

Viscosity of Melts of the System LiF—KF—K₂NbF₇

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The viscosity of melts of the system LiF—KF—K₂NbF₇ has been measured by means of the computerized torsion pendulum method. The viscosity increases from KF through LiF to K₂NbF₇. Additivity of logarithms of viscosity was adopted as the ideal behaviour of the mixture. Deviations from such additive behaviour in the KF—K₂NbF₇ binary system as well as in the LiF—KF—K₂NbF₇ ternary one are most probably due to the chemical interaction $\text{K}_2\text{NbF}_7(\text{l}) + \text{KF}(\text{l}) \leftrightarrow \text{K}_3\text{NbF}_8(\text{l})$. The chemical equilibrium of this reaction is characterized by the dissociation degree of K₃NbF₈. At 1100 K it attains the value $\alpha_0 = 0.45$. In the ternary system, statistically significant ternary interaction does not take place.

The study of viscosity of the melts of the system LiF—KF—K₂NbF₇ 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 metallic base [1]. From the theoretical point of view it is possible from the viscosity knowledge to draw some conclusions on the structure and on the ionic composition of these melts.

No data on the viscosity of the individual binary systems or on the ternary system LiF—KF—K₂NbF₇ can be found in the literature. However, the phase diagram [2], the density [3], and the surface tension [4] of this system was measured quite recently. In the system KF—K₂NbF₇ the intermediate compound K₃NbF₈, melting congruently at 770 °C, is formed. This compound divides the ternary system LiF—KF—K₂NbF₇ into two simple eutectic ones, the coordinates of the two ternary eutectic points being e_1 : 22.3 mole % LiF, 9.4 mole % KF, 68.3 mole % K₂NbF₇; $t_e = 649$ °C, e_2 : 45.5 mole % LiF, 51.7 mole % KF, 2.8 mole % K₂NbF₇; $t_e = 486$ °C.

The aim of the present work was to supplement the existing physicochemical data and to determine the viscosity of the melts of the ternary system LiF—KF—K₂NbF₇. On the basis of the obtained data the excess viscosity was calculated and the information on the mutual interaction of components as well as on possible chemical reactions was elucidated.

EXPERIMENTAL

For the preparation of samples the following chemicals were used: LiF (Lachema), KF (Merck), and K₂NbF₇ (Aldrich), all of reagent quality. LiF was dried at 600 °C for 2 h, KF and K₂NbF₇ were dried

in vacuum at 130 °C for one day. All handling of salts was done in the glove box under a dry inert atmosphere.

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 was described in detail in [5]. The platinum cylinder with the diameter of 15 mm and the height of 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 SAPI-1 minicomputer.

The measured melt of 25 cm³ in volume, placed in a platinum crucible, was inserted in a resistance furnace. After melting of the sample the pendulum was immersed in the melt, 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 %.

Table 1. Regression Coefficients a , b and the Standard Deviations of Approximation of the Temperature Dependence of the Viscosity (Eqn (1)) of Investigated Melts of the System LiF—KF—K₂NbF₇

x_{LiF}	x_{KF}	$x_{\text{K}_2\text{NbF}_7}$	a	$b \cdot K$	SD $\cdot 10^3$	Temperature range/K
1.000	0.000	0.000	-1.694	2624	0.07	1140—1330
0.850	0.150	0.000	-2.035	2910	0.48	1050—1210
0.700	0.300	0.000	-2.428	3220	1.92	940—1090
0.500	0.500	0.000	-2.664	3410	2.03	830—970
0.350	0.650	0.000	-2.684	3400	1.97	930—1060
0.200	0.800	0.000	-2.553	3230	0.72	1038—1180
0.000	1.000	0.000	-2.462	3094	1.94	1120—1320
0.750	0.000	0.250	-2.860	3940	0.98	1030—1120
0.563	0.187	0.250	-3.273	4404	6.96	1030—1140
0.375	0.375	0.250	-3.097	4126	13.5	1010—1120
0.187	0.563	0.250	-2.770	3770	5.15	1040—1110
0.000	0.750	0.250	-2.640	3600	4.26	1030—1090
0.500	0.000	0.500	-3.540	4780	12.3	1060—1150
0.375	0.125	0.500	-3.559	4847	10.1	1070—1200
0.250	0.250	0.500	-3.352	4641	7.95	1030—1130
0.125	0.375	0.500	-3.030	4290	2.51	930—1050
0.000	0.500	0.500	-2.880	4190	2.59	1000—1130
0.000	0.250	0.750	-3.480	4960	1.84	1020—1100
0.125	0.125	0.750	-3.738	5223	1.90	940—1060
0.250	0.000	0.750	-3.880	5268	0.30	1010—1110
0.000	0.000	1.000	-4.131	5718	3.16	980—1080

