

On solid solutions in the system $\text{LiF}-\text{Na}_3\text{AlF}_6$ *

^aI. KOŠTENSKÁ, ^bJ. ČORBA, and ^aM. MALINOVSKÝ

^aDepartment of Inorganic Technology, Slovak Technical University,
880 37 Bratislava

^bInstitute of Inorganic Chemistry, Slovak Academy of Sciences,
809 34 Bratislava

Received 26 November 1973

Accepted for publication 5 February 1974

The quasi-binary system $\text{LiF}-\text{Na}_3\text{AlF}_6$ has been studied using the methods of TA and X-ray phase analysis. It has been found that there is a eutectic point (85.0 ± 1) mole % LiF , (15.0 ± 1) mole % Na_3AlF_6 , $T_E = (696 \pm 1)^\circ\text{C}$ in the system. On the side of Na_3AlF_6 there is a narrow region of limited solid solutions containing up to 6 mole % LiF , 94 mole % Na_3AlF_6 at the eutectic temperature. The results of TA and X-ray phase analysis are consistent with the conclusions which follow from the thermodynamic analysis of the course of liquidus curve of Na_3AlF_6 in the vicinity of the temperature of fusion of pure cryolite in the studied system.

Lithium fluoride appears to be one of the most promising additions to the electrolytes for aluminium production [1, 2]. Therefore it is topical to investigate the interaction between LiF and the usually used constituents of these electrolytes, particularly Na_3AlF_6 .

The system $\text{LiF}-\text{Na}_3\text{AlF}_6$ may be considered as a quasi-binary section of the ternary reciprocal system $\text{Li,Na} \parallel \text{F,AlF}_6$. This system has been studied six times [3–8] up to now. However, there are great differences among the published results (Table 1). *Chu* and *Belyaev* [3] have investigated only the course of the liquidus curve in the system and the coordinates of the eutectic point by the visual-polythermic analysis. *Holm* [4] and later *Jenssen* [5] have determined also the character of the system. According to these authors the system is a simple eutectic one. They investigated the system by TA and DTA methods. *Kuvakin* [6] used the TA method and he found that the system is eutectic with a broad region of solid solutions of LiF in Na_3AlF_6 . However, comparing his results with those of the other authors, the temperature of the eutectic crystallization seems to be very low. *Matiašovský* and *Malinovský* [7] found on the basis of TA and X-ray phase analysis also an extensive solid solution on the side of Na_3AlF_6 . *Holm* [8] in his other work has found a not too broad region of solid solutions of LiF in Na_3AlF_6 . Because of serious discrepancies in published results it has been decided to examine once more the discussed system.

* Presented at the 2nd Czechoslovak Seminar on "Molten Salt Systems", Bratislava, April 11–12, 1973.

Table 1

The main parameters of LiF—Na₃AlF₆ system according to different authors

M.p. [°C]		T_E [°C]	Eutectic composition [mole %]		Type of diagram	Remarks (extent of solid solution of LiF in Na ₃ AlF ₆)	Ref.
Na ₃ AlF ₆	LiF		LiF	Na ₃ AlF ₆			
1002	845	700	83.5	16.5	—	Liquidus only	[3]
1011	848	693	—	—	SES	—	[4]
1011	848	693	84.6	15.4	SES	—	[5]
1000	848	665	75	25	ES	43 mole %	[6]
1004	847	700	85.6	14.4	ES	70 mole %	[7]
1010	848	694	85	15	ES	12 mole %	[8]
1008	848	696	85	15	ES	6 mole %	This work

SES — simple eutectic system; ES — eutectic system.

One of the most interesting is the question of the existence of limited solid solutions in the studied system. The existence of limited solid solutions in the system LiF—NaF which can be considered to some extent as an analogue of the LiF—Na₃AlF₆ system favours the idea of the existence of the limited solid solutions in the system under study. In the LiF—NaF system there are limited solid solutions on the side of NaF up to (4 ± 1) mole % LiF, (96 ± 1) mole % NaF at the temperature of the eutectic crystallization [9, 10]. Therefore the problem of the existence of the solid solution in the system LiF—Na₃AlF₆ has been studied carefully in this work.

