PHYSICO-CHEMICAL PROPERTIES OF MOLTEN $LiF-AlF_3$ MIXTURES

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Dedicated to Professor S. Škramovský on the occasion of his 70th birthday.

Received January 7th, 1971

The phase equilibria, the densities and the electrical conductivities of molten binary $LiF-AlF_3$ mixtures have been investigated up to 48–50 mol% AlF_3. The obtained results enabled us to calculate the dissociation degree of the AlF_6^{3-} anions in this system using two different approaches.

The study of the system $LiF-AlF_3$ seems to be of interest from both the theoretical and technical point of view. Theoretically, the structure of $LiF-AlF_3$ mixtures is interesting with regard to the analogy between this system and the well-known system $NaF-AlF_3$. From the technical aspect, the system $LiF-AlF_3$ is important regarding the possibility of utilisation of lithium salts, namely LiF and Li_3AlF_6, as additives to the aluminium electrolyte. The well-known paper dealing with the investigation of the phase equilibria in the system $LiF-AlF_3$ was published by Fedotieff and Timofeev[1] nearly 40 years ago. Therefore it seemed to be useful to verify the presented data. The density of molten $LiF-AlF_3$ mixtures has not yet been systematically studied. The electrical conductivity of molten system under consideration was measured by Daněk and coworkers[2]. On the basis of the obtained data which are important concerning the physico-chemical properties of those melts also some conclusions regarding the structure of lithium cryolite melts could be done.

EXPERIMENTAL

For the preparation of samples, reagent-grade lithium fluoride with the melting point 847 ± 1°C was used. Aluminium fluoride was prepared by sublimation of a calcined product in a platinum apparatus according to Matiašovský and coworkers[3]. The concentration range of investigation was limited by 48–50 mol % AlF_3 because of a comparatively intense evaporation from the melt at higher concentration of aluminium fluoride. For the measurement of the temperature a Pt/Pt10Rh thermocouple was used.

The phase equilibria in the studied system were determined by means of the TA method and the X-ray phase analysis. In the TA determination, the total weight of the sample was 20 g.

The density was established using the well-known hydrostatic method. A spherical platinum sinker (diameter 25 mm) was suspended from an analytical balance pan by a platinum wire (diameter 0·3 mm). The samples (100 g) were placed in a platinum crucible. For a detailed description of the apparatus and the measuring techniques see Paučírová[4]. Molten lithium cryolite as well as molten mixtures with a high content of lithium cryolite tend to rise on the platinum wire on which the sinker is suspended due to their excellent wetting ability with respect to platinum. For this reason the sinker was submerged into the melt just before every run.

The electrical conductivity was determined using the method proposed by Daněk and coworkers[2]. The measuring cell consisted of a platinum crucible and two disk electrodes made of bright platinum (diameter 5 mm). The distance between the electrodes was 12 mm. With the aid of a micrometric screw the electrodes were submerged simultaneously with an accuracy of ±0·01 mm into the melt. The Thomson double bridge was used for the measurement of the resistance in the melt. All measurements were carried out with 10 mA current. The standard deviation of a single measurement was less than ±2%.

It was shown that the measurements should be performed using such a frequency at which the measured resistance R_x of the melt is equal to the proper ohmic resistance of the melt, R_0. For LiF the constant value of the resistance was attained at appr. 18 kHz and for lithium cryolite at 15 kHz. Thus the frequency 18 kHz was used in the measurement of the specific conductivity of LiF–AlF$_3$ mixtures[2].

RESULTS AND DISCUSSION

The results of the study of the phase equilibria are presented graphically in Fig. 1. It is evident that there exists a congruently melting compound, lithium cryolite Li_3AlF_6, in the system with the melting point 782 ± 1°C. Thus the system LiF–AlF$_3$ can be divided into two independent systems, LiF–Li_3AlF_6 and Li_3AlF_6–AlF$_3$.

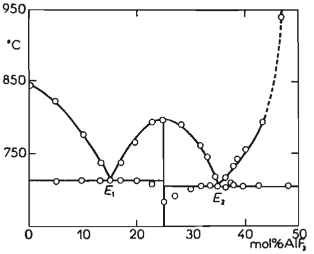

FIG. 1

Phase Diagram of the System LiF–AlF$_3$

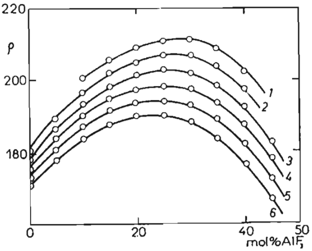

FIG. 2

Density (ϱ, g cm^{-3}) Isotherms of Molten LiF–AlF$_3$ Mixtures 1 800, 2 850, 3 900, 4 950, 5 1 000, 6 1 050°C.

The partial system LiF–Li_3AlF_6 is a simple eutectic system, with no detectable solid solutions. The eutectic point has the composition 85·0 mol% LiF and 15·0 mol% AlF_3 and the eutectic temperature is 711 ± 1°C.

