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Liquid Crystals

Publication details, including instructions for authors and subscription information:

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To cite this Article Harrison, William J. , McDonald, Malcolm P. and Tiddy, Gordon J. T.(1990) 'Phase behaviour of lithium and sodium salts of phenylstearic acid', *Liquid Crystals*, 7: 4, 509 – 515

To link to this Article: DOI: 10.1080/02678299008033827

URL: <http://dx.doi.org/10.1080/02678299008033827>

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Phase behaviour of lithium and sodium salts of phenylstearic acid

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(Received 4 October 1989; accepted 16 November 1989)

Phenylstearic acid, prepared from oleic acid and benzene, using the Friedel-Crafts reaction, has been confirmed to be a reproducible mixture of twelve positional isomers. Lithium and sodium salts of this acid are semi-crystalline solids which behave in many ways like pure single substances. The thermotropic polymorphism of these soaps has been studied using DSC and polarizing microscopy (as well as X-ray diffraction and ^7Li NMR spectroscopy for the former soap). Both soaps exhibit characteristic stepwise melting behaviour and form stable reversed hexagonal mesophases at elevated temperatures, in contrast to the lamellar phases exhibited by the unsubstituted soaps.

1. Introduction

Most of the factors governing the formation and stability of liquid-crystalline phases occurring in surfactant-water systems (such as electrostatic interactions, surfactant head-group hydration, steric repulsions and alkyl chain conformations) have been studied extensively and are understood qualitatively [1, 2]. Few fundamental studies have been made of concentrated binary surfactant-hydrocarbon mixtures in spite of their widespread use in industry and their special relevance to the field of soap-thickened lubricating greases. At room temperature the crystalline alkali metal and alkaline earth fatty acid soaps show little solubility in hydrocarbons. When heated, the soaps alone undergo a process of complex, stepwise melting in which first the hydrocarbon chains and then the polar groups undergo progressive disordering [3, 4, 5]. At higher temperatures, hydrocarbons can be dissolved in limited amounts in the disordered hydrocarbon regions of the soap while the polar groups largely retain their crystalline order [6].

In a DTA study of several lithium stearate-oil systems, Cox (7) demonstrated that in each of the systems the number and nature of the phases found were remarkably similar to those in the solvent free soap. At room temperature lithium stearate was essentially insoluble in the oils used since the first transition temperature of the solid soap (116°C) remained constant at all soap-oil compositions. However, Honig and

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Singletery reported that the alkali and alkaline earth phenylstearates (derived from the Friedel–Crafts reaction between oleic acid and benzene) are readily soluble in aromatic solvents at room temperature [8]. The solutions formed are shear-birefringent, highly viscous and slightly non-newtonian in flow.

It was considered that these systems would form a convenient starting point for the study of binary surfactant-hydrocarbon mixtures. In order to characterize fully such systems it is also necessary to study the thermotropic behaviour of the anhydrous soaps. In the present paper we describe the thermotropic behaviour of one of these soaps, lithium phenylstearate, (LiPS), and a future publication will describe the lyotropic behaviour of LiPS in hydrocarbon solvents. The phenylstearic acid obtained from the Friedel–Crafts reaction is a mixture of twelve isomers with substitution at the C_6 to C_{17} positions on the fatty acid chain.

2. Experimental section

2.1. Materials

Phenylstearic acid was prepared by the Friedel–Crafts reaction of oleic acid (BDH Biochemicals, 92 per cent minimum assay) with an excess of benzene, using aluminium chloride as the catalyst under anhydrous conditions [9, 10]. The purest phenylstearic acid fraction, obtained as a very pale yellow oil at room temperature, was collected between 212°C and 217°C at 0.05 to 0.10 mm Hg (typical yield 28.1 per cent). Micro-analysis gave the results: calculated for $C_{24}H_{40}O_2$: C 79.94 per cent, H 11.18 per cent; found: C 80.02 per cent, H 11.19 per cent for this fraction. Refractive index for the purest fraction, $n_D^{20} = 1.4900$. Nicolet and de Milt [9] reported $n_D^{20} = 1.4905$ for their purest fraction which was collected at 250°C and 4 mm Hg. Analysis of the purest acid fraction in our laboratories by GLC of the alkyl aryl ketones obtained by chromic acid oxidation confirmed the isomeric composition of the acid [11] and our results are within ± 1 mol% of those obtained by Smith *et al.* [12, 13], for ten of the twelve isomers and ± 1.5 mol% for the other two.

