

Viscosity of the Molten System $\text{KF—KCl—K}_2\text{TiF}_6$

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Received 26 May 1995

The viscosity of the melts of the system $\text{KF—KCl—K}_2\text{TiF}_6$ has been measured by means of the computerized torsional pendulum method.

In the ternary system at constant temperature the viscosity increases from KCl through KF and from the binary system KF—KCl to K_2TiF_6 .

Additivity of the logarithms of viscosity was adopted as the ideal behaviour of the mixture. Negative deviations from such additive behaviour were found in the binary system KF—KCl probably due to the nonrandom mixing of the anions. Positive deviations from the ideal behaviour were found in the binaries $\text{KF—K}_2\text{TiF}_6$ and $\text{KCl—K}_2\text{TiF}_6$ probably due to the formation of larger TiF_7^{3-} and $\text{TiF}_6\text{Cl}^{3-}$ anions, respectively.

Statistically significant ternary interaction indicates the pronounced formation of both TiF_7^{3-} and $\text{TiF}_6\text{Cl}^{3-}$ anions also in the ternary system.

The system $\text{KF—KCl—K}_2\text{TiF}_6$ is a part of the quaternary system $\text{KF—KCl—KBF}_4\text{—K}_2\text{TiF}_6$, which is a promising electrolyte in the electrochemical synthesis of TiB_2 , especially when coherent coatings on metallic bases have to be prepared [1]. From the theoretical point of view, considerations on the structure, *i.e.* the ionic composition of the melts, can be also made on the basis of the viscosity data.

The thermodynamic analysis of the phase diagram of the system KF—KCl was made in [2]. The authors of this work claimed that it is a simple eutectic system. The viscosity of this system has been studied in [3].

The phase diagram of the system $\text{KF—K}_2\text{TiF}_6$ was studied in [4]. The congruently melting compound K_3TiF_7 with the melting temperature of 1048 K is formed in this system. The zero value of the tangent to the K_3TiF_7 liquidus curve at $x(\text{K}_2\text{TiF}_6) = 0.5$ indicates that this compound undergoes at melting a considerable thermal dissociation. The dissociation degree calculated on the basis of the experimentally determined phase diagram is $\alpha_0 = 0.64$ [5], which is in a very good accordance with the values obtained on the basis of the density data, $\alpha_0(1000 \text{ K}) = 0.6$ and $\alpha_0(1100 \text{ K}) = 0.7$ [6]. The viscosity of the system $\text{KF—K}_2\text{TiF}_6$ was measured in [7], where the positive values of the excess viscosity probably due to the formation of larger TiF_7^{3-} have been determined.

The phase diagram of the system $\text{KCl—K}_2\text{TiF}_6$ was studied in [8]. Like in the previous system, the congruently melting compound $\text{K}_3\text{TiF}_6\text{Cl}$ with the melting temperature of 964 K is formed in this system. $\text{K}_3\text{TiF}_6\text{Cl}$ undergoes at melting a considerable thermal dissociation with $\alpha_0 = 0.81$ at 1100 K, which was confirmed also by the density measurement [6].

The phase diagram of the ternary system $\text{KF—KCl—K}_2\text{TiF}_6$ has been measured in [9] and the density in [6]. From the results of both works the formation of congruently melting compounds K_3TiF_7 and $\text{K}_3\text{TiF}_6\text{Cl}$ also in the ternary system was confirmed.

In the present work the viscosity of the melts of the binary system $\text{KCl—K}_2\text{TiF}_6$ and of the ternary system $\text{KF—KCl—K}_2\text{TiF}_6$ was measured. On the basis of the obtained data the values of the excess viscosity were calculated to get information on the interaction of the components and the possible chemical reactions.

