Phase Diagrams of Binary Alkanoate Systems with Common Cation: Potassium Isobutyrate-Propionate, and Sodium Butyrate-Isobutyrate

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The phase diagrams of the binary mixtures of mesogenic potassium isobutyrate with non-mesogenic potassium propionate and mesogenic sodium butyrate with non-mesogenic sodium isobutyrate have been investigated by differential thermal analysis and hot stage polarization microscopy. Both systems have one eutectic and one metatectic phase equilibriums. Pecularities of liquid crystal formation in binary alkanoate systems with common alkali metal cation are discussed and compared with those of systems with common anion.

Introduction

During the last years many data on phase diagrams of the binaries of metal alkanoate salts with common anion were obtained [1–6]. These systems are of interest because ionic liquid crystals may be formed in them. Among the binaries studied are systems with one or both components mesogenic [2–4], as well as systems with individually non-mesogenic components [4–6]. As for systems of metal alkanoates with common cation, few phase diagrams of binaries showing liquid crystals are known [1]. All information on more than 100 alkanoate binaries with common cation [1] was obtained until 1976 by authors who were unaware of the possibility of liquid crystal formation. Therefore these systems be reinvestigated in light of possible mesophase formation.

In the present work the phase diagram of the binaries potassium propionate – isobutyrate and sodium butyrate – isobutyrate have been studied. There exist no data on the phase transition temperatures of the first system, while the second system was investigated by N. Sokolov with the visual polythermal method [1]. This author claimed the existence of a continuous series of solid solutions, with a minimum at 221 °C and 72.5 mol% sodium isobutyrate, but he said nothing about the mesogenicity of sodium butyrate and completely ignored the range of mesophase existence. Hence he interpreted the mesophase clearing temperatures as the melting temperatures.

Experimental

All salts were prepared by the method described in [3, 4]. They were free from any water and acid, as evidenced by their IR-spectra. The binary mixtures were prepared by melting the preweighed components under argon. Samples were stored in argon 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 α-Al_2O_3 powder as reference substance were used to obtain thermograms on heating, the heating rates being 2.5 °C/min. A polarization microscope "Amplival" with "Boëmius" hot stage was used to identify the mesophases and isotropic liquid phases and thus to determine the temperatures of the isotropic melt – mesophase and isotropic – crystal transitions.

The temperatures of phase transitions of the pure salts, synthesized in our laboratory, were in good agreement with the literature data [7]. Potassium isobutyrate had a solid-solid transition at 151 °C, melted at 281 °C with formation of mesophase A and then cleared at 353 °C. Potassium propionate had a solid-solid transition at 80 °C and melted at 365 °C. Sodium butyrate had three solid-solid transitions at 178 °C, 226 °C and 235 °C, melted at 254 °C with formation of smectic A mesophase and then cleared at 324 °C. Sodium isobutyrate melted at 254 °C without solid-solid transitions.

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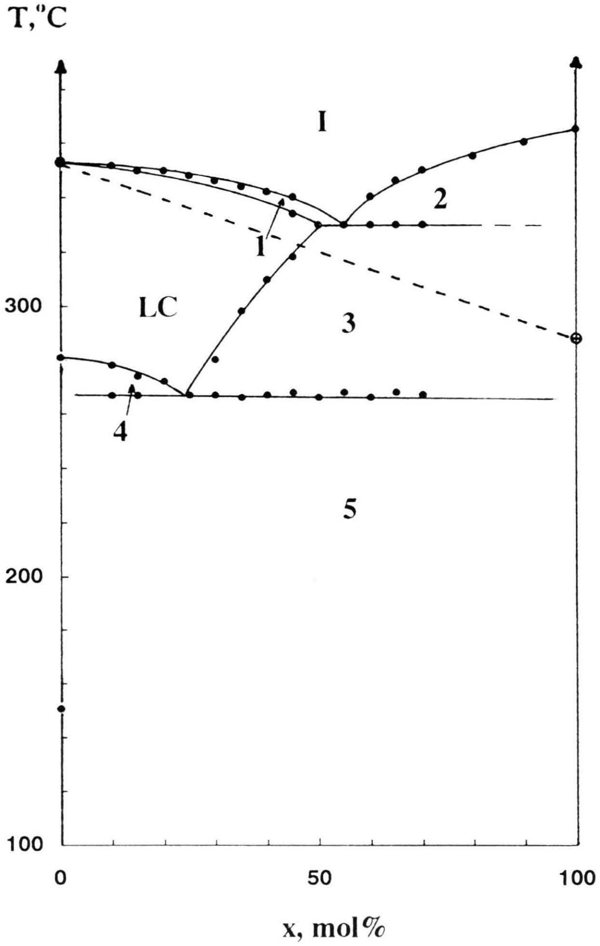

Fig. 1. Phase diagram of

$\{x\,(CH_3)_2CHCOOK + (100 - x)\,C_2H_5COOK\}$.

I: isotropic melt, LC: liquid crystalline smectic A phase. Arabic numerals stand for heterogeneous two-phase regions as follows: 1: (I + LC), 2: (I + K_{KPr}), 3: (LC + K_{KPr}), 4: (LC + K_{KIso}), 5: (K_{KIso} + K_{KPr}), where K_{Iso} and K_{KPr} are the solid phases of pure potassium isobutyrate and propionate, respectively. The crossed circle indicates the estimated latent mesophase clearing temperature of potassium propionate [4]. The dashed straight line joins the apparent and latent clearing temperatures of the pure components.

