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The thermotropic liquid crystals formed by anhydrous sodium ricinoleate

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The polymorphism of sodium ricinoleate has been examined using differential scanning calorimetry, optical microscopy and low angle X-ray diffraction. There are three low temperature phases, separated by small transition enthalpies, where the molecules are packed in layers with little molecular disorder. At high temperatures (> 160°C), two semi-molten mesophases are formed. Both have distinct optical textures under polarizing microscopy, that of the highest temperature phase being the typical fan pattern of a hexagonal phase. X-ray diffraction shows that this phase is comprised of hexagonally packed oblate spheroids arranged in layers according to an ABAB type pattern. It has not been reported previously for surfactants. The head groups form the cores of the spheroids with molten alkyl chains filling the remaining space. In the lower temperature mesophase, the head groups pack into rods joined in fours to give layers of a tetragonal array. The layers stack to give a body centred tetragonal structure. Again, the head groups form the rod cores, while alkyl chains fill the remaining space.

1. Introduction

The formation of themotropic mesophases in alkali and alkaline earth metal soaps has been investigated extensively [1–4]. The mesophase behaviour changes with a change in the valancy of the cations, the nature of polar groups and the nature of the hydrocarbon moiety. Sodium ricinoleate (NaR) is a C-18 carboxylate with a *cis*-double bond at the 9–10 carbons and a hydroxy group at the 12th carbon atom. We have established the significant effects of this mid-chain polarity on the micellar properties and the lyotropic mesophases of NaR [5, 6]. The Krafft boundary is lower, the micelles are smaller and the hexagonal phase melts at a much lower temperature than is observed with typical long-chain soaps. Also, the hexagonal and lamellar phases are separated by a 'reentrant' micellar solution rather than a bicontinuous cubic phase. This behaviour, typical of a short chain surfactant, occurs because the 12-OH group resides at the micelle surface, giving an effective micelle radius of *c*. seven carbon atoms. The structural features of NaR may be expected to have significant effects also on the thermotropic phases. In this study we report the effects of this mid-chain polarity on the thermotropic phase transitions and compare the results with those for a saturated C-18 soap, sodium stearate (NaSt), and an unsaturated C-18 soap sodium oleate (NaOl).

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The techniques used include polarizing optical microscopy, differential scanning calorimetry (DSC) and low angle X-ray diffraction.

2. Experimental

2.1. *Materials and methods*

Pure sodium ricinoleate ($>99\cdot9$ per cent) was prepared by saponifying pure methyl ricinoleate as described elsewhere [5]. The maximum moisture content was <1 wt% estimated by thermogravimetric analysis. The infrared spectrum of NaR was recorded by KBr pellet technique on a Perkin–Elmer FTIR spectrophotometer. The optical properties were studied using a Carl Zeiss Jena polarizing optical microscope equipped with a Linkam hot stage and a camera. The DSC transition temperatures and enthalpies were determined using a Mettler TA 3000 thermal analysis system with associated control unit TC10 TA processor. The samples were sealed in aluminium pans and measurements were made at scanning rates of $10^\circ\,\mathrm{min}^{-1}$ with nitrogen as purge gas.

The low angle X-ray scattering data were obtained using a Siemens Kristalloflex-8110 diffractometer. Similar measurements were carried out on beam line 7·2 at the SERC Synchrotron Radiation Laboratory at Daresbury (UK). Both the sets of data agreed with experimental error.

3. Results

3.1. *Differential scanning calorimetry*

The DSC thermogram of NaR on heating (see figure 1) showed minor transitions over the temperature range 80–120°C, and four major transitions between 120–220°C when the material completely melts to an isotropic liquid. During the first heating, the twin peaks between 160–190°C were not resolved. However, the thermograms on subsequent heating/cooling cycles were reproducible (see figure 1). The transition temperature (T_t) and the corresponding enthalpies (ΔH) for NaR and other C-18 soaps, sodium stearate (NaSt) [2] and sodium oleate (NaOl) [2] are summarized in table 1.

