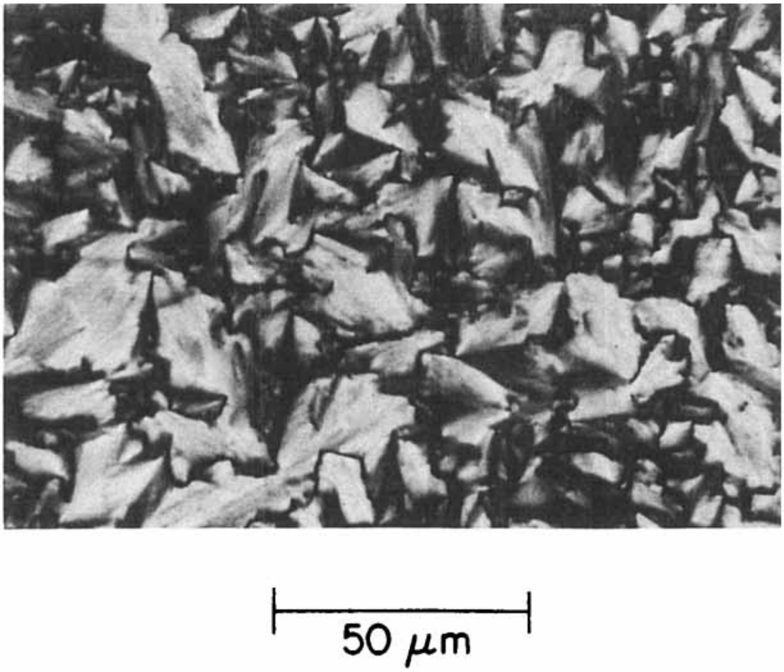

FIGURE 2a Simple fan textures observed under crossed polars for the mesophase of sodium *n*-butyrate.

In all salts the interference colors increase in Newton's scale[17] with increasing temperature. The color change is similar for the *n*-alkyl salts, changing from greyish-blue at low temperatures to pale yellows at high temperatures. This corresponds to a change of about only half of the first order on Newton's scale. This assignment of position on Newton's scale is confirmed by observations using parallel polars. Sodium isovalerate, in marked contrast to the *n*-alkyl carboxylates, exhibits color changes through the entire first order and up slightly into the second order before reaching the isotropic phase. Specifically, the colors change from greyish-blue near T_F to yellow at T_V (263°C). We note here the temperature, T_V, indicates the point of change in the slope of molar volume with temperature.[2] From T_V to T_{CL} the colors change much more rapidly with temperature from yellow all the way up to blue. Importantly, the interference colors and the extent of change of interference colors are reproducible for each compound when different melt preparations are used.

In Table II the transition temperatures obtained in this study are

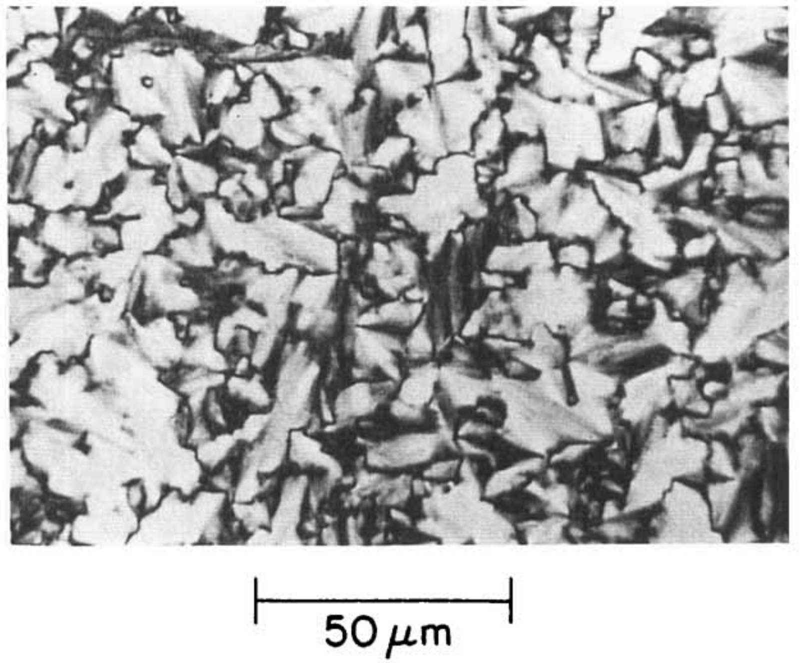

FIGURE 2b Sodium *n*-valerate.

