Phase Diagrams of Binary Systems of Non-Mesogenic Components: Caesium–Sodium and Caesium–Lithium Iso-Butyrates

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The phase diagrams of the binary systems given in the title have been studied by differential thermal analyses and hot stage polarization microscopy. Smectic liquid crystals are found in some composition ranges of the binary with sodium iso-butyrate. The liquid crystal appearance in this system is explained by latent mesomorphism of both components and by the additional electrostatic stabilization of the ionic mesophase because of dissimilar cation interactions. The unlike conditions for the exhibition of latent mesomorphism of caesium isobutyrate in the two systems is discussed.

Introduction

Many short-chain alkanoic acid salts form thermotropic mesophases or so-called ionic liquid crystals [1, 2]. Bilayer smectic ordering in these mesophases is stabilized by electrostatic forces acting between the ions while the molecular shape is not so essential as for molecular mesogens.

It is known that some alkali alkanoates, while individually non-mesogenic, form binary systems with liquid crystalline phases [3, 4]. This effect may be due to latent (virtual) mesomorphism of one or the two components as well as complex formation when mesogenic ions are formed. So, the formation of liquid crystals in the binary systems from non-mesogenic sodium, potassium and caesium propionates is a consequence of the latent mesomorphism of the sodium and potassium propionates [3], but in the system derived from non-mesogenic lithium and caesium propionates it is a consequence of ion complex formation [4]

Lithium, sodium and caesium iso-butyrates do not form a mesophase under fusion [5, 6]. The iso-butyrate anion has the same radius of repulsion envelope as the propionate anion (2.82 Å [7]). Thus the formation of mesophase may be presumed in the binary systems of caesium and sodium or caesium and lithium iso-butyrates. Moreover the assumption is well substantiated by the results of our previous work [5], where latent mesomorphism for sodium and caesium iso-butyrate have been found and the latent mesophase clearing temperatures have been estimated (224 °C for sodium iso-butyrate and 272 °C for caesium iso-butyrate).

The phase diagrams of binary systems caesium–sodium and caesium–lithium iso-butyrate have been studied in the present work with a view to discover the formation of induced liquid crystalline phase. There exist no data on the phase transition temperatures of these systems in literature.

Experimental

Lithium, sodium and caesium iso-butyrates were prepared by the general method described in [6]. The salts obtained were free from any water or acid, as evidenced by their IR-spectra. The pure salts as well as the binary mixtures, prepared by melting the preweighed components under argon, were stored in vacuum before the measurements.

The phase diagrams were determined by means of both polythermal polarization microscopy and differential thermal analysis. A Paulik-Paulik-Erdey derivatograph (Q-1500 D) with a Pt-Pt/Rh thermocouple and Al_2O_3 powder as reference substance were used to obtain thermograms on heating, the heating rates being 2.5 °C/min. DTA-samples weighing 0.7–1.2 g were sealed under vacuum in special Pyrex containers. A polarization microscope "Amplival" with hot stage "Boëmius" was used to identify mesophases and isotropic liquid phase and so to determine the temperatures of isotropic melt-mesophase and isotropic melt-crystal transitions.

The solid-to-solid transitions and melting temperatures for the pure salts synthesized in our laboratory

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were in excellent agreement (±1 °C) with the accepted data [6]. Lithium iso-butyrate had a solid-to-solid transition at 163 °C and melted at 230 °C. Sodium iso-butyrate melted at 254 °C without solid-to-solid transitions. The thermal properties of caesium iso-butyrate were not known. From our data it melted at 320 °C and had two solid-to-solid transitions at 85 °C and 198 °C. No mesomorphic was revealed in melting of the pure salts.

Results and Discussions

In Figs. 1 and 2 the phase diagrams for the binary systems studied are represented.