On heating, the first two minor transitions are accompanied by very small enthalpies suggesting that phases 1 and 2 are crystal modifications. The third transition could be the crystal to liquid crystal transition where the alkyl chains are in a molten state. But the enthalpy change of this transition ($2\cdot2\,\mathrm{kJ\,mol^{-1}}$) appears to be too low to be characteristic of melting of alkyl chains [2, 6]. Hence this is probably another crystal to crystal transition. Thus phase 3 may be another crystal phase or a very ordered mesophase where the alkyl chains are only partially melted. The sharpness and large enthalpies of the two transitions at 160–190°C suggest that a significant fraction of the NaR molecule is becoming mobile. The magnitude of ΔH for the second transition also suggests that the phase structures of 4 and 5 are significantly different. The last transition involves the largest enthalpy change (about 45 per cent of the total ΔH), and is a transition where the mesophase melts to an isotropic liquid. For conventional soaps, it is generally accepted that multiple transitions reflect a complex melting process where first the hydrocarbon chains and then the polar groups undergo progressive disordering [7–10]. Thus in the present case, there appears to be a considerable order within the head-groups prior to the formation of the liquid. The total enthalpy of transition (ΔH_{tot}) from crystal to isotropic liquid is considerably smaller as compared to NaSt and NaOl (see table 1).

On cooling no hysteresis effects were observed except for the 5/4 phase transition. This leads to a 20° increase in the stability range of phase 5. The total enthalpy change is not significantly different from that in the heating cycle.

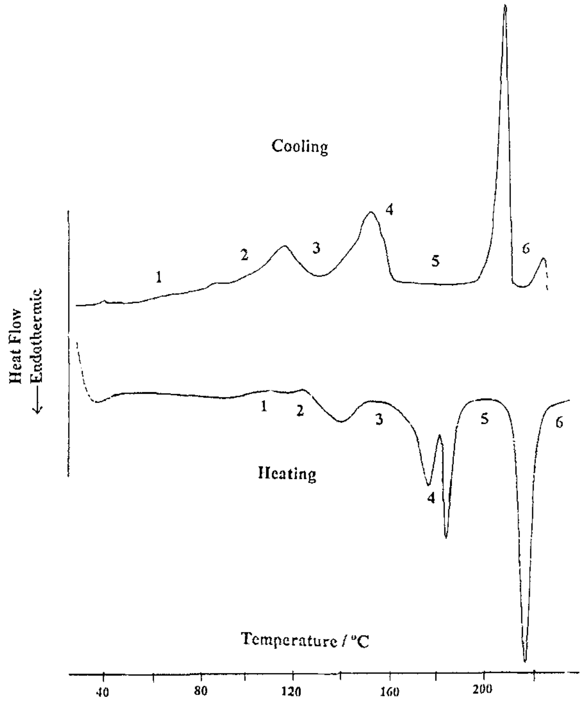


Figure 1. The differential scanning calorimetry (DSC) thermograms of anhydrous sodium ricinoleate on heating and cooling. The numbers 1–6 refer to the various new phases formed (see text).