The measurement was carried out in the temperature interval of approximately 100 K starting at 20—30 K above the temperature of primary crystallization. In the cross-sections with constant mole ratio $n(\text{LiF}) : n(\text{KF}) = 3, 1, \text{ and } 0.33$, figurative points with constant content of 25, 50, and 75 mole % K₂NbF₇ were chosen for the measurement in the ternary system.

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

$$\ln\{\eta\} = a + \frac{b}{T} \quad (1)$$

where η is the viscosity in mPa s and T is the temperature in K. The values of the constants a and b , obtained by the linear regression analysis, together with the values of the standard deviations of approximation and the measured temperature range for the investigated melts are given in Table 1.

RESULTS AND DISCUSSION

For the elucidation of the structure of the investigated system from the viscosity measurement the additivity of the logarithms of viscosity was adopted as the "ideal" behaviour. This approach is based on the validity of the Arrhenius equation for viscosity and on the additivity of the activation energy of viscous flow. To describe the excess viscosity, the Redlich—Kister's type equation was used. Then for the real ternary system at constant temperature it holds

$$\begin{aligned} \eta &= \eta_{\text{id}} + \eta_{\text{ex}} = \\ &= \eta_1^{x_1} \eta_2^{x_2} \eta_3^{x_3} + \sum_{i \neq j}^3 x_i x_j \sum_{n=0}^m A_{nij} x_j^n + B x_1^a x_2^b x_3^c \end{aligned} \quad (2)$$

where η_i 's are viscosities of pure components, x_i 's are their mole fractions, η_{ex} is the viscosity excess, and a, b, c are integers in the range 1—3. The first term represents the "ideal" behaviour, the second one the interaction of components in the binary systems, and the third one the ternary interaction. The calculation of coefficients η_i , A_{nij} , and B 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)—KF(2)—K₂NbF₇(3) was obtained in the form

$$\eta = \eta_1^{x_1} \eta_2^{x_2} \eta_3^{x_3} + A_{012} x_1 x_2 + A_{013} x_1 x_3 + A_{123} x_2 x_3^2 \quad (3)$$

