Viscosity of Melts of the System KCl—KBF$_4$—K$_2$TiF$_6$

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The viscosity of melts of the system KCl—KBF$_4$—K$_2$TiF$_6$ has been measured by means of the computerized torsional pendulum method. The viscosity of KCl is higher than that of KBF$_4$ at the same temperature, most probably due to the substantial overheating of KBF$_4$. In the ternary system the viscosity increases with increasing content of K$_2$TiF$_6$.

Additivity of logarithms of viscosity was adopted as the ideal behaviour of the mixture. Negative deviations from such additive behaviour were found in the binary system KCl—KBF$_4$ probably due to the breaks of the weak B—Cl—B bridges caused by the excess of Cl$^-$ ions. Positive deviations from the ideal behaviour were found in the binaries KCl—K$_2$TiF$_6$ and KBF$_4$—K$_2$TiF$_6$ due to the formation of larger anions TiF$_6$Cl^{3-} and TiF$_7^{3-}$ caused by the reactions

$$K_2TiF_6(l) + KCl(l) = K_3TiF_6Cl(l)$$

$$KBF_4(l) + K_2TiF_6(l) = K_3TiF_7(l) + BF_3(g)$$
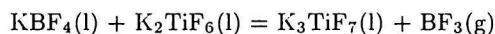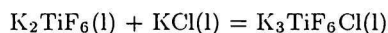
Statistically significant ternary interaction confirmed that the above chemical reactions take place also in the ternary system.

The study of viscosity of the melts of the system KCl—KBF$_4$—K$_2$TiF$_6$ is interesting from the practical as well as from the theoretical point of view. This system is a part of the quaternary system KF—KCl—KBF$_4$—K$_2$TiF$_6$ the melts of which are used as electrolytes for the electrochemical deposition of smooth and adherent TiB$_2$ layers on metallic bases [1]. From the theoretical point of view it is possible from the viscosity knowledge to draw some conclusions on the structure, resp. the ionic composition of these melts.

The phase diagram of the boundary binary system KCl—KBF$_4$ was studied in [2]. It is a simple eutectic system with the eutectic point at 75 mole % KBF$_4$ and 737 K. The density of this system was measured in [3].

The phase diagram of the binary system KCl—K$_2$TiF$_6$ was measured in [4]. The congruently melting compound K$_3$TiF$_6$Cl with the melting point of 964 K is formed in the system. This compound undergoes at melting an extended thermal dissociation. The volume properties of the system KCl—K$_2$TiF$_6$ were studied in [5]. It was found that this system exhibits in the whole concentration range negative volume excess.

The phase diagram of the system KBF$_4$—K$_2$TiF$_6$ was studied in [6]. It is a simple eutectic system, the coordinates of the eutectic point being 28 mole % K$_2$TiF$_6$ and 721 K. The density of this system was measured in [7].

The phase diagram of the ternary system KCl—KBF$_4$—K$_2$TiF$_6$ was measured in [8]. The congruently

melting compound K$_3$TiF$_6$Cl, formed in the system, divided the ternary system into two simple eutectic ones. The measurement of the volume properties of this system was performed in [9] and two different regions, one with volume expansion and one with volume contraction were found.

The viscosity of the boundary binary systems KCl—KBF$_4$, KCl—K$_2$TiF$_6$, and KBF$_4$—K$_2$TiF$_6$ was measured in [10—12]. It was found that the system KCl—KBF$_4$ exhibits negative deviation while the systems KCl—K$_2$TiF$_6$ and KBF$_4$—K$_2$TiF$_6$ positive deviations from the accepted additivity of the logarithms of viscosity course.

The aim of the present work was the determination of the viscosity of the melts of the ternary system KCl—KBF$_4$—K$_2$TiF$_6$. On the basis of the obtained data the excess viscosity was calculated and the information on the mutual interactions of components as well as on possible chemical reactions was elucidated.

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 [13]. 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

Table 1. Regression Coefficients a, b, and the Standard Deviations σ of Approximation of the Temperature Dependence of Logarithm of Numerical Value of the Viscosity of the System KCl—KBF_4—K_2TiF_6