listed with those results determined by NMR,[10,11] DSC[2,12] and PM[13] studies. The best agreement is obtained by the NMR studies done in this laboratory. Due to the large size of the quartz, NMR sample cells (10 mm Dia. × 10 mm), wall effects should not significantly affect the transition temperatures obtained by the NMR studies. Good agreement is also obtained with the DSC studies, although there appears to be some discrepancy in temperature calibration in one of the DSC studies.[12] As can also be seen from Table II, T_{CL} for sodium isovalerate and sodium *n*-butyrate from this study is higher than obtained by other techniques. Conversely, this effect does not appear as pronounced for the longer chain *n*-alkyl carboxylates. This would suggest that surfaces stabilize the mesophase of sodium isovalerate and sodium *n*-butyrate to a much larger degree than for the other *n*-alkyl carboxylates. The cause for this behavior, however, is not presently understood.

IV. DISCUSSION

The smectic A or neat structure of the ionic mesophase agrees with the results from x-ray data[3] on sodium isovalerate and sodium *n*-butyrate

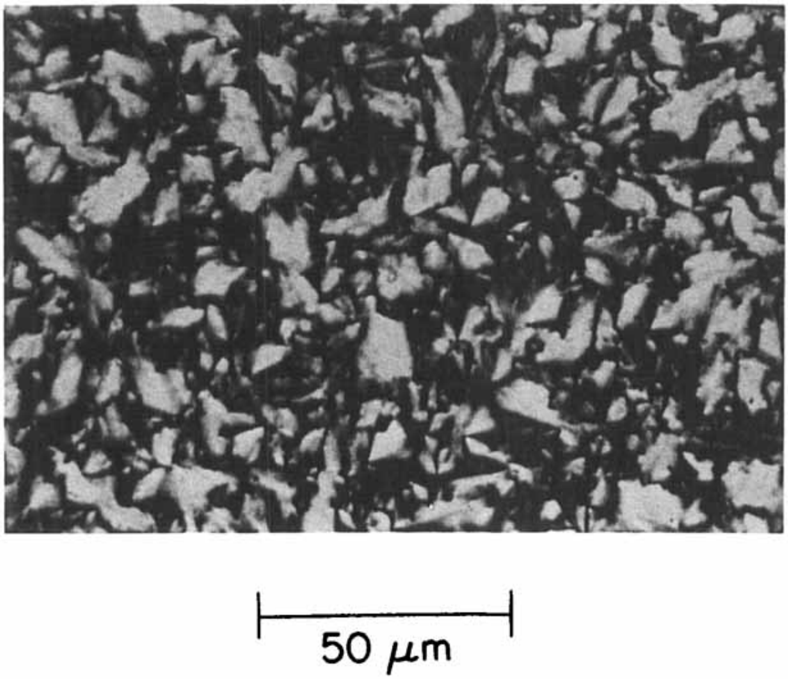

FIGURE 2c Sodium hexanoate.

which suggest a bilayer arrangement of anions. In Figure 4 we present such a structure based on the results of our NMR studies.[8-11] It is noteworthy that the mesophase for all compounds studied appears homogeneous. In other words, there are not domains of structured liquid within an isotropic medium, but only a liquid crystalline structure is present.

