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Thermotropic Ionic Liquid Crystals VI. Structural Parameters of Solid and Liquid Crystal Phases of Anhydrous Short-Chain Sodium Alkanoates

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Thermotropic ionic liquid crystals

VI. Structural parameters of solid and liquid crystal phases of anhydrous short-chain sodium alkanoates

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Unit cell constants were determined from powder X-ray diffraction photographs taken of several anhydrous short-chain sodium alkanoates at room temperature. The temperature dependence of the bilayer spacing in the alkanoates was determined over the range 25–300°C. Overall changes in bilayer spacings between the solid and the neat phase were found to be much smaller than in long-chain alkanoates. A correspondence was noted between the room temperature lateral packing area and the ^{23}Na quadrupole coupling constant in the mesophase. The mesophase bilayer spacing was consistent with a structural model in which the tilted anion chain rotates on a cone.

1. Introduction

Thermotropic mesophases of anhydrous alkali metal alkanoates have long been observed [1]. Typically these salts undergo a series of phase transitions when heated from the room temperature crystalline state, passing through various intermediate phases (for example, 'waxy', 'superwaxy') to the 'neat' mesophase, and on to the clear, 'isotropic' liquid [2]. X-ray diffraction [3] and polarization microscopy [4, 5] studies have shown that the neat phase has a bilayer smectic A structure.

The crystalline phases of soaps, like the neat phase, display a bilayer structure [6, 7]. However, Skoulios and Luzzati [3] found that the structure of the intermediate phases of long-chain Na alkanoates was different. The polar head groups in double layers form ribbons of finite width and indefinite length, the ribbons being arranged parallel in a regular array with the hydrocarbon chains fanning out to fill the space between them. It has been suggested by Busico *et al.* [8] that the ionic groups rearrange themselves from a double-layered configuration to a single layer when entering the neat phase.

While the structure of long-chain alkanoates has been extensively studied, spatial parameters of anhydrous short-chain alkanoates in any phase are generally not available. The room temperature cell constants of potassium *n*-alkanoates [7] with $n_c \geqq 4$ and silver *n*-alkanoates [6] with $n_c \geqq 6$, even n_c only, have been reported. Duruz *et al.* measured the densities [9] and the bilayer spacings [10] in sodium *n*-butyrate and sodium isovalerate in the temperature range 100–300°C.

In our previous studies of anhydrous short-chain sodium alkanoates in the neat phase [5, 11–13], we have noted the effect of anion size and shape on the motions of both anion and cation, the quadrupole coupling constant of ^{23}Na, the smectic domain size, and the order parameter. In order to understand trends in these properties we made assumptions about physical parameters such as lateral packing area. The purpose of the present study was to determine the crystal structure of these alkanoates, as a starting point for the understanding of the mesophase structure, and to extend our knowledge of the thermal evolution of the short-chain alkanoates from the crystalline state to the neat phase. We show that the lateral packing area and the chain tilt observed in the crystalline solid correlate with properties of the mesophase.

Alkali metal alkanoates do not readily form crystals large enough for single-crystal X-ray structure determination [14]. We have had to rely upon powder diffraction data, which while more ambiguous than single-crystal data, can provide reasonable cell constants. X-ray diffraction was also used to measure bilayer spacings as a function of temperature in the solid and neat phases.

2. Experimental section

The salts studied were sodium *n*-butyrate (Na C_4), sodium *n*-valerate (Na C_5), sodium hexanoate (Na C_6), sodium heptanoate (Na C_7), sodium isovalerate (Na i-C_5), sodium 3-methylpentanoate (Na 3-MeC_5) and sodium 4-methylpentanoate (Na 4-MeC_5), prepared in this laboratory [12].

Room temperature powder diffraction photographs were taken of anhydrous, acid-free sodium alkanoates contained in a 0·7 mm diameter Lindemann glass capillary, using a Debye–Scherrer camera of radius 57·3 mm. Samples were exposed to Ni-filtered CuKα radiation for 5–6 hours.

