Intermolecular Forces in the NaF + KF + K_2NbF_7 System: Investigation of Surface Tension and Viscosity

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The surface tension and viscosity of the NaF (1) + KF (2) binary system and of the NaF (1) + KF (2) + K_2NbF_7 (3) ternary system have been measured over the whole concentration range under an inert atmosphere. A modified Redlich–Kister type equation has been used for the description of the viscosity dependence on the composition. The surface tension of the NaF (1) + KF (2) + K_2NbF_7 (3) system changes continually and decreases from K_2NbF_7 through KF to NaF. The viscosity of the NaF (1) + KF (2) + K_2NbF_7 (3) system decreases from K_2NbF_7 through NaF to KF. In the case of excess surface tension, the system behavior is ideally close to the KF-rich side, and for excess viscosity, the behavior is ideally close to the NaF-rich side.

Introduction

Niobium is a shiny gray, ductile refractory metal, which has many industrial applications. It is used especially in electronics and metallurgy for production of special alloys. Niobium metal is manufactured by the aluminothermic reduction of the oxide followed by electron beam refining.[1] Electrolytic deposition from molten salts represents an alternative way for niobium production.[2–5]

Many authors have already determined physicochemical as well as electrochemical properties of different fluoroniobium molten systems. The authors have devoted their works to the investigation of the phase diagram,[6–21] density,[22–24] viscosity,[25–27] surface tension,[28–30] and NMR.[31,32] The electrochemical behavior of fluoroniobium melts was determined in the literature.[33–51] The knowledge of these properties is fundamental for the industrial process of niobium electrodeposition from molten salts.

Phase equilibrium of the the NaF (1) + KF (2) + K_2NbF_7 (3) system was determined for the first time by McCawley and Barclay.[9] Due to the presence of a congruently melting compound in the KF (2) + K_2NbF_7 (3) binary system, two ternary eutectics occur in the NaF (1) + KF (2) + K_2NbF_7 (3) system, with the following coordinates

$$\begin{aligned} e_1 &: x_1 = 0.30,\ x_2 = 0.05,\ x_3 = 0.65;\ T = 925\ \text{K} \\ e_2 &: x_1 = 0.27,\ x_2 = 0.53,\ x_3 = 0.20;\ T = 936\ \text{K} \end{aligned} \quad (1)$$

where e_1 and e_2 represent eutectic points and x_i is a molar fraction of the corresponding component.

Density of the NaF (1) + KF (2) + K_2NbF_7 (3) system has been investigated recently by Mlynariková et al.[52] The authors observed a maximum in density for this ternary system at the KF (2) + K_2NbF_7 (3) binary around $x_2 = 0.50$.

In the present work, the surface tension of the NaF (1) + KF (2) and NaF (1) + KF (2) + K_2NbF_7 (3) systems was determined using the maximum bubble pressure method, and the viscosity of the same systems was measured using the torsion pendulum method. Corresponding data for the KF (2) + K_2NbF_7 (3) and NaF (1) + K_2NbF_7 (3) binary systems have been reported elsewhere,[28,31] and these data have been used for the calculation of the surface tension and viscosity of the NaF (1) + KF (2) + K_2NbF_7 (3) system in the present work.

Table 1. 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 NaF (1) + KF (2) + K_2NbF_7 (3) System

			a	*b*	sd	*T*
x_1	x_2	x_3	(mN·m^{-1})	(mN·m^{-1}·K^{-1})	(mN·m^{-1})	K
1.000	0.000	0.000	264.96	0.0749	0.14	1294 to 1370
0.750	0.250	0.000	285.11	0.0943	0.29	1203 to 1296
0.500	0.500	0.000	303.88	0.125	0.18	1126 to 1184
0.250	0.750	0.000	231.71	0.0709	0.29	1090 to 1185
0.000	1.000	0.000	215.65	0.0718	0.20	1158 to 1251
0.000	0.000	1.000	164.14	0.0817	0.59	1043 to 1150
0.190	0.560	0.250	196.62	0.0726	0.46	1039 to 1118
0.375	0.375	0.250	254.63	0.1276	1.05	1037 to 1127
0.560	0.190	0.250	434.49	0.2728	0.83	1107 to 1203
0.375	0.125	0.500	233.41	0.1182	0.38	1003 to 1099
0.250	0.250	0.500	190.36	0.0736	0.96	1002 to 1097
0.125	0.375	0.500	205.77	0.0923	0.35	1032 to 1127
0.125	0.125	0.750	196.88	0.0979	0.23	993 to 1088
0.185	0.065	0.750	220.68	0.1192	0.26	984 to 1080
0.065	0.185	0.750	252.73	0.1489	0.81	1000 to 1097