It is evident from domain size estimates that the mesophase of sodium isovalerate is far more stable than the mesophases of the sodium *n*-alkyl carboxylates studied. The assumption that larger domains imply greater stability is also consistent with the lower fusion temperature, T_F, observed for sodium isovalerate. Among the series of *n*-alkyl carboxylates, the neat phase of sodium *n*-butyrate is the most stable having the largest domains. The domain size and stability decrease with increasing chain length. Since electrostatic forces dominate the stabilization of the mesophase,[3,9,10] it is reasonable to assume longer chain lengths and consequently larger spaced bilayers[10,11,18,19] reduce the forces of one layer to the next. This, however, does not explain the stability difference (factor of 25) between sodium isovalerate and sodium *n*-butyrate for which x-ray long spacings are nearly equal.[3]

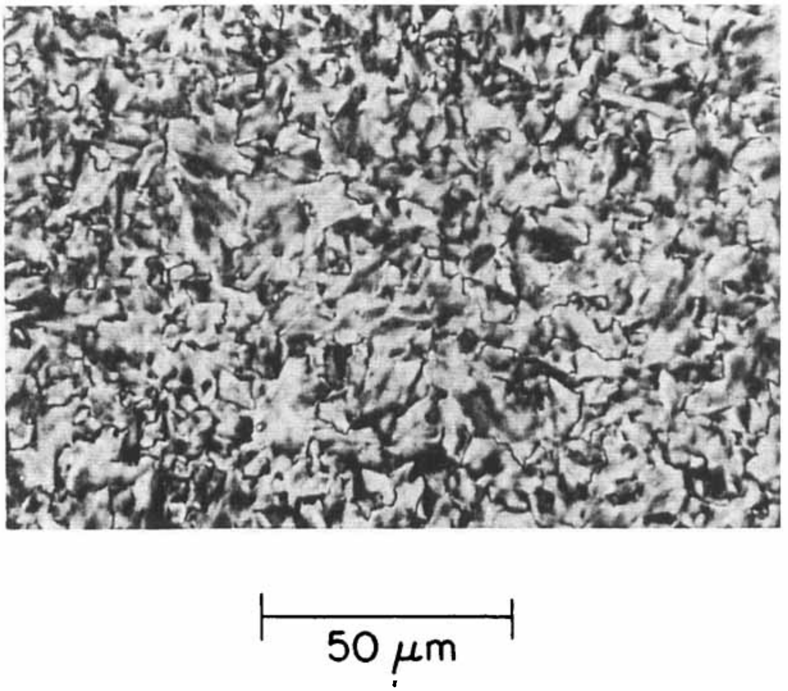

FIGURE 2d Sodium heptanoate.

The relative retardation, R, which is related to interference color, is given for uniaxial systems when $\Delta n \ll n_e, n_o$ by the expression[17]

$$R = d \sin^2 \phi (n_e - n_o) = d \sin^2 \phi \, \Delta n, \tag{1}$$

where d is the sample thickness, n_o and n_e are the refractive indices for the ordinary and extraordinary rays, respectively, Δn is the birefringence and ϕ is the angle between the incident light ray and the optic axis.

That the appearance of textures remains constant with varying temperature for a particular heating or cooling cycle indicates the do-

TABLE I

Estimated domain size in the smectic melts

Compound	Domain size (μm)
Sodium isovalerate	500
Sodium *n*-butyrate	20
Sodium *n*-valerate	15
Sodium hexanoate	10
Sodium heptanoate	7

