Cryoscopy of B_2O_3 in Molten Alkali Metal Fluorides

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The mechanism of dissolution of boron oxide in LiF, NaF, and KF and the ionic structure of created molten mixtures were studied by the cryoscopic method. The investigation was carried out in B_2O_3 mole fraction region from 0 to 5 mole %. The results of cryoscopic measurements have been confirmed by X-ray analysis and by infrared spectroscopy as well. It was found that alkali metal tetraborate, alkali metal metaborate, and boron trifluoride are created in the molten systems $LiF—B_2O_3$ and $NaF—B_2O_3$. Gaseous BF_3 is evaporated from the melt. Except alkali metal cations the anions F^-, BO_2^-, and $B_4O_7^{2-}$ are present in the melt. In the system $KF—B_2O_3$ boron oxide reacts with KF under the formation of potassium tetraborate and potassium tetrafluoroborate. The ionic structure of created molten mixtures is given by the presence of potassium cations and anions F^-, $B_4O_7^{2-}$, and BF_4^-. The presence of the metaborate anions, BO_2^-, was not proved by spectral methods, however, it cannot be excluded in melts with low concentration of boron oxide.

Cryoscopy is one of the various indirect methods often used for determination of chemical reactions in melts on the basis of which the ionic composition can be predicted [1]. From an analysis of the liquidus curves in a simple binary system (A—B) it follows that the melting point depression of the component A affected by an addition of the component B can be expressed by the equation

$$-\Delta T(A) = R\{T(\text{fus, A})\}^2/\Delta H(\text{fus, A})x(B)k_{St} \quad (1)$$

where $-\Delta T(A)$ is the melting point depression of substance A, $x(B)$ is the mole fraction of substance B, k_{St} is Stortenbeker factor for component B [2], R is the gas constant and $\Delta H(\text{fus, A})$ is enthalpy of melting of substance A at melting temperature.

In this type of solutions [3, 4], the Stortenbeker factor is numerically equal to the number of new particles which are introduced to the substance A by one molecule of substance B. Eqn (1) is a limiting relation which is valid exactly only for $x(B) \to 0$. A tangent (k_0) of the liquidus curve for an infinite diluted solution is given by the limit of the differentiation of eqn (1) according to $x(B)$ for $x(B) \to 0$

$$\lim_{x \to 0} \frac{d\Delta T}{dx(B)} = -R\{T(\text{fus, A})\}^2/\Delta H(\text{fus, A}) \, k_{St} = k_0 \quad (2)$$

On the basis of the known value k_{St} the mechanism of dissolution of boron oxide in molten alkali metal fluorides and the ionic structure of the originated solutions can be determined.

An analysis of the phase diagram of the molten system $LiF—B_2O_3$ is published in [5, 6]. A congruently melted compound $LiF \cdot B_2O_3$ with m.p. = 840 °C was identified in the system. This compound creates with LiF an eutectic point at 33.3 mole % B_2O_3 and eutectic temperature 798 °C. In the B_2O_3

composition region from 5 to 23 mole % an existence of two liquidus phases is declared [6].

The system $NaF—B_2O_3$ was studied as a part of quaternary reciprocal system $BF_3—NaF—Na_2O—B_2O_3$ [7]. Two crystal phases $2NaF \cdot B_2O_3$ and $NaF \cdot B_2O_3$ were determined in the stable diagonal $NaF—B_2O_3$ of the above reciprocal system.

The phase diagram of the system $KF—B_2O_3$ is described in [6]. It was declared as a simple eutectic system. The authors explain the dissolution of B_2O_3 in potassium fluoride by the chemical reaction under the formation of potassium tetrafluoroborate and potassium tetraborate.

In this work the mechanism of dissolution of boron oxide in molten alkali fluorides (LiF, NaF, KF) and the ionic structure of created melts are studied by the cryoscopic method.

EXPERIMENTAL

For the sample preparation (total amount 20 g) the following chemicals were used: LiF, NaF, and KF (anal. grade, Lachema, Brno) and B_2O_3 (anal. grade, Fluka).

A homogenized sample was melted in a platinum crucible placed in a resistance furnace. The temperature was measured using a Pt/Pt10Rh thermocouple. The cooling curves were recorded by means of data acquisition computer system. The applied scheme made it possible to measure the temperature differences with the relative accuracy ± 0.3 K. The cooling rate of the sample did not exceed 1 K min^{-1}.

