Liquid Crystals and Glasses in Binary Systems from Sodium and Alkali-Earth Metal Butyrates

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The temperature and composition ranges of liquid crystal and glass formation have been established for the binary mixtures of mesogenic sodium butyrate with non-mesogenic magnesium, calcium and strontium butyrates by means of differential thermal analysis and hot stage polarization microscopy. The formation of a vitreous optically anisotropic mesophase has been found for binaries of sodium butyrate with calcium and strontium butyrates.

Introduction

Many alkali short-chain alkanoates and their binary mixtures form so-called ionic liquid crystals or mesophases [1–4]. But there are no data on binaries of alkanoates with asymmetrically charged metal cations, such as univalent alkali and divalent alkali-earth metal cations. Such systems may be very interesting and useful since not only ionic mesophases but glasses with optically isotropic and anisotropic properties may be formed there.

In the present work the phase diagrams of the binary systems of mesogenic sodium butyrate with non-mesogenic magnesium, calcium and strontium butyrates have been studied in order to determine the temperature and concentration ranges of liquid crystal and glass formation. As known [5, 6], pure magnesium, calcium and strontium butyrates do not form mesophases but supercool and easily form glasses.

Experimental

Sodium, magnesium, calcium and strontium butyrates were prepared by the method described in [5, 6]. All salts 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 and then recrystallizing them at 80 °C during several hours or days, if it was needed. Samples were stored in argon before the measurements.

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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 was used to obtain thermograms on heating, the heating rates being 2.5 °C/min. 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 temperatures of phase transitions for pure salts synthesized in our laboratory were in good agreement with the literature data [5, 6]. 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. Magnesium, calcium and strontium butyrates had no solid-solid transitions and melted into a viscous isotropic liquid at 296 °C, 335 °C and 409 °C, respectively.

Results and Discussion

In Figs. 1–3 the phase diagrams for binary systems studied are represented.

$$x\,C_3H_7COONa + (100\text{-}x)\,(C_3H_7COO)_2Mg$$

As seen in Fig. 1, three branches of the melting curve intersect in two eutectic points at 200 °C, $x = 45$ mol% and 206 °C, $x = 78$ mol%. A congruently melting complex (D) with probable composition $3\,C_3H_7COONa\,(C_3H_7COO)_2Mg$ has a flat and

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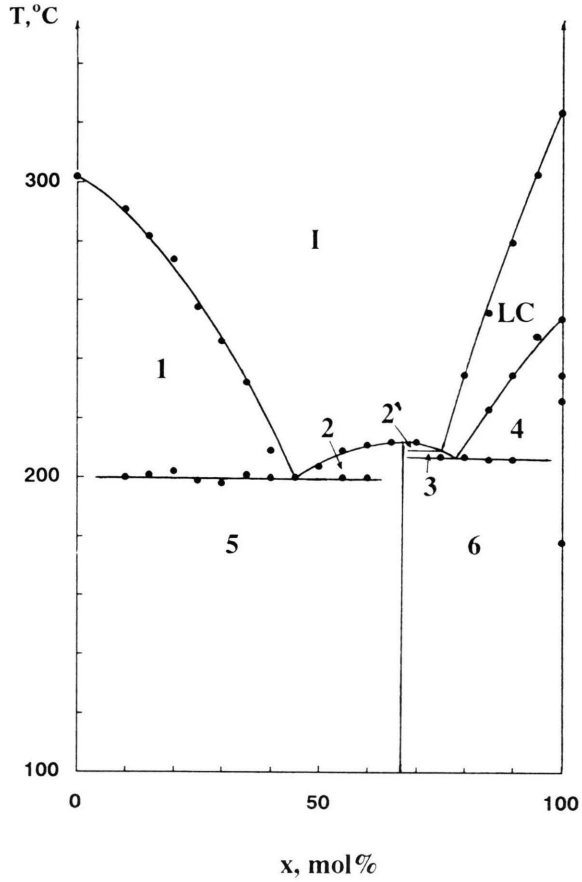

Fig. 1. Phase diagram of
$\{x\,C_3H_7COONa + (100\text{-}x)(C_3H_7COO)_2Mg\}$.
I: isotropic melt, LC: liquid crystalline phase. Arabic numerals stand for heterogeneous two-phase regions as follows: 1: $(I + K_{Mg})$, 2 and 2′: $(I + K_D)$, 3: $(LC + K_D)$, 4: $(LC + K_{Na})$, 5: $(K_{Mg} + K_D)$, 6: $(K_{Na} + K_D)$, where K_{Mg} and K_{Na} are solid phases of pure magnesium and sodium butyrates, K_D is the solid phase of the congruently melting complex.

