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Phase Equilibria, Volume Properties, Surface Tension, and Viscosity of the $(\mathrm{FLiNaK})_{\mathrm{eut}} + K_2NbF_7$ Melts

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Physicochemical properties of the system $(\mathrm{FLiNaK})_{\mathrm{eut}}$ (1) + K_2NbF_7 (2) were investigated. Phase equilibria were studied by a thermal analysis method. Density of the investigated system was measured by the Archimedean method. On the basis of these data, molar volumes were calculated for selected temperatures, and the partial molar volume of K_2NbF_7 in $(\mathrm{FLiNaK})_{\mathrm{eut}}$ was evaluated adopting the value $\bar{V}_2/\mathrm{cm}^3\cdot\mathrm{mol}^{-1} = (121.1 \pm 0.4)$ at 1073 K, indicating volume contraction. Surface tension was measured by the maximal bubble pressure method, and viscosity was measured using the computerized torsion pendulum method.

Introduction

Molten fluoride systems of niobium have been extensively analyzed to obtain data on basic physicochemical properties comprising phase diagrams, density, surface tension, or viscosity. The most complete set of data on the mentioned properties is available for the systems MF + K_2NbF_7 (MF = LiF + NaF,[1−6] LiF + KF,[7−11] NaF + KF[12−15]). From this set of data, some comparison can be done on the influence of different cations on the studied properties. Moreover, all of these data can be used in practical applications during electrolysis of molten mixtures.[16]

Systems that consist of fluorides of alkaline metals, fluoroniobates, with the addition of its oxide have also been investigated[17−22] with the purpose of incorporating additional components that would influence the electroactivity of the molten mixture.

Extensive corrosion activity at high temperature represents relatively important disadvantages in the use of these systems. The lowering of the working temperature can be achieved by substitution of a binary fluoride system with a eutectic ternary system $(\mathrm{LiF} + \mathrm{NaF} + \mathrm{KF})_{\mathrm{eut}}$ (1) = $\mathrm{FLINAK}_{\mathrm{eut}}$. An investigation of the above system with respect to practical applications was done previously.[23,24]

The objective of this work was to extend the data set of physicochemical properties also for the most acceptable system $(\mathrm{FLiNaK})_{\mathrm{eut}}$ (1) + K_2NbF_7 (2) from an industrial point of view.

Experimental Section

For the preparation of mixtures, the following chemicals were used: LiF (Ubichem, p.a.), NaF (Merck, 99 %), KF (Fluka, 99.5 %), and K_2NbF_7 (prepared in the Institute of Chemistry KSC RAS, Apatity, Russia, min. 99.5 %). LiF and NaF were dried at 773 K for 2 h, and KF and K_2NbF_7 were dried under vacuum at 403 K for 24 h. Handling of all salts was done in a glovebox under dry nitrogen atmosphere (Messer 99.99 %).

The phase equilibrium of the investigated system was determined by means of a thermal analysis (TA) method. Detailed descriptions of the experimental device can be found elsewhere.[2,19] Temperatures of particular thermal effects for certain compositions are summarized in Table 1.

Table 1. Experimental Characteristic TA Temperatures in the Molten $(\mathrm{FLiNaK})_{\mathrm{eut}}$ (1) + K_2NbF_7 (2) System

x_1	T_1/K	T_2/K	T_{pk}/K
1.0			725
0.975	723		729
0.925	724		769
0.85	723		845
0.75	719		914
0.7	721		916
0.65		902	920
0.6			900
0.5		908	933
0.4		896	947
0.3		900	954
0.2		901	970
0.1		908	982
0.0			994

The density of the studied melts was measured using the Archimedean method. Both arrangement of the experimental device and measuring procedure have been described in detail elsewhere.[25] The temperature dependence of the density of particular mixtures was expressed in the form of the linear equation

$$\rho = a - bT \qquad (1)$$

where $\rho/\mathrm{g}\cdot\mathrm{cm}^{-3}$ is density and T/K is the temperature. For each measurement, one heating and two cooling curves were recorded. For each curve, coefficients $a/\mathrm{g}\cdot\mathrm{cm}^{-3}$ and $b/\mathrm{g}\cdot\mathrm{cm}^{-3}\cdot\mathrm{K}^{-1}$ were obtained from the linear regression. The values of the constants a and b together with the standard deviations of approximations ($\mathrm{sd}/\mathrm{g}\cdot\mathrm{cm}^{-3}$) obtained by the linear regression analysis of the experimentally obtained data are summarized in Table 2.

