Phase Diagrams of Mesogenic Binary Systems of Cobalt(II) and Univalent Metal Octanoates

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The phase diagrams of binary systems of cobalt(II) octanoate and lithium, sodium, potassium, and thallium(I) octanoates have been studied by differential thermal analysis and polythermal polarization microscopy. In all systems, continuous or limited liquid crystalline solutions of smectic modification are formed. The temperature and composition ranges of the formation of liquid crystals and glasses have been determined.

Key words: Liquid Crystal; Glass; Metal Alkanoate; Phase Diagram.

1. Introduction

Metal alkanoates are typical representatives of ionic metallomesogens, which form thermotropic and lyotropic liquid crystals, optically isotropic and anisotropic (mesomorphic) glasses [1, 2]. Mesomorphic alkanoate glasses, which are a supercooled smectic liquid crystalline phase, are of special interest for the creation of modern optical materials and media for laser generation/modulation and holographic information recording [3]. The problem of creating a low-melting vitrifiable mesomorphic metal alkanoate composition can be solved by composing multicomponent systems and synthesizing low-melting glass-forming mesogenic metal alkanoates. It is known that among metal alkanoates, some bivalent metal alkanoates, such as lead, cadmium, and 3d-transition metal alkanoates, have the lowest melting points and the ability to supercool and vitrify [4 – 11]. However, there are no data in literature to date on the systematic investigation of the thermophysical properties of systems based on 3d-transition metal alkanoates; there is only information on phase equilibria in systems based on 3d-transition metal (cobalt, manganese, nickel, and copper) decanoates with lead decanoate [12] and cobalt laurate with lanthanum laurate [13].

In this work, phase equilibria in binary systems of bivalent cobalt octanoate and univalent lithium, sodium, potassium, and thallium octanoates have been studied to determine the temperature and composition ranges of the ionic mesophase and the glass formation. These systems can be very interesting and useful due to the possibility to obtain on this basis anisotropic materials with special optical and nonlinear optical characteristics.

2. Experimental

Materials. Lithium, sodium, potassium, and thallium(I) octanoates were prepared by the interaction of metal carbonates with octanoic acid in methanol; the salts obtained were recrystallized several times from hot methanol. Cobalt(II) octanoate was prepared by metathesis with the addition of saturated aqueous solutions of cobalt chloride to a solution of potassium octanoate in water, then washed more than once with hot water and dried in a vacuum oven at 50 °C for a day.

Infrared (IR) spectra for metal alkanoates were recorded in potassium bromide (KBr) pellets, at room temperature, on a Perkin–Elmer BX FTIR spectrometer over the range of 4000 – 400 cm^{-1}. These data have evidenced that all salts synthesized were free from any water and acid.

Carbon and hydrogen contents were determined via microanalysis (Tab. 1), cobalt contents by complexometric titration (Co: 17.15% found, 17.08% calc.). Since there is an excellent agreement between exper-

Table 1. Elemental analyses for metal octanoates.

Compound	Carbon (%)		Hydrogen (%)	
	Experimental	Calculated	Experimental	Calculated
$(C_7H_{15}COO)_2Co$	55.19	55.66	8.82	8.70
$C_7H_{15}COOLi$	63.86	64.04	10.09	10.00
$C_7H_{15}COONa$	57.48	57.86	9.11	9.03
$C_7H_{15}COOK$	52.35	52.74	8.36	8.23
$C_7H_{15}COOTl$	27.27	27.65	4.39	4.32

imental and calculated values, it is reasonable to conclude that the compounds are of high purity.

The phase transition temperatures of the pure salts synthesized in our laboratory (cobalt(II), alkali metal and thallium(I) octanoates) were in good agreement (± 2 °C) with the literature data [14, 15]. So, it is a perfect evidence of purity and individuality of all these salts.

The binary mixtures were prepared by melting the preweighed components under argon atmosphere and then recrystallizing them at 80 °C during several hours or days, if it was needed. Samples were stored in argon before the measurements.

