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RUBIDIUM AND LITHIUM BUTANOATES BINARY PHASE DIAGRAM
Formation of a stable lyotropic liquid crystal phase and two mixed salts

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The temperature and enthalpy *vs.* composition diagrams of the binary system [$xC_3H_7CO_2Li+(1–x)C_3H_7CO_2Rb$], where x=mole fraction, were determined by differential scanning calorimetry (DSC). This binary systems displays the formation of two mixed salts with a composition 1:1 and 1:2, which melt incongruently at T_{fus}=590.5 K, with $\Delta_{fus}H_m$=11.6 kJ mol^{-1}, and congruently at T_{fus}=614.5 K, with $\Delta_{fus}H_m$=20.2 kJ mol^{-1}, respectively. The phase diagram also presents an ionic liquid-crystalline phase in a wide temperature range: 95 K.

Keywords: *binary phase diagram, eutectic and peritectic points, lithium butanoate, lyotropic liquid crystal, mixed salts, rubidium butanoate*

Introduction

Many studies of the thermodynamic behavior of organic salts have been achieved in the last 50 years [1, 2], providing important information in the characterization of different mesophases. This family of substances joins properties of both ionic salts and organic compounds and the interest of the different phases (solid, lyotropic and thermotropic mesophases, and also ionic liquid phases) of metallic *n*-alkanoates [3] (MCn hereafter, where *M* corresponds to the metallic cation and *n* to the total number of carbons of the alkyl chain) is still increasing. Ionic liquids [4–6] are known to be promising materials for their application as non-volatile solvents. IUPAC defines them as the materials melting under 100ºC to ionic liquids. Organic salt mixtures usually melt above this temperature, but about hundred degrees lower than the pure salts, though.

Such salts, composed of organic ions, can often exhibit mesomorphic behaviour. This mesogenic aspect of metal alkanoates is due to the anisotropy in the electric charge distribution in the organic anions rather than to a geometrical anisotropy [7]. These ionic liquid crystal (ILC), are much more ordered ionic solvents than the regular ionic liquids, combining the properties of both phases.

Although many pure salts are not still studied, the combination of some well-known salts can improve some properties, for example the formation of mixed salts or a lyotropic liquid crystal phase in a wide range of temperature [8–10]. Thus, some binary systems have been reported: in the case of the lithium and sodium butanoates [11], and lithium and cesium butanoates [12]. In principle, the one studied here must be similar to these, but differences will be discussed later.

Pure lithium [3, 13–15] and rubidium [3, 14, 16] alkanoates have been widely studied. It was found that no member of the lithium series is thermotropic mesogen, and the first member in the rubidium series behaving like that is the *n*-pentanoate. That it is to say, none of the pure components of the system studied here shows an ILC phase. The first aim of this paper was to find lyotropic mesomorphism [10, 17] mixing two non thermotropic salts. Many binary systems with common cations or common anions with alkali alkanoates as one of the components were reviewed and critically evaluated [10, 18]. The presence and identification of mesophases have not been done in several of the phase diagrams studied in [18], and more work on the lyotropic ionic liquid crystal phases should be developed to understand them in more extent.

A better knowledge of the association, aggregation and phase behavior in these non-aqueous systems from thermodynamic viewpoint may be valuable for describing the interactions occurring in different colloidal and surfactant systems, in particular in the aqueous ones, for which Krafft point, critical micellar concentration and other structural properties have been reported by many authors.

The aim of the present paper is to present a complete study of the phase diagram formed between the rubidium and lithium butanoates over the whole composition range (0 to 100 mol% of lithium salt), by means of DSC technique, explaining in particular the

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problems found related to the preparation and handling the pure compounds and its mixtures. A further target is to provide a good definition of the mixed salts (in both systems) and the lyotropic liquid crystal region, for this diagram.

