

Structure and Properties of the KF—KCl—KBF₄ Melts

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On the basis of the phase diagram, density, conductivity, and viscosity measurements as well as the direct spectroscopic analysis, the structure of the KF—KCl—KBF₄ melts has been elucidated. From the physicochemical analysis it follows that a significant ternary interaction of all anions present in the melt takes place. The deviation from the ideal behaviour is due to the break off of the relatively weak B—F—B bonds between the BF₄⁻ tetrahedra, the mixing of anions with different ionic radius, as well as the exchange of the fluorine atoms in the BF₄⁻ tetrahedra for the chlorine ones. The presence of [BF_{4-n}Cl_n]⁻ anions was confirmed by means of the IR spectroscopy of quenched samples.

The molten system KF—KCl—KBF₄ is interesting as the possible electrolyte for electrochemical boriding of steels [1] and along with K₂TiF₆ as electrolyte for the electrochemical synthesis of titanium diboride, especially to obtain protective layers on metallic substrates [2]. The knowledge of the structure of these melts is needed for the deeper understanding of the mechanism of the electrochemical processes involving electrodeposition of boron and the formation of titanium diboride on the electrode surface.

The interaction of components and the possible chemical reactions, which may take place in the melt, affect the ionic composition, thus determining 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. In the phase diagram of the system KBF₄—KCl, determined in [5], the formation of the congruently melting compound 11KBF₄ KCl was suggested. However, the existence of this compound was not confirmed in the later investigation [6]. The phase diagram of the ternary system KF—KCl—KBF₄ was measured in [7]. The system is a simple eutectic one with the coordinates of the eutectic point of 19.2 mole % KF, 18.4 mole % KCl, 61.4 mole % KBF₄ and the eutectic temperature 695 K.

Among the physicochemical properties, the density of the binary system KF—KCl [8] and of the pure component KBF₄ [9] as well as the conductivity of the binary melts KF—KCl [8] and KF—KBF₄ [10] have been measured. However, the conductivity data of the latter system seem to be unreliable. The density of the ternary melts KF—KCl—KBF₄ was measured in [11],

the electrical conductivity in [12], and the viscosity in [13].

The aim of the present work was to elucidate the structure of the KF—KCl—KBF₄ melts by means of a complex analysis of the physicochemical properties as well as the determination of the character of the possible interaction components using spectroscopic methods.

Computational Procedure

For the dependence of the temperature of primary crystallization $T_{pc}(i)$ on the composition the simplified Le Chatelier—Shreder's equation is valid ($\Delta H_f(i) = \text{const}$, $i = 1, 2, 3$)

$$T_{pc}(i) = \frac{\Delta H_f(i) + RT_{pc}(i) \ln \gamma(i)}{\frac{\Delta H_f(i)}{T_f(i)} - R \ln x(i)} \quad (1)$$

where $T_f(i)$ and $\Delta H_f(i)$ are the temperature and the enthalpy of fusion of the pure i -th component, respectively, $x(i)$ and $\gamma(i)$ are the mole fraction and the activity coefficient of the i -th component in the mixture, respectively.

For the dependence of the excess molar Gibbs energy of mixing on composition in the ternary system, which is needed for the calculation of the activity coefficients of components, the following relation was considered

$$\Delta G_{\text{ter}}^{\text{ex}} = \sum_{\substack{j=1 \\ i \neq j}}^3 \sum_{n=1}^5 A_n x_i x_j^n + B x_1 x_2 x_3 + \sum_{\substack{i,j,k=1 \\ i \neq j \neq k}}^3 C_i x_i^2 x_j x_k \quad (2)$$

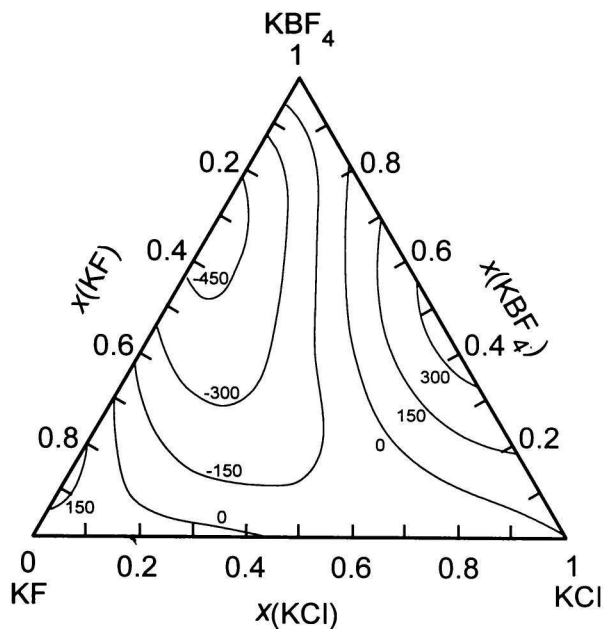


Fig. 1. The excess molar Gibbs energy (J mol^{-1}) of the molten system KF—KCl—KBF₄.

