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ON THE IONIC EQUILIBRIUM BETWEEN COMPLEXES IN MOLTEN FLUOROALUMINATES

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We discuss theoretically (i) the effect of the alkali cation species on the ionic equilibrium between $(\text{AlF}_6)^{3-}$ and $(\text{AlF}_4)^-$ complexes in molten alkali fluoroaluminates, and (ii) the possible presence of $(\text{AlF}_5)^{2-}$ complexes in molten cryolite, in relation to very recent Raman scattering experiments by Gilbert and Materne.

KEY WORDS: Raman scattering, molten cryolite.

In a previous publication¹ (hereafter referred to as I) two of us have proposed a statistical mechanical model for the equilibrium between $(\text{AlF}_6)^{3-}$ and $(\text{AlF}_4)^-$ complexes in liquid $(\text{AlF}_3)_c(\text{NaF})_{1-c}$ mixtures over the composition range $c \leq 0.5$. The relevant data are from Raman scattering experiments by Gilbert, Mamantov and Begun², showing that the Raman spectrum of Al-alkali fluoride mixtures in the composition range $0.375 \leq c \leq 0.5$ contains two partially overlapping but distinct peaks, that they attributed to the above two species in relative concentration varying with composition. These authors further reported that in molten cryolite (Na_3AlF_6 , i.e. $c = 0.25$) at $T = 1288$ K the Raman scattering spectrum contains a main peak, that they attributed to the $(\text{AlF}_6)^{3-}$ species, with a high-frequency shoulder due to the $(\text{AlF}_4)^-$ species in relative concentration of order $20 \div 25\%$. The theoretical results in I were in overall good agreement with this interpretation of the Raman data and also offered a natural explanation for the different complexing behaviours of Al-alkali fluorides and chlorides, i.e. for the fact that the $(\text{AlCl}_4)^-$ coordination is stable in the latter systems.

Very recently Gilbert and Materne³ have reported new Raman scattering spectra from Al-alkali fluoride melts in the composition range $c \leq 0.25$. Their data show that (i) the high-frequency shoulder attributed to the $(\text{AlF}_4)^-$ species in molten Na_3AlF_6 is no longer seen on replacing Na by Li and is resolved as a separate peak on replacing Na by K, and (ii) the distribution of intensity in the main spectral peak in $(\text{AlF}_3)_c(\text{NaF})_{1-c}$ mixtures undergoes shifts on decreasing c below $c = 0.25$. They attribute the latter observation to the presence of two bands under the main spectral peak, that they separate by suitable fitting procedures, and propose as the most probable explanation for these two bands coexistence of $(\text{AlF}_6)^{3-}$ and $(\text{AlF}_5)^{2-}$ species. In the

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present work we show that the theoretical model presented in I accounts for the observed alkali-ion effect on the equilibrium between $(\text{AlF}_4)^-$ and higher complexes in molten fluoroaluminates, and discuss theoretically the question of an equilibrium between $(\text{AlF}_6)^{3-}$ and $(\text{AlF}_5)^{2-}$ species in molten cryolite.

The model developed in I treats the dissociation equilibrium



in the melt as being determined by the balance between the difference in binding of the two species in vacuo and the difference in their gain of free energy from Coulomb interactions in the melt. The equilibrium in the melt at temperature T and molar volume v is described by the equation

$$\frac{x_6}{x_4 x_{\text{F}}^2} = \left(\frac{h^2}{2\pi k_B T v^{2/3}} \right)^3 \left[\frac{m_{\text{Al}} + 6m_{\text{F}}}{(m_{\text{Al}} + 4m_{\text{F}})m_{\text{F}}^2} \right]^{3/2} \exp \left[-\frac{F_{64}(x_6)}{k_B T} \right] \quad (2)$$

where x_6 , $x_4 = c - x_6$ and $x_{\text{F}} = 1 - 2c - 2x_6$ are the molar fractions of $(\text{AlF}_6)^{3-}$, $(\text{AlF}_4)^-$ and free F^- ions, the m 's are the atomic masses and

$$F_{64}(x_6) = f_{64} + \left(\frac{\partial F_{\text{ex}}}{\partial x_6} \right)_{T,v,c} \quad (3)$$

