Phase Diagrams of Binary Systems of Some Alkali Iso-Butyrates with One Mesogenic Component

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The phase diagrams of the binary mixtures of mesogenic potassium iso-butyrate with non-mesogenic lithium-, sodium-, and caesium iso-butyrate have been investigated by differential thermal analysis and hot stage polarization microscopy. The temperature and concentration ranges of liquid crystal formation have been established. Sodium and caesium iso-butyrate have been found to possess latent mesogenic properties.

Introduction

Some alkali short-chain alkanoates are known to form so-called ionic liquid crystals or mesophases [1]. Among the alkali iso-butyrates only the potassium salt is mesogenic [2], but the other alkali iso-butyrates may be potentially mesogenic. Their latent mesogenicity may show up in binary mixtures with a common anion, as was found in studying the phase diagrams of alkali propionates, which are individually non-mesogenic [3].

There exist no data on the phase diagrams of the binary systems under study. The system potassium-sodium iso-butyrate was studied by Sokolov, et al. [4], but these authors measured only the temperatures of the phase transition from liquid to crystal or mesophase and interpreted them as melting temperatures in all cases, because they were unaware of or ignored the existence of liquid crystals.

In the present work the phase diagrams of the binary systems of mesogenic potassium iso-butyrate with non-mesogenic lithium-, sodium-, and caesium iso-butyrate have been studied in order to determine the temperature and concentration ranges of liquid crystal formation and to estimate the latent mesophase clearing temperatures of the potentially mesogenic components.

Experimental

Lithium-, sodium-, potassium-, and caesium iso-butyrates were prepared by the method described in [5]. The obtained salts 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 α-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 phases and thus to determine the temperatures of the isotropic melt – mesophase and isotropic – crystal transitions.

The solid–solid transition, melting and mesophase clearing temperatures for the pure salts synthesized in our laboratory were in excellent agreement with the data in [2, 5]. Lithium iso-butyrate had solid–solid transition at 163 °C and melted at 230 °C. Sodium iso-butyrate melted at 254 °C without solid–solid transitions. Potassium iso-butyrate had a solid–solid transition at 151 °C, melted at 281 °C with formation of mesophase which then cleared at 353 °C. The thermal properties of caesium iso-butyrate have not been described in the literature. From our data it melts at 320 °C and has two solid–solid transitions at 85 °C and 198 °C.

The liquid crystals, studied by microscopic observation, showed to be smectic A since they formed the characteristic continuous confocal-conical texture [6, 7].

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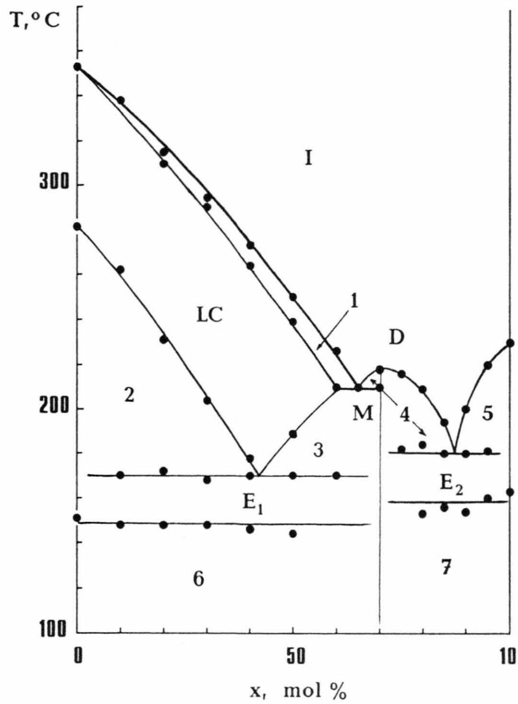

Fig. 1. Phase diagram of $\{x(CH_3)_2CHCOOLi+(100-x)(CH_3)_2CHCOOK\}$. I: isotropic melt, LC: liquid crystalline phase, D: distectic point, M: metatectic point, E_1 and E_2: eutectic points. Arabic numerals stand for heterogenous two-phase regions as follows: 1: (I+LC), 2: $(LC+K_K)$, 3: $(LC+K_D)$, 4: $(I+K_D)$, 5: $(I+K_{Li})$, 6: (K_K+K_D), 7: $(K_{Li}+K_D)$, where K_K and K_{Li} are solid phases of pure potassium and lithium iso-butyrate, K_D: solid phase of congruently melting complex.

