Raman Spectra of Molten Mixtures Containing Aluminium Fluoride. II. Dissociation of AlF_6^{3-}

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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

$$AlF_6^{3-} \rightleftharpoons AlF_4^- + 2F^- \quad (1)$$

gave the best description of the cryolite peak in the phase diagram of NaF and AlF_3. The same result was found for the corresponding lithium system.[2,3] Holm [4] interpreted the total value of ΔH_{mix} in the system NaF-AlF_3 as due to the dissociation of the cryolite anion into AlF_3 and F^- in the composition range $0 < X_{AlF_3} < 0.25$. Dewing [5] found that NaF-$NaAlF_4$ mixtures may be described for all values of X_{AlF_3} as a regular solution the two ions F^- and AlF_4^-. Deviations near the $NaAlF_4$ composition were explained by the formation of $Al_2F_7^-$.

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 AlF_6^{3-} as the main complex in the system LiF-Li_3AlF_6. In order to test the existence of other species proposed in the cryolite melts, compositions in the system Li_3AlF_6-AlF_3 should be investigated. In this paper we report the results of a Raman spectroscopic investigation of the Li_3AlF_6-AlF_3 eutectic melt. After completion of the present work we became aware of a Raman investigation of the sodium system.[7,8]

Results. The experiments were performed according to a procedure previously described.[6] The only change in the experimental design was the introduction of a cylindric platinum liner in the Raman cell in order to increase the Raman intensity. The spectrum obtained at 730 °C for the molten Li_3AlF_6-AlF_3 eutectic mixture, LiF + 35.5 mol % AlF_3,[9] 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 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-Li_3AlF_6 eutectic mixture [6] 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.

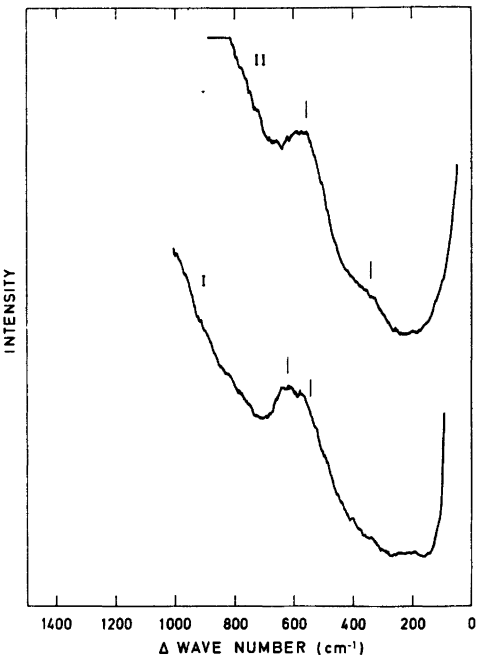

Fig. 1. The Raman spectra of the molten $Li_3AlF_6 - AlF_3$ (I) and LiF-Li_3AlF_6 (II) eutectic mixtures at 730 °C. The band widths were 20 cm^{-1} (curve I) and 25 cm^{-1} (curve II). Sensitivity: 1000 cps. Scan speed: 0.2 cm^{-1}/s. Period: 50 s.

Discussion. The 620 cm^{-1} band is assigned to the ν_1 frequency of the AlF_4^- 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 AlF_6^{3-}. This result is within the uncertainty limits of our first value, 556 ± 5 cm^{-1}. In NaF-AlF_3 mixtures,[7,8] the corresponding frequencies were found to be 622 and 555 cm^{-1}.

Since no definite sign of species other than AlF_6^{3-} and AlF_4^- was found, the dissociation (1) is used in a description of the melt mixtures in the composition range LiF-$LiAlF_4$. Thus the melt is considered as being composed of a cation mixture and a mixture of the anionic entities AlF_6^{3-}, AlF_4^- and F^-. This represents a Temkin model, but not necessarily an ideal one.

