Experimental study of the phase equilibria in the systems $NaCl—NaF—Na_3FSO_4$ and $NaCl—Na_2SO_4—Na_3FSO_4$

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Received 12 November 1982

Accepted for publication 15 August 1983

Phase equilibria in the ternary systems $NaCl—NaF—Na_3FSO_4$ and $NaCl—Na_2SO_4—Na_3FSO_4$ have been investigated using the thermal analysis method. Both systems were found to be simple eutectic systems, the coordinates of the ternary eutectic points being: system $NaCl—NaF—Na_3FSO_4$: 62.0 mole % NaCl, 11.4 mole % NaF, 26.6 mole % Na_3FSO_4, $T(E) = 898$ K; system $NaCl—Na_2SO_4—Na_3FSO_4$: 54.6 mole % NaCl, 31.8 mole % Na_2SO_4, 13.6 mole % Na_3FSO_4, $T(E) = 869$ K.

Исследованы фазовые равновесия в тройных системах $NaCl—NaF—Na_3FSO_4$ и $NaCl—Na_2SO_4—Na_3FSO_4$ с помощью метода термического анализа. Оказалось, что обе системы относятся к простому эвтектическому типу, причем координатами тройных эвтектических точек являются: для системы $NaCl—NaF—Na_3FSO_4$: 62,0 мольных % NaCl, 11,4 мольных % NaF, 26,6 мольных % Na_3FSO_4, $T(E) = 898$ K; для системы $NaCl—Na_2SO_4—Na_3FSO_4$: 54,6 мольных % NaCl, 31,8 мольных % Na_2SO_4, 13,6 мольных % Na_3FSO_4, $T(E) = 869$ K.

In the aluminium production nowadays great attention is being paid to the possibility of decreasing the operating temperature of the electrolysis in order to decrease the energy consumption, increase the current efficiency and reduce the fluorine emissions [1]. To this purpose various additives, among them NaCl, to the electrolyte are being tested. On the other hand, the aluminium electrolyte always contains Na_2SO_4 which reacts with NaF under formation of sodium fluorosulfate, Na_3FSO_4. This substance thermally dissociates to a high degree [2] according to the equation

$$Na_3FSO_4 \rightleftarrows NaF + Na_2SO_4$$

the equilibrium constant of the dissociation being

$$K_{\text{dis}(Na_3FSO_4)} = \frac{a(NaF)\cdot a(Na_2SO_4)}{a(Na_3FSO_4)}$$

An increase of the cryolite ratio (C.R.) leading to an increase of the NaF activity would result in a decrease of the activity of Na_2SO_4. This might exert a positive influence on the current efficiency as a higher ratio of detrimental SO_4^{2-} anions would be bonded as Na_3FSO_4 [1]. Besides, an increase of C.R. would result in reduced fluorine emissions. This may explain our interest in the systems NaCl—NaF—Na_3FSO_4 and NaCl—Na_2SO_4—Na_3FSO_4.

The above systems represent subsystems of the ternary system NaCl—NaF—Na_2SO_4. The phase equilibria in this system have been first investigated by *Wolters* [3] in 1910 and reexamined by *Mukimov* [4] in 1940. Both the authors agree on the formation of a congruently melting compound, Na_3FSO_4, in the binary system NaF—Na_2SO_4. The section connecting the figurative point of Na_3FSO_4 with the NaCl apex is a stable section dividing the phase diagram of the system NaCl—NaF—Na_2SO_4 into two simple eutectic systems, *viz.* NaCl—NaF—Na_3FSO_4 and NaCl—Na_2SO_4—Na_3FSO_4. The data on the ternary eutectics

Table 1

Characteristic data on the system NaCl—NaF—Na_3FSO_4

x(E)/mole %			T(E)/K	Ref.
NaCl	NaF	Na_3FSO_4		
62.30	14.20	23.50	893	[3]
60.30	16.10	23.60	897	[4]
62.00	11.40	26.60	898	This paper

Table 2

Characteristic data on the system NaCl—Na_2SO_4—Na_3FSO_4

x(E)/mole %			T(E)/K	Ref.
NaCl	Na_2SO_4	Na_3FSO_4		
51.70	35.90	12.40	867	[3]
50.00	38.70	11.30	875	[4]
54.60	31.80	13.60	869	This paper

presented by the above authors are given in Tables 1 and 2. The differences between the two sets of data obviously surpass possible experimental errors, this being one more reason for the systems to be reexamined.

Experimental

The phase equilibria in the ternary systems have been investigated by means of the thermal analysis (TA). The following chemicals were used: NaCl, anal. grade (Lachema, Brno), m.p. = 1073.8 K [5]; Na_2SO_4, anal. grade (Lachema, Brno), m.p. = 1157.8 K [5]; NaF, anal. grade (Lachema, Brno), m.p. = 1266.5 K (value determined at the Institute of Inorganic Chemistry, Centre for Chemical Research, Slovak Academy of Sciences, Bratislava).

The salts were weighed-in into a Pt crucible, the total weighed-in amount being 20 g. The temperature was measured by means of a PtRh10—Pt thermocouple and the cooling curves have been registered using a recorder EZ—11. The cooling rate did not surpass 2 K min^{-1}.

