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Formation of smectic mesophases in binary systems of short chain alkanoic acid salts

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The formation of thermotropic ionic smectic liquid crystals in binary systems of lithium and caesium acetates, propionates and butyrates has been discovered. Mesomorphism of mixed melts of non-mesogenic components results from the formation of complex anions. Correlations between anion mesogenic properties and its size, shape, anisotropy in the Coulomb charge distribution as well as the nature of the surrounding cations are discussed.

1. Introduction

The salts of short chain alkanoic acids form thermotropic ionic liquid crystals which are generally smectics. The abnormality of these liquid crystal compounds consists of their high electrostatic charge concentration, small particle size of the medium (ions) and the absence of any pronounced anisometry in the mesogenic alkanoate anions. Ionic mesophases give a unique possibility for studying the influence of Coulomb interactions on liquid crystal formation. Ubbelohde was the first to discover and investigate liquid-crystalline behaviour of alkali metal short chain alkanoates ($C_nH_{2n+1}COOM$ with $n \leqslant 7$) [1, 2]. Following him a few other investigators have studied the physico-chemical properties and structure of these salt mesophases [3-10].

Our work has shown [11], that there is a relationship between ionic mesophase formation on the one hand and the radius and charge of the cation as well as the chain length of the alkanoate anion on the other. It is a matter of common experience that in pure salt melts the alkanoate anion exhibits mesogenic properties provided $n \geqslant 3$, i.e. starting from the butyrate homologue. It is stated though in the work by Roth *et al.* [3] that sodium propionate ($n = 2$) has a liquid crystal phase over a narrow temperature range. However these authors seem to have mistaken a solid-solid transition for a solid-liquid crystal transition. Our investigation of the thermal behaviour of sodium propionate by means of thermal analysis and polarization microscope undoubtedly has shown the absence of any mesophase in the pure melt.

To establish the rules of liquid crystal formation in ionic media is an important problem to be solved. The role of various processes responsible for the appearance and stabilization of the ionic mesophase in mixed molten salts such as the electrostatic charge density distribution and hydrogen bond formation have been demonstrated in our former work [12, 13]. The influence of such processes as ion complex formation on the appearance of liquid crystals in binary systems of lithium and caesium alkanoates is discussed here. In addition the question of the minimum chain length of the alkanoate anion sufficient for the creation of liquid crystal ordering in the melt is considered.

2. Experimental

Lithium and caesium salts of formic (LiForm and CsForm), acetic (LiAc and CsAc), propionic (LiPr and CsPr) and butyric (LiBut and CsBut) acids were prepared by the generally accepted method [3, 6]. Binary mixtures were prepared in a dry box under an argon atmosphere. All further manipulations with samples investigated were also carried out in the inert atmosphere to minimize their decomposition at high temperatures. Solid–mesophase and mesophase–isotropic phase transition temperatures for the binary salt systems were determined from the temperature dependence of the electrical conductivity and polarized light transmission of the sample as well as from differential thermal analysis data. All of the methods used are described in detail in [11]. The liquid crystal phases were identified using a polarizing microscope.

The salts synthesized appeared to be non-mesomorphic in accord with literature data [14].

3. Results and discussion

Phase diagrams of the binary mixtures LiForm–CsForm, LiAc–CsAc, LiPr–CsPr and LiBut–CsBut are shown in figure 1 (*a*), (*b*), (*c*), (*d*). As is shown in this figure, all of the diagrams studied are of a distectic type and indicate the existence of congruently melting complexes, the composition of the solid complex being $Cs[Li_2(C_nH_{2n+1}COO)_3]$.

LiForm–CsForm mixture. Three branches of the melting curve intersect in two eutectic points at 423 K and 30 mol % CsForm and at 393 K and 60 mol % CsForm. No liquid-crystalline phases were found for this system. The solid complex melts at 448 K.

LiAc–CsAc mixture. The composition range for the existence of ionic mesophase is 25–45 mol % CsAc. Polymesomorphic transitions have not been detected in this system. The solid complex melts at 566 K and exhibits a mesophase up to 572 K. The strong supercooling revealed in this system allowed us to observe the liquid crystal phase down to 400 K between a slide and a cover slip using a microscope in the regime of slow cooling. Supercooled ionic liquid crystals which do not recrystallize at room temperature may be obtained by fast cooling of the mesomorphic melt in liquid nitrogen. The eutectic points in this system are located at 513 K and 12 mol % CsAc and at 408 K and 76 mol % CsAc.

LiPr–CsPr mixture. The composition range over which the mesophase appears is 26–80 mol % CsPr. The solid complex melts at 637 K and has a clearing temperature of 657 K. Dilution of the complex with one of the system components decreases the thermal stability of the mesophase. The eutetic points are found at 568 K and at 496 K and 71 mol % CsPr. Only one liquid-crystalline phase was revealed over the entire temperature range of the mesophase.