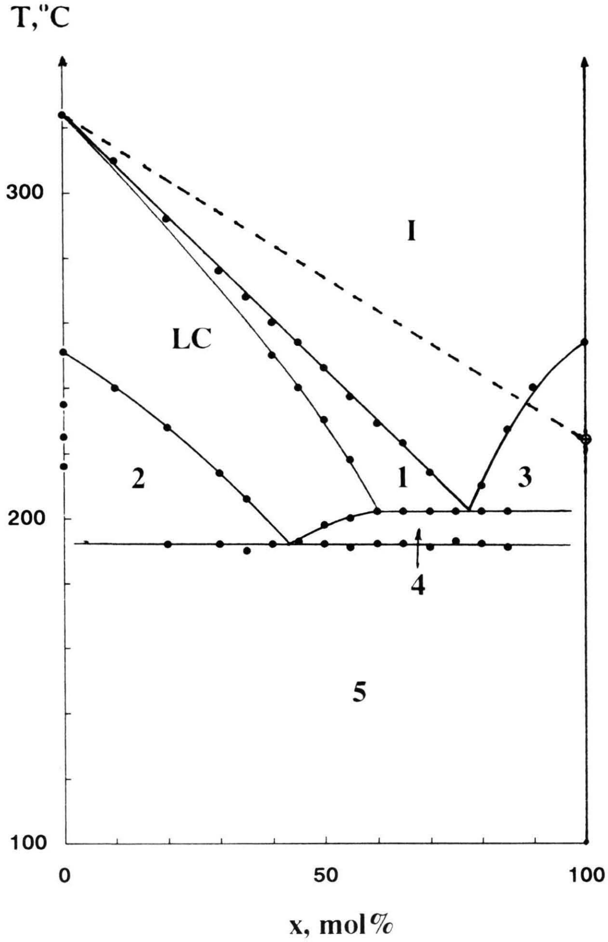

Fig. 2. Phase diagram of

$\{x\,C_3H_7COONa + (100 - x)(CH_3)_2CHCOONa\}$.

I: isotropic melt, LC: liquid crystalline smectic A phase. Arabic numerals stand for heterogeneous two-phase regions as follows: 1: (I + LC), 2: (I + K_{NaB}), 3: (I + K_{NaIso}), 4: (LC + K_{NaIso}), 5: (K_{NaB} + K_{NaIso}), where K_{NaB} and K_{NaIso} are the solid phases of pure sodium butyrate and isobutyrate, respectively. The crossed circle indicates the estimated latent mesophase clearing temperature of sodium isobutyrate [3]. The dashed straight line joins the apparent and latent clearing temperatures of the pure components.

Results and Discussion

In Figs. 1–2 show the obtained phase diagrams.

$$\underline{x\,(CH_3)_2CHCOOK + (100 - x)\,C_2H_5COOK}\,.$$

As seen in Fig. 1, two branches of the melting curve intersect in an eutectic point at 266 °C, $x = 24$ mol%. The liquid crystalline solutions (LC), identified as smectic A phase, are formed according to the eutectic reaction:

$$K_{KIso} + K_{KPr} \overset{266\,^{\circ}C}{=} LC\,,$$

where K_{KIso} and K_{KPr} are the solid phases of potassium isobutyrate and propionate, respectively. Potassium isobutyrate forms a homogeneous mesophase with potassium propionate up to $x = 50$ mol%.

The mesophase clearing curve intersects the melting curve in a metatectic point at 330 °C and $x = 55$ mol%. In this invariant point phase coexists with two liquids, isotropic and mesomorphic.

$x\,C_3H_7COONa + (100 - x)(CH_3)_2CHOONa$.

The phase diagram is presented in Figure 2. The homogeneous mesomorphic phase (LC), identified as smectic A, exists over the wide composition range $0 < x < 60$ mol%. The liquid crystalline solutions are formed following to the eutectic reaction:

$$K_{NaB} + K_{NaIso} \overset{192\,^\circ C}{=} LC\,,$$

where K_{NaB} and K_{NaIso} are solid phases of sodium butyrate and isobutyrate, respectively. The melting curve has one eutectic point at 192 °C, $x = 44$ mol%. The metatectic point is observed at 202 °C, $x = 78$ mol%.

In the binary systems studied, one component is mesogenic and the other is non-mesogenic but possesses latent mesomorphic properties. So, as was shown in [3, 4], potassium propionate and sodium isobutyrate have latent mesophase clearing points at 287 °C and 224 °C, respectively.

From Fig. 1 may be seen that replacement of isobutyrate anion by propionate anion in mesogenic potassium isobutyrate leads to a smooth decrease in the mesophase clearing temperature, and the clearing curve has slightly positive deviations from the straight line joining the apparent and latent mesophase clearing points of the pure components. In the second system the situation is different (Figure 2). Here the replacement of butyrate anion by isobutyrate anion gives rise to a fairly sharp decrease in the mesophase clearing temperature, and the clearing curve has negative deviations from the straight line joining the apparent and latent mesophase clearing points of the pure components.

In the first system both components have anions with approximately the same radii of the repulsion envelope (2.82 Å), while in the other system the components have anions with dissimilar radii (2.82 Å and 3,46 Å) [8]. It is known [3–5] that in the systems with common anion and two apparently or potentially mesomorphic components there are large positive deviations of the clearing curve from the straight line joining the apparent or latent clearing temperatures of the two components, the deviations being the larger, the greater the difference in cationic radii. Thus the mesomorphic behavior of the binaries having a common cation differs from the one of systems with common anion. From the present results follows that the ionic mesophase is destabilized and destroyed when the component with an anion differing in size from the anion of the first component is added.

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