Results and discussion

The phase equilibria in the systems NaCl—NaF—Na_3FSO_4 and NaCl—Na_2SO_4—Na_3FSO_4 have been studied in the following way: Two sets of altogether 19 sections of the first order were selected in each system:

(i) Sections connecting the NaF or Na_2SO_4 apex and the figurative points with x/mole % NaCl: 10, 20, 30, 40, 50, 60, 70, 80, and 90 in the binary system Na_3FSO_4—NaCl. All points on the individual sections of this group are characterized by a constant $x(Na_3FSO_4):x(NaCl)$ ratio;

(ii) Sections connecting the NaCl apex with the figurative points in the binary system NaF—Na_3FSO_4 or Na_2SO_4—Na_3FSO_4 with x/mole % NaF or Na_2SO_4: 10, 20, 30, 40, 50, 60, 70, 80, and 90. All points of the individual sections of this group are characterized by a constant $x(Na_3FSO_4):x(NaF)$ or $x(Na_3FSO_4):x(Na_2SO_4)$ ratio.

The figurative points of samples submitted to the TA correspond to intersections of these two groups of sections. Besides, sections connecting the Na_3FSO_4 apex with the figurative points in the binary systems NaCl—NaF and NaCl—Na_2SO_4 with x/mole % NaF or $Na_2SO_4 = 50$ were investigated in order to increase the accuracy in the determination of the course of the lines of monovariant equilibrium. Altogether, 81 and 83 ternary mixtures have been investigated in the systems NaCl—NaF—Na_3FSO_4 and NaCl—Na_2SO_4—Na_3FSO_4, respectively. The phase diagrams of the ternary systems are shown in Figs. 1 and 2.

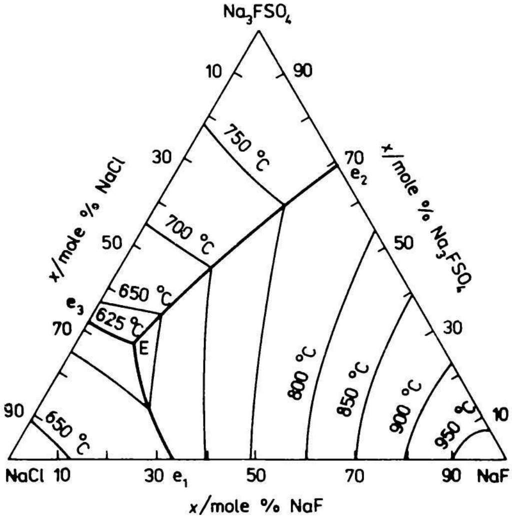

Fig. 1. Phase diagram of the system NaCl—NaF—Na_3FSO_4.

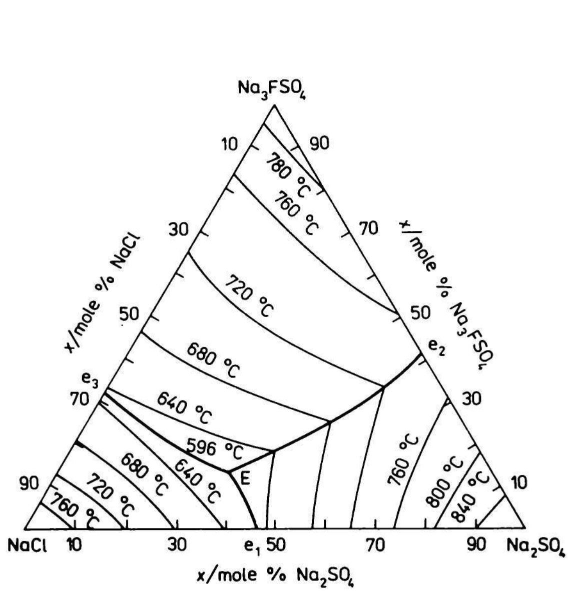

Fig. 2. Phase diagram of the system NaCl—Na_2SO_4—Na_3FSO_4.

It has been confirmed that the investigated systems NaCl—NaF—Na_3FSO_4 and NaCl—Na_2SO_4—Na_3FSO_4 are simple eutectic systems. The coordinates of the ternary eutectic points are presented in Tables 1 and 2. The differences between the determined eutectic compositions and temperatures, and the corresponding data reported by *Wolters* [3] and *Mukimov* [4] apparently are due to the rather low accuracy of the visual method used in the previous investigations.

Objective criteria of the accuracy of the determined values with respect to the incidental errors are given by relations derived from the mathematical statistics [6]. These relations hold on the assumption that

(i) all results have the same statistical weight,

(ii) the functional dependence of the statistical weight on the parameters of the set is known.

In this case, however, none of the above conditions is fulfilled and therefore, these relations cannot be utilized since a correct selection of data from the basic set in the evaluation of the accuracy of the course of the liquidus and solidus lines determined by the TA is rather difficult. Generally, it may be stated that the reliability of results depends on the composition of the investigated mixture. The closer is this composition to the apexes of the concentration triangle, the lower is the reliability of determination of the temperatures of the secondary and tertiary crystallizations and the higher is the reliability of the determined temperature of the primary crystallization.

In the system NaCl—NaF—Na_3FSO_4 the figurative point with mole fractions 25.0 mole % NaCl, 37.5 mole % NaF, and 37.5 mole % Na_3FSO_4, which is close to the line of the monovariant crystallization NaF + Na_3FSO_4 and to the ternary eutectic point, has been selected in order to check the reproducibility of the determined values. Three parallel samples have been weighed-in with an accuracy of ± 0.0002 g and submitted to the TA. The differences between the determined temperatures of the primary crystallization were ± 2 K, while the temperatures of the secondary and tertiary crystallizations agreed within ± 0.5 K.

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Translated by K. Matiašovský