Theoretical

It can be proved [11] that if there is a limited solid solution on the base of component B in the system A—B (see Fig. 1) then it holds

$$\ln \frac{a_B^l}{a_B^s} = \frac{\Delta H_B^f}{R} \left[\frac{1}{T_B^f} - \frac{1}{T_B} \right], \quad (1)$$

where a_B^l is the activity of component B in liquid solution, which is saturated at T_B^f with solid solution of B in A (point "1" in Fig. 1), a_B^s is the activity of component B in the solid solution A + B at the temperature T_B (point "2" in Fig. 1), ΔH_B^f is the enthalpy of fusion of pure component B, T_B^f is the temperature of fusion of pure component B, T_B is the temperature of primary crystallization of the solid solution A + B, the composition of which corresponds to the point "2" (Fig. 1).

Relation (1) was derived on the assumption that $\Delta C_p^{l/s}$ of component B equals zero. Because we shall analyze the course of the liquidus and solidus curves near the point T_B^f the mistake caused by this simplification is negligible.

It follows from eqn (1) that the ratio a^l/a^s is only a function of the parameters, which are characteristic of pure substance B (and of course of temperature).

If the difference $1 - x_B^l$ is small (x_B^l being the mole fraction of component B in the liquid phase of the system A—B which is at T_B in equilibrium with the limited solid

solution on the basis of substance B), the function $a_B^1 = f(x_B^1)$ can be expressed with sufficient accuracy by means of the universal relationship [12]:

$$a_B^1 = (x_B^1)k_{A/B}^{St} \quad (2)$$

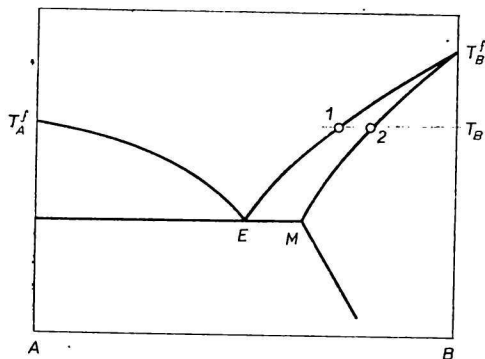


Fig. 1. Scheme of the phase diagram of a binary system A-B having limited solid solution on the base of component B.

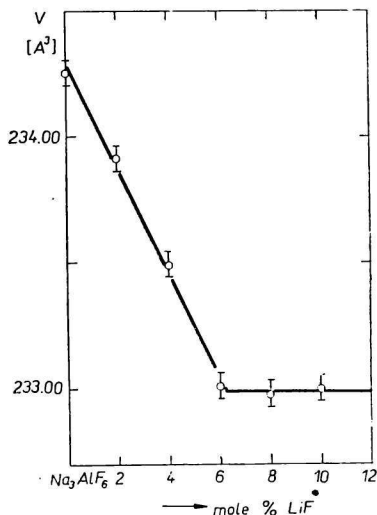


Fig. 2. Change in the volume of the unit cell of Na_3AlF_6 owing to the formation of the solid solution of LiF in Na_3AlF_6 .

where $k_{A/B}^{St}$ is the Stortenberg correction factor [13, 14]. It is equal to the number of new particles which appear in the system formed by pure liquid substance B when 1 molecule of substance A is added.

An analogous equation can be applied in order to express the functional dependence $a_B^s = f(x_B^s)$. Here x_B^s is the mole fraction of component B in the limited solid solution saturated at T_B with substance B. The Stortenberg correction factor has in this case an analogous meaning as it has been explained above. Thus

$$a_B^s = (x_B^s)k_{A/B}^{St} \quad (3)$$

Inserting from eqns (2) and (3) into eqn (1) we obtain

$$k_{A/B}^{St} \ln x_B^1 = \Delta H_B^f (1/T_B^f - 1/T_B) / R + k_{A/B}^{St} \ln x_B^s \quad (4)$$

Because $x_B^s < 1$ one can write formally

$$k_{A/B}^{St} \ln x_B^s = \Delta H_B^s (1/T_B^f - 1/T_B) / R \quad (5)$$

The quantity $\Delta H_B^s > 0$ has the same physical dimensions as ΔH_B^f .