Phase Diagram Determination. 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 at a rate of 2.5 °C min^{-1}. 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 crystal–mesophase or isotropic (T_{melting}), and isotropic–mesophase (T_{clearing}) transitions.

3. Results and Discussion

3.1. Properties of Metal Octanoates

IR spectroscopy. Infrared spectroscopy of long chain metal alkanoates provides information on metal coordination, chain conformation, and packing. The IR-spectrum for cobalt(II) octanoate is shown in Figure 1. It is similar in many respects to spectra of other metal octanoates. For example, vibrational absorptions for methylene (CH_2) and methyl (CH_3) groups are found in the region of 2960 – 2855 cm^{-1}. Also, a progression of regularly spaced bands in the region of 1380 – 1100 cm^{-1}, assigned to the wagging vibrations of the CH_2 group, are typical for long aliphatic chains and point to a substantial part of the chains being in the all-trans conformation. The number of absorptions in this region of the spectrum is also related, empirically, to the number of carbon atoms in the hydrocarbon chains [4]. Additionally, there is a relatively strong band at ≈ 1000 cm^{-1} (ν(C–C)), C–C stretch adjacent to the CH_2 group located near 920 cm^{-1} in the coordinated compound. The absence of a carbonyl absorption band in the region of 1730 cm^{-1} and its replacement by carbonyl absorptions in the region of 1500, 1400, 690, and 540 cm^{-1} indicates that there is a complete resonance in the C–O bonds of the carbonyl group as a result of coordination between metal and carboxylate group; as well as the absence of free acid. Further, the absence of hydroxyl absorption bands in the region of 3500 – 3300 cm^{-1} confirms that the compounds are indeed anhydrous.

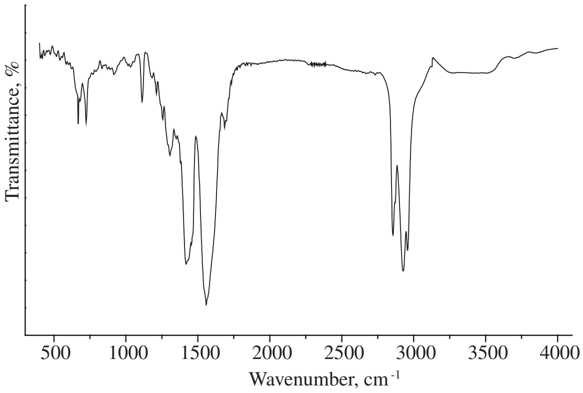

Fig. 1. Room temperature infrared spectra for cobalt(II) octanoate.

The important carbonyl absorptions that point to a possible molecular structure are the asymmetric stretch, $\nu_{as}(COO) \approx 1570 - 1560\ cm^{-1}$, and the symmetric stretch, $\nu_s(COO) \approx 1425 - 1410\ cm^{-1}$. Additionally, the frequencies and relative positions of the symmetric and asymmetric bands ($\Delta\nu = \nu_{as} - \nu_s$) are interpreted by several authors as indicative of carboxylate–metal ion coordination [8, 10, 11]. For example, the frequency shifts of these bands relative to those of the free carboxylate ion depend on metal to

Table 2. Frequencies of main IR bands and COO^- separation (cm^{-1}) for metal octanoates.

Compound	Frequencies of main IR bands, cm^{-1}				$\Delta\nu$ (COO^-)
	$\nu_{as}(COO^-)$	$\nu_s(COO^-)$	$\nu_{as}(CH_2)$	$\nu_s(CH_2)$	
$(C_7H_{15}COO)_2Co$	1560	1425	2930 2960	2855 2875	135
$C_7H_{15}COOLi$	1570	1425	2930 2960	2855 2875	145
$C_7H_{15}COONa$	1565	1415	2930 2960	2860 2880	150
$C_7H_{15}COOK$	1565	1410	2920 2950	2850 2870	155
$C_7H_{15}COOTl$	1565	1410	2930 2960	2860 2880	155