For the temperature study, dry, acid-free, degassed sodium alkanoate samples were sealed under vacuum in 0·7 mm diameter Lindemann glass capillaries and mounted in a Mettler FP 52 thermal microscopy stage which had been modified for X-ray use. A Mettler FP 5 temperature control unit allowed heating or cooling rates as slow as 0·2°C/min, with a maximum temperature of 300°C. Temperature was monitored by means of a thermocouple located within 3 mm of the sample. The hot stage was mounted on a Huber diffractometer. The geometry of the stage limited the accessible 2θ range to about $\pm 12^\circ$ (spacings $> 7{\cdot}4$ Å for CuKα). The X-ray source was an Elliot GX 21 rotating anode with a copper target. Typically a 2θ range of 2–8° (11–44 Å) was scanned at 0·05°/0·5 min using a scintillation detector.

Powder densities were measured at room temperature in a Quantachrome micropycnometer with a dry nitrogen overpressure.

3. Results

The room temperature powder diffraction lines were indexed using Vand's first graphical method for long-spacing compounds [15]. An indexing scheme had to satisfy the following criteria: (1) all observed lines indexed; (2) agreement with observed density; (3) reasonable number of molecules per unit cell; and (4) reasonable lateral spacings. A further consideration was consistency in unit cell type among the various sodium soaps. Cell constants were refined by means of a least-squares routine. The results are found in table 1. In the case of sodium 4-methylpentanoate, an alternative indexing scheme yields an orthorhombic cell with $a = 8{\cdot}61$ Å, $b = 11{\cdot}54$ Å, $c = 16{\cdot}02$ Å, and $\varrho_{\mathrm{calc}} = 1{\cdot}153\,\mathrm{g\,cm^{-3}}$. While the calculated density of the orthorhombic cell agrees better than that of the monoclinic cell with the observed density $1{\cdot}149\,\mathrm{g\,cm^{-3}}$, the orthorhombic scheme does not account for some diffraction lines so well. In addition, the 8·61 Å lateral spacing (4·3 Å for one molecule) may pack the branched chains too closely. The powder diffraction pattern of Na 4-MeC_5 is given

Table 1. Summary of powder X-ray results.

Salt	a/Å	b/Å	c/Å	α/deg.	β/deg.	γ/deg.	ϱ/g cm^{-3}		S/Å^2
							Calc.	Obs.	
Na C_4†	7·41	5·21	14·07	90	90	90	1·346	1·362	19·3
Na C_5†	7·79	5·23	15·71	90	91·2	90	1·288	1·311	20·4
Na C_6‡	4·02	5·06	18·75	93·5	93·4	87·1	1·209	1·205	20·3
Na C_7†	8·77	4·79	20·02	90	90	90	1·202	1·197	21·0
Na *i*-C_5§	19·92	4·82	14·66	90	98·9	90	1·186	1·175	24·0
Na 3-MeC_5§	20·06	5·14	15·94	90	98·8	90	1·130	1·150	25·8
Na 4-MeC_5§	19·70	5·15	16·06	90	96·5	90	1·134	1·149	25·3

† Four molecules/unit cell.
‡ Two molecules/unit cell.
§ Eight molecules/unit cell.

Table 2. Powder diffraction pattern of sodium 4-methylpentanoate.

Line	Strength	(n/d) obs./Å^{-1}	Index	(n/d) calc./Å^{-1}
1	vs	0·0626	001	0·627
2	ms	0·0852	101	0·0852
3	m	0·1249	002 201	0·1254 0·1258
4	vw	0·1406	102	0·1406
5	vw	0·1589	$30\bar{1}$‡	0·1589
6	w	0·1738	202 301	0·1705 0·1720
7	w	0·1842	$30\bar{2}$‡	0·1866
8	m	0·1942	010	0·1943
9	mw	0·2055	†	—
10	m	0·2205	210 401 203	0·2195 0·2204 0·2240
11	mw	0·2322	012 211 $12\bar{2}$	0·2312 0·2314 0·2337
12	m	0·2500	†	—
13	vw	0·2965	†	—
14	vw	0·3121	105 005‡	0·3117 0·3134
15	mw	0·3229	†	—
16	vw	0·3326	511 $51\bar{2}$ 503	0·3325 0·3338 0·3339
17	w	0·3442	602‡	0·3441
18	vw	0·3564	†	—
19	w	0·3716	†	—
20	vw	0·3871	†	—
21	vw	0·4402	†	—
22	vw	0·4990	†	—
23	vw	0·5239	†	—