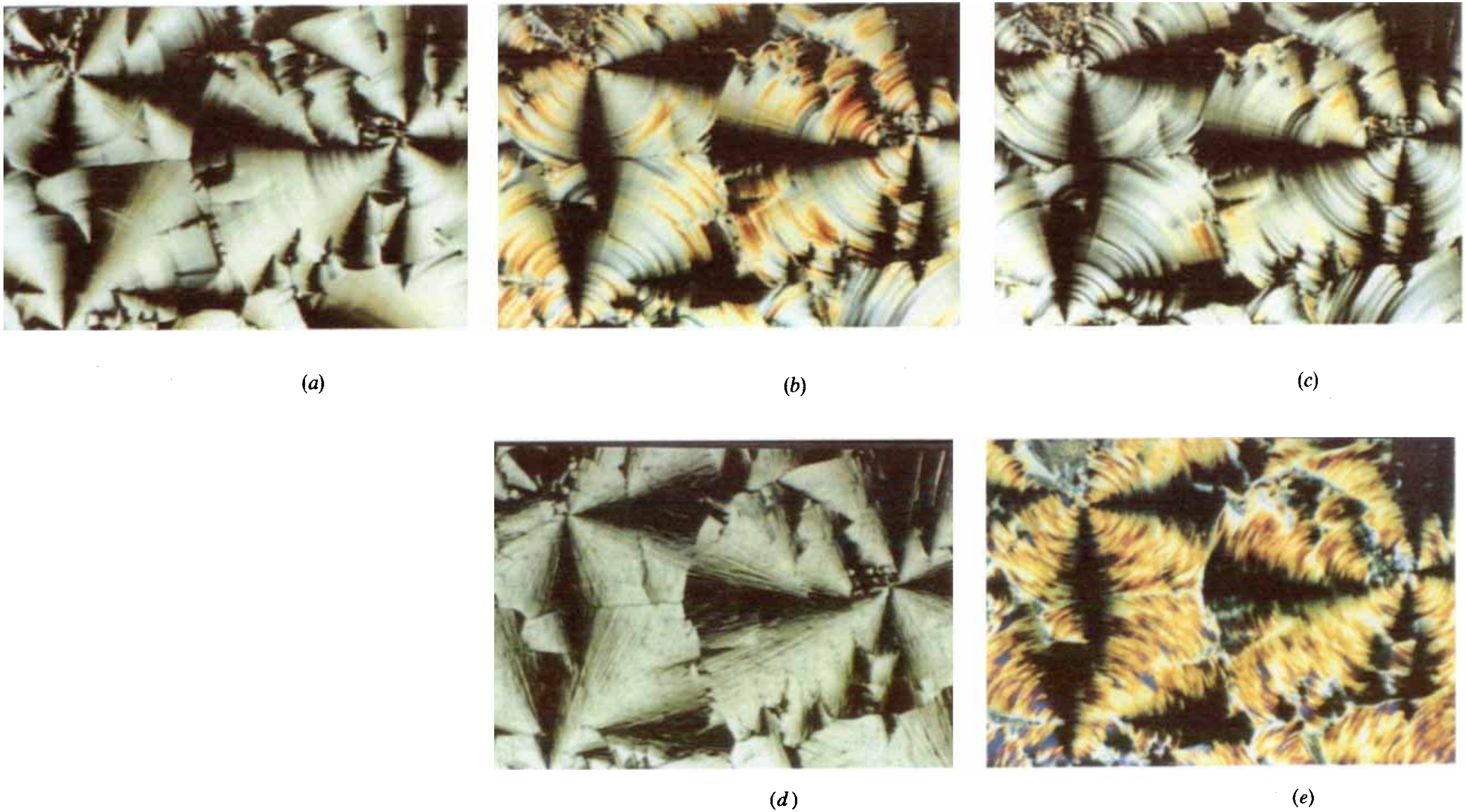
Table 1. Transition temperatures (T_t°C) and enthalpies of transitions (ΔH/kJ mole^{-1}) (in parentheses) in C_{18} sodium soaps

Stearate†	Oleate†	Ricinoleate‡ Heating	Ricinoleate‡ Cooling
89 (3·9)	40 (6·7)	63 (1·0)	210 (10·5)
114 (21·6)	66 (1·3)	115 (<0·05)	158, 153 (6·1)
134 (16·8)	115 (12)	125 (2·2)	120 (3·2)
208 (6·7)	187 (3·7)	160, 183 (8·9)	87 (0·2)
238 (6·5)	202 (3·6)	213 (10·2)	
280 (2·2)	237 (8·0)		
ΔH_{tot} **57·7**	**35·3**	**22·3**	**20·0**

†Data from [2 (*a*)].
‡Present work; transition temperatures taken as the onset temperatures of DSC peaks.

