Density of the Molten System $KCl—KBF_4—K_2TiF_6$

M. CHRENKOVÁ, V. DANĚK, and A. SILNÝ

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

Received 17 November 1999

The density of the melts of the system $KCl—KBF_4—K_2TiF_6$ has been measured using the Archimedean method. The molar volume, the partial molar volume, and the excess molar volume of the melts at 1000, 1100, and 1200 K were calculated on the basis of the obtained density data and the possible chemical interactions of components have been considered. The dependence of the molar volume on composition was described using the regression equation

$$V = x_1V_1 + x_2V_2 + x_3V_3 + x_1x_3A_{013} + x_2x_3(A_{023} + A_{123}x_3) + x_1x_2x_3^2B$$

The significant mutual interaction of all three components was found in the investigated system.

The study of the volume properties of the melts of the system $KCl—KBF_4—K_2TiF_6$ is a part of the complex investigation of the physicochemical properties of the quaternary system $KF—KCl—KBF_4—K_2TiF_6$, which can be used as the electrolyte in the electrochemical synthesis of TiB_2, especially when coherent coatings on metallic bases have to be prepared [1]. From the theoretical point of view, considerations on the structure, *i.e.* the ionic composition of the melts, on the basis of the volume properties can be made.

The phase diagram of the system $KCl—KBF_4$ has been studied in [2]. It was found that it is a simple eutectic system with the coordinates of the eutectic point 75 mole % KBF_4 and 737 K. The density of this system has been studied in [3].

The phase diagram of the system $KCl—K_2TiF_6$ was studied in [4, 5]. The congruently melting compound formed in this system, K_3TiF_6Cl, with the melting temperature of 964 K, divides the above system into two simple eutectic ones. The coordinates of the respective eutectic points are: 30.7 mole % K_2TiF_6, 925 K and 64.8 mole % K_2TiF_6, 943 K. The zero value of the tangent of the K_3TiF_7 liquidus curve at $x(K_2TiF_6) = 0.5$ indicates that this compound undergoes at melting a considerable thermal dissociation. The dissociation degree calculated on the basis of the experimentally determined phase diagram is $\alpha_0 = 0.78$ [6], which is in a very good accordance with the values obtained on the basis of the density data, $\alpha_0(1000\ K) = 0.71$ and $\alpha_0(1100\ K) = 0.81$ [7].

The phase diagram of the system $KBF_4—K_2TiF_6$ has been studied in [8]. It is a simple eutectic system with the coordinates of the eutectic point 28 mole % K_2TiF_6 and 721 K. The density of this system was measured in [9].

The phase diagram of the ternary system $KCl—KBF_4—K_2TiF_6$ has been measured in [10]. The intermediate compound K_3TiF_6Cl is formed in this system. The $K_3TiF_6Cl—KBF_4$ joint divides the ternary system into two simple eutectic ones. The coordinates of the two ternary eutectic points are as follows: 24.1 mole % KCl, 62.1 mole % KBF_4, 13.8 mole % K_2TiF_6, 920 K and 6.5 mole % KCl, 62.5 mole % KBF_4, 31.0 mole % K_2TiF_6, 687.5 K.

In the present work the density of the melts of the ternary system $KCl—KBF_4—K_2TiF_6$ was determined. The molar volumes and the excess molar volumes were calculated on the basis of the obtained data. From the course of these volume functions the information on the interactions of components and the possible chemical reactions between them was obtained.

EXPERIMENTAL

For the preparation of samples the following chemicals were used: KCl (Lachema), KBF_4 and K_2TiF_6 (both Fluka), all anal. grade. KCl was dried at 880 K for 2 h, KBF_4 and K_2TiF_6 were dried in vacuum at 430 K for 6 h. In the ternary system cross-sections with the constant ratio $x(KCl)/x(KBF_4) = 3$, 1, and 0.333 with the content of 25 mole %, 50 mole % , and 75 mole % K_2TiF_6 were chosen for the measurement.

