Mesophase and Glass Formation in Binary Systems of Caesium and Alkali-Earth Metal Butyrates

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The phase diagrams of the binary systems of non-mesomorphic components such as caesium–magnesium, caesium–calcium and caesium–barium butyrates have been studied by differential thermal analysis and hot stage polarization microscopy. Smectic liquid crystals are found in some composition ranges of the binaries with calcium and barium butyrates. The liquid crystal appearance in these systems is explained by the exhibition of latent mesomorphism of caesium butyrate. Glasses are obtained in all systems studied, the formation of vitreous optical anisotropic mesophase being revealed only for binary from caesium and barium butyrates.

Key words: Phase Diagram; Mesophase; Glass; Metal Alkanoate.

Introduction

Many alkali short-chain alkanoates are known to form so-called ionic liquid crystals or mesophases [1–2]. Some of them have latent (virtual) mesomorphic properties that can be exhibited in binary systems [3]. During the last years many data on phase diagrams of the binaries of alkali alkanoates with common anion were obtained [4, 5]. But there are few data on phase diagrams of binaries from metal alkanoates with asymmetric charged cations such as, for example, univalent alkali and divalent alkali-earth metal cations [6]. Such systems may be very interesting and useful since not only ionic mesophases but glasses with optical isotropic and anisotropic properties may be formed there.

In the present work the phase diagrams of the binary systems of caesium butyrate with magnesium, calcium and barium butyrates have been studied in order to discover the formation of induced liquid crystalline phases and determine the composition ranges of mesophase and glass existence. There exist no data on the phase transition temperatures of these systems in literature. As known [6, 7], pure magnesium, calcium and barium butyrates do not form liquid crystals but supercool and form glasses easily on cooling their liquid phases. Pure caesium butyrate does not form either a mesophase or glass [8] but is should be expected to possess the latent mesomorphic properties just like other caesium alkanoates do, for example, caesium propionate and isobutyrate [9, 10]

Experimental

Caesium, magnesium, calcium and barium butyrates were prepared by the methods described in [7, 8]. 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.

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 "Boemius" 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 [6–8]. No mesophase was revealed on melting of the pure salts. Caesium butyrate has a solid-solid transition at 76 °C and melts at 353 °C. Magnesium and calcium butyrates have no solid-solid transitions and melt into viscous isotropic liquids at 296 °C and 335 °C, respectively. Barium butyrate exhibits a complicated thermal behavior: it undergoes a solid-solid transition at 161 °C, melts at 246 °C, then immediately solid-

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ifies, and remelts at a higher temperature (316 °C). As was shown in [11], the addition of a second component such as sodium butyrate to barium butyrate stabilized the liquid which had appeared with the first melting of barium butyrate.

Results and Discussion

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

$x\,C_3H_7COOCs + (100-x)\,(C_3H_7COO)_2Mg$

As seen in Fig. 1, three branches of the melting curve intersect in two eutectic points at 248 °C, $x = 18$ mol% and at 233 °C, $x = 65$ mol%. A congruently melting complex (D) with probable composition $2\,C_3H_7COOCs \cdot 3(C_3H_7COO)_2Mg$ has a flat and weakly-defined distectic maximum at 258 °C which indicates a high degree of complex dissociation in the melt.

No liquid crystals have been obtained in this system. Glasses may be observed in the composition range from pure magnesium butyrate up to $x = 30$ mol%, no optical anisotropic glasses being obtained in this system.

$x\,C_3H_7COOCs + (100-x)\,(C_3H_7COO)_2Ca$

The phase diagram is presented in Figure 2. The melting curve has two eutectic points at 218 °C, $x = 46$ mol% and at 298 °C, $x = 84$ mol%. There is a peritectic point at 268 °C, $x = 22$ mol%. The phase diagram indicates the formation of a congruently and an incongruently melting complex, D and P, with the probable compositions $3\,C_3H_7COOCs \cdot 3(C_3H_7COO)_2Ca$ and $C_3H_7COOCs \cdot 4(C_3H_7COO)_2Ca$, respectively.

The intermediate homogeneous liquid crystal solution (LC), identified as smectic A, is formed in the system according to the eutectic reaction between the solid phases of caesium butyrate and complex D at 298 °C.

The metatectic points, where a solid phase coexists with two liquids, isotropic and mesomorphic, are observed at 316 °C, $x = 79$ mol% and 310 °C, $x = 86$ mol%. The region where mesophase and isotropic melt are found to coexist in our experiments is 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 $0\ \text{mol\%} < x < 50$ mol%. Optical anisotropic glasses have not been obtained in this system.