The first term describes the binary and the last two the ternary interactions. The coefficients A_n , B , and C_i were calculated using the multiple linear analysis method, the statistical importance of the individual coefficients being checked by means of Student's criterion at the 0.95 confidence level. The experimental data on the temperatures of primary crystallization were taken from our previous work [7]. From the data given in [7] it follows that a significant ternary interaction is present. The excess molar Gibbs energy of mixing of the molten system KF—KCl—KBF₄ is shown in Fig. 1. The calculation was performed assuming $\Delta_{\text{fus}}H_i \neq f(T)$ and $\Delta G_{\text{ter}}^{\text{ex}} \neq f(T)$.

On the basis of the density data given in [11] the values of the molar volumes were calculated. The concentration dependence of the molar volume was described by the equation

$$V = \sum_{i=1}^3 V_i x_i + \sum_{\substack{j=1 \\ i \neq j}}^3 x_i x_j (A_{ij} + B_{ij} x_j) + C x_1 x_2 x_3 \quad (3)$$

The first term represents the ideal behaviour, the second and the third one the binary and ternary interaction, respectively, *i.e.* the excess molar volume. By means of the multiple linear analysis and omitting the statistically unimportant terms at the 0.95 confidence level the following equation at 1100 K was obtained

$$\begin{aligned} V/(\text{cm}^3 \text{ mol}^{-1}) = & \\ & = 30.109x_{\text{KF}} + 49.842x_{\text{KCl}} + 75.290x_{\text{KBF}_4} + \\ & + 0.906x_{\text{KF}}x_{\text{KCl}} + 4.384x_{\text{KF}}x_{\text{KBF}_4} + \\ & + 2.627x_{\text{KCl}}x_{\text{KBF}_4} - 14.632x_{\text{KF}}x_{\text{KCl}}x_{\text{KBF}_4} \end{aligned} \quad (4)$$

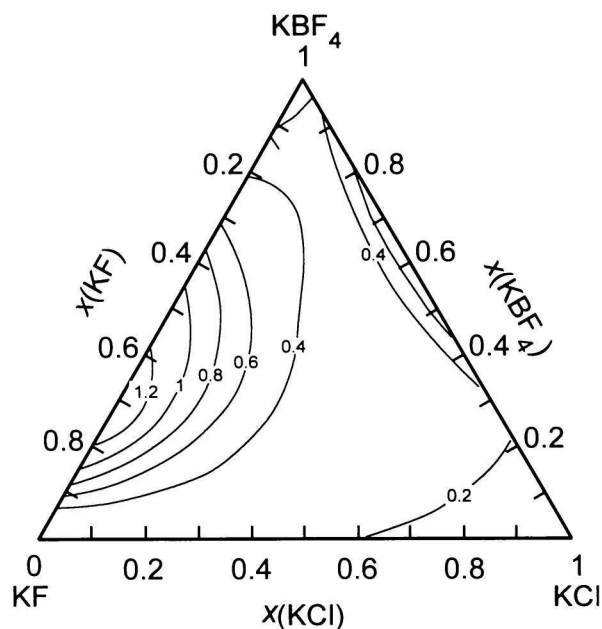


Fig. 2. The excess molar volume ($\text{cm}^3 \text{ mol}^{-1}$) of the molten system KF—KCl—KBF₄ at the temperature of 1100 K.

The standard deviation of the fit is $0.166 \text{ cm}^3 \text{ mol}^{-1}$. The coefficients B , which relate to the second-order deviation from the additivity in the binary systems, were found to be statistically unimportant. On the other hand, like in the phase diagram study, the last term, which represents the ternary interaction, is statistically important. The excess molar volume of the molten system KF—KCl—KBF₄ is shown in Fig. 2.