The surface tension and viscosity of the NaF (1) + KF (2) + K_2NbF_7 (3) system have not been investigated so far. The surface tension and viscosity of the NaF (1) + KF (2) and NaF (1) + KF (2) + K_2NbF_7 (3) systems have been calculated for (1073, 1123, and 1173) K.

The aim of this work was to measure surface tension and viscosity in order to complete these missing experimental data. In the future, they can be used for comparison of the surface tension and viscosity of similar fluoroniobium systems like LiF−NaF−K_2NbF_7 and LiF−KF−K_2NbF_7.

All compounds present in the melt are dissociated into cations and anions at working temperatures, and they are responsible for the changes in the physicochemical properties of the melts.

Experimental

For the preparation of samples, the following chemicals were used: NaF (Merck 99.9 %), KF (Lachema 99.5 %), and K_2NbF_7

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10.1021/je700606f CCC: $40.75
Published on Web 02/29/2008

Table 2. Regression Coefficients *a* and *b* and the Standard Deviations (sd) of the Viscosity of Investigated Melts of the NaF (1) + KF (2) + K_2NbF_7 (3) System

			a	*b*	sd·10^3	*T*
x_1	x_2	x_3	mPa·s	mPa·s·K	mPa·s	K
1	0	0	−2.052	3123	1	1290 to 1400
0.000	1.000	0.000	−2.382	3014	7	1153 to 1273
0.000	0.000	1.000	−4.131	5718	15	1023 to 1173
0.250	0.750	0.000	−2.566	3303	1	1133 to 1273
0.500	0.500	0.000	−2.380	3230	3	1233 to 1273
0.750	0.250	0.000	−2.200	3155	1	1120 to 1253
0.560	0.190	0.250	−2.414	3570	1	1103 to 1233
0.375	0.375	0.25	−2.530	3651	4	1033 to 1173
0.19	0.56	0.25	−2.607	3691	3	993 to 1133
0.375	0.125	0.5	−2.876	4238	1	1013 to 1163
0.25	0.25	0.5	−2.861	4199	2	983 to 1123
0.125	0.375	0.5	−2.953	4269	11	1013 to 1163
0.125	0.125	0.75	−4.060	5720	2	973 to 1123
0.185	0.065	0.75	−3.900	5430	5	973 to 1123
0.065	0.185	0.75	−4.250	5870	3	993 to 1153

(prepared in the Institute of Chemistry KSC RAS, Apatity, Russia, min. 99.5 %). NaF was dried at 600 °C for 2 h, and KF and K_2NbF_7 were dried under vacuum at 130 °C for 24 h. Handling of all salts was done in a glovebox under a dry nitrogen atmosphere (Messer 99.99 %).

The arrangement of the experimental devices and the measuring procedures have been described in detail elsewhere.[53,54]

The temperature dependence of the surface tension of particular mixtures was expressed by the linear equation

$$\gamma = a - bT \tag{2}$$

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

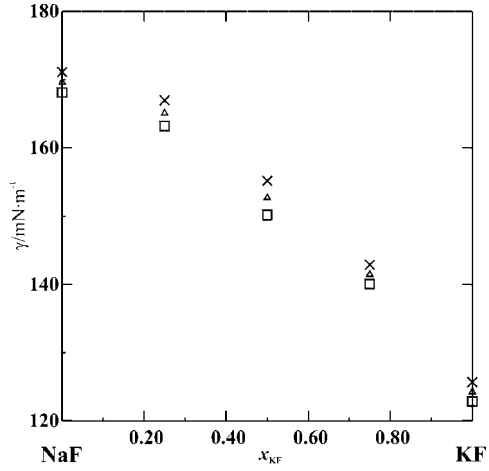

Figure 1. Surface tension in the NaF (1) + KF (2) system: ×, 1253 K; Δ, 1273 K; □, 1293 K.