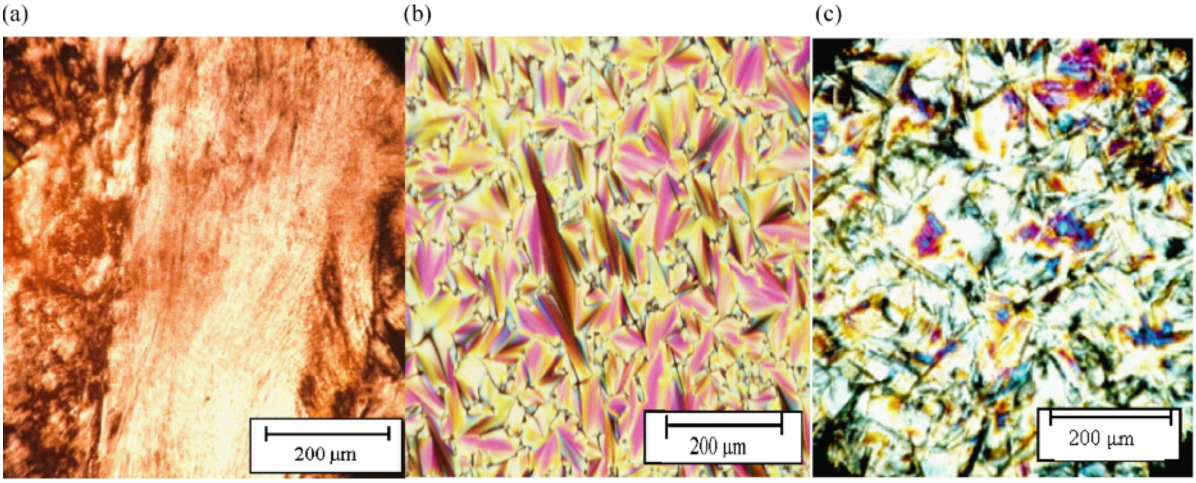

Fig. 2 (colour online). Textures observed by polarizing light microscopy with crossed polars for: (a) mesophase of cobalt(II) octanoate at 115 °C; (b) mesophase of thallium(I) octanoate at 170 °C; (c) mesophase of equimolar mixture of cobalt(II) and thallium(I) octanoates at 115 °C, on cooling from the isotropic melt.

ligand coordination. A summary of all the ν_{as}, ν_s, and $\Delta\nu$ data for metal octanoate synthesized in our laboratory is presented in Table 2. Investigated metal octanoates have a $\Delta\nu$ in the region of 135 – 155 cm^{-1} that testifies to the ionic bidentate mode of coordination [8].

Thermal properties. The phase transition temperatures of the pure salts synthesized in our laboratory (cobalt, alkali metal, and thallium octanoates) were in good agreement (± 2 °C) with the literature data [14, 15]. So, cobalt(II) octanoate $(C_7H_{15}COO)_2Co$ melts at 95 °C to form a smectic mesophase, which is a birefringent liquid with feebly marked microscopic texture (Fig. 2a), and then vitrifies on cooling. The mesophase clearing temperature of the cobalt(II) octanoate has been determined at 164 °C. Lithium octanoate $C_7H_{15}COOLi$ melts into an isotropic liquid at 258 °C without mesophase formation. Sodium octanoate $C_7H_{15}COONa$ has a solid–solid transition at 123 °C and forms a smectic mesophase at 220 °C, which then forms an isotropic liquid at 332 °C. Potassium octanoate $C_7H_{15}COOK$ has a solid–solid transition at 54 °C and forms a smectic mesophase at 282 °C, which then forms a liquid at 440 °C. Thallium(I) octanoate $C_7H_{15}COOTl$ forms a smectic mesophase with fan texture, typical for a smectic A phase, (Fig. 2b) at 140 °C, which clears at 220 °C.

