

PHYSICOCHEMICAL ANALYSIS OF INORGANIC SYSTEMS

The LiCl–KCl Binary System

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Abstract—Liquidus temperatures in the LiCl–KCl system in the composition range from 0 to 100 mol % KCl have been measured for 16 samples using the methods of oscillation phase analysis and thermal analysis. The melting points of the components and the eutectic composition of the system have been refined.

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In recent years, the eutectic of the lithium chloride–potassium chloride binary system attracts more attention as a low-temperature and low-viscosity electrolyte for electric power cells and for refining metals [1, 2].

The LiCl–KCl system was studied experimentally at the beginning of the 20th century [3, 4] and later [5–9] as part of ternary and quaternary chloride systems. Fairly large differences were observed both in the melting point (from 348 [7] to 360°C [8]) and in the eutectic composition (from 40.5 [3] to 42.5 [5] mol % KCl).

EXPERIMENTAL

We carried out measurements on 16 samples in the composition range from 0 to 100 mol % KCl. Phase transformations of the system were studied on an experimental setup combining oscillation phase analysis (OPA) [10–12] and thermal analysis (TA). Samples 30–40 g in weight were prepared from starting reactants (lithium chloride monohydrate and potassium chloride of special purity grade) preliminary dried at 150–200°C for 2–3 h. In the measuring cell, we used a platinum crucible 45 mm in diameter and 50 mm in height. The melt height was ~30 mm. To prevent segregation, samples after melting were stirred via nitrogen bubbling.

The sample temperature was measured using a Pt–Pt/Rh thermocouple in a platinum case immersed into the melt to a depth of ~20 mm. DTA curves were recorded using an N-307 x, y recorder at a heating rate of 5 K/min.

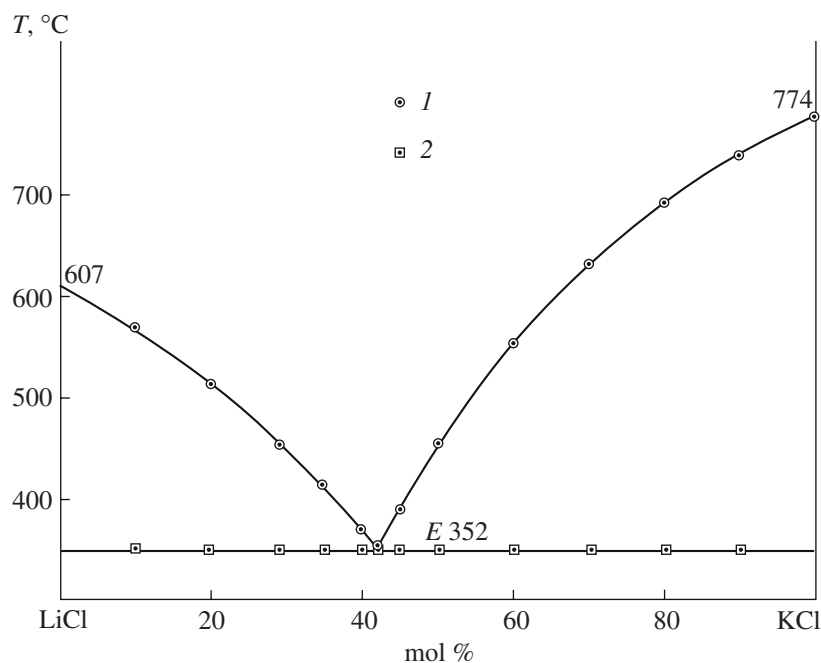
The measurement error of the liquidus temperature and melting points was $\pm 2^\circ\text{C}$ K [10]. Pt–Pt/Rh thermocouples were calibrated at the Novosibirsk Institute of Metrology.

RESULTS AND DISCUSSION

The results of measurements are presented in the table and in figure. By our data, the eutectic melts at

Temperatures of phase equilibria in the LiCl–KCl system

Composition, mol % KCl	t_L (LiCl), °C	t_E , °C	t_L (KCl), °C
0	607		
10	568	353	
20	512	352	
29	452	352	
34.9	416	352	
39.9	371	352	
41.4	357	352	
42	–	352	357
45	–	352	390
45.1	–	352	392
50	–	352	454
60	–	353	553
70	–	351	631
80	–	352	688
89.91	–	350	736
100	–	–	774



Phase diagram of the lithium chloride–potassium chloride system: (1) OPA data and (2) TA data. Regions of solid solutions near the components are not shown.

352°C and contains 41.8 mol % KCl and 58.2 mol % LiCl. The melting points of lithium chloride (607°C) and potassium chloride (774°C) coincide with data in [7, 9, 13] (606 and 774°C, respectively), but differ from the values recommended in [14] for LiCl (610°C) and KCl (770°C). We did not verify the homeomorphous transformation in lithium chloride found in [7, 13]. The liquidus lines in the figure were constructed by averaging equations $T_L(\text{LiCl}) = 607.2 - 3.4198x - 0.063255x^2$ (with the mean-square deviation from the experimental points $\sigma = 2.4^\circ\text{C}$) and $T_L(\text{KCl}) = 773.97 - 3.4562(100 - x) - 0.023368(100 - x)^2 - 0.00071877(100 - x)^3$ (with $\sigma = 1.9^\circ\text{C}$), where x is the KCl content in molar percent and temperature is expressed in degrees Celsius.

The liquidus temperature on the lithium chloride side is described well in the context of the regular solution model [15] with $\sigma = 2.5^\circ\text{C}$ with the use of the value of 19.75 kJ/mol [14] recommended for the enthalpy of melting of LiCl and fitting parameter $\omega = -16.13$ kJ/mol (the energy of mutual exchange). We failed to describe the liquidus line on the potassium chloride side even with the use of the subregular solution model, probably, because of the existence of an extended region of solid solutions.

Our experiment did not confirm the existence of the precrystallization endotherm preceding the crystallization of the pure potassium chloride melt [16]. In our opinion, the precrystallization endotherm found in [16] is associated either with the specific features of the tem-

perature control system and redistribution of thermal fluxes in the DTA setup or with considerable impurity levels in the sample. For example, our KCl sample was of high-purity grade and contained 0.2% NaCl, whereas that used in [16] was less pure (of pure grade).

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