Volume properties of molten KF—KCl—KBF_4 system

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Using the Archimedean method the densities of melts in the KF—KCl—KBF_4 system were determined. The temperature dependences of the density of individual mixtures were described by linear functions $\varrho = a - bT$. On the basis of the measured densities the molar volumes and the excess molar volumes at the temperatures of 1000, 1100, and 1200 K were calculated. The dependence of the molar volume on composition was described using the regression equation

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

It was found that the molar volumes of the investigated melts are close to the additive values.

The study of the volume properties of the KF—KCl—KBF_4 melts is a part of the complex investigation of the physicochemical properties of the molten quaternary system KF—KCl—KBF_4—K_2TiF_6. This system is interesting as electrolyte for the electrochemical synthesis of titanium diboride [1].

The phase diagrams of the boundary binary systems may be found in the literature [2—4]. In all cases they are simple eutectic systems. The coordinates of the eutectic point in the KF—KCl system are 47 mole % KF and 976 K, in the KF—KBF_4 system 74.5 mole % KBF_4 and 733 K and in the KCl—KBF_4 system 75 mole % KBF_4 and 737 K. From these data it follows that no additional compounds are formed in the binary systems. *Daněk et al.* [5] studied the reactions of KBF_4 in molten alkali chlorides by means of the cryoscopic method. The measurements have been carried out at low contents of KBF_4. It was found that in molten LiCl, and partly also in NaCl, an exchange of fluorine by chlorine in KBF_4 under formation of volatile BCl_3 takes place. On the other hand, in the presence of molten potassium chloride KBF_4 seems to be stable. This finding was confirmed also by the thermodynamic calculation [5]. In the ternary system KF—KCl—KBF_4 only the density values of the binary KF—KCl system [2] and of the pure KBF_4 component [6] are known.

Experimental

The densities of the KF—KCl—KBF_4 melts were measured using the Archimedean method. A platinum ball with the diameter of 25 mm was used as measuring body. The temperature dependence of the volume of the ball was determined by calibration on the basis of known values of the density of molten NaCl and KCl. The density measurement was carried out using an adapted analytical balance connected with a control and computer unit SAPI-1. The detailed description of the device used and the control program is given in [7]. The experimental error of the density measurement was less than 0.2 %. The densities were measured in the binary KF—KBF_4 and KCl—KBF_4 systems and in the sections of the ternary system KF—KCl—KBF_4 with a constant mole ratio $n(KF) : n(KCl) = 0.33, 1, 3$. In the boundary systems as well as in the individual sections the figurative points with 25, 50, and 75 mole % KBF_4 were selected. The density data of the melts in the binary KF—KCl system were taken from the literature [2].

Anal. grade KF, KCl, and KBF_4 were used for the preparation of samples.

The temperature dependences of the experimentally determined density values of the investigated melts were described by the linear functions

$$\varrho = a - bT \qquad (1)$$

The constants a and b and the standard deviations of the experimental data from eqn (*1*) are given in Table 1. On the basis of these data the molar and excess molar volumes of the investigated melts were calculated.

It was shown [8] that the molar volume of the ternary melts can be calculated on the basis of knowledge of the volume properties of the boundary binary systems. The calculation is based on the assumption that the excess molar volume in the ternary system may be specified as a sum of the excess contributions of the individual binary systems

$$V^E = x_1x_2(A_{12} + B_{12}x_2) + (A_{23} + B_{23}x_3) + (A_{31} + B_{31}x_1) \qquad (2)$$

where V^E is the calculated excess molar volume of the ternary system, x_i are the mole fractions of the components and A_{ij} and B_{ij} are empirical constants which may be determined from the experimental data on the molar volumes in the boundary binary systems. These constants are functions of the temperature.

Results and discussion

The densities of the molten KF—KCl—KBF_4 mixtures at 1100 K are shown in Fig. 1. The density of the pure KBF_4 is by 7.5 % higher than the value determined in [3]. However, authors of the cited work used most probably a mixture of KBF_4 and KBF_3OH, which is formed when the preparation method used in [3] is employed [9].