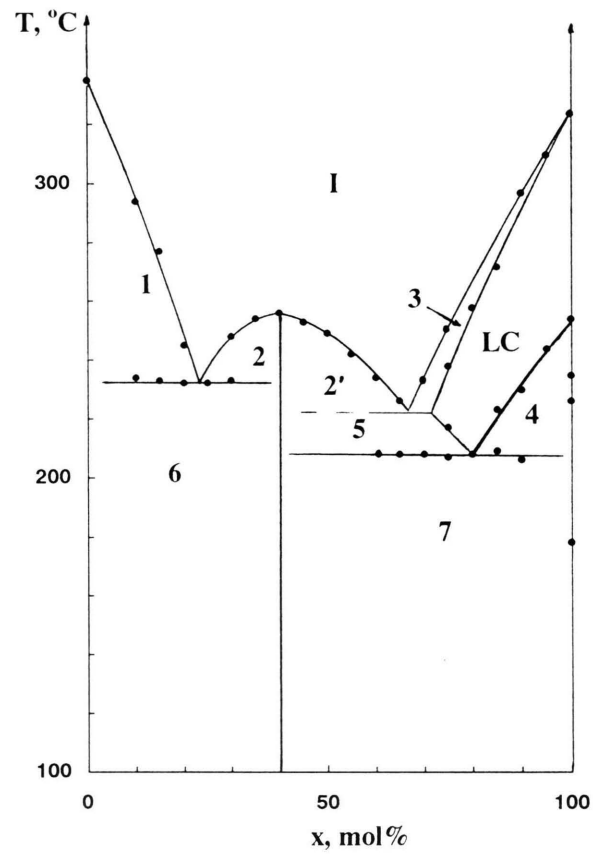

Fig. 2. Phase diagram of
$\{x\,C_3H_7COONa + (100\text{-}x)(C_3H_7COO)_2Ca\}$.
I: isotropic melt, LC: liquid crystalline phase. Arabic numerals stand for heterogeneous two-phase regions as follows: 1: $(I + K_{Mg})$, 2 and 2′: $(I + K_D)$, 3: $(I + LC)$, 4: $(LC + K_{Na})$, 5: $(LC + K_D)$, 6: $(K_{Ca} + K_D)$, 7: $(K_{Na} + K_D)$ where K_{Ca} and K_{Na} are solid phases of pure calcium and sodium butyrates, K_D is the solid phase of the congruently melting complex.

weakly-defined distectic maximum which is indicative of a high degree of complex formation in the melt.

Liquid crystal solution or mesophase (LC) is formed in the system following the eutectic reaction:

$$K_{Na} + K_D \overset{206\,^\circ C}{=} LC,$$ where K_{Na} and K_D are solid phases of sodium butyrate and complex D, respectively.

An invariant point at 210 °C, $x = 76$ mol% is a metatectic point where two liquids, isotropic and mesomorphic, coexist with solid phase.

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.

It is found that glass formation in the system may be observed in the composition range 0 mol% $< x <$ 60 mol%. Optical anisotropic glasses have not been obtained in this system.

$x\,C_3H_7COONa + (100\text{-}x)(C_3H_7COO)_2Ca$

The phase diagram is presented in Figure 2. The melting curve has two eutectic points at 233 °C,

