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Viscosity of the System LiF + NaF + K_2NbF_7

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The viscosity of melts of the system LiF + NaF + K_2NbF_7 has been measured by means of the computerized torsion pendulum method. The viscosity increases from LiF through NaF to K_2NbF_7. Deviations from the additivity of logarithms were considered. The measurement of viscosity in the investigated system has shown that a significant ternary interaction exists in the melts, which can be ascribed to the formation of the $[NbF_8]^{3-}$ anions.

Introduction

The study of viscosity of the melts of the system LiF (1) + NaF (2) + K_2NbF_7 (3) is interesting from the practical as well as from the theoretical point of view. The melts of this system are promising electrolytes for the electrochemical deposition of smooth and adherent niobium layers on a metallic base.[1] From the theoretical point of view it is possible to draw from viscosity knowledge some conclusions on the structure and on the ionic composition of these melts.

The phase diagram of the system LiF (1) + NaF (2) was studied previously.[2−4] The authors of those studies found that it is a simple eutectic system with the coordinates of the eutectic point at $x_2 = 0.39$ and 649 °C. The phase diagram of the system LiF (1) + K_2NbF_7 (3) has been determined.[5,6] The system LiF (1) + K_2NbF_7 (3) is a simple eutectic with a calculated eutectic point at $x_3 = 0.72$ and 670 °C. The phase diagram of the system NaF (2) + K_2NbF_7 (3) has been studied in refs 7 and 8. The authors of both works found that they are simple eutectic systems with the coordinates of the eutectic points at $x_2 = 0.37$ and 657 °C,[7] and $x_2 = 0.335$ and 647 °C.[8]

The densities of the systems LiF (1) + NaF (2)[9] and LiF (1) + K_2NbF_7 (3)[10] have been studied. The viscosity of the system LiF (1) + NaF (2) has been studied[11,12] but has been measurement in the present work. The system LiF (1) + K_2NbF_7 (3) has been studied.[13]

In the present work the viscosity of the ternary system LiF (1) + NaF (2) + K_2NbF_7 (3) has been measured. On the basis of the results, deviations of the viscosity from additive behavior on a logarithmic basis were calculated. Results have been interpreted in terms of interaction of components and possible chemical reaction.

Experimental Section

The torsion pendulum method based on the measurement of the logarithmic decrement of damping, caused by the friction in the melt, was used for the viscosity measurement. The measuring device has been described in detail.[14] The platinum cylinder with the diameter 15 mm and the height 20 mm was used as the measuring body. The oscillations of the pendulum system were followed by means of two fixed phototransistors, placed in the path of a light beam reflected from a mirror attached to the pendulum. The viscosity values were computed on-line using a Pentium processor.

Table 1. Regression Coefficients *a* and *b* and the Standard Deviations of the Approximation of the Temperature Dependence of the Viscosity (Eq 1) of Investigated Melts of the System LiF (1) + NaF (2) + K_2NbF_7 (3)

x_1	x_2	x_3	*a*	*b*	10^3(SD)·	*T*/K
1.000	0.000	0.000	−1.808	2755	1.23	1130−1310
0.250	0.750	0.000	−2.045	3059	0.922	1160−1320
0.500	0.500	0.000	−1.994	2961	0.792	1130−1320
0.750	0.250	0.000	−1.907	2848	0.975	1130−1320
0.000	1.000	0.000	−2.052	3123	1.310	1290−1400
0.750	0.000	0.250	−2.860	3940	0.980	1030−1120
0.563	0.187	0.250	−2.880	3928	10.84	1030−1100
0.375	0.375	0.250	−2.830	3898	6.08	1020−1140
0.187	0.563	0.250	−2.740	3836	2.43	1050−1160
0.000	0.750	0.250	−2.659	3829	2.43	1170−1270
0.500	0.000	0.500	−3.540	4780	12.3	1060−1150
0.375	0.125	0.500	−3.487	4713	4.88	1020−1140
0.250	0.250	0.500	−3.402	4636	2.97	1020−1140
0.125	0.375	0.500	−3.300	4554	8.14	960−1060
0.000	0.500	0.500	−3.170	4450	3.60	1050−1170
0.125	0.125	0.750	−5.145	6828	20.38	1010−1100
0.250	0.000	0.750	−3.880	5268	0.300	1010−1110
0.000	0.000	1.000	−4.131	5718	3.16	980−1080