The phase composition of individual cooled melts was determined by the X-ray diffraction analysis and by infrared spectroscopy as well.
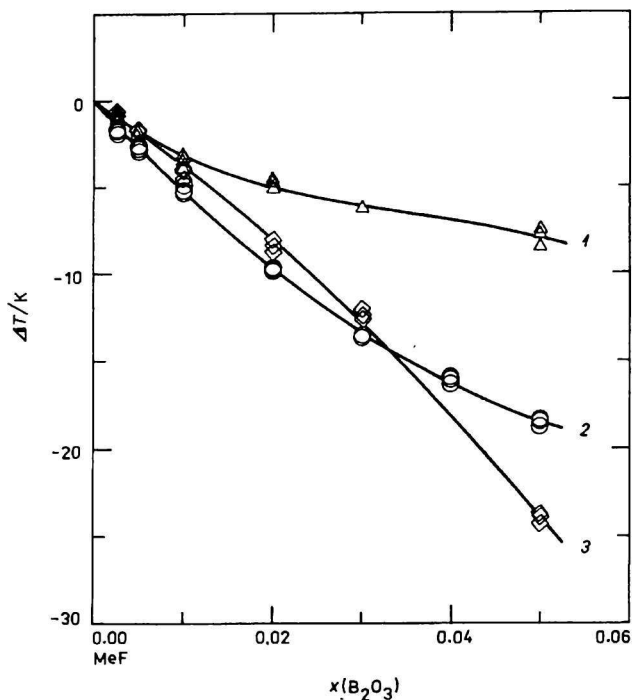
Fig. 1. Melting point depression of alkali metal fluorides as a function of the boron oxide content. *1*. LiF—B_2O_3; *2*. NaF—B_2O_3; *3*. KF—B_2O_3.

RESULTS

In Fig. 1 the experimentally determined dependences of temperatures of primary crystallization of alkali metal fluorides on mole fraction of boron oxide are shown. The values ΔT represent the difference between the melting point temperature of pure alkali metal fluorides and the temperature of primary crystallization of molten mixtures. From the tangents of the experimental liquidus curves in the melting point of the pure solvent the values of Stortenbeker factor have been calculated according to eqn (*1*). The values of k_{St} are summarized in Table 1. In calculations the published thermodynamic data [8] were used.
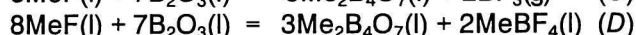
X-Ray diffraction analysis and infrared spectroscopy were carried out in all tested systems. The samples contained 10, 20, and 30 mole % B_2O_3. The presence of alkali metal tetraborate was proved in all samples. Alkali metal metaborates were present in the mixtures based on LiF and NaF. In the system KF—B_2O_3 the presence of $K_2B_4O_7$ and KBF₄ was proved by both X-ray analysis and IR spectroscopy.

Table 1. Experimental Values of Stortenbeker Factor k_{St} in Molten Mixtures of Alkali Metal Fluorides and Boron Oxide for $x(B_2O_3) \rightarrow 0$

Mixture	LiF—B_2O_3	NaF—B_2O_3	KF—B_2O_3
k_{St}	1.05	1.42	0.9

DISCUSSION

On the basis of the results of spectroscopic measurements the following chemical reactions can be suggested in molten mixtures of alkali metal fluorides and boron oxide

$$3MeF(l) + 2B_2O_3(l) = 3MeBO_2(l) + BF_3(g) \quad (A)$$
$$4MeF(l) + 2B_2O_3(l) = 3MeBO_2(l) + KBF_4(l) \quad (B)$$
$$6MeF(l) + 7B_2O_3(l) = 3Me_2B_4O_7(l) + 2BF_3(g) \quad (C)$$
$$8MeF(l) + 7B_2O_3(l) = 3Me_2B_4O_7(l) + 2MeBF_4(l) \quad (D)$$

The calculated values of Gibbs energy, $\Delta_r G$, and equilibrium constants of the above chemical reactions at 1200 K are in Table 2. The thermodynamic data of LiBF₄ and NaBF₄ for 1200 K are not published in accessible literature, so the values of $\Delta_f G°$ have been estimated ($\Delta_f G°(LiBF_4) = -1300$ kJ mol⁻¹, $\Delta_f G°(NaBF_4) = -1450$ kJ mol⁻¹) [9]. It is suggested on the basis of the values $\Delta_r G$ of reactions (*A*) through (*D*) that the various reaction schemes are applied during the dissolution of boron oxide in the melts of individual alkali fluorides resulting in different ionic composition of solutions which influences the course of the liquidus curves (Fig. 1). The determination of the reaction schemes was done by the comparison of the experimental curve with the theoretical one, calculated for the given chemical reaction according to eqn (*1*), and by the comparison of the experimentally determined k_{St} with theoretical value of k_{St}. With respect to the very low concentration of B_2O_3 in tested melts, the ideal behaviour of molten mixtures has been assumed.