The density of the investigated melts was measured using the Archimedean method. The platinum sphere with the diameter of 20 mm, suspended on the Sartorius automatic analytical balance by means of the platinum wire of 0.3 mm in diameter, was used as the measuring body. The dependence of the sphere volume on temperature was determined by calibration using molten NaCl and KCl. The experimental error in the density measurement did not exceed 0.4 %. For the

Table 1. Coefficients *a* and *b* in Eqn (*1*) and the Standard Deviations, σ, of the Fit for the Investigated Melts of the System KCl(1)—KBF_4(2)—K_2TiF_6(3)

Composition			a	$b \cdot 10^4$	$\sigma \cdot 10^4$
x_1	x_2	x_3	g cm^{-3}	g/(cm^3 °C)	g cm^{-3}
System KCl—KBF_4 [3]					
1.000	0.000	0.000	2.1373	5.849	1.5
0.750	0.250	0.000	2.2117	6.205	2.4
0.500	0.500	0.000	2.2411	5.974	2.1
0.250	0.750	0.000	2.3018	6.171	1.8
0.000	1.000	0.000	2.3536	6.205	4.3
System KCl—K_2TiF_6 [7]					
0.750	0.000	0.250	2.4839	6.247	1.9
0.500	0.000	0.500	2.5909	6.062	4.8
0.250	0.000	0.750	2.6988	6.117	3.1
0.000	0.000	1.000	2.7715	6.102	2.2
System KBF_4—K_2TiF_6 [9]					
0.000	0.750	0.250	2.6198	7.684	3.2
0.000	0.500	0.500	2.7719	7.800	3.9
0.000	0.250	0.750	2.9561	8.500	5.5
System KCl—KBF_4—K_2TiF_6					
0.563	0.187	0.250	2.4508	5.999	3.0
0.375	0.375	0.250	2.5235	6.643	2.9
0.187	0.563	0.250	2.5320	6.595	4.6
0.375	0.125	0.500	2.6373	6.270	1.8
0.250	0.250	0.500	2.6271	6.230	1.8
0.125	0.375	0.500	2.6603	6.700	2.5
0.187	0.063	0.750	2.7209	6.185	1.6
0.125	0.125	0.750	2.7071	6.102	4.8
0.063	0.187	0.750	2.7108	6.116	6.2

measuring device control and the evaluation of experimental data the on-line PC XT computer was used. The detailed description of the measuring device used is given in [11].

The measurements were carried out in the temperature interval of approximately 150 K starting at 10—20 K above the temperature of primary crystallization. The density values were automatically registered every 30 s by the measuring device yielding approximately 30—50 density values for each composition. The measurement of every melt composition was 1—2 times repeated. Thus, the temperature dependences of the density are presented in the form of the linear equations

$$\rho = a - b \cdot T \qquad (1)$$

where ρ is the density in g cm^{-3} and T is the temperature in K. The values of the constants a and b together with the standard deviations of approximations, obtained by the linear regression analysis of the experimentally obtained data, are given in Table 1. The original density data are available at the first author on request.

RESULTS AND DISCUSSION

The density of the molten system KCl—KBF_4—K_2TiF_6 at the temperature of 1100 K is shown in Fig. 1. From the figure it follows that the density of the melts increases from KCl through KBF_4 to K_2TiF_6. The densities of melts of the boundary binary systems were taken from [3, 7, 9].

The molar volume of the ternary system is given by the equation

$$V = V_{\mathrm{id}} + V^{\mathrm{E}} = \sum_{i=1}^{3} x_i V_i + V^{\mathrm{E}} \qquad (2)$$

where V_i is the molar volume of pure component at the given temperature, x_i is its mole fraction, and V^{E} is the excess molar volume.

