Electrical conductivity of the melts of the system KF—KCl—KBF$_4$

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The electrical conductivity of the melts of the ternary system KF—KCl —KBF$_4$ has been measured using a four-electrode method. The temperature dependences of the conductivity were described by second-order polynomials of the type $\varkappa = a + bT + cT^2$ On the basis of the experimental values of the conductivity and density the molar and excess molar conductivities of the investigated system were calculated. The dependence of the molar conductivity on composition was described by the equation

$$\lambda = \sum A_i x_i + \sum_i \sum_{\substack{j \\ i \neq j}} x_i x_j (B_{ij} + C_{ij} x_j) + x_1 x_2 x_3 D$$

Like in the case of the volume properties there is a significant mutual interaction of all three components in the investigated system.

The study of the electrical conductivity of the melts of the system KF—KCl —KBF$_4$ is a continuation of the complex investigation of the physicochemical properties of the quaternary system KF—KCl—KBF$_4$—K$_2$TiF$_6$. This system is interesting as the electrolyte for the electrochemical synthesis of titanium diboride [1].

The density of the system KF—KCl—KBF$_4$ has been described in [2]. The basic characteristics of the phase diagrams of the boundary binary systems are summarized in [2] as well. Only the electrical conductivities of the binary systems KF—KCl [3] and KF—KBF$_4$ [4] are known, however the values of the latter seem to be unreliable.

In the present work the measurement of the electrical conductivity of the melts of the system KF—KCl—KBF$_4$ using the four-electrode method was realized. On the basis of the obtained conductivity values the molar and excess molar conductivities were calculated. The character of interaction between the components is discussed.

Experimental

The conductivity measurement was realized using the four-electrode method [5]. In this method the potential gradient of the electrical field of known intensity created using one pair of electrodes is measured by means of the another pair of electrodes. The measurement is realized at two depths of immersion of the electrodes. For conductivity calculation the following equation holds

$$\varkappa = \frac{\ln 2}{2\pi} \frac{R_1 - R_2}{R_1 R_2 \Delta W} F \qquad (1)$$

where R_1 and R_2 are the average resistance values at both depths of immersion, ΔW is the immersion difference and F is a factor close to unity, which takes into account the influence of the measuring vessel walls on the distribution of electrical field. The detailed description of the conductivity device is given in [6].

The measurement was realized in a resistance furnace. The temperature of the melt was measured using a Pt/PtRh10 thermocouple, the voltage of which was transferred in a computer controlling unit SAPI-1. The electrodes made of PtIr10 alloy with a diameter of 0.5 mm were fixed in a four-hole corundum capillary. The depths of immersion of electrodes used were $W_1 = 5$ mm and $W_2 = 10$ mm. The depth of immersion was fixed in the first position by means of adjustable holding device. The second immersion was realized by an electromagnet. ΔW was adjusted by a micrometric screw with an accuracy 0.01 mm.

The conductivity measurement was carried out in the temperature range of 950—1150 K. The measured melt, with a volume of ca. 40 cm^3, was placed in a Pt crucible. The conductivity was determined in the binary systems KF—KBF$_4$ and KCl—KBF$_4$ and in the cross-sections of the ternary system with a constant mole ratio $n(KF):n(KCl) = 0.33, 1, 3$. In the binary systems as well as in the cross-sections the mixtures with 25, 50, and 75 mole % KBF$_4$ were examined. The conductivity of the system KF—KCl was taken from [3]. The reagent grade KF, KCl, and KBF$_4$ were used for the sample preparation.

The temperature dependences of the experimentally determined conductivity values were described by second-order polynomials using the least-squares method. The polynomial constants as well as the standard deviations of the experimental points are given in Table 1. On the basis of these data the molar conductivities were calculated according to the equation

$$\lambda = \varkappa V \qquad (2)$$

where $\varkappa$ is the conductivity and V is the molar volume of the melt in question. The molar volumes of the melts under investigation were taken from [2].