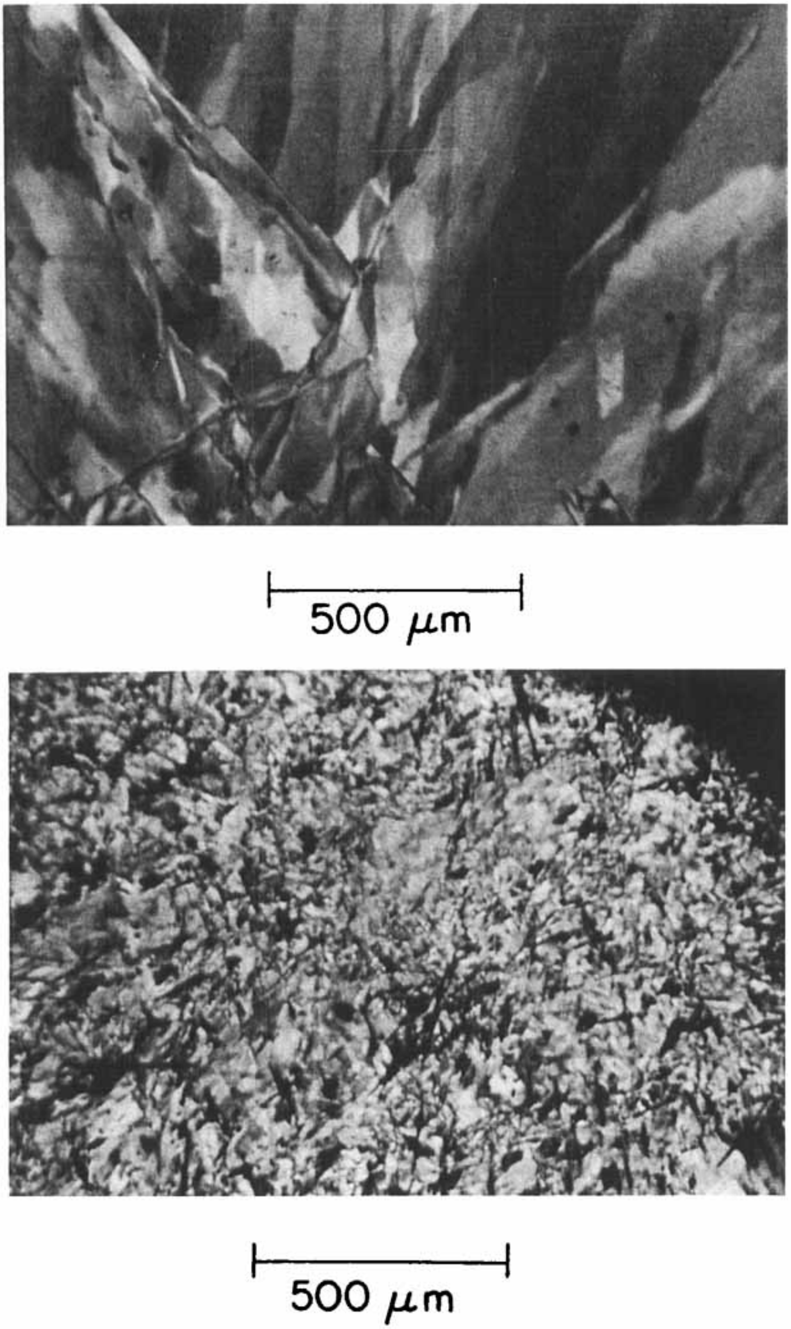

FIGURE 3 Textures obtained for solid I(a) and solid II(b) sodium *n*-butyrate under crossed polars.

TABLE II

Transition temperatures (°C) and temperature interval, ΔT, of mesophase stability for the compounds studied.

Sodium *n*-butyrate			Sodium isovalerate			Sodium *n*-valerate			Sodium hexanoate			Sodium heptanoate				
T_F[b]	T_{CL}[c]	ΔT[d]	T_F	T_{CL}	ΔT	T_F	T_{CL}	ΔT	T_F	T_{CL}	ΔT	T_F	T_{CL}	ΔT	Method[a]	Reference
262	321	59	—	—	—	241	344	103	235	361	126	242	363	121	PM	Baum *et al.*[13]
252	324	72	188	280	92	229	353	124	232	358	126	238	361	123	DSC	Ubbelohde *et al.*[2,12]
252	324	72	188	280	92	237	364	127	245	368	123	248	374	126	NMR	Bonekamp *et al.*[10,11]
264	333	69	188	289	101	237	361	124	243	373	130	250	378	128	PM	This work