The second partial system, Li_3AlF_6–AlF_3, seems to be also a simple eutectic one with the eutectic point at 65·0 mol% LiF and 35·0 mol% AlF_3. The temperature of the eutectic crystallization was found to be 708 ± 2°C. Special attention was paid to the possibility of the existence of the compounds $Li_5Al_3F_{14}$ and/or $LiAlF_4$, *i.e.*, the lithium analogues of compounds which were described in the system NaF–AlF_3 by Abramov and coworkers[5] and by Grjotheim and coworkers[6]. However, according to Malinovský and coworkers[7], none of these substances could be detected by the applied methods. The isotherms of the density of molten LiF–AlF_3 mixtures in the temperature range 800–1050°C are plotted in Fig. 2.

The molar volumes of mixtures and the partial molar volumes of both constituents in the system LiF–Li_3AlF_6 at 1000°C are plotted in Fig. 3. The molar excess volume, *i.e.*, $\Delta V^{ex} = V^{real} - V^{id}$ for every arbitrary composition of the melt at 1000°C in the same partial system is shown in Fig. 4.

The value of the maximum excess volume in per cent with respects to the ideal volume, V^{id}, in the system LiF–Li_3AlF_6 is less than −2%. From this point of view, this system does not differ very much from an ideal system.

The same calculation in the partial system Li_3AlF_6–AlF_3 showed that the maximum excess volume is −15%. However, as reported by Paučírová[4], if this result was re-

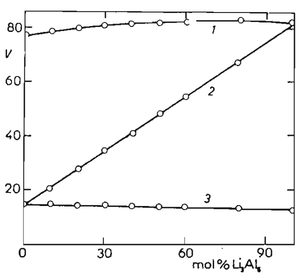

FIG. 3

Dependence of the Molar Volume V (cm^3 mol^{-1}) and the Partial Molar Volumes $\overline{V}$ on Composition for LiF–Li_3AlF_6 Mixtures at 1000°C

1 $\overline{V}$(LiF), 2 V, 3 $\overline{V}$(Li_3AlF_6).

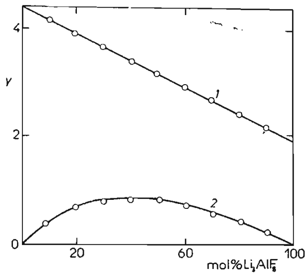

FIG. 4

Dependence of the Excess Volume ΔV^E and of the Expression $\Delta V^E/x_2(1 - x_2)$ on Composition for LiF–Li_3AlF_6 Mixtures at 1000°C

1 $y = \Delta V^E$, 2 $y = \Delta V^E/x_2(1 - x_2)$.

calculated into the coordinates Li_3AlF_6–$LiAlF_4$, this quantity became three times lower, *i.e.*, -5%.

On the basis of the measured values of the resistance of the melt the polytherms of the specific conductivities were obtained. The specific conductivity of LiF at 900°C was found to be $8{\cdot}52\ \Omega^{-1}\ cm^{-1}$, this being in a very good agreement with the value reported by Yim and Feinleib[8]. The same holds for the value of the specific conductivity of Li_3AlF_6 which was found to be $4{\cdot}19\ \Omega^{-1}\ cm^{-1}$ at 1000°C. In both cases the differences are within the reported limits of accuracy of the measurement.

In Fig. 5 the isotherms of the specific conductivity of LiF–AlF_3 mixtures are presented. They are slightly convex with respect to the concentration axis. On the basis of measured values the dependence of the energies of activation of the specific conductivities of LiF, Li_3AlF_6 and for comparison also those of NaF, on temperature, are calculated (Fig. 6). It is interesting to note the comparatively small value of the activation energy of the specific conductivity of lithium cryolite.

The problem of the structure, *i.e.*, of the particles which are present in the melt, is of great interest. So far, two indirect procedure were suggested, one by Grjotheim[9], the other by Frank and Foster[10].

Grjotheim's method is based on the analysis of the shape of liquidus curves. One assumes that each molecule of Li_3AlF_6 dissociates with the formation of three cations Li^+ and of a mixture of anions AlF_6^{3-}, AlF_4^- and F^- according to the scheme:

$$Li_3AlF_6 \rightarrow 3\,Li^+ + (1-\beta)\,AlF_6^{3-} + \beta\,AlF_4^- + 2\beta\,F^-$$

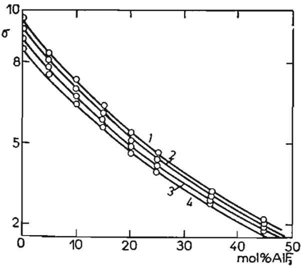

FIG. 5

Isotherms of the Specific Conductivity $\sigma\ (\Omega^{-1}\ cm^{-1})$ of Molten LiF–AlF_3 Mixtures
1 1050, *2* 1000, *3* 950, *4* 900°C.