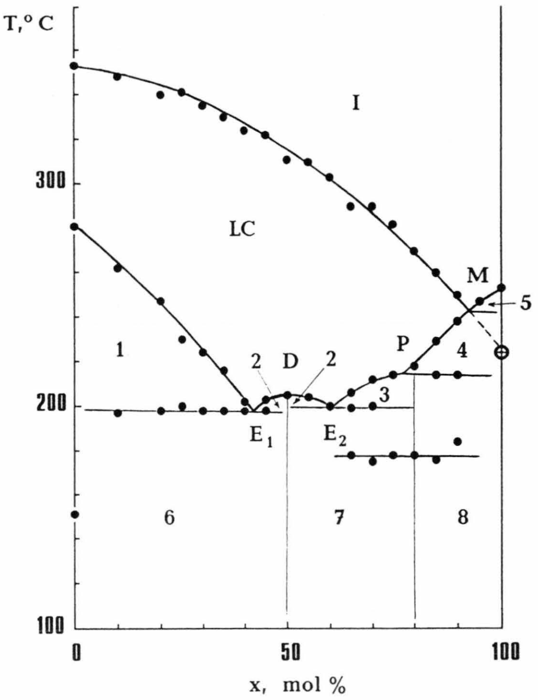

Fig. 2. Phase diagram of $\{x(CH_3)_2CHCOONa+(100-x)(CH_3)_2CHCOOK\}$. P: peritectic point. As to other letter symbols see the caption of Figure 1. Arabic numerals stand for heterogenous two-phase regions as follows: 1: $(LC+K_K)$, 2: $(LC+K_D)$, 3: $(LC+K_P)$, 4: $(LC+K_{Na})$, 5: $(I+K_{Na})$, 6: (K_K+K_D), 7: (K_D+K_P), 8: $K_P+K_{Na})$, where K_K and K_{Na} are solid phases of pure potassium and sodium iso-butyrates, K_D and K_P are solid phases of complexes, melting congruently and incongruently, respectively. Crossed circle is the latent mesophase clearing temperature of the pure component obtained by extrapolation (dotted line) of the clearing curve.

Results and Discussion

In Figs. 1, 2, and 3 the phase diagrams for the binary systems studied are represented.

$x(CH_3)_2CHCOOLi+(100-x)(CH_3)_2CHCOOK$

As seen in Fig. 1, three branches of the melting curve intersect in two eutectic points at 170 °C, $x=42$ mol% (E_1) and at 181°C, $x=87$ mol% (E_2). An invariant point M at 210 °C, $x=65$ mol% is a metatectic point, where two liquids, isotropic and mesomorphic, coexist with solid phase. The phase diagram indicates the formation of a congruently melting complex with the probable composition $7(CH_3)_2CHCOOLi \cdot 3(CH_3)_2CHCOOK$ (D). Liquid crystalline solution or mesophase (LC) is formed in the system following the eutectic reaction: $K_K+K_D \overset{181\,°C}{=} LC$, where K_K and K_D are solid phases of potassium iso-butyrate and complex D, respectively.

Potassium iso-butyrate forms a liquid crystalline solution with lithium iso-butyrate up to $x=60$ mol%. The phase diagram does not allow to expect that lithium iso-butyrate has latent mesogenic properties, which is in good agreement with the empiric rule [1] according to which the metal alkanoates can not form ionic liquid crystals if their cation is smaller than the sodium cation.

$x(CH_3)_2CHCOONa+(100-x)(CH_3)_2CHCOOK$

The phase diagram is presented in Figure 2. The liquid crystalline phase exists over the wide composition range 0 mol% $< x <$ 93 mol%. This fact is indicative of latent mesogenicity of a non-mesogenic component. So, the latent mesophase clearing temperature for sodium iso-butyrate may be estimated approximately by the extrapolation of the mesophase clearing curve to $x = 100$ mol% (224 °C).

The region where mesophase and isotropic melt coexist is found in our experiments to be smaller than 1 °C and is not marked in the diagram. The mesophase clearing curve intersects the melting curve in the metatectic point M at 244 °C, $x = 93$ mol%.

