A Theoretical Study of the Stabilization of the $(AlF_5)^{2-}$ Complex Anion by Alkali Counterions

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We evaluate the relative stability of various states of coordination for the aluminium ion by fluorines in M_nAlF_{n+3} microclusters, with M = Li, Na or K and n = 2 or 3. The calculations use ionic model interactions which have been adjusted and tested against experimental data and *ab initio* calculations on the $(AlF_4)^-$ anion and on $MAlF_4$ clusters. We confirm earlier results showing that the fivefold $(AlF_5)^{2-}$ anion is stabilized by the counterions and assess the sensitivity of this result to the details of the model as well as the effect of alkali substitution. We evaluate the variation of the breathing mode frequency of the complex anions in these clusters for comparison with Raman scattering data from liquid mixtures ofAlF_3 and MF in the basic range of composition.

Key words: Charged Clusters; Structure of Associated Liquids.

1. Introduction

Raman scattering spectra and thermodynamic measurements on liquid $(MF)_{1-x}$ - $(AlF_3)_x$ mixtures (with M = Li, Na or K and $x \leq 0.5$) have been interpreted as giving evidence for the coexistence of the $(AlF_4)^-$, $(AlF_5)^{2-}$, and $(AlF_6)^{3-}$ anions in varying relative concentrations as the composition is varied [1 - 5]. There has been much interest in metal halide complexes because of applications in such areas as high-temperature industrial processes and catalysis, and the uncommon fivefold coordination of a trivalent metal ion in $(AlF_5)^{2-}$ has drawn considerable attention.

In recent studies some of us [6, 7] have evaluated the relative stability of various isolated $(AlF_{n+3})^{n-}$ and Na_nAlF_{n+3} microclusters (with n = 1, 2 or 3) and drawn attention to the role of the Na counterions in stabilizing different states of coordination for Al. In particular, for the Na_3AlF_6 cluster these calculations showed that the energy minimum corresponding to a fivefold coordinated Al combined with three double-bridged Na counterions and one F coion is deeper than the minimum corresponding to sixfold coordinated Al with three triple-bridged Na counterions.

In this work we extend these calculations to M_nAlF_{n+3} clusters with different alkalis. We use an ionic model which was first developed for Al chloride clusters [8], where it accounts for the electron-shell deformability of the halogens through a reduced valence and through electrical and overlap polarizabilities. In a later adaptation to the $MAlF_4$ molecules, an account of the electrical polarization of the alkali ions has been added [9]. Indeed, while the polarizability of the Li ion is completely negligible and that of the Na ion is quite small, the polarizability of the heavier alkalis is larger than that of the fluorine ion. For all details on the model and its parameters the reader should consult [8] and [9]. We only emphasize that for fluorides the model has been adjusted and tested against data from electron diffraction [10] and Raman scattering [11] as well as from *ab initio* molecular orbital results on $MAlF_4$ molecules [12].

Here we apply without further adjustments the model determined in [9] to evaluate the isolated

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M_2AlF_5 and M_3AlF_6 clusters with M = Li, Na or K. For each cluster various structures allowing for fourfold, fivefold or sixfold coordination of the Al ion by fluorines are examined. We report only on those structures which are both zero-force and mechanically stable configurations of the ionic assembly (*i. e.* do not have any imaginary frequency). We also test the sensitivity of the structural predictions on M_nAlF_{n+3} clusters to details regarding short-range overlap repulsions and polarization terms for the alkali counterions.

2. Structure and Cohesive Energy of M_nAlF_{n+3} Clusters

With regard to the bonding of the alkali to fluorines in the $MAlF_4$ clusters it was found [9] that, whereas a twofold edge-bridged configuration is strongly favoured for Li in $LiAlF_4$, edge-bridging and face-bridging become energetically equivalent as one moves from Na to the heavier alkalis. This is yet another example of a well known general rule for ionic structures: increasing size of positive ions favours higher coordination and is not wholly balanced by the parallel increase of their polarizability. The equivalence between edge-bridging and face-bridging in $MAlF_4$ for M = K, Rb or Cs was interpreted as implying that these clusters can almost be viewed as a diatomic molecule composed of M^+ and $(AlF_4)^-$ units in a state of almost free relative rotation.