Like for the molar volume, the concentration dependence of the molar conductivity was described by the general equation

$$\lambda = \sum_{i=1}^3 \lambda_i x_i + \sum_{\substack{j=1 \\ i \neq j}}^3 x_i x_j (A_{ij} + B_{ij} x_j) + C x_1 x_2 x_3 \quad (5)$$

Again the first term represents the additive behaviour, the second and the third one the binary and ternary interaction, respectively, *i.e.* the excess molar conductivity. Using the multiple linear regression analysis of the conductivity data the following equation at 1100 K was obtained [12]

$$\begin{aligned} \lambda/(\text{S cm}^2 \text{ mol}^{-1}) = & \\ & = 95.990x_{\text{KF}} + 114.297x_{\text{KCl}} + 120.268x_{\text{KBF}_4} - \\ & - 21.444x_{\text{KF}}x_{\text{KCl}}^2 - x_{\text{KF}}x_{\text{KBF}_4}(99.675 - 59.675x_{\text{KF}}) + \\ & + 84.398x_{\text{KF}}x_{\text{KCl}}x_{\text{KBF}_4} \end{aligned} \quad (6)$$

The standard deviation of the fit is $1.384 \text{ S cm}^2 \text{ mol}^{-1}$. Again a significant mutual interaction of all three components was found. The excess molar conductivity of the molten system KF—KCl—KBF₄ is shown in Fig. 3.

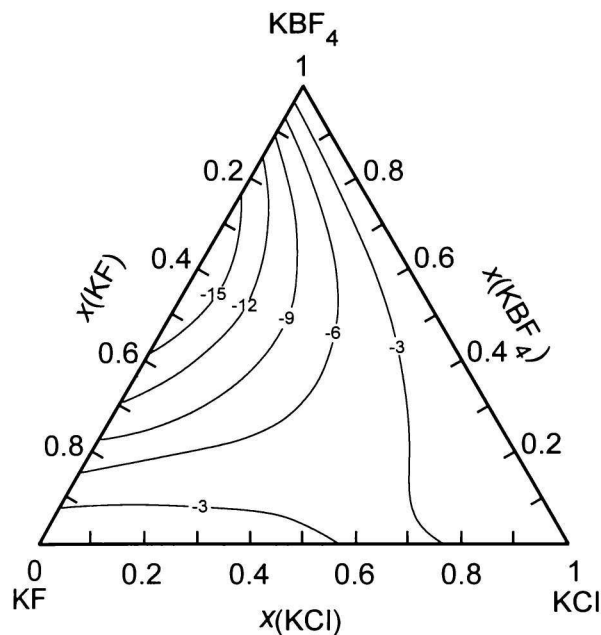


Fig. 3. The excess molar conductivity ($\text{S cm}^2 \text{mol}^{-1}$) of the molten system KF—KCl— KBF_4 at the temperature of 1100 K.

The viscosity of the melts of the system KF—KCl— KBF_4 was described by the equation

$$\eta = \prod_{i=1}^3 \eta_i^{x_i} + \sum_{i \neq j}^3 x_i x_j \sum_{n=0}^k A_{nij} x_j^n + B x_1^k x_2^l x_3^m \quad (7)$$

where the first term represents the adopted "ideal" behaviour, *e.g.* the additivity of logarithms of viscosity, and the second and third terms the binary and ternary interactions, respectively. Using the multiple linear regression analysis of data published in [13] the following final equation at 1100 K was obtained

$$\begin{aligned} \eta / (\text{mPa s}) = & 1.431^{x_{\text{KF}}} 0.953^{x_{\text{KCl}}} 0.638^{x_{\text{KBF}_4}} - \\ & - 0.562 x_{\text{KF}} x_{\text{KCl}} - 0.501 x_{\text{KF}} x_{\text{KBF}_4} - 0.541 x_{\text{KCl}} x_{\text{KBF}_4} - \\ & - 4.576 x_{\text{KF}} x_{\text{KCl}} x_{\text{KBF}_4} \end{aligned} \quad (8)$$

The standard deviation of the fit is 0.019 mPa s. Again a significant ternary interaction was found. The excess viscosity of the investigated system is shown in Fig. 4.

EXPERIMENTAL

Infrared spectra of KBF_4 and of the quenched molten KBF_4 —KCl (1 : 1 mole ratio) mixtures were measured using a Perkin—Elmer 983G spectrophotometer. The mid-infrared spectra were recorded at 300 K from KBr pellets or samples mullied in Nujol. To record the weak infrared bands in the 600—900 cm^{-1} region, 0.5 mm thick pellets were pressed from pure materials.

