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# Phase Diagram of the Binary System of Barium and Sodium *n*-Butanoates

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The phase diagram of the binary system of barium and sodium *n*-butanoates has been studied by differential thermal analysis, hot stage polarization microscopy, and small angle X-ray diffraction. Pure barium *n*-butanoate exhibits a complicated thermal behavior: it melts at 519 K, then immediately solidifies, and remelts at a higher temperature (589 K). The addition of a second component like sodium *n*-butanoate stabilizes the liquid which appears with the first melting of barium *n*-butanoate. This melt exists up to the temperature of the second melting, which may be called the clearing point because this liquid has been found to be slightly anisotropic and to have local bilayer smectic order. The temperature and concentration ranges of formation of the liquid crystalline smectic A solutions has been established. These liquid crystalline solutions are formed as a result of the eutectic reaction at 425 K. In this binary system, glass formation has been discovered in the composition range 0 to 70 mol % of Na *n*-butanoate.

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## Introduction

Phase diagrams of binary systems of metal alkanoates are known to be fairly complicated due to the strong interaction between the components which often leads to the formation of different stable and metastable solid and/or liquid crystalline phases (Franzosini, 1988). From the group of metal alkanoate binaries with a common short-chain anion, only the systems formed with alkali metals are described in the literature (Mirnaya *et al.*, 1990, 1993, 1995a,b). There are no data on phase diagrams of binaries from alkanoates with asymmetrically charged metal cations, such as, for example, alkanoates of alkali and alkali-earth metals. But these systems may be very interesting and useful, due to the possibility of the formation of smectic ordered glasses with valuable physical and optical properties (Mirnaya *et al.*, 1989).

In the present work the phase diagram of the binary system of the mesogenic barium and sodium *n*-butanoates has been studied in order to determine the temperature and concentration ranges of the liquid crystal region and of glass formation. It is known (Ferloni *et al.*, 1976) that pure barium *n*-butanoate easily forms a glass upon cooling the liquid phase. Moreover it was found that it exhibits a very specific and strange thermal behavior, because on heating it undergoes a solid-to-solid transformation at 434 K, it melts at 520 K, and then immediately recrystallizes into a new solid phase which in turn remelts at 586 K (Ferloni *et al.*, 1976). Similar sequences of melting, solidifying, and remelting at a higher temperature were reported previously (Findlay, 1951). In connection with such behavior it is very interesting to study the effect of the addition of a second component on the phase transitions in the mixtures.

## Experimental Section

Barium and sodium *n*-butanoates were prepared according to the method described in a previous work (Mirnaya *et al.*, 1993). Both salts were free from any water and acid, as evidenced by their IR spectra. The binary mixtures were prepared by melting known masses of the components under argon and then recrystallizing them at 353 K during several hours or days, if it was needed. The extent of crystallinity was determined by means of X-ray diffraction. Samples were stored in argon before the measurements.

The phase diagram was investigated by means of both polythermal polarization microscopy and differential thermal analysis (DTA). A Paulik−Paulik−Erdey derivatograph (Q-1500 D) with α-$Al_2O_3$ powder as the reference substance was used to obtain thermograms on heating, the heating rates being 2.5 K $min^{-1}$. The temperature was measured with a precision of ±1 K.

A polarization microscope “Amplival” with a “Boëmius” hot stage was used to identify mesophases and isotropic liquid phases, thus determining the temperatures of the isotropic melt−mesophase and isotropic−crystal transitions.

Small angle X-ray diffraction measurements were used in some cases to estimate bilayer spacings and to prove the formation of mesophases such as smectic liquid crystals or locally ordered melts. A special device AMUR (Ni-filtered Cu Kα radiation) was used for these purposes.

The temperatures of the phase transitions for the pure salts synthesized in our laboratory were in good agreement (about ±1 K) with the literature data (Ferloni *et al.*, 1976; Franzosini, 1988). Sodium *n*-butanoate displays three main solid−solid transitions at 450, 499, and 508 K, melts at 527 K with formation of a smectic A mesophase, and then clears at 597 K. Barium *n*-butanoate undergoes a solid-to-solid phase transition at 434 K and exhibits melting at 519 K, forming a liquid or a mesophase. This first melting is followed by immediate recrystallization, and this solid phase melts at 589 K with formation of an optically isotropic viscous liquid. The latter value is 3 K higher than that found in the mentioned work (Ferloni *et al.*, 1976).

