Density of melts of the systems NaCl—KCl—$SrCl_2$ and NaF—NaCl—$SrCl_2$

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Temperature dependence of density of two ternary molten systems NaCl—KCl—$SrCl_2$ and NaF—NaCl—$SrCl_2$ was investigated. On the basis of knowledge of density of boundary binary systems density of the ternary system was calculated. The agreement between experimental and calculated set of data is very good.

Была измерена температурная зависимость плотности двух трехкомпонентных расплавов NaCl—KCl—$SrCl_2$ и NaF—CaCl—$SrCl_2$. На основании плотности граничных бинарных систем была рассчитана плотность тройных систем. Совпадение экспериментальных и расчетных значений очень хорошее.

Melts containing strontium chloride can be used for modification of silumin or as electrolytes for preparation of master alloy of strontium with aluminium [1—7]. Density of these melts ranges in broad interval of values from 1.455 g cm^{-3} (density of KCl at 900°C) to 2.696 g cm^{-3} (density of $SrCl_2$ at 900°C). Therefore it follows that density of the melts of ternary mixtures can be higher or lower in comparison with density of aluminium (2.31 g cm^{-3} at 900°C). If the densities of metal and melt do not differ very much metal flows in the melt, which is advantageous for kinetics of the modification process of silumin based on the exchange chemical reaction between silumin and melt. On the other hand, if we wish to prepare an alloy of aluminium with strontium by electrolysis then it is preferable to work with molten mixtures having density different from that of metal. Therefore, it is desirable to have metal either on the bottom of the electrolytic cell or on the level of the electrolyte, because only these conditions assure high current efficiency [8, 9].

Experimental determination of density of ternary systems of molten salts is a time-consuming procedure (the same being true about all other physicochemical properties) and, therefore, it is not surprising that complete data on physicochemical properties of molten mixtures containing more than two components are rather scarce. In order to diminish the number of necessary experiments, we used for planning of experimental work and for treatment of experimental data the mathematical procedure which had been proposed and tested in [10].

Results and discussion

The temperature dependence of density of some molten mixtures of the systems NaCl—KCl—$SrCl_2$ and NaF—NaCl—$SrCl_2$ was determined by the Archimedean method. The experimental apparatus is described in detail in papers [11, 12]. Principle of the measurements consists in automated outweighing of platinum ball immersed in melt. The signal of balance together with signal of thermocouple are recorded on paper tape and then treated using a programmable calculator HP 9821A. Temperature was measured using a PtRh10—Pt thermocouple. Chemicals used (NaCl, KCl, NaF, $SrCl_2$) were of anal. grade and they were dried before using, which is especially important in the case of $SrCl_2$. The literature data on the temperature of primary crystallization of the system NaF—NaCl—$SrCl_2$ were not known with sufficient precision and therefore it was necessary to determine also this parameter for the chosen mixtures. The method of thermal analysis was used.

The experimental results on density of the systems NaCl—KCl—$SrCl_2$ and NaF—NaCl—$SrCl_2$ are summarized in Tables 1 and 2. The coefficients of temperature dependence of density were determined from experimental data using a least-squares method. The uncertainty of the used Archimedean method is estimated to be 0.5%.

In paper [10] it has been shown that density of melts of a ternary system 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 excess molar volume of ternary system can be expressed as a sum of contributions of boundary binary systems

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

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

System NaCl—KCl—$SrCl_2$

Data on the density of melts of binary systems were taken from literature [13—15]. The constants describing molar volume of melts of these binary systems are summarized in Table 3. It follows that concerning volume properties the systems are almost ideal and therefore it can be expected that the deviation from ideality will be small also in the corresponding ternary system. The comparison of experimental data on molar volume with the calculated ones confirmed this assumption. The value of V^E does not exceed the uncertainty of the measurement.

Table 1

Density of melts of the system NaCl—KCl—$SrCl_2$
$\varrho/(g\ cm^{-3}) = a + bt/°C$

mole % NaCl	mole % KCl	mole % $SrCl_2$	a	$-b \cdot 10^4$	Temperature interval, °C	Standard deviation, $\sigma \cdot 10^4$
16.66	16.66	66.66	2.87235	5.70442	690—790	1.03294
16.66	66.66	16.66	2.20462	5.52282	640—800	1.33711
33.33	33.33	33.33	2.45874	5.62483	600—800	1.16477
66.66	16.66	16.66	2,22133	5.33314	730—800	1.00514

Table 2

Density of melts of the system NaF—NaCl—$SrCl_2$
$\varrho/(g\ cm^{-3}) = a + bt/°C$

mole % NaCl	mole % $SrCl_2$	mole % NaF	tpc/°C	a	$-b \cdot 10^4$	Temperature interval, °C	Standard deviation, $\sigma \cdot 10^4$
66	—	34	676.5	1.95346	3.77277	700—850	1.01440
—	70	30	790.0	3.03173	5.36641	800—990	1.20713
40	30	30	762.0	2.53157	5.21524	775—910	1.27840
80	10	10	751.0	2.55342	4.98032	760—900	1.83364

tpc — temperature of primary crystallization.

