Raman Spectra of Molten Mixtures Containing Aluminium Fluoride. II. Dissociation of AlF₆⁻

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Both ideal 1–4 and regular solution models 5 have been adapted to explain the thermodynamic data of the alkali fluoride-aluminium fluoride melts. In the sodium system Grjotheim 1 found that the dissociation reaction

\[ \text{AlF}_6^- \leftrightarrow \text{AlF}_4^- + 2\text{F}^- \]  

(1)

gave the best description of the cryolite peak in the phase diagram of NaF and AlF₆. The same result was found for the corresponding lithium system. 2,3 Holm 4 interpreted the total value of \( \Delta H_{\text{mix}} \) in the system NaF-AlF₆ as due to the dissociation of the cryolite anion into AlF₆ and F⁻ in the composition range 0 < \( X_{\text{AlF}_6} \) < 0.25. Dewing 5 found that NaF-NaAlF₆ mixtures may be described for all values of \( X_{\text{AlF}_6} \) as a regular solution the two ions F⁻ and AlF₆⁻. Deviations near the NaAlF₆ composition were explained by the formation of Al₃F₁₀⁻.

All these calculations, however, are based on model assumptions and are as such only indirect indications of melt species. In a previous investigation 6 we reported the ion AlF₆⁻ as the main complex in the system LiF-Li₃AlF₆. In order to test the existence of other species proposed in the cryolite melts, compositions in the system Li₃AlF₆-AlF₆ should be investigated. In this paper we report the results of a Raman spectroscopic investigation of the Li₃AlF₆-AlF₆ eutectic melt. After completion of the present work we became aware of a Raman investigation of the sodium system. 1,6

Results. The experiments were performed according to a procedure previously described. 6

The only change in the experimental design was the introduction of a cylindrical platinum liner in the Raman cell in order to increase the Raman intensity. The spectrum obtained at 730 °C for the molten Li₃AlF₆-AlF₆ eutectic mixture, LiF + 35.5 mol % AlF₆, is presented in Fig. 1. Two peaks at 545 ± 10 and 620 ± 10 cm⁻¹ were found by subtraction of the background and by resolution of the band complex into two approximate Gaussian curves. The

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Fig. 1. The Raman spectra of the molten Li₃AlF₆—AlF₆ (I) and LiF-Li₃AlF₆ (II) eutectic mixtures at 730 °C. The band widths were 20 cm⁻¹ (curve I) and 25 cm⁻¹ (curve II). Sensitivity: 1000 cps. Scan speed: 0.2 cm⁻¹/s. Period: 50 s.

Band positions were determined from six spectra. There were signs of additional bands at ~220 and ~350 cm⁻¹. For comparison, the spectrum of the LiF-Li₃AlF₆ eutectic mixture 4 also is given in Fig. 1. The ratio of the peak intensities \( I_{545}/I_{620} \) was calculated from the average of four spectra to be 1.0 ± 0.1. Uncertainties in melt compositions are included in this limit.

Discussion. The 620 cm⁻¹ band is assigned to the \( \nu_1 \) frequency of the AlF₆⁻ tetrahedron. The frequency agrees well with 630 ± 20 cm⁻¹ estimated in our previous publication. 6 The band at 545 ± 10 cm⁻¹ is attributed to the totally symmetric stretching frequency of AlF₆⁻. This result is within the uncertainty limits of our first value, 556 ± 5 cm⁻¹. In NaF-AlF₆ mixtures, 1,6 the corresponding frequencies were found to be 622 and 555 cm⁻¹.

Since no definite sign of species other than AlF₆⁻ and AlF₆⁻ was found, the dissociation (1) is used in a description of the melt mixtures in the composition range LiF-Li₃AlF₆. Thus the melt is considered as being composed of a cation mixture and a mixture of the anionic entities AlF₆⁻, AlF₄⁻, and F⁻. This represents a Temkin model, but not necessarily an ideal one.
The following expression then is valid for the stoichiometric dissociation constant \( K \) of reaction (1) in the system LiF-AlF₃:

\[
K = \frac{[(1+P) - X_{\text{AlF}}^{2-}] (2 + 4P)^3}{P[(1+P) - X_{\text{AlF}}^{2-}] (1 + 3P)^3}
\]

where \( P \) is the ratio between the concentrations of AlF\(^{2-}\) and AlF\(^4-\). The expression is derived by a procedure similar to that described for KCl-AlCl₃ melts.\(^{18,19}\) For pure cryolite, LiAlF₄, \( P \) is related to the dissociation degree \( \alpha_0 \) of AlF\(^{2-}\) through

\[
P = \frac{X_{\text{AlF}}^{2-}}{X_{\text{AlF}}^{2-}} = \frac{1 - 2\alpha_0}{\alpha_0}
\]