Experimental

Materials

Lithium *n*-butanoate

A slight different method from the one described in [11, 12] was used for the synthesis of the lithium *n*-butanoate; it was obtained by reaction between lithium hydroxide ($LiOH{\cdot}H_2O$, Fluka, ≥99%), instead of lithium carbonate, and the butyric acid (Fluka, ≥99.5%), using ethanol (Merck, ≥99.8%) as solvent. The salt was recrystallized for several times in methanol (Merck, 99.8%) and precipitated with 2-propanol (Panreac, 99%). The purity of the synthesized product determined by DSC was 99.97 %.

Rubidium butanoate

For the synthesis of the rubidium butanoate, the most common method [11] was followed: it was prepared by chemical reaction between rubidium carbonate (Aldrich, 99%) and butyric acid (Fluka, ≥99.5%), but, due to the deliquescent nature of the RbC4, dry ethanol (Merck, ≥99.8%) was used to avoid ionized water. The solvent had to be eliminated by a rotavapor, and the recrystallization was carried out in *n*-butanol (Sigma, ≥99%), and then washing the RbC4 with *n*-heptane (Aldrich, 99%); finally the product was vacuum dried and maintained at 425 K, due to the high hygroscopicity of the RbC4. Rubidium salts, in general, are highly hygroscopic, or even deliquescent (e. g., RbI and RbOH, or this RbC4).

A 99.98 % of purity for the RbC4 was evaluated by DSC.

Mixture preparation

In order to cover the whole composition range, 18 mixtures (weighing about 0.3 g, each) were prepared by adding a known amount of LiC4 and an approximated one of RbC4 in Pyrex phials. The mixture was vacuum dried at 425 K, because the deliquescent behavior of the RbC4, maintained in an inert atmosphere (with dry $N_2(g)$), cooled to room temperature and weighed to calculate the exact molar fraction. For this reason, it was really difficult to get a specific mixture (e. g., the exact compositions of the two mixed salts or the eutectic).

The molar fractions were prepared and homogenized in solution of dry methanol (Merck, 99.8%), and then the solvent was removed with a rotavapor; mixture was finally high vacuum dried, again at 425 K, in order to get a homogeneous powder. The mixtures thus obtained are real physical mixtures of both components, being necessary the register a second heating in order to obtain their stable behaviour. The estimated error in the molar fraction x was at most ±0.002.

Methods

Differential scanning calorimetry

A TA Instruments DSC, Model Q10 has been used in this work. Tightly sealed aluminum volatile pans (in atmosphere of $N_{2(g)}$) were used to scan at different heating rates (usually at 5 K min^{-1}, again in dry nitrogen atmosphere). A MT5 Mettler microbalance was used to weigh the samples, of about 10 mg (with an error of ±0.01 mg), each. The calorimeter was calibrated in temperature using standard samples of In and Sn, supplied by TA (purity >99.999% and >99.9%, respectively), and of benzoic acid (purity >99.97%), supplied by the former NBS (lot 39i), and in enthalpy with the standard In and Sn samples already described.

Optical microscopy

To identify the nature of the different phases (solid, liquid crystal, or isotropic liquid), a Carl Zeiss-Jena polarizing optical microscope (model Zeiss Jenalab pol-30-G0527), equipped with a LINKAM hot stage (model THMS600), connected to a LINKAM programmable temperature-controller (model TMS94), was used.

Results and discussion

Pure components

The thermal behavior of LiC4 and RbC4 in the superambient region was reported in previous works [11, 12]. Molar heat capacities and relevant thermodynamic functions of the LiC4 determined by equilibrium adiabatic calorimetry and DSC, from 6 to 480 K, have been published [12], with a thorough description of the phase transformations and of the stepwise melting process occurring in this compound. The data obtained by DSC, on the LiC4 used in the present work, are in fair agreement with those provided previously. The experimental results obtained for the pure substances, used in the preparation of the mixtures, are listed in Table 1.