Table 3

Values of constants A, B ($cm^3\ mol^{-1}$) used for the calculation of excess molar volumes in the systems NaCl—KCl—$SrCl_2$ and NaF—NaCl—$SrCl_2$

System	700°C		800°C		Ref.
	A	*B*	*A*	*B*	
NaCl—KCl	0.23045	0.86108	—	—	[13]
KCl—$SrCl_2$	9.58766	− 15.46380	—	—	[15]
NaCl—$SrCl_2$	2.53286	− 1.94327	2.14578	− 1.52455	[14]
NaF—NaCl	—	—	0.83075	—	[17]*
$SrCl_2$—NaF	—	—	4.55672	—	*

* Calculated from the data given in Table 2.

That is why density of the ternary system was calculated on the basis of assumption of ideal behaviour of this system. The calculated density of ternary system at 700°C is plotted in Fig. 1. The region of existence of a liquid phase at 700°C is marked out in agreement with the phase diagram [16].

Comparison of the experimental and calculated values of density and molar volumes of the melt of given system at 700°C is presented in Table 4. It should be

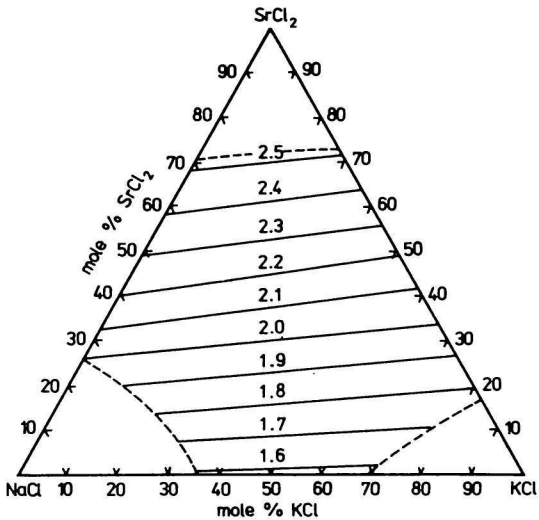

Fig. 1. Density of melts (ϱ/g cm^{-3}) of the ternary system NaCl—KCl—$SrCl_2$ calculated at temperature 700°C.

Dashed lines mark out the regions of primary crystallization of corresponding components.

Table 4

Comparison of the experimental and calculated values of densities and molar volumes of the ternary system NaCl—KCl—$SrCl_2$ at 700°C

mole % NaCl	mole % KCl	V_{exp} $cm^3\ mol^{-1}$	V_{calc} $cm^3\ mol^{-1}$	ϱ_{exp} $g\ cm^{-3}$	ϱ_{calc} $g\ cm^{-3}$	$\frac{V_{exp} - V_{calc}}{V_{exp}} 100$
16.66	16.66	51.70	51.88	2.473	2.464	− 0.35
16.66	66.66	47.23	47.21	1.818	1.819	0.04
33.33	33.33	47.08	46.89	2.065	2.073	0.40
66.66	16.66	(42.12)	41.58	(1.848)	1.872	1.28

Data in brackets were obtained by extrapolation of experimental values to temperature 700°C.

Table 5

Comparison of the experimental and calculated values of densities and molar volumes of the ternary system NaF—NaCl—$SrCl_2$ at 800°C

mole % NaF	Mole % NaCl	V_{exp} $cm^3\ mol^{-1}$	V_{calc} $cm^3\ mol^{-1}$	ϱ_{exp} $g\ cm^{-3}$	ϱ_{calc} $g\ cm^{-3}$	$\frac{V_{exp} - V_{calc}}{V_{exp}} 100$
30	40	39.51	39.23	2.114	2.129	0.71
10	80	38.06	38.28	1.755	1.745	− 0.58

pointed out that the experimental data ϱ_{exp} for temperature 700°C were calculated from the temperature dependence of density as it is given in Table 1. It follows that the difference between the experimental and calculated values does not exceed 1%. It can be shown that similar counclusion can be drawn for the whole studied temperature range.

System NaF—NaCl—$SrCl_2$

The molar volumes and empirical constants A, B for this system were determined on the basis of literature data [14, 17] which were complemented by our measurements (Table 2). The empirical constants describing deviation of volume of the system from ideality are given in Table 3. Because the region of existence of a liquid phase at 800°C is relatively narrow the graphical dependence of density on composition of the system is not presented. The corresponding data on density can be obtained on the basis of constants presented in this paper.

It can be stated that the volume behaviour of these melts is not also too far from ideality. In this case, however, the application of proposed mathematical formalism contributes substantially to the improvement of agreement between experimental and calculated data. Using this procedure, the difference between experimental and calculated values does not exceed 1% (Table 5).

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