Enthalpy of Mixing of Melts in the KF—K_2TiF_6 System

I. NERÁD, L. KOSA, E. MIKŠÍKOVÁ, and K. ADAMKOVIČOVÁ

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

Relative enthalpies of melts in the system KF—K_2TiF_6 at mole fractions of K_2TiF_6 equal to 0.25, 0.50, 0.75, and 1.0 have been determined from drop calorimetry measurements at the temperature 1198 K. The enthalpies of mixing and excess entropies of mixing have been calculated from experimental data. The $\Delta_{mix}H$ has been found to be negative in the whole composition range of the system. The exothermic effect at mixing reaches minimum of -4.9 kJ mol^{-1} at the composition around $x(K_2TiF_6) = 0.52$. The course of $\Delta_{mix}H$ curve indicates the tendency to association of the particles in the melt, producing more complex structural units.

The system KF—K_2TiF_6 is a subsystem of the important quaternary system KF—KCl—KBF_4—K_2TiF_6, the melts of which may be used as electrolytes in the electrochemical synthesis of TiB_2, especially when coherent coatings on metallic bases have to be prepared [1]. The above system is also important for electrochemical deposition of the titanium metal [2].

The knowledge of the structure, especially of the ionic composition of these electrolytes is important for the understanding of the mechanism of electrochemical processes. The kinds of electroactive species, present in the melt, are considerably influenced by the melt composition and the interaction of the ionic components. Some considerations concerning the potential ionic composition of the melts and types of interactions between end member ionic constituents can be done indirectly on the basis of the known physicochemical properties of the melts.

The phase diagram of the system KF—K_2TiF_6 was studied by *Chernov* and *Ermolenko* [3]. The congruently melting compound K_3TiF_7 with the melting temperature 1048 K, is formed in this system. The zero value of the tangent to the liquidus curve at $x(K_2TiF_6) = 0.5$ indicates that this compound undergoes considerable thermal dissociation at melting.

Recently several papers dealing with some physicochemical properties have been published. *Daněk et al.* [4] studied densities of the binary system melts as part of the ternary system KF—KCl—K_2TiF_6. They found out that the formation of the K_3TiF_7 compound does not affect substantially the volume properties of the melts. The excess molar volume of the KF—K_2TiF_6 system is slightly positive at 1100 K. This indicates that either this compound dissociates to a considerable degree in the melt, or the volumes of the ions TiF_6^{2-} and TiF_7^{3-} are fairly similar. The dissociation degree $\alpha = 0.7$ at 1100 K and dissociation enthalpy of

K_3TiF_7 equal to 52.4 kJ mol^{-1} have been calculated in the above paper.

The dissociation degree $\alpha = 0.64$ was calculated on the basis of the experimentally determined phase diagram [2]. In spite of the dissociation, however, the concentration of the TiF_7^{3-} complex anions in the system was still comparable with the concentration of the TiF_6^{2-} anions [2].

Positive deviations from the additivity of the logarithms of viscosity were found in the system KF—K_2TiF_6 [5, 6]. These results also support the assumption about the formation of the TiF_7^{3-} anions in the melt.

These results of the physicochemical analysis of the melt properties show that the most characteristic feature of these melts seems to be the formation of the more complex, thermodynamically less stable ionic species TiF_7^{3-} with lowered symmetry of the coordination sphere. The presence of these anions facilitates most probably the electroreduction of titanium ions on the cathode.

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

EXPERIMENTAL

The anal. grade purity $KF \cdot 2H_2O$ (Lachema) was dried under vacuum in the presence of P_2O_5 for about three weeks at ambient temperature, and subsequently for 5 h at 453 K. K_2TiF_6 of anal. grade (Fluka) was dried for 4 h at 473 K. The prepared mixtures were melted at temperatures about 20 K above liquidus

temperature at particular compositions. The cooled samples were then loaded into platinum crucibles in a dry box. The crucibles were then closed by soldering with gold to prevent any contact of the samples with ambient atmosphere. The method has been described in detail in [7]. Tightness of the crucibles was checked by weighting before each calorimetric measurement.