The first term on the right-hand side of Eq. (3) is the difference in binding free energy for the two species in vacuo, which by itself would lead to complete dissociation of $(\text{AlF}_6)^{3-}$, while the second term, which is the change in the excess free energy F_{ex} of the melt on dissociation of an $(\text{AlF}_6)^{3-}$ unit, stabilizes these triply charged units relative to the singly charged $(\text{AlF}_4)^-$ units. The balance between these two free energies in Al-Na fluoride melts, as calculated in I from ionic-model treatments of the two species in vacuo and a statistical mechanical treatment of the liquid in the mean spherical approximation (MSA), is such as to yield only limited dissociation of $(\text{AlF}_6)^{3-}$ as a function of composition, in substantial agreement with the data of Gilbert *et al.*²

The stabilizing effect on the more highly charged species in the melt is clearly mainly due to the alkali counterions. The excess number of these counterions in the first-neighbour shell of $(\text{AlF}_6)^{3-}$ is on average higher than in that of $(\text{AlF}_4)^-$, so as to compensate for the excess negative charge carried by the former species. The resulting gain in Coulomb interaction energy for the more highly charged species is expected to decrease with increasing size of the alkali counterion, since the screening length of the liquid is correspondingly increased. This leads to a shift of the dissociation equilibrium in Eq. (1) towards increased relative concentration of $(\text{AlF}_4)^-$ with increasing size of the alkali counterion, as we demonstrate by calculations on Li, Na and K fluoroaluminates. The input data for our calculations at two temperatures⁴⁻⁶ are collected in Table 1, while Table 2 reports our results for the equilibrium in Eq. (1). These results agree with the observations of Gilbert and Materne³ on the changes in the Raman scattering spectrum on replacing Na by Li or K.

Table 1 Values of molar volumes ($\text{\AA}^3/\text{molecule}$), differences in binding free energies in vacuo (kcal/mol) and hard diameters (\AA)^a.

$v_{\text{Li}_3\text{AlF}_6}$	$v_{\text{Na}_3\text{AlF}_6}$	$v_{\text{K}_3\text{AlF}_6}$	f_{64}	f_{65}	f_{54}
30.2	37.9	49.8	216	167	50
33.5	41.9	55.1	211	164	47

σ_{Li}	σ_{Na}	σ_{K}	σ_{F}	$\sigma_{(\text{AlF}_6)^{3-}}$	$\sigma_{(\text{AlF}_4)^-}$	$\sigma_{(\text{AlF}_5)^{2-}}$
1.86	2.24	2.68	2.27	4.96	5.06	5.08
1.90	2.28	2.72	2.31	5.00	5.10	5.12

^a The two numerical values reported for each quantity refer to 1053 K and to 1288 K. The molar volumes are obtained for Na_3AlF_6 from data of Grjotheim *et al.*, Ref. 4, and estimated for the other systems by linear interpolation. The diameters of alkali and fluorine ions are taken from the work of Senatore *et al.*, Ref. 5, on molten alkali halides. The parameters for $(\text{AlF}_6)^{3-}$ and $(\text{AlF}_4)^-$ are taken from I, while those for $(\text{AlF}_5)^{2-}$ are evaluated in the present work.