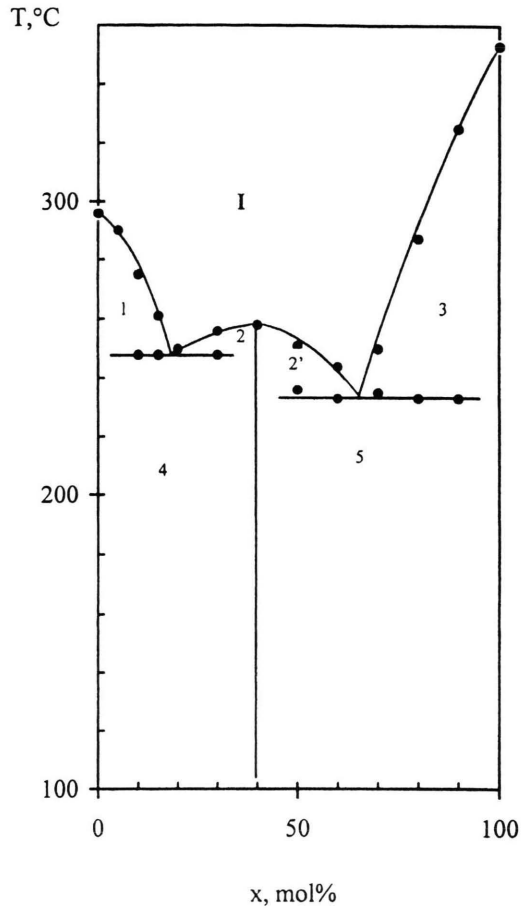

Fig. 1. Phase diagram of $\{x\,C_3H_7COOCs + (100-x)\,(C_3H_7COO)_2Mg\}$. I: isotropic melt. Arabic numerals stand for heterogeneous two-phase regions as follows: 1: $(I + K_{Mg})$, 2 and 2′: $(I + K_D)$, 3: $(I + K_{Cs})$, 4: $(K_{Mg} + K_D)$, 5: $(K_{Cs} + K_D)$, where K_{Mg} and K_{Cs} are the solid phases of pure magnesium and caesium butyrates, K_D is the solid phase of the congruently melting complex.

$x\,C_3H_7COOCs + (100-x)\,(C_3H_7COO)_2Ba$

The phase diagram presented in Fig. 3 is indicative of the formation of a congruently melting complex D with the probable composition $C_3H_7COOCs \cdot 2(C_3H_7COO)_2Ba$. There exist two eutectic points at 222 °C, $x = 17$ mol%, and at 164 °C, $x = 66$ mol%. There is a peritectic point at 208 °C, $x = 75$ mol% and transition point at 246 °C, $x = 13$ mol%. The phase diagram shows the formation of an incongruently melting complex P with the probable composition $4\,C_3H_7COOCs \cdot (C_3H_7COO)_2Ba$.

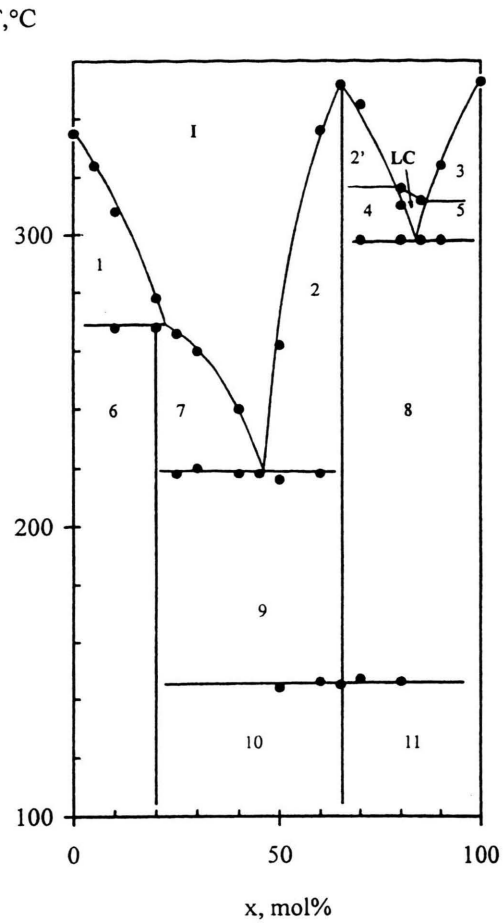

Fig. 2. Phase diagram of $\{xC_3H_7COOCs + (100-x)\ (C_3H_7COO)_2\ Ca\}$. I: isotropic melt, LC: liquid crystalline phase. Arabic numerals stand for heterogeneous two-phase regions as follows: 1: $(I + K_{Ca})$, 2 and 2′: $(I + K_{D1})$, 3: $(I + K_{Cs})$, 4: $(LC + K_{D1})$, 5: $(LC + K_{Cs})$, 6: $(K_{Ca} + K_P)$, 7: $(I + K_P)$, 8: $(K_{Cs} + K_{D1})$, 9: $(K_P + K_{D1})$, 10: $(K_P + K_{D2})$, 11: $(K_{Cs} + K_{D2})$, where K_{Ca} and K_{Cs} are the solid phases of pure calcium and caesium butyrates, K_{D1} and K_{D2} are the polymorphic solid modifications of the congruently melting complex, K_P is the solid phase of the incongruently melting complex.