The melt, 22.5 cm^3 in volume, was placed in a platinum crucible and inserted in a resistance furnace. After melting of the sample, the pendulum was immersed in the melt, and the surface of the melt was kept always 2 mm over the top of the cylinder. The depth of immersion was continuously monitored and controlled using the electrical contact. The additional damping, caused by the cylinder-carrying rod, was eliminated in the computational procedure. The computer controlled the whole measuring device, including the furnace temperature. After all the input data and the required temperature profile were inserted, the measurement of the viscosity at the desired temperatures was performed automatically. All temperature-dependent variables (oscillation period in gas, dimensions of the cylinder, damping in gas, density of the measured liquid, moment of inertia of the oscillating system) were 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 measurement was carried out in the temperature interval of approximately 120 K starting at (20 to 30) K

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Table 2. Experimental Data on the Viscosity of the Molten System LiF (1) + NaF (2) + K_2NbF_7 (3)

			η/mPa·s		
x_1	x_2	x_3	1100 K	1150 K	1200 K
0	1	0	2.195	1.940	1.733
0.25	0.75	0	2.088	1.850	1.656
0.5	0.5	0	2.009	1.787	1.605
0.75	0.25	0	1.977	1.767	1.594
1	0	0	2.006	1.799	1.628
0	0	1	2.907	2.319	1.885
0.75	0	0.25	2.058	1.761	1.527
0.563	0.187	0.25	1.996	1.709	1.482
0.375	0.375	0.25	2.041	1.750	1.519
0.187	0.563	0.25	2.111	1.814	1.578
0	0.75	0.25	2.275	1.956	1.702
0.5	0	0.5	2.238	1.852	1.558
0.375	0.125	0.5	2.220	1.843	1.553
0.25	0.25	0.5	2.207	1.839	1.556
0.125	0.375	0.5	2.316	1.935	1.640
0	0.5	0.5	2.400	2.013	1.713
0.25	0	0.75	2.482	2.016	1.665
0	0.25	0.75	2.614	2.132	1.768
0.125	0.125	0.75	2.260	1.744	1.375

Table 3. Coefficients A_{nij} and B and the Standard Deviations of the Approximation of the Composition Dependence of the Viscosity of the System LiF (1) + NaF (2) + K_2NbF_7 (3) at Different Temperatures

coefficient/ mPa·s	T/K = 1100	T/K = 1150	T/K = 1200
A_{120}	−0.350 ± 0.021	−0.317 ± 0.015	−0.291 ± 0.012
A_{023}	−0.472 ± 0.028	−0.421 ± 0.019	−0.378 ± 0.016
A_{103}	−0.776 ± 0.044	−0.817 ± 0.037	−0.818 ± 0.033
B_1	−27.116 ± 4.149	−30.399 ± 3.452	−31.095 ± 3.097
B_2	147.478 ± 23.583	168.624 ± 19.841	174.008 ± 17.890
B_3	−193.421 ± 30.284	−221.177 ± 25.699	−228.200 ± 23.259
SD	0.015	0.012	0.010

above the temperature of primary crystallization. The results of some of these measurements at certain temperatures are summarized in Table 2.

For the preparation of samples, the following chemicals were used: LiF (Lachema), NaF (Merck), and K_2NbF_7 (prepared in Apatity), all of reagent quality. LiF was dried at 600 °C for 2 h; NaF and K_2NbF_7 were dried in a vacuum at 130 °C for 1 day. All handling of salts was done in the glovebox under a dry inert atmosphere.

The temperature dependence of the viscosity of the individual melts was described using the equation

$$\ln(\eta/\mathrm{mPa \cdot s}) = a + b/(T/\mathrm{K}) \qquad (1)$$

The values of the constants a and b, obtained by the linear regression analysis, together with the values of the standard deviations of the approximation and the measured temperature range for the investigated melts are given in Table 1. Data for the system LiF (1) + K_2NbF_7 (3) were take from ref 12.

Results and Discussion

Several equations for the analysis of the viscosity dependency on the composition can be suggested. One of them arising from Redlich−Kister's type equation has been used.[15]

$$\eta = \sum_{i=1}^{3} x_i \eta_i + \sum_{i^1 j}^{3} x_i x_j (A_{ij} + B_{ij} x_j + C_{ij} x_j^2) + \sum_{i^1 j^1 k}^{3} x_i x_j x_k (A_{ijk} + B_{ijk} x_k) \qquad (2)$$