$x(CH_3)_2CHCOONa + (100-x)(CH_3)_2CHCOOCs$

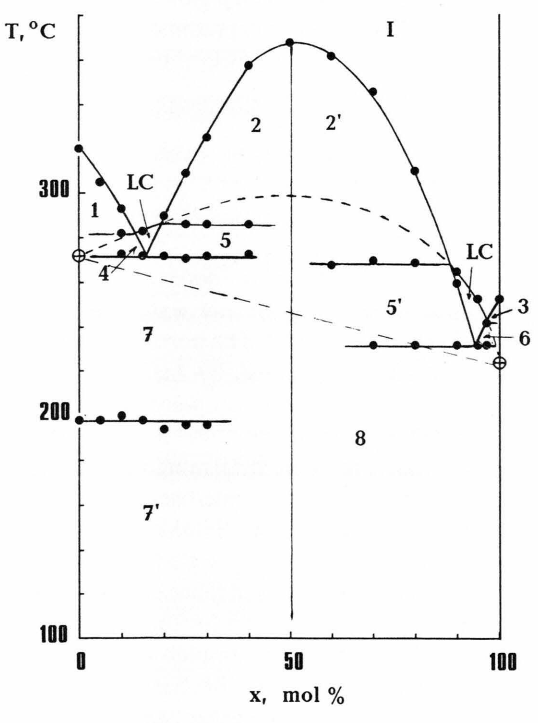

Fig. 1. Phase diagram of $\{x(CH_3)_2CHCOONa + (100-x) \cdot (CH_3)_2CHCOOCs\}$. The homogeneous regions of isotropic melt and liquid crystalline phases are marked by I and LC. Arabic numbers stand for two-phase regions as follows. 1: $(I + K_{Cs})$, 2 and 2′: $(I + K_D)$, 3: $(I + K_{Na})$, 4: $(LC + K_{Cs})$, 5 and 5′: $(LC + K_D)$, 6: $(LC + K_{Na})$, 7 and 7′: $(K_{Cs} + K_D)$, 8: $(K_{Na} + K_D)$, where K_{Cs} and K_{Na} are the solid phases of caesium and sodium iso-butyrate, and K_D is the solid phase of the congruently melting complex. The crossed circles indicate the estimated latent mesophase clearing temperatures [5]. For the dashed lines see text.

As seen in Fig. 1, three branches of the melting curve intersect in two eutectic points at 272 °C, $x = 15$ mol% and at 232 °C, $x = 95$ mol%. The phase diagram indicates the formation of a congruently melting complex D with equimolar composition ($x = 50$ mol%), the distectic maximum being at 369 °C.

Homogeneous mesomorphic liquid phases are found to exist in two ranges; 13 mol% $< x <$ 19 mol% and 89 mol% $< x <$ 97 mol%, i.e., near to the eutectic points. As shown by microscopic observation, the mesophase seems to be smectic A. So, on cooling the isotropic melt, birefringent domains, so-called battonets, forming the continuous confocal-conical texture which is typical for smectic A phases of short-chain alkali alkanoates [3, 5, 8], have been seen for all samples in the above composition ranges. The mesophase or liquid crystaline solutions (LC) are formed in both composition ranges of the system ac-

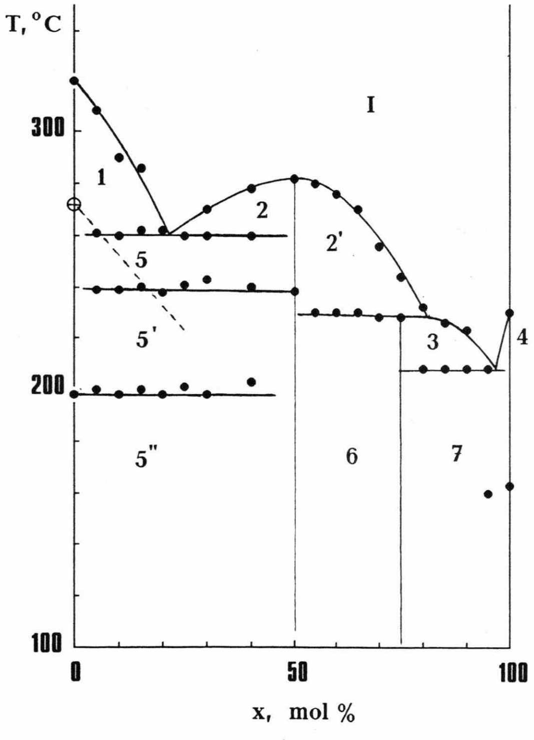

Fig. 2. Phase diagram of $\{x(CH_3)_2CHCOOLi + (100-x) \cdot (CH_3)_2CHCOOCs\}$. The region is isotropic melt is marked by I. Arabic numbers stand for two-phase regions as follows. 1: $(I + K_{Cs})$, 2 and 2′: $(I + K_D)$, 3: $(I + K_P)$, 4: $(I + K_{Li})$, 5, 5′ and 5″: $(K_{Cs} + K_D)$, 6: $(K_D + K_P)$, 7: $(K_P + K_{Li})$, 8: $(K_{Na} + K_D)$, where K_{Cs} and K_{Li} are the solid phases of caesium and lithium iso-butyrate, K_D and K_P are solid phases of complexes, melting congruently and incongruently, respectively. The crossed circle is the latent mesophase clearing temperature of the pure component according to [5]. The dashed line designates conventionally the latent mesophase clearing line.

cording to the corresponding eutectic reactions

$$K_{Cs} + K_D \overset{272\,^\circ C}{\rightleftharpoons} LC \quad \text{or} \quad K_{Na} + K_D \overset{232\,^\circ C}{\rightleftharpoons} LC,$$

where K_{Cs}, K_{Na} and K_D are the solid phases of caesium and sodium iso-butyrates and complex D, respectively.

