

Thermodynamic properties of liquids in the system KF–KBF₄

I. Nerád*, L. Kosa, K. Adamkovičová, I. Proks

Institute of Inorganic Chemistry, Slovak Academy of Sciences, 842 36 Bratislava, Slovak Republic

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Abstract

Relative enthalpies of melts in the system KF–KBF₄ at mole fractions of KBF₄ equal to 0.35, 0.42, 0.60 and 0.80 have been determined from drop-calorimetry measurements at temperatures up to 1082 K. The temperature dependences of relative enthalpies of melts have been found to be linear. The heat capacities of melted mixtures indicate a positive deviation from additivity. The enthalpy of mixing shows a negative deviation from ideality in the entire composition range of the system. The exothermic effect at mixing reaches its minimum of about -3 kJ mol^{-1} at the composition around $x(\text{KBF}_4) = 0.7$. Negative enthalpy of mixing is explained by forming of individual BF₄⁻ ions, following the breaking of B–F–B bridges in KBF₄ melt during the mixing process. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The KF–KBF₄ is an important subsystem of KF–KCl–KBF₄ and KF–KCl–KBF₄–K₂TiF₆ systems that are of interest as electrolytes for electrochemical boring of metals and electrochemical synthesis of titanium diboride, respectively [1,2]. The knowledge of the physicochemical properties and ionic composition of these electrolytes is important for the understanding of the mechanism of electrochemical processes. Recently, several papers dealing with some physicochemical properties of melts in KF–KBF₄ system have been published.

Chrenková and Daněk [3] measured densities of melts in KF–KBF₄ system by the Archimedean method. They found the excess molar volume to be

positive with a maximum of about $1.25 \text{ cm}^3 \text{ mol}^{-1}$ at $x(\text{KBF}_4)$ around 0.25 and at $T = 1100 \text{ K}$, representing about 3% of the corresponding molar volume. They concluded that the volume expansion on mixing is probably a consequence of a nonrandom mixing of complex anions BF₄⁻ with the simple F⁻ ones due to the different size of both types of ions.

The data on electrical conductivity of melts in KF–KBF₄ system have been published by Janz [4] and Chrenková et al. [5]. The molar electrical conductivity of melts in this system exhibits a considerable negative deviation from additivity. The minimum value of excess molar conductivity at 1100 K is $-20.2 \text{ S cm}^2 \text{ mol}^{-1}$ at $x(\text{KBF}_4) = 0.5$ [5]. The considerable decrease of molar conductivity in the KF–KBF₄ system was found to be a consequence of anionic interactions in the melt due to mixing of anions with different size and shape [5].

Additivity of logarithms of viscosities of pure component melts was adopted as the ideal behaviour

*Corresponding author. Fax: +421 7 59410444; e-mail: uachnera@savba.sk

of the solution by Daněk and Nguyen [1]. Negative deviation from such ideal behaviour has been determined in KF–KBF₄ system. The composition dependence of viscosity is asymmetrical, the minimum being shifted slightly to the KBF₄ rich region at 1100 K. In pure KBF₄ melt BF₄[−] tetrahedra tend to link, forming relatively weak B–F–B bonds. Introducing F[−] ions into the KBF₄ melt by addition of KF, the B–F–B bridges break which leads to the lowering of viscosity and the negative deviation from ideal behaviour [1].

The excess molar Gibbs energy of mixing in ternary KBF₄–KF–KCl and KF–KBF₄–K₂TiF₆ system melts was estimated by Patarák and Daněk [6] and Chrenková et al. [7], respectively, using phase diagrams of the systems and enthalpies of fusion of pure components. According to data from Ref. [7], the minimum value of $\Delta_{\text{mix}}G^E$ in KF–KBF₄ binary melt is about -0.6 kJ mol^{-1} at $x(\text{KBF}_4)$ around 0.7.