3.2. Phase Diagrams of Binary Systems

In Figures 3 – 6 the phase diagrams for the binary systems investigated are represented. In all systems, the existence of liquid crystalline phases has been established. These mesophases, studied by mi-

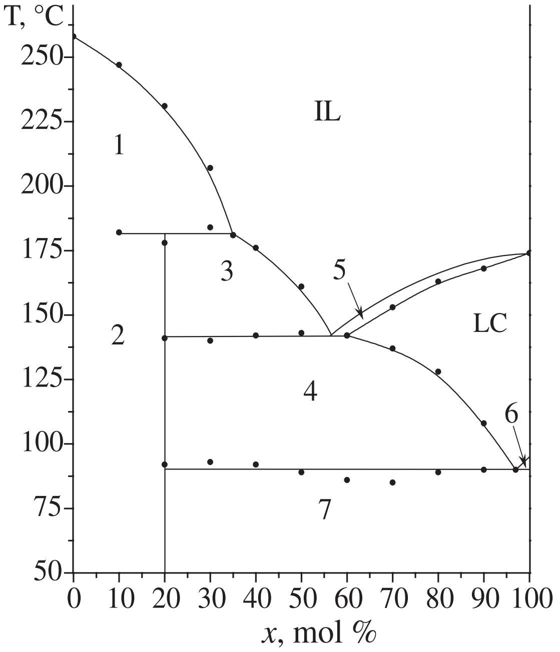

Fig. 3 (colour online). Phase diagram of the binary system $\{x\,(C_7H_{15}COO)_2Co + (100-x)\,C_7H_{15}COOLi\}$. Here and in Figures 4–6 the homogeneous regions of isotropic melt and liquid crystalline phases are marked by IL and LC, respectively. Arabic numbers stand for heterogeneous two-phase regions as follows. 1: $(IL + K_{Li})$, 2: $(K_{Li} + K_P)$, 3: $(K_P + IL)$, 4: $(LC + C_P)$, 5: $(LC + IL)$, 6: $(LC + K_{Co})$, 7: $(K_P + K_{Co})$, where K_{Li} and K_{Co} are the solid phases of lithium and cobalt(II) octanoates, and K_P is the solid phase of incongruently melting compound.

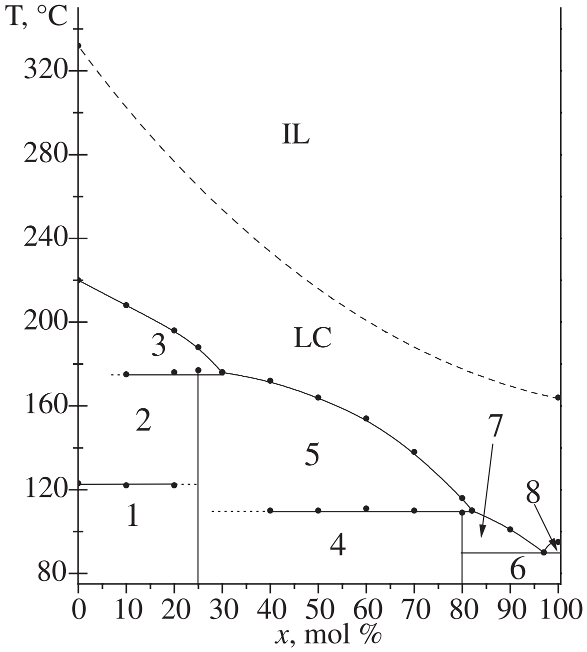

Fig. 4 (colour online). Phase diagram of the binary system $\{x\,(C_7H_{15}COO)_2Co + (100-x)\,C_7H_{15}COONa\}$. 1: $(K_{Na1} + K_{P1})$, 2: $(K_{Na2} + K_{P1})$, 3: $(K_{Na2} + LC)$, 4: $(K_{P1} + K_{P2})$, 5: $(LC + K_{P1})$, 6: $(K_{P2} + K_{Co})$, 7: $(LC + K_{P2})$, 8: $(LC + K_{Co})$, where K_{Na} and K_{Co} are the solid phases of sodium and cobalt(II) octanoates, and K_{P1} and K_{P2} are the solid phases of the incongruently melting compounds P_1 and P_2.

croscopic observation, showed to be smectic A since they formed the characteristic continuous confocal-conical or fan texture [16] as can be seen, for example, from Figure 2c, which illustrates a texture of mesophase in the binary system of cobalt(II) and thallium(I) octanoates.