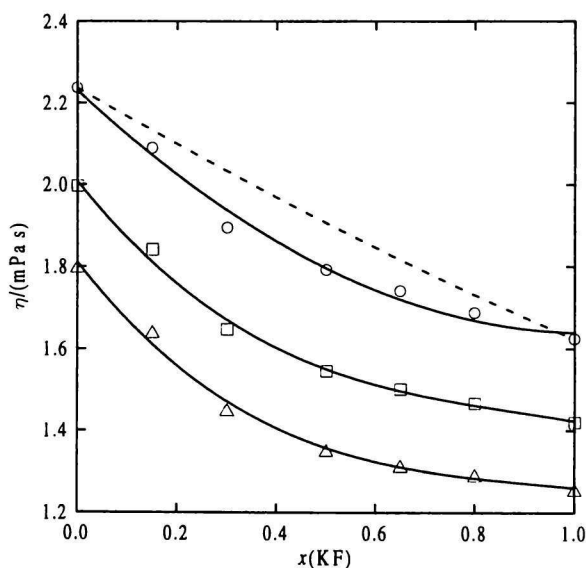
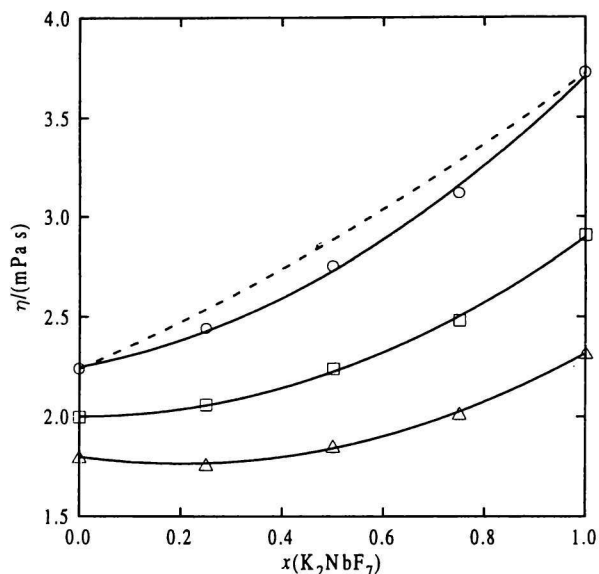
The obtained regression coefficients of eqn (3) as well as the standard deviations of approximation for the investigated system at the temperatures of 1050 K, 1100 K, and 1150 K are given in Table 2.

The viscosity of the system LiF—KF is shown in Fig. 1. Surprisingly, there are no literature data on the viscosity of this system available. The viscosity decreases from LiF to KF. The higher viscosity of LiF compared with that of KF can be ascribed to the ability of LiF to form associates with F—F bridges. This effect obviously overlaps the effect of the different cation size. From the values of the individual coefficients it follows that there is only simple mutual interaction in the binary system LiF—KF (coeff. A_{012}) caused by the exchange of cations in the next neighbour surrounding.

The viscosity of the system LiF—K₂NbF₇ is shown in Fig. 2. From the phase diagram study it follows that it is a simple eutectic system and forms the stable di-

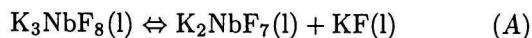
Table 2. Coefficients η_i , A_{nij} , and the Standard Deviations of Approximation of the Composition Dependence of the Viscosity of the System LiF(1)—KF(2)—K₂NbF₇(3) at Different Temperatures

Coefficient	Temperature		
	1050 K	1100 K	1150 K
mPa s			
η_1	2.535 ± 0.051	2.237 ± 0.043	1.997 ± 0.057
η_2	1.881 ± 0.053	1.624 ± 0.041	1.420 ± 0.054
η_3	4.889 ± 0.066	3.724 ± 0.061	2.907 ± 0.081
A_{012}	-0.294 ± 0.147	-0.408 ± 0.118	-0.484 ± 0.102
A_{013}	-0.304 ± 0.159	-0.518 ± 0.128	-0.640 ± 0.111
A_{123}	4.051 ± 0.310	3.480 ± 0.249	3.029 ± 0.216
SD	0.071	0.057	0.049


Fig. 1. Viscosity of the system LiF—KF. ○ 1050 K, □ 1100 K, △ 1150 K, - - - ideal behaviour.

Fig. 2. Viscosity of the system LiF—K₂NbF₇. ○ 1050 K, □ 1100 K, △ 1150 K, - - - ideal behaviour.

agonal of the reciprocal system Li⁺, K⁺//F⁻, NbF₇²⁻. Thus, the viscosity increases monotonously from LiF to K₂NbF₇. The negative value of the regression coefficient A_{013} corresponding to the interaction in the binary system LiF—K₂NbF₇ refers to the absence of any formation of more voluminous species probably due to the strong polarization effect of the lithium cation.

