TEMPERATURE DEPENDENCE OF THE DEGREE OF DISSOCIATION OF THE ANION AlF_6^{3-} IN MOLTEN Li_3AlF_6 AND Na_3AlF_6
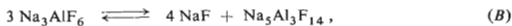
K. Matiašovský, M. Paučírová and M. Malinovský

Institute of Inorganic Chemistry,
Slovak Academy of Sciences, Bratislava

Temperature dependence of the degree of dissociation of the complex anion AlF_6^{3-} in molten Li_3AlF_6 and Na_3AlF_6 has been examined by measuring the values of densities of the molten mixtures $LiF–AlF_3$ and $NaF–AlF_3$. The enthalpy of dissociation of the complex anion AlF_6^{3-} was calculated from these dependences.

From the phase diagrams of the system[1-5] $LiF–AlF_3$ and $NaF–AlF_3$ (see[6-10]), as well as from the measured density values of these molten mixtures[11-15] it is evident that in both systems a compound of the type M_3AlF_6 (M = Li or Na) is formed with a congruent melting point. The shape of maximum on the phase diagrams $MF–AlF_3$ indicates partial dissociation of the compounds M_3AlF_6 in molten state. According to the literature, up to now mainly the dissociation of the complex anion AlF_6^{3-} in molten Na_3AlF_6 has been investigated[16-26]. In solving this problem we considered different dissociation schemes of which the most probable, with respect to the components of the system and to the products formed, are the following ones

$$Na_3AlF_6 \rightleftharpoons 3\,NaF + AlF_3 , \qquad (A)$$

$$3\,Na_3AlF_6 \rightleftharpoons 4\,NaF + Na_5Al_3F_{14} , \qquad (B)$$

$$Na_3AlF_6 \rightleftharpoons 2\,NaF + NaAlF_4 . \qquad (C)$$

On the basis of experimentally determined density values, Pearson and Waddington[16] calculated the degree of dissociation, α, for scheme (A) at 1000 and 1100°C to be 0·2 and 0·3, respectively. Using the same method, Abramov and coworkers[24] calculated the value of α at 1000°C to be 0·15. Contrary to this, Frank and Foster[25] attained a very good agrement between their measured density values and those calculated according to scheme (C) at 1000°C for $K = 0·09$ ($\alpha = 0·35$) up to concentrations of 30 mol% AlF_3. From the temperature dependence of α they calculated, using the relation $d\ln K/dT = \Delta H/RT^2$, the enthalpy of dissociation to be 22 kcal/mol. Veťukov[26] determined from the isotherm of molar volumes of molten system $NaF–NaAlF_4$ the degree of dissociation of molten Na_3AlF_6 $\alpha = 0·25$ at 1000°C. The employed procedure, however, was criticized by Paučírová and coworkers[27]. In the papers[27,28] the dissociation of the AlF_6^{3-} ion was calculated according to scheme (C). The values of K and α at 1000°C found by Paučírová and coworkers[27] are 0·06 and 0·3, respectively.

In the present work, the temperature dependence of the degree of dissociation of the complex anion AlF_6^{3-} in molten Li_3AlF_6 and Na_3AlF_6 has been determined

on the basis of the measured density data of molten MF–AlF₃ mixtures and the enthalpy of dissociation of AlF_6^{3-} has been calculated.

EXPERIMENTAL

For the preparation of the LiF–AlF₃ and NaF–AlF₃ mixtures LiF and NaF "for single crystals" were used. Pure AlF₃ (99.5%) was prepared by sublimation of a technical product[29]. The density of the melts was determined using hydrostatic method[30] with an accuracy of ±0.2%. The degree of dissociation of the complex anion AlF_6^{3-} in molten Li₃AlF₆ was determined by comparing the experimentally found densities of the melts[15] with the values, calculated according to the method suggested by Frank and Foster[25]. In both cases the following dissociation scheme was accepted

$$M_3AlF_6 \rightleftarrows 2\,MF + MAlF_4 \,. \qquad (D)$$

For various selected values of the equilibrium constant K the corresponding compositions of the melts (the hypothetical equilibrium concentration of MF, MAlF₄ and M₃AlF₆) were calculated. For each value of K the density ϱ of the corresponding MF–AlF₃ mixtures was calculated using the equation

$$\varrho = 100/[A(MF) + A(M_3AlF_6) + A(MAlF_4)] \,, \qquad (I)$$

where $A(i) = \varphi_i/\varrho_i$, φ_i is the content of component i in weight %.