This study aims to investigate the enthalpic properties of liquids in KF–KBF₄ system, as a function of temperature and composition. On the base of these data and already known physicochemical properties of the melts we will try to discuss the character of anionic interactions and corresponding structural changes in the melts due to the mixing process.

2. Experimental

2.1. Sample preparation

The analytical grade purity KF (Lachema) was dried for several days under vacuum in presence of P₂O₅ at ambient temperature, and subsequently 5 h at 450 K. KBF₄ analytical grade (Fulka) was dried at 680 K for 4 h. The prepared mixtures were melted at temperatures about 20 K above liquidus temperature at particular compositions. The liquidus temperatures have been adopted from a phase diagram by Barton et al. [2]. Rapidly cooled samples were then loaded into platinum crucibles in a dry box. The platinum crucibles with samples were subsequently soldered using gold. A special technique for loading samples into the crucibles through a small hole and for soldering of crucibles was developed, to prevent wetting of samples during manipulation.

2.2. Calorimetric measurements

Relative enthalpies $H_{\text{rel}} = H(T) - H(298 \text{ K})$ of melts at mole fractions $x(\text{KBF}_4) = 0.35, 0.42, 0.60$ and 0.80 have been measured using a high temperature drop calorimeter described by Proks et al. [8]. The compositions of the samples were chosen with regard to the composition interval of the stable liquid phase available for chosen temperatures. The highest temperature for measurements was 1082 K. The lower limit was about 20 K above the liquidus temperature at particular composition. Closing of the samples in Au soldered Pt crucibles should prevent the violation of stoichiometry due to escaping of gaseous decomposition products on heating during calorimetric measurements. The tightness of the crucibles was checked by weighing before and after each calorimetric measurement. To keep the tightness of the crucibles at high temperatures was the largest experimental problem that influenced significantly the choice of the highest temperature and the number of correctly performed measurements.

3. Results and discussion

Temperature dependences of relative enthalpies of melts have been found to be linear. Measured relative enthalpies along with data smoothed by linear regression and standard deviations of the calculated values are listed in Tables 1–4. The given standard deviations have been calculated by the law of propagation of errors using variances of both coefficients of fitted linear temperature dependences as well as covariance between them.

The heat capacities of melted mixtures have been determined by differentiation of analytical expressions fitted to measure relative enthalpy data. The

Table 1
Relative enthalpies of melt at composition $x(\text{KBF}_4) = 0.35$

T/K	$h_{\text{rel}}/(\text{J g}^{-1})$	$h_{\text{calc}}/(\text{J g}^{-1})$	$\sigma(h_{\text{calc}})/(\text{J g}^{-1})$
1042	1125.5	1123.8	1.6
1052	1134.5	1136.8	1.2
1062	1149.8	1149.8	1.0
1081	1174.9	1174.4	1.9

Table 2
Relative enthalpies of melt at composition $x(\text{KBF}_4) = 0.42$

T/K	$h_{\text{rel}}/(\text{J g}^{-1})$	$h_{\text{calc}}/(\text{J g}^{-1})$	$\sigma(h_{\text{calc}})/(\text{J g}^{-1})$
1001	1077.5	1071.3	3.2
1001	1068.8	1071.3	3.2
1026	1099.0	1104.0	2.2
1054	1137.0	1140.6	2.1
1054	1143.4	1140.6	2.1
1082	1173.7	1177.3	3.1
1082	1182.9	1177.3	3.1

Table 3
Relative enthalpies of melt at composition $x(\text{KBF}_4) = 0.60$

T/K	$h_{\text{rel}}/(\text{J g}^{-1})$	$h_{\text{calc}}/(\text{J g}^{-1})$	$\sigma(h_{\text{calc}})/(\text{J g}^{-1})$
894	910.9	910.5	1.2
914	938.1	936.7	1.1
944	975.0	976.0	0.9
993	1037.9	1040.1	0.9
1062	1132.0	1130.5	1.6

Table 4
Relative enthalpies of melt at composition $x(\text{KBF}_4) = 0.80$

T/K	$h_{\text{rel}}/(\text{J g}^{-1})$	$h_{\text{calc}}/(\text{J g}^{-1})$	$\sigma(h_{\text{calc}})/(\text{J g}^{-1})$
793	779.4	779.4	5.2
904	924.5	926.5	1.8
964	1007.7	1006.1	1.5
1022	1085.9	1083.0	2.2
1072	1146.8	1149.3	3.7

evaluated values are partially within the uncertainty limits of the determination. Nevertheless, a tendency to positive deviation from additivity is clearly signified.