3.2. *Optical microscopy*

Optical textures were observed under a polarizing microscope during cooling from the liquid and subsequent heating cycles. NaR melts at about 220°C to an isotropic liquid with some very slight degree of decomposition. On cooling, a focal conic, fan-like texture characteristic of a hexagonal phase is observed from 217 to 160°C (see figure 2 (*a*)). This supports the DSC observation that on cooling, the phase 5 exists in this temperature range. The optical texture indicates a phase with hexagonal symmetry



(*a*) (*b*) (*c*)

(*d*) (*e*)

Figure 2. Optical textures of anhydrous sodium ricinoleate observed by polarizing optical microscopy (magnification ×75) during cooling and heating cycles. (*a*) A focal conic, fan-like texture observed on cooling the isotropic liquid from 217° to 160°C (189°C). (*b*) Increased birefringence and prominent concentric rings on cooling below 160°C (158°C). (*c*) Appearance of fine vertical striations and diminished birefringence of reheating to 180°C (175°C). (*d*) Fan-like texture above 188°C on heating (189°C). (*e*) 'Solid' texture formed on cooling at and below 150°C.

[11]. Below 160°C the texture consists of prominent rings (see figure 2 (*b*)), which indicate a significant change in the phase structure [12] to an ordered layered phase.

On re-heating from 151° to 175°C, the optical texture remains similar to that below 160°C on cooling. With increasing temperature, vertical striations gradually appear within the concentric rings, and the birefringence is reduced (phase 4, figure 2 (*c*)), but the overall pattern remains. However, at 189°C a sudden change to a fan-like texture (figure 2 (*d*)) occurs (phase 5) which lasts to 217°C when the sample melts to an isotropic liquid. If the phase 5 is re-cooled without melting, then at 160°C the 'solid' texture reforms, but with a marked increase in birefringence (see figure 2 (*e*)). This texture remains on cooling to room temperature.

These observations are in agreement with the DSC results and suggest that phase 5 is a type of hexagonal phase, whereas phases 1 to 3 are layered phases (smectic or crystalline).

3.3. *X-ray and IR measurements*

X-ray diffraction studies were carried out on the powdered anhydrous NaR; the sample was melted prior to the measurements. From 25° to 115°C, the diffraction pattern—see table 2—was characteristic of a bilayer crystal structure. The diffraction pattern consisted of sharp reflections up to the 8th order. The interlayer distance remained constant at 43·2 Å throughout the temperature range studied. This value is comparable to those for other fatty acid soaps [13]. At higher angles, two intense and somewhat broad reflections of average spacings 4·5 Å and 4·2 Å were observed. These reflections are associated with CH_2–CH_2 or interchain reflections [14]. In the hydrocarbons, a single, broad peak at 4·5–4·6 Å is indicative of liquid chains and a peak at 4·2 Å is associated with the hexagonal chain-packing [15].

The IR spectrum of NaR at room temperature showed a single peak at *c*. 720 cm^{-1} which is indicative of either hexagonal or triclinic packing of the molecules [16]. The tilt angle of 60° suggests that it is triclinic packing. Moreover, this packing may be easily deformed locally and is thus flexible to the space requirements of substituted polar groups and branches [17].

At 150°C (phase 3), the X-ray pattern is fairly similar to that at lower temperatures. However, at higher angles, the two reflections at 4·5 Å and 4·2 Å were replaced by (at least) three somewhat broad reflections at *c*. 4·5 Å. Some degree of alkyl chain order must be present since the reflections are much sharper than those from liquid alkanes. This supports the conclusion from the DSC data that the alkyl chains still remain partially ordered. The low angle reflections indicate a bilayer structure with an interlayer spacing of 39·8 Å, which suggests a thinning of the bilayer die to the 'partial' disordering of the alkyl chains. Because of the hysteresis in the transitions between phases 4 and 5, diffraction patterns were recorded in the temperature sequence 200°C (cooled from the melt), 170°C, 150°C, 170°C and 200°C. The 170°C pattern obtained on cooling showed that a mixture of phases 4 and 5 was present. Hence the data for phase 4 are taken from the heating run, while those for phase 5 are the same, whether taken on heating or initial cooling.