† More than three probable indices.
‡ Additional indices possible.

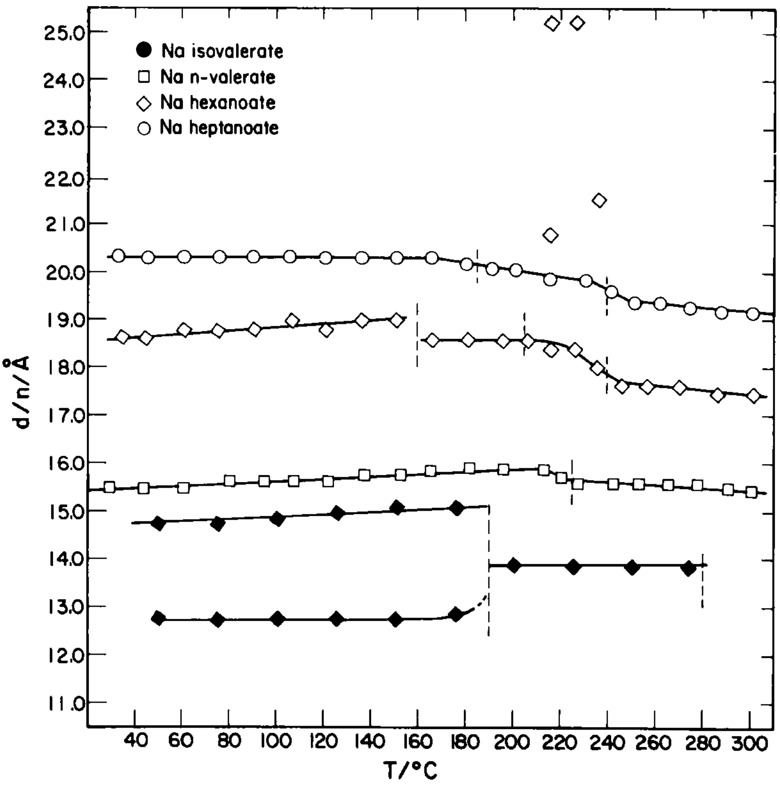

Figure 1. Equilibrium long spacings as a function of temperature in anhydrous sodium alkanoates. The sodium hexanoate points in the range 205–240°C probably correspond to the dimensions of the superwaxy phase ribbon structure.

in table 2 in terms of the reciprocal spacings

$$n/d = 2\sin\theta/\lambda, \tag{1}$$

together with possible indices in a monoclinic system.

In the temperature study, it was found that the positions of the diffraction lines depended somewhat on the rate at which the sample had been cooled from the previous high temperature. The powder patterns in the room temperature samples may therefore not represent equilibrium crystal structures, since those samples were prepared from powders which had previously been cooled rapidly from a drying temperature ≧ 180°C. Samples in the temperature studies were always cooled at a rate of 0·2°C/min, so that spacing data were reproducible between temperature runs.

Long spacings ($\geqq 11$ Å) of Na C_5, Na C_6, Na C_7, Na i-C_5, Na 3-MeC_5, and Na 4-MeC_5 from room temperature to 300°C are shown in figures 1 and 2. No temperature study was performed on NaC_4. The longest spacing for both straight and branched-chain salts in the room-temperature crystal is the 001 line, i.e. the bilayer spacing. The second longest spacing for Na i-C_5 and Na 3-MeC_5 corresponds to the $10\bar{1}$ line. In table 3 the equilibrium bilayer spacing in the temperature study at 40°C, $1/c^*$, is compared with the bilayer spacing calculated from the cell constants, $c \sin\alpha \sin\beta$, for all compounds.

