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Phase diagram of the system LiF–Na_3AlF_6–Na_3FSO_4. Experimental study and calculation

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Abstract

Experimental data on solid–liquid phase equilibria in the binary system Na_3AlF_6–Na_3FSO_4 and ternary system LiF–Na_3AlF_6–Na_3FSO_4 are presented. A model of molten salt mixtures based on the assumption of the existence of ionic assemblies is applied to this system and the temperatures of primary crystallization of LiF, Na_3AlF_6 and Na_3FSO_4 were calculated. Good agreement between the experimental and calculated data was achieved.

INTRODUCTION

Sodium sulphate is often present in different amounts in the cryolite-based electrolytes used for electrowinning of aluminium. The behaviour of sulphates in the electrolyte is not well understood [1]. In this paper we present experimental data on the solid–liquid equilibria in the ternary system LiF–Na_3AlF_6–Na_3FSO_4 and the binary system Na_3AlF_6–Na_3FSO_4. The experimental temperatures of primary crystallization are compared with calculations based on the model of molten salt mixtures.

EXPERIMENTAL

Phase equilibria in the ternary system LiF–Na_3AlF_6–Na_3FSO_4 were studied by the "cooling curves" method. The temperature was measured by a PtRh10–Pt thermocouple. The cooling rate was 1.2–2.5 K min^{-1} and the thermoelectric voltage of the thermocouple was sampled at 10 s intervals and stored in computer memory. The "cooling curves" obtained were numerically treated and the reproducibility in determination of equilibrium temperatures was about 0.3 K. The investigated samples (15 g) were placed in a platinum crucible.

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The thermocouple was calibrated using the melting temperatures of pure salts: NaF, θ(fus) = 993.5°C (this standard was supplied by the Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava); NaCl, θ(fus) = 800.8°C [2]; Na_2SO_4, θ(fus) = 884.8°C [3]; KCl, θ(fus) = 771°C [2] and the melting temperatures of eutectic mixtures: KCl–K_2SO_4, θ(eut) = 685°C [4] and NaCl–Na_2SO_4, θ(eut) = 628°C [5].

RESULTS AND DISCUSSION

The experimental phase diagrams of the systems Na_3AlF_6–Na_3FSO_4 and LiF–Na_3AlF_6–Na_3FSO_4 are plotted in Figs. 1 and 2, respectively. (Numerical data will be supplied by the authors on request.) It follows that the binary system Na_3AlF_6–Na_3FSO_4 is of a simple eutectic type with no formation of solid solutions being observed. The eutectic point has the parameters θ(eut) = 765.5°C, $x(Na_3AlF_6) = 0.12$, $x(Na_3FSO_4) = 0.88$. The phase diagrams of the other binary systems, i.e. LiF–Na_3AlF_6 and LiF–Na_3FSO_4 have been published already [6,7]. Our data are in good agreement with the cited papers. In these systems the existence of solid solutions of LiF in Na_3AlF_6 and Na_3FSO_4, respectively, is reported. Formation of solid solutions to the same extent was observed in the ternary system LiF–Na_3AlF_6–Na_3FSO_4. The parameters of the ternary eutectic point are 65.0 mol.% LiF, 6.5 mol.% Na_3AlF_6, 28.5 mol.% Na_3FSO_4; θ(eut) = 606°C.

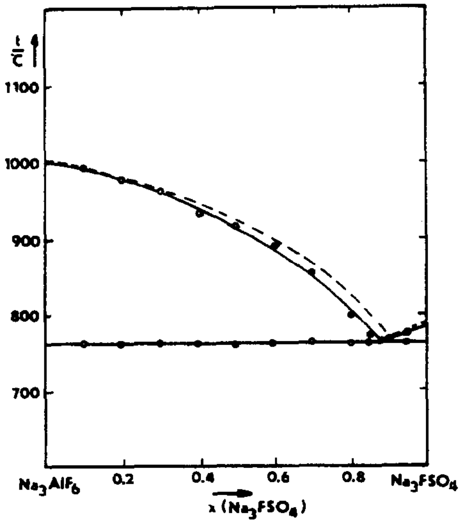

Fig. 1. Phase diagram of the system Na_3AlF_6–Na_3FSO_4. Key: ———, experimental; - - - - - -, calculated.