LiBut–CsBut mixture. Ionic mesophase is found in the composition range of 17–85 mol % CsBut. The solid complex melts at 646 K and forms a mesophase with a clearing temperature of 653 K. No polymesomorphism was established for this mixture. Three branches of the melting curve intersect in two eutetic points at 573 K and 5 mol % CsBut and at 533 K and 80 mol % CsBut.

Liquid-crystalline phases formed by all of the systems studied are shown by microscopic observation to be smectic modifications. The texture of the smectic mesophase obtained throughout all the phase diagrams is either schlieren or mosaic. The mesophase was formed, on cooling the isotropic melt, as fast growing and colour varying clouds, bâtonnets were not revealed in either experiment. The thermal

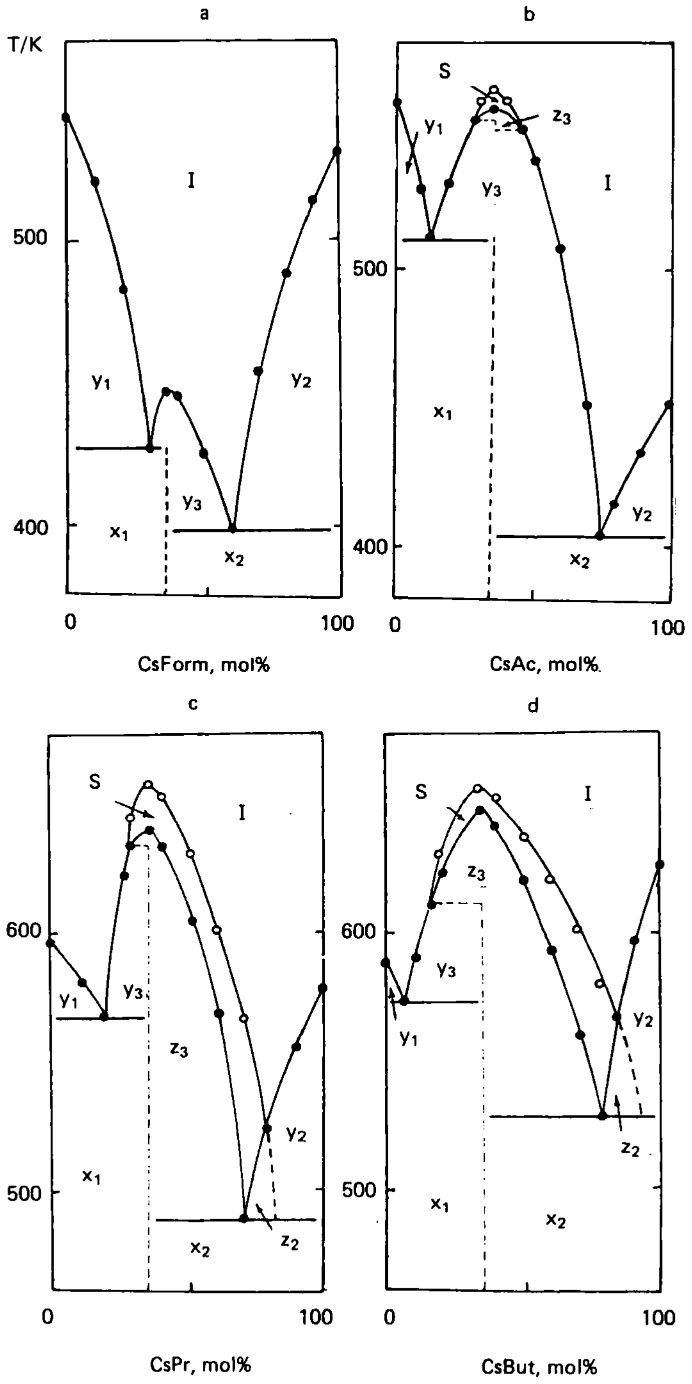

Figure 1. Phase diagram of the Li(C_nH_{2n+1}COO)–Cs(C_nH_{2n+1}COO) mixtures with $n = 0$ (*a*), 1 (*b*), 2 (*c*) and 3 (*d*), the open and shaded circles being smectic–isotropic liquid (S–I) and solid–smectic (C–S) or isotropic liquid (C–I) transitions. The two phase regions are marked in the following way: $x_1 = (C_1 + C_3)$, $x_2 = (C_2 + C_3)$, $y_1 = (C_1 + I)$, $y_2 = (C_2 + I)$, $y_3 = (C_3 + I)$, $z_2 = (C_2 + S)$, $z_3 = (C_3 + S)$, where 1, 2 and 3 refer to the lithium salt, caesium salt and complex, respectively. The eutectic lines are marked by solid straight lines.

instability of the mixtures have inhibited our attempts to confirm this phase assignments using other techniques.

