Physicochemical properties of the molten system Na_3AlF_6—K_3AlF_6—Al_2O_3 II. Density

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Dedicated to Associate Professor K. Matiašovský, DrSc., in honour of his 60th birthday

Temperature dependence of density of the Na_3AlF_6—K_3AlF_6—Al_2O_3 melts was investigated by the Archimedean method. On the basis of the knowledge of density of boundary systems, density of the ternary system was calculated. The agreement between experimental and calculated set of data is very good. Partial molar volumes of infinitely diluted alumina in molten Na_3AlF_6 and K_3AlF_6 are 68.49 $cm^3\ mol^{-1}$ and 54.77 $cm^3\ mol^{-1}$, respectively, at the temperature of 1000 °C.

No data on the density of the systems K_3AlF_6—Al_2O_3 and Na_3AlF_6—K_3AlF_6—Al_2O_3 are available in literature. Only density of the system Na_3AlF_6—Al_2O_3 has been studied extensively [1—3]. Data on the density of molten K_3AlF_6 [4, 5] and density of the molten binary system Na_3AlF_6—K_3AlF_6 [5, 6] are available. However, there are remarkable differences between different authors. According to paper [4] temperature dependence of density of molten K_3AlF_6 can be described by the relationship

$$\varrho/(\mathrm{g\ cm^{-3}}) = 2.770 - 7.398 \times 10^{-4}\ T/\mathrm{K} \qquad (1)$$

It follows that at 1000 °C $\varrho(K_3AlF_6, l) = 1.828$ g cm^{-3}. *Fernandez et al.* [5] have reported the value of 1.891 g cm^{-3}. Thus the difference exceeds 3 %. This can be explained by experimental difficulties encountered in the investigation of the systems containing K_3AlF_6, *viz.* high partial evaporation.

Experimental

In this work density was measured by the "Archimedean method" The apparatus is described in detail in [7]. Platinum ball of diameter 20 mm was used and its mass in the

melt was recorded by authomatic balance as a function of the temperature. Temperature was measured by Pt—Pt10Rh thermocouple. Samples were prepared in the same way and from the same chemicals as it has been described in [8].

The experimentally determined dependences of the density of the investigated melts on the temperature were described by the linear equation

$$\varrho = a - b\theta \tag{2}$$

The values of the constants a and b were calculated by the least-squares method and are given in Table 1.

Table 1

Coefficients a and b in the equation $\varrho = a + b\theta$ and the standard deviations of the experimental densities σ of the Na_3AlF_6—K_3AlF_6—Al_2O_3 melts

$x(Na_3AlF_6)$	$x(K_3AlF_6)$	$x(Al_2O_3)$	a / g cm^{-3}	$-b \cdot 10^4$ / g cm^{-3} °C	$\sigma \cdot 10^4$ / g cm^{-3}
1	0	0	3.097	9.820	1.4
0.8	0.2	0	3.007	9.580	2.3
0.6	0.4	0	2.940	9.460	2.0
0.4	0.6	0	2.933	9.800	1.8
0.2	0.8	0	2.835	9.135	2.5
0	1	0	2.768	8.778	2.1
0.97	0	0.03	3.061	9.602	2.3
0.94	0	0.06	3.031	9.400	2.5
0.88	0	0.12	2.934	8.603	2.1
0.82	0	0.18	2.879	8.203	1.8
0.76	0	0.24	2.808	7.600	3.0
0	0.95	0.05	2.679	8.002	2.5
0	0.88	0.12	2.633	7.600	2.4
0	0.78	0.22	2.614	7.403	2.8
0	0.61	0.39	2.503	6.205	2.5
0.20	0.60	0.20	2.634	7.200	2.2
0.40	0.40	0.20	2.727	7.601	1.8
0.60	0.20	0.20	2.639	6.200	1.9

Results and discussion

The system Na_3AlF_6—K_3AlF_6

Experimental density data on the molten system Na_3AlF_6—K_3AlF_6 at 1000 °C and 1050 °C are plotted in Fig. 1. They are in good agreement with literature [5]. Molar volume of the melt of this system behaves almost ideally.

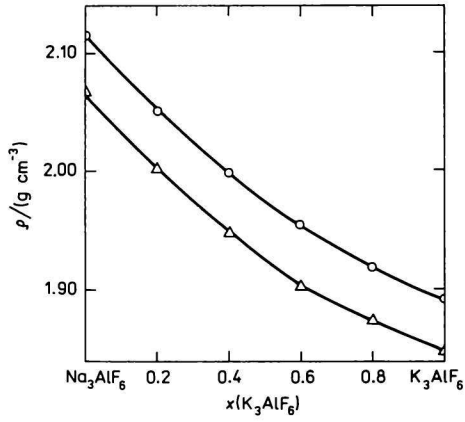

Fig. 1. Density of the molten binary system Na_3AlF_6—K_3AlF_6.
○ at 1000 °C; △ at 1050 °C.

Deviation of molar volume of the melts of this binary system from additivity does not exceed 0.52 %.