x_{KCl}	x_{KBF_4}	$x_{K_2TiF_6}$	a	b 10^{-3} K^{-1}	σ 10^3
1.000	0.000	0.000	−2.785	4.911	8.88
0.750	0.250	0.000	−3.339	3.499	5.40
0.500	0.500	0.000	−3.159	3.124	4.70
0.250	0.750	0.000	−3.428	3.234	4.16
0.000	1.000	0.000	−3.068	2.874	6.95
0.750	0.000	0.250	−2.651	3.267	1.79
0.500	0.000	0.500	−2.745	3.838	3.80
0.250	0.000	0.750	−2.991	4.492	4.76
0.000	0.000	1.000	−2.947	4.835	3.38
0.000	0.750	0.250	−3.033	3.417	1.55
0.000	0.500	0.500	−2.710	3.660	2.46
0.000	0.250	0.750	−3.335	4.870	4.00
0.563	0.187	0.250	−3.724	4.220	2.56
0.375	0.375	0.250	−3.578	3.953	5.99
0.187	0.563	0.250	−3.917	4.144	11.74
0.375	0.125	0.500	−3.221	4.262	3.09
0.250	0.250	0.500	−3.826	4.785	9.35
0.125	0.375	0.500	−4.117	5.036	7.27
0.187	0.063	0.750	−3.402	4.910	8.88
0.125	0.125	0.750	−3.380	4.922	8.78
0.063	0.187	0.750	−3.615	5.174	1.58

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 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 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 1 %.

For the preparation of samples the following chemicals were used: KCl, KBF_4, and K_2TiF_6, all Fluka, anal. grade. The chemicals 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 cross-sections with the constant

ratio $x(KCl)/x(KBF_4) = 3$, 1, and 0.333 were chosen for the measurement. In the boundary binary systems and in the above-mentioned cross-sections the figurative points with the content of 25 mole %, 50 mole %, and 75 mole % K_2TiF_6 were selected.

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

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

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, for the investigated melts are given in Table 1.

RESULTS AND DISCUSSION

The iso-lines of constant viscosity of the system KCl—KBF_4—K_2TiF_6 at the temperature of 1100 K are shown in Fig. 1. It may be seen from the figure that the viscosity increases from KBF_4 through KCl to K_2TiF_6. The surprisingly low viscosity of KBF_4 at the given temperature can be explained as the consequence of the appreciable overheating of KBF_4 in comparison with KCl and K_2TiF_6.

For the suggestion of the possible structure of the given ternary system from the viscosity measurement the viscosity course in the "ideal system" has to be defined in a proper way. In the present work 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

Table 2. Coefficients η_i, A_{nij}, B, and the Standard Deviations of Approximation of the Concentration Dependence of Viscosity of the System KCl—KBF_4—K_2TiF_6

Quantity	Temperature/K		
mPa s	1000	1050	1100
$\{\eta_{KCl}\}$	1.287	1.104	0.960
$\{\eta_{KBF_4}\}$	0.822	0.715	0.631
$\{\eta_{K_2TiF_6}\}$	6.907	5.419	4.342
$\{A_{112}\}$	-0.763 ± 0.221	-0.700 ± 0.163	-0.644 ± 0.151
$\{A_{013}\}$	-4.502 ± 0.318	-3.274 ± 0.224	-2.427 ± 0.199
$\{A_{023}\}$	-4.744 ± 0.308	-3.446 ± 0.219	-2.549 ± 0.195
B	-57.151 ± 11.550	-62.285 ± 8.185	-63.784 ± 7.304
$\{\sigma\}$	0.051	0.037	0.033
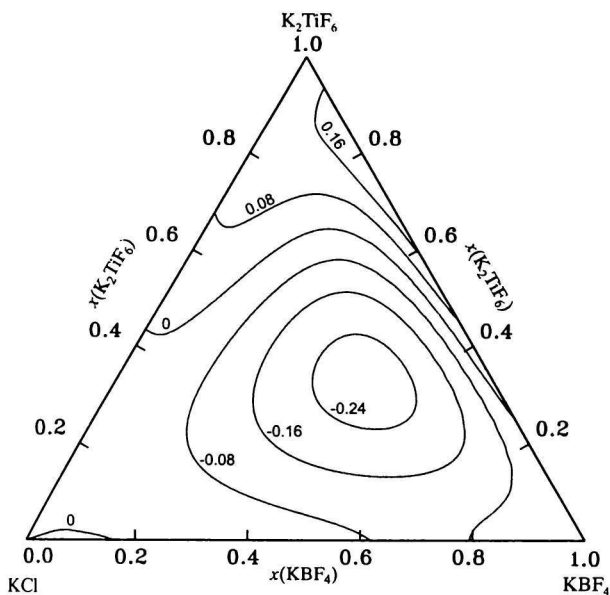
Fig. 1. Viscosity of the system KCl—KBF_4—K_2TiF_6 at the temperature of 1100 K. Numerical values are $\eta/(\text{mPa s})$.

flow. For the ternary system at constant temperature it then holds

$$\ln\{\eta_{id}\} = x_1 \ln\{\eta_1\} + x_2 \ln\{\eta_2\} + x_3 \ln\{\eta_3\} \quad (2)$$

resp.