The surface tension of the $(\mathrm{FLiNaK})_{\mathrm{eut}}$ (1) + K_2NbF_7 (2) melts was determined using the maximum bubble pressure method. A description of the experimental device with measuring procedure can be found in another published work.[27] The temperature dependence of the surface tension of particular mixtures was expressed by the linear equation

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$$\gamma = a - bT \qquad (2)$$

where γ/mN·m^{-1} is the surface tension and T/K is the temperature. The values of the constants a/mN·m^{-1} and b/mN·m^{-1}·K^{-1} in eq 2 obtained from the linear regression analysis, together with the values of the standard deviations of approximation (sd/mN·m^{-1}) for the investigated $(FLiNaK)_{eut}$ (1) + K_2NbF_7 (2) melts, are given in Table 3.

The viscosity of the $(FLiNaK)_{eut}$ (1) + K_2NbF_7 (2) system was measured using the torsion pendulum method. Both the arrangement of the experimental device and the corresponding measuring procedure have been described in detail elsewhere.[28] The temperature dependence of the viscosity of the individual melts was described using the equation

$$\ln\{\eta\} = a + b/\mathrm{T} \qquad (3)$$

where $\{\eta\}$ is the numerical value of the viscosity expressed in mPa·s and T/K is temperature. The values of the constants a/mPa·s and b/mPa·s·K obtained by linear regression analysis, together with the values of the standard deviations of approximation (sd) and the measured temperature range for the investigated melts, are summarized in Table 4.

Results and Discussion

The schematic phase diagram of the $(FLiNaK)_{eut}$ (1) + K_2NbF_7 (2) system is shown in Figure 1. On the right part of the phase diagram, the temperatures of primary crystallization decrease with increasing content of $(FLiNaK)_{eut}$ (1) up to $x_1 = 0.60$. The average eutectic temperature in this range is $T_1 = 902$ K. In the concentration range $x_1 = 0.60$ to 0.75, temperature of primary crystallization slowly increases and reaches an almost constant value. It indicates the presence of an immiscibility gap that is analogous to the phase diagram of the LiF + K_2NbF_7 system published by Kartsev,[7] or there can be a crystallization area of one of the basic components or a crystallization area of a compound that can be formed in the system because the studied system is a cross-cut of the quaternary system. From $x_1 = 0.75$ to 1.00, the temperatures of primary crystallization descend with increasing content of $(FLiNaK)_{eut}$ (1). The average temperature of the second thermal effect observed in the concentration range $x_1 = 0.70$ to 0.975 is $T_2 = 722$ K.

Table 2. Composition, x_i, Regression Coefficients, a and b, and the Standard Deviations (sd) of the Density, ρ, of the Investigated $(FLiNaK)_{eut}$ (1) + K_2NbF_7 (2) System

x_1	a g·cm^{-3}	b·10^4 g·cm^{-3} K^{-1}	sd·10^4 g·cm^{-3}	T K	ref
1.00	2.579	6.2	2.9	940 to 1170	26
0.80	3.014	7.0	6.7	940 to 1050 (c)	
0.80	2.962	6.3	19.7	970 to 1080 (h)	
0.80	3.012	6.9	7.1	980 to 1080 (c)	
0.50	3.256	8.3	4.5	960 to 1100 (c)	
0.50	3.166	7.4	21.6	960 to 1090 (h)	
0.50	3.246	8.2	2.3	960 to 1090 (c)	
0.25	3.436	9.1	10.2	1000 to 1150 (c)	
0.25	3.354	8.3	41.0	1000 to 1100 (h)	
0.25	3.379	8.7	7.0	1000 to 1110 (c)	
0.00	3.577	10.9	11.5	1023 to 1133	8