EXPERIMENTAL

The torsional 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 [10]. 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

Table 1. Coefficients *a* and *b* of the Temperature Dependence of the Logarithms of Viscosity of Individual Melts and the Standard Deviations of the Approximations (Composition in mole fractions)

x_{KF}	x_{KCl}	$x_{\text{K}_2\text{TiF}_6}$	<i>a</i>	<i>b</i> · 10 ⁻³ /K	<i>s</i> · 10 ³
1.000	0.000	0.000 ^a	-2.462	3.094	1.94
0.750	0.250	0.000 ^a	-2.800	3.267	1.96
0.500	0.500	0.000 ^a	-2.901	3.205	4.66
0.250	0.750	0.000 ^a	-2.875	3.106	5.02
0.000	1.000	0.000 ^a	-2.785	3.011	0.16
0.750	0.000	0.250 ^b	-2.443	3.389	2.25
0.500	0.000	0.500 ^b	-2.496	3.805	1.77
0.250	0.000	0.750 ^b	-2.660	4.330	2.29
0.000	0.000	1.000 ^b	-2.915	4.797	3.41
0.000	0.250	0.750	-2.991	4.492	4.76
0.000	0.500	0.500	-2.745	3.838	3.80
0.000	0.750	0.250	-2.651	3.267	1.79
0.167	0.083	0.750	-2.753	4.352	1.38
0.125	0.125	0.750	-2.785	4.359	1.29
0.083	0.167	0.750	-2.813	4.354	2.53
0.333	0.167	0.500	-2.718	3.970	2.53
0.250	0.250	0.500	-2.712	3.919	2.08
0.167	0.333	0.500	-2.791	3.976	2.08
0.500	0.250	0.250	-2.682	3.460	3.94
0.375	0.375	0.250	-2.692	3.422	3.67
0.250	0.500	0.250	-2.774	3.475	3.47

a) According to Ref. [3]; b) according to Ref. [7].

in the computational procedure. The whole measuring system, including the furnace temperature, was controlled by the computer. After all the input data and the required temperature profile were inserted, the measurement of the viscosity at the chosen 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 1 %.

For the preparation of samples the following chemicals were used: KF, KCl (both Lachema), and K₂TiF₆ (Fluka), all anal. grade. KF was dried in vacuum at 400 K in the presence of P₂O₅ for two weeks, KCl and K₂TiF₆ were dried at 680 K for 2 h. All handling and storage of the chemicals was done in the glove box.

The measurements were carried out in the temperature interval of approx. 100 K starting at 20–30 K above the temperature of primary crystallization. In the ternary system the cross-sections with the constant ratio $x(\text{KF})/x(\text{KCl}) = 0.5, 1, \text{ and } 2$ were chosen for the measurement. In the binary system KCl—K₂TiF₆ and in the above-mentioned cross-sections the figurative points with the content of 25 mole %, 50 mole %, and 75 mole % K₂TiF₆ were selected.

The temperature dependences of the viscosity of the individual melts were described using the equation

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

where η is the viscosity in mPa s and T is the temper-

ature 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 of eqn (1), for the investigated melts are given in Table 1.

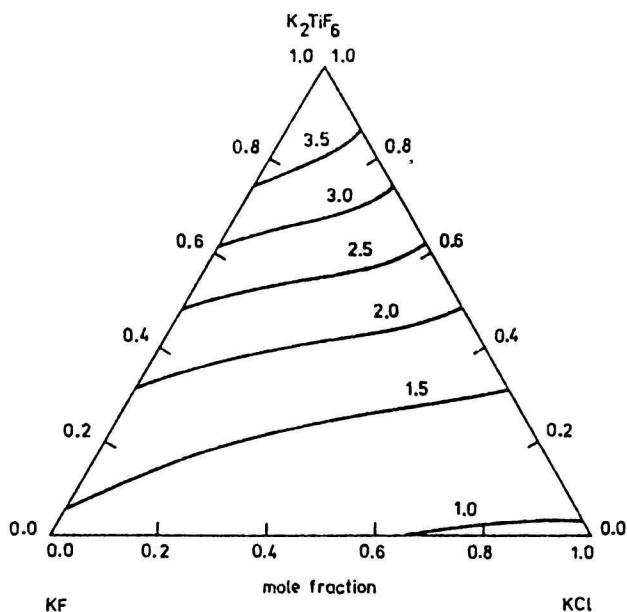


Fig. 1. Iso-viscosity lines of the system KF—KCl—K₂TiF₆ at the temperature of 1100 K.