Results and discussion

The measured conductivity values of pure KF and KCl are in a good agreement with the literature data [3], only the conductivity of KBF$_4$ was found

Table 1

Coefficients a, b, and c in the equation $\varkappa = a + bT + cT^2$ and the standard deviations of the experimental points in the system KF—KCl—KBF$_4$

$x(KF)$	$x(KCl)$	$x(KBF_4)$	$\dfrac{-a}{S\,cm^{-1}}$	$\dfrac{b\ 10^3}{S\,cm^{-1}K^{-1}}$	$\dfrac{-c\cdot 10^6}{S\,cm^{-1}K^{-2}}$	$\dfrac{\sigma\cdot 10^2}{S\,cm^{-1}}$
1	0	0	−2.660	−1.392	−1.173	0.55
0	1	0	3.989	9.019	3.000	0.48
0	0	1	2.419	6.198	2.345	2.13
0.25	0	0.75	2.642	6.322	2.330	0.76
0.50	0	0.50	1.310	3.584	0.825	2.16
0.75	0	0.25	2.301	6.373	2.034	1.41
0	0.25	0.75	2.546	6.609	2.494	0.65
0	0.50	0.50	0.462	2.472	0.311	1.36
0	0.75	0.25	−2.535	−2.751	−2.096	1.26
0.063	0.187	0.75	15.780	32.680	15.316	1.85
0.125	0.125	0.75	1.821	4.825	1.510	0.84
0.187	0.063	0.75	5.508	11.155	4.590	1.21
0.125	0.375	0.50	4.262	10.189	4.246	1.23
0.25	0.25	0.50	3.958	9.979	3.392	0.86
0.375	0.125	0.50	2.839	6.663	2.248	1.25
0.187	0.563	0.25	5.863	13.221	5.472	0.86
0.375	0.375	0.25	2.582	6.746	2.244	1.54
0.563	0.187	0.25	9.134	19.351	8.260	0.74

to be approx. 6 % higher than the value published in [4]. Similarly as in the density study [2], this discrepancy may be ascribed to the unsatisfactory purity of KBF$_4$ used in the cited work. From the results of the measurement it follows that KF exhibits the greatest influence on the conductivity increase.

The dependence of the molar conductivity of the system KF—KCl—KBF$_4$ on composition was described by the general equation

$$\lambda = \sum A_i x_i + \sum_{i \neq j}\sum x_i x_j (B_{ij} + C_{ij}x_j) + x_1 x_2 x_3 D \tag{3}$$

where A_i are the molar conductivities of pure components, the constants B_{ij} and C_{ij} describe the binary interactions and the constant D reflects the interaction of all three components. Using a multiple linear regression analysis and by neglecting the statistically nonimportant terms (on the 0.95 confidence level) the following equation

$$\lambda = A_1 x(KF) + A_2 x(KCl) + A_3 x(KBF_4) + C_{12}x(KF)x^2(KCl) +$$
$$+ x(KF)x(KBF_4)[B_{13} + C_{13}x(KF)] + Dx(KF)x(KCl)x(KBF_4) \tag{4}$$

Table 2

Regression coefficients ($S\,cm^2\,mol^{-1}$) for eqn (*4*) in the system
KF—KCl—KBF$_4$ at 1000 K and 1100 K

Coefficient	1000 K	1100 K
A_1	83.334	95.990
A_2	99.881	114.297
A_3	106.321	120.688
C_{12}	−35.315	−21.444
B_{13}	−95.946	−99.675
C_{13}	68.454	59.978
D	83.856	84.398
σ	1.054	1.384

was obtained. The values of the regression coefficients and the standard deviations of the experimental points for the temperatures 1000 K and 1100 K are given in Table 2. The molar conductivity of the ternary system KF—KCl—KBF$_4$ is shown in Fig. 1. On the basis of the molar conductivity values the excess molar conductivities were calculated using the relation

$$\lambda^E = \lambda - \lambda_{ad} = \lambda - \sum x_i \lambda_i^\circ \tag{5}$$