Inserting from eqn (5) into eqn (4) and rearranging we get

$$k_{A/B}^{St} \ln x_B^1 = (\Delta H_B^f + \Delta H_B^s) (1/T_B^f - 1/T_B) / R$$

or

$$k_{A/B}^{St} \ln x_B^1 = \Delta H_B^* (1/T_B^f - 1/T_B) / R. \quad (6)$$

Evidently

$$\Delta H_B^* = \Delta H_B^f + \Delta H_B^s.$$

The cryometric treatment of the data concerning the course of the liquidus curve of B enables us to determine the value of the slope of the tangent to the liquidus curve at the melting point of pure component B. This quantity will be denoted as $k_B^{0,1}$. It follows from eqn (6) that

$$k_B^{0,1} = \lim_{x_B \rightarrow 1} (dT/dx_B) = R(T_B^f)^2 k_{A/B}^{St} / \Delta H_B^*. \quad (7)$$

In the case of the system $\text{LiF}-\text{Na}_3\text{AlF}_6$, the first component yields Li^+ and F^- ions, the second one the ions Na^+ , AlF_6^{3-} , F^- and most probably also AlF_4^- [15]. Thus if $A = \text{LiF}$, $B = \text{Na}_3\text{AlF}_6$, then $k_{A/B}^{St} = 1$ (i.e., Li^+). If $A = \text{Na}_3\text{AlF}_6$, $B = \text{LiF}$, then $k_{A/B}^{St} = 4$ (i.e., three ions Na^+ and one ion Al^{3+} , probably in the form of complex anions AlF_6^{3-} and AlF_4^-).

Because $\Delta H_B^f < \Delta H_B^*$, the slope $k_B^{0,1}$ is smaller if there exist limited solid solutions than if there are no solid solutions in the system at all. Consequently if the difference $\Delta H_B^* - \Delta H_B^f$ where ΔH_B^f is the enthalpy of fusion of pure B determined e.g. from calorimetric measurements is greater than the admissible experimental error it follows that there is a region of solid solutions near the point T_B^f . Therefore a careful cryometric treatment of the course of the liquidus curve near the melting point of a given component indicates the existence of limited solid solutions based on the given component.

Experimental

LiF of grade "for single crystals", m.p. 848°C was used. Cryolite was prepared from NaF of grade "for single crystals", m.p. 992°C and from AlF_3 prepared by sublimation of pure salt in a platinum apparatus [16]. Temperature was measured by means of Pt/Pt10Rh thermocouple calibrated by means of melting points of pure K_2SO_4 (1069°C), NaF (992°C), Na_2SO_4 (884.8°C), NaCl (800.8°C), KCl (772°C), and eutectic mixture 81 mole % $\text{KCl} + 19$ mole % LiF (718°C). The mixtures of salts (20 g weighed-in) were melted in a platinum crucible with a minimal over-heating. The signal of thermocouple was registered by a compensating recorder EZ 11. The cooling rate was $1-3^\circ\text{C}/\text{min}$. Twenty-nine inner mixtures of the $\text{LiF}-\text{Na}_3\text{AlF}_6$ system have been investigated. The results which are important from the point of view of the existence of limited solid solutions are presented in Table 2.

The samples for X-ray phase analysis were prepared in the following way: 10 g of salt mixture was melted in a Pt crucible with minimal over-heating above the melting temperature and after thorough stirring the mixture was cooled with the rate $1-2^\circ\text{C}/\text{min}$ to 690°C , i.e. slightly below the temperature of the eutectic crystallization. The sample was kept for 30 min at this temperature. Then the crucible was cooled in crushed ice which proved to be a better cooling medium than solid CO_2 . Then the solidified sample was crushed and studied by X-ray analysis.