The molar enthalpies of mixing have been determined, using measured enthalpies of melts and published enthalpic data of pure component liquids [9] by the equation

$$\Delta_{\text{mix}}H(\text{melt}) = H_{\text{rel}}(\text{melt}) - [1 - x(\text{KBF}_4)] \times H_{\text{rel}}(\text{KF}) - x(\text{KBF}_4)H_{\text{rel}}(\text{KBF}_4) \quad (1)$$

where $H_{\text{rel}}(\text{melt})$ is the measured relative enthalpy of melt at temperature T and composition $x(\text{KBF}_4)$,

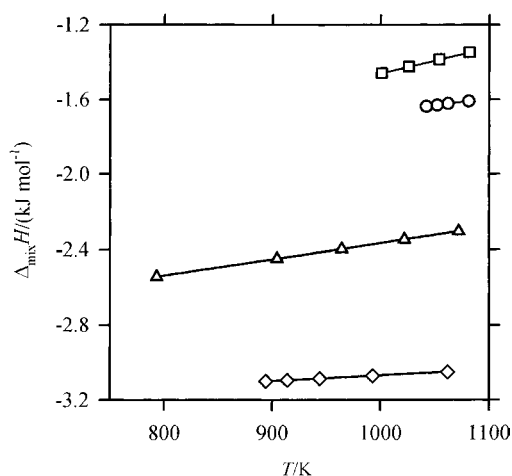


Fig. 1. Temperature dependences of molar enthalpy of mixing of melts in KF–KBF₄ system at compositions $x(\text{KBF}_4) = 0.35$ – circles, 0.42 – squares, 0.60 – diamonds and 0.80 – triangles.

$H_{\text{rel}}(\text{KF})$ and $H_{\text{rel}}(\text{KBF}_4)$ are enthalpies of pure component liquids at temperature T , and $x(\text{KBF}_4)$ is the mole fraction of KBF₄ in the melt. Total crystallisation of melts during quite quick cooling in the drop calorimeter was assumed.

In Fig. 1, the enthalpies of mixing for melts of considered compositions are plotted versus temperature. The H_{rel} data smoothed by linear regression were used to calculate $\Delta_{\text{mix}}H$ values. It can be seen in this figure, that the temperature dependences of the enthalpy of mixing are distinctly influenced by the composition.

The composition dependence of the enthalpy of mixing at 1050 K is shown in Fig. 2. Error bars correspond to standard deviations of the impute $\Delta_{\text{mix}}H$ values. The curve in this figure has been obtained fitting the $\Delta_{\text{mix}}H$ data by third order polynomial. The constrains $y_0 = 0$ and $y_0 + y_1 + y_2 + y_3 = 0$, y_i being coefficients of the regression polynomial, were used by regression analysis. Weighted regression was used, weights being equal to $1/\sigma^2$ of the impute values of $\Delta_{\text{mix}}H$. Standard deviations for $\Delta_{\text{mix}}H$ were equal to those for H_{rel} , due to zero values of errors for pure component relative enthalpies considered to calculate standard deviations of the calculated values of the enthalpy of mixing. Fig. 2 shows that negative deviation from ideality takes place in the whole composition interval of the system. The mini-