[a] PM-polarization microscopy; NMR; DSC-differential scanning calorimetry
[b] Melting temperature (solid-mesophase)
[c] Clearing temperature (mesophase-isotropic liquid)
[d] Temperature interval of mesophase stability

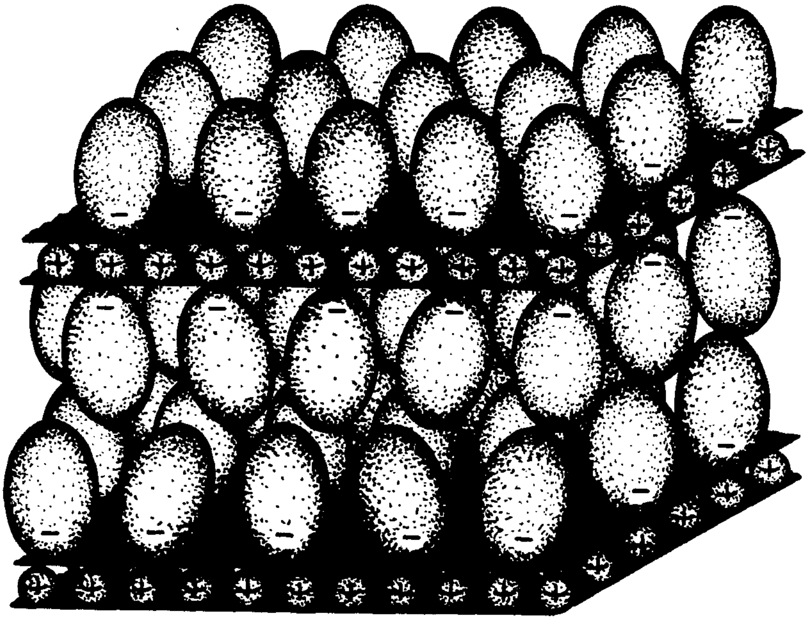

FIGURE 4 Model of the ionic mesophase of sodium isovalerate. Sodium ions are represented with positive signs and the carboxylate groups are denoted by the negative signs.

main size and sample orientation do not change with temperature for a cover slip preparation. This strongly implies that sample thickness remains nearly constant with temperature. Furthermore, the reproducibility of both *location* and *range* of interference colors for different cover slip preparations of the same compound demonstrates either that R is relatively insensitive to possible variations in sample thickness and orientation or that there may be a preferred orientation and sample thickness necessary to obtain a single interference color. Therefore, since $d \sin^2 \phi = k$, a constant, Eq. (1) may be written as

$$R(T) = k\,\Delta n(T).$$

This allows us to relate the change in R and Δn (eliminating k with values at T_F) by

$$\frac{R_T - R_F}{R_F} = \frac{\Delta n_T - \Delta n_F}{\Delta n_F} \qquad (2)$$

where R_T and Δn_T represent values at an arbitrary T. We conclude, therefore, that the relative change in retardation or interference color monitors the relative change in birefringence. It is noteworthy that the relative change in birefringence is a parameter which may be meaningfully compared between compounds.

For the mesophases of the sodium *n*-alkyl carboxylates R increases from about 150 mμ at T_F to about 200 mμ at T_{CL}. For sodium isovalerate $R_F = 130$ mμ and increases to 640 mμ at T_{CL} with nearly half of the change occurring in the 17°C region from T_V to T_{CL}. To our best knowledge, such a large temperature coefficient for color change has only been seen previously with cholesteric liquid crystals.[20] The temperature dependence of the relative retardation is plotted in Figure 5 for sodium isovalerate. We note here that it is necessary to recalibrate the observed temperature because of the surface effects. It is assumed that $T_F)_{\mathrm{exp}} = 188°\mathrm{C}$ becomes $T_F)_{\mathrm{plot}} = 188°\mathrm{C}$ and $T_{CL})_{\mathrm{exp}} = 289°\mathrm{C}$ becomes $T_{CL})_{\mathrm{plot}} = 280°\mathrm{C}$ and a linear relationship exists for intermediate temperatures. Similar plots of R vs. T may not be made for the *n*-alkyl carboxylates due to the limited resolution of Newton's scale. It is clear that the relative changes in birefringence over the entire mesophase is nearly a factor of 4 larger for sodium isovalerate than for sodium *n*-butyrate. This gives an overall birefringence temperature coefficient