It should be borne in mind that the dissociation process in Eq. (1) is taking place in a dense liquid medium and may thus be visualized as a series of microscopic diffusion steps in which two F^- ions leave the first coordination shell of the Al^{3+} ion in an $(\text{AlF}_6)^{3-}$ unit to join the excess Na^+ ions in the next coordination shell and to undergo further diffusional rearrangements. The statistical mechanical averages involved in our evaluation of F_{ex} imply that intermediate configurations that may resemble an $(\text{AlF}_5)^{2-}$ unit in the liquid are not neglected altogether, but have a relatively short lifetime and therefore no special weight. On the other hand, a long-lived intermediate $(\text{AlF}_5)^{2-}$ species would imply a rather specific kinetics of the dissociation process, in which the two F^- ions are released over sufficiently different time scales for the intermediate state to attain equilibrium. While we have no access to such kinetic questions in our approach, we may assume that the kinetics is of the necessary type and ask whether $(\text{AlF}_5)^{2-}$ units could be stable on thermodynamic grounds.

To this end we need first to assess the binding of an $(\text{AlF}_5)^{2-}$ unit in vacuo. We do so by the same polarizable-ion model that was used in I for $(\text{AlF}_6)^{3-}$ and $(\text{AlF}_4)^-$. We assume that the $(\text{AlF}_5)^{2-}$ unit has the shape of a trigonal bipyramid with the Al^{3+} ion at its centre, as an intermediate shape between the $(\text{AlF}_6)^{3-}$ octahedron and the $(\text{AlF}_4)^-$ tetrahedron. The calculation yields approximately equal Al-F bond

Table 2 Equilibrium between $(\text{AlF}_6)^{3-}$ and $(\text{AlF}_4)^-$ in molten fluoroaluminates.

	$T = 1053 \text{ K}$			$T = 1288 \text{ K}$		
	x_6	x_4	F_{64}^a	x_6	x_4	F_{64}^a
Li_3AlF_6	0.25	0.00	-79	0.24	0.01	-83
Na_3AlF_6	0.24	0.01	-64	0.22	0.03	-71
K_3AlF_6	0.20	0.05	-54	0.15	0.10	-62

^a Values of the activation energy $F_{64}(x_6)$ at equilibrium, in kcal/mol.

lengths for the fluorine ions in the basal plane (1.78 Å) and at the apices (1.81 Å) and a binding energy of 1420 kcal/mol relative to free ions, with a substantial contribution from fluorine polarization (56 kcal/mol). The above values should be compared with those given in I for the $(\text{AlF}_4)^-$ unit (1.71 Å and 1476 kcal/mol) and for the $(\text{AlF}_6)^{3-}$ unit (1.90 Å and 1247 kcal/mol). The estimated values for the effective diameter of the $(\text{AlF}_5)^{2-}$ unit in the melt and for the free energy differences f_{65} and f_{54} between this unit and the others in vacuo are given in Table 1.

With the above estimates we can now evaluate the dissociation equilibria



in molten cryolite. The melt is treated in the MSA as a five-component fluid consisting of $(\text{AlF}_6)^{3-}$, $(\text{AlF}_5)^{2-}$ and $(\text{AlF}_4)^-$ units in molar fractions x_6 , x_5 and x_4 respectively, free F^- ions in molar fraction $x_{\text{F}} = 1 + 2c - 6x_6 - 5x_5 - 4x_4$ and Na^+ ions in molar fraction $(1 - c)$. The excess free energy of the liquid is thus obtained as a function $F_{\text{ex}}(x_6, x_5, x_4)$, subject to the restriction $x_6 + x_5 + x_4 = c$. The equilibrium equations are

$$\frac{x_6}{x_5 x_{\text{F}}} = \left(\frac{h^2}{2\pi k_{\text{B}} T v^{2/3}} \right)^{3/2} \left[\frac{m_{\text{Al}} + 6m_{\text{F}}}{(m_{\text{Al}} + 5m_{\text{F}})m_{\text{F}}} \right]^{3/2} \exp \left[- \frac{F_{65}(x_6, x_4)}{k_{\text{B}} T} \right] \quad (5)$$

