Density and Viscosity of the $(LiF + NaF + KF)_{eut}$ (1) + K_2TaF_7 (2) + Ta_2O_5 (3) Melts

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The density and the viscosity of the melts of the system $(LiF + NaF + KF)_{eut}$ (1) + K_2TaF_7 (2) + Ta_2O_5 (3) have been investigated up to $x_3 = 0.02$ and $x_2 = 0.15$. The density of the melts has been measured using an Archimedean method. On the basis of the measured densities, the molar volumes of the melts and the partial molar volume of K_2TaF_7 in binary $(LiF + NaF + KF)_{eut}$ (1) + K_2TaF_7 (2) system have been calculated. The viscosity of the melts of the investigated system has been measured using the computerized torsion pendulum method. The viscosity data was fit to modified Redlich−Kister's equation.

Introduction

Tantalum is an excellent material for surface treatment (coating) of steel materials for the chemical industry due to its high hardness and corrosion resistance in wet acidic conditions.[1] For these applications, it is necessary to prepare high-purity tantalum metal.[2] Fluoride melts based on tantalum have been investigated as media suitable for industrial applications. For industrial application, the determination of the physicochemical properties of fluorides melts is very important.

The system $(LiF + NaF + KF)_{eut}$ (1) + K_2TaF_7 (2) + Ta_2O_5 (3) {$(LiF + NaF + KF)_{eut}$(1) = $FLINAK_{eut}$ (1)} has the potential to be used as an electrolyte in the electrochemical production of tantalum.[1,2] The phase equilibrium of the binary systems LiF + K_2TaF_7 has been measured in ref 3. The system LiF (1) + K_2TaF_7 (2) is a simple eutectic with the coordinates of the eutectic point at $x_2 = 0.840$ with a liquid immiscibility in the interval $x_2 = 0.250$ to 0.520. The system NaF (1) + K_2TaF_7 (2) has been studied in ref 4. It is a simple eutectic system with the coordinates of the eutectic point at mole fraction of K_2TaF_7 from (63 to 66) % and the eutectic temperature at (925 to 935) K. The phase diagram of the binary system KF (1) + K_2TaF_7 (2) has been studied in refs 5 and 6. The congruently melting compound K_3TaF_8 gives rise to two eutectic points.The first eutectic point with the coordinates of the eutectic point in the interval $x_2 = 0.220$ to 0.240, at (991 to997) K, and *the* second eutectic point with the coordinates at $x_2 = 0.700$ and temperature at (968 to 970) K.

The phase diagram of the system KF (1) + Ta_2O_5 (2) up to $w_2 = 0.350$ ($x_2 = 0.661$) has been determined.[7] The coordinates of the eutectic point at $w_2 = 0.018$ ($x_2 = 0.0024$) at 1126 K have been reported. The formation of $KTaO_3$ has been observed in the system.

The phase diagram of the binary system K_2TaF_7 (1) + Ta_2O_5 (2) up to $x_2 = 0.275$ has been studied.[7] The coordinates of the eutectic point are at $x_2 = 0.165$ at 853 K.

Two reports of the whole ternary system KF (1) + K_2TaF_7 (2) + Ta_2O_5 (3) can be found in the literature.[6,7] The ternary point at $w_1 = 0.30$ ($x_1 = 0.745$), $w_2 = 0.63$ ($x_2 = 0.232$), and $w_3 = 0.07$ ($x_3 = 0.023$) at 1045 K was reported.[7] The alternative eutectic point is at $x_1 = 0.775$, $x_2 = 0.205$, and $x_3 = 0.002$, at 991 K.[7] The same authors have reported also a peritectic point at $x_1 = 0.870$, $x_2 = 0.085$, and $x_3 = 0.045$ at 1037 K.