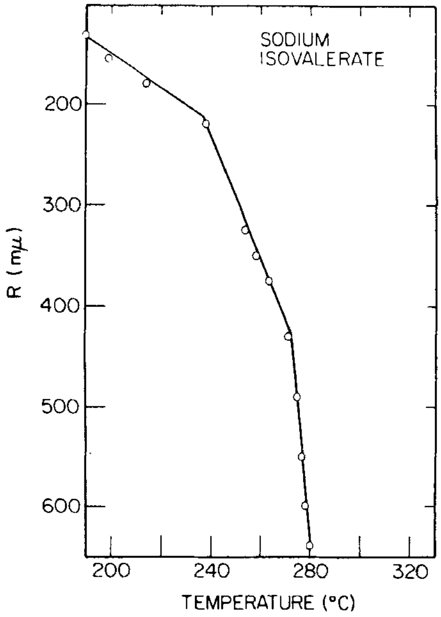

FIGURE 5 Temperature dependence of estimated relative retardation, R, for sodium isovalerate.

for sodium isovalerate which is more than a factor of 3 larger than obtained for sodium *n*-butyrate.

Numerous studies[20] have related anisotropy changes of material and/or molecular structure to refractive index and birefringence. To describe changes in molecular structure with temperature for liquid crystalline systems, the order parameter, S, may be used where

$$S = \tfrac{1}{2}\langle 3\cos^2\theta - 1\rangle \tag{3}$$

and θ is the angle between the molecular long axis and the order director of the liquid crystal. Importantly, $S = 1$ corresponds to complete anion alignment, whereas $S = 0$ corresponds to "random" orientation. Following Subramhanyam and Krishnamurti,[21] for a nematic phase the refractive indices may be written

$$n_e^2 - 1 = 4\pi N\alpha_e(1 - N\alpha_e\gamma_e)^{-1} \tag{4}$$

and

$$n_o^2 - 1 = 4\pi N\alpha_o(1 - N\alpha_o\gamma_o)^{-1} \tag{5}$$

where N is the number of molecules per unit volume, γ_e and γ_o are internal field constants, and the effective polarizabilities, α_e and α_o, corresponding to the electric vector parallel and perpendicular to the optic axis, respectively, are given by

$$\alpha_e = 1/3(\alpha_\parallel - \alpha_\perp)(2S + 1) + \alpha_\perp \tag{6}$$

and

$$\alpha_o = 1/3(\alpha_\parallel - \alpha_\perp)(1 - S) + \alpha_\perp \tag{7}$$

where $\alpha_\parallel$ is the molecular polarizability along the long molecular axis and $\alpha_\perp$ is the average molecular polarizability perpendicular to the long axis. For a uniaxial smectic A or neat phase we expect these above equations to be a good approximation. It is also noteworthy that both refractive indices decrease with decreasing density as can be seen from Eqs. (4) and (5). The birefringence, on the other hand, is nearly density independent.

From NMR studies[10] of sodium isovalerate and sodium *n*-butyrate carried out in our laboratory, S is estimated to decrease from about .38 to .1 with increasing temperature for the region T_V to T_{CL} of sodium isovalerate and for the entire mesophase of sodium *n*-butyrate. Furthermore, S is estimated to be about .65 near T_F for sodium isovalerate. These order parameters are plotted with temperature in Figure 6 for sodium isovalerate and sodium *n*-butyrate. The temperatures where