Table 3. Calculated Values of Surface Tension of Pure Components, γ_i, Coefficients A_{nij}, and the Standard Deviations of the Fit, sd, for the NaF (1) + KF (2) + K_2NbF_7 (3) System

coefficient	temperature		
mN·m^{-1}	1073 K	1123 K	1173 K
γ_1	183 ± 6	188 ± 5	184 ± 5
γ_2	136 ± 4	133 ± 3	128 ± 3
γ_3	79 ± 3	72 ± 2	66 ± 2
A_{013}	−99 ± 2	−421 ± 7	−472 ± 7
A_{113}	−	997 ± 27	1142 ± 26
A_{213}	−	−746 ± 25	−859 ± 25
sd	2	4	4

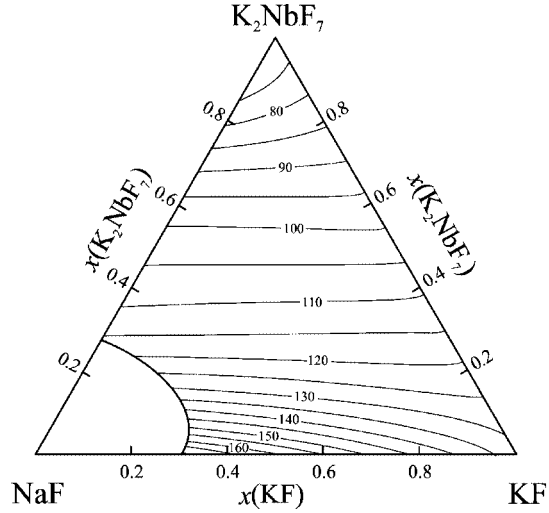

Figure 2. Surface tension of the NaF (1) + KF (2) + K_2NbF_7 (3) system at the temperature of 1123 K. Values are in mN·m^{-1}.

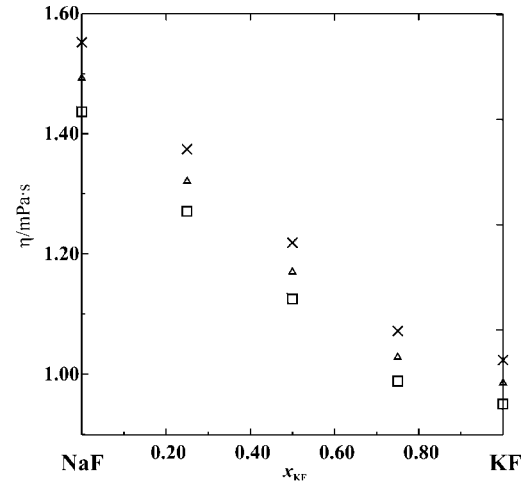

Figure 3. Viscosity of the NaF (1) + KF (2) system: ×, 1253 K; Δ, 1273 K; □, 1293 K.

Table 4. Coefficients A_{nij} and *B* and the Standard Deviations of the Viscosity of the System NaF (1) + KF (2) + K_2NbF_7 (3) at Different Temperatures

coefficient	temperature		
(mPa·s)	1073 K	1123 K	1173 K
ln{η_{NaF}}	0.84 ± 0.02	0.71 ± 0.02	0.59 ± 0.01
ln{η_{KF}}	0.42 ± 0.01	0.29 ± 0.01	0.19 ± 0.01
ln{$\eta_{K_2NbF_7}$}	1.22 ± 0.03	0.97 ± 0.02	0.73 ± 0.01
ln A_{212}	−	−	−0.35 ± 0.10
ln A_{023}	0.81 ± 0.11	0.88 ± 0.10	1.40 ± 0.21
ln B_{111}	−	−	1.62 ± 0.43
sd	0.03	0.03	0.02

approximation (sd/mN·m^{-1}), for the investigated NaF (1) + KF (2) + K_2NbF_7 (3) melts are given in Table 1.