The molar volume of the ternary melts can be calculated in two ways. It may be assumed that the excess molar volume of the ternary system at constant temperature, V^{E}, is a sum of the excess molar volumes of the boundary binary systems

$$V^{\mathrm{E}} = \sum_{i \neq j}^{3} x_i x_j \sum_{n=0}^{k} A_{nij} x_j^n \qquad (3)$$

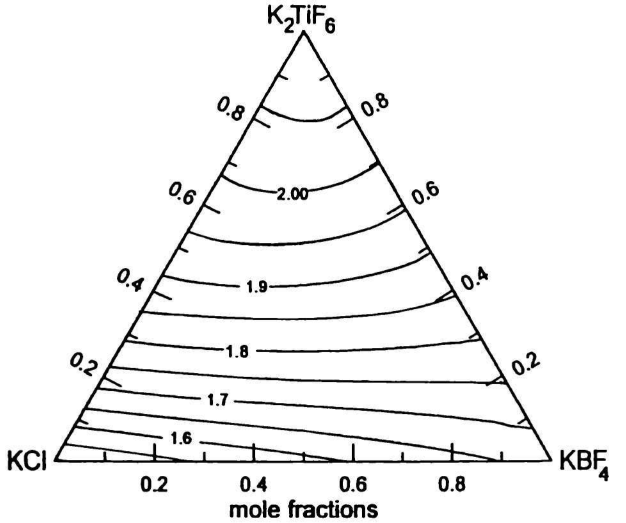

Fig. 1. Iso-density lines ($\rho/(\text{g cm}^{-3})$) of the system KCl—KBF$_4$—K$_2$TiF$_6$ at the temperature of 1100 K.

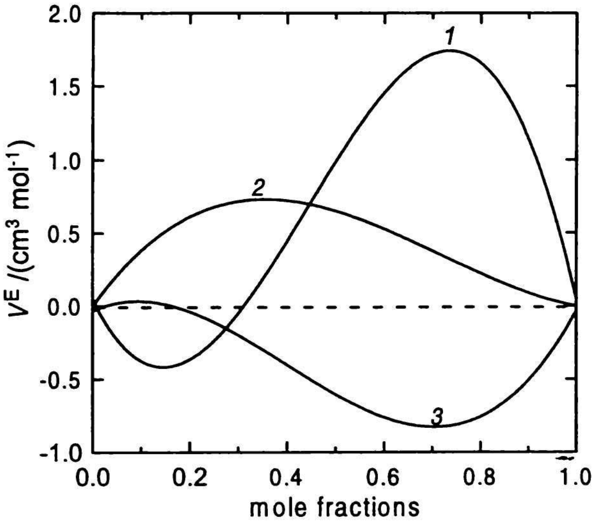

Fig. 2. Excess molar volumes in the boundary binary systems at the temperature of 1100 K. *1.* KBF$_4$—K$_2$TiF$_6$; *2.* KCl—KBF$_4$; *3.* KCl—K$_2$TiF$_6$.

In eqn (*3*), x_i and x_j are the mole fractions of components, A_{nij} are coefficients, and n is adjustable integer of the excess molar volume, calculated from the experimental data of the individual boundary binary systems. Coefficients A_{nij} depend on temperature. This approach is suitable in that case, when the ternary interaction is not present and the deviation from the additivity in the ternary system is due to the binary interactions only.

The coefficients A_{nij} in eqn (*3*) for the system KCl—KBF$_4$—K$_2$TiF$_6$ were calculated from the excess molar volumes of the boundary binary systems (see Fig. 2). The detailed description of the computational procedure is given in [12]. For the dependence of the molar volume in the ternary system KCl(1)—KBF$_4$(2)—K$_2$TiF$_6$(3) on composition at the temperature of 1100 K the following final equation was obtained

$$\begin{aligned}\frac{V}{\text{cm}^3\ \text{mol}^{-1}} &= 49.885x_1 + 75.367x_2 + 114.347x_3 + \\ &+ x_1x_2\,(0.430 + 4.231x_2) + \\ &+ x_2x_3\,(14.527 - 20.641x_3) + \\ &+ x_3x_1\,(0.881 - 6.762x_1) \qquad (4)\end{aligned}$$

When ternary interaction may be expected, the molar volume of the ternary system can be calculated on the basis of the experimental data of the whole ternary system in one step. The dependence of the molar volume of the ternary system on composition at constant temperature can be described by the equation

$$V = \sum_{i=1}^{3} x_iV_i + \sum_{i\neq j}^{3} x_ix_j \sum_{n=0}^{k} A_{nij}x_j^n + Bx_1^px_2^qx_3^r \quad (5)$$

where p, q. r, and n are adjustable integers. The first term represents ideal behaviour, the second one describes the binary interactions, and the third one the interaction of all three components.