From 150° to 200°C the spectra showed partial orientation effects, with some lower angle reflections oriented along the equator and the high angle diffuse band oriented along the meridian. The sample tube long axis was oriented along the equator. We deduce that the phases 4 and 5 are unlikely to have conventional layer structures, since this would imply that the layers are perpendicular to the tube surface, an unlikely event. The diffraction pattern at 170°C (phase 4) was characterized by nine sharp reflections at

Table 2. X-ray spacings in sodium ricinoleate at 25°–115°C.

d/Å	Intensity†	*hkl*
43·3	vvs	001
21·5	s	002
14·6	vs	003
10·8	s	004
8·6	m	005
7·2	s	006
6·2	w	007
5·4	w	008
4·6	s,broad‡	
4·1	s,broad‡	

Average interlayer spacing = 43·2 Å indicates a bilayer structure with molecules arranged head-to-head and tail-to-tail and tilted by 60° with respect to the bilayer normal (†vvs, very very strong; vs, very strong; s, strong, m, medium w, weak; vw, very weak. ‡Probably alkyl chain reflections].

low angles and a diffuse ring at 4·5 Å, the latter indicating disorder in alkyl chains (see table 3). Of the nine sharp reflections, six intense lines are in the ratio 1 : 2 : 3... etc., suggesting a layered structure with an interlayer spacing of 39·0 ± 0·1 Å. However, the presence of additional lines is evidence of a more complex structure than a simple lamellar phase. Using a Bunn Chart for a tetragonal lattice [18], all the reflections may be indexed, although there are several possible fits which require distinguishing.

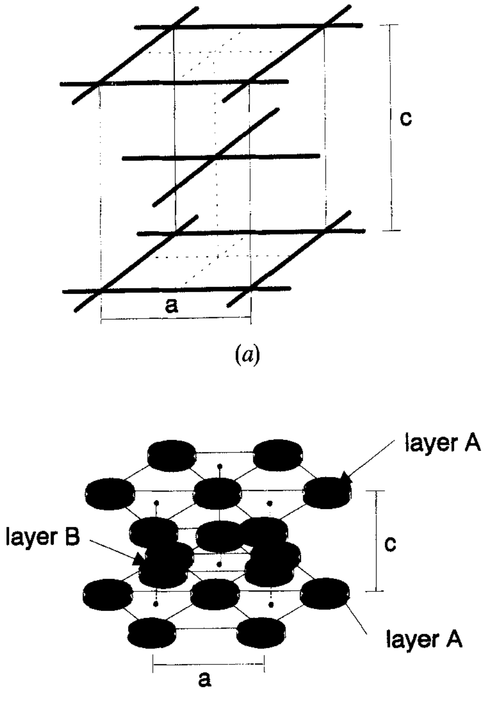
The first is a simple tetragonal lattice with $a = 36{\cdot}4$ Å and $c = 39{\cdot}0$ Å. The structure is very close to cubic symmetry and would probably have a low birefringence. It also has a problem in that the diagonal of the unit cell is ∼64 Å, which is considerably larger than the length of two all-*trans* NaR chains (50 Å). Therefore, there would be a difficulty in filling the centre of the unit cell. For these reasons the structure is considered to be unlikely. No simple tetragonal structure has been previously reported in the literature for any surfactant/lipid system.

A second indexation is to a body centred tetragonal structure, illustrated in figure 3 (*a*), with $a = 51{\cdot}5$ Å and $c = 78{\cdot}0$ Å. A phase having this structure was first found for one of the mesophases of anhydrous long chain calcium soaps by Luzzati *et al.* [19], and referred to as phase T. The structure consists of finite rods containing the head groups linked together four by four to give a planar two-dimensional network. The space between the rods is filled by disordered alkyl chains. Since the alkyl chains form a continuous region, this is a 'reversed' phase. It can be visualized as a lamellar structure where the polar layers contain hydrocarbon-filled holes arranged on a tetragonal lattice. The 'holes' in one layer are located opposite rod-junction zones in the neighbouring layers. The interlayer spacing is 39·0 Å ($= c/2$) and is comparable to that of the lower temperature lamellar structure (phase 3) which has a layer spacing of 39·8 Å. Once again there is a problem with the structure when it is considered in relation to the NaR chain length and volume. There would be difficulty in filling the centres of the hydrocarbon 'holes' at a reasonable hydrocarbon density. A third indexation to a similarly centred tetragonal structure, summarized in table 3, provides a satisfactory structure with $a = 26{\cdot}5$ Å and $c = 78{\cdot}0$ Å. Here the distance between one corner of the tetragonal cell and the centre rod junction is about 43 Å, which can be easily bridged by