Table 1 Thermodynamic data for RbC4

	This work				Literature [10]		
Compound	Transition	T/K	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}	T/K	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
LiC4	SI–IL	591.0±0.5	21.1±0.1	35.7±0.2	591.7	20.8	35.2
	SIII–SII	–	–	–	346±2	1.0	2.9
RbC4	SII–SI	465.4±0.6	2.4±0.1	5.0±0.2	466	2.3	1.0±0.1
	SI–IL	655.6±0.4	17.8±0.2	27.1±0.3	652	15.7	24.2

- Lithium butanoate: only a fusion, reported in Table 1, was measured by DSC, in agreement (0.5% of difference) with the data given by Ferloni *et al.* [11] for the same compound.
- Rubidium butanoate: measurements began at 425 K, so the two first solid-to-solid transitions of the pure salts were not observed; the SII-to-SI transition and the fusion were measured, instead, at the little higher values of temperature and enthalpy for the melting processes than previous studies [11]. Thermodynamic data for RbC4 are given in Table 1.

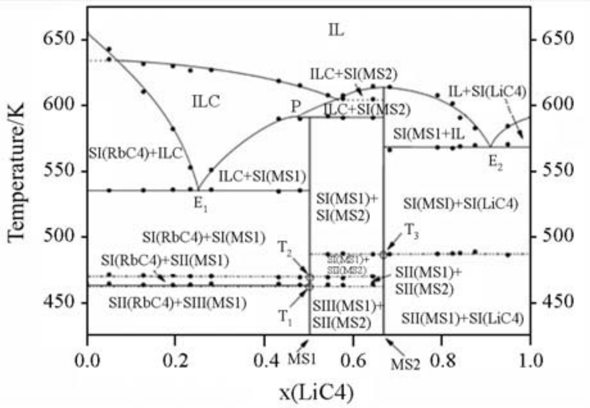


Fig. 2 T *vs.* composition plot for the LiC4+RbC4 system, showing the eutectic points (E_1 and E_2), the peritectic point (P), and the solid-to-solid transition for MS1 (X_1 and X_2) and MS2 (X_3)

Binary systems

As it was said in section 2.2, 18 mixtures (including the pure compounds, LiC4 and RbC4) were prepared to study this binary system. The heat flow output values from the calorimeter are given in 'watts per gram of mixture'. The curves were 'normalized' multiplying these data by the average molecular mass, in order to transform them into 'watts per mole of mixture'. This allows doing the areas (enthalpies) of the transitions comparable one to another, in a three dimensional representation (Fig. 1).

In Fig. 2 the complete T *vs.* x phase diagram is illustrated. In all the defined regions, except in the isotropic liquid (*IL*) and in the lyotropic ionic liquid crystal (*ILC*), two conjugated phases are present, i.e., *SI*(RbC4)+*ILC*: means ionic liquid crystal and the solid I phase of the RbC4 separation. ΔH *vs.* x phase diagram (shown in Fig. 3), related to the considered equilibria, has been developed following the Tammann's method, used commonly in any phase diagram to find exactly the characteristic points, plotting enthalpies (per mole of mixture) *vs.* composition for each process (i.e. eutectic reaction) [19, 20].

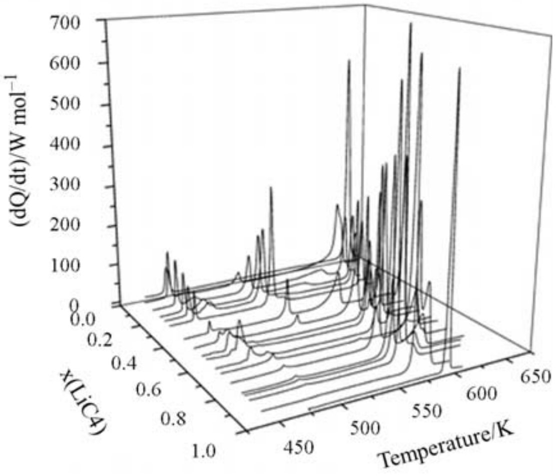
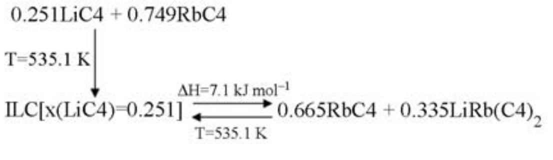


Fig. 1 3D-plot (heat flow *vs.* composition *vs.* temperature) for the LiC4+RbC4 system