The specific relative enthalpies $h_{rel} = h(1198\ K) - h(298\ K)$ of melts at mole fractions $x(K_2TiF_6)$ equal to 0.25, 0.50, 0.75, and 1.0 have been measured using a high-temperature drop calorimeter. In this equipment the sample is heated in the calorimetric furnace at the chosen temperature T and subsequently dropped into a calorimetric block, kept at 298 K. The measured quantity is determined evaluating the heat lost of the block into its surrounding after the sample has been dropped. Details are described by *Proks et al.* [8].

RESULTS AND DISCUSSION

The measured specific relative enthalpies along with arithmetic means and standard deviations of the observed values are listed in Table 1. The experimental error in the relative enthalpy measurement did not exceed 0.8 %.

The molar enthalpies of mixing have been determined, using measured enthalpies of melted mixtures of chosen composition, measured enthalpy of the K_2TiF_6 melt, and enthalpy of KF melt obtained from Ref. [9] by the equation

$$\Delta_{mix}H(melt) = H_{rel}(melt) - [1 - x(K_2TiF_6)]H_{rel}(KF) - x(K_2TiF_6)H_{rel}(K_2TiF_6) \quad (1)$$

where $H_{rel}(melt)$ is the molar relative enthalpy of melt at temperature T and composition $x(K_2TiF_6)$, $H_{rel}(KF)$ and $H_{rel}(K_2TiF_6)$ are molar relative enthalpies of pure component liquids at temperature T, and $x(K_2TiF_6)$ is the mole fraction of K_2TiF_6 in the melt. The $H_{rel,\phi}$ data were used to calculate $\Delta_{mix}H$ values. The total crystallization of the melts during rapid cooling in the drop calorimeter was assumed.

The composition dependence of the molar enthalpy of mixing has been calculated by fitting the $\Delta_{mix}H$ data by a third-order polynomial. The weights used by the linear regression analysis were proportional to the reciprocal values of variances of molar enthalpies of mixing. The following equation has been obtained

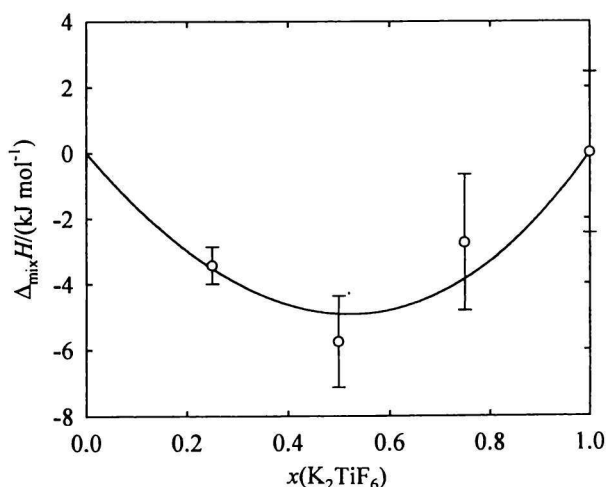$$\Delta_{mix}H/(kJ\ mol^{-1}) = -17.9341x(K_2TiF_6) + 14.4106[x(K_2TiF_6)]^2 + 3.5235[x(K_2TiF_6)]^3 \quad (2)$$

with the standard error of estimate $\sigma = 0.3\ kJ\ mol^{-1}$.

The composition dependence of the molar enthalpy of mixing at 1198 K, along with the experimental $\Delta_{mix}H$ data is shown in Fig. 1. The error bars represent 2σ values of the $\Delta_{mix}H$ data, calculated using $\sigma(H_{rel})$ values

Table 1. Relative Enthalpies of Melts at Temperature 1198 K

$x(K_2TiF_6)$	h_{rel}	$h_{rel,\phi}$	$\sigma(h_{rel,\phi})$
	$J\ g^{-1}$	$J\ g^{-1}$	$J\ g^{-1}$
1	1101.6	1091.9	7.3
	1096.8		
	1090.6		
	1085.6		
	1084.8		
0.75	1105.5	1097.6	8.3
	1102.2		
	1096.1		
	1086.6		
0.50	1108.3	1105.0	7.2
	1110.0		
	1096.7		
0.25	1173.7	1170.5	3.6
	1171.0		
	1166.6		
0	1357.5*		

*Ref. [9].