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

$$\ln\{\eta\} = a + b/T \tag{3}$$

where {η} 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 given in Table 2.

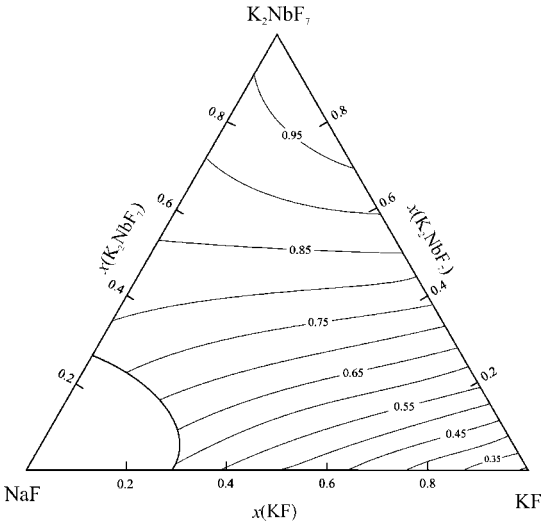

Figure 4. Viscosity, $\ln\{\eta\}$, of the NaF (1) + KF (2) + K_2NbF_7 (3) system at the temperature of 1123 K. Values are expressed in logarithm scale.

Results and Discussion

Surface Tension. The concentration dependence of the surface tension of the NaF (1) + KF (2) binary system at the temperatures (1253, 1273, and 1293) K is shown in Figure 1. The addition of KF to the NaF caused a decrease of the surface tension of NaF. Surface tension of the NaF (1) + K_2NbF_7 (3) and KF (2) + K_2NbF_7 (3) molten system was recently determined in refs 28 and 29. The authors found out that the surface tension decreases with increasing content of K_2NbF_7.

For the surface tension of the real ternary system, it can be written

$$\gamma = \sum_{i=1}^{3} \gamma_i x_i + \sum_{\substack{i=1 \\ i\neq j}}^{3} \left(x_i x_j \sum_{n=0}^{s} A_{nij} x_j^n \right) + x_1 x_2 x_3 \sum_{p,g=0}^{2} B_{pq} x_2^p x_3^q \quad (4)$$

In eq 4, γ_i's/mN·m^{-1} are the surface tensions of pure components and x_i's are their mole fractions in the mixture. Coefficients p and q are integers in the range 0 to 2. The first term represents the contribution of pure compounds, the second the interactions in the binary systems, and the third the interactions of all three components. The last two terms in eq 4 represent excess surface tension.

The calculation of the coefficients A_{nij}/mN·m^{-1} and B_{pq}/mN·m^{-1} for the NaF (1) + KF (2) + K_2NbF_7 (3) system was performed using a multiple linear regression analysis, omitting the statistically nonimportant terms on the 0.99 confidence level. More details can be found in previously published work.[29,30]

For the concentration dependence of the surface tension of the NaF (1) + KF (2) + K_2NbF_7 (3) system for the temperature 1123 K, the following final equation was obtained

$$\gamma = \gamma_1 x_1 + \gamma_2 x_2 + \gamma_3 x_3 + x_1 x_3 A_{013} + x_1 x_3^2 A_{113} + x_1 x_3^3 A_{213} \quad (5)$$

The calculated values of the surface tension of pure components, γ_i, coefficients A_{nij}, and the standard deviation (sd) of approximation at the three temperatures (1073, 1123, and 1173) K are given in Table 3. As can be seen, no ternary terms are present as they are statistically unimportant. From eq 5, it results that the excess surface tension is almost ideal close to pure KF.

