Density of the molten system LiCl–NaCl–KCl

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The temperature dependence of density of the molten binary system LiCl–NaCl and of four figurative points of the ternary system LiCl–NaCl–KCl was determined. On the basis of knowledge of volume properties of three binary boundary systems the molar volume of ternary system was calculated. Comparison of experimental and calculated densities shows very good agreement between these two sets of data.

Экспериментально была определена температурная зависимость плотности бинарной системы LiCl–NaCl и четырех расплавов фигуративных точек тройной системы LiCl–NaCl–KCl. Исходя из объемных свойств предельных двойных систем, был рассчитан мольный объем тройной системы и был сравнен с экспериментальными значениями. Соответствие экспериментальных и рассчитанных значений плотностей очень хорошее.

Density of molten salts of the system LiCl–NaCl–KCl was measured using the Archimedean method. The experimental apparatus was described previously [1, 2]. The signal from automatic balance, on which a platinum ball immersed in the melt is suspended, was punched together with information on temperature onto the paper tape and it was consequently treated on off-line Programmable Calculator HP 9821A. Temperature was measured by a PtRh10–Pt thermocouple. Chemicals used were of anal. grade. Sodium chloride and potassium chloride were dried at temperature 600°C, lithium chloride was purified by double crystallization: it crystallized from aqueous solution at 120°C as almost anhydrous salt and the rest of moisture was removed in vacuum drier at 130°C.

The experimental data on density are summarized in Table 1. The coefficients of temperature dependence of density were calculated from experimental data using the least squares method.

In [3] we have shown that density of ternary melts can be calculated with good approximation on the basis of knowledge of volume properties of boundary binary systems. The calculation is based on the assumption that the excess molar volume in ternary system can be calculated as a sum of contributions of boundary binary systems

Table 1

Density of the molten system LiCl–NaCl–KCl
$\varrho/(\mathrm{g\ cm^{-3}}) = a + bt/°C$

mole % LiCl	mole % NaCl	mole % KCl	a	$-b \cdot 10^4$	Temperature interval °C	Standard deviation
100	0	0	1.67509	3.17031	620—760	9.73831×10^{-4}
0	100	0	1.95315	5.01899	820—940	5.92442×10^{-5}
0	0	100	1.93316	5.37806	790—950	5.16267×10^{-5}
25	75	0	1.89740	4.67213	770—910	1.67393×10^{-4}
50	50	0	1.87309	4.76675	620—780	1.21277×10^{-4}
75	25	0	1.81487	4.50271	560—690	2.59112×10^{-4}
16.66	16.66	66.66	1.92438	5.32368	755—895	9.50460×10^{-5}
16.66	66.66	16.66	1.90862	4.87144	815—900	1.17457×10^{-4}
33.33	33.33	33.33	1.89617	5.04757	720—850	1.11627×10^{-4}
66.66	16.66	16.66	1.79647	4.27233	800—920	1.01688×10^{-3}

$$V^E = x_1x_2(A_{12} + B_{12}x_2) + x_2x_3(A_{23} + B_{23}x_3) + x_3x_1(A_{31} + B_{31}x_1) \qquad (1)$$

where V^E is the calculated excess molar volume of the ternary system, x_1, x_2, and x_3 are the mole fractions of components, A, B are the empirical constants determined from experimental data obtained for binary systems. These constants are functions of temperature and pressure.

From eqn (*1*) it follows that if one of the mole fractions equals zero we obtain the relation which describes the dependence of V^E on composition in a binary system

$$V^E = x_ix_j(A_{ij} + B_{ij}x_j) \qquad (2)$$

x_i, x_j are the mole fractions of the first and of the second component in the corresponding binary system.

The values of empirical constants describing the deviation of molar volume from additivity in the binary systems LiCl–NaCl, NaCl–KCl, and KCl–LiCl are for temperature 800°C summarized in Table 2. From the low values of constants it follows that all the binary systems behave almost ideally as far as the volume properties are concerned.

Table 2

Coefficients of the empirical relation (*2*) for the description of concentration dependence of V^E/cm^3 mol^{-1}

System	*A*	*B*	Ref.
LiCl–NaCl	0.830654	−1.03721	This paper, [4]*
NaCl–KCl	0.244381	0.874922	[5]
KCl–LiCl	0.701721	−0.280335	[5]

* In [4] there are given density values for the molten mixture 50 mole % LiCl + 50 mole % NaCl. The data are in very good agreement with the results presented here.

On the basis of eqn (*1*) excess molar volume of the ternary system can be calculated. Molar volume is given as the sum of ideal molar volume, which is defined as $x_1V_1^0 + x_2V_2^0 + x_3V_3^0$ (V^0 being the molar volume of pure components), and the excess molar volume. The calculated values of molar volume and of density are compared with experimental data in Table 3. It follows that in the most unfavourable case the difference does not exceed the reported limit of uncertainty of density measurement, *i.e.* 0.5% [5, 6].

Except the angle in the vicinity of LiCl the agreement between experimental and calculated values is in the limit of experimental error, *i.e.* 0.2%. The extraordinary good agreement in the region of NaCl and KCl can be explained by two reasons:

— both melts KCl and NaCl are often used for calibration of the Archimedean method for density measurements,
— density of these melts was carefully studied in the course of Standard Program [7] and, therefore, precise experimental data could be used.

Table 3

Comparison of experimental and calculated values of molar volumes and densities at four figurative points of the ternary mixture LiCl–NaCl–KCl; $t = 800°C$

LiCl mole %	NaCl mole %	V_{exp}	V_{calc}	ϱ_{exp}	ϱ_{calc}
16.66	16.66	44.385	44.503	1.498	1.496
16.66	16.66	38.482	38.481	1.519	1.519
33.33	33.33	39.175	39.211	1.492	1.491
66.66	16.66	34.651	34.510	1.455	1.461

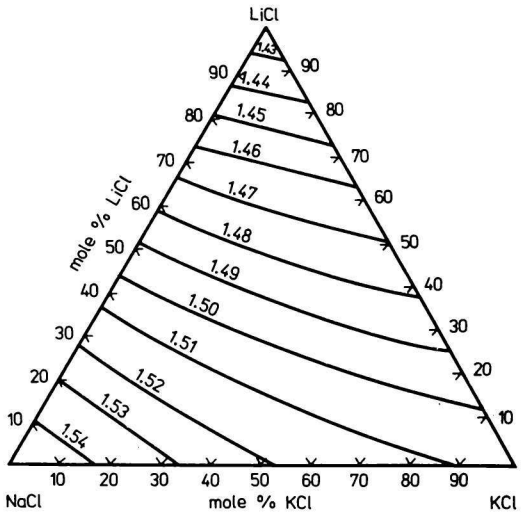

Fig. 1. Isodensity curves in the system LiCl–NaCl–KCl at 800°C.

The calculated dependence of density on composition in the ternary system LiCl–NaCl–KCl at 800°C is drawn in Fig. 1. However, on the basis of data presented in this paper, it is possible to obtain the density values within the studied temperature interval, which can supply chemical engineering data needed for the choice of suitable medium for electrochemical reaction and accumulation of energy.

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