As follows from the phase diagrams (see figure 1) the smectic ordering in the alkanoate salt melt appears to be due to complex formation. The great difference in the polarizing ability of lithium and caesium cations promotes the formation of the $[Li_2(C_nH_{2n+1}COO)_3]^-$ complex anion. In consequence each of the non-mesogenic component system discussed may be divided in two sub-systems with the component pairs: a mesogenic salt such as $Cs[Li_2(C_nH_{2n+1}COO)_3]$ and a non-mesogenic salt such as $Li(C_nH_{2n+1}COO)$ or $Cs(C_nH_{2n+1}COO)$.

The ionic complex possesses the maximum mesophase thermostability and its dilution with the pure non-mesogenic salt results in the depression of the clearing temperature analogous to the situation which takes place in binary liquid-crystalline molecular systems with one mesogenic component and without specific chemical interaction between both components [15]. Thus the existence of the $[Li_2(C_nH_{2n+1}COO)_3]^-$ complex anion determines liquid crystal formation in the salt melt complex anions having mesogenic properties if they are formed from an alkanoate anion with $n \geqslant 1$. The complex anion formed by the formate anion does not seem to be mesogenic. It means that this anion is not capable of liquid crystal ordering of the melt whatever the surrounding cation is. We consider that this kind of non-mesomorphism results from the absence of any pronounced anisotropy of the Coulomb charge distribution, which is created in the other alkanoate homologues by the alkyl chain. The present study demonstrates that this chain may include the single methyl group.

Earlier it was established that pure metal alkanoates form mesomorphic melt under following conditions: metal cation radius to mesogen anion radius must not exceed 0·4, when the metal cation polarizing ability (z/r^2) is less than 1·05. In accord with this rule caesium salts of *n*-alkanoic acids starting with the capronate form liquid crystals. The question is whether this rule holds for the caesium salt with the mesogenic complex anion. The most probable structure for the lithium–alkanoate complex anion is sketched in figure 2. It should be noted that the second order symmetry main axes of the alkanoate anions have a dominant parallel reciprocal orientation. Such kind of anion arrangement follows from NMR studies of molten alkali metal alkanoate mixtures [16]. According to these NMR measurements the reciprocal orientation of anions along their main symmetry axes is enhanced as the difference in radii of the

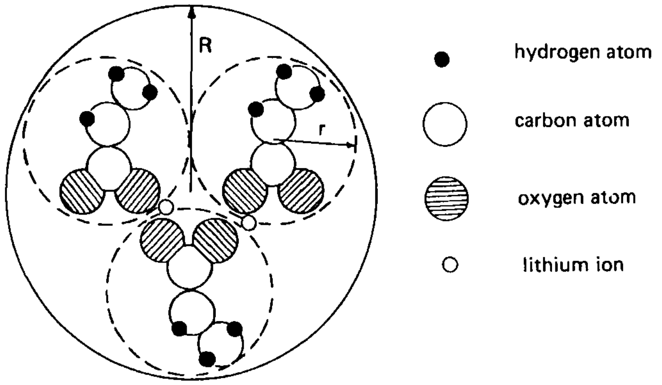

Figure 2. A sketch illustrating the possible arrangement of the carboxylate and lithium ions in the complex anion $Li_2(C_nH_{2n+1}COO)_3^-$ with $n = 2$; r and R are the radii of the repulsion envelopes of the carboxylate and complex anions, respectively.

uncommon metal cations in the binary melts increases. The maximum difference in the size of cations occurs for the binary melt of lithium and caesium salts and therefore the parallel reciprocal orientation of the alkanoate anions in the complex anion is most stable.

Using the radii (r) of the pseudo-spherical repulsion envelopes of short chain alkanoate anions determined by Duruz *et al.* [17] we estimate the radius of the lithium-alkanoate complex anion (R). The lithium cation is sufficiently small to fit into the interstices between the alkanoate anions without their separation and so the radius of the complex anion may be taken to equal the radius of the sphere enveloping the three touching spherical repulsion envelopes of the alkanoate anions (see figure 2), i.e. $R = 2{\cdot}15r$. In that case the lithium-acetate complex anion radius equals 5·6 Å and the ratio of the caesium cation radius to the complex anion radius in $Cs(Li_2Ac_3)$ is equal to 0·3, i.e. it does not exceed 0.4 in accord with the previously mentioned rule. The ratio of the cation–anion radii in the homologous caesium salts with the lithium–alkanoate complex anion is much less than 0·3 if $n \geqslant 2$.

Thus our investigation has shown that the rule concerning the cation–anion radii relation in the salt mesophase holds for caesium salts with mesogenic complex anion when $n = 1, 2$ and 3. In addition liquid crystals may be expected to be formed in melts of the homologous compounds $Cs[Li_2(C_nH_{2n+1}COO)_3]$ if $n \geqslant 4$. We believe that such data will be found in future experimental work.

It is clear from the preceding discussions that ionic interactions in molten systems from non-mesogenic salts may give rise to electrostatic charge redistribution and the formation of new complex ions or ensemble of ions which create micro-ordering in the salt melt and ensure the appearance of a liquid-crystalline phase.

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