In the present work, the density and the viscosity of the melts of the system $FLINAK_{eut}$ (1) + K_2TaF_7 (2) + Ta_2O_5 (3) have been investigated up to $x_2 = 0.150$ and $x_3 = 0.002$. On the basis of the measured density values, the molar volumes of the melts and partial molar volume of K_2TaF_7 in the binary system $FLINAK_{eut}$ (1) + K_2TaF_7 (2) have been calculated. The viscosity of the $FLINAK_{eut}$ (1) + K_2TaF_7 (2) and the $FLINAK_{eut}$ (1) + K_2TaF_7 (2) + Ta_2O_5 (3) systems have been measured using the torsion pendulum method. Results obtained from viscosity measurement heve been used to describe the dependence of the viscosity on concentration at constant temperature (973 K). The working temperature should be as low as possible so that energy consumptiom would be acceptable. This low temperature results in a low solubility of Ta_2O_5 only up to $x_3 = 0.02$.

Experimental Section

For preparation of the samples the following chemicals heve been used: LiF (Lachema, 99 %), NaF (Fluka, 99.9 %), KF (Merck, 99.9 %). and K_2TaF_7 and Ta_2O_5 (prepared in Institute of Chemistry KSC RAS, Apatity, Russia, min. 99 %). LiF and NaF have been dried at 873 K for 2 h; KF and K_2TaF_7 have been dried in a vacuum at 403 K for 1 day.

The density of the investigated melts has been measured using the Archimedean method. A platinum vessel suspended in a platinum wire of 0.3 mm diameter, attached below an electronic balance unit, has been used as the measuring body. The temperature dependence of the volume of the vessel has been determined by calibration, using molten NaCl and KF, all of analytical grade purity. The temperature has been measured using a Pt−Pt10Rh thermocouple calibrated at the melting points of NaCl and KF. A detailed description of the apparatus has been published.[8]

Density. The necessary amount of the mixture (50 g) was placed in the Pt crucible and then quickly transferred into the furnace that has been preheated at 573 K, positioned just below

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Table 1. Constants *a* and *b* in the Temperature Dependence of Density (eq 1) and the Standard Deviations of Approximations of Investigated Samples of the System $FLINAK_{eut}$ (1) + K_2TaF_7 (2) + Ta_2O_5 (3)