In the system $\{x\,(C_7H_{15}COO)_2Co + (100-x)\,C_7H_{15}COOLi\}$, the formation of an incongruently melting compound (P) of the probable composition $(C_7H_{15}COO)_2Co \times 4C_7H_{15}COOLi$ has been established. As is seen from Figure 3, a limited liquid crystalline solution is formed in the system following the eutectic reaction between the solid phases of cobalt(II) octanoate and the incongruently melting compound P and exists over the range $60\,\text{mol}\,\% \le x \le 100\,\text{mol}\,\%$. The melting curve has an eutectic point at 90 °C, $x = 97$ mol %, and a peritectic point at 181 °C, $x = 35$ mol %. The mesophase clearing curve intersects the melting curve at 140 °C, $x = 57$ mol %. At this invariant point, the solid phase coexists with two liquids: isotropic and mesomorphic. Therefore this invariant may be called metatectic point. In the range $10\,\text{mol}\,\% < x \le 100\,\text{mol}\,\%$, supercooling of melts takes place to form glasses: either optically isotropic glasses in the range $10\,\text{mol}\,\% < x < 60\,\text{mol}\,\%$ or optically anisotropic mesomorphic glasses in the range $60\,\text{mol}\,\% < x \le 100\,\text{mol}\,\%$. The addition of nonmesogenic lithium octanoate into a mesophase of cobalt octanoate leads to a destruction of this mesophase. As is seen from Figure 3, there is a decrease in mesophase thermostability and then its full disappearance at 43 mol % $C_7H_{15}COOLi$.

The phase diagram of the binary system $\{x\,(C_7H_{15}COO)_2Co + (100-x)\,C_7H_{15}COONa\}$, presented in Figure 4, indicates the formation of two incongruently melting compounds of the probable composition $(C_7H_{15}COO)_2Co \times 3C_7H_{15}COONa$ (P_1) and $4(C_7H_{15}COO)_2Co \times C_7H_{15}COONa$ (P_2). Two

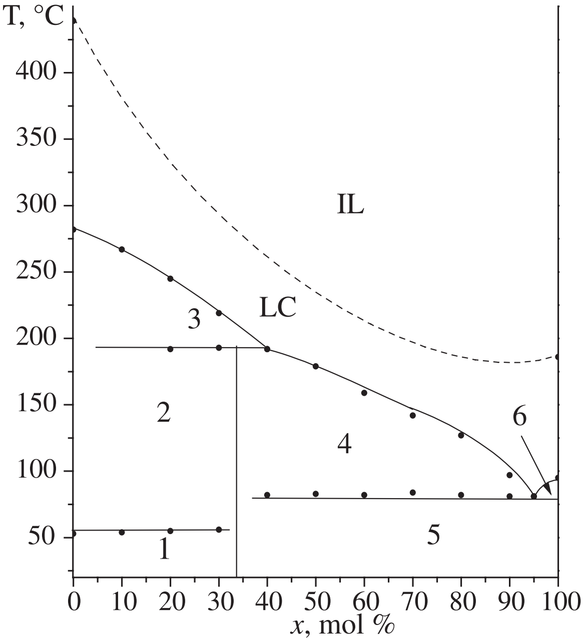

Fig. 5 (colour online). Phase diagram of the binary system $\{x\,(C_7H_{15}COO)_2Co + (100 - x)\,C_7H_{15}COOK\}$. 1: $(K_{K1} + K_P)$, 2: $(K_{K2} + K_P)$, 3: $(K_{K2} + LC)$, 4: $(LC + K_P)$, 5: $(K_P + K_{Co})$, 6: $(LC + K_{Co})$, where K_K and K_{Co} are the solid phases of potassium and cobalt(II) octanoates, and K_P is the solid phase of incongruently melting compound.