The samples contained 0, 2, 4, 6, 8, and 10 mole % LiF , rest Na_3AlF_6 .

A Phillips diffractometer (goniometer PW 1050 and generator PW 1130) was used for the measurements. The X-ray radiation was obtained from a Cu anode tube with a Ni filter at 45 kV and 20 mA. The divergence and scatter slits were 1° and the receiving slit 0.1 mm. The time constant of the recorder $T = 4$, goniometer speed $1/4^\circ 2\theta/\text{min}$,

chart speed 1200 mm/hr. Silicon was used as the inner standard for the measurements of lattice parameters. The refinement of the lattice parameters of Na_3AlF_6 was done on the basis of twelve diffraction lines from the region of angles $46-35^\circ 2\theta$. Five diffraction records were done for each sample. The refinement of the lattice parameters was done using the least square method according to *Lindquist's* program [17].

Table 2

TA data concerning the system $\text{LiF}-\text{Na}_3\text{AlF}_6$

LiF [mole %]	Na_3AlF_6 [mole %]	Temperature [°C]	
		Primary crystallization	Eutectic crystallization
100	—	848	—
99.75	0.25	843	690
99.50	0.50	840	694
99.25	0.75	836	695
99.0	1.0	833	696
98.0	2.0	819	696
97.0	3.0	807	696
96.0	4.0	795	696
95.0	5.0	785	697
86.0	14.0	703	696
85.0	15.0	—	696
10.0	90.0	999	—
7.5	92.5	1000	—
5.0	95.0	1003	—
4.0	96.0	1004	—
2.0	98.0	1005.5	—
1.0	99.0	1007	—
—	100	1008	—

The existence of limited solid solutions has been proved also by the X-ray analysis. It has been found that the volume of the elementary cell of pure Na_3AlF_6 equals $234.25 \pm 0.1 \text{ \AA}^3$. The volume of the elementary cell of the solid solution containing 94 mole % $\text{Na}_3\text{AlF}_6 + 6$ mole % LiF is $233.00 \pm 0.1 \text{ \AA}^3$. The decrease is fluent and the volume of the elementary cell remains constant despite a further increase in concentration of LiF (Fig. 2).

Discussion

A. Region with high concentration of LiF

From the results of TA it follows that there are no solid solutions on the side of LiF. The eutectic halt has been found on the cooling curve even at the concentration 99.75 mole % LiF, 0.25 mole % Na_3AlF_6 .

By the cryometric treatment of the experimental results of TA it was found that ΔH^* (LiF) = $6243 \text{ cal mol}^{-1}$, which differs from the calorimetric value of ΔH^c reported by Douglas and Dever [18] *i.e.* $6471 \text{ cal mol}^{-1}$ by 3.5%, this being in the limits of experimental error.

B. Region with high concentration of Na_3AlF_6

From the results of TA it follows that the eutectic halt cannot be found on the cooling curves if the mixtures contain more than 90 mole % Na_3AlF_6 .

By the cryometric treatment of the results of TA for the liquidus curve of Na_3AlF_6 it has been found that ΔH^* (Na_3AlF_6) = 35 500 cal mol⁻¹, which differs from the calorimetric value ΔH^r = 25 640 cal mol⁻¹ [19] by 38.4%. Even if the value of ΔH^r (Na_3AlF_6) = 27 600 cal mol⁻¹ reported by Kelley [20] was used, ΔH^* (Na_3AlF_6) would be by 28.6% greater. The difference $\Delta H^* - \Delta H^r$ exceeds in this case about three times the possible experimental error.

Thus from the cryoscopic measurements it follows that the solid solutions based on Na_3AlF_6 do exist.

