Liquid Crystals in Binary Systems of Lead Decanoate with Zinc or Cadmium Decanoate

T. A. Mirnaya, L. S. Sudovtsova, and G. G. Yaremchuk

The V. Vernadski Institute of General and Inorganic Chemistry of the Ukrainian Academy of Sciences, 32-34 Prospect Palladina, 03680 Kiev-142, Ukraine

Reprint requests to Dr. T. A. M., Fax: (38 044) 444 30 70; E-mail: mirnaya@ionc.kar.net

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The phase transition temperatures were determined by differential thermal analysis and hot stage polarization microscopy between room temperature and the isotropic liquid region for the binary systems of lead (II) decanoate with zinc (II) or cadmium (II) decanoate. The boundaries of the liquid crystal formation in these systems were found.

Key words: Phase Diagram; Mesophase; Metal Alkanoate.

Introduction

Many univalent metal alkanoates and their binary mixtures are known to form thermotropic smectic liquid crystals [1, 2]. The phase transition temperatures of these salts are fairly well studied [2 - 4], but there are few data on the phase behavior of divalent metal alkanoates. Only, the thermophysical properties of the homologous series of cupric and lead alkanoates were studied thoroughly. Information about other divalent metal alkanoates is scarce. In the literature there are no data on phase diagrams of binaries from metal alkanoates with common anion and dissimilar divalent metal cations.

In the present work the phase diagrams of the binary systems of lead (II) decanoate with zinc and cadmium (II) decanoates have been studied in order to determine the temperature and concentration ranges of liquid crystalline phase formation. As known, pure lead decanoate forms a thermotropic smectic A phase. Thermal properties and phase transitions for zinc and cadmium decanoates are not available from the literature.

Experimental

The lead (II), zinc (II) and cadmium (II) decanoates were prepared following a method described in [5, 6]. It consists in the metathesis of the potassium cation of potassium decanoate in methanol solution by lead (II), zinc (II) or cadmium (II) cations, respectively, added as nitrates dissolved in a small amount of water. The potassium decanoate had been prepared previously by interaction of potassium carbonate with the decanoic acid dissolved in methanol.

The divalent metal decanoates were finally purified through several recrystallizations from benzene and dried in a vacuum heater at 50 °C for 6 h. All synthesized salts were free from 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 room temperature during several hours or days. Samples were stored in argon before the measurements.

The phase diagrams were determined 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 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.

Results and Discussion

The temperatures of the phase transitions of pure lead decanoate synthesized in our laboratory were in good agreement (about ± 1 °C) with the literature

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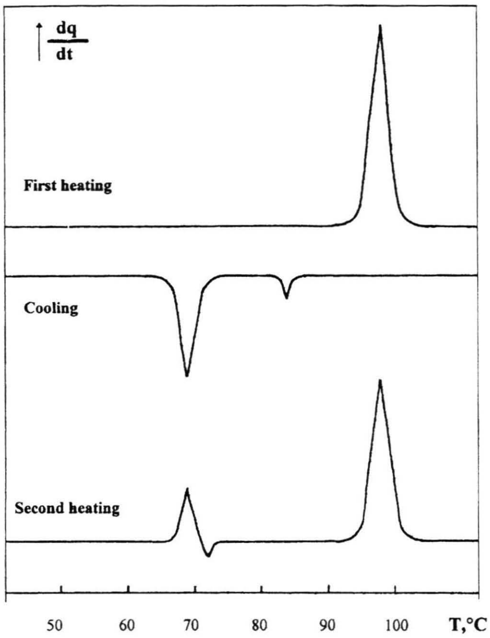

Fig. 1. Thermal behaviour of cadmium decanoate: DTA thermograms; heating rate = 2.5 °C/min.

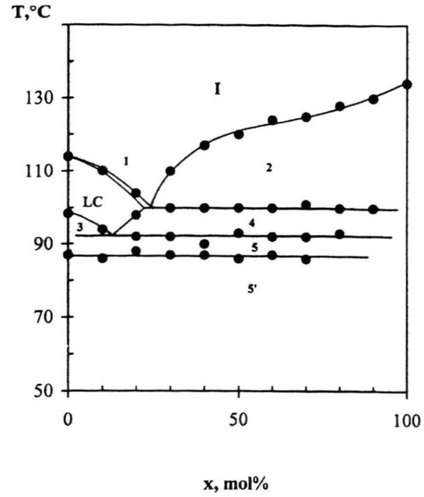

Fig. 2. Phase diagram of $\{xC_9H_{19}COOZn + (100 - x)(C_9H_{19}COO)_2Pb\}$: I: isotropic melt, LC: liquid crystalline phase. Arabic numerals stand for heterogeneous two-phase regions as follows: 1: (I + LC), 2: (I + K_{Zn}), 3: (LC + K_{Pb}), 4: (LC + K_{Zn}), 5 and 5': (K_{Pb} + K_{Zn}), where K_{Pb} and K_{Zn} are the solid phases of pure lead and zinc decanoates

data [5]. It has a solid-solid transition at 87 °C, melts at 98.5 °C with formation of a smectic A mesophase and then clears at 114 °C.