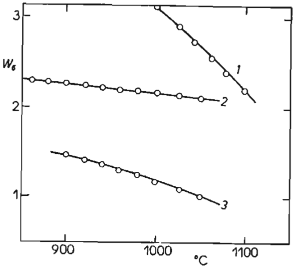

FIG. 6

Polytherms of the Activation Energy W_σ (kcal mol^{-1}) of the Specific Conductivity of Individual Fluorides
1 NaF, *2* LiF, *3* Li_3AlF_6.

where β is the degree of dissociation of the anions AlF_6^{3-} in pure molten Li_3AlF_6.

Assuming that Temkin's model of ideal ionic solutions holds for the melt under consideration and that the equilibrium dissociation constant of AlF_6^{3-} as well as the enthalpy of melting of Li_3AlF_6, $\Delta H^f(Li_3AlF_6)$, are temperature independent, we obtain for the dissociation constant:

$$K(AlF_6^{3-}) = \frac{x(AlF_4^-) \, . \, x^2(F^-)}{x(AlF_6^{3-})} = \frac{4\beta^3}{(1-\beta)(1+2\beta)^2} \, . \qquad (1)$$

For the liquidus curve of lithium cryolite it is valid that

$$\ln a(Li_3AlF_6) = [\Delta H^f(Li_3AlF_6)]/R \, [(T^f_{id})^{-1} - (T^f_{exp})^{-1}] \, , \qquad (2)$$

where $a(Li_3AlF_6)$ is the activity of lithium cryolite in the melt and T^f_{id} and T^f_{exp} are the ideal and the experimentally determined melting points of pure lithium cryolite, respectively.

The addition of LiF, the complete dissociation of which is assumed, to molten lithium cryolite will change its dissociation degree from β to δ. If the mole fraction of lithium cryolite in the mixture with lithium fluoride is x, then the dissociation constant of the anions AlF_6^{3-} in the considered mixture is expressed as

$$K(AlF_6^{3-}/LiF) = (1 + 2x\delta - x)^2 \, \delta/(1-\delta)(1+2x\delta)^2 \, . \qquad (3)$$

The liquidus temperature T of lithium cryolite can be computed from the following equation

$$T^{-1} = (T^f_{id})^{-1} - R[\Delta H^f(Li_3AlF_6)]^{-1} \ln \frac{x(1-\delta)}{1+2x\delta} \, . \qquad (4)$$

The procedure for calculation is as follows: Upon chosing the dissociation degree β and inserting it into Eqs (*1*) and (*2*) one can compute $K(AlF_6^{3-})$ and T^f_{id}. Because $K(AlF_6^{3-}) = K(AlF_6^{3-}/LiF)$, it is possible to calculate the term δ from Eq. (*3*) for a chosen value of x. Inserting this value of x and the corresponding value of δ into Eq. (*4*) one obtains the theoretical liquidus temperature of Li_3AlF_6 in the mixture with LiF. The agreement between the calculated and experimental data is the criterion for the correct choice of the degree of dissociation, β, of the pure molten Li_3AlF_6. A similar treatment was applied to the molten mixtures Li_3AlF_6–AlF_3.

Frank and Foster's method is based on the density measurements. Let N be the mol fraction of LiF in the mixture LiF–AlF_3, n the number of mol of hypothetic undissociated cryolite at equilibrium. Asuming that the activities of all substances are equal to their mol fractions, it can easily be shown that the expression for the equilibrium constant is as follows:

$$K = \frac{a^2(\mathrm{LiF})\,.\,a(\mathrm{LiAlF_4})}{a(\mathrm{Li_3AlF_6})} = \frac{(2N - 1 - 2n)^2\,(1 - N - n)}{n(N - 2n)^2} \tag{5}$$

and the density of the molten mixture is expressed by

$$d^{-1} = A\,.\,d^{-1}(\mathrm{Li_3AlF_6}) + B\,.\,d^{-1}(\mathrm{LiAlF_4}) + C\,.\,d^{-1}(\mathrm{LiF})\,, \tag{6}$$

where A denotes wt% Li_3AlF_6, B wt% $LiAlF_4$ and C wt% LiF.

In this procedure of calculation arbitrary values of K are chosen and Eq. (5) is solved for the term n. We are then able to calculate the wt% of all constituents in the mixture. Furthermore, choosing a series of arbitrary, but reasonable, values of density of the hypothetic undissociated cryolite we may calculate the density of the mixture from Eq. (6). The agreement between the calculated and measured values of the density of the mixtures under consideration is the criterion for the correct choice of K and $d(Li_3AlF_6)$. Both methods yield practically the same value for the degree of dissociation of the anion AlF_6^{3-} in pure lithium cryolite: 0·30–0·35. These values are close to those found for sodium cryolite.

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Translated by the author (K. M.).