Table 3. Regression Coefficients a and b of the Temperature Dependence of the Surface Tension and the Standard Deviation of Approximation (sd) of Individual Melts of the $(FLiNaK)_{eut}$ (1) + K_2NbF_7(2) System

x_1	a mN·m^{-1}	b mN·m^{-1}·K^{-1}	sd mN·m^{-1}	T K	ref
1.00	272.61	0.10	0.03	770 to 1040	26
0.80	176.55	0.05	0.53	960 to 1050	
0.50	221.45	0.11	0.60	950 to 1050	
0.25	206.75	0.11	0.34	980 to 1050	
0.00	164.14	0.08	0.59	1043 to 1150	15

Table 4. Regression Coefficients a and b and the Standard Deviations (sd) of the Viscosity of Investigated Melts of the $(FLiNaK)_{eut}$ (1) + K_2NbF_7(2) System

x_1	a/mPa·s	b/mPa·s·K	sd·10^2/mPa·s	T/K	ref
1.00	−3.52	4327	2.4	770 to 1025	
0.80	−3.10	4149	0.6	950 to 1072	
0.50	−3.43	4810	0.3	710 to 830	
0.25	−4.23	5774	0.3	1055 to 1170	
0.00	−4.42	6091	0.3	1035 to 1150	22

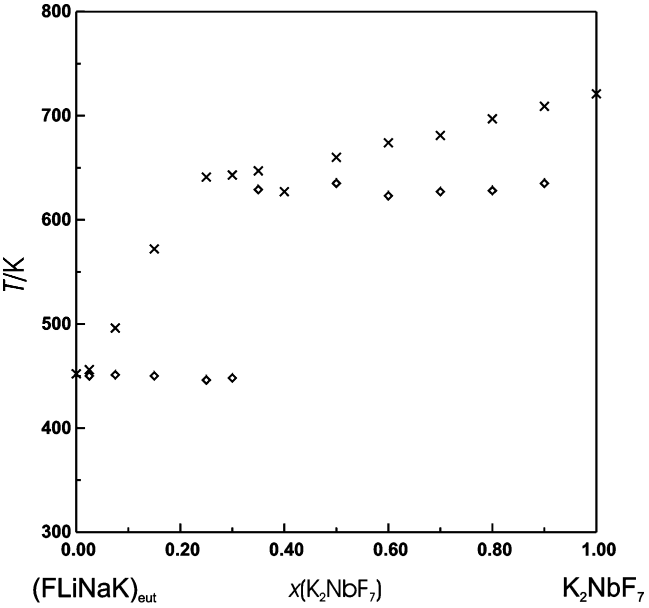

Figure 1. Schematic phase diagram of the $(FLiNaK)_{eut}$ (1) + K_2NbF_7 (2) system.

Table 5. Calculated Data of the Density, ρ, and the Molar Volume, V, of the Molten $(FLiNaK)_{eut}$ (1) + K_2NbF_7 (2) System

x_1	ρ_{1023K} g·cm^{-3}	ρ_{1073K} g·cm^{-3}	ρ_{1123K} g·cm^{-3}	$V_{1023\,K}$ cm^3·mol^{-1}	$V_{1073\,K}$ cm^3·mol^{-1}	$V_{1123\,K}$ cm^3·mol^{-1}
1.00	1.941	1.910	1.879	21.274	21.621	21.980
0.80	2.307	2.273	2.239	40.688	41.291	41.913
0.50	2.406	2.367	2.327	71.771	72.969	74.207
0.25	2.450	2.407	2.364	97.305	99.038	100.834
0.00	2.460	2.405	2.350	123.640	126.449	129.389

Three different temperatures (1023 K, 1073 K, and 1123 K) were selected for calculation of the isothermal density and molar volume. Calculated values based on experimental data are summarized in Table 5. The graphical representation of concentration dependences of the density and molar volume of the $(FLiNaK)_{eut}$ (1) + K_2NbF_7 (2) system at three chosen temperatures are shown in Figures 2 and 3, respectively. In both cases, densities and molar volumes increase with increasing content of K_2NbF_7 (2) for all three selected temperatures. The concentration dependence of the molar volume of the investigated system for the temperature $T = 1073$ K can be described by the following equation

$$V^{1073}/\mathrm{cm^3{\cdot}mol^{-1}} = (5.3x_2^2 + 100.0x_2 + 21.5)$$
$$\mathrm{sd/cm^3{\cdot}mol^{-1}} = 0.4 \qquad (4)$$