The system M_3AlF_6—Al_2O_3

Density of the molten binary system K_3AlF_6—Al_2O_3 at temperatures of 1000 °C and 1050 °C is plotted in Fig. 2. It is evident that up to about 15 mole % of alumina the density of molten mixture K_3AlF_6—Al_2O_3 decreases. At higher content of alumina it starts to increase. Thus it is remarkably different from behaviour of the system Na_3AlF_6—Al_2O_3. The second significant feature is that the dependences of density on the content of alumina in the system K_3AlF_6—Al_2O_3 at different temperatures are different from the similar plot in the system Na_3AlF_6—Al_2O_3. This indicates a different type of oxofluoride complexes in these systems.

The molar volumes of the molten systems Na_3AlF_6—Al_2O_3 and K_3AlF_6—Al_2O_3 can be described by eqns (*3*—*5*). It follows that the dependence of molar volume of the system K_3AlF_6—Al_2O_3 on the content of alumina is linear. The least-squares method gives ($x(Al_2O_3) < 0.4$)

$$V/(\mathrm{cm^3\,mol^{-1}}) = 54.77 + 82.57\,x(K_3AlF_6) \qquad \sigma = 0.43 \qquad (3)$$

In the system Na_3AlF_6—Al_2O_3 ($x(Al_2O_3) < 0.25$) the polynomial of the second order has to be used for the description of the dependence of molar volume on composition

$$V/(\mathrm{cm^3\,mol^{-1}}) = 99.31 - 32.12\,x(Al_2O_3) - 30.65\,x^2(Al_2O_3) \quad \sigma = 0.041 \quad (4)$$

Similar fit with the experimental data can be obtained using the polynomial of the third order omitting the linear term

$$V/(\mathrm{cm^3\ mol^{-1}}) = 63.62 + 76.25\,x^2(\mathrm{Na_3AlF_6}) - 40.56\,x^3(\mathrm{Na_3AlF_6})$$

$$\sigma = 0.031 \qquad (5)$$

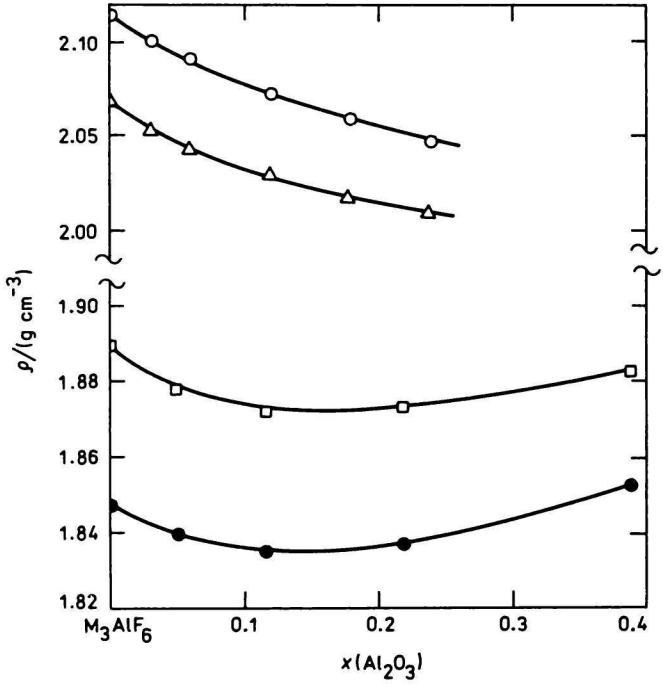

Fig. 2. Density of the molten binary systems M_3AlF_6—Al_2O_3.
○ Na_3AlF_6—Al_2O_3 at 1000 °C; △ Na_3AlF_6—Al_2O_3 at 1050 °C; □ K_3AlF_6—Al_2O_3 at 1000 °C;
● K_3AlF_6—Al_2O_3 at 1050 °C.

Partial molar volumes of alumina in molten mixture can be calculated according to the equation

$$V(\mathrm{Al_2O_3}) = V + x(\mathrm{Na_3AlF_6})\left[\frac{\partial V}{\partial x(\mathrm{Al_2O_3})}\right]_{T,p} \qquad (6)$$

It follows that in the system K_3AlF_6—Al_2O_3 at 1000 °C

$$V(\mathrm{Al_2O_3}) = 54.77\ \mathrm{cm^3\ mol^{-1}}$$

In the system Na_3AlF_6—Al_2O_3

$$V(Al_2O_3) = 36.53 + 30.65\,x^2(Na_3AlF_6)$$

or

$$V(Al_2O_3) = 63.62 - 76.25\,x^2(Na_3AlF_6) + 81.12\,x^3(Na_3AlF_6)$$

It follows that in the case of the system Na_3AlF_6—Al_2O_3 both treatments of data give very close values of the partial molar volume of alumina infinitely diluted solution. ($V(Al_2O_3) = 67.18$ cm^3 mol^{-1} or 68.49 cm^3 mol^{-1}.) This is significantly higher value than that corresponding to the partial molar volume of alumina in molten K_3AlF_6. This confirms the assumption [8] that oxofluoride complexes formed at dissolution of alumina in the melts of Na_3AlF_6 and K_3AlF_6, respectively, are of different composition.