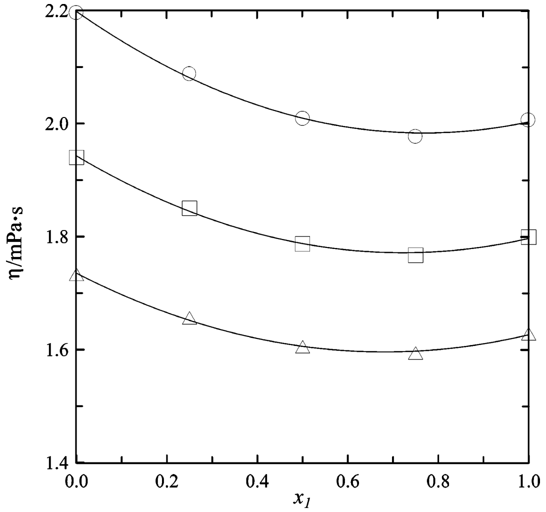

Figure 1. Viscosity of the system LiF (1) + NaF (2): ○, 1100 K; □, 1150 K; △, 1200 K.

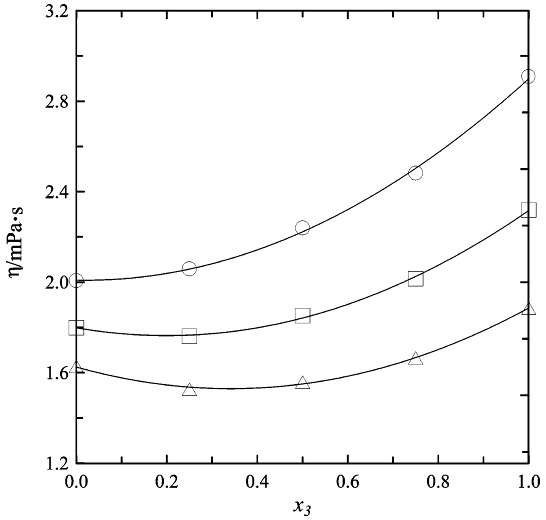

Figure 2. Viscosity of the system LiF (1) + K_2NbF_7 (3): ○, 1100 K; □, 1150 K; △, 1200 K.

Authors considered that the third term represents interactions of all three components, the second term represents the binary interactions, and the first term 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 the total derivative. Thus, the additivity rule cannot be used. On the other hand, this property is thermally activated. Consequently, the additivity of the activation energies can be assumed. Thus, the sum of viscosities of pure components in logarithm values multiplied by their mole fractions can be used as "additive" behavior. For the description of the viscosity of the three component system, the following equation can be used.[13]

$$\eta = \eta_{\mathrm{id}} + \eta_{\mathrm{ex}} = \eta_1^{x_1} \eta_2^{x_2} \eta_3^{x_3} + \sum_{i \neq j}^{3} x_i x_j \sum_{n=0}^{m} A_{nij} x_j^n + \sum_{i,j,k}^{3} B_{abc} x_i^a x_j^b x_k^c \qquad (3)$$

where η_i is the viscosity of the pure component, x_i is the mole fraction, η_{ex} is the viscosity ternary and binary correction, and a, b, and c are integers in the range 1−3.

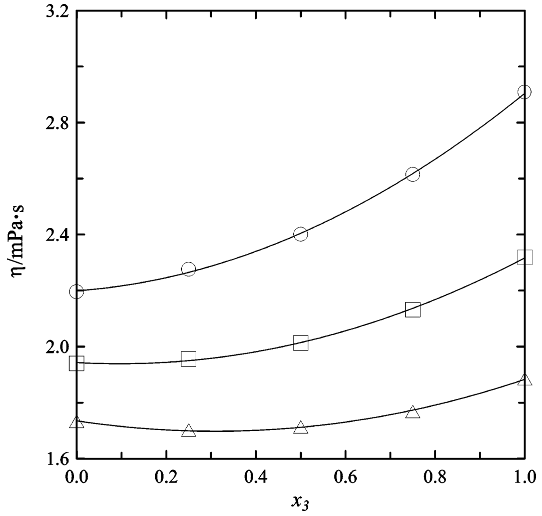

Figure 3. Viscosity of the system NaF (2) + K_2NbF_7 (3): ○, 1100 K; □, 1150 K; △, 1200 K.