By differentiating eq 4 according to x_2 and introducing the results into the equation

$$\bar{V}_2 = V + x_1\left(\frac{\partial V}{\partial x_2}\right) \qquad (5)$$

the concentration dependence of the partial molar volume of K_2NbF_7 can be extracted in the form

$$\bar{V}_2^{1073}/\text{cm}^3\cdot\text{mol}^{-1} = (126.427 - 5.285x_1^2) \qquad (6)$$

For $x_1 \rightarrow 1$, the partial molar volume of K_2NbF_7 (2) in an infinitely diluted solution adopts the value $\bar{V}_2/\text{cm}^3\cdot\text{mol}^{-1} = (121.1 \pm 0.4)$ at 1073 K. This value is slightly lower than the molar volume of pure K_2NbF_7 (2), $V_2 = 126.4\ \text{cm}^3\cdot\text{mol}^{-1}$, at 1073 K. It indicates volume contraction when K_2NbF_7 (2) is immersed in the $(\text{FLiNaK})_{\text{eut}}$ (1). The explanation of this observation was presented by Mlynáriková.[29]

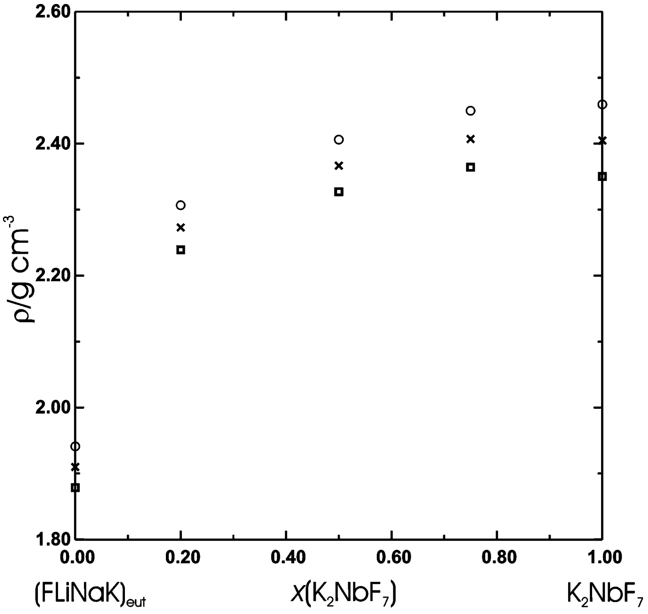

Figure 2. Density, ρ, of the $\text{FLINAK}_{\text{eut}}$ (1) + K_2NbF_7 (2) system: ○, 1023 K; ×, 1073 K; □, − 1123 K.

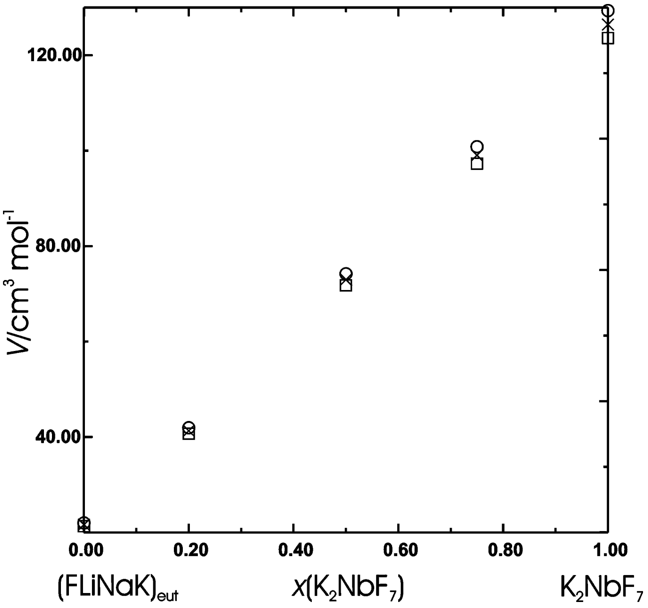

Figure 3. Molar volume, *V*, of the $\text{FLINAK}_{\text{eut}}$ (1) + K_2NbF_7 (2) system: □, 1023 K; ×, 1073 K; ○, 1123 K.

