

# Viscosity of the System KF—KCl—KBF<sub>4</sub>

V. DANĚK and D. K. NGUYEN

*Institute of Inorganic Chemistry, Slovak Academy of Sciences,  
SK-842 36 Bratislava*

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The viscosity of the melts of the system KF—KCl—KBF<sub>4</sub> has been measured by means of the computerized torsional pendulum method.

Additivity of the logarithms of viscosity was adopted as the ideal behaviour of the mixture. Negative deviations from such additive behaviour were found in all the boundary binary and ternary systems.

In the pure KBF<sub>4</sub> melt BF<sub>4</sub><sup>-</sup> tetrahedra tend to link, forming relatively weak B—F—B bonds. Introducing F<sup>-</sup> ions into the KBF<sub>4</sub> melt by addition of KF, the B—F—B bridges break off, which leads to the lowering of the viscosity and the negative deviation from the ideal behaviour in the KF—KBF<sub>4</sub> system. Introducing Cl<sup>-</sup> ions into the KBF<sub>4</sub> melt, the exchange of fluoride atoms in the BF<sub>4</sub><sup>-</sup> tetrahedron for the chloride ones according to the general scheme



takes place. Consequently, the less stability of the B—Cl—B bridges and the lower concentration of the B—F—B ones lead to the negative deviation of the viscosity course in the KCl—KBF<sub>4</sub> system. These processes take place obviously in the ternary system as well.

The molten system KF—KCl—KBF<sub>4</sub> is an alternative electrolyte for electrochemical boriding of steels [1] and along with K<sub>2</sub>TiF<sub>6</sub> serves as the electrolyte for the electrochemical synthesis of titanium diboride, especially when coherent deposits on metallic substrates have to be prepared [2]. The knowledge of the structure of these melts is needed for the understanding of the mechanism of the electrochemical process involving electrodeposition of boron and the synthesis of titanium diboride on the electrode surface. The interaction of components and the possible reactions which may take place in the melt affect the ionic composition, thus affecting the kind of the electroactive species. The suitable choice of the electrolyte composition may prevent the formation of volatile compounds which leads to undesirable exhalations and lowers the efficiency of the process.

The phase diagrams of the boundary binary systems may be found in the literature [3—6]. In all cases they are the simple eutectic systems. The phase diagram of the ternary system KF—KCl—KBF<sub>4</sub> was measured in [7]. The system is a simple eutectic one with the coordinates of the eutectic point of 19.4 mole % KF, 19.2 mole % KCl, 61.4 mole % KBF<sub>4</sub> and the temperature of the eutectic crystallization of 695 K.

From among the physicochemical properties the density of the ternary system KF—KCl—KBF<sub>4</sub> was measured in [8] and the electrical conductivity in [9]. On the basis of the physicochemical analysis [7—9] the substitution of the fluoride atoms in the BF<sub>4</sub><sup>-</sup> tetrahedron by the chloride ones was suggested.

In the present work the viscosity of the melts of the system KF—KCl—KBF<sub>4</sub> 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 cm<sup>3</sup> 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 con-

trolled 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: KF (Lachema), KCl and  $\text{KBF}_4$  (both Fluka), all anal. grade. KF was dried in vacuum at 400 K in the presence of  $\text{P}_2\text{O}_5$  for two weeks, KCl and  $\text{KBF}_4$  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  $x(\text{KF})/x(\text{KCl}) = 3, 1$ , 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  $\text{KBF}_4$  content of 25 mole %, 50 mole %, and 75 mole % were selected.

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

$$\ln \left( \frac{\eta}{\text{mPa s}} \right) = a + \frac{b}{T} \quad (1)$$

where  $\eta$  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.