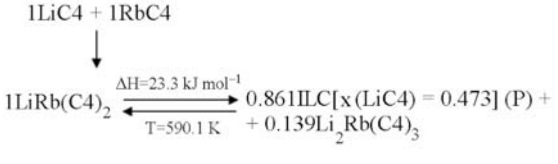
The most characteristic processes in this binary system (eutectic and peritectic reactions) are:

First eutectic reaction (E_1):



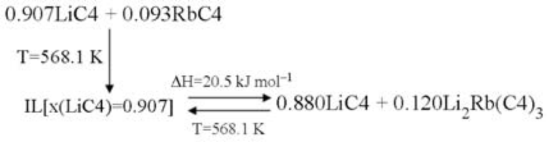
Scheme 1

Peritectic reaction (P):



Scheme 2

Second eutectic reaction (E_2):



Scheme 3

Two important features clearly are present in this phase diagram: a) the formation of two mixed salts (with a rate of 1:1 and 2:1, for LiC4:RbC4) and b) the existence of a very wide region of a lyotropic ionic liquid crystal phase (ILC in Fig. 2).

LiRb(C4)$_2$ and Li$_2$Rb(C4)$_3$ mixed salts

Two mixed salts come out in this system: LiRb(C4)$_2$ and Li$_2$Rb(C4)$_3$ (MS1 and MS2, respectively, in Fig. 2). Although it was very difficult to prepare a specific molar fraction exactly, as already mentioned in 2.2., these intermediate compounds are clearly detected when building up the Tammann diagram (*H vs. x*, Fig. 3). LiRb(C4)$_2$ presents two solid-to-solid transitions at T_1=462.3 K and T_2=470.0 K (with ΔH=0.8 and 8.0 kJ mol^{-1}, per mole of mixed salt, or 0.4 and 4.0 kJ mol^{-1} per mole of mixture, respectively). These two transitions are represented by dash-dot lines, and appear as invariants (constant temperature) in the range of its existence at both sides of T_1 and T_2 in plot 2. This first phase transition is very close to the SII-to-SI transition of RbC4 invariant, and this problem was solved with the aid of the *H vs. x* diagram. This salt melts incongruently, as it is described in the peritectic reaction, at 590.1 K with ΔH=23.3 kJ mol^{-1} (per mole of mixed salt, or 11.7 kJ mol^{-1} per mole of mixture).

Li$_2$Rb(C4)$_3$ shows only one solid-to-solid transition at T_3=486.9 K, with an enthalpy of 2.1 kJ mol^{-1} per mole of mixed salt (0.7 kJ mol^{-1} per mole of mixture) and it's also represented as a dash-dot line. This salt has a congruent melting point at 613.7 K with and enthalpy of 60.8 kJ mol^{-1} per mole of mixed salt (20.3 kJ mol^{-1} per mole of mixture).

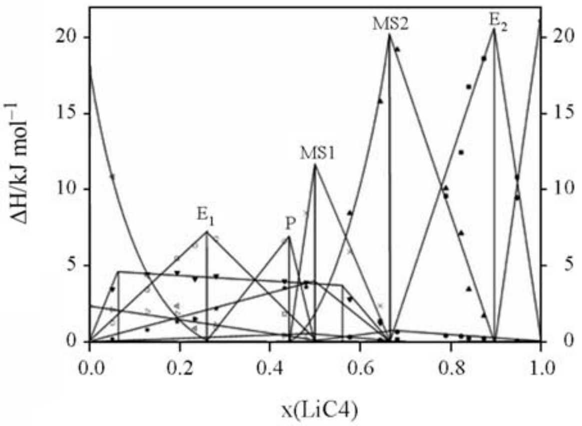


Fig. 3 ΔH (per mole of mixture) *vs.* composition plot for the LiC4+RbC4 system, for the following transitions: ◁ – solubilization of the RbC4; ▼ – clearing of the ILC phase; ▷ – SII-to-SI transition of the RbC4; □ – first eutectic reaction (E_1); ★– SII-to-SI transition for MS1; + – SIII-to-SII transition for MS1; × – solubilization of MS1; ◇ – peritectic reaction (P); ▲ – solubilization of MS2; ● – SII-to-SI transition for MS2; ■ – second eutectic reaction (E_2); ◆ – solubilization for LiC4

Lyotropic liquid crystal phase (ILC)

These non-thermotropic alkanoates (LiC4 and RbC4) form a very large lyotropic ionic liquid crystal region, which goes in its ampler intervals from *x* (LiC4)=0.07 to 0.57, and from *T*=535 to 628 K. This means that the melting point of the RbC4 diminishes about 120 K at *x* (LiC4)=0.251.