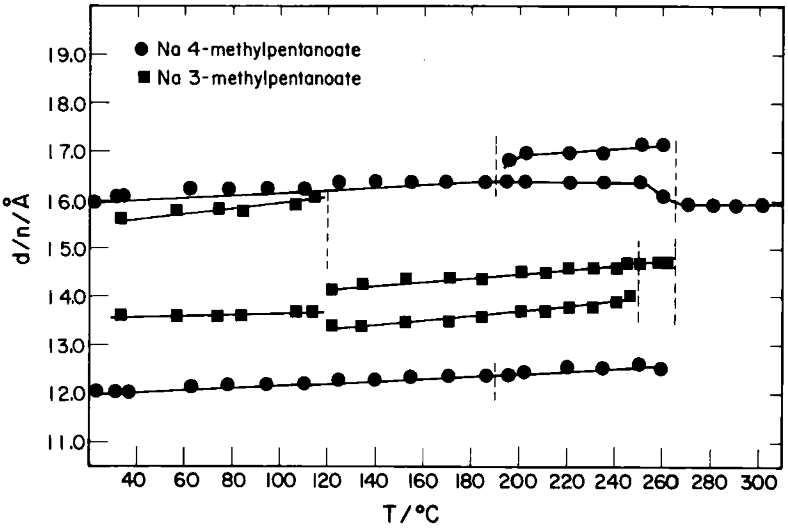

Figure 2. Equilibrium long spacings as a function of temperature in anhydrous sodium methylpentanoates.

Table 3. Comparison of powder cell constants and bilayer spacings from temperature study at 40°C.

Salt	$c \sin\alpha \sin\beta$ (calc.)/Å	$1/c^*$ (obs.)/Å
Na C_4	14·07	14·08†
Na C_5	15·70	15·49
Na C_6	18·68	18·61
Na C_7	20·02	20·32
Na *i*-C_5	14·48	14·73
Na 3-MeC_5	15·75	15·63
Na 4-MeC_5	15·96	16·07

† Duruz and Ubbelohde [10].

Table 4. Phase transitions from X-ray data.

Salt	Temperature/°C	Transition type
Na C_5	225	Solid–neat
Na C_6	160	Solid–solid
	205	Solid–superwaxy
	240	Superwaxy–neat
Na C_7	185	Solid–superwaxy
	240	Superwaxy–neat
Na *i*-C_5	190	Solid–neat
	280	Neat–isotropic
Na 3-MeC_5	120	Solid–solid
	250	Solid–neat
	265	Neat–isotropic
Na 4-MeC_5	190	Solid–solid
	265	Solid–neat

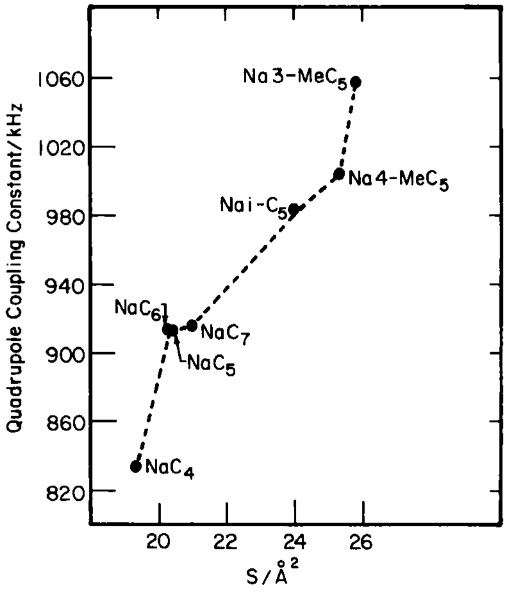

Figure 3. Correlation between lateral packing area S in the room temperature crystal and ^{23}Na quadrupole coupling constant in the mesophase at 275°C.