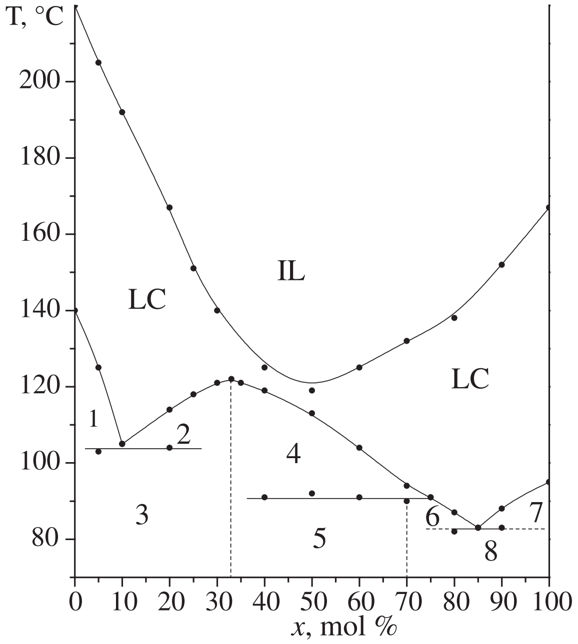

Fig. 6 (colour online). Phase diagram of the binary system $\{x\,(C_7H_{15}COO)_2Co + (100 - x)\,C_7H_{15}COOTl\}$. 1: $(LC + K_{Tl})$, 2: $(LC + K_D)$, 3: $(K_{Tl} + K_D)$, 4: $(LC + K_D)$, 5: $(K_D + K_P)$, 6: $(LC + K_P)$, 7: $(LC + K_{Co})$, 8: $(K_P + K_{Co})$, where K_{Tl} and K_{Co} are the solid phases of thallium(I) and cobalt(II) octanoates, and K_P and K_D are the solid phase of incongruently and congruently melting compounds, respectively.

branches of the melting curve intersect at the eutectic point at 90 °C, $x = 97$ mol %. There are two peritectic points at 180 °C, $x = 30$ mol %, and at 110 °C, $x = 82$ mol %. Continuous liquid crystalline solutions are formed in the system by the eutectic reaction between the solid phases of cobalt(II) octanoate and the incongruently melting compound P_2. It was experimentally impossible to construct a mesophase clearing curve in all composition ranges of the system since the mesophase texture for some binary mixtures was pseudoisotropic when observed by polarized light microscopy apparently because of a strong tendency to homeotropic orientation of liquid crystalline domains.

Supercooling and formation of optically anisotropic (mesomorphic) glasses were observed in the composition range 30 mol % $< x \le$ 100 mol %.

Figure 5 shows a phase diagram of the binary system $\{x\,(C_7H_{15}COO)_2Co + (100 - x)\,C_7H_{15}COOK\}$. Formation of an incongruently melting compound (P) of the probable composition $(C_7H_{15}COO)_2Co \times 2C_7H_{15}COOK$ has been established in the system. Continuous liquid crystalline solutions are formed by the eutectic reaction between the solid phases of cobalt(II) octanoate and the compound P. The eutectic point has been established at 80 °C, $x = 95$ mol %, and the peritectic point at 192 °C, $x = 40$ mol %. As in the case of the cobalt and sodium octanoates system, it was impossible to construct a mesophase clearing curve in all composition ranges of the system because of the pseudoisotropic texture of the mesophase of binary mixtures.

Supercooling and formation of optically anisotropic (mesomorphic) glasses were observed in the concentration range 30 mol % $< x \le$ 100 mol %.