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

where η_i are viscosities of pure components and x_i are their mole fractions. For the real system it can be then written

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

where η_{ex} is the viscosity excess. The excess viscosity defined in such a way may already yield the information on the structure of the investigated system and

it can be expressed in the form of Redlich—Kister's type equation

$$\eta_{ex} = \sum_{i \neq j}^{3} x_i x_j \sum_{n=0}^{k} A_{nij} x_j^n + B x_1^a x_2^b x_3^c \quad (5)$$

The first term represents the interactions in the binary systems while the second one describes the interaction of all three components. The calculation of coefficients A_{nij} and B for the chosen temperature was performed using the multiple linear regression analysis omitting the statistically unimportant terms on the 0.99 confidence level. The final equation for the viscosity in the investigated system is in the form

$$\eta = \eta_1^{x_1} \eta_2^{x_2} \eta_3^{x_3} + A_{112} x_1 x_2^2 + A_{013} x_1 x_3 +$$
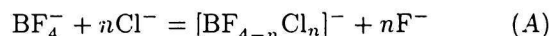$$+ A_{023} x_2 x_3 + B x_1 x_2^2 x_3^2 \quad (6)$$

The obtained regression coefficients of eqn (6) as well as the standard deviations of approximations for the investigated system at the temperatures of 1000 K, 1050 K, and 1100 K are given in Table 2. The first term in eqn (6) represents the "ideal" behaviour. The viscosity excess was calculated according to the relation

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

where η is the viscosity calculated according to eqn (6) and η_{id} was calculated according to eqn (3).

The viscosity excess in the ternary system KCl—KBF_4—K_2TiF_6 calculated according to eqn (7) for the temperature of 1100 K is shown in Fig. 2. The viscosity excess for the individual binary systems is shown in Fig. 3.

From Fig. 2 it can be seen that there are two different regions in the viscosity course of the ternary system KCl—KBF_4—K_2TiF_6. The first region with lower K_2TiF_6 concentration exhibits negative viscosity excess while the second one, with higher K_2TiF_6 concentration, shows positive viscosity excess. With regard to the fact that the investigated system has

Fig. 2. Excess viscosity in the system KCl—KBF$_4$—K$_2$TiF$_6$ at the temperature of 1100 K. Numerical values are $\eta_{ex}/$(mPa s).

Fig. 3. The viscosity excess for the individual binary systems. *1.* KCl—KBF$_4$; *2.* KCl—K$_2$TiF$_6$; *3.* KBF$_4$—K$_2$TiF$_6$

a common cation, the observed deviations from the "ideal" behaviour can be ascribed to the mutual interactions of anions only.

In the binary system KCl—KBF$_4$ the most probable interaction is the exchange of the fluorine atoms of the BF$_4^-$ tetrahedra for the chlorine ones according to the general scheme

$$\text{BF}_4^- + n\text{Cl}^- = [\text{BF}_{4-n}\text{Cl}_n]^- + n\text{F}^- \qquad (A)$$

and the presence of the $[\text{BF}_{4-n}\text{Cl}_n]^-$ mixed anions in the melts can be expected. The less stable B—Cl—B bonds, as well as the lower concentration of the stronger B—F—B ones lead to the negative deviations of the viscosity (see curve *1* in Fig. 3). In the region of the high KBF$_4$ concentration the exchange reaction (A) is shifted to the right.

In the boundary binary system KCl—K$_2$TiF$_6$ the compound K$_3$TiF$_6$Cl is formed according to the reaction

$$\text{K}_2\text{TiF}_6(\text{l}) + \text{KCl}(\text{l}) = \text{K}_3\text{TiF}_6\text{Cl}(\text{l}) \qquad (B)$$
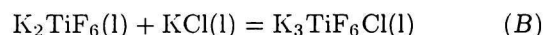
$$\Delta_r G^\circ_{1000 \text{ K}} = 0.587 \text{ kJ mol}^{-1}$$

However, K$_3$TiF$_6$Cl is less stable, its dissociation degree at the temperature of 1100 K attains the value $\alpha_0 = 0.81$, and its influence on the viscosity course is low. Thus the positive deviation of the viscosity is observable only at high concentration of K$_2$TiF$_6$ (see curve *2* in Fig. 3).

In the last boundary binary system KBF$_4$—K$_2$TiF$_6$ the following chemical reaction can be suggested

$$\text{KBF}_4(\text{l}) + \text{K}_2\text{TiF}_6(\text{l}) = \text{K}_3\text{TiF}_7(\text{l}) + \text{BF}_3(\text{g}) \qquad (C)$$
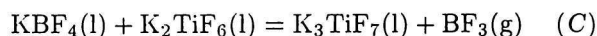
$$\Delta_r G^\circ_{1100 \text{ K}} = 10.71 \text{ kJ mol}^{-1}$$

The originating K$_3$TiF$_7$ subsequently thermally dissociates according to the equation

$$\text{K}_3\text{TiF}_7(\text{l}) \Leftrightarrow \text{K}_2\text{TiF}_6(\text{l}) + \text{KF}(\text{l}) \qquad (D)$$
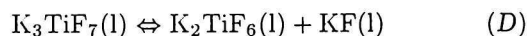
$$\Delta_r G^\circ_{1100 \text{ K}} = 0.963 \text{ kJ mol}^{-1}$$

The lower dissociation degree of K$_3$TiF$_7$ at 1100 K, calculated from the density data, $\alpha_0 = 0.70$ [5], the relatively low positive value of the Gibbs energy of reaction (C), as well as the escape of gaseous BF$_3$ document the higher stability of K$_3$TiF$_7$ in the investigated system causing the positive deviation of viscosity from the "ideal" behaviour.

