Phase Diagrams of Binary Systems of Some Alkali Propionates

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The phase diagrams of the binary systems sodium–potassium, sodium–caesium, and potassium–caesium propionates have been investigated by differential thermal analysis and hot-stage polarization microscopy. Smectic liquid crystals in the systems with sodium propionate have been discovered. Liquid crystal formation in binaries of two non-mesomorphic components is explained by latent mesomorphism which is shown to be inherent to both sodium and potassium propionate.

Introduction

The thermal properties of pure alkali propionates have been studied in some detail by different investigators in a variety of ways [1, 2]. None of these salts is found to form liquid crystals or so-called mesophases under melting, i.e. is apparently mesomorphic, as distinguished from the homologues of metal alkanoates with longer aliphatic chain length such as alkali butyrates or valerates. As well known [3, 4], the latter belong to a special family of thermotropic ionic liquid crystals whose existence and stability are highly sensitive to the nature of the metal cation, the size of the alkanoate anion and the character of the interionic interactions.

There is an empiric rule [4], according to which the short-chain alkanoic acid salts may form enantiotropic mesophases or may have latent mesomorphic properties, i.e. be potential mesogens, when the ratio of cation to anion radii does not exceed 0.5. Also the cation polarizing ability must not exceed 1.05 as with the sodium cation, or at least must be smaller than the polarizing ability of the lithium cation, whose alkanoate salts are known [1–4] to form no liquid crystals due to the alkanoate anion size. In accordance with the above rule, sodium and potassium propionates have to possess latent mesomorphic properties since the ratios of the crystallographic radii of their cations (0.97 Å for Na^+ and 1.33 Å for K^+) to the radius of the propionate anion repulsion envelope, estimated by Duruz et al. as 2.82 Å [5], do not exceed 0.5.

On this basis one should expect that a mesophase appears in some concentration-temperature region of the binary system of metal propionates which has sodium propionate or potassium propionate as one of the two components, if the solidus curve being lower than the latent mesophase clearing temperature curve.

In the present work the phase diagrams of the binary systems of potentially mesogenic sodium and potassium propionates as well as sodium or potassium propionate with caesium propionate, where only one component is potentially mesogenic, have been studied. There exist no data on the phase transition temperatures of the last two binaries, while the system of sodium with potassium propionate was investigated by Sokolov et al. with the visual polythermal method [6, 7]. However, these authors were unaware of the possibility of liquid crystal formation in metal alkanoate systems and hence have interpreted the mesophase clearing temperature curve as the solidus curve even in binaries of two mesogenic components, such as sodium and potassium butyrates or valerates [2]. Thus in most cases the results obtained by the above authors must be reinvestigated in light of the possibility of mesophase formation.

Experimental

Sodium, potassium and caesium propionates were synthesized by neutralization of the metal carbonates with propionic acid. After evaporation of the aqueous solutions, the salts were recrystallized from ethanol, then washed with either ethyl ether or acetone and dried in a vacuum oven for 48 h at ≈120 °C. The salts obtained were free from any water and acid, as evi-

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denced 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 with a Paulik-Paulik-Erdey derivatograph (Q-1500 D). A Pt−Pt/Rh thermocouple and 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 possible mesophases and isotropic liquid phases and so to determine the temperatures of isotropic melt−mesophase and isotropic melt−crystal transitions.

Our DTA-apparatus turned out to be little sensitive to the mesophase−isotropic melt transitions for all samples studied, perhaps due to the small enthalpies of these transitions. Thus the data on these transition temperatures were obtained mainly by microscopic observation in polarizing light with crossed polaroids.

The solid-to-solid transition and melting temperatures for the pure salts synthesized in our laboratory were in excellent agreement with the accepted data [1, 2]. Sodium propionate had two solid-to-solid transitions at 197 °C and 221 °C and then melted at 289 °C. Potassium propionate had a solid-to-solid transition at 80 °C and melted at 365 °C. Caesium propionate melted at 307 °C and exhibited two solid-to-solid transitions at 41 °C and 146 °C. No mesomorphic phase was revealed in melting of the pure salts.

Results and Discussion

In Figs. 1, 2, and 3 the phase diagrams for the binary system studied are represented. All of them demonstrate intricate solidus lines and indicate the formation of both congruently and incongruently melting complexes. In addition, the formation of mesophase is observed in the systems with sodium propionate.