Table 3. X-ray spacings for sodium ricinoleate at 170° (phase 4). Indexation to body centred tetragonal lattice (see figure 3(*a*)) with $a = 26{\cdot}5 \pm 0{\cdot}3$ Å and $c = 78{\cdot}0 \pm 0{\cdot}2$ Å.

d_{obs}/Å	Intensity†	*hkl*	d_{cal}/Å	Percentage error
39·2	vvs	002	39·0	0·51
19·7	s	004	19·5	1·01
18·1	vw	103	18·6	2·76
17·1	s	112	16·9	1·17
13·4	vw	200	13·3	0·74
		114	13·5	0·74
12·9	vs	006	13·0	0·77
		202	12·5	3·1
9·8	m	008	9·8	0
7·8	m	0010	7·8	0
6·5	w	0012	6·5	0
4·6	diffuse‡			

†Symbols as for table 2.
‡Alkyl chain reflection.



(*a*)

(*b*)

Figure 3. Schematic representation of reverse tetragonal L_α^h (T_2) phase and hexagonally packed oblate spheroids. (*a*) L_α^h (T_2) phase: Rods of finite length containing the headgroups linked together four by four giving a planar two-dimensional network. The space between rods is filled by disordered alkyl chains; the 'holes' in one layer are located opposite rod-junction zones in neighbouring layers. (*b*) Oblate spheroids packed hexagonally in layers in an ABAB pattern.

two NaR molecules, given that is it unlikely that their head groups are located precisely on the (0, 0, 0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ positions.

Until recently the report [9] of Luzzati *et al.*, remained the only observation of this structure. However, during the past 2–3 years, there have been a number of reports [19–22] of a phase of this type in aqueous surfactant systems where the aqueous polar region forms a tetragonal array of holes in lamellar bilayers. Here also the holes are packed in a body centred array. Since the structure consists of surfactant layers, it closely resembles the L_α phase. We have suggested [22] the label L_α^h (T_1) for this structure (h, 'holes'; T_1, normal, i.e. water-continuous (body centred) tetragonal array). Hence for phase 4 we suggest the label L_α^h (T_2).

In the original work on anhydrous soaps, the tetragonal phase of calcium stearate [19] was bounded, to higher temperature, by a hexagonal (H_2) phase in which long cylindrical rods containing the head groups were hexagonally arrayed in a paraffinic matrix. This acted as the precursor to the higher temperature isotropic phase. In NaR at 200°C (phase 5), the diffraction pattern consists of an increased number of lines (17) as well as a diffuse reflection at 4·5 Å see table 4. The presence of many sharp lines indicates a high degree of order within the mosophase. Using Bunn Charts, the pattern may be indexed to a hexagonal structure which is consistent with the optical texture. However, the structure is not a simple hexagonal phase of infinite rod aggregates as mentioned above. The many additional reflections and the high degree of order suggest a more complex structure.

In the anhydrous strontium stearate system, a rhombohedral structure was observed between a lower temperature lamellar and a higher temperature cubic (V_2) phase followed by an H_2 phase [1, 9]. Here the rods containing the head groups are connected three by three in layers to form a hexagonal network; the layers are then stacked in an ABCA arrangement. In the NaR system we have been unable to find a satisfactory rhombohedral indexation of phase 5. Several indexations are possible, but all are to hexagonal lattices with an ABAB type of stacking. The most satisfactory indexation to phase 5 is a hexagonal lattice with $a = 31{\cdot}8$ Å and $c = 41{\cdot}6$ Å. The absence of a rhombohedral phase in NaR may be because the system passes through a tetragonal phase, with its alternating layer structure acting as a promoter for an ABAB type structure, rather than passing directly from a lamellar structure which might allow the ABCA structure.