x_1	x_2	x_3	a/g·cm^{-3}	$\bar{a}$	b·10^4/g·cm^{-3}·K^{-1}	$\bar{b}$	SD·10^4	$\overline{SD}$·10^4	T/K
1.000	**0.000**	**0.000**		**2.5793**		**6.240**		**2.5**	**933−1163**
1.000	0.000	0.000	2.5790		6.239		2.0		933−1163
1.000	0.000	0.000	2.5803		6.232		3.3		933−1163
1.000	0.000	0.000	2.5785		6.249		2.2		933−1163
0.990	**0.010**	**0.000**		**2.6750**		**6.187**		**7.2**	**873−1023**
0.990	0.010	0.000	2.6754		6.199		6.9		873−1023
0.990	0.010	0.000	2.6964		6.189		6.7		873−1023
0.990	0.010	0.000	2.6532		6.173		8.0		873−1023
0.970	**0.030**	**0.000**		**2.8360**		**6.001**		**4.1**	**923−1033**
0.970	0.030	0.000	2.8366		5.995		3.1		923−1033
0.970	0.030	0.000	2.8416		6.025		5.2		923−1033
0.970	0.030	0.000	2.8299		5.983		4.0		923−1033
0.950	**0.050**	**0.000**		**2.8876**		**5.492**		**8.5**	**913−1073**
0.950	0.050	0.000	2.8893		5.322		7.4		913−1073
0.950	0.050	0.000	2.8943		5.643		9.3		913−1073
0.950	0.050	0.000	2.8793		5.511		8.8		913−1073
0.900	**0.100**	**0.000**		**3.1923**		**6.803**		**5.1**	**913−1063**
0.900	0.100	0.000	3.1992		6.912		4.0		913−1063
0.900	0.100	0.000	3.1844		6.703		6.5		913−1063
0.900	0.100	0.000	3.1934		6.794		4.9		913−1063
0.850	**0.150**	**0.000**		**3.3727**		**7.249**		**4.1**	**923−1073**
0.850	0.150	0.000	3.3709		7.259		2.8		923−1073
0.850	0.150	0.000	3.3627		7.290		5.4		923−1073
0.850	0.150	0.000	3.3845		7.198		4.1		923−1073
0.976	**0.018**	**0.006**		**2.9911**		**8.192**		**3.8**	**933−1053**
0.976	0.018	0.006	2.9950		8.094		2.8		933−1053
0.976	0.018	0.006	2.9939		8.251		5.5		933−1053
0.976	0.018	0.006	2.9845		8.232		3.2		933−1053
0.960	**0.030**	**0.010**		**3.0175**		**7.596**		**8.98**	**943−1063**
0.960	0.030	0.010	3.0182		7.532		7.5		943−1063
0.960	0.030	0.010	3.0243		7.705		10.2		943−1063
0.960	0.030	0.010	3.0099		7.550		9.3		943−1063
0.920	**0.060**	**0.020**		**3.0587**		**5.524**		**7.3**	**943−1043**
0.920	0.060	0.020	3.0679		5.543		6.7		943−1043
0.920	0.060	0.020	3.0753		5.531		8.3		943−1043
0.920	0.060	0.020	3.0329		5.499		6.8		943−1043
0.973	**0.024**	**0.003**		**2.9154**		**6.849**		**9.7**	**953−1053**
0.973	0.024	0.003	2.9133		6.869		8.3		953−1053
0.973	0.024	0.003	2.9319		6.856		10.5		953−1053
0.973	0.024	0.003	2.9009		6.821		10.3		953−1053
0.955	**0.040**	**0.005**		**3.0738**		**7.906**		**5.5**	**943−1063**
0.955	0.040	0.005	3.0709		7.910		4.9		943−1063
0.955	0.040	0.005	3.0705		7.913		7.2		943−1063
0.955	0.040	0.005	3.0801		7.894		4.4		943−1063
0.910	**0.080**	**0.010**		**2.9138**		**4.169**		**6.59**	**953−1053**
0.910	0.080	0.010	2.9045		4.159		5.5		953−1053
0.910	0.080	0.010	2.9281		4.151		7.5		953−1053
0.910	0.080	0.010	2.9089		4.198		6.7		953−1053
0.972	**0.026**	**0.002**		**2.9293**		**7.317**		**9.1**	**923−1053**
0.972	0.026	0.002	2.9295		7.310		6.6		923−1053
0.972	0.026	0.002	2.9140		7.311		13.2		923−1053
0.972	0.026	0.002	2.9445		7.329		7.5		923−1053
0.953	**0.043**	**0.003**		**3.0083**		**7.565**		**3.6**	**923−1063**
0.953	0.043	0.003	3.0159		7.612		2.4		923−1063
0.953	0.043	0.003	2.9992		7.462		5.6		923−1063
0.953	0.043	0.003	3.0099		7.621		2.7		923−1063

the measuring body, where the sample was held under an atmosphere of dried nitrogen. The sample was introduced into a shaft furnace, and a Pt−Pt10Rh thermocouple inside the crucible was also used to indicate the melting of the sample. The depth of immersion was controlled using the electrical contact. The measurements were carried out in a temperature interval depending on the temperature of primary crystallization of the measured mixture. The samples were heated to the upper temperature, and then the cooling direction was performed down to the lowest temperature. The measurements was carried out in the temperature interval of approximately (100 to 150) K. The density results were automatically recorded by the measuring device every 3 s for each melt. For each measurement, one heating and two cooling curves were recorded. For each errorless curve, coefficients a and *b* together with the stardand deviations of aproximations obtained by the linear regression analysis of the experimentally obtained data, are summarized in Table 1.