The viscosity of the system KF—K₂NbF₇ is shown in Fig. 3. In this system, the congruently melting intermediate compound K₃NbF₈ is formed, which is shown by the positive deviation from the ideal behaviour (coeff. A_{123}). This compound is, however, not stable and dissociates partially according to the reaction



Thus, reaction (A) affects the chemical equilibrium, which is characterized by the degree of dissociation of reaction (A), α_0 .

Providing the ideal viscosity course is described by

eqn (2), there is the possibility to calculate α_0 by simulating the real viscosity course in the binary system KF—K₂NbF₇ at the equilibrium using the equation

$$\eta_{\text{calc}} = \frac{x(\text{KF})}{\eta_{\text{KF}}} \frac{x(\text{K}_2\text{NbF}_7)}{\eta_{\text{K}_2\text{NbF}_7}} \frac{x(\text{K}_3\text{NbF}_8)}{\eta_{\text{K}_3\text{NbF}_8}} \quad (4)$$

where $\eta(\text{KF})$ and $\eta(\text{K}_2\text{NbF}_7)$ is the viscosity of KF and K₂NbF₇, respectively, $\eta(\text{K}_3\text{NbF}_8)$ is the hypothetical viscosity of pure nondissociated K₃NbF₈, and x_i 's are the equilibrium mole fractions of KF, K₂NbF₇, and K₃NbF₈ in the mixture. $\eta(\text{K}_3\text{NbF}_8)$ can be roughly estimated from the values of the viscosity of both other components. For every composition it is possible to calculate the equilibrium mole fractions of constituents KF, K₂NbF₇, and K₃NbF₈ for every chosen value of α_0 and $\eta(\text{K}_3\text{NbF}_8)$. The correct value of α_0 is obtained by the condition

$$\sum_{i=1}^n (\eta_{\text{calc},i} - \eta_{\text{exp},i})^2 = \min \quad (5)$$

The detailed calculation procedure is described *e.g.* in

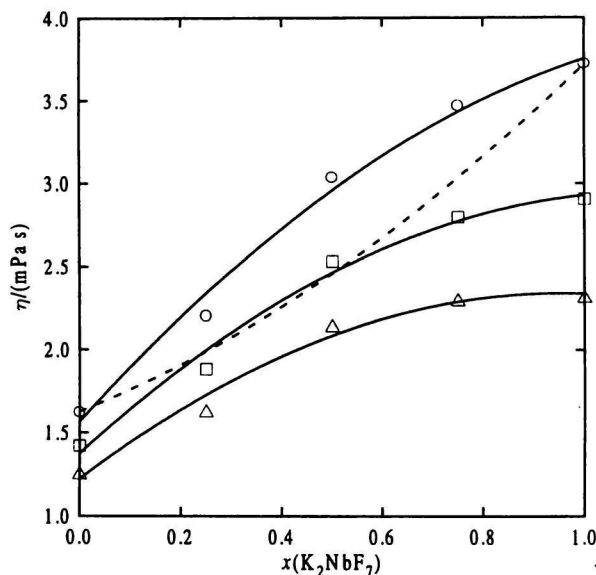


Fig. 3. Viscosity of the system KF—K₂NbF₇. ○ 1050 K, □ 1100 K, △ 1150 K, --- ideal behaviour.

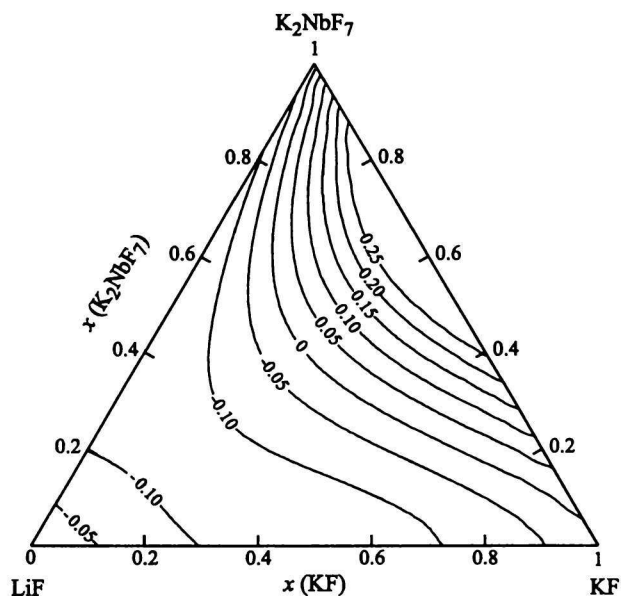


Fig. 5. Excess viscosity in the system LiF—KF—K₂NbF₇ at the temperature of 1100 K. Values are in mPa s.