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**Table 1. Phase Transition Temperatures in Binary Mixtures of $(n\text{-}C_3H_7COO)_2Ba$ (A) + $n\text{-}C_3H_7COONa$ (B)**

| $x_B$ | $T$/K | $x_B$ | $T$/K |
|---|---|---|---|
| 0.00 | 434 | 0.45 | 426 |
| | 519 | | 446 |
| | 589 | | |
| 0.05 | 425 | 0.50 | 425 |
| | 445 | | 445 |
| | 511 | | |
| 0.10 | 425 | 0.55 | 425 |
| | 445 | | 445 |
| | 479 | | 477 |
| | 501 | | |
| 0.15 | 422 | 0.60 | 425 |
| | 447 | | 453 |
| | 480 | | 497 |
| | 493 | | |
| 0.20 | 427 | 0.65 | 425 |
| | 445 | | 443 |
| | 479 | | 482 |
| | | | 510 |
| 0.25 | 423 | 0.70 | 425 |
| | 447 | | 453 |
| | 479 | | 458 |
| | | | 508 |
| | | | 526 |
| 0.30 | 425 | 0.80 | 450 |
| | 445 | | 484 |
| | 480 | | 537 |
| 0.35 | 425 | 0.90 | 452 |
| | 446 | | 497 |
| | 477 | | 576 |
| 0.40 | 425 | 1.00 | 451 |
| | 445 | | 499 |
| | 468 | | 508 |
| | | | 527 |
| | | | 597 |

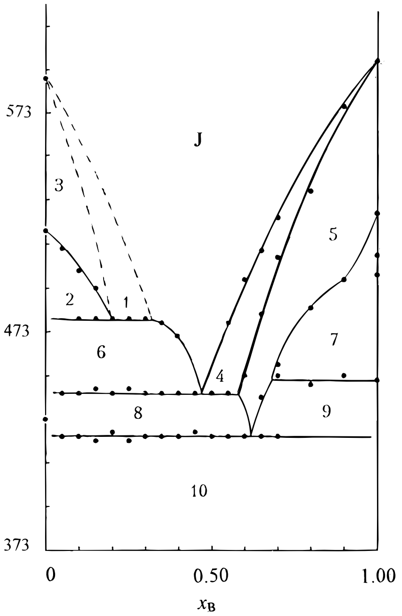

**Figure 1.** Phase diagram of $(n\text{-}C_3H_7COO)_2Ba$ (A) + $n\text{-}C_3H_7COONa$ (B): (•) DTA data. **1**, (J + M); **2**, (M + $K_{Ba}$); **3**, M; **4**, (J + SmA); **5**, SmA; **6**, (J + $K_{Ba}$); **7**, (SmA + $K_{Na2}$); **8**, (SmA + $K_{Ba}$); **9** , (SmA + $K_{Na}$); **10**, ($K_{Ba}$ + $K_{Na}$). J = isotropic melt, M = homogeneous nonspecified mesomorphic liquid, SmA = homogeneous smectic A liquid crystalline phase, $K_{Ba}$ = solid phase of barium butanoate, and $K_{Na}$ and $K_{Na2}$ = lower temperature and higher temperature solid modifications of sodium butanoate. The dashed lines designate conventionally the heterogeneous two-phase region (1) dividing the isotropic (J) and nonspecified mesomorphic (3) melts.

## Results and Discussion

The experimental transition temperatures measured by DTA on the mixtures of the binary system [$(n\text{-}C_3H_7COO)_2Ba$ + $n\text{-}C_3H_7COONa$] are reported in Table 1, and the phase diagram is illustrated in Figure 1. It has been obtained upon heating because on cooling the formation of glasses, which has been observed in a wide concentration range ($0 > x > 0.70$) prevents the detection of the transition phenomena. The glasses were fairly stable and it was necessary to keep them in a furnace at about 353 K during several days to yield fully recrystallized samples.

The phase diagram shows a eutectic point at 425 K, $x$ = 0.62. The homogeneous liquid crystalline solution identified as the smectic A phase (SmA) exists over the range $0.58 < x < 1.00$. The above solution (SmA) is formed in the system following the eutectic reaction: $K_{Na} + K_{Ba}$ = SmA, where $K_{Na}$ and $K_{Ba}$ are solid phases of sodium and barium $n$-butanoates. The liquid crystalline solution has the same microscopic texture (confocal-conical) as the well-known smectic A mesophase of pure sodium $n$-butanoate.