Phase transitions evident in the diffraction data are summarized in table 4. Very broad, weak lines corresponding to the neat phase 001 reflection were visible in the isotropic phase of Na i-C_5 and Na 3-MeC_5 up to 300°C.

4. Discussion

The unit cell types for the sodium n-alkanoates, deduced from the room-temperature X-ray diffraction data, were orthorhombic for Na C_4 and Na C_7, monoclinic for Na C_5, and triclinic for Na C_6. The differences in crystal system among these salts may be due to the varying thermal histories of the samples. Triclinic unit cells with dimensions similar to those of Na C_6 were reported for even-carbon silver n-alkanoates [6]; also known are orthorhombic cells for Na C_7–Na C_{12} inclusive [16], and monoclinic cells ($P2_1/a$ space group) for the even-carbon potassium n-alkanoates [7]. Systematic absences in the indexing for Na C_5 are consistent with the $P2_1/a$ space group. All three branched-chain salts appear to crystallize in a monoclinic form, in which $c \sin \beta$ is the bilayer spacing and four molecules are arranged side by side along the a axis in each layer. Since eight molecules are contained in a monoclinic cell which should hold four repeating units, we suggest that the repeating unit is composed of two independent conformations of the molecule.

The two largest spacings seen in the sodium isovalerate diffraction pattern were about 15 Å and 12·8 Å in the solid phase. On the other hand, Duruz and Ubbelohde [10] reported only a single line at 12·5 Å. Possibly their samples of sodium isovalerate crystallized in a different configuration in which the 001 line was extinguished.

We can calculate the lateral packing area S in the crystalline state from the cell constants

$$S = ab \sin \gamma / n, \tag{2}$$

where n is the number of molecules per half-layer; calculated values of S are found in table 1. Interestingly, as shown in figure 3, the lateral packing areas of the seven sodium alkanoates at room temperature fall in the same order as the ^{23}Na quadrupole coupling constants at about 275°C, the point of overlap of all mesophase ranges [12]. We have explained this trend in terms of an ionic bilayer structure for the neat phase in which each sodium ion on the average is surrounded by four carboxylate groups in the same half-layer and one carboxylate group in the opposite half-layer [12]. When the electric field gradient along the bilayer normal, V_{zz}, is calculated using the nearest COO$^-$ group in the opposite half-layer, the four nearest neighbor Na$^+$–COO$^-$ pairs, and the four second nearest Na$^+$–COO$^-$ pairs, it is found that $|V_{zz}|$ increases in magnitude with increasing lateral distances [12]. The quadrupole coupling constant is directly proportional to $|V_{zz}|$ [17].

Lateral packing areas of ~24 Å and ~29 Å for Na C_4 and Na *i*-C_5, respectively, in the neat phase [10] represent approximately a 25 per cent increase over the room temperature value: sufficient for fairly unhindered molecular rotation, but not indicative of a change to a single-layer arrangement of all ionic groups.

In contrast to the long-chain alkanoates, the bilayer spacings in the short-chain sodium alkanoates undergo relatively little change when heated from the room temperature crystal to the mesophase. The decrease in mesophase bilayer spacing relative to the maximum crystalline bilayer spacing ranges from 2·6 per cent for Na C_5 to 8·3 per cent for Na 3-MeC_5; this may be compared with a 16 per cent decrease for Na laurate (C_{12}) and a 39 per cent decrease for Na palmitate (C_{16}). In the crystalline phase, the bilayer spacing remains constant or increases slightly with temperature; the linear expansion coefficient is no more than $3{\cdot}3 \times 10^{-4}$/°C. Contraction of the bilayer is evident in the superwaxy phase of Na C_6 and Na C_7. The spacings at ~ 18·5 Å and longer in the Na C_6 superwaxy phase might correspond to the two-dimensional lattice of the 'structure á rubans' [3].