RESULTS AND DISCUSSION

The iso-viscosity lines of the system KF—KCl—K₂TiF₆ at the temperature of 1100 K are shown in Fig. 1. From the figure it is obvious that the viscosity of the ternary melts increases from KCl through KF and from the binary system KF—KCl to K₂TiF₆. The higher viscosity of KF compared with that of KCl is also due to the presence of F—F bridges in the KF melt.

The composition and temperature dependence of viscosity of real solutions can be described by the general equation

$$\ln\{\eta\} = f\left(x_i, \frac{1}{T}\right) \quad (2)$$

To get some information on the structure of the melt it is very important to define the viscosity course of the ideal solution. The additivity of the logarithms of viscosity has been frequently supposed to obey the ideal behaviour [11, 12]. This assumption is based on the validity of the Arrhenius plot for the viscosity and on the additivity of activation energies of viscous flow. For the ternary system it may be then written

$$\ln\{\eta_{id}\} = x_1 \ln\{\eta_1\} + x_2 \ln\{\eta_2\} + x_3 \ln\{\eta_3\} \quad (3)$$

or

$$\eta_{id} = \eta_1^{x_1} \cdot \eta_2^{x_2} \cdot \eta_3^{x_3} \quad (4)$$

where η_i 's are the viscosities of pure components and x_i 's are their mole fractions in the mixture.

Taking into account eqn (1), for the viscosity of the three-component system we can then write

$$\begin{aligned} \ln\{\eta\} = & \sum_{i=1}^3 x_i \left(A_i + \frac{1}{T} A_{iT} \right) + \\ & + \sum_{i \neq j}^3 x_i x_j \sum_{n=0}^k x_j^n \left(B_{ijn} + \frac{1}{T} B_{ijTn} \right) + C x_1^p x_2^r x_3^s \end{aligned} \quad (5)$$

The first term represents the ideal behaviour, the next one the interactions in the binary systems, both in dependence on temperature, while the last term describes the interaction of all three components as temperature-independent. The calculation of the coefficients $A_i, A_{iT}, B_{ijn}, B_{ijTn}$, and C was performed using the multiple linear regression analysis, omitting the statistically nonsignificant terms on the 0.95 confidence level. The following final equation was obtained

$$\begin{aligned} \ln\{\eta\} = & A_1 x_1 + A_2 x_2 + A_3 x_3 + \\ & + \frac{1}{T} (A_{1T} x_1 + A_{2T} x_2 + A_{3T} x_3) + \\ & + (B_{120} x_1 x_2 + B_{132} x_1 x_3^2 + B_{232} x_2 x_3^2) + \\ & + \frac{1}{T} (B_{12T0} x_1 x_2 + B_{13T2} x_1 x_3^2 + B_{23T2} x_2 x_3^2) + \\ & + C x_1^2 x_2^3 \end{aligned} \quad (6)$$

Table 2. Coefficients $A_i, A_{iT}, B_{ijn}, B_{ijTn}$, and C and the Standard Deviation of Approximation of the Concentration and Temperature Dependence of the Viscosity of the Ternary System KF—KCl—K₂TiF₆

Coefficient	Value $\pm s$ in coefficient
A_1	-2.438 ± 0.014
A_2	-2.777 ± 0.022
A_3	-1.948 ± 0.129
A_{1T}/K	3068 ± 17
A_{2T}/K	3002 ± 24
A_{3T}/K	3641 ± 150
B_{120}	-1.000 ± 0.068
B_{132}	-5.728 ± 1.585
B_{232}	-11.20 ± 1.55
B_{12T0}/K	620.1 ± 73.4
B_{13T2}/K	8072 ± 1820
B_{23T2}/K	13390 ± 1782
C	21.20 ± 2.42
s in eqn (6)	7.1×10^{-4}

The regression coefficients of eqn (6), $A_i, A_{iT}, B_{ijn}, B_{ijTn}$, and C and the standard deviation of approximation are given in Table 2. The validity of eqn (6) is in the temperature interval 700—1300 K.