Lithium phenylstearate was prepared by neutralising an ethanolic solution of the parent acid to a phenolphthalein end point by addition of a carbonate-free, 50 per cent aqueous ethanol solution of lithium hydroxide monohydrate. After removal of the solvents and drying under vacuum over phosphorus pentoxide at 110°C for 48 hours, the salt was isolated as a near white, waxy solid. The drying procedure was repeated periodically to maintain the soap in an anhydrous state, even though infrared studies by Kagarise [14] showed that LiPS is not hygroscopic. The infrared spectrum of the dried soap also showed that it contained no free acid. A sample of sodium phenyl stearate was also prepared by the procedure outlined above. Microscope observations were made using a Vickers M41 Photoplan polarizing microscope equipped with a Kofler hot-stage. DSC thermograms were recorded using the Mettler TA3000 Thermal Analysis System. Samples were contained in standard aluminium crucibles and a slow stream of nitrogen was passed through the chamber containing the sample and reference crucibles to prevent oxidative decomposition at high temperatures. First order transition temperatures were taken systematically as the apex of the curve of milliwatts input (ordinate) versus temperature (abscissa). For second order transitions the temperature recorded corresponded to 50 per cent completion of the transition.

X-ray diffraction experiments in the small-angle region were carried out using a Kratky camera equipped with a slit collimation system. Samples were contained in a screw assembly glass cell of 2 mm thickness. Elevated temperatures were attained by

electrical heating of the sample holder using an Anton-Parr K-HR temperature control unit which controlled the sample temperature to $\pm 1.5^\circ\text{C}$. Samples were held at each temperature for approximately 20 min to allow equilibration before data collection was started. The data was smoothed, desmeared to compensate for slit collimation effects [15] and fitted using computer methods to yield the characteristic Bragg spacings and peak intensities.

^7Li N.M.R. spectra were recorded using a Bruker WP 80 SY pulsed spectrometer operating at a resonance frequency of 31.14 MHz. Peak widths were measured at half maximum intensity. Room temperature ^7Li spectra were obtained at sample temperatures of $30 \pm 1^\circ\text{C}$. For the temperature dependence studies, a Bruker BVT-1000 control unit maintained the temperature at the sample to $\pm 0.5^\circ\text{C}$. All samples were thermally equilibrated at each new temperature for at least 20 min.

3. Results

3.1. Polarizing microscopy

At room temperature, LiPS can be pressed out between a microscope slide and cover slip to produce regions with a patchy, non-geometric, dully birefringent texture which exhibits partial extinction as the microscope stage is rotated. According to Rosevear [16] and Tiddy [17] similar textures may be exhibited by middle (hexagonal) mesophases. The sample passes through an apparent melting transition between 150° and 160°C accompanied by a marked decrease in rigidity and an increase in the extent of the birefringent texture. Fine striations develop in the sample at approximately 200°C and a general decrease in the intensity of the birefringence is observed, accompanied by a further decrease in viscosity to a liquid-like state. As the temperature is raised slowly to about 240°C , the spectacular birefringent focal conic texture of a fused hexagonal mesophase develops [16]. This fan-like texture was observed up to the melting point at approximately 370°C . A similar sequence of events was observed on heating a sample of anhydrous NaPS, the development of the fan-like texture occurring at about 260°C .

3.2. Differential scanning calorimetry

The thermograms recorded on heating samples of anhydrous LiPS between -170°C and the isotropic melt were characterized by a low temperature second order transition, H1, and three first order transitions, denoted H2, H3 and H4 in order of increasing temperature. Figure 1 shows a typical heating thermogram recorded at a rate of 5°C min^{-1} . The table lists the mean and standard deviation values for the observed transition temperatures and the corresponding enthalpy changes for fifteen samples. The thermotropic polymorphism of anhydrous NaPS appeared similar to that of LiPS, except for an additional transition, H5 at 121.5°C . For LiPS and NaPS, the H3 transition occurs at 227.0°C and 259.0°C respectively and represents the fusion of the polar groups and the formation of a reversed hexagonal mesophase, usually denoted M_2 or H_2 . In sodium stearate, fusion of the polar groups to give a lamellar mesophase occurs at approximately 260°C [3]. It has been found in this laboratory that at 226.5°C lithium stearate also forms a very short-lived lamellar mesophase when reheated from 217.5°C after cooling from the melt [21]. Hence the temperatures at which the polar groups of lithium and sodium carboxylates fuse to form liquid-crystalline phases seem to be independent of the types of mesophase formed. The formation of the reversed hexagonal phases in LiPS and NaPS has