The molar volumes of the molten KF—KCl—KBF_4 mixtures were calculated according to the relation

$$V = \frac{\sum_i x_i M_i}{\varrho} \tag{3}$$

where x_i and M_i are the mole fractions and the molar masses of the individual components, respectively. From the molar volumes the excess molar volumes were calculated according to the equation

$$V^E = V - V_{id} = V - \sum_i x_i V_i^\circ \tag{4}$$

where V_i° are the molar volumes of the pure components.

The excess molar volumes in the boundary binary KF—KBF_4 and KCl—KBF_4 and in the ternary KF—KCl—KBF_4 systems are shown in Figs. 2 and 3, respectively. The maximum V^E value, 1.25 $cm^3 mol^{-1}$, in the boundary KF—KBF_4 system at *ca.* 25 mole % KBF_4, represents 2.9 % of the corresponding molar volume. In the KCl—KBF_4 system a lower volume expansion with a maximum at *ca.* 70 mole % KBF_4 may be observed. The positive values of the excess molar volumes are probably caused by the nonrandom mixing of the

Table 1

Coefficients a and b in the equation $\varrho = a - bT$ and the standard deviations of the experimental densities σ of the investigated KF—KCl—KBF_4 melts

x(KF)	x(KCl)	x(KBF_4)	a / g cm^{-3}	$b\ 10^3$ / g cm^{-3} K^{-1}	$\sigma \cdot 10^4$ / g cm^{-3}
0	0	1.00	2.3536	0.6205	4.3
0.25	0	0.75	2.3738	0.6215	3.3
0.50	0	0.50	2.4340	0.6573	3.7
0.75	0	0.25	2.4983	0.6685	2.5
1.00	0	0	2.6806	0.6750	2.1
0	0.25	0.75	2.3018	0.6171	1.8
0	0.50	0.50	2.2411	0.5974	2.1
0	0.75	0.25	2.2117	0.6052	2.4
0	1.00	0	2.1373	0.5849	1.5
0.063	0.187	0.75	2.3221	0.6150	4.5
0.125	0.125	0.75	2.3410	0.6202	3.2
0.187	0.063	0.75	2.3910	0.6600	2.8
0.125	0.375	0.50	2.3610	0.6599	2.2
0.25	0.25	0.50	2.3848	0.6601	3.1
0.375	0.125	0.50	2.2610	0.5913	1.9
0.187	0.563	0.25	2.2180	0.5675	2.7
0.375	0.375	0.25	2.3687	0.6551	2.8
0.563	0.187	0.25	2.3765	0.5950	1.8

complex anion BF_4^- with the simple F^- and Cl^- ones due to the different magnitude of both types of ions. The formation of more complex anions may not be excluded either. Very small negative values of the excess molar volume were found in the KF—KCl boundary system [1].

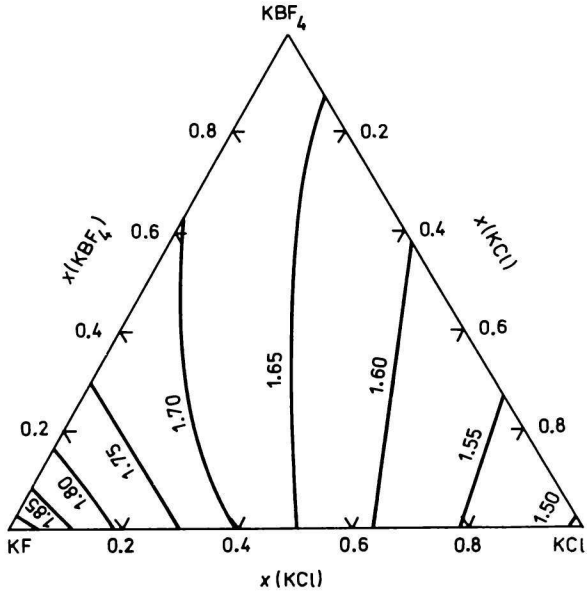

Fig. 1. Densities of the melts of the KF—KCl—KBF_4 system at 1100 K.