Combination of eqns (2) and (3) and introduction of \( X_{\text{AlF}}^{2-} = 1/4 \) yield

\[
K = 4\alpha_0/(1 + 2\alpha_0)(1 - \alpha_0)
\]

At a constant temperature, the relationship between \( P, \alpha_0 \) and \( X_{\text{AlF}}^{2-} \) is given by eqns. (2) and (4) provided the activity coefficient term is constant. This assumption is not as rigid as the ideal mixture approximation. The value \( \alpha_0 \) at a temperature \( T \) may be used as a frame of reference for the function \( P = P(X_{\text{AlF}}^{2-}) \).

According to Wolkenstein's bond polarization theory, the mean molecular polarization derivative is a bond property (see Chantry\(^{11}\)). It follows that the mol fraction ratio may be calculated from\(^{10,12}\)

\[
\frac{X_{\text{AlF}}^{2-}}{X_{\text{AlF}}^{2-}} = \frac{k}{P} = P = P
\]

with \( k = 1/1.9 \). The value \( k = 4/6 \) was used by Solomons et al.,\(^{13}\) but they did not take the difference in \( \nu \), frequencies between the two species into account. The Al–F bonds in the two species are assumed similar. Gilbert et al.\(^{14}\) found that the coefficient \( k \) should be between 1/2.0 and 1/2.1 in the NaF-AlF₃ system. By using the value \( k = 1/2.0 \) and inserting 1.0 for the intensity ratio \( I_{\text{AlF}}^{2-}/I_{\text{AlF}}^{2-} \) at \( X_{\text{AlF}}^{2-} = 0.355 \), the result \( P = 0.5 \) is obtained. This gives \( K = 3.4 \times 10^{-3} \) from eqn. (2) and \( \alpha_0 = 0.24 \) from eqn. (4) at 730 °C. This result is consistent with previous investigations of the LiF-LiAlF₄ eutectic mixture\(^{1,4} \) which gave no sign of AlF\(^{2-}\). By taking into consideration the uncertainty of the observed intensity ratio, the uncertainty of \( \alpha_0 \) is calculated to be \( \pm 0.06 \). It is a linear relationship between \( \alpha_0 \) and \( P \) at \( X_{\text{AlF}}^{2-} = 0.355 \) and therefore the upper and lower limits are equal.

The effect of changing the temperature from 730 °C to the melting temperature of lithium cryolite, 782 °C, may be estimated by using the value \( A\nu = 50.5 \) J/mol at 700 °C which Holm and Holm\(^{9} \) have calculated for the dissociation AlF\(^{2-}\) = AlF\(^{4-}\) + 3F\(^-\). Van't Hoff's equation then leads to an increase in \( \alpha_0 \) of about 10 % when the undercooled liquid is heated to the melting point.

The obtained value of \( \alpha_0 \) is in reasonable agreement with the thermodynamic values \( \alpha_0 = 0.35 \) and \( \alpha_0 = 0.40 \) reported by Malinovsky and Vrebenska\(^{1,4} \) and with \( \alpha_0 = 0.20 \) given by Jønsen.\(^2 \) The thermodynamic values refer to 782 °C. Good correspondence with thermodynamic results also are found in the recent Raman investigations by Gilbert et al.,\(^4 \) of NaF-AlF₃ melts. They found \( K = 3 \times 10^{-4} \) at 780 °C.

To conclude, the dissociation of AlF\(^{2-}\) in cryolite melts is found to follow the equilibrium reaction AlF\(^{2-}\) = AlF\(^{4-}\) + 3F\(^-\) with \( K = 3 \times 10^{-4} \) and \( \alpha_0 = 0.24 \pm 0.06 \) at 730 °C in the lithium system. These values are based on a Temkin model and a scattering efficiency (\( \nu_1 \)) of AlF\(^{2-}\) two times greater than of AlF\(^{4-}\).

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