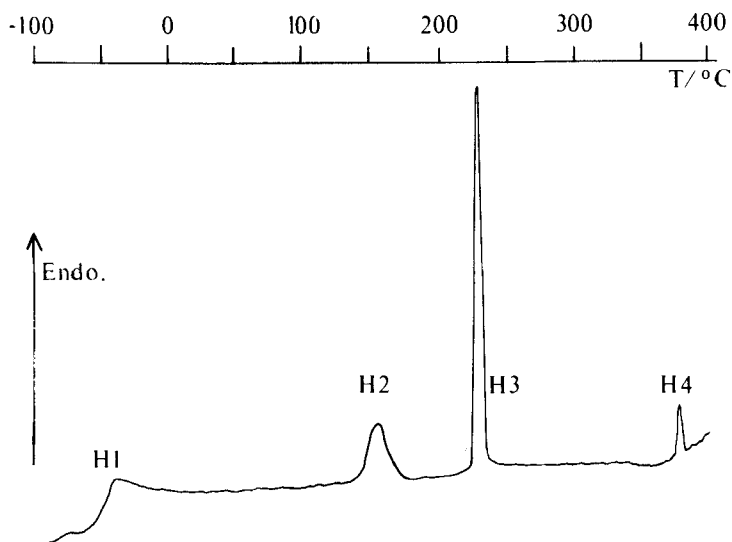


Figure 1. DSC heating thermogram for anhydrous LiPS; heating rate, $5^{\circ}\text{C min}^{-1}$.

been confirmed by polarising microscopy, X-ray diffraction and N.M.R. linewidth measurements.

The temperature ranges of stability of the anhydrous H_2 mesophases of LiPS and NaPS (about 144°C and 154°C , respectively) far exceed those of the lamellar phases of lithium and sodium stearates (approximately 1°C [21] and 25°C [3], respectively). Assuming a similar bonding of the polar groups in the two mesophases, then the increased stability of the mesophases in the phenylstearates may be explained in terms of a greater average separation between, and therefore greater freedom of thermal motion by, highly disordered neighbouring chains in the cylindrical aggregates of the reversed hexagonal phase, than in the planar double layers of the lamellar phase.

Table 1. Phase transition temperatures and enthalpies for lithium and sodium phenyl stearate.

Transition	LiPS		NaPS	
	$T/^{\circ}\text{C}$	$\Delta H/\text{kJ mol}^{-1}$	$T/^{\circ}\text{C}$	$\Delta H/\text{kJ mol}^{-1}$
H1	-49.9 ± 1.1	—	-49.8 ± 1.0	—
H5	—	—	121.5 ± 9.2	1.6 ± 0.5
H2	154.8 ± 3.3	6.0 ± 0.5	187.7 ± 4.2	3.3 ± 0.3
H3	227.0 ± 1.0	11.2 ± 0.4	259.0 ± 0.9	10.9 ± 0.7
H4	370.6 ± 1.1	0.93 ± 0.09	412.9 ± 1.3	1.0 ± 0.2

3.3. N.M.R. spectroscopy

The ^7Li N.M.R. powder spectrum of anhydrous LiPS at 22°C consists of a central line flanked by two equally spaced satellites. The quadrupole splitting (as measured from satellite to central peak) was 20 ± 1 kHz, of a similar order of magnitude to splittings reported for polycrystalline lithium phosphide [18] and lithium niobate [19]. Because of the small amplitude of the quadrupole splitting satellites and the consequent difficulty in measuring accurately, it was decided to