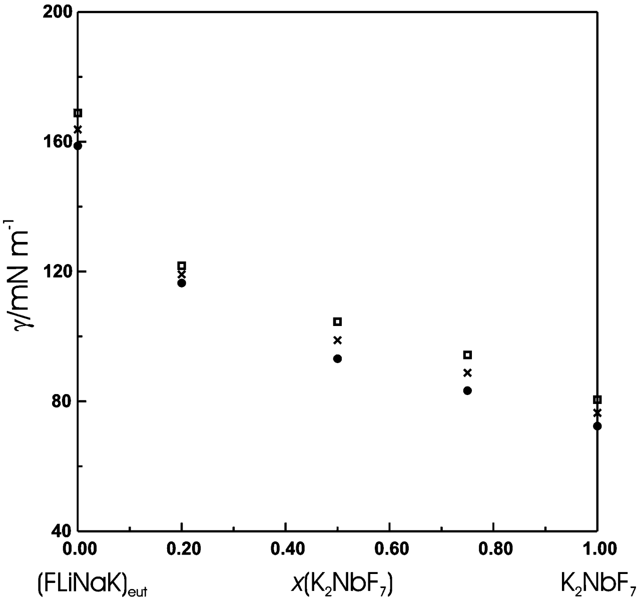

Figure 4. Surface tension in the $\text{FLINAK}_{\text{eut}}$ (1) + K_2NbF_7 (2) system: □, 1023 K; ×, 1073 K; ●, 1123 K.

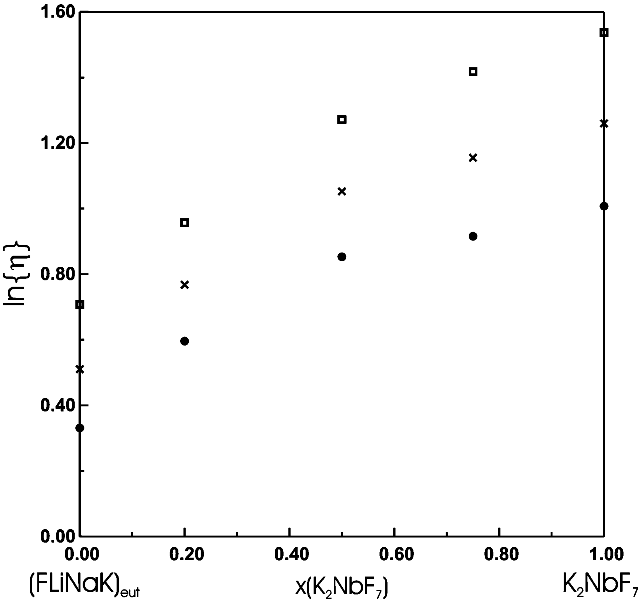

Figure 5. Viscosity ln{η} of the $\text{FLINAK}_{\text{eut}}$ (1) + K_2NbF_7 (2) system: □, 1023 K; ×, 1073 K; ●, 1123 K.

The concentration dependences of the surface tension of the molten $(\text{FLiNaK})_{\text{eut}}$ (1) + K_2NbF_7 (2) system at the temperatures 1023 K, 1073 K, and 1123 K are shown in Figure 4. The addition of K_2NbF_7 (2) to the $(\text{FLiNaK})_{\text{eut}}$ (1) caused a decrease in the surface tension of $(\text{FLiNaK})_{\text{eut}}$ (1). It means that K_2NbF_7 (2) is a surface active component in $(\text{FLiNaK})_{\text{eut}}$ (1).

The concentration dependences of the viscosity for the $(\text{FLiNaK})_{\text{eut}}$ (1) + K_2NbF_7 (2) system at the temperatures 1023 K, 1073 K, and 1123 K are shown in Figure 5. The viscosity in the $(\text{FLiNaK})_{\text{eut}}$ (1) + K_2NbF_7 (2) system increases continually from $(\text{FLiNaK})_{\text{eut}}$ (1) to K_2NbF_7 (2).

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