The calculation of the theoretical liquidus curve was carried out on the basis of the consideration that the chemical reaction between the basic fluoride melt and boron oxide runs up to the certain limit defined by the degree of conversion, α. The thermodynamic equilibrium constant K was calculated for every possible reaction in the given system according to the relation $-\Delta_r G = RT \ln K$ and it was compared with the equilibrium constant $K(\alpha)$ calculated on the basis of the chosen degree of conversion. In the case when the value $K(\alpha)$ was equal to the thermodynamic equilibrium constant K, the equilibrium concentration of alkali metal fluoride in the melt was evaluated and the melting point depression ΔT was calculated according to the relation (*1*). The values ΔT were compared with the experimental data.

The results of spectroscopic measurements and thermodynamic analysis (Table 2) indicate that in the system LiF—B_2O_3 the dissolution of boron oxide runs according to the chemical reactions (*A*) and (*C*). Fig. 2 shows the theoretical and experimental values of ΔT as a function of the boron oxide content in the melt. The calculation was carried out for both the case when BF₃ remains dissolved in

Table 2. Calculated Values of Gibbs Energies and Equilibrium Constants of Reactions (A) through (D) for Individual Systems

Reaction	Quantities	$LiF—B_2O_3$	$NaF—B_2O_3$	$KF—B_2O_3$
A	$\Delta_r G/kJ$	14.9	85.1	− 42.7
	K	2.2×10^{-1}	2.0×10^{-4}	72.2
B	$\Delta_r G/kJ$	212.2	176.6	− 41.1
	K	5.8×10^{-10}	2.1×10^{-8}	61.5
C	$\Delta_r G/kJ$	− 11.9	83.5	− 205.7
	K	3.3	2.3×10^{-4}	9.0×10^{8}
D	$\Delta_r G/kJ$	383.1	266.5	− 202.7
	K	2.1×10^{-17}	2.5×10^{-12}	6.7×10^{8}

the melt and the case when BF_3 is evaporated from the melt (in this case $\alpha = 1$). The value of Stortenbeker factor of the experimental curve for $x(LiF) \rightarrow 1$ ($k_{St} = 1.05$) is between the values of the theoretical curves calculated for the reaction (A) ($k_{St} = 1.99$) and for the reaction (C) ($k_{St} = 0.91$). For this reason the simultaneous equilibrium of the reactions (A) and (C) was calculated. It was found that the theoretical liquidus curve calculated for the reaction scheme

$$3LiF(l) + 3B_2O_3(l) = LiBO_2(l) + \\ + Li_2B_4O_7(l) + BF_3(g) \quad (E)$$

fits the experimental results best. The value of Stortenbeker factor calculated for the reaction (E) is 0.99. The calculations showed that with increasing content of B_2O_3 in the mixture the reaction (C) be-

comes dominating. This is in good agreement with X-ray analysis results where the peaks representing $LiBO_2$ gradually disappeared. The increase of the temperature of primary crystallization (cf. curve 2 (Fig. 2)) can be caused by the evaporation of BF_3 from the melt and by the presence of the small amount of higher polyborates not identified by the spectroscopic methods. The evaporation of BF_3 is confirmed by the evolution of gas from the melts with higher content of boron oxide.