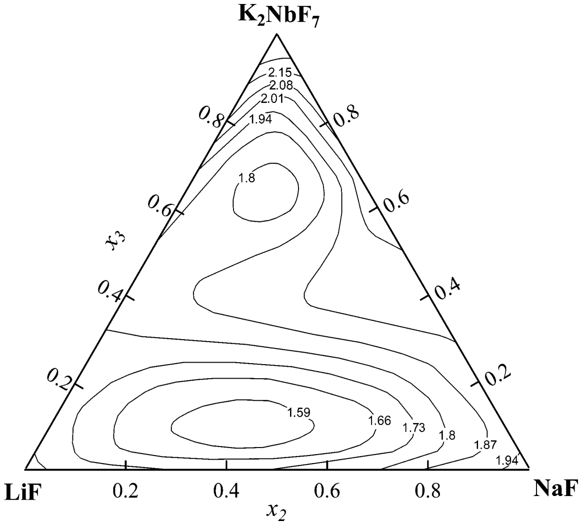

Figure 4. Viscosity of the system LiF (1) + NaF (2) + K_2NbF_7 (3) at the temperature of 1150 K. Values are in mPa·s.

Someone can have a restriction about the physical interpretation of eq 3; thus, we suggest its modification in the following form

$$\ln\{\eta\} = \ln\{\eta_{id}\} + \ln\{\eta_{ex}\} = \sum_{i=1}^{3} x_i \ln\{\eta_i\} + \sum_{i\neq j}^{3} (x_i x_j \sum_{n=0}^{m} A_{nij} x_j^n) + \sum_{i,j,k}^{3} B_{i},j,k x_i^a x_j^b x_k^c \quad (4)$$

where generally the second and third terms may represent not ideal behavior viscosity in logarithmic values. The calculation of the coefficients η_i, A_{nij}, and B_{abc} for the chosen temperature was performed using the multiple linear regression analysis omitting the statistically nonimportant terms on the 0.99 confidence level. The final equation for the viscosity in the investigated system LiF (1) + NaF (2) + K2NbF$_7$ (3) was obtained in the form

$$\eta = \eta_1^{x_1}\eta_2^{x_2}\eta_3^{x_3} + A_{120}x_1x_2 + A_{023}x_2x_3 + A_{103}x_1x_3 + B_1x_1x_2x_3 + B_2x_1x_2x_3^2 + B_3x_1x_2x_3^3 \quad (5)$$

The obtained regression coefficients of eq 5 as well as the standard deviations of the approximation for the investigated system at the temperatures 1100 K, 1150 K, and 1200 K are given in Table 3.

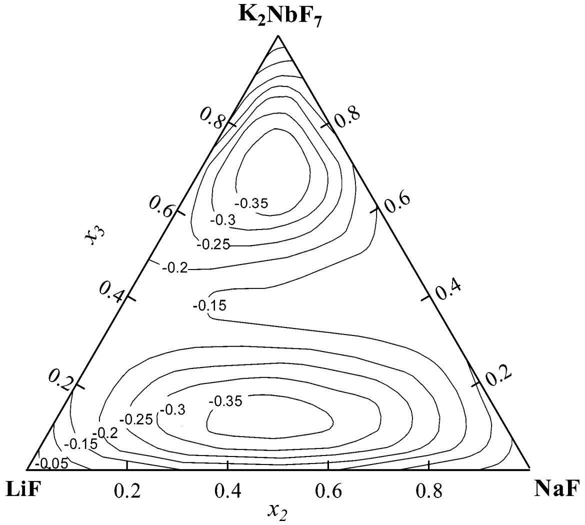

Figure 5. Excess viscosity in the system LiF (1) + NaF (2) + K_2NbF_7 (3) at the temperature of 1150 K. Values are in mPa·s.

The viscosity of the system LiF (1) + NaF (2) is shown in Figure 1. The viscosity decreases from NaF to LiF.

The viscosity of the system LiF (1) + K_2NbF_7 (3)[13] is shown in Figure 2. From the phase diagram study it follows that it is a simple eutectic system and forms the stable diagonal of the reciprocal system Li^+, K^+//F^-, NbF_7^{2-}. Thus, the viscosity increases monotonically from LiF to K_2NbF_7. The viscosity of the system NaF (2) + K_2NbF_7 (3) is shown in Figure 3. The viscosity increases monotonically from NaF to K_2NbF_7.

The viscosity of the ternary system LiF (1) + NaF (2) + K_2NbF_7 (3) at the temperature 1150 K is shown in Figure 4. It may be seen from the figure that the viscosity increases from LiF through NaF to K_2NbF_7. The viscosity excess (ternary and binary correction) in the ternary system LiF (1) + NaF (2) + K_2NbF_7 (3), calculated for the temperature 1150 K according to eq 3, is shown in Figure 5. From the figure it can be seen that is only negative excess viscosity; values were obtained with the minimum localized in the vicinity of the figurative point of K_3NbF_8.

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