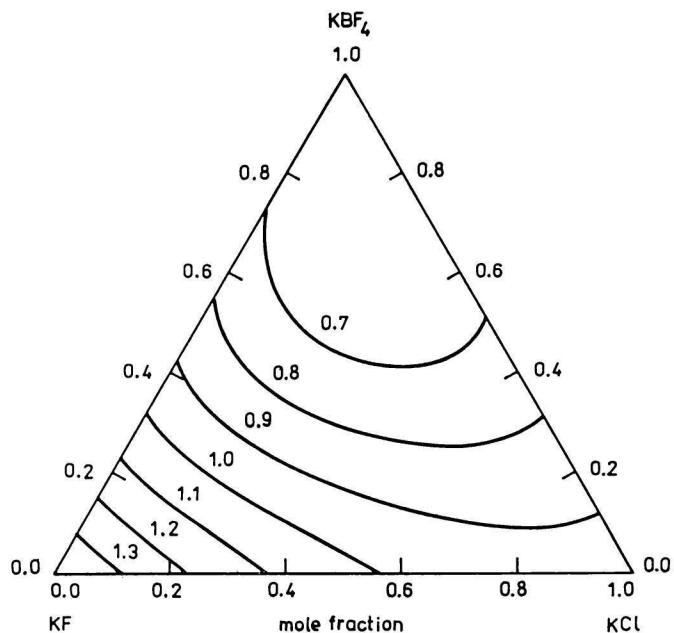
## RESULTS AND DISCUSSION

The iso-viscosity lines of the system KF—KCl— $\text{KBF}_4$  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  $\text{KBF}_4$  through KF to KCl. Surprisingly low seems to be the viscosity of  $\text{KBF}_4$ , however, there is a substantial overheating of the  $\text{KBF}_4$  melt at 1100 K when compared with those of KF and KCl.

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 logarithm 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

**Table 1.** Coefficients  $a$  and  $b$  of the Temperature Dependence of the Viscosity and the Standard Deviations of the Approximations

$x_{\text{KF}}$	$x_{\text{KCl}}$	$x_{\text{KBF}_4}$	$a$	$b$	$10^{-3}/\text{K}$	$s$	$10^3$
1.000	0.000	0.000	-2.462	3.094	1.94		
0.750	0.250	0.000	-2.800	3.267	1.96		
0.500	0.500	0.000	-2.901	3.205	4.66		
0.250	0.750	0.000	-2.875	3.106	5.02		
0.000	1.000	0.000	-2.785	3.011	0.16		
0.750	0.000	0.250	-1.467	1.735	3.47		
0.500	0.000	0.500	-3.084	3.130	4.78		
0.250	0.000	0.750	-3.145	3.060	3.12		
0.000	0.000	1.000	-3.046	2.857	2.14		
0.000	0.750	0.250	-3.339	3.499	5.40		
0.000	0.500	0.500	-3.159	3.124	4.70		
0.000	0.250	0.750	-3.428	3.234	4.16		
0.563	0.187	0.250	-3.262	3.513	5.98		
0.375	0.375	0.250	-3.315	3.425	5.57		
0.187	0.563	0.250	-3.370	3.456	1.53		
0.375	0.125	0.500	-3.521	3.515	6.45		
0.250	0.250	0.500	-3.550	3.436	2.32		
0.125	0.250	0.500	-3.550	3.436	2.32		
0.187	0.063	0.750	-3.526	3.515	3.08		
0.125	0.125	0.750	-3.445	3.234	2.24		
0.063	0.187	0.750	-3.446	3.230	1.69		



**Fig. 1.** Iso-viscosity lines of the system KF—KCl— $\text{KBF}_4$  at the temperature of 1100 K.

additivity of activation energies of viscous flow. For the ternary system it may be then written

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

or

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

where  $\eta_i$ 's are the viscosities of pure components and  $x_i$ 's are their mole fractions in the mixture. For real solutions we can then write

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

The excess viscosity defined in such a way already gives the information on the structure of the melt and may be expressed in the form of the Redlich—Kister type excess function