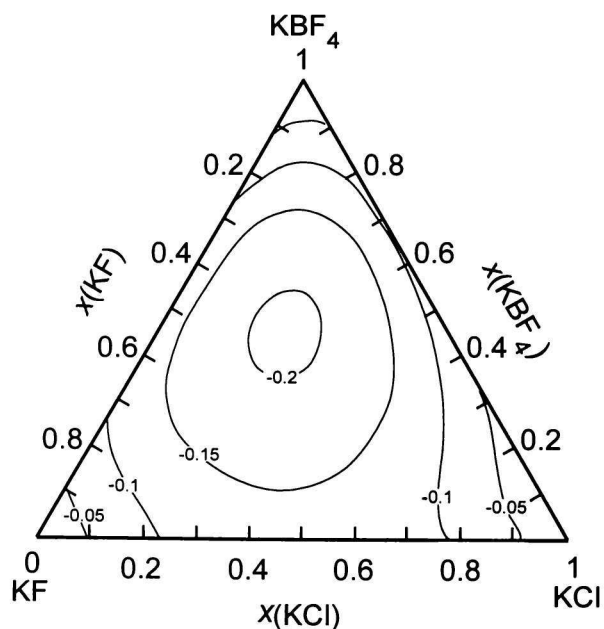


Fig. 4. The excess viscosity (mPa s) of the molten system KF—KCl— KBF_4 at the temperature of 1100 K.

RESULTS AND DISCUSSION

The interaction of components found may be of different origin. With regard to the fact that the investigated system has a common cation, the determined deviations from the ideal behaviour must be a consequence of the anionic interaction. First of all a different character of interaction has to be considered in the boundary binaries KF— KBF_4 and KCl— KBF_4 .

In the pure KBF_4 melt BF_4^- tetrahedra tend to link, forming relatively weak B—F—B bonds. The strength of this bond depends strongly on temperature. Introducing F^- ions into the KBF_4 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_4 system. Besides, the mixing of small anions F^- with relatively large BF_4^- ones takes place. In systems of this type the deviation from additivity is proportional to the fractional difference in the ionic radii of the different anions [7]. Therefore a relatively large deviation from ideality may be achieved, which was confirmed either by the density [11], conductivity [12], and viscosity [13] measurements.

An opposite interaction effect takes place in the system KCl— KBF_4 . There is the mixing of two relatively large and polarizable anions BF_4^- and Cl^- . Like in the systems of alkali metal chlorides, bromides, and iodides with a common cation, no important deviations from additivity were found in these systems [3, 14]. Such behaviour was confirmed also in the system KCl— KBF_4 by the density [11], conductivity [12], and viscosity [13] measurements. On the other hand, intro-

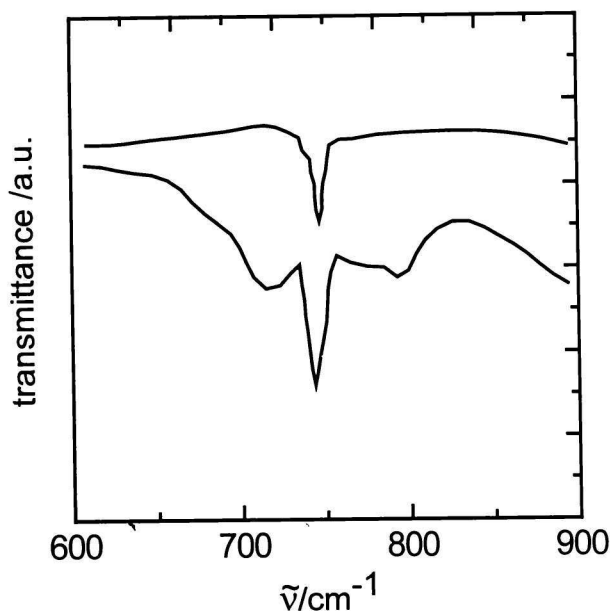
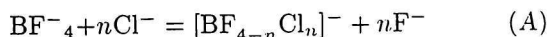


Fig. 5. The IR spectra of KBF_4 and of the quenched molten $\text{KBF}_4\text{--KCl}$ (1 : 1 mole ratio) mixture.

ducing Cl^- ions into the KBF_4 melt, the exchange of fluorine atoms in the BF_4^- tetrahedra for the chlorine ones according to the general scheme



and the possible presence of the $[\text{BF}_{4-n}\text{Cl}_n]^-$ mixed anions may be achieved. Consequently, the lower stability of the B—Cl—B bridges and the lower concentration of the B—F—B ones lead to the negative deviations of the properties in the KCl--KBF_4 system. This explanation is supported also by the asymmetric course of the excess viscosity which is due to the shift of reaction (A) to the right side in the region of high concentration of KBF_4 .