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The following expression then is valid for the stoichiometric dissociation constant K of reaction (1) in the system $LiF\text{-}AlF_3$:

$$K = \frac{[(1+P) - X_{AlF_3}^{\circ}\,(2+4P)]^2}{P[(1+P) - X_{AlF_3}^{\circ}\,(1+3P)]^2} \quad (2)$$

where P is the ratio between the concentrations of AlF_6^{3-} and AlF_4^-. The equation is derived by a procedure similar to that described for $KCl - AlCl_3$ melts.[10,11] For pure cryolite, Li_3AlF_6, P is related to the dissociation degree α_0 of AlF_6^{3-} through

$$P = \frac{X_{AlF_6^{3-}}}{X_{AlF_4^-}} = \frac{1-\alpha_0}{\alpha_0} \quad (3)$$

Combination of eqns (2) and (3) and introduction of $X_{AlF_3}^{\circ} = 1/4$ yield

$$K = 4\alpha_0^3/(1+2\alpha_0)^2(1-\alpha_0) \quad (4)$$

At a constant temperature, the relationship between P, α_0 and $X_{AlF_3}^{\circ}$ 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 α_0 at a temperature T may be used as a frame of reference for the function $P = P\,(X_{AlF_3})$.

According to Wolkenstein's bond polarizability theory, the mean molecular polarizability derivative is a bond property (see Chantry [12]). It follows that the mol fraction ratio may be calculated from [10–12]

$$\frac{X_{AlF_6^{3-}}}{X_{AlF_4^-}} = k\frac{I_{AlF_6^{3-}}}{I_{AlF_4^-}} = P \quad (5)$$

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 ν_1 frequencies between the two species into account. The Al – F bonds in the two species are assumed similar. Gilbert *et al.*[8] found that the coefficient k should be between 1/2.0 and 1/2.1 in the $NaF\text{-}AlF_3$ system. By using the value $k = 1/2.0$ and inserting 1.0 for the intensity ratio $I_{AlF_6^{3-}}/I_{AlF_4^-}$ at $X_{AlF_3}^{\circ} = 0.355$, the result $P = 0.5$ is obtained. This gives $K = 3.4 \times 10^{-2}$ from eqn. (2) and $\alpha_0 = 0.24$ from eqn. (4) at 730 °C. This result is consistent with previous investigations of the $LiF\text{-}Li_3AlF_6$ eutectic mixture [6,8] which gave no sign of AlF_4^-. By taking into consideration the uncertainty of the observed intensity ratio, the uncertainty of α_0 is calculated to be ± 0.06. It is a linear relationship between α_0 and P at $X_{AlF_3}^{\circ} = 0.355$ 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,[2] may be estimated by using the value $\Delta H = 50.3$ J/mol at 700 °C which Holm and Holm [9] have calculated for the dissociation $AlF_6^{3-} = AlF_3 + 3F^-$. Van't Hoff's equation then leads to an increase in α_0 of about 10 % when the undercooled liquid is heated to the melting point.

The obtained value of α_0 is in reasonable agreement with the thermodynamic values $\alpha_0 = 0.35$ and $\alpha_0 = 0.40$ reported by Malinovsky and Vrebenska [2,14] and with $\alpha_0 = 0.20$ given by Jenssen.[3] The thermodynamic values refer to 782 °C. Good correspondence with thermodynamic results also are found in the recent Raman investigations by Gilbert *et al.*[7,8] of $NaF\text{-}AlF_3$ melts. They found $K = 3 \times 10^{-3}$ at 780 °C.

To conclude, the dissociation of AlF_6^{3-} in cryolite melts is found to follow the equilibrium reaction $AlF_6^{3-} \rightleftharpoons AlF_4^- + 2F^-$ with $K = 3 \times 10^{-2}$ and $\alpha = 0.24 \pm 0.06$ at 730 °C in the lithium system. These values are based on a Temkin melt model and a scattering efficiency (ν_1) of AlF_6^{3-} two times greater than of AlF_4^-.

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