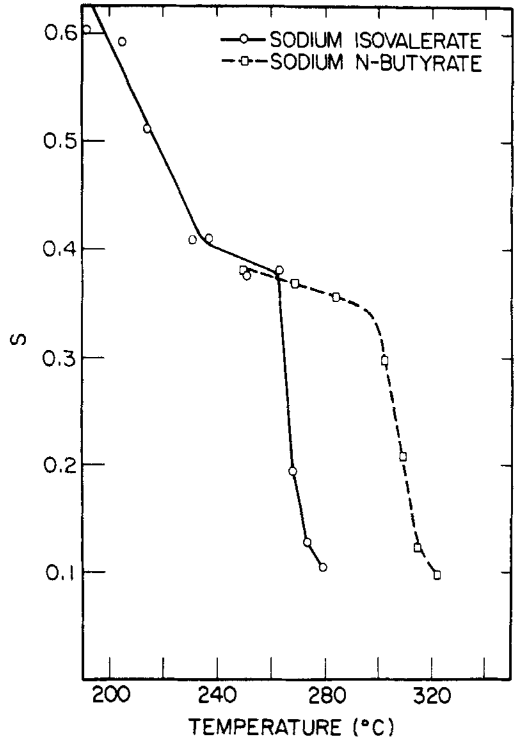

FIGURE 6 Temperature dependence of estimated order parameters, *S*, for sodium isovalerate and sodium *n*-butyrate.[10]

slope changes occur in *S* are 237°C and 263°C for sodium isovalerate. Importantly, these temperatures are nearly identical to those where changes in temperature dependence occur for the birefringence of sodium isovalerate. It is interesting that the overall change in order parameter is about twice as large for sodium isovalerate as it is for sodium *n*-butyrate over the entire mesophase. This disparity between compounds in magnitude of change is also seen in relative birefringence. The causes of change in order parameter temperature coefficient at 237°C for sodium isovalerate and at 295°C for sodium *n*-butyrate are presently not understood. The change in order parameter at T_V for sodium isovalerate as discussed earlier however, corresponds to a change in slope of molar volume. We expect that the order parameters of the remaining *n*-alkyl carboxylate anions have nearly the same magnitude and temperature dependence as for sodium *n*-butyrate in view of the similar birefringence behavior.

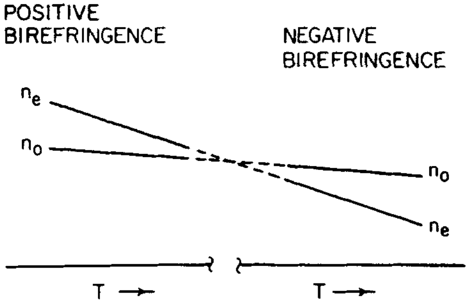

FIGURE 7 Schematic representation for temperature dependence of indices of refraction. For discussion, see text.

It has been found for the neat phases of thallium *n*-alkyl carboxylates that n_e always has a larger temperature coefficient than n_o.[18] Since we have nearly the same chain lengths, it is reasonable to suppose that this is also the case for sodium alkyl carboxylates. As discussed below, this means that increasing birefringence with increasing temperature may only be explained if the birefringence is negative. This has only been seen previously for cholesteric liquid crystals[20] and the shorter chain lengths of the thallium *n*-alkyl carboxylates.[18]

Following the argument given by Pelzl and Sackmann,[18] two competing effects determine the overall polarizability anisotropy, $\alpha_e - \alpha_o$, of the material. The layer arrangement for the smectic liquid crystal contributes a negative anisotropy and the hydrocarbon chains perpendicular to the layers contribute a postive anisotropy. For long chain lengths the positive polarizability anisotropy contribution is dominant and the birefringence is positive. This is the case for most smectic and nematic liquid crystals. For shorter chain lengths, as studied in this work, the layers dominate the overall anisotropy and the birefringence is negative. A decrease of S means an α_e decrease and an α_o increase. Consequently n_e decreases more than n_o decreases (including density effects) and the birefringence increases with increasing temperature. This behavior is shown schematically in Figure 7.

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