The constants V_i, A_{nij}, and B in eqn (*5*) were calculated using the multiple linear regression analysis. Omitting the statistically nonimportant terms on the 0.99 confidence level, the following equation was obtained

$$\begin{aligned}V &= x_1V_1 + x_2V_2 + x_3V_3 + x_1x_3A_{013} + \\ &+ x_2x_3\,(A_{023} + A_{123}\,x_3) + x_1x_2x_3^2B \qquad (6)\end{aligned}$$

The values of constants V_i, A_{nij}, and B in eqn (*6*) as well as the standard deviations of approximation for the temperatures 1000 K, 1100 K, and 1200 K are given in Table 2.

Considering the linear temperature dependence of the molar volumes of pure components, V_i, as well as of the coefficients A_{nij} and B, the following equation can be written

$$\begin{aligned}V &= \sum_{i=1}^{3} x_i\,(V_i + V_i'T) + \sum_{i\neq j}^{3} x_ix_j\cdot \\ &\cdot \sum_{n=0}^{k} x_j^n\,(A_{nij} + A_{nij}'T) + x_i^px_2^qx_3^r\,(B + B'T) \quad (7)\end{aligned}$$

The dependence of the molar volume of the ternary system KCl—KBF$_4$—K$_2$TiF$_6$ on composition and temperature according to eqn (*7*) was calculated using the multiple linear regression analysis as well. The following final equation was obtained

Table 2. Coefficients V_i, A_{nij}, and B of Eqn (*6*) and the Standard Deviations of the Fit for the Composition Dependence of the Molar Volume of the System KCl—KBF$_4$—K$_2$TiF$_6$

Coefficient	1000 K	1100 K	1200 K
$V_1/(\mathrm{cm^3\ mol^{-1}})$	48.075 ± 0.195	49.985 ± 0.188	52.013 ± 0.251
$V_2/(\mathrm{cm^3\ mol^{-1}})$	73.114 ± 0.263	75.844 ± 0.254	78.796 ± 0.339
$V_3/(\mathrm{cm^3\ mol^{-1}})$	111.114 ± 0.465	114.478 ± 0.446	117.825 ± 0.589
$A_{013}/(\mathrm{cm^3\ mol^{-1}})$	−2.242 ± 1.536	−3.581 ± 1.474	−4.030 ± 1.951
$A_{023}/(\mathrm{cm^3\ mol^{-1}})$	5.908 ± 2.955	9.026 ± 2.857	12.235 ± 3.807
$A_{123}/(\mathrm{cm^3\ mol^{-1}})$	−13.604 ± 6.063	−13.017 ± 5.851	−10.961 ± 7.779
$B/(\mathrm{cm^3\ mol^{-1}})$	−53.370 ± 22.320	−74.556 ± 21.491	−111.430 ± 28.539
$\sigma/(\mathrm{cm^3\ mol^{-1}})$	0.378	0.364	0.484

Table 3. Experimental and Calculated Molar Volumes in the System KCl—KBF$_4$— K$_2$TiF$_6$ at 1100 K and the Standard Deviations of the Fit