The low excess molar volumes in the ternary KF—KCl—KBF_4 system indicate that the molar volume in the investigated system differs only slightly from the additive values. That is why the molar volumes in the ternary system were calculated according to eqn (*2*). The constants A_{ij} and B_{ij} calculated from the experimental densities of the boundary binary systems are given in Table 2. The experimental and calculated molar volumes are compared in Table 3. From the comparison it follows that the differences are less than 1 % but in all cases higher than the experimental error. From this fact it follows that beside the contributions of the binary interactions the ternary interactions have also to be considered for a more exact evaluation. Therefore the dependence of the molar volume on composition was described with the more common equation

$$V = \sum_i V_i^{\circ} x_i + \sum_{\substack{i \\ i \neq j}} \sum_j x_i x_j (A_{ij} + B_{ij} x_j) + x_1 x_2 x_3 C \qquad (5)$$

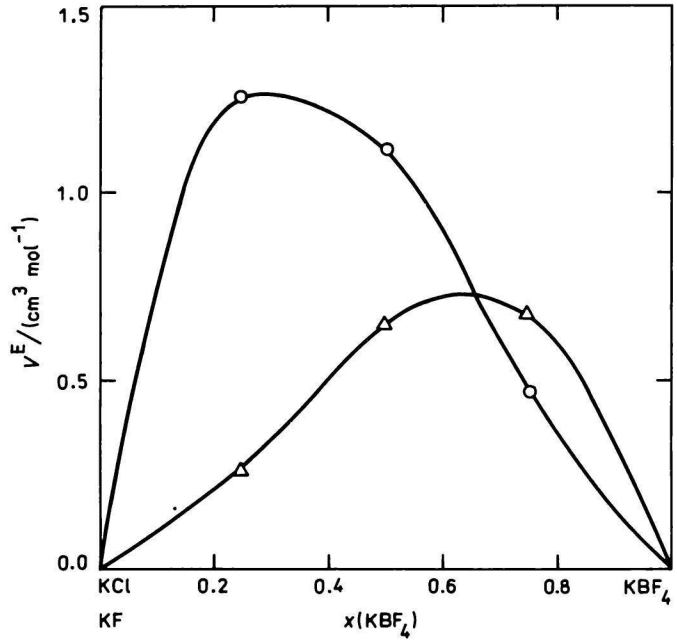

Fig. 2. Excess molar volumes of the molten binary KF—KBF_4 and KCl—KBF_4 mixtures at 1100 K. ○ KF—KBF_4; △ KCl—KBF_4.

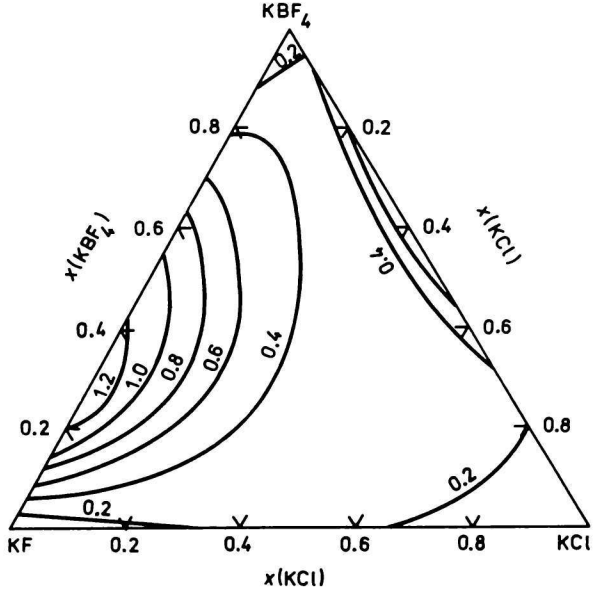

Fig. 3. Excess molar volumes of the molten ternary KF—KCl—KBF_4 mixtures at 1100 K.