The temperature dependencies of the density can be expressed in the form of the linear equation

$$\rho/\mathrm{g\cdot cm^{-3}} = a - bT/\mathrm{K} \qquad (1)$$

where ρ is the density and T is the temperature.

The torsion pendulum method based on the measurement of the logarithmic decrement of damping, caused by the friction in the melt, has been used for the viscosity measurement. The measuring device has been described in detail elsewhere.[9] The platinum cylinder with the diameter of 15 mm, and the height of 20 mm has been used as the measuring body. The oscillations of the pendulum system have been registered by means of two

Table 2. Constants a' and b' in the Temperature Dependence of Viscosity (eq 2) and the Standard Deviations of Approximations of Investigated Samples of the System FLINAK$_{eut}$ (1) + K_2TaF_7 (2) + Ta_2O_5 (3)

x_1	x_2	x_3	a'/mPa·s	b'/mPa·s·K	SD·10^3	T/K
1.000	0.000	0.000	−3.0489	3847	5.2	933−1163
0.990	0.010	0.000	−3.0783	3898	8.2	873−1023
0.950	0.050	0.000	−2.2734	3235	6.9	913−1073
0.900	0.100	0.000	−3.0885	4045	3.1	913−1063
0.850	0.150	0.000	−2.9285	3866	6.9	923−1073
0.976	0.018	0.006	−2.9073	3797	8.4	933−1053
0.960	0.030	0.010	−2.9427	3868	10.4	943−1063
0.920	0.060	0.020	−2.2101	3270	4.9	943−1043
0.973	0.024	0.003	−3.0090	3851	6.9	953−1053
0.955	0.040	0.005	−2.8895	3784	4.2	943−1063
0.910	0.080	0.010	−2.9979	3972	4.1	953−1053
0.972	0.026	0.002	−2.9063	3774	8.3	923−1053
0.9534	0.0433	0.0033	−3.0116	3900	6.3	923−1063

phototransistors, placed in the path of a light beam reflected from a mirror attached to the pendulum. The measurements have been carried out in the temperature interval of approximately (100 to 150) K. The measurement in the cooling direction has been performed until the temperature of approximatly 20 K above the temperature of primary crystallization.

Viscosity. The necessary amount of the mixture (50 g) has been placed in the Pt crucible and then quickly transferred into the furnace that has been preheated at 573 K, positioned just below the measuring body, where the sample has been held under an atmosphere of dried nitrogen. After melting of the sample, the pendulum has been immersed in the melt, and the surface of the melt has been kept always 2 mm over the top of the cylinder. The depth of immersion controlled using the electrical contact. The whole measuring device, including the furnace temperature has been controlled by computer. After all the input data and the required temperature profile have been inserted, the measurement of the viscosity at the desired temperatures has been performed automatically. All temperature-dependent variables (oscillation period in gas, dimensions of the cylinder, damping in gas, density of the measured liquid, and moment of inertia of the oscillating system) have been expressed in the form of polynomials and calculated for the actual experimental temperature. The experimental error in the viscosity measurement did not exceed 2.5 %.

The temperature dependence of the viscosity of individual melts have been described by the equation:

$$\ln(\eta/\text{mPa·s}) = a' + b'/(T/\text{K}) \tag{2}$$

where η is the viscosity and T is the temperature. The values of the constants a' and b', obtained by the linear regression analysis, together with the values of standard deviations of approximation for the investigated melts are given in Table 2.

Results and Discussion

Density Measurements and Volume Properties. (a) System FLINAK$_{eut}$ (1) + K_2TaF_7 (2). The density of the system FLINAK$_{eut}$ (1) + K_2TaF_7 (2) was found to increase monotonically with increasing content of K_2TaF_7 (Figure 1). The molar volume at definite composition and temperature has been calculated according to the expression:

$$V_i = \frac{\sum_i x_i M_i}{\rho_i} \tag{3}$$

where V_i is the molar volume at definite composition and temperature in cm^3·mol^{-1}, x_i is the mole fraction, M_i is the atomic mass g·mol^{-1}, and ρ_i is the density at definite composition and temperature.