Composition			$V_i/(\mathrm{cm^3\ mol^{-1}})$			
x_1	x_2	x_3	exp	Eqn (*4*)	Eqn (*6*)	Eqn (*8*)
0.563	0.187	0.250	70.094	70.991	70.219	70.100
0.375	0.375	0.250	75.510	76.563	75.355	75.409
0.187	0.563	0.250	80.115	81.963	80.821	81.004
0.375	0.125	0.500	84.081	85.034	84.076	84.167
0.250	0.250	0.500	87.584	89.048	87.398	87.449
0.125	0.375	0.500	91.805	92.606	91.303	91.393
0.187	0.063	0.750	98.905	99.826	98.503	99.207
0.125	0.125	0.750	100.406	101.421	100.530	100.630
0.063	0.187	0.750	102.203	102.966	102.420	102.420
	$\sigma/(\mathrm{cm^3\ mol^{-1}})$		-	1.130	0.364	0.343

$$\begin{aligned}
&\frac{V}{\mathrm{cm^3\ mol^{-1}}} = \\
&= x_1\left(29.642 + 1.846 \times 10^{-2}T/\mathrm{K}\right) + \\
&+ x_2\left(44.229 + 2.859 \times 10^{-2}T/\mathrm{K}\right) + \qquad (8)\\
&+ x_3\left(78.485 + 3.196 \times 10^{-2}T/\mathrm{K}\right) + 3.951x_1x_2^2 + \\
&+ x_1x_3\left(8.692x_3 - 5.137 \times 10^{-3}T/\mathrm{K}\right) - \\
&- x_2x_3\left(2.628 - 2.916 \times 10^{-2}T/\mathrm{K}\right) - 7.614x_1x_2x_3^2
\end{aligned}$$

The standard deviation of approximation of eqn (*8*) $\sigma = 0.343\ \mathrm{cm^3\ mol^{-1}}$.

From the comparison of the experimentally determined values of the molar volumes of the ternary system KCl—KBF$_4$—K$_2$TiF$_6$ with those calculated according to eqns (*4*), (*6*), and (*8*) given in Table 3 it follows that the differences, when considering binary interactions only $V_{(4)}$, surpass the experimental error, indicating so the presence of ternary interaction. On the other hand, when the ternary interaction was taken into account, the standard deviation of approximation agreed well with the experimental error.

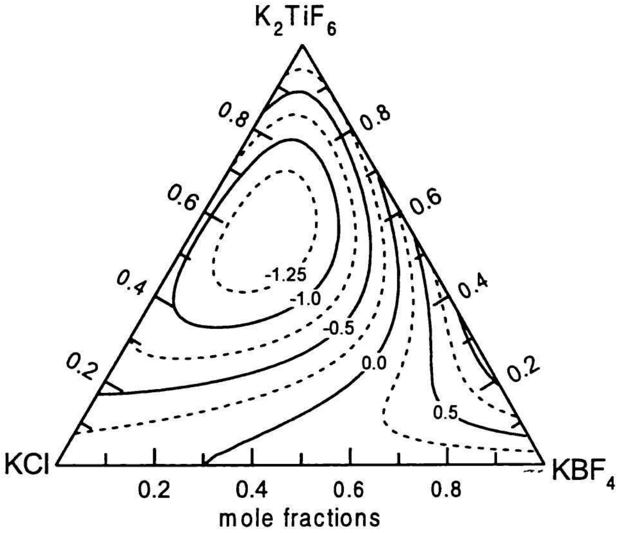

Fig. 3. Iso-lines of excess molar volume ($V/(\mathrm{cm^3\ mol^{-1}})$) in the system KCl—KBF$_4$—K$_2TiF_6$ at the temperature of 1100 K.

From the calculated values of the excess molar volumes it follows that from the volume properties point of view the binary system KCl—KBF$_4$ differs only a little from the additive behaviour, which is in agreement with the results given in [3]. In the systems KBF$_4$—K$_2$TiF$_6$ and KCl—K$_2$TiF$_6$ the deviations from the ideal behaviour are higher. In the former system the deviations are positive, while in the latter one they are negative (*cf.* Fig. 2).