The surface tension of the ternary system NaF (1) + KF (2) + K_2NbF_7 (3) at the temperature 1123 K is shown in Figure 2. Since the melting temperature of pure NaF is high (1269 K), the area where eq 5 is valid is crosshatched. It is obvious that the surface tension continually increases from K_2NbF_7 through KF to NaF. Although in the KF (2) + K_2NbF_7 (3) binary system, a congruently melting compound, K_3NbF_8, takes place,[8] its presence has no influence on the surface tension.

Viscosity. The concentration dependence of the viscosity for the NaF (1) + KF (2) binary system at the temperatures (1253, 1273, and 1293) K is shown in Figure 3. The viscosity in the NaF (1) + KF (2) system decreases continually from NaF to KF. Results for the viscosity of the NaF (1) + K_2NbF_7 (3) and KF (2) + K_2NbF_7 (3) systems were published in refs 25 and 26. The viscosity in both binary systems increases with increasing content of K_2NbF_7.

The concentration dependence of the viscosity of different melts has been studied by many authors.[55–59] Several equations describing the viscosity dependence on composition were suggested. Redlich–Kister type equations seem to be the best choice for the description of the viscosity of the ternary system where complex anions may form. In the case of transport properties like viscosity, the ideal behavior is not physically defined, since we deal with scalar quantities, which do not possess the total derivative. Thus, the additivity of the activation energies can be assumed. Thus, the sum of viscosities of pure components in logarithm values multiplied by their mole fraction can be used as "additive" behavior (see eq 6). Detailed information about the way of calculation is presented in ref 60.

$$\ln\{\eta\} = \ln\{\eta_{id}\} + \ln\{\eta_{ex}\} = \sum_{i=1}^{3} x_i \ln\{\eta_i\} + \sum_{i\neq j}^{3} \left(x_i x_j \sum_{n=0}^{m} A_{nij} x_j^n \right) + \sum_{i,j,k}^{3} B_{i,j,k} x_i^a x_j^b x_k^c \quad (6)$$

Viscosity of the whole ternary system at the temperature 1123 K was described by the following equation

$$\ln\{\eta\} = x_1 \ln\{\eta_1\} + x_2 \ln\{\eta_2\} + x_3 \ln\{\eta_3\} + A_{023} x_2 x_3 \quad (7)$$

The obtained regression coefficients of eq 7 and their standard deviations for the investigated system at the temperatures of (1073, 1123, and 1173) K are given in Table 4. As can be seen, no ternary terms are present as they are statistically unimportant. From eq 7, it results that the excess viscosity is almost ideal close to pure NaF. The viscosity of the ternary system NaF (1) + KF (2) + K_2NbF_7 (3) at the temperature of 1123 K is shown in Figure 4. Due to the high melting point of NaF, the validity of eq 7 is graphically restricted according to the phase diagram[10] in Figure 4. From Figure 4, it may be seen that the viscosity increases from KF through NaF to K_2NbF_7. The formation of the congruently melting compound K_3NbF_8[8] in the KF (2) + K_2NbF_7 (3) system has no influence on viscosity. This result is similar to the result obtained from surface tension determination. In the case of the density investigation of the NaF (1) + KF (2) + K_2NbF_7 (3) system,[52] the authors noticed a maximum of the density for this ternary system at the KF (2) + K_2NbF_7 (3) binary at around $x_2 = 0.50$. It was connected with volume contraction caused by the formation of the K_3NbF_8 compound.

If a higher surface tension component is added to one of low surface tension, it tends to be less concentrated in the surface layer and has only a slight influence on the surface tension. It means that NaF and KF should concentrate in the bulk, while NbF_7^{2-} should concentrate in the surface layer. It could be noted that the size of the cation (Na^+, K^+) influences the surface tension, as well.

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Received for review October 18, 2007. Accepted January 27, 2008. The present work was financially supported by the Scientific Grant Agency of the Ministry of Education of the Slovak Republic and the Slovak Academy of Sciences under the No. 2/6179/26.

JE700606F