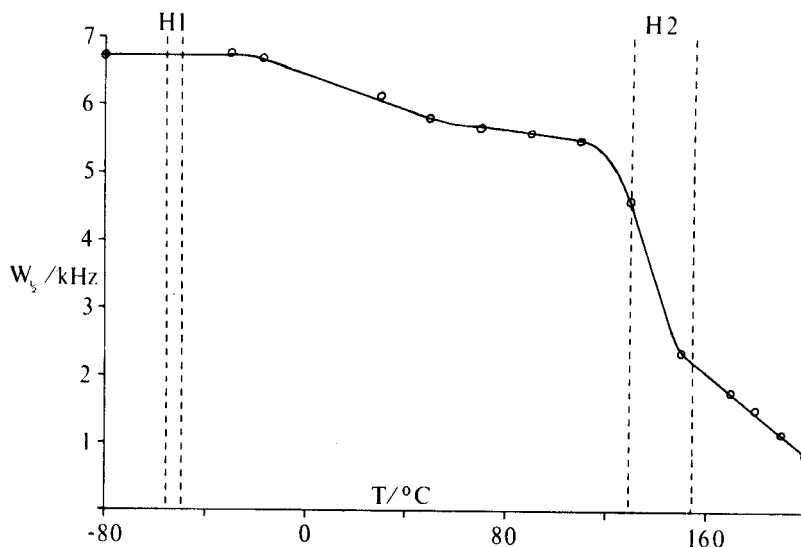


Figure 2. Variation of $W_{1/2}$, the ${}^7\text{Li}$ N.M.R. linewidth, with temperature for anhydrous LiPS.

observe instead the temperature dependence of the ${}^7\text{Li}$ central line width, $W_{1/2}$, over the range from -80°C to $+200^\circ\text{C}$, (see figure 2). Between -80°C and -17°C , $W_{1/2}$ is essentially constant and not affected by the second order transition H1. At room temperature, $W_{1/2}$ is of the same order as that of lithium niobate [19], suggesting a quasi-crystalline arrangement for the polar groups of LiPS. With increasing temperature, $W_{1/2}$ decreases very slowly up to 130°C (the onset of transition H2) when there is a sudden, sharp decrease from 4.60 kHz at 130°C to 2.35 kHz at 150°C . Between 150°C and 200°C (the maximum attainable temperature), $W_{1/2}$ continues to decrease gradually to a final value of about 0.85 kHz .

3.4. X-ray diffraction

At room temperature LiPS gave a small angle diffraction pattern with four sharp reflections corresponding to spacings of 31.1 , 17.8 , 15.8 , and 11.6 \AA whilst NaPS gave spacings of 31.8 , 18.2 , 15.9 and 11.9 \AA . In the high angle region both soaps gave a diffuse reflection at approximately 4.6 \AA . The low angle spacings are almost exactly in the ratio, $1 : 1/\sqrt{3} : 1/\sqrt{4} : 1/\sqrt{7}$, consistent with structures having two-dimensional hexagonal symmetry. For a soap in the anhydrous state, a reversed hexagonal structure (containing rod-like aggregates with a polar core dispersed in a hydrocarbon continuum) is the most favourable.

Figure 3 shows the variation of the hexagonal lattice parameter, a , ($2d_1/\sqrt{3}$), with temperature. The results indicate that over the temperature range from 28°C to 270°C , the reversed hexagonal structure of LiPS was maintained (as evidenced by the continued presence of the $1/\sqrt{3}$ and $1/\sqrt{4}$ spacings at both 190°C and 240°C) but that important structural modifications occurred at the first order H2 and H3 transitions detected calorimetrically (represented on the graph by vertical bands covering the temperature range from the onset of each transition to the point of 50 per cent completion). These results show a gradual, small increase in a across the temperature range, caused by thermal expansion of the hexagonal lattice, and abrupt decreases in a , corresponding to the transitions H2 and H3.