Fig. 1. Composition dependence of the enthalpy of mixing at 1198 K.

$$\sigma(\Delta_{mix}H(melt)) =$$
$$= \sqrt{[\sigma(H_{rel}(melt))]^2 + [x(K_2TiF_6)]^2[\sigma(H_{rel}(K_2TiF_6))]^2} \quad (3)$$

It can be seen in Fig. 1 that the negative deviation from ideality takes place in the whole composition range of the system. The minimum of about $-4.9\ kJ\ mol^{-1}$ is reached at $x(K_2TiF_6)$ around 0.52. This course of the $\Delta_{mix}H$ curve indicates a tendency to association of particles in the melt due to the interactions between anions present in the melts of pure components. We can assume an equilibrium of the
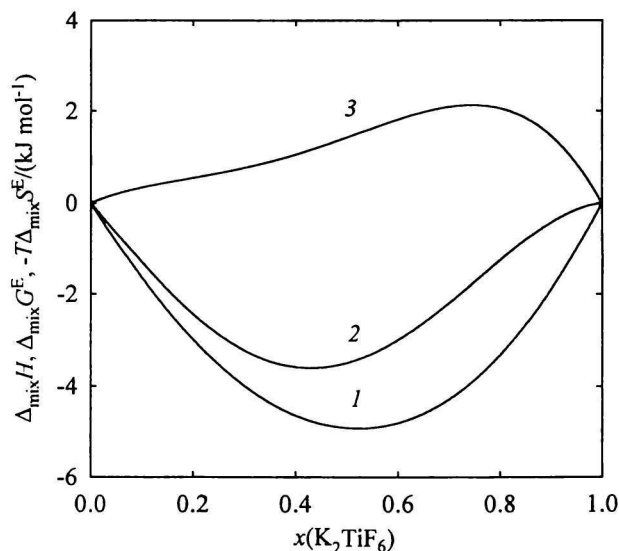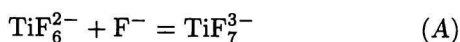
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Fig. 2. Excess mixing properties. *1.* $\Delta_{mix}H$, *2.* $\Delta_{mix}G^{E}$, *3.* $-T\Delta_{mix}S^{E}$.

type

$$TiF_6^{2-} + F^- = TiF_7^{3-} \qquad (A)$$

in this melt. The negative enthalpy of mixing indicates that a part of the TiF$_7^{3-}$ anions is expected to stay undissociated at equilibrium in the melt at the considered temperature. This is in accordance with the values of the degree of dissociation determined on the basis of thermodynamic analysis and volume properties of the melts [2, 4]. The assumption on the arising of the more complex particles in the melt is also consistent with the measured positive excess viscosity [5].

The composition dependence of the excess mixing properties of melts at 1198 K is plotted in Fig. 2. The $-T\Delta_{mix}S^{E}$ curve was determined using the molar excess Gibbs energy of mixing function from [10]. Negative excess entropy of mixing implies increased ordering of the melt. Note that in [10] a model for $\Delta_{mix}G^{E}$ with temperature-independent constants was used.

CONCLUSION

The calorimetric study of the enthalpic properties of liquids in the KF—K$_2$TiF$_6$ system has shown that the negative deviation from ideality at mixing takes place in the whole composition range of the system. This indicates a tendency to association of particles in the melt due to the interactions between anions present in the melts of pure components. The negative enthalpy of mixing indicates that a part of the TiF$_7^{3-}$ anions in the melt is not dissociated at the considered temperature. These conclusions are consistent with other physicochemical properties of the melts, *e.g.* density, viscosity, and phase equilibria.

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