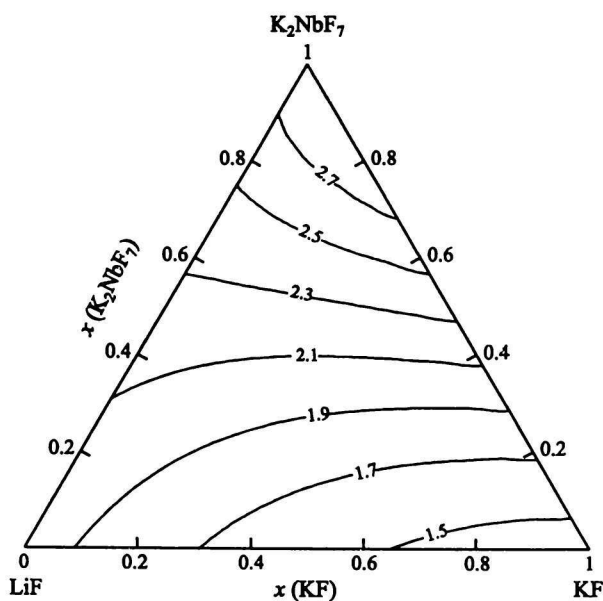


Fig. 4. Viscosity of the system LiF—KF—K₂NbF₇ at the temperature of 1100 K. Values are in mPa s.

[6]. The results of calculation are given in Table 3.

From the calculated values of the dissociation degree of reaction (*A*) it follows that the thermal stability of K₃NbF₈ decreases with increasing temperature. Thus the positive deviation of the viscosity is more expressed at lower temperatures. From the temperature dependence of α₀ the dissociation enthalpy of K₃NbF₈ was calculated and the value Δ_{dis}H_{K₃NbF₈} = -17.3

Table 3. Calculated Values of Dissociation Degree, α₀, the Equilibrium Constant of Reaction (*A*), and the Viscosity of Nondissociated K₃NbF₈

<i>T</i> /K	$\eta(\text{K}_3\text{NbF}_8)$ mPa s	<i>K</i>	α ₀	α ₀ *	α ₀ **
1050	4.01	0.468	0.42	0.61	0.44
1100	3.55	0.510	0.45	0.55	
1150	3.20	0.556	0.49	0.38	

* From density measurements [3]; ** from phase diagram calculation [2].

kJ mol⁻¹ was obtained. In Table 3 the calculated degree of dissociation is compared also with that obtained from the density and phase diagram measurement [2]. As may be seen from the table, the calculated degree of dissociation agrees well with that from the phase diagram calculation (α₀ = 0.44), while the values from the density measurement decrease with increasing temperature. This course is most probably unrealistic and may be caused by the inappropriate estimation of the density of nondissociated compound K₃NbF₈.

The viscosity of the ternary system LiF—KF—K₂NbF₇ at the temperature of 1100 K is shown in Fig. 4. It may be seen from the figure that the viscosity increases from KF through LiF to K₂NbF₇. The viscosity excess in the ternary system LiF—KF—K₂NbF₇, calculated for the temperature of 1100 K according to eqn (3), is shown in Fig. 5. From the figure

it can be seen that there is only one positive viscosity excess, the maximum of which is localized in the vicinity of the figurative point of K₃NbF₈. This observation confirms the very probable formation of K₃NbF₈ also in the ternary melts, which is the general feature of this system.

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