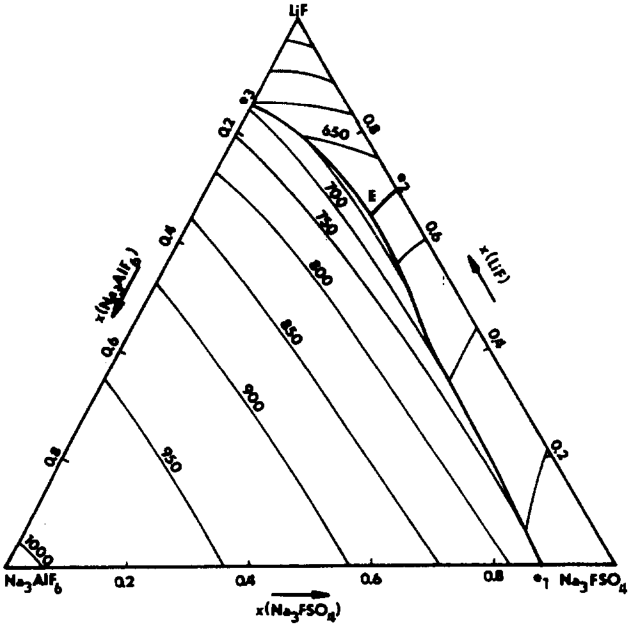

Fig. 2. Experimental phase diagram of the system $LiF–Na_3AlF_6–Na_3FSO_4$.

The equilibrium temperature of the primary crystallization can be calculated according to the Le Chatelier–Shreder equation

$$\ln a_{A,l} = \frac{\Delta H_m^{\ominus}}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right) \tag{1}$$

where $\Delta H_m^{\ominus}$ is the standard molar enthalpy of melting of pure substance A, T_m (K) is the temperature of melting of pure component, and T is the equilibrium temperature of primary crystallization of A. It is assumed that the difference in heat capacity between solid and liquid A is so small that it can be neglected. (This is a reasonable assumption when $T_m - T < 100$ K.) In those cases where A forms a solid solution with other components, the expression on the left-hand side of eqn. (1) is replaced by $\ln(a_{A,l}/a_{A,s})$.

It follows that for calculation of the equilibrium temperature of primary crystallization it is necessary to know the activity of the components in a particular molten mixture.

It is assumed that, in the first approximation, the activity equals the model mole fraction of a given component and that the ideal thermodynamic behaviour of the molten mixture $LiF–Na_3AlF_6–Na_3FSO_4$ can be described under the following assumptions.

(i) The molten mixture consists of ionic assemblies $Li^+ \cdot F^-$, $Na^+ \cdot F^-$, $3Na^+ \cdot AlF_6^{3-}$, $3Na^+ \cdot FSO_4^{3-}$, $2Na^+ \cdot SO_4^{2-}$, $2Li^+ \cdot SO_4^{2-}$, $3Li^+ \cdot AlF_6^{3-}$, $Na^+ \cdot AlF_4^-$, and $Li^+ \cdot AlF_4^-$.

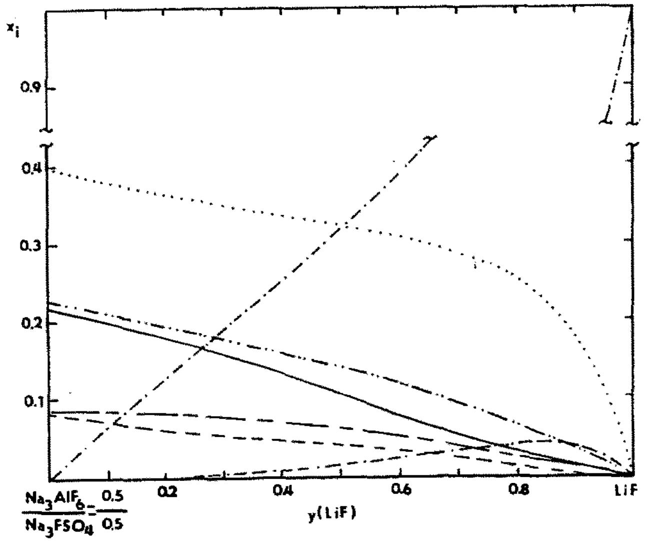

Fig. 3. Dependence of model mole fractions $x(i)$ on the weighed-in mole fraction y(LiF) in the section 50 mol.% Na_3AlF_6/50 mol.% Na_3FSO_4–LiF. Key: ——, Na_3AlF_6; - - - - -, Na_3FSO_4; ·–·–·, LiF; ······, NaF; –··–··, Na_2SO_4; -·-·-·, Li_3AlF_6; - —— - —— -, $NaAlF_4$.