Given a hexagonal ABAB arrangement for phase 5, there remains the question of its precise structure. Two arrangements are possible. The head groups could aggregate again to form rods which again connect with each other three by three to form a hexagonal network within a plane, i.e. the rhombohedral structure, but with only ABAB packing. Secondly the head groups might aggregate together into disc shapes (oblate spheroids) which pack onto a hexagonal lattice. This structure is rather similar to one proposed by Skoulios, i.e., a hexagonal version of the orthorhombic body centred phase [10]. It could also be thought of as being closely related to the I_2 cubic phase comprising small reversed micelles which occurs with lipids and soap/alcohol mixtures at low water contents [19]. Given the volume fraction of the headgroups (*c.* 5–10 per cent) the rod network can be ruled out because the rods have too small a diameter for reasonable stability of a crystalline arrangement. Hence the disc shape inverse micelle model is the preferred structure. The oblate spheroids are hexagonally packed in planes of average thickness 20·8 Å. Within a plane, the centre–centre separation of the spheroids is 31·8 Å. From the volume of the unit cell, we estimate that each spheroid contains *c.* 30 NaR molecules. It is clear that a considerable alkyl chain

Table 4. X-ray spacings in sodium ricinoleate at 200°C (phase 5). The pattern is indexed to a hexagonal lattice (see figure 3 (*b*)) with $a = 31{\cdot}8$ Å and $c = 41{\cdot}6$ Å.

Reflections given by $\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{C^2}$.

d_{obs}/Å	Intensity†	*hkl*	d_{calc}/Å	Percentage error‡
27·8	vvs	100	27·5	0·92
20·8	m	002	20·8	—
15·9	vs	110	15·9	—
13·9	vs	200	13·77	0·95
12·9	m	201	13·07	1·33
12·2	vs	103	12·39	1·5
10·5	m	004	10·40	0·97
10·2	m	211	10·10	1·00
9·2	m	300	9·18	0·10
8·9	vw	301	8·96	0·65
8·6	m	114	8·70	1·19
8·2	vw	213	8·32	1·50
		204	8·30	1·19
7·8	vw	220	7·95	1·90
		310	7·64	2·11
7·5	vw	222	7·44	0·81
7·1	vw	205	7·13	0·36
6·4	vw	320	6·32	1·27
6·2	vw	314	6·16	0·69

†Symbols as for table 2.
‡Calculated error in Q ($Q = 2\pi/d$).

disorder is required to fill the spaces between the polar cores of the spheroids. Also, the cross-section of the polar groups is *c.* 36 Å^2 in the crystal. The area occupied by the flattened spheres is 411·6 Å^2. This is too small to accommodate 15 double layered headgroups with a packing similar to that in the crystal. Clearly, the polar region is thicker than in the crystal arrangement. Also, it simply is not possible for all the headgroups to have identical locations. The detailed molecular arrangements within the polar cores remains a subject for further study.

With this structure the description so far has assumed a model where the OH groups do not participate in the polar cores. The average layer separation (20·8 Å) is not much larger than the length of NaR in the wicket conformation. Hence it is possible that some 12-OH groups could be present in the polar region. Their presence could help to screen electrostatic interactions between carboxylate groups and to reduce sodium carboxylate/alkyl chain contacts, both being energetically favourable. However, the 31·8 Å separation between spheres within the planes does require some 12-OH groups not to be included in the core. Also, the large ΔH of the 5/6 transition indicates that a considerable order remains in the headgroup region; hence the OH groups would be required to fit into a regular lattice. The presence of OH groups in the polar region in phase 5 remains an open question, but on balance it appears to be unlikely.

It is surprising that the layers form an ABAB pattern rather than ABCABC. A possible explanation for this might arise from the electrostatic interactions between the polar micelle cores. The ordered arrays of charges could give rise to attractions between micelles in every other layer; these are favoured in the ABAB pattern. Work on related surfactants and theoretical studies are required for further understanding of the structure.

The structure proposed for phase 5 is novel and has not been reported previously for any surfactant system. As mentioned above, structurally, it is fairly closely related to the I_2 cubic phase comprised of small reversed micelles that occurs with lipids and soap/alcohol mixtures at low water contents [19]. The *oblate* spheroidal nature arises from the residual order in the polar groups. Clearly before the structure can be accepted, it requires confirmation by other techniques.