RESULTS AND DISCUSSION

From both the literature data and the results of our own measurements it follows that partial dissociation of molten cryolite can best be expressed in terms of the dissociation scheme (C)[9,10,25]. The compound NaAlF₄ was identified by Howard[31] in quenched vapours. The existence of the complex anion AlF_4^- in molten cryolite was determined by cryoscopic[32] and spectroscopic[23] measurements and the presence of the compound NaAlF₄ in the melt is also supported by the studies of vapour composition[33,34] and of vapour pressure[34,35] of the melt close to the cryolite composition. On the other hand, the existence of the anion $Al_3F_{14}^{5-}$, as suggested by Cochran[22], or of an other complex anion is not probable. The corresponding compound, Na₅Al₃F₁₄ (chiolite), though it does not exist in the system NaF–AlF₃ as an incongruently melting compound, decomposes at 739°C to form Na₃AlF₆ and AlF₃ (see[9]). It has been confirmed spectroscopically[23] at 1030°C that no complex anions $Al_3F_{14}^{5-}$ are present in the melt which excludes the possibility of dissociation according to scheme (B). Calculated values of K and α which are in the best agreement with the density values obtained by direct measurement for dissociation scheme (C) are presented in Table I. Contrary to the results of Frank and Foster[25] the calculated values for both systems are in good accordance with the measured ones only in the concentration range up to 20 mol% of AlF₃. Good agreement in the region of higher AlF₃ concentrations (up to 30 mol%) as referred in paper[25], is the result of an inadequate application of additivity of molar volumes and of the unreally

TABLE I

Equilibrium Constant K of the Reaction $M_3AlF_6 \rightleftarrows 2\,MF + MAlF_4$ and the Dissociation Degree α at Different Temperatures, t

System	NaF–AlF$_3$			LiF–AlF$_3$			
t, °C	1 000	1 050	1 100	900	950	1 000	1 050
K	0·07	0·09	0·10	0·04	0·05	0·06	0·07
α	0·32	0·35	0·36	0·25	0·28	0·30	0·32

high extrapolated value of the density[15] of NaAlF$_4$. With respect to the relatively high differences between the experimental and the calculated values it cannot be excluded that in the region of higher AlF$_3$ concentrations the mechanism of dissociation might be different from schemes (A) to (C). The degree of dissociation of Na$_3$AlF$_6$ as determined in the present work is in fairly good agreement with the values given in papers[16,25], whereas the value[23] 0·8, seems to be too high. The dependence $\log K$–$1/T$ for molten systems LiF–AlF$_3$ and NaF–AlF$_3$ has a linear course. The enthalpies of dissociation, calculated from its slopes, are $\Delta H(\mathrm{Li_3AlF_6}) = 11\cdot2$ kcal/mol and $\Delta H(\mathrm{Na_3AlF_6}) = 10\cdot7$ kcal/mol, respectively. The calculated value of the enthalpy of dissociation of molten Na$_3$AlF$_6$ is approximately one half of the value given by Frank and Foster[25]. This value, however, agrees within the limits of experimental errors with the corresponding value for Li$_3$AlF$_6$.

According to Malinovský[36], Li$_3$AlF$_6$ and Na$_3$AlF$_6$ are thermodynamically analogous compounds having a equal entropy of fusion, which allows us to expect very close values of their enthalpies of dissociation. The calculated values confirm this assumption.

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Translated by V. Čermáková.