The excess viscosity has been calculated according to the relation

$$\eta_{ex} = \eta - \eta_{id} \quad (7)$$

where η was calculated according to eqn (6) and η_{id} according to eqn (4). The excess viscosity defined in

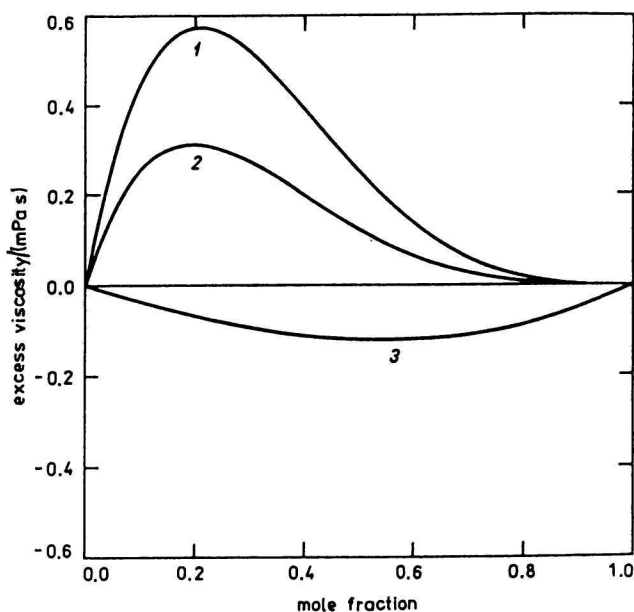


Fig. 2. Excess viscosity of the boundary binary systems at the temperature of 1100 K. 1. K₂TiF₆—KF; 2. K₂TiF₆—KCl; 3. KF—KCl.

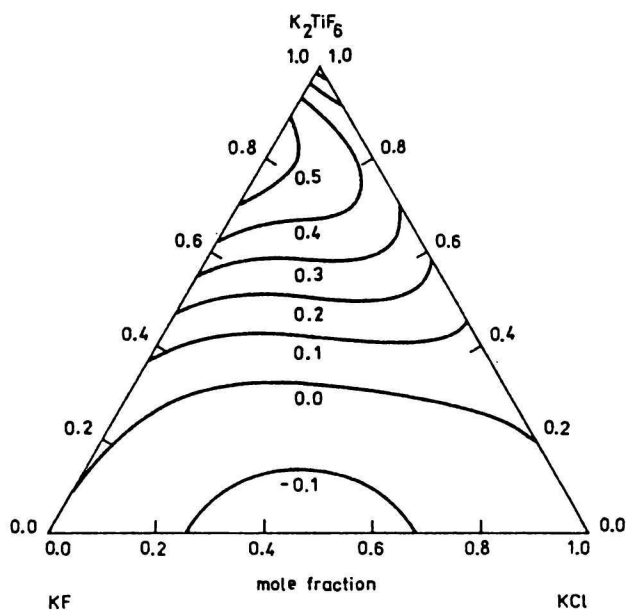


Fig. 3. Isolines of excess viscosity of the system KF—KCl—K₂TiF₆ at the temperature of 1100 K.

such a way already gives the information on the structure of the melt.

From the data given in Tables 1 and 2 the course of the excess viscosity in the binary systems may be drawn (Fig. 2). In the binary system KF—KCl negative deviations from the adopted ideal behaviour were observed, which may be due to the nonrandom mixing of the anions.

In the binary system KF—K₂TiF₆ the anion TiF₇³⁻ is formed [4], which increases the viscosity of the melt. Therefore the excess viscosity in this system is positive. Similar conclusions may be drawn for the system KCl—K₂TiF₆, where the anion TiF₆Cl³⁻, formed in this system [8], increases the viscosity as well.

The isolines of excess viscosity of the ternary system KF—KCl—K₂TiF₆ are shown in Fig. 3. From the figure it follows that the formation of anions TiF₇³⁻ and TiF₆Cl³⁻, respectively, takes place also in the ternary system. From the positive value of the statistically significant ternary interaction, described by coefficient *C* in eqn (6), it follows that the degrees of their thermal dissociation in the ternary system decrease.

Acknowledgements. The present work was financially supported by the Grant Agency for Science of the Slovak Republic under the No. 2/1164/94.

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Translated by V. Daněk