It can be assumed on the basis of both the spectroscopic measurements and the course of the experimental liquidus curves that the mechanism of dissolution of B_2O_3 in molten sodium fluoride is similar to that in lithium fluoride. Fig. 3 shows the experimental temperatures of primary crystallization together with the theoretical liquidus curves calcu-
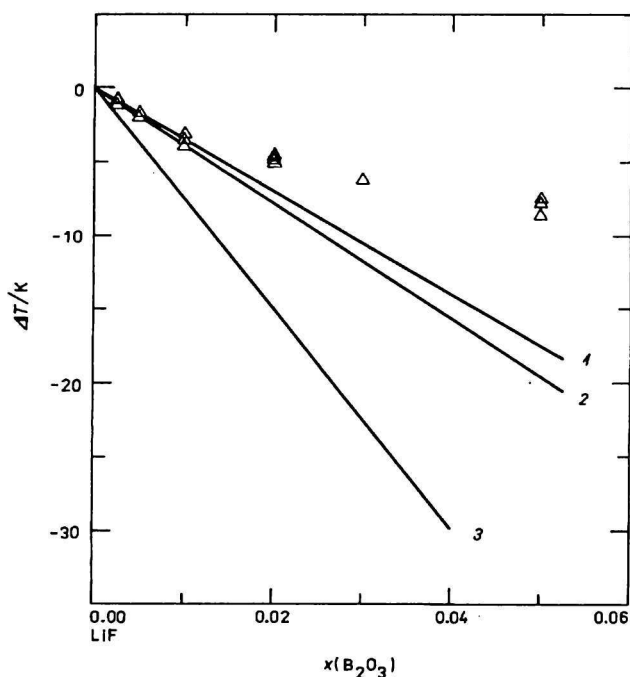

Fig. 2. Theoretical liquidus curves of the system $LiF—B_2O_3$ calculated for the reactions (A), (C), and (E). Δ Experimental points. *1*. Reaction (C) (BF_3 is dissolved in the melt) $k_{St} = 0.91$; *2*. reaction (E) (BF_3 is dissolved in the melt) $k_{St} = 0.99$; *3*. reaction (A) (BF_3 is dissolved in the melt) $k_{St} = 1.99$.
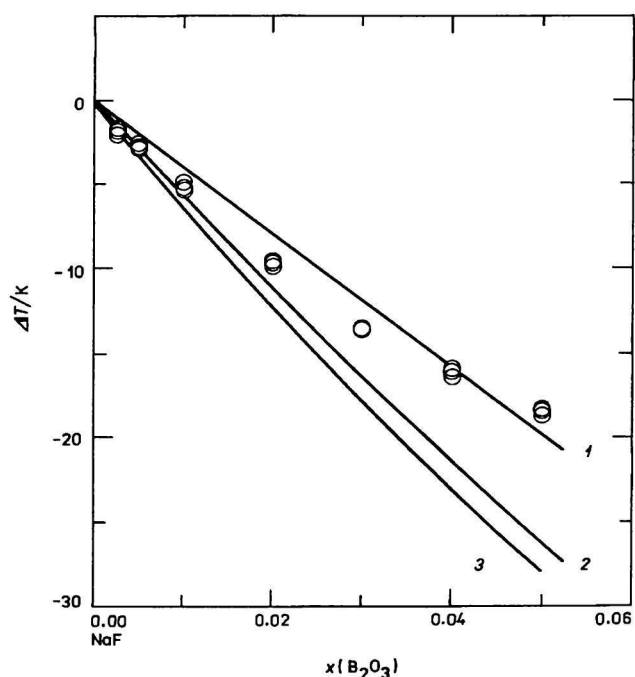
Fig. 3. Theoretical liquidus curves of the system $NaF—B_2O_3$ calculated for the reactions (A), (C), and (F). o Experimental points. *1*. Reaction (C) (BF_3 is dissolved in the melt) $k_{St} = 0.94$; *2*. reaction (F) (BF_3 is dissolved in the melt) $k_{St} = 1.43$; *3*. reaction (A) (BF_3 is dissolved in the melt) $k_{St} = 1.62$.
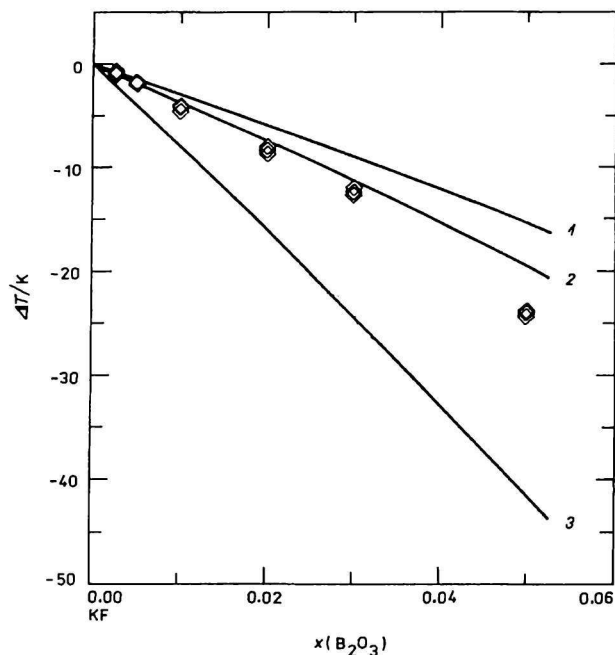
Fig. 4. Theoretical liquidus curves of the system $KF-B_2O_3$ calculated for the reactions (*B*), (*D*), and (*G*). ◇ Experimental points. *1*. Reaction (*D*) k_{St} = 0.74; *2*. reaction (*G*) k_{St} = 0.91; *3*. reaction (*B*) k_{St} = 1.98.