The latent mesophase clearing temperatures for pure sodium and caesium iso-butyrates estimated in our previous work [5] are marked in Fig. 1 by crossed circles. They are joined by a dashed straight line. As a rough approximation, the experimental values of mesophase clearing temperatures in the two ranges of the mesophase existence and the latent mesophase clearing temperatures for the pure components may be joined by a curve, designated in the figure by the dashed curve. So, this curve is the mesophase clearing curve composed of both the latent and apparent mesophase clearing temperatures.

The mesophase clearing curve intersects the melting curve in four invariants points at 281 °C, $x = 13$ mol%, at 286 °C, $x = 19$ mol%, at 268 °C, $x = 89$ mol%, and at 243 °C, $x = 97$ mol%, where solid phase coexists with two liquids, isotropic and mesomorphic. Therefore these invariants may be called metatectic points.

As seen in Fig. 1, the mesophase clearing curve exhibits a large positive deviations from additivity, i.e. from the straight line joining the latent mesophase clearing temperatures of the pure components. As results from [8], this effect may be due to the additional stabilization of the binary ionic mesophase by electrostatic forces associated with dissimilar alkali cation interactions.

Thus, the formation of liquid crystals in the binary system of non-mesogenic sodium and caesium iso-butyrate results from the following: in some composition ranges the melting temperature is lower than the latent mesophase clearing curve, the effect being possible due to the positive deviation of the mesophase clearing curve from additivity. The electrostatic interactions of dissimilar metal cations are thus a fairly important factor in inducing the liquid crystalline phase when one or both components of the binary are potentially mesogenic.

$x(CH_3)_2CHCOOLi + (100 - x)(CH_3)_2CHCOOCs$

The phase diagram is presented in Figure 2. No mesomorphic phase is formed in this system. The melting curve has two eutectic points at 260 °C, $x = 22$ mol% and at 208 °C, $x = 97$ mol%. There is a peritectic point at 228 °C, $x = 81$ mol%. The phase diagram is indicative of the formation of a congruently melting complex D with equimolar composition, as well as an incongruently melting complex P with the probable composition $3(CH_3)_2CHCOOLi \cdot (CH_3)_2CHCOOCs$. The system has only one homogeneous region: isotropic melt. In all other regions the isotropic melt coexists with a solid phase, or two solid phases coexist.

In the binary systems from non-mesogenic linear alkanoates of lithium and caesium the liquid crystal formation is due to the formation of a mesogenic complex, melting congruently [4, 9]. As seen in Fig. 1, the congruently melting complex, which is formed in the system of lithium and caesium iso-butyrates is not mesogenic. The reason of the unlike behaviour of the linear and branched alkanoate systems seems to be the dissimilar structure of the complexes formed there and here. Indeed, the mesogenic properties of *n*-alkanoate complexes $Cs[Li_2(C_nH_{2n+1}COO)_3]$ are associated with the structure of the complex anion $[Li_2(C_nH_{2n+1}COO)_3]^-$ meeting the requirements of the anisotropy in the Coulomb charge distribution and of the presence of a dipole moment across the long symmetry axis. In the iso-butyrate system the complex $Cs\{Li[(CH_3)_2CHCOO]_2\}$ is not mesogenic because there is no dipole moment across the long symmetry axis in the complex anion $\{Li[(CH_3)_2CHCOO]_2\}^-$.

The possibility of mesophase induction in the system lithium–caesium isobutyrate, which is the exhibition of the latent mesomorphism of caesium iso-butyrate in adding the second component is found not to exist. Lithium iso-butyrate, like other lithium short-chain alkanoates [6], does not possess latent mesomorphic properties, and hence its addition to the potentially mesogenic caesium iso-butyrate is bound to cause a sharp linear decrease in the latent mesophase clearing temperature [10], designated conventionally in the figure by the dashed line. So, as may be seen, the melting temperatures in the system can not become lower than the probable latent mesophase clearing temperatures, thereby enabling the latent mesophase of caesium iso-butyrate to become apparent.

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