Figure 6 shows a phase diagram of the binary system $\{x\,(C_7H_{15}COO)_2Co + (100 - x)\,C_7H_{15}COOTl\}$. Continuous liquid crystal solutions of smectic A modification are formed in the system (Fig. 2c). The melting-point curve has two eutectic points at 104 °C, $x = 10$ mol %, and at 83 °C, $x = 85$ mol %. There is a peritectic point at 91 °C, $x = 75$ mol %. The phase diagram indicates the formation of a congruently melting compound of the probable composition $(C_7H_{15}COO)_2Co \times 2C_7H_{15}COOTl$ (D) and an incongruently melting compound of the probable composition $7(C_7H_{15}COO)_2Co \times 3C_7H_{15}COOTl$ (P). The clearing temperature curve for the mesophase has a well-defined minimum at 120 °C, $x = 50$ mol %. The two-phase region of coexisting mesophase with isotropic liquid was under 2 °C in our experiments and is not shown in the diagram. Supercooling and formation of optically anisotropic (mesomorphic) glasses were observed in the concentration range $60 \text{ mol \%} < x \leq 100 \text{ mol \%}$.

The components of the binary systems studied are known to be representatives of ionic metallomesogens, liquid–crystalline ordering in which results from the anisotropic nature of electrostatic cation–anion interactions [2]. As has been found [1], pure metal alkanoates possess apparent or latent mesogenic properties when their ionic parameters satisfy the empirical relation, which was called ionic mesogenicity rule and can be expressed in terms of the following inequality: $(z_c/z_a)(L_a/r_c) > 3$, at $r_c > 0.6$ Å , where z_c and z_a are anion and cation charges, L_a is the alkanoate anion length, and r_c the metal cation radius. The metal octanoates studied satisfy this rule. So, $C_7H_{15}COOLi$ has $r_c < 0.6$ Å, namely 0.59 Å [17], and it is not mesogenic. The remaining salts possess mesogenic properties. So, for $(C_7H_{15}COO)_2Co$, where $L_a = 11.5$ Å [2], $r_c = 0.79$ Å [17], and $(z_c/z_a)(L_a/r_c) = 7.67$; for $C_7H_{15}COONa$, where $r_c = 0.99$ Å [17], $(z_c/z_a)(L_a/r_c) = 11.62$; for $C_7H_{15}COOK$, where $r_c = 1.39$ Å [17], $(z_c/z_a)(L_a/r_c) = 11.62$; and for $C_7H_{15}COOTl$, where $r_c = 1.5$ Å [17], $(z_c/z_a)(L_a/r_c) = 7.67$.

From this point of view it is clear that binary mixtures of $(C_7H_{15}COO)_2Co$ with $C_7H_{15}COONa$, $C_7H_{15}COOK$, and $C_7H_{15}COOTl$ satisfy the ionic mesogenicity rule in all composition ranges, and hence they form continuous liquid crystalline solutions. In the case of the system $\{x\,(C_7H_{15}COO)_2Co + (100-x)\ C_7H_{15}COOLi\}$ there is only a limited liquid crystalline solution based on cobalt(II) octanoate as far as an increase in the lithium cation percentage in this system causes a destruction of liquid crystalline cation–anionic ordering in accordance with the ionic mesogenicity rule.

4. Conclusions

Thus, the study of phase equilibria in cobalt octanoate based binary systems showed that replacing the bivalent cobalt cation by an univalent metal (lithium, sodium, potassium, thallium) cation results in the formation of congruently and/or incongruently melting compounds. Mesogenic sodium, potassium, and thallium(I) octanoates have unlimited solubility in cobalt(II) octanoate mesophase in accordance with the ionic mesogenicity rule, and nonmesogenic lithium octanoate is only partly soluble in it. When studying the phase behaviour of binary systems based on cobalt(II) octanoate with alkali metal and thallium(I) octanoates, formation of optically anisotropic mesomorphic glasses has been established; these glasses absorb light in the visible wavelength range [18], making it possible to use them as universal liquid crystalline matrices in the creation of novel photorefractive and nonlinear optical liquid crystalline materials.

Acknowledgements

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