and

$$\frac{x_5}{x_4 x_{\text{F}}} = \left(\frac{h^2}{2\pi k_{\text{B}} T v^{2/3}} \right)^{3/2} \left[\frac{m_{\text{Al}} + 5m_{\text{F}}}{(m_{\text{Al}} + 4m_{\text{F}})m_{\text{F}}} \right]^{3/2} \exp \left[- \frac{F_{54}(x_5, x_6)}{k_{\text{B}} T} \right], \quad (6)$$

where

$$F_{65}(x_6, x_4) = f_{65} + \left(\frac{\partial F_{\text{ex}}}{\partial x_6} \right)_{x_5, x_4} - \left(\frac{\partial F_{\text{ex}}}{\partial x_5} \right)_{x_6, x_4} \quad (7)$$

and

$$F_{54}(x_5, x_6) = f_{54} + \left(\frac{\partial F_{\text{ex}}}{\partial x_5} \right)_{x_4, x_6} - \left(\frac{\partial F_{\text{ex}}}{\partial x_4} \right)_{x_5, x_6} \quad (8)$$

The derivatives in Eqs. (7) and (8) are at constant T , v , and c .

Of course, both the doubly and the triply charged species are stabilized by screening in the ionic liquid relative to the singly charged species, but with the input parameters given in Table 1 we find that the stabilization of $(\text{AlF}_5)^{2-}$ is insufficient to yield an appreciable concentration of this species. At $T = 1288$ K we find $x_6 = 0.21$, $x_5 = 0.01$ and $x_4 = 0.03$. We should, however, point out that comparable amounts of $(\text{AlF}_6)^{3-}$ and $(\text{AlF}_5)^{2-}$ would be found by changes in our input parameters which, though rather large, cannot be excluded: for instance, by destabilizing the $(\text{AlF}_6)^{3-}$ unit in vacuo by some 15 kcal/mol or by decreasing the effective diameter of $(\text{AlF}_5)^{2-}$ by some 0.2 Å. We recall in this connection that the reliability of our calculations for isolated species can only be tested through their results for bond lengths and vibrational frequencies⁶, and that there is some arbitrariness in the way

we estimate the effective diameter of a complex from the halogen-halogen bond length.

In summary, the observed effects of the alkali counterion on the equilibrium between $(\text{AlF}_4)^-$ and more highly charged complexes are easily accounted for within our model. On the other hand, on purely thermodynamic grounds and leaving aside the dissociation kinetics, our best *a priori* estimate of input parameters suggests that intermediate $(\text{AlF}_5)^{2-}$ units may be present in molten cryolite only as relatively short-lived configurations. Nevertheless, the free energy balance is sufficiently delicate, compared with the crudeness of our estimations, to exclude coexistence of $(\text{AlF}_6)^{3-}$ and $(\text{AlF}_5)^{2-}$ species. We also take the occasion to point out that the scenario that two of us have recently proposed for processes of structure breaking and electron localization in molten cryolite under addition of sodium metal⁷ (i.e. dissociation of higher complexes and formation of Al ions in reduced valence states) would be substantially unchanged if $(\text{AlF}_5)^{2-}$ complexes were present in the ionic melt.

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References

1. Z. Akdeniz and M. P. Tosi, *Phys. Chem. Liquids*, **21**, 127 (1990).
2. B. Gilbert, G. Mamantov and G. M. Begun, *J. Chem. Phys.*, **62**, 950 (1975).
3. B. Gilbert and T. Materne, *Appl. Spectr.*, **44**, 299 (1990).
4. K. Grjotheim, C. Krohn, M. Malinovsky, K. Matiasovsky and J. Thonstad, *Aluminium Electrolysis* (Aluminium-Verlag GmbH, Düsseldorf, 1977).
5. G. Senatore, M. Parrinello and M. P. Tosi, *Phil. Mag.*, **B41**, 595 (1980).
6. Wang Li and M. P. Tosi, *N. Cimento*, **10 D**, 1497 (1988).
7. Z. Akdeniz and M. P. Tosi, *Phil. Mag.*, in the press.