(ii) In an ideal molten mixture the ionic assemblies mix randomly.

(iii) The model mole fractions can be calculated from the equilibria of reactions between ionic assemblies in the molten state (for simplicity, the components are written in molecular form).

In the case of the ternary system $LiF–Na_3AlF_6–Na_3FSO_4$ the following set of reaction schemes and corresponding equilibrium constants have been chosen: $Na_3AlF_6 = NaAlF_4 + 2NaF$, $K_1 = 0.06$ [1], $Na_3FSO_4 = Na_2SO_4 + NaF$, $K_2 = 1.123$ [8], $LiF + Na_2SO_4 = Li_2SO_4 + 2NaF$, $K_3 = 0.01$ [9], $NaAlF_4 + LiF = LiAlF_4 + NaF$, $K_4 = 0.05$ [10], $LiAlF_4 + 2LiF = Li_3AlF_6$, $K_5 = 50$ [10]. Temperature dependence of the equilibrium constants has been neglected in this approximation. (This is not a major simplification; it is used only to facilitate numerical calculation.) The equilibrium constants K_1, K_2, K_4 and K_5 were obtained from comparison of the experimental and calculated phase diagrams of the corresponding systems. It should be pointed out that a choice of other dissociation schemes of Na_3AlF_6 can lead to different values of constants describing thermal dissociation of sodium cryolite. The equilibrium constant K_3 was calculated from $\Delta_f G^{\ominus}$ values of pure components [9] at 1000 K.

For illustration, the model composition corresponding to the section of the ternary phase diagram $LiF–Na_3AlF_6–Na_3FSO_4$ with mole ratio $n(Na_3AlF_6)/n(Na_3FSO_4) = 1$ is shown in Fig. 3.

The calculated phase diagram of the binary system $Na_3AlF_6–Na_3FSO_4$ is presented in Fig. 1. In this calculation the model activity of Na_3AlF_6 in

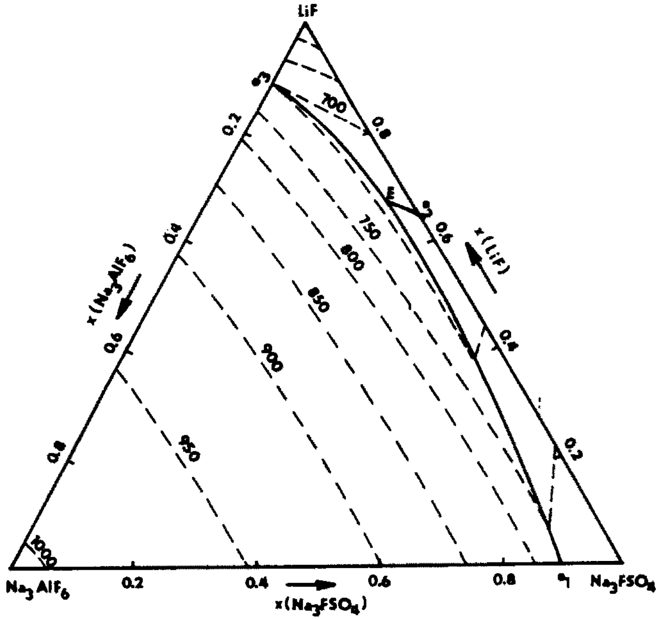

Fig. 4. Calculated phase diagram of the system LiF–Na_3AlF_6–Na_3FSO_4.

eqn. (1) is defined by the relationship [11]

$$a(Na_3AlF_6,l) = x(Na_3AlF_6,l)/x^{o}(Na_3AlF_6,l)$$

where $x^{o}(Na_3AlF_6,l)$ denotes the model mole fraction of non-dissociated sodium cryolite in the pure melt of Na_3AlF_6. It can be readily shown that this approach is similar to that using the hypothetical melting temperature of thermally dissociating compounds [12]. The activity of Na_3FSO_4 was estimated in the same way. As follows from Fig. 1 the agreement between the experimental and calculated phase diagrams of the system Na_3AlF_6–Na_3FSO_4 is good.

In Fig. 4 the calculated phase diagram of the ternary system LiF–Na_3AlF_6–Na_3FSO_4 is presented. No correction for the existence of solid solutions has been made. Nevertheless it can be seen that also in this case the experimental and calculated phase diagrams are in reasonably good agreement. This supports the thermodynamic model presented here.

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