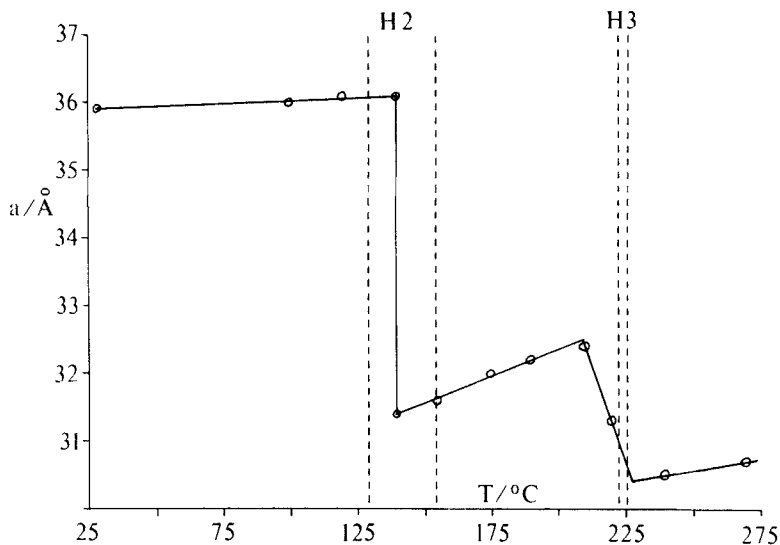


Figure 3. Variation of a , the hexagonal lattice parameter of anhydrous LiPS, with temperature.

4. Discussion

Anionic soaps and surfactants with branched lipophilic groups frequently do not crystallise and the pure anhydrous salts, of which Aerosol OT is the best known example, exist as mesophases of the fused type at room temperature [20]. High and low angle X-ray diffraction results for LiPS and NaPS suggest a similar behaviour at room temperature.

The reversible second order glass-type transition at approximately -50°C for both LiPS and NaPS occurs at a similar temperature to the major melting endotherm of the isomeric phenylstearic acid mixture (-57.3°C) and is therefore considered to involve melting of the hydrocarbon chains. Crystallization of the chains below this temperature is unlikely to occur because of the large number of isomers in the mixture, particularly since each isomer is a racemic mixture of two enantiomers. The different isomers will have a tendency to form separate crystals. Since there is insufficient time for nucleation of all the different crystals, glass formation occurs. This is supported by the invariance of the ^7Li N.M.R. linewidth values during the H1 transition.

The transitions H2 and H3 are both of higher enthalpy than we should expect for fused mesophases. Since the hydrocarbon chains are in a liquid-like state at room temperature, these transitions are attributed mainly to a polymorphism of the polar groups which must be in a quasi-crystalline state at lower temperatures, as suggested by the ^7Li N.M.R. linewidths.

Since substitution of the planar phenyl group on the fatty acid chain does not occur at positions close to the polar groups, we expect little steric repulsion between the substituted chains close to the polar groups at the lower temperatures. In the anhydrous state the polar groups of LiPS and NaPS may be held together by coulombic forces and by coordination bonds between the alkali metal ion and the two equivalent carboxylate oxygens, as suggested by Honig and Singleterry for the linear polymeric structure of the alkali metal phenyl stearates in benzene [8]. For the

solvent-free, anhydrous soaps the hexagonal phases may result from a grouping of a number of these polymeric chains into cylinders possessing polar cores. The room temperature structures of both LiPS and NaPS are therefore regarded as semi-crystalline reversed hexagonal phases.

The H2 transition observed for LiPS by DSC is attributed to a polymorphic rearrangement of the polar groups to a second semi-crystalline reversed hexagonal phase. The pronounced decrease in the ^7Li N.M.R. linewidth may be associated with the onset of limited rotational or translational motion within the polar regions of the hexagonally packed cylinders. The sharp decrease in lattice parameter indicates that this motion also results in a decrease in the centre-to-centre distance of the cylinders, by allowing a sudden increase in the conformational freedom of the hydrocarbon chains.

The enthalpy of the final transition observed by DSC for both LiPS and NaPS (approximately 1 kJ mol^{-1}) is of the order expected for a liquid crystal to isotropic melt and is almost identical to that observed for the melting of the reversed hexagonal mesophase of Aerosol OT.

The authors wish to thank Jeff Rockcliffe for assistance with the N.M.R. measurements at Port Sunlight and Mark Flanagan and Phil Smith for assistance with the X-ray diffraction measurements, also at Port Sunlight. We wish to thank the science and Engineering Research Council and Unilever Research, Port Sunlight Laboratory for financial assistance to one of us (W.J.H.).

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