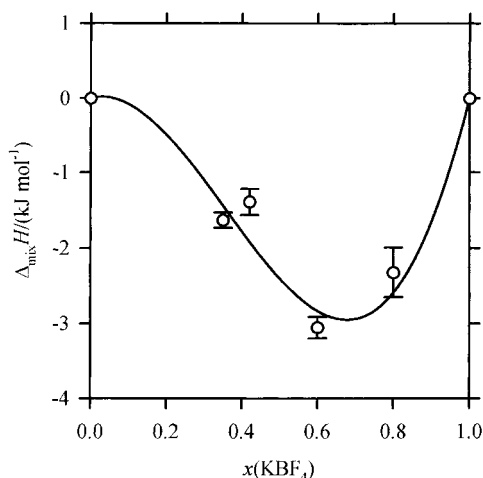
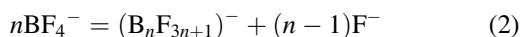


Fig. 2. Composition dependence of molar enthalpy of mixing at temperature 1050 K. The error bars represent $\sigma(H_{\text{rel,calc}})$ values at 1050 K.

imum of about -3 kJ mol^{-1} is reached at $x(\text{KBF}_4)$ around 0.7.

Accepting the hypothesis that BF_4 tetrahedra in the melt of pure KBF_4 are partially linked through B–F–B bridges due to bridging fluorine [1] we can assume an equilibrium of the type



in this melt. This means that one individual F^- ion originates from building of each B–F–B bridge. Thus in the KBF_4 melt individual BF_4^- ions may only exist in the presence of certain amount of F^- ions. Introducing additional F^- ions into this melt by addition of KF the equilibrium of the reaction (2) is shifted to the left. This process is exothermic.

These results are consistent with measured negative excess viscosity [1], negative excess electrical conductivity [5] and volume expansion on mixing [3].

The composition dependences of the excess mixing properties of melts in KF– KBF_4 system at 1050 K are plotted in Fig. 3. The $-T\Delta_{\text{mix}}S^{\text{E}}$ curve was determined using molar excess Gibbs energy of mixing function taken from Ref. [7]. Negative excess entropy of mixing implies increased ordering of the melt. The maximum of ordering is shifted towards the KBF_4 rich side of the system. Note that in Ref. [7] a model for $\Delta_{\text{mix}}G^{\text{E}}$ with temperature independent coefficients was used.

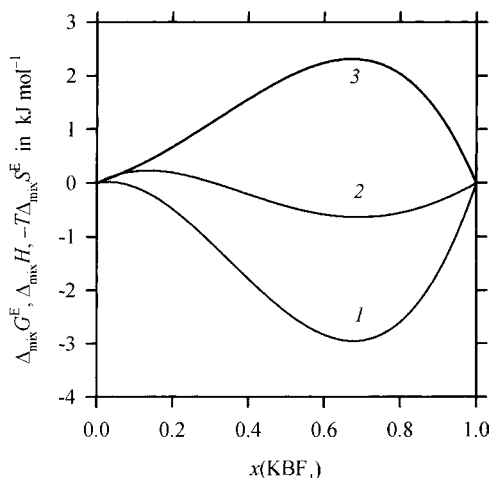


Fig. 3. Composition dependences of excess mixing properties at 1050 K. (1) $\Delta_{\text{mix}}H$, (2) $\Delta_{\text{mix}}G^{\text{E}}$ [7] and (3) $-T\Delta_{\text{mix}}S^{\text{E}}$.

4. Conclusions

The calorimetric study of the enthalpic properties of liquids in KF– KBF_4 system has shown that enthalpy of mixing is negative in the whole composition interval of the system. The minimum is about -3 kJ mol^{-1} at the composition around $x(\text{KBF}_4) = 0.7$. This result supports the conception of the formation of individual BF_4^- ions as a result of breaking of B–F–B bridges in KBF_4 melt due to introduction of F^- ions into the KBF_4 melt by addition of KF during the mixing process. This assumption is consistent with excess entropy of mixing and with already known viscosity, electrical conductivity and molar volume data.

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