Sodium 3-methylpentanoate undergoes a phase transition at 115°C in which the bilayer spacing seems to decrease discontinuously. However, we lack the complete diffraction pattern necessary to assign indices to the observed lines at ~ 14·1 Å and ~ 13·4 Å. It is possible that the 16 Å bilayer spacing remains in the structure, but the 001 line is absent due to a change in the point group symmetry. On the other hand, the continuity of the 14 Å line with the neat phase 001 line would tend to indicate that it is the bilayer spacing in the intermediate phase.

The bilayer spacing at any temperature up to 300°C is considerably shorter than twice the length of the all-trans molecule. Chain tilt at an angle of approximately 35° accounts for the difference at room temperature [7]. Subsequent changes in the bilayer spacing with heating could be the result of changing tilt angle, chain kinking, molecular vibrations and reorientations, and thermal expansion of bond lengths and van der Waals radii; the last effect, however, is probably negligible [18]. The tilt angle could either increase or decrease, counteracting or reinforcing the tendency of chain kinking and other reorientations to decrease the bilayer spacing. Since the homologous series of short-chain *n*-alkanoates show no consistent trend in the thermal evolution of the bilayer spacing, it is likely that several factors contribute simultaneously at high temperatures.

Quite possibly the molecules remain tilted even in the neat phase [19, 20]. The uniaxial nature of the neat phase—smectic A rather than smectic C—may be due to free molecular rotation about the bilayer normal. In an earlier paper [13] we noted that the observed mesophase bilayer spacing *d* of Na C_4 to Na C_7 agreed closely with the spacings calculated for all-trans chains tilted and rotating on a cone at an angle

Table 5. Comparison of calculated and observed bilayer-spacings, using l measured from molecular models and the tilt angle θ_t extracted from the order parameter according to equation (3).

		At 260°C		At 300°C	
	l/Å	$2l\cos\theta_t$/Å	d/Å	$2l\cos\theta_t$/Å	d/Å
n-Butyrate	8·08	13·9	13·8†	13·7	13·6†
n-Valerate	9·44	15·9	15·6	15·6	15·5
Hexanoate	10·7	17·8	17·7	17·4	17·5
Heptanoate	12·0	19·7	19·4	19·2	19·2

† Duruz and Ubbelohde [10].

θ_t extracted from the order parameter S_{CD}

$$\cos\theta_t = [\tfrac{1}{3}(4S_{CD} + 1)]^{1/2}. \qquad (3)$$

These results are reviewed in table 5. The tilt angles θ_t fall in the range 30–38°, very similar to the room temperature case.

Finally, the persistence of a broad, weak bilayer spacing line in the clear liquid phase, as seen in Na i-C_5 and Na 3-MeC_5, has been ascribed either to wall effects [10] or to a fluid lamellar structure [3, 21].

5. Conclusions

In our X-ray diffraction studies of spatial parameters of short-chain sodium alkanoates, we have found some close correspondences between the room temperature crystal structure and mesophase properties. The size of the ^{23}Na quadrupole coupling constant, which is expected to depend positively upon the lateral packing area in the mesophase, was found to be related to the room temperature lateral packing area. Bilayer spacings were found to change relatively little over the temperature range 25–300°C, spanning several phases. We conclude that the neat phases of short-chain alkanoates resemble their crystalline phases to a greater extent than do long-chain alkanoates. This difference in behaviour may be due to the reduced influence of thermal agitation for shorter chains.

Our conclusion is further supported by the fact that the lateral packing areas in sodium *n*-butyrate and sodium isovalerate increase by only about 25 per cent from the room temperature crystal to the neat phase, as compared to the near doubling of the lateral packing area in long-chain *n*-alkanoates ($n_c \geq 12$). High temperature density measurements of other short-chain alkanoates would be useful in determining their lateral packing areas in the neat phase, in order to establish with greater certainty whether the ionic double layer remains, or is replaced by some other structure [8] at elevated temperatures.

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