The thermal properties of zinc and cadmium decanoates are not available from the literature. No thermotropic mesophase was revealed on melting of these pure salts in our experiments. Zinc decanoate melts into a viscous isotropic liquid at 134 °C, which supercools easily without the formation of a mesomorphic state.

Cadmium decanoate exhibits monotropic liquid crystalline behaviour (Figure 1). It melts at 98 °C, then under cooling it forms a monotropic smectic A mesophase at 84 °C and solidifies at 69 °C. During a second heating, cadmium decanoate melts at 69 °C and recrystallizes immediately to the stable original crystalline state that transforms to the isotropic liquid at 98 °C.

In Fig. 2 the phase diagram for binary system $\{xC_9H_{19}COOZn + (100 - x)(C_9H_{19}COO)_2Pb\}$ is represented. As seen in the figure, two branches of the melting curve intersect in the eutectic point at 92 °C, x = 13 mol%.

The homogeneous liquid crystal solution (LC), identified as smectic A, is formed in the system according to the eutectic reaction between the solid phases of lead and zinc decanoates at 92 °C. The mesophase clearing curve intersects the melting curve

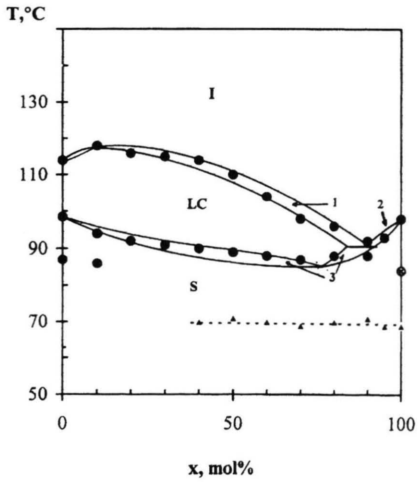

Fig. 3. Phase diagram of $\{xC_9H_{19}COOCd + (100 - x)(C_9H_{19}COO)_2Pb\}\}$: I: isotropic melt, LC: liquid crystalline phase, S: solid solution. Arabic numerals stand for heterogeneous two-phase regions as follows: 1: (I + LC), 2: (I + S), 3: (LC + S). The crossed circle shows the monotropic mesophase clearing temperature of the pure cadmium decanoate upon cooling. The dashed line designates the transformation of a metastable solid phase formed upon cooling to the stable crystal phase.

in the metatectic point at 100 °C, $x = 25$ mol%. In this the invariant solid phase coexists with two liquids, isotropic and mesomorphic.

It is found that glass formation in the system may be observed in the composition range 60 mol% $< x \leq$ 100 mol%.

The phase diagram for the binary system $\{xC_9H_{19}COOCd + (100-x)(C_9H_{19}COO)_2Pb\}$ is presented in Figure 3. It should be noted that these data have been obtained on heating. On cooling the liquid crystals are formed in a whole concentration range of the system owing to the existence of monotropic mesophase in pure cadmium decanoate, the vitreous mesophases being obtained in the range 70 mol% $< x \leq$ 100 mol%.

Continuous solid solutions are found to be formed in the system with a minimum at 86 °C, $x = 75$ mol%. There exists the homogeneous liquid crystal solution (LC), identified as smectic A, in the range 0 mol% $\leq x <$ 85 mol%. The mesophase clearing curve intersects the melting curve in the metatectic point at 92 °C, $x =$ 10 mol%.

The peculiarity of this system is the existence of a phase transformation at 69 °C in the range 40 mol% $< x \leq$ 100 mol%. The DTA peak intensity for this transition is maximum in pure cadmium decanoate previously melted (Figure 1). With increase in the content of lead decanoate in binary mixtures the peak intensity decreases and then disappears at $x <$ 40 mol%. So, the transition at 69 °C seems to be related to the melting of a metastable crystalline phase of cadmium decanoate with its further immediate recrystallization to the stable original crystalline state.

The systems studied in this work demonstrates the complexity of the thermal behaviour of divalent metal alkanoates. As shown, they can form thermotropic and monotropic mesophases, metastable crystal phases and isotropic and mesomorphic glasses.

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