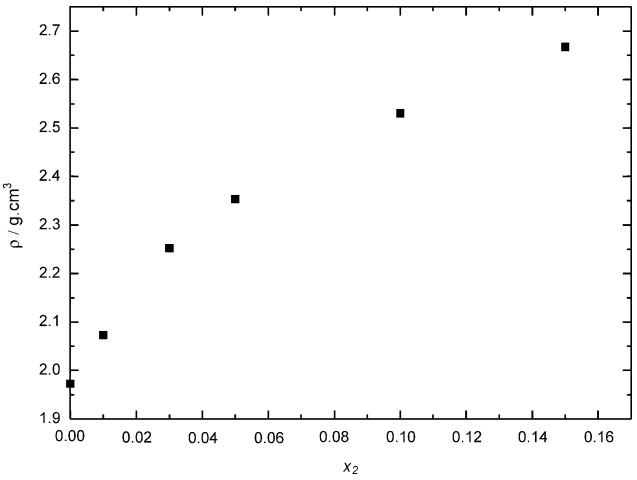

Figure 1. Density, ρ, of the system FLINAK$_{eut}$ (1) + K_2TaF_7 (2) at temperature 973 K.

The concentration dependence of the molar volume of this system at 973 K can be described by the second-order polynomial:

$$V/\text{cm}^3\text{·mol}^{-1} = (20.9 + 75.7x_2 + 134.9x_2^2)$$

$$\text{SD} = 0.3\ \text{cm}^3\text{·mol}^{-1} \tag{4}$$

Differentiating eq 4 according to x_2 and inserting into the equation

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

the expression for the partial molar volume of K_2TaF_7 is obtained:

$$\bar{V}_2/\text{cm}^3\text{·mol}^{-1} = (231.6 - 134.9\,x_1^2) \tag{6}$$

For the partial molar volume of K_2TaF_7 in the infinitely diluted solution ($x_1 \rightarrow 1$), the value $\bar{V}_2 = 96.7$ cm^3·mol^{-1} was calculated. It is impossible to decide whether volume contraction or volume expansion should be considered as the working temperature is much lower than the melting point of pure K_2TaF_7.

(b) System FLINAK$_{eut}$ (1) + K_2TaF_7 (2) + Ta_2O_5 (3). The concentration dependence of the molar volume in the "ternary" system FLINAK$_{eut}$ (1) + K_2TaF_7 (2) + Ta_2O_5 (3) on composition at constant temperature can be described by the general equation:

$$V = \sum_{i=1}^{3} x_i V_i + \sum_{i\neq j}^{3} x_i x_j \sum_{n=0}^{k} A_{nij} x_j^n + B_m x_1^p x_2^q x_3^r \tag{7}$$

where p, q, and r are adjustable integers. The first term represents ideal behavior, and the next terms represent the excess volume (deviation from ideal behavior). The constants V_i, A_{nij}, and B_m in eq 7 were calculated using the multiple linear regression analysis omitting the statistically nonimportant terms on the 0.95 confidence level. At 973 K the following equation

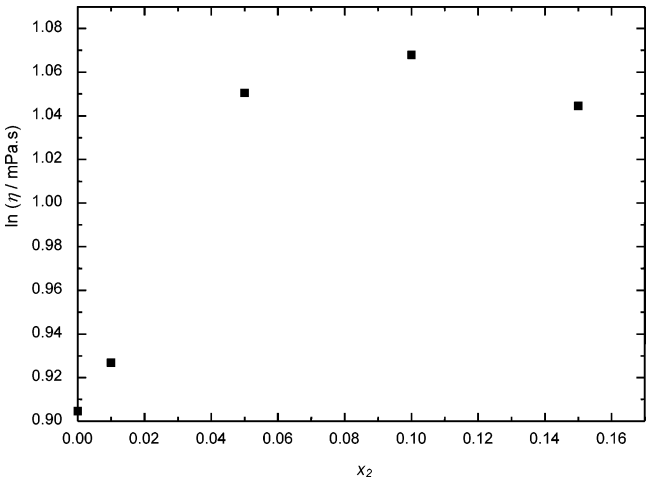

Figure 2. Viscosity, ln η, of the system FLINAK$_{eut}$ (1) + K_2TaF_7 (2) at temperature 973 K.