In the binary system KF--KCl the origin of the negative deviations of properties may be sought in the mutual influence of the dissociation degree of components, described in detail in the dissociation model of the electric conductivity of molten salts mixtures [14].

The negative deviations of the properties, found in the ternary system KF--KCl--KBF_4 , have obviously the same origin as it was described for the boundary binary systems. As follows from the course of the excess molar Gibbs energy of mixing (Fig. 1), the excess molar volume (Fig. 2), the excess molar conductivity (Fig. 3), and the excess viscosity (Fig. 4) in the investigated system, the maximum interaction effect is localized near the KF--KBF_4 boundary.

The anionic interaction according to the reaction (A) was confirmed by means of the infrared spectroscopy method. The IR spectra of KBF_4 and that

of the quenched molten $\text{KBF}_4\text{--KCl}$ (1 : 1 mole ratio) mixture are shown in Fig. 5. With the exception of the 600—900 cm^{-1} region, the mid-infrared spectra of both samples are almost identical. In agreement with the earlier study of the alkali metal tetrafluoroborates [15], common vibrations can be assigned to crystalline KBF_4 . Significant differences have been observed only in the 600—900 cm^{-1} region. It can be seen that beside the $\nu(1)$ vibration corresponding to KBF_4 , the quenched molten $\text{KBF}_4\text{--KCl}$ mixture produces two additional peaks at 760 cm^{-1} and 796 cm^{-1} with a shoulder at 770 cm^{-1} . It may be assumed that these peaks arise due to the different B—F and B—Cl stretching vibrations in the $[\text{BF}_{4-n}\text{Cl}_n]^-$ anions. The substitution of the fluorine atom by the chlorine one in the coordination sphere of the BF_4^- anion in the molten KF--KCl--KBF_4 mixtures was thus confirmed. However, the type of the mixed anion had not been determined either by physicochemical analysis or by spectroscopic method.

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REFERENCES

1. Matiašovský, K., Daněk, V., and Makyta, M., *Koroze a ochrana materiálu* 20, 63 (1978).
2. Matiašovský, K., Grjotheim, K., and Makyta, M., *Metall.* 42, 1196 (1988).
3. Sangster, J. and Pelton, A. D., *J. Phys. Chem. Ref. Data* 16, 506 (1987).
4. Barton, C. J., Gilpatrick, L. O., Bornmann, J. A., Stone, H. H., McVay, T. N., and Insley, H., *J. Inorg. Nucl. Chem.* 33, 337 (1971).
Samsonov, V. G., Obolonchik, V. A., and Kulichkina, G. N., *Khim. Nauka Prom.* 4, 804 (1959).
5. Daněk, V., Votava, I., Chrenková-Paučířová, M., and Matiašovský, K., *Chem. Zvesti* 30, 841 (1976).
6. Patarák, O. and Daněk, V. *Chem. Papers* 46, 91 (1992).
7. Janz, G. J., Tomkins, R. P. T., and Allen, C. B., *J. Phys. Chem. Ref. Data* 8, 125 (1979).
8. Cantor, S., McDermonnt, D. P., and Gilpatrick, L. O., *J. Chem. Phys.* 52, 4600 (1970).
9. Janz, G. J., *J. Phys. Chem. Ref. Data* 17, 3 (1989).
10. Chrenková, M. and Daněk, V. *Chem. Papers* 45, 213 (1991).
11. Chrenková, M., Hura, M., and Daněk, V. *Chem. Papers* 45, 739 (1991).
12. Daněk, V. and Nguyen, D. K., *Chem. Papers* 49, 64 (1995).
13. Chrenková, M. and Daněk, V. *Chem. Papers* 44, 329 (1990).
14. Bates, J. B. and Quist, A. S., *Spectrochim. Acta* 31(A), 1317 (1975).

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