Table 2

Constants A_{ij} and B_{ij} in eqn (*2*) used for the calculation of the molar volume in the KF—KCl—KBF_4 system at 1100 K

System	A_{ij} / $cm^3\ mol^{-1}$	B_{ij} / $cm^3\ mol^{-1}$
KF—KCl	1.166413	−0.456778
KCl—KBF_4	0.330480	4.432162
KBF_4—KF	0.339923	8.366192

Table 3

Experimental and calculated molar volumes in the KF—KCl—KBF_4 system at 1100 K

x(KF)	x(KCl)	x(KBF_4)	V_{exp} / $cm^3\ mol^{-1}$	$V_{1,calc}$ / $cm^3\ mol^{-1}$	$V_{2,calc}$ / $cm^3\ mol^{-1}$
0.187	0.063	0.75	66.078	65.711	65.893
0.125	0.125	0.75	66.923	66.983	66.961
0.063	0.187	0.75	68.060	68.294	68.103
0.375	0.125	0.50	55.906	56.014	55.852
0.25	0.25	0.50	57.949	58.330	58.109
0.125	0.375	0.50	60.332	60.743	60.566
0.563	0.187	0.25	45.426	45.853	45.508
0.375	0.375	0.25	49.281	49.390	49.075
0.187	0.563	0.25	52.964	52.963	52.840

$V_{1,calc}$ — molar volume calculated according to eqn (*2*); $V_{2,calc}$ — molar volume calculated according to eqn (*6*); standard deviations for the individual sets: $\sigma_1 = 0.298\ cm^3\ mol^{-1}$, $\sigma_2 = 0.152\ cm^3\ mol^{-1}$

Table 4

Experimental molar volumes of pure components and the regression coefficients in eqn (*6*). The dimension of all values is in $cm^3\ mol^{-1}$

T/K	$V°$(KF)	$V°$(KCl)	$V°$(KBF_4)	A_1	A_2	A_3
1000	28.969	48.023	72.649	29.109	47.953	72.595
1100	29.978	49.900	75.344	30.109	49.842	75.290
1200	31.060	51.952	78.247	31.161	51.890	78.212
T/K	B_1	B_2	B_3	C	σ	
1000	0.983	3.805	2.592	−13.511	0.135	
1100	0.906	4.384	2.627	−14.632	0.166	
1200	0.751	5.031	2.780	−16.070	0.210	

By means of the regression analysis and omitting the statistically unimportant members the equation in the form

$$V = A_1 x(\mathrm{KF}) + A_2 x(\mathrm{KCl}) + A_3 x(\mathrm{KBF_4}) + B_1 x(\mathrm{KF})\, x(\mathrm{KCl}) + \\ + B_2 x(\mathrm{KF})\, x(\mathrm{KBF_4}) + B_3 x(\mathrm{KCl})\, x(\mathrm{KBF_4}) + C x(\mathrm{KF})\, x(\mathrm{KCl})\, x(\mathrm{KBF_4}) \quad (6)$$

was obtained. The molar volumes of pure components, the regression coefficients A_i, B_i, and C as well as the standard deviations of the experimental data from eqn (*6*) for temperatures of 1000, 1100, and 1200 K are given in Table 4. In all cases the values of the standard deviations are lower or comparable with the experimental error. Coefficients A_i (eqn (*6*)) correspond evidently to the molar volumes of the pure components. The constants B_{ij}, which relate to the second-order deviation from the additivity in the binary systems (*cf.* eqn (*2*)), seem to be statistically unimportant. On the other hand, the last member representing in the investigated system the interaction of the third order, is of greater significance. The experimental and calculated molar volumes are compared in Table 3.

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