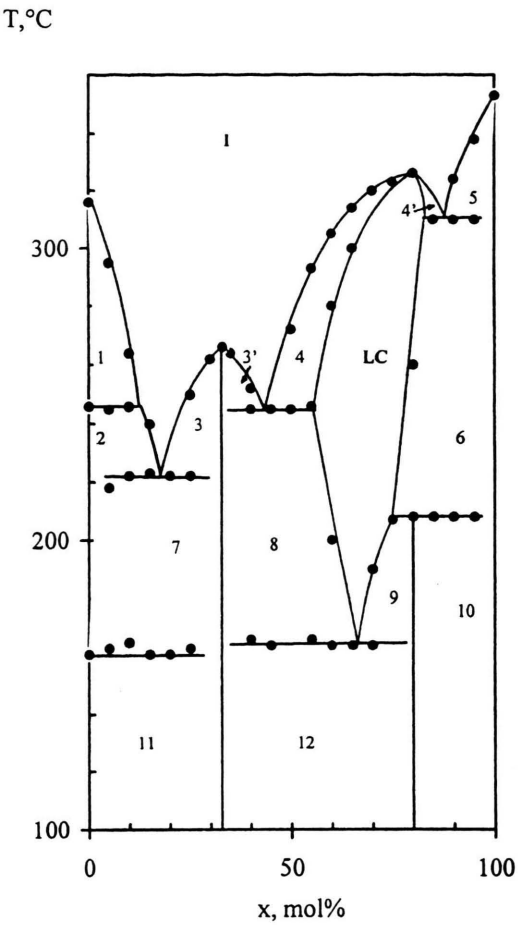

Fig. 3. Phase diagram of $\{xC_3H_7COOCs + (100-x)\ (C_3H_7COO)_2\ Ba\}$. I: isotropic melt, LC: liquid crystalline phase. Arabic numerals stand for heterogeneous two-phase regions as follows: 1: $(I + K_{Ba1})$, 2: $(I + K_{Ba2})$, 3 and 3′: $(I + K_D)$, 4 and 4′: $(I + LC)$, 5: $(I + K_{Cs})$, 6: $(LC + K_{Cs})$, 7: $(K_{Ba2} + K_D)$, 8: $(LC + K_D)$, 9: $(LC + K_P)$, 10: $(K_P + K_{Cs})$, 11: $(K_{Ba3} + K_P)$, 12: $(K_P + K_D)$, where K_{Ba1}, K_{Ba2} and K_{Ba3} are the polymorphic solid modifications of pure barium butyrate, K_{Cs} is the solid phase of pure caesium butyrate, K_D and K_P are solid phases of complexes, melting congruently and incongruently, respectively.

The intermediate homogeneous liquid crystal solution (LC), identified as smectic A, is formed in the system following to the eutectic reaction at 164 °C between the solid phases of congruently and incongruently melting complexes D and P.

The mesophase clearing curve intersects the melting curve in two metatectic points at 245 °C, $x = 44$ mol% and 310 °C, $x = 88$ mol%. It has a maximum at 326 °C, $x = 80$ mol%.

Glasses may be obtained in the composition range from pure barium butyrate up to $x = 80$ mol%, vitreous mesophases being obtained in the range 50 mol% $< x < 80$ mol%.

In contrast to the earlier studied binary system of barium and sodium butyrate [11], the addition of caesium butyrate to barium butyrate does not stabilize the liquid which appears with the first melting of barium butyrate at 246 °C and immediately recrystallizes. It may be specified by the large difference in radii of sodium and caesium cations. As seen in Fig. 3, there is a solid-solid transition at 246 °C in binaries of barium and caesium butyrates in the composition range 0 mol% $< x \leq 14$ mol%.

From Figs. 1–3 follow that the addition of barium and calcium butyrates to caesium butyrate results in mesophase formation but there is no mesophase induction in the system of caesium and magnesium butyrates. As can be seen from the figures, the concentration and temperature range of induced mesophase in binaries with caesium butyrate is the greater, the larger the alkali-earth metal radius and the closer it is to caesium cation radius. Caesium butyrate is known to have latent mesomorphic properties, [3] and his latent mesophase clearing temperature is estimated to be ≈286 °C [12]. Formation of complexes with high content of caesium butyrate in binaries with calcium and barium butyrates favors the exhibition of latent mesophase of caesium butyrate due to the melting temperatures in these systems becoming lower than the probable latent mesophase clearing temperatures in the composition ranges not far from $x = 100$ mol%. It should be noted that the induced mesophase clearing temperatures in both systems discussed lie higher than the latent mesophase clearing temperature of caesium butyrate (286 °C) and even increase when adding calcium or barium butyrates in some concentration range. This may mean that presence of a small amount of barium and calcium cations in mesophase based on caesium butyrate increases its ordering and thermal stability. Moreover, this fact may be indicative of latent mesomorphic properties of complexes formed in binaries with calcium and barium butyrates.

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