where λ_i° are the molar conductivities of the pure components. The excess molar conductivity of the studied system is shown in Fig. 2.
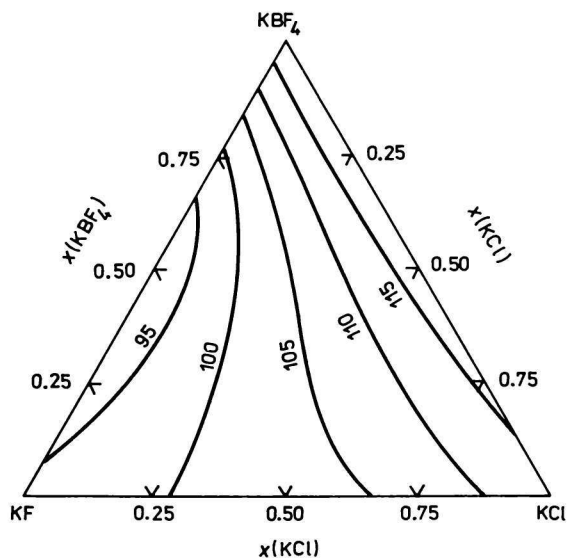

Fig. 1. Molar conductivity of the molten ternary system KF—KCl—KBF$_4$ at the temperature of 1100 K.

The molar conductivity of the binary systems KF—KCl and KCl—KBF$_4$ shows little negative deviations from the additive course. The maximum deviation in the system KF—KCl is -3.1 S cm^2 mol^{-1}, which represents 2.95 % of the molar conductivity value. In the system KCl—KBF$_4$ the molar conductivity has almost a linear course. The differences are within the experimental error. On the other hand, the system KF—KBF$_4$ exhibits a considerable negative deviations from additivity. The maximum λ^E value is -20.2 S cm^2 mol^{-1} at 50 mole % KBF$_4$, which represents 23 % of the molar conductivity value.
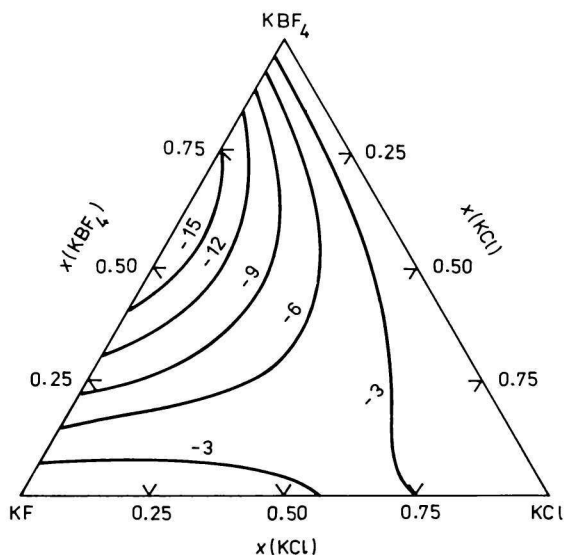

Fig. 2. Excess molar conductivity of the molten ternary system KF—KCl—KBF$_4$ at the temperature of 1100 K.

The different course of the dependence of the molar conductivity in the systems KF—KBF$_4$ and KCl—KBF$_4$ on composition can be explained by a different character of interaction in the above systems. With regard to the fact that both systems have a common cation the resulting conductivity course must be a consequence of the anionic interaction. In the system KF—KBF$_4$ the mixing of small anions F$^-$ with relatively large BF$_4^-$ ones takes place. In the systems of this kind the deviation from additivity is proportional to the fractional difference in ionic radii of the different anions [7]. The molar conductivity of this system exhibits a deep minimum.

Two different interaction effects are present in the system KCl—KBF$_4$. First of all there is the mixing of two relatively large and polarizable anions, like e. g. in the systems of chlorides, bromides and iodides of alkali metals with a common cation [6]. In these systems no important deviations from additivity were found. On the other hand, the replacement of the fluoride atoms in the BF$_4^-$

tetrahedron by chloride ones and the possible presence of the $BF_xCl_y^-$ and F^- anions may not be excluded. More mobile F^- anions obviously contribute to the conductivity increase. Both effects result in the linear dependence of the molar conductivity on composition.

Using the multiple linear regression analysis a significant mutual interaction of all three anions was found in the ternary system KF—KCl—KBF_4. Similar behaviour was found also in the study of the volume properties of the investigated system [2].

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