$xC_2H_5COONa + (100-x)C_2H_5COOK$

As seen in Fig. 1, three branches of the melting curve intersect in two eutectic points at 260 °C, $x = 87$ mol% and at 290 °C, $x = 37$ mol%. There is a peritectic point at 300 °C, $x = 30$ mol%. The phase diagram indicates the formation of a congruently melting complex with equimolar composition ($x = 50$ mol%), i.e. $C_2H_5COONa \cdot C_2H_5COOK$ (D), as well as an incongruently melting complex with probable composition $C_2H_5COONa \cdot 4\,C_2H_5COOK$ (P). Complex D has three solid-to-solid transitions at 172 °C, 203 °C, and 230 °C, which are observed in the range 15 mol% < x < 85 mol%. The flat maximum of the solidus curve is indicative of a high degree of dissociation of complex D in the melt.

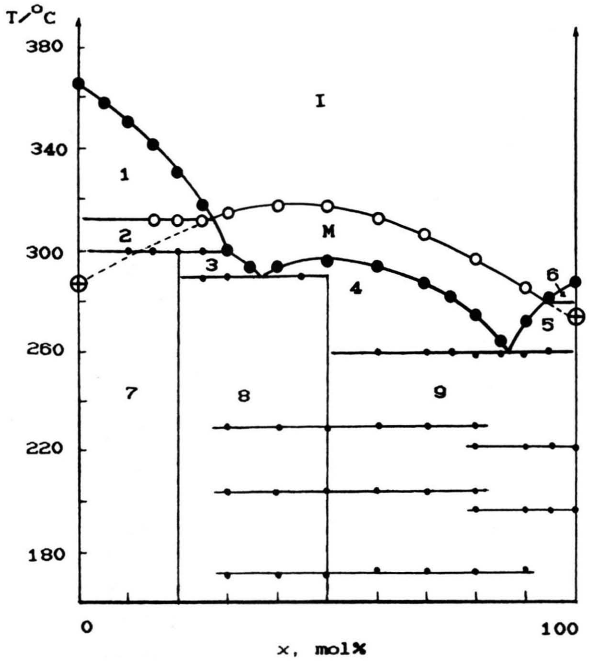

Fig. 1.
Phase diagram of $\{xC_2H_5COONa + (100-x)C_2H_5COOK\}$. Open circles are the experimental data obtained by polarization microscopy only. Full circles are the experimental data obtained by the DTA-method, the large circles being the DTA-data confirmed by polarization microscopy. Crossed circles are the latent mesophase clearing temperatures of the pure components obtained by extrapolation (dotted line) of the clearing temperature curve. One-phase regions for isotropic melt and mesophase are marked by I and M. Arabic numbers stand for heterogeneous two-phase regions, as for the corresponding compositions, see text.

There exists a homogeneous mesomorphic liquid phase in the range 27 mol% < x < 94 mol%. The mesophase was shown by microscopic observation to be smectic A. So, on cooling the isotropic melt, the appearance of birefringent domains, so-called bâton-

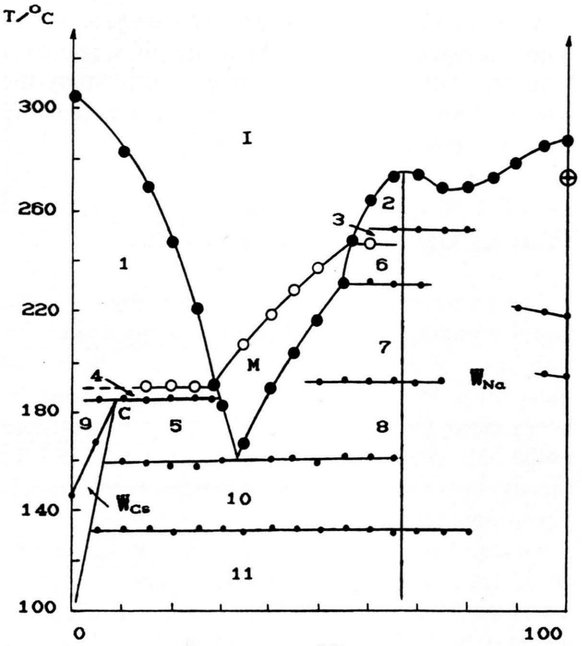

Fig. 2.
Phase diagram of $\{x\mathrm{C_2H_5COONa}+(100-x)\mathrm{C_2H_5COOCs}\}$. As for the open, small full, and large full circles and the crossed circle see the caption of Figure 1. I, M, W_{Cs}, and W_{Na} stand for homogeneous one-phase regions while arabic numbers stand for heterogeneous two-phase ones. For explanations see text. Point C designates the equilibrium between the mesophase and two solid phases.