lated for the reactions (*A*) and (*C*). The values of thermodynamic equilibrium constants of these reactions are small (Table 2) but the great surplus of NaF and the gradual evaporation of BF_3 allow the fast establishing of the reaction equilibrium. This is confirmed also by the good reproducibility of the cryoscopic measurements.

The values of Stortenbeker factor in the limit $x(NaF) \rightarrow 1$ of the reactions (*A*) and (*C*) are 0.94 and 1.62, respectively. It indicates that, similarly to the previous melt, both the reactions (*A*) and (*C*) are applied in dissolution of boron oxide in NaF. Fig. 3 shows the theoretical curve (curve 2) calculated for the reaction

$$15NaF(l) + 11B_2O_3(l) = 13NaBO_2(l) +$$
$$+ Na_2B_4O_7(l) + 5BF_3(g) \quad (F)$$
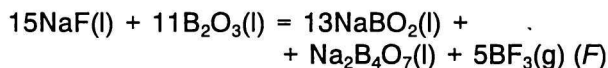
The value of Stortenbeker factor of this curve is 1.43 which is in good agreement with the experimental value 1.42.

The analysis of calculations of liquidus curves shows that the reaction (*B*) is dominating at low concentrations of B_2O_3. On the other hand, with increasing concentration of boron oxide in the melt the reaction (*C*) dominates in the mechanism of dissolution. This is also confirmed by the IR spectroscopy in the mixture containing 30 mole % B_2O_3 where the peaks representing $NaBO_2$ were not registered.

The course of the experimental liquidus curve of the system $KF-B_2O_3$ (Fig. 1) is different when compared to the course of experimental curves of the two previous systems. This fact together with the results

of spectroscopic measurements indicates that boron oxide reacts with potassium fluoride according to the chemical reactions (*B*) and (*D*) under the formation of KBF_4 which is dissolved in the melt. In Fig. 4 the experimental and theoretical liquidus curves calculated for the reactions (*B*) and (*D*) are shown together with the curve calculated for the reaction

$$32KF(l) + 25B_2O_3(l) = 6KBO_2(l) +$$
$$+ 9K_2B_4O_7(l) + 8KBF_4(l) \quad (G)$$
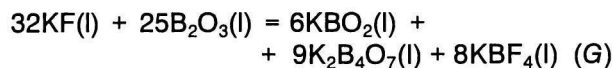
The value of Stortenbeker factor of the theoretical liquidus curve calculated for the reaction (*G*) is 0.91 which is close to the experimental value 0.90. This indicates that in the mixtures with low content of boron oxide the dissolution runs according to eqn (*G*). The calculations of the simultaneous equilibrium of reactions (*B*) and (*D*) proved that, as in the two previous systems, with increasing content of B_2O_3 in the mixture potassium tetraborate is preferentially created. This was confirmed by both X-ray and IR spectroscopy where the presence of metaborate anions was not recorded.

CONCLUSION

It can be concluded on the basis of the above discussion that during the dissolution B_2O_3 reacts with the basic fluoride melt under the formation of metaborate and tetraborate of alkali metals, while the content of alkali metal tetraborates increases with increasing concentration of boron oxide in basic melt. As a further product of these chemical reactions in the systems $LiF-B_2O_3$ and $NaF-B_2O_3$ is boron trifluoride, BF_3, which is evaporating from the melt. In the system $KF-B_2O_3$ potassium tetrafluoroborate, KBF_4, is created in the melt. The ionic structure of the individual molten systems is determined by their chemical composition.

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