This ILC phase was observed by optical microscopy, and is shown in Fig. 4. It presents a fan shape texture, typical of a 'smectic A like' or neat phase, similar to the smectic A phase in the molecular liquid

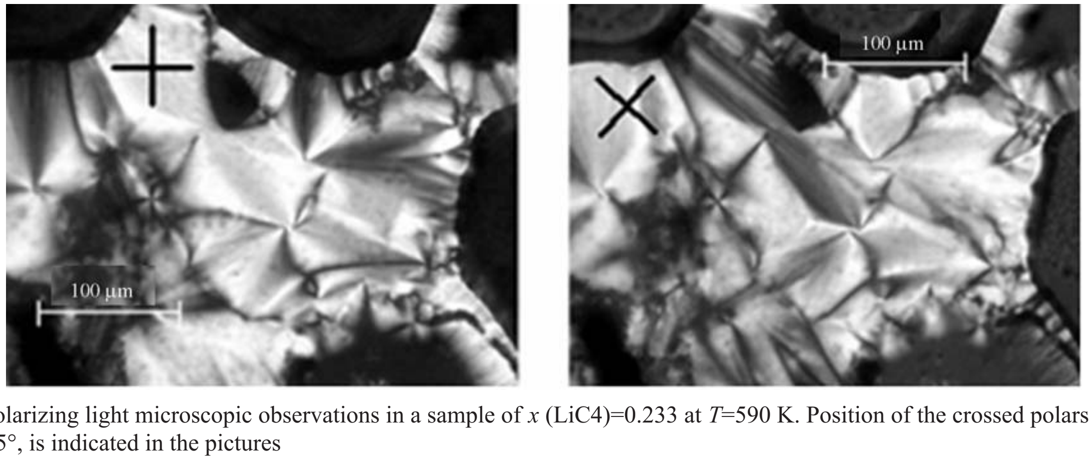


Fig. 4 Polarizing light microscopic observations in a sample of *x* (LiC4)=0.233 at *T*=590 K. Position of the crossed polars, rotated 45°, is indicated in the pictures

crystals [21]. Most of thermotropic metal alkanoates show this liquid crystal phase [1, 18].

Conclusions

The solved RbC4+LiC4 binary system permits the comparison with the NaC4+LiC4 and CsC4+LiC4 systems, reported in [8, 9].

First of all, a lyotropic liquid crystal phase can be clearly detected in all these diagrams, although the NaC4 is already thermotropic. The appearance of thermotropism in the pure salts obviously depends on the size of the cations, and on the length of the alkyl chain as well [14]. Maintaining the latter constant, it is easy to think that the appearance of lyotropism will be determined by the ratio of cation sizes. However, it seems that the correlation to establish the existence of lyotropic liquid crystal for mixtures consists in an average value of the cation size more than in its difference of size. Consistent with this idea, the wider range of composition for this phase appears just in the lithium and rubidium butanoates system.

On the other hand, there is no mixed salt for the NaC4+LiC4 system, whereas RbC4+LiC4 and CsC4+LiC4 ones present two (1:1 and 1:2) and one (1:2), respectively. It looks like the difference in the cation size would help to form an ordered 1:1 or 1:2 stoichiometry ionic crystals. The variation in the composition must depend on the difference in size of the cations, according to the logical variation of the ion volume from Cs to Na.

For both reasons, to measure the KC4+LiC4 system will be very significant, because it is probably the junction of both behaviours. Moreover, it would complete this series of phase diagrams between lithium and the rest of alkali metal butanoates.

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