has been obtained (note: equation is valid in the composition range <0, 2> mole Ta_2O_5; <0, 15> mole K_2TaF_7):

$$V/\mathrm{cm}^3\cdot\mathrm{mol}^{-1} = 20.7\,x_1 + 115.1\,x_2 + 1751.7\,x_2x_3$$

$$\mathrm{SD} = 0.4\ \mathrm{cm}^3\cdot\mathrm{mol}^{-1} \qquad (8)$$

Viscosity Measurements. The viscosity of the system FLINAK$_{eut}$ (1) + K_2TaF_7 (2) is shown in Figure 2. The viscosity shows a maximum at $x_2 = 0.1$.

The concentration dependence of the viscosity of different melts has been studied by many authors.[10−12] Several equations describing the viscosity of complicated systems have been suggested. In the present case, if we assume formation of anion complexes in the melt, the Redlich−Kister-type equations seem to be the most convenient to describe the viscosity of the ternary system. We used the following Redlich−Kister-type equation to describpe of the viscosity of the system:[13]

$$\eta = \sum_{i=1}^{3} \eta_i x_i + \sum_{i\neq j}^{3} (x_i x_j \sum_{n=0}^{n} A_{nij} x_j^{\,n}) + \sum_{a,b,c}^{m} B_m x_1^{\,a} x_2^{\,b} x_3^{\,c} \qquad (9)$$

Authors considered that the third terms represent interactions of all three components, the second term represents the binary interactions, and the first terms should represent ideal behavior.

In the case of transport properties such as viscosity, the ideal behavior is not physically defined since we deal with scalar quantities, which do not possess a total derivative. Thus, the additivity rule cannot be used. On the other hand, this property is thermally activated. Consequently, the additivity of activation energies can be assumed. Thus, the sum of viscosities of pure components in logarithm values multiplied by their mole fraction can be modeled be an "additive" behavior:[13,14]

$$\ln \eta = \ln \eta_{\mathrm{id}} + \ln \eta_{\mathrm{ex}} = \sum_{i=1}^{3} x_i \ln \eta_i + \sum_{i\neq j}^{3} (x_i x_j \sum_{n=0}^{m} A_{nij} x_j^{\,n}) + \sum_{i,j,k}^{3} B_m x_i^{\,a} x_j^{\,b} x_k^{\,c} \qquad (10)$$

Equation 10 describes the dependence of the viscosity on the composition (viscosity is in logarithm value). The terms with coefficients A_{nij} and B_{abc} represent non-ideal behavior of the viscosity ("excess viscosity").

The calculation of the coefficients ln η_i, A_{nij}, and B_{abc} for the chosen temperature has been performed using the multiple linear regression analysis omitting the statistically non-important terms on the 0.95 confidence level. The final equation for the viscosity of the investigated system FLINAK$_{eut}$ (1) + K_2TaF_7 (2) + Ta_2O_5 (3) at the temperature of 923 K has been obtained in the form:

$$\ln \eta = 0.90\,x_1 + 0.90\,x_2 + 3.22\,x_1x_2 - 13.97\,x_1x_2^{\,2} + 399.15\,x_1x_3^{\,2}$$

$$\mathrm{SD} = 0.02 \qquad (11)$$

The final equations of the concentration dependence of the molar volume and the viscosity in the "ternary" system FLINAK$_{eut}$ (1) + K_2TaF_7 (2) + Ta_2O_5 (3) versus composition gives results in good agreement with measured data.

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