A transition point is found at 451 K, $x$ = 0.68, where equilibrium exists between the lower and higher temperature solid polymorphs of sodium $n$-butanoate and mesophase SmA. This means that barium $n$-butanoate in the solid state is soluble in neither polymorph of sodium $n$-butanoate.

The invariant point at 445 K, $x$ = 0.47, is a metatectic point, where two liquids, the isotropic and the mesomorphic (SmA) ones, coexist with the solid phase. Another invariant point is observed at 480 K, $x$ = 0.20. It seems to be a metatectic point, because there exists one solid phase with two liquids, isotropic and nonspecified mesomorphic (M).

This mesomorphic phase M occurring in the mixtures corresponds to the first liquid which is formed on melting and immediately recrystallizes in pure barium $n$-butanoate. It is formed on cooling the isotropic melt of this salt. But addition of a small amount of a second salt (we have started from $x$ = 0.2) gives rise to stabilization of this liquid phase M so that it exists from the melting point up to the clearing temperature. Microscopic observations show that the mesophase M is a slightly anisotropic liquid. Small angle X-ray diffraction curves for this mesophase obtained by either heating the mixtures or supercooling the molten pure barium $n$-butanoate and the mixtures display a form which is characteristic of the nonoriented smectic mesophase near a clearing point or for a locally ordered structured melt. The diffraction maximum has been discovered in the angle range $2\theta$ = 6.2−6.3°, which is indicative of the mesophase bilayer spacing 13.98 Å.

On the other hand, the thermograms are not sensitive to the transitions from liquid M to isotropic liquid. Thus, the curve between regions 3 and 1, as well as that between regions 1 and J, is marked in Figure 1 by dotted lines. The equilibria defined by these lines can be observed by microscopic observation.

The powder X-ray diffraction patterns of pure barium and sodium $n$-butanoates taken at room temperature have shown that the bilayer spacings in their crystal phases are equal to 14.6 Å and 14.08 Å, respectively. The mesophase bilayer spacing in pure sodium $n$-butanoate is equal to 13.8 Å, which closely resembles that of the mesophase bilayer spacings in binary salt mixtures (13.98 Å).

Figure 2 represents the bilayer spacings as a function of temperature in two binary mixtures studied as typical examples. As it is shown, a transition from crystal to mesophase occurs in all binary mixtures at approximately 423 K, which is indicative of the formation of a liquid crystalline eutectic.

The obtained phase diagram shows that the liquid, which is metastable in pure barium $n$-butanoate, becomes stable

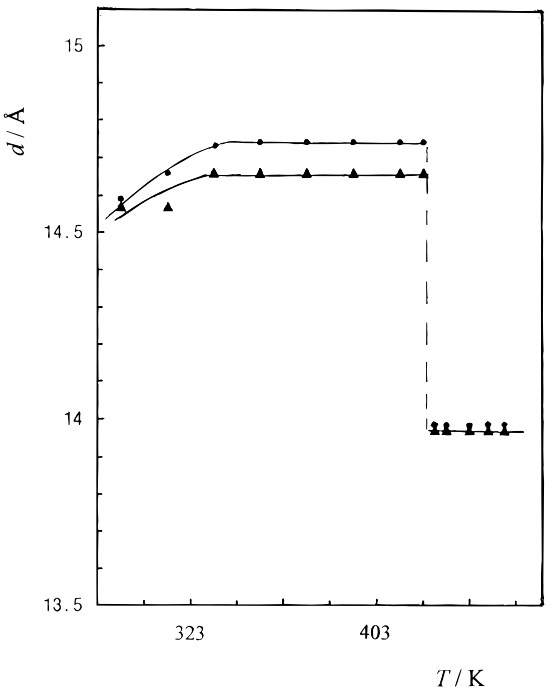

**Figure 2.** Bilayer spacings as a function of temperature in the binary mixtures of $(n\text{-}C_3H_7COO)_2Ba$ (A) + $n\text{-}C_3H_7COONa$ (B): $x = 0.40$ (•); $x = 0.60$ (▲)

in the presence of sodium *n*-butanoate and this liquid is mesomorphic or locally ordered. The decrease in the mesophase clearing temperature in adding sodium *n*-butanoate to barium *n*-butanoate and vice versa indicates that the second component decreases the extent of melt ordering which exists in each pure component. It means that the ion arrangement of the mesophase rich in sodium *n*-butanoate differs from that of the mesophase rich in barium *n*-butanoate. However, both mesophases display a bilayer smectic structure, as evidenced by their X-ray diffraction patterns.

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