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

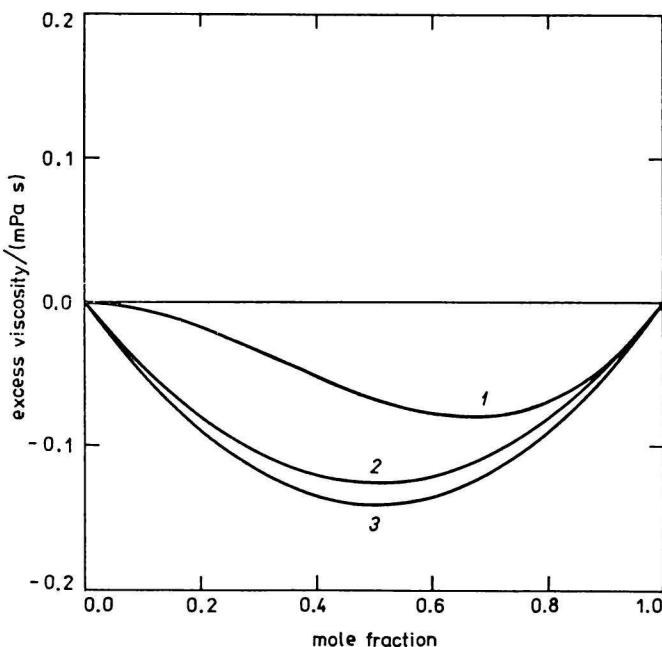
The first term represents the interactions in the binary system, while the second one describes the interaction of all three components. The calculation of the coefficients  $A_{nij}$  and  $B$  for the system KF—KCl—KBF<sub>4</sub> was performed using the multiple linear regression analysis, omitting the statistically nonimportant terms on the 0.95 confidence level. The following final equation was obtained

$$\begin{aligned} \eta = & \eta_1^{x_1} \cdot \eta_2^{x_2} \cdot \eta_3^{x_3} + A_{12} x_1 x_2 + A_{13} x_1 x_3 + \\ & + A_{23} x_2 x_3 + B x_1 x_2 x_3^2 \end{aligned} \quad (6)$$

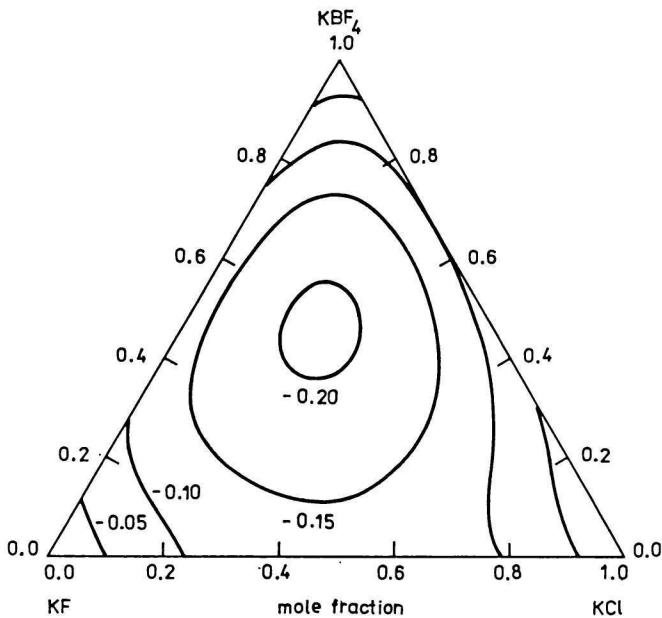
The regression coefficients as well as the standard deviations of approximations for the temperatures of 1000 K, 1050 K, and 1100 K are given in Table 2. The excess viscosity of the individual binary systems at 1100 K is shown in Fig. 2 and the isotherms of the excess viscosity of the ternary system KF—KCl—KBF<sub>4</sub> are shown in Fig. 3.