The excess molar volume of the ternary system

KCl—KBF$_4$—K$_2$TiF$_6$ is shown in Fig. 3. Like in the ternary system KF—KBF$_4$—K$_2$TiF$_6$ [9], two different regions are present in the investigated system: the region of volume expansion with the maximum in the binary system KBF$_4$—K$_2$TiF$_6$ at approximately 25 mole % K$_2$TiF$_6$ and 75 mole % KBF$_4$ and the region of volume contraction with the maximum at approximately 60 mole % K$_2$TiF$_6$, 20 mole % KCl, and 20 mole % KBF$_4$. On the basis of this fact, as well as from the coefficient B in eqn (7), the ternary interaction may be supposed to exist in the melts of the system KCl—KBF$_4$—K$_2$TiF$_6$.

In [9] it was suggested that in the molten system KBF$_4$—K$_2$TiF$_6$ the following chemical reaction takes place

$$\mathrm{KBF_4(l) + K_2TiF_6(l) = K_3TiF_7(l) + BF_3(g)} \qquad (A)$$
$$\Delta_r G^0_{1100\,\mathrm{K}} = 10.71\ \mathrm{kJ\ mol^{-1}}$$

The originating compound K$_3$TiF$_7$ dissociates thermally according to the reaction

$$\mathrm{K_3TiF_7(l) = K_2TiF_6(l) + KF(l)} \qquad (B)$$
$$\Delta_r G^0_{1100\,\mathrm{K}} = 0.963\ \mathrm{kJ\ mol^{-1}}$$

The additive compound K$_3$TiF$_6$Cl, which is formed in the binary system KCl—K$_2$TiF$_6$, dissociates thermally as well, according to the scheme

$$\mathrm{K_3TiF_6Cl(l) = K_2TiF_6(l) + KCl(l)} \qquad (C)$$
$$\Delta_r G^0_{1100\,\mathrm{K}} = 0.587\ \mathrm{kJ\ mol^{-1}}$$

The Gibbs energy of reaction (C) was calculated from the equilibrium constant of this reaction in [7].

In the ternary system KCl—KBF$_4$—K$_2$TiF$_6$ the next chemical reaction is possible

$$\mathrm{KCl(l) + 2\,K_2TiF_6(l) + KBF_4(l) =}$$
$$\mathrm{= K_3TiF_7(l) + K_3TiF_6Cl(l) + BF_3(g)} \qquad (D)$$
$$\Delta_r G^0_{1100\,\mathrm{K}} = 12.05\ \mathrm{kJ\ mol^{-1}}$$

The originating additive compounds dissociate thermally according to reactions (B) and (C). The Gibbs energy of reaction (D) was calculated on the basis of the Gibbs energies of reactions (B) and (C), as well as of the formation Gibbs energies of KCl, KBF$_4$, and BF$_3$ given in [13]. The relatively low positive value of the reaction Gibbs energy and the observed minor escape of gaseous BF$_3$ indicate that even the reaction (D) takes probably place in the ternary melts.

Acknowledgements. The present work was financially supported by the Grant Agency for Science of the Slovak Republic under No. 2/7205/98.

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. Pap. 45*, 213 (1991).
4. Aotani, K., Hasegava, K., and Miyazawa, Y., *J. Electrochem. Soc. Jpn. 27*, 117 (1959).
5. Chernov, R. V. and Ermolenko, P. M., *Zh. Neorg. Khim. 18*, 1372 (1973).
6. Daněk, V. and Matiašovský, K., *Z. Anorg. Allg. Chem. 570*, 184 (1989).
7. Daněk, V., Šiška, J., and Matiašovský, K., *Chem. Pap. 42*, 753 (1988).
8. Chrenková, M., Patarák, O., and Daněk, V., *Thermochim. Acta 273*, 157 (1996).
9. Chrenková, M., Daněk, V., and Ngyen, D. K., *Z. Phys. Chem. 194*, 51 (1996).
10. Chrenková, M., Patarák, O., and Daněk, V., *Chem. Pap. 49*, 167 (1995).
11. Silný, A., *Sdělovací technika 38*, 101 (1990).
12. Fellner, P. and Chrenková-Paučírová, M., *Chem. Zvesti 33*, 705 (1979).
13. Stuhl, D. P. and Prophet, H., *JANAF Thermochemical Tables*, 2nd Edition. NSRDS, Nat. Bur. Stand., Washington, 1971.