These structures show a clear progression with increasing temperature. From 25°C to 115°C there is a bilayer crystal structure with a layer spacing $d = 43{\cdot}2$ Å. At higher temperature (150°C), the alkyl chains are partially melted and there is a bilayer structure with $d = 39{\cdot}8$°C. At 170°C the structure is centred tetragonal—essentially a network of rods joined four by four in planes, with the rod junction of one layer over the hydrocarbon 'hole' in the neighbouring plane. The layer spacing here is 39·0 Å, whilst the side by side separation of the rods in a plane is 26·5 Å. Finally at 200°C the network has broken up into oblate spheroidal reversed micelles packed in layers.

4. Discussion

In the forthcoming discussion we compare the thermotropic phase behaviour of NaR with other sodium soaps—sodium stearate (NaSt) and sodium oleate (NaOl). NaOl is structurally closer to NaR in that it has a *cis*-double bond at the 9, 10 carbon atoms, while NaSt is a 'normal' soap with a saturated alkyl chain.

The early works by Vold *et al.* [2], Pacor *et al.* [6] and Madelmont *et al.* [3], suggest that NaSt and NaOl undergo six to eight thermotropic phase transitions, whereas NaR undergoes six before melting to the isotropic liquid. NaR clearly forms fewer phases with lower transition temperatures and a smaller total enthalpy change (see table 1). These observations can be related to the structural differences between these soaps. NaSt being a saturated soap has a compact packing of molecules in the crystal. The packing becomes increasingly less compact in NaOl and NaR which have an unsaturation or an unsaturation and a hydroxy group in the middle of the molecules. Also, in the liquid state, the polar OH group is expected to reside close to, or among, the sodium carboxylate moieties; hence the conformational freedom of the alkyl chain is severely restricted. Thus the enthalpy change for the lower temperature transitions of NaR, which are due mainly to hydrocarbon melting (< 165°C), are much smaller than with NaSt or NaOl. However, the higher temperature transitions (< 165°C) all have similar total enthalpies (*c.* 15 kJ mole^{-1}), as expected if they arise mainly from melting of the polar headgroups. It is somewhat astonishing that the 12-OH substituent of NaR does not disrupt this simple pattern, perhaps indicating that the 12-OH group does not penetrate the headgroups in the mesophases.

The most striking difference between NaR and conventional soaps is the absence of a 'neat' L_α phase at high temperatures. However, we note that while a conventional L_α phase does form for NaSt just prior to final melting, NaOl has a large heat for this transition (which is also 40° lower). This implies that there is significant headgroup order in the highest temperature mesophase for both NaOl and NaR. Clearly, on melting they form a reversed micellar structure rather than L_α because of their increased negative curvature in the non-polar region (see below). This prevents the occurrence of extensive bilayers where headgroup and chain areas are equal. (Oleate chains are well known to induce negative micelle curvature; for example, monoolein forms inverse bicontinuous cubic (V_2) and hexagonal (H_2) phases at temperatures where monostearin forms only the L_α phase [23–25].

If the headgroups maintain a considerable degree of order within the phases 4 and 5, then this will prevent the incorporation of the 12-OH group in the polar region, unlike the behaviour in the aqueous mesophases [5]. The large dimensions required for the alkyl chains to fill all the spaces between the polar groups in both phases supports this conclusion, since the chains are required to have extended conformations. The sequence of phase transformations is then seen as a competition between the disordering influence of an increasing conformational freedom of the chains on increasing the temperature and the ionic forces between the 'semi-crystalline' headgroups which retain order. This results in the occurrence of smaller surfactant aggregates with increased chain disorder, until the headgroups finally melt, when the isotropic liquid phase occurs.

To summarize, NaR forms fewer mesophases with lower heats and transition temperatures than conventional soaps. This is attributed to poor packing of the 12-OH group and the 9–10 double bond in the crystal, along with the conformational restrictions caused by the requirement of the sodium carboxylate groups to maintain some crystalline order within the mesophases. This gives rise to the formation of two unusual phases of type L_α^h (T_2) and oblate spheroids packed in alternating layers.

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