**Table 2.** Coefficients  $\eta_i$ ,  $A_{ij}$ , and  $B$  and the Standard Deviations of Approximations of the Concentration Dependence of the Viscosity of the Ternary System KF—KCl—KBF<sub>4</sub>

Coefficient	1000 K	1050 K	1100 K
$\eta_{\text{KF}}/(\text{mPa s})$	1.882	1.625	1.421
$\eta_{\text{KCl}}/(\text{mPa s})$	1.253	1.086	0.953
$\eta_{\text{KBF}_4}/(\text{mPa s})$	0.827	0.722	0.638
$A_{12}/(\text{mPa s})$	$-0.625 \pm 0.091$	$-0.593 \pm 0.061$	$-0.562 \pm 0.050$
$A_{13}/(\text{mPa s})$	$-0.788 \pm 0.091$	$-0.694 \pm 0.061$	$-0.501 \pm 0.051$
$A_{23}/(\text{mPa s})$	$-0.562 \pm 0.165$	$-0.565 \pm 0.110$	$-0.541 \pm 0.092$
$B/(\text{mPa s})$	$-2.369 \pm 1.909$	$-2.920 \pm 1.275$	$-4.576 \pm 1.062$
$s/(\text{mPa s})$	0.035	0.026	0.019



**Fig. 2.** Excess viscosity of the boundary binary systems at the temperature of 1100 K. 1. KCl—KBF<sub>4</sub>; 2. KF—KBF<sub>4</sub>; 3. KF—KCl.



**Fig. 3.** Excess iso-viscosity lines of the system KF—KCl—KBF<sub>4</sub> at the temperature of 1100 K.

From Fig. 2 it follows that in all three binary systems negative deviations from the ideal behaviour were observed. With regard to the fact that the investigated system has a common cation, the observed deviations from the ideal behaviour must be a consequence of the anionic interaction only.

In the pure KBF<sub>4</sub> melt BF<sub>4</sub><sup>-</sup> tetrahedra tend to link, forming relatively weak B—F—B bonds. The strength of this bond depends strongly on temperature, lowering substantially the viscosity of KBF<sub>4</sub> with the increasing temperature. Introducing F<sup>-</sup> ions into the KBF<sub>4</sub> melt by addition of KF, the B—F—B bridges break off, which leads to the lowering of the viscosity and the negative deviation from the ideal behaviour in the KF—KBF<sub>4</sub> system (curve 2 in Fig. 2).

Similar situation may be observed in the binary system KCl—KBF<sub>4</sub>. Introducing Cl<sup>-</sup> ions into the KBF<sub>4</sub> melt the exchange of fluoride atoms in the BF<sub>4</sub><sup>-</sup> tetrahedron for the chloride ones according to the general scheme



and the possible presence of the [BF<sub>4-n</sub>Cl<sub>n</sub>]<sup>-</sup> mixed anions may be achieved. Consequently, the less stability of the B—Cl—B bridges and the lower concentration of the B—F—B ones lead to the negative deviation of the viscosity course in the KCl—KBF<sub>4</sub> system (curve 1 in Fig. 2). This explanation is supported also by the asymmetric course of the excess viscosity which is due to the shift to the right of eqn (A) in the region of high concentration of KBF<sub>4</sub>.

In the binary system KF—KCl the origin of the negative deviation, like in the case of the electric conductivity, may be sought in the mutual influence of the dissociation degree, described in detail in the dissociation model of the electric conductivity of molten salts mixtures [13, 14].

The negative deviations of the viscosity found in the ternary system KF—KCl—KBF<sub>4</sub> have obviously the same origin as it was described for the boundary binary systems. As it follows from Fig. 3, the maximum deviation is localized near the KF—KBF<sub>4</sub> boundary,

which was observed also in the study of the phase equilibria [7], density [8], and electric conductivity [9]. The exchange reaction according to eqn (A) was confirmed using the IR spectroscopy investigations in [15].

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