In this connection the results of X-ray phase analysis are conclusive. From Fig. 2 it follows that the volume of the unit cell of Na_3AlF_6 changes as the solid solution of LiF in Na_3AlF_6 is formed. This result confirms again the existence of limited solid solutions of LiF in Na_3AlF_6 . At the eutectic temperature the range of the solid solutions is up to 6 mole % LiF, 94 mole % Na_3AlF_6 . This result is in agreement with the results of TA as well as with the cryometric data.

Consequently it may be stated that the system LiF– Na_3AlF_6 is quasi-binary with the eutectic point having coordinates 85.0 mole % LiF, 15.0 mole % Na_3AlF_6 and temperature T_E = 696°C.

On the side of Na_3AlF_6 there is a limited solid solution with limit concentration at T_E equal to 6 mole % LiF, 94 mole % Na_3AlF_6 according to X-ray data. The TA data seem to indicate a some broader extent of solid solution, approx. up to 10 mole % LiF, 90 mole % Na_3AlF_6 .

The results reported in this paper are thus in very good agreement with the data by Holm [8] concerning the coordinates of the eutectic point E in the system LiF– Na_3AlF_6 and in an acceptable agreement concerning the extent of limited solid solution of LiF in Na_3AlF_6 .

The previous data by Holm [4] as well as by Jenssen [5] who have claimed the simple eutectic character of the LiF– Na_3AlF_6 system have not been confirmed.

The data by Kuvakin [6] concerning both the composition and temperature of the eutectic point and the extent of solid solution seem to be erroneous.

The data reported by Matiašovský and Malinovský [7] on the extent of solid solution of LiF in Na_3AlF_6 are evidently too high.

References

1. Lewis, R. A., *J. Metals* **19**, 30 (1967).
2. Vol'berg, A. A., Tararin, S. V., Litvinenko, I. F., and Nikitin, V. Ja., *Tsvet. Metal.* **1968**, 63.
3. Chu, Y. I. and Belyaev, A. I., *Izv. Vyssh. Ucheb. Zaved., Tsvet. Metal.* **1959**, 59.
4. Holm, J. L., *Lic. Thesis*. NTH, Trondheim, 1963; cited from [5].
5. Jenssen, B., *Lic. Thesis*. NTH, Trondheim, 1969.
6. Kuvakin, M. A., *Zh. Neorg. Khim.* **14**, 282 (1969).
7. Matiašovský, K. and Malinovský, M., *Hutn. Listy* **24**, 515 (1969).
8. Holm, J. L., *Thesis for a Doctor's Degree*. NTH, Trondheim, 1971.
9. Holm, J. L., *Acta Chem. Scand.* **19**, 638 (1965).
10. Matiašovský, K., Čakajdová, I., and Malinovský, M., *Chem. Zvesti* **19**, 513 (1965).

11. Malinovský, M., Koštenská, I., and Galová, M., *Collect. Czech. Chem. Commun.* **38**, 2823 (1973).
12. Malinovský, M. and Koštenská, I., *Chem. Zvesti* **28**, 498 (1974).
13. Malinovský, M., *Chem. Zvesti* **23**, 801 (1969).
14. Malinovský, M., *Chem. Zvesti* **23**, 809 (1969).
15. Malinovský, M. and Vrbenská, J., *Collect. Czech. Chem. Commun.* **36**, 567 (1971).
16. Matiašovský, K., Malinovský, M., Pliško, E., and Kubík, C., *Chem. Zvesti* **14**, 487 (1960).
17. Lindquist, O. and Wengelin, F., *Ark. Kemi* **28**, 179 (1967).
18. Douglas, T. B. and Dever, J. L., *J. Amer. Chem. Soc.* **76**, 4826 (1954).
19. Stull, D. R. and Prophet, H., *JANAF Thermochemical Tables*. US Depart. Comm. Natl. Bur. Stand., Washington, 1971.
20. Kelley, K. K., *Bureau of Mines, Bull.* 584. US Govern. Print. Off., Washington, 1960.

Translated by P. Fellner