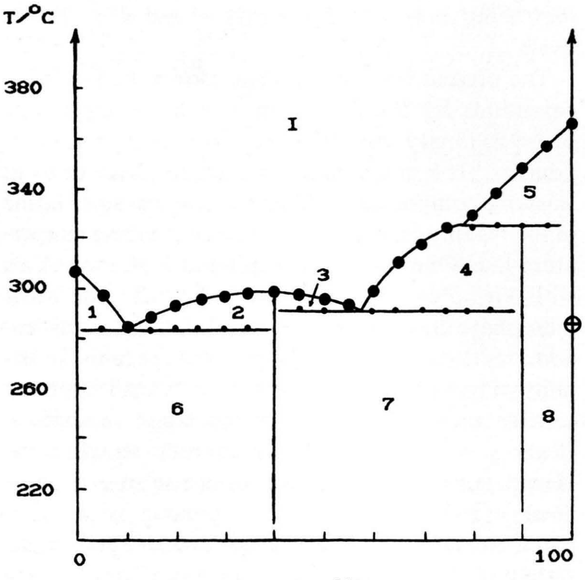

Fig. 3.
Phase diagram of $\{x\mathrm{C_2H_5COOK}+(100-x)\mathrm{C_2H_5COOCs}\}$. As for the meaning of the circles and numbers see the caption of Figure 1. The region of isotropic melt is marked by I.

nets, forming the continuous focal-conical texture which is characteristic of smectic phase A [8], has been seen for all samples in the above composition range. Moreover the mesophase obtained in the system discussed was found to be continuously miscible with the known smectic phase A of sodium butyrate, which exists in the same temperature interval as the identified mesophase does [3, 9].

The mesophase clearing curve intersects the solidus curve in two invariant points at 312 °C, $x = 27$ mol% and at 290 °C, $x = 94$ mol%, where three phases, solid, mesophase and isotropic melt coexist. Except in the isotropic melt and in the mesophase, marked in Fig. 1 as I and M, two phases coexist in all other regions of the phase diagram, such as solid and solid (S + S), solid and mesophase (S + M) and solid and isotropic melt (S + I). These heterogeneous regions are marked in the figure by arabic numbers, which mean the following: 1: $(S_K + I)$, 2: $(S_K + M)$, 3: $(S_P + M)$, 4: $(S_D + M)$, 5: $(S_{Na} + M)$, 6: $(S_{Na} + I)$, 7: $(S_K + S_P)$, 8: $(S_P + S_D)$, 9: $(S_{Na} + S_D)$, where S_K and S_{Na} are solid phases of pure potassium and sodium propionates, S_D and S_P are solid phases of complexes D and P, melting congruently and incongruently, respectively. Regions were the isotropic melt coexists with a mesophase are not revealed in our experiments.

A comparison of the present results with earlier findings [6, 7] by Sokolov et al. has shown that the above authors determined only the temperatures of the equilibrium of the isotropic melt with a solid or mesophase but considered all of them as solidus temperatures.

The latent mesophase clearing temperatures for the potentially mesogenic sodium and potassium propionates may be estimated approximately by the extrapolation of the mesophase clearing curve to $x = 100$ mol% (274 °C) and $x = 0$ mol% (287 °C), respectively. It will be noted that the value of latent mesophase clearing temperature for sodium propionate obtained in this work agrees fairly well with that obtained in studying the phase diagram of sodium and barium propionates [10].

$x\mathrm{C_2H_5COONa} + (100-x)\mathrm{C_2H_5COOCs}$

The phase diagram is presented in Figure 2. The existence of a homogeneous liquid crystalline phase is observed in the range 28 mol% $< x <$ 56 mol%. The identification of the mesophase has been carried out in the same way as for the above system. This mesophase has been established to be also smectic A. Since the mesophase makes its appearance rather far from pure sodium propionate ($x < 56$ mol%), it is not worthwhile to estimate the latent mesophase clearing temperature for this potential mesogen. Thus, it is essential to use here the value that has been obtained in studying the system of sodium and potassium propionates, i.e. 274 °C.

There is an eutectic point at 160 °C, $x = 34$ mol%. The phase diagram indicates the formation of a congruently melting complex with $x = 67$ mol%, i.e. $2\,C_2H_5COONa \cdot C_2H_5COOCs$ (D), which has four solid-to-solid transitions at 132 °C, 193 °C, 232 °C and 254 °C that are missing for the pure components. There are four transition invariant points: at 190 °C, $x = 28$ mol% and 248 °C, $x = 56$ mol%, where the isotropic melt (I), mesophase (M) and solid (S) coexist, and at 186 °C, $x = 30$ mol% and 232 °C, $x = 55$ mol%, where mesophase coexists with two solid phases.