In the ternary system KCl—KBF$_4$—K$_2$TiF$_6$ the following chemical reaction can take place

$$\text{KCl}(\text{l}) + 2\text{K}_2\text{TiF}_6(\text{l}) + \text{KBF}_4(\text{l}) =$$

$$= \text{K}_3\text{TiF}_7(\text{l}) + \text{K}_3\text{TiF}_6\text{Cl}(\text{l}) + \text{BF}_3(\text{g}) \qquad (E)$$
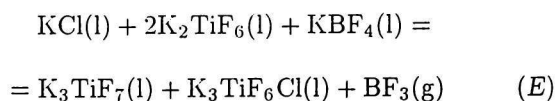
$$\Delta_r G^\circ_{1100 \text{ K}} = 12.05 \text{ kJ mol}^{-1}$$

The Gibbs energy of reaction (E) was calculated on the basis of the Gibbs energy of reactions (B), (C), and (D) as well as of the Gibbs energies of formation of KCl, KBF$_4$, and BF$_3$ given in [14]. With regard
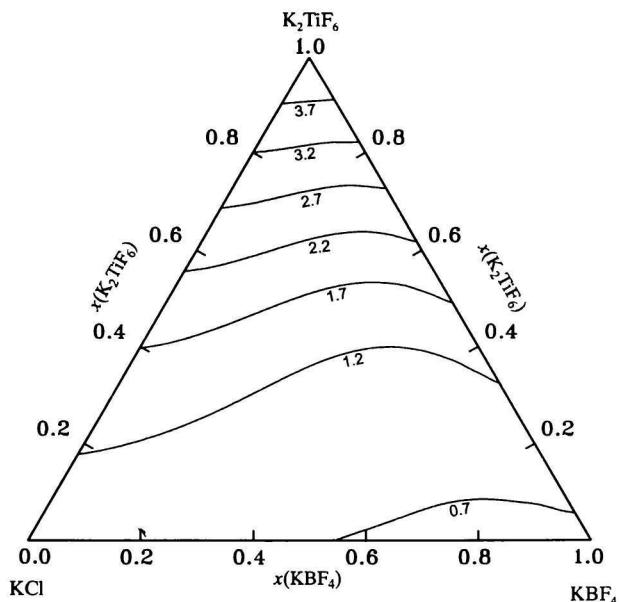
to its relatively low positive value and the escape of gaseous BF_3 the reaction (E) takes probably place also in the ternary system.

REFERENCES

1. Matiašovský, K., Grjotheim, K., and Makyta, M., *Metall. 42*, 1192 (1988).
2. Daněk, V., Votava, I., Chrenková-Paučírová, M., and Matiašovský, K., *Chem. Zvesti 30*, 841 (1976).
3. Chrenková, M. and Daněk, V *Chem. Papers 45*, 213 (1991).
4. Chernov, R. V. and Ermolenko, P. M., *Zh. Neorg. Khim. 18*, 1372 (1973).
5. Daněk, V., Šiška, J., and Matiašovský, K. *Chem. Papers 42*, 753 (1988).
6. Chrenková, M., Patarák, O., and Daněk, V., *Thermochim. Acta 273*, 157 (1996).
7. Chrenková, M., Daněk, V., and Nguyen, D. K., *Z. Phys. Chem. 194*, 51 (1996).
8. Chrenková, M., Patarák, O., and Daněk, V., *Chem. Papers 49*, 167 (1995).
9. Chrenková, M., Daněk, V., and Silný, A., *Ber. Bunsenges. Phys. Chem.*, in press.
10. Daněk, V. and Nguyen, D. K., *Chem. Papers 49*, 64 (1995).
11. Nguyen, D. K. and Daněk, V., *Chem. Papers 50*, 4 (1996).
12. Silný, A., Daněk, V and Nguyen, D. K., *Ber. Bunsenges. Phys. Chem. 99*, 985 (1995).
13. Silný, A., *Sdělovací technika 38*, 101 (1990).
14. Stuhl, D. P and Prophet, H., *JANAF Thermochemical Tables*, 2nd Edition. NSRDS, Nat. Bur. Stand., Washington, 1971.

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