The ternary system Na_3AlF_6—K_3AlF_6—Al_2O_3

Measurement of physicochemical properties of multicomponent systems is a time-consuming procedure. It has been shown [9, 10] that the number of necessary experimental measurements of density of the molten system can be remarkably lowered if a model for calculation of this parameter is used. For the calculation only the data on density of the binary systems are required. If the model successfully describes volume properties of the system only limited number of the experimental data is necessary for evaluation of fit of calculation and experiment. The procedure of calculation has been described in [9]. It is based on definition of the excess molar volume

$$V^E = V - \sum_i x_i V_i^\circ \tag{7}$$

where V is the molar volume of system, x_i are the mole fractions of components and V_i° are the molar volumes of pure substances. It is assumed that at constant temperature the excess molar volume can be described with sufficient precision by the relationship

$$V^E = x_i x_j (A_{ij} + x_j B_{ij}) \tag{8}$$

Thus for the ternary molten mixture it follows that

$$V_{123} = x_1 V_1^\circ + x_2 V_2^\circ + x_3 V_3^\circ + x_1 x_2 (A_{12} + B_{12} x_2) + \\ + x_2 x_3 (A_{23} + B_{23} x_3) + x_3 x_1 (A_{31} + B_{31} x_1) \tag{9}$$

A_{ij}, B_{ij} are the adjustable parameters of the model which have to be obtained from the experimental data on molar volume of binary mixtures. It is assumed

that no ternary terms are required for description of the dependence of molar volume on composition of the ternary system.

It is obvious that the only problem with application of this model to the system Na_3AlF_6—K_3AlF_6—Al_2O_3 is the determination of the molar volume of alumina. From the physical point of view the problem is in that alumina actually does not exist in the melt. It forms a wide spectrum of oxofluoride complexes [1, 11] in cryolite-based melts. The used model is, however, so flexible that we can use for calculation a hypothetical molar volume of alumina. By extrapolation of experimental data (molar volumes or partial molar volumes) we got at 1000 °C that $V°(Al_2O_3) \approx 60.0$ cm^3 mol^{-1} [9]. Using this value of molar volume of alumina the empirical constants A_{ij}, B_{ij} were calculated using the least-squares method. The values of these constants are summarized in Table 2.

Table 2

Values of the constants A, B used for the calculation of excess molar volumes in the system Na_3AlF_6—K_3AlF_6—Al_2O_3 at 1000 °C

System	A	B
	cm^3 mol^{-1}	cm^3 mol^{-1}
Na_3AlF_6—K_3AlF_6	2.4808	0.2816
K_3AlF_6—Al_2O_3	8.8683	−44.8436
Al_2O_3—Na_3AlF_6	−34.8830	45.3004

Comparison of experimentally measured density of melts of the system Na_3AlF_6—K_3AlF_6—Al_2O_3 with calculations (Table 3) proved that the deviation does not exceed experimental error in determination of density of this system. This allows us to assume that the model gives reasonable results in the whole studied composition range. The calculated density of the molten ternary system Na_3AlF_6—K_3AlF_6—Al_2O_3 at 1000 °C is presented in Fig. 3. (The region near pure Na_3AlF_6 corresponds to an undercooled melt.)

Table 3

Comparison of the experimental and calculated values of densities of the ternary system Na_3AlF_6—K_3AlF_6—Al_2O_3 at 1000 °C

$x(Na_3AlF_6)$	$x(K_3AlF_6)$	$x(Al_2O_3)$	ϱ_{exp}	ϱ_{calc}
			g cm^{-3}	g cm^{-3}
0.60	0.20	0.20	2.019	2.015
0.40	0.40	0.20	1.965	1.970
0.20	0.60	0.20	1.914	1.922

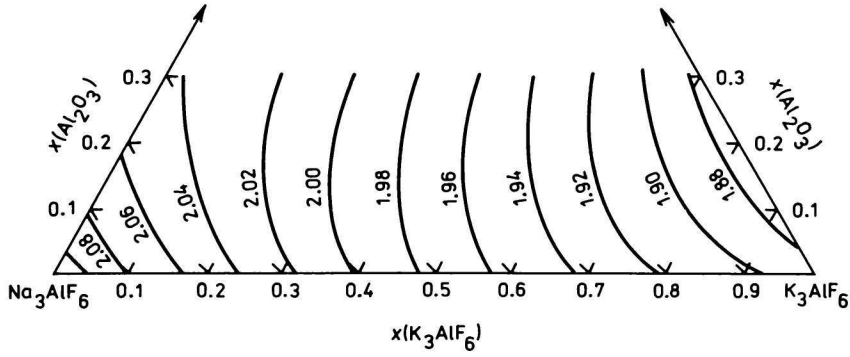

Fig. 3. Density of the molten ternary system Na_3AlF_6—K_3AlF_6—Al_2O_3, calculated at the temperature 1000 °C.

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