A feature of this system consists in the formation of continuous solid solutions (W_{Na}) between complex D and pure sodium propionate in the range 67 mol% $< x <$ 100 mol% with a minimum at 269 °C, $x = 77$ mol%. Moreover, complex D seems to form solid solutions (W_{Cs}) with one polymorphic modification of caesium propionate, namely S_{Cs2} which exists at $T < 146$ °C. This conclusion follows from general analyses of the phase equilibrium lines. The fact that the eutectic line and the solid-to-solid transition line for complex D at 132 °C are detected up to $x = 10$ mol% and $x =$ 5 mol%, respectively, is indicative of both the absence of any incongruently melting complex and the formation of a solid solution on the basis of only one solid polymorph of caesium propionate. An appropriate construction has given an invariant point C where three phases coexist: a high temperature solid modification of caesium propionate (S_{Cs1}), mesophase (M) and solid solution (W_{Cs}).

Thus one can see in Fig. 2 four homogeneous regions: I, M, W_{Na}, and W_{Cs}. All other regions of the phase diagram are two-phase ones. They are marked in the figure by arabic numbers as follows: 1: ($I + S_{Cs1}$), 2: ($I + S_{D1}$), 3: ($I + S_{D2}$), 4: ($M + S_{Cs1}$), 5: ($M + W_{Cs}$), 6: ($M + S_{D2}$), 7: ($M + S_{D3}$), 8: ($M + S_{D4}$), 9: ($S_{Cs1} + W_{Cs}$), 10: ($S_{D4} + W_{Cs}$), 11: ($S_{D5} + W_{Cs}$), where $S_{D1} + S_{D5}$ are polymorphic solid modifications of complex D. It will be noted that the regions where the isotropic melt coexists with the solid solution W_{Na} or the mesophase are very narrow and are not detected experimentally.

Since the addition of caesium propionate to potentially mesogenic sodium propionate gives rise to a liquid crystalline phase, it is of interest to study the binary system of caesium propionate with potentially mesogenic potassium propionate.

$xC_2H_5COOK + (100-x)C_2H_5COOCs$

The phase diagram is presented in Figure 3. No liquid crystalline phase is observed in any concentration range of this system. The reason may be in that the solidus line for all values of x lies well above the latent mesophase clearing temperature for potassium propionate which is, as stated above, equal to ≈ 287 °C, thereby not enabling the latent mesomorphic properties of potassium propionate to be exhibited.

As seen from Fig. 3, three branches of the melting curve intersect in two eutectic points at 284 °C, $x = 11$ mol% and 294 °C, $x = 57$ mol%. There is a peritectic point at 326 °C, $x = 78$ mol%. The phase diagram is indicative of the formation of a congruently melting complex, $2\,C_2H_5COOK \cdot 3\,C_2H_5COOCs$, as well as an incongruently melting complex with the probable composition $9\,C_2H_5COOK \cdot C_2H_5COOCs$. The system has only one homogeneous region: the isotropic melt. In all other regions the isotropic melt coexists with a solid phase, or two solid phases coexist, they being marked in figure by 1–5 and 6–8, respectively.

The present investigation has shown the following conditions for the formation of a liquid crystalline phase in binary salt mixtures of nonmesogenic components: (1) a potential mesomorphism of both or at least one component, (2) a markedly lower solidus line in the region of the latent mesophase clearing temperature line. One should bear in mind that, in systems with one potentially mesogenic component, the latent mesophase clearing temperature has the general tendency to decrease rather sharply, and hence the possibility of mesophase formation must depend upon the relative rates of decrease in the latent mesophase clearing temperature and the melting temperature. Hence, these processes have given rise to a positive result in the system (Na, Cs) propionate, i.e. a mesophase has been realized, but to a negative one in the system (K, Cs) propionate. On the other hand, in systems with two potentially mesogenic components having a common alkanoate anion, such as (Na, K) propionate, there is the possibility of not only a smooth decrease in the latent mesophase clearing temperature but also an increase up to values which even exceed the melting temperatures of one or both components. As stated in [4], this effect may result from the additional electrostatic stabilization of liquid crystalline ordering due to dissimilar metal cation interactions in the binary system. It is clear that, the closer the latent mesophase clearing temperatures to the melting temperatures of pure potentially mesogenic components and the closer the former to each other, the wider is the concentration-temperature range in which the mesophase can be formed.

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