The melting curve has two eutectic points at 198 °C, $x = 42$ mol% (E_1), and at 200 °C, $x = 60$ mol% (E_2). There exists a peritectic point P at 214 °C, $x = 77$ mol%. A congruently melting complex with equimolar composition ($x = 50$ mol%), i.e. $(CH_3)_2CHCOONa \cdot (CH_3)_2CHCOOK$ (D), has a flat and weakly-defined distectic maximum which is indicative of a high degree of dissociation of the complex D in the melt. An incongruently melting complex with probable composition $4(CH_3)_2CHCOONa \cdot (CH_3)_2CHCOOK$ seems to have a solid–solid transition at 178 °C which is detected in the range 60 mol% $< x <$ 90 mol%.

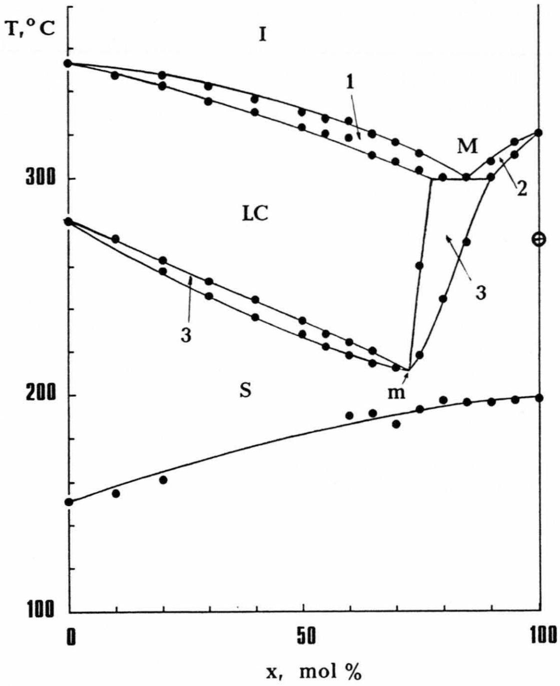

Fig. 3. Phase diagram of $\{x(CH_3)_2CHCOOCs + (100-x)(CH_3)_2CHCOOK\}$. S: solid solutions, m: minimum of melting curve. As to other letter symbols see the caption of Figure 1. Arabic numerals stand for heterogenous two-phase regions as follows: 1: (I + LC), 2: (I + S), 3: (LC + S). As for the meaning of the crossed circle see the caption of Figure 2.

$x(CH_3)_2CHCOOCs + (100-x)(CH_3)_2CHCOOK$

The phase diagram presented in Figure 3 indicates the formation of continuous solid solutions with a minimum (m) at 209 °C, $x = 72$ mol%. The liquid crystalline solutions are formed under fusion of the solid solutions, and the homogeneous liquid crystalline phase extends from pure potassium iso-butyrate up to $x = 78$ mol%.

The metatectic point M, where solid phase coexists with two liquids, isotropic and mesomorphic, is observed at 300 °C, $x = 86$ mol%. The smooth decrease in the mesophase clearing temperature on adding caesium iso-butyrate to potassium iso-butyrate is indicative of latent mesogenicity of caesium iso-butyrate. As estimated by extrapolation of the mesophase clearing curve to $x = 100$ mol%, the latent mesophase clearing temperature for caesium iso-butyrate is approximately 272 °C.

The present investigation has shown that the addition of lithium-, sodium-, and caesium iso-butyrates to potassium iso-butyrate gives rise to a decrease of its mesophase thermostability and at last to the disappearance of the liquid crystalline phase in the systems. However the velocity of the decrease in the mesophase clearing temperature depends on the nature of the metal cation of the non-mesogenic component. So, it is maximum in the case of the system with lithium iso-butyrate and minimum in the case of the binary with caesium iso-butyrate. The addition of lithium salt leads to a practically linear drop of the mesophase clearing temperature as with the known liquid crystalline systems with one mesogenic component [8]. But there is a smooth non-linear variation of the mesophase clearing temperature with composition in the binaries where sodium- or caesium iso-butyrates have been added to potassium iso-butyrate. In these cases the mesophase clearing curve exhibits large positive deviations from the straight line joining the apparent and latent mesophase clearing temperatures of the pure components. As stated in [1, 9], this effect may be due to the additional electrostatic stabilization of the binary mesophase at the expense of the interaction of dissimilar metal cations.

It should be noted that a marked decrease in both upper and lower temperature boundaries of mesophase existence is observed in all systems studied. Moreover a considerable increase in the temperature range of mesophase existence is established over the composition regions near eutectic points or a minimum of the melting curve.

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