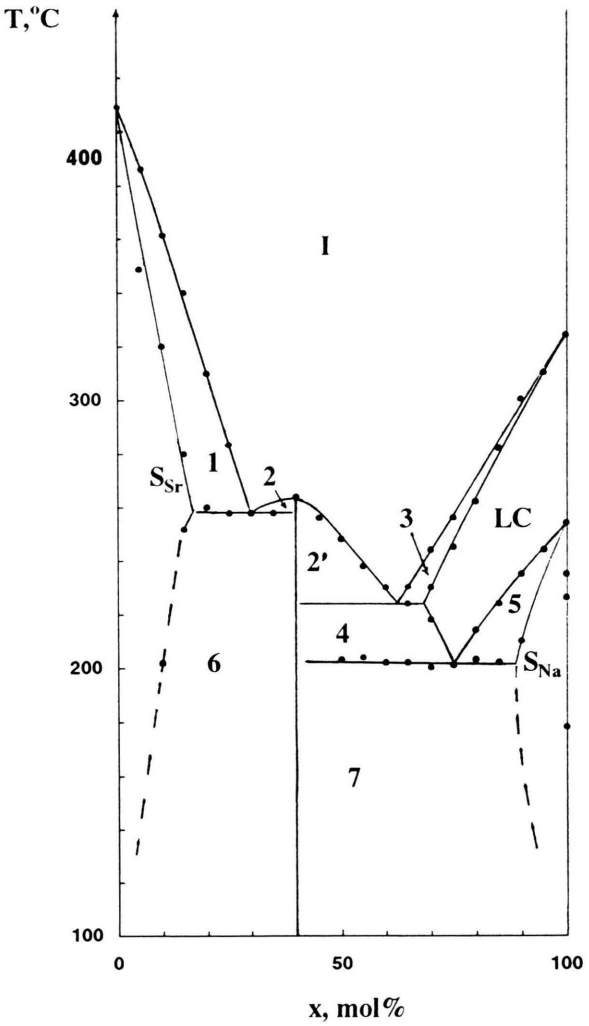

Fig. 3. Phase diagram of
$\{x\,C_3H_7COONa + (100\text{-}x)(C_3H_7COO)_2Sr\}$.
I: isotropic melt, LC: liquid crystalline phase, S_{Sr} and S_{Na}: solid solutions of sodium butyrate in strontium butyrate and vice versa, respectively. Arabic numerals stand for heterogeneous two-phase regions as follows: 1: $(I + S_{Sr})$, 2 and 2′: $(I + K_D)$, 3: (I + LC), 4: $(LC + K_D)$, 5: $(LC + S_{Na})$, 6: $(S_{Sr} + K_D)$, 7: $(S_{Na} + K_D)$, where K_D is the solid phase of the congruently melting complex.

$x = 23$ mol%, and 208 °C, $x = 80$ mol%. The phase diagram indicates the formation of a congruently melting complex (D) with the probable composition $2\,C_3H_7COONa\ 3(C_3H_7COO)_2Ca$.

The homogeneous liquid crystal solution (LC) is formed in the system according to the eutectic reaction between the solid phases of sodium butyrate and complex D at 208 °C.

The metatectic point, where solid phase coexists with two liquids, isotropic and mesomorphic, is observed at 222 °C, $x = 66$ mol%.

Under cooling the isotropic melt is found to form glassy phase in the composition range: 0 mol% $< x <$ 85 mol%.Optically anisotropic vitreous mesophases have been obtained in the composition range 66 mol% $< x <$ 85 mol%.

$x\,C_3H_7COONa + (100\text{-}x)(C_3H_7COO)_2Sr$

The phase diagram presented in Fig. 3 is indicative of the formation of a congruently melting complex D with the probable composition $2\,C_3H_7COONa\ 3(C_3H_7COO)_2Sr$. There exist two eutectic points at 258 °C, $x = 30$ mol% and 202 °C, $x = 75$ mol%.

A liquid crystal solution (LC) is formed in the system following to the eutectic reaction ar 202 °C between the solid phases of sodium butyrate and complex D.

The mesophase clearing curve intersects the melting curve in the metatectic point at 224 °C, $x = 63$ mol%.

Glasses may be obtained in the system in the composition range from pure strontium butyrate up to $x = 80$ mol%, the vitreous mesophases being obtained in the range 63 mol% $< x <$ 80 mol%.

From Figs. 1–3 follows that the addition of nonmesogenic alkali-earth metal butyrates to mesogenic sodium butyrate results to a decrease in the mesophase clearing temperature and finally to the disappearance of liquid crystals in the mixtures. Homogeneous liquid crystalline solution disappears on adding to pure sodium butyrate 24 mol% magnesium butyrate, 28 mol% calcium butyrate or 32 mol% strontium butyrate. So, magnesium salt has the largest effect in destroying the mesophase of sodium butyrate.

It should be noted that magnesium butyrate forms a congruently melting compound with the probable composition $Na_2Mg(C_3H_7COO)_4$, in contrast to calcium and strontium butyrates which form compounds with the composition $Na_2Ca_3(C_3H_7COO)_8$ and $Na_2Sr_3(C_3H_7COO)_8$, respectively. The concentration range of glass formation in the binary system of sodium and magnesium butyrate is smaller than in the two other systems. Moreover mixtures with magnesium butyrate do not form optically anisotropic glassy mesophases. Thus, we can state that the interionic interaction in the binary system of sodium and magnesium butyrates is stronger than that in binaries of sodium and calcium or strontium butyrates.

Acknowledgements

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