As we move to the higher clusters (M_2AlF_5 and M_3AlF_6), we add one or two MF molecules to $MAlF_4$ and examine all possible coordinations of the aluminium ion which are allowed by the available number of fluorines. The shift in relative stability of edge-bridged and face-bridged configurations for the alkali counterions from Li to K, that we have recalled just above for $MAlF_4$, is also a determining factor in the structure of the higher clusters.

2.1. The M_2AlF_5 Clusters

The states of fourfold and fivefold coordination for the Al ion are both mechanically stable at this composition. Twofold coordination is preferred for Li and the threefold one for K, while both are found for Na. Table 1 illustrates the structures that we have found in the case of Na_2AlF_5 by reporting the bond lengths between near neighbours. In all cases there are some minor distortions in the shape of the complex anion relative to a perfect prism, as well as some differences in the three bond lengths for a threefold coordinated alkali. However, at high temperature such structural details will be averaged out by the thermal motions of the counterions around the complex anion.

Table 1. Bond lengths between near neighbours in Na_2AlF_5 (in Å). The first column shows the state of coordination of Al, and the other columns report the Al-F and Na-F bond lengths with their multiplicities.

	Al	Na_1	Na_2
4-fold:	1.65, 1.70 twice, 1.72	1.92, 2.19	1.95, 2.40 twice
5-fold:	1.69, 1.78 twice, 1.80 twice	1.99, 2.04	1.99, 2.04
5-fold:	1.74 twice, 1.77, 1.80 twice	1.99, 2.04	2.07, 2.34 twice

Table 2. Energy differences between the fourfold ground state and the fivefold excited states in M_2AlF_5 (eV).

Li_2AlF_5	Na_2AlF_5	K_2AlF_5
0.64	0.70	0.60

In all cases the fourfold coordination is found to be the ground state (see Table 2). The energy differences between the different states of coordination for the alkali ions are at the level of a few hundredths of an eV and have been neglected in Table 2.

We have examined the dependence of our results on the detailed form of the overlap repulsive interactions between the alkali and the fluorine ions in the case of Na_2AlF_5, by carrying out calculations based on different expressions from studies of the cohesive properties of alkali halide crystals [13] (see [9] for the details). The absolute values of the cohesive energy of each structure are shifted upwards by about 0.1 eV upon replacing the TF potential by the FT potential, but the energy differences are affected only at the level of 0.01 eV or so.

The role of alkali polarization is instead rather relevant in clusters containing the heavier alkalis. We have examined it by repeating the calculations for K_2AlF_5 after setting to zero the polarizability of K^+ and refitting the other model parameters to $KAlF_4$. The energy difference reported in Table 2 for K_2AlF_5 is moved up to almost 1 eV. However, such energy shifts are small in Na_2AlF_5 and totally negligible in Li_2AlF_5.

2.2. The M_3AlF_6 Clusters

States of fourfold, fivefold and sixfold coordination for the Al ion are mechanically stable at this com-

Table 3. Bond lengths between near neighbours in Na_3AlF_6 (in Å). The first column shows the state of coordination of Al, and the other columns report the Al-F and Na-F bond lengths with their multiplicities; tw = twice.

Al	Na_1	Na_2, Na_3
4-fold: 1.65, 1.70 tw, 1.72	1.97 tw	1.91, 2.30, 2.59
5-fold: 1.74 tw, 1.77, 1.80 tw	1.99, 2.06	1.97, 2.23, 2.32
6-fold: 1.77 tw, 1.78, 1.91 tw, 1.96	2.13 tw, 2.24	2.03, 2.21 tw

Table 4. Energy differences between the fourfold ground state and the fivefold and sixfold excited states in M_3AlF_6 (eV).

	Li_3AlF_6	Na_3AlF_6	K_3AlF_6
Fivefold:	0.57	0.43	0.30
Sixfold:	1.37	1.16	1.0

position. The distributions of near-neighbour bond lengths in these states are illustrated in Table 3 for the Na_3AlF_6 clusters. Comparison of these results with those in Table 1 shows that the change in composition (aside from suppressing the first of the two fivefold states in Table 1) does not alter the Al-F bond lengths. To this extent one may look upon the $(AlF_4)^-$ and $(AlF_5)^{2-}$ anions as units whose structure is almost ideally independent of their environment.

The sixfold-Al clusters have different stable shapes depending on the alkali counterions. In the case of Li the cluster conforms to the naive idea of a perfect octahedron with three edge-bridged counterions. However, it is evident from Table 3 that in the case of Na the stable structure of the sixfold cluster is quite different from this ideal picture. In fact, each Na counterion has three fluorine near neighbours (see Table 3). Higher symmetry will be established as rotational diffusion of the counterions around the complex anion sets in at high temperature.

The fourfold coordination state is again the ground state of M_3AlF_6 in all cases, with the fivefold state being higher by several tenths of an eV and the sixfold one still higher by about 1 eV. The energy differences between these different states of coordination are shown in Table 4. Thus, after inclusion of alkali polarization our calculations confirm our earlier finding [7] that the fivefold state is at least energetically competitive with, and probably more strongly bound than the sixfold state at this composition.

Finally, our results for the M_3AlF_6 clusters are rather more sensitive to the details of the model. The energy differences shown in Table 4 for Na_3AlF_6 move up by 0.05 - 0.1 eV upon replacing the TF potential by the FT potential in dealing with the Na-F overlap repulsive energy. Even more strikingly, the energy differences shown in Table 4 for K_3AlF_6 move up to 0.46 eV (fivefold state) and to 1.49 eV (sixfold state) upon neglecting the polarization of the K^+ ion.

Table 5. Calculated frequencies of the breathing mode of the complex anions in various neutral clusters (in cm^{-1}).

		Li_nAlF_{n+3}	Na_nAlF_{n+3}	K_nAlF_{n+3}
$(AlF_4)^-$	$n = 1$:	613 - 624	621	627
	$n = 2$:	616 - 633	634	641
	$n = 3$:	625 - 662	641	641
$(AlF_5)^{2-}$	$n = 2$:	528	553	551
	$n = 3$:	558	553	552
$(AlF_6)^{3-}$	$n = 3$:	496	453	458

3. Breathing-mode Frequencies of the Complex Anions

We have noticed in Sect. 2 that the calculated structural parameters of the $(AlF_4)^-$ and $(AlF_5)^{2-}$ complex anions show little sensitivity to the environment. Table 5 illustrates the same issue with regard to dynamical structure, by reporting the calculated values of the frequency of the breathing mode of $(AlF_4)^-$, $(AlF_5)^{2-}$ and $(AlF_6)^{3-}$ in the various M_nAlF_{n+3} clusters with M = Li, Na or K. In the Li clusters the interaction with the vibrations of the complex anion is appreciable, and indeed it appears that the breathing mode of the isolated $(AlF_4)^-$ tetrahedron may be split into two as indicated in Table 5. However, for the Na and K clusters the effect of the environment on the breathing mode of the complex anion seems to be quite small.

For a comparison with experimental data we refer to the work on the Raman spectrum of $KF\text{-}AlF_3$ melts by Robert *et al.* [4], who assign bands at 622, 555 and 515 cm^{-1} to $(AlF_4)^-$, $(AlF_5)^{2-}$ and $(AlF_6)^{3-}$, respectively. It can be seen from Table 5 that there is good agreement with these data for the first two anions, whereas for $(AlF_6)^{3-}$ there remains a discrepancy between theory on isolated clusters and experiment on molten mixtures. There also is agreement with the experimental evidence [4] showing that the influence of the counterion on the vibrations of the complex anions is strongest for Li and weakest for K.

4. Summary and Concluding Remarks

Most of the results that we have presented in this work on isolated microclusters are consistent with the thermodynamic and Raman scattering evidence which is available on liquid $(MF)_{1-x}$ - $(AlF_3)_x$ mixtures in the basic range of composition from the equimolar melt ($x = 0.5$) to the composition corresponding to cryolite ($x = 0.25$).

Specifically, we find that (i) the $(AlF_4)^-$ anion remains energetically competitive with the higher complexes as the fluorine content increases; and (ii) the $(AlF_5)^{2-}$ anion is at least energetically competitive with the $(AlF_6)^{3-}$ anion down to composition $x = 0.25$. These stability properties of the complex anions are crucially dependent on the presence of the alkali counterions. Nevertheless, the $(AlF_4)^-$ and$(AlF_5)^{2-}$ anions can almost be viewed as well defined units having structural and dynamical identities of their own. Of course, one might expect that in molten mixtures the $(AlF_6)^{3-}$ complex anion will eventually become the dominant species at very high dilution of AlF_3 ($x \to 0$).

The above properties hold independently of the details of the theoretical model for the clusters that we have evaluated – although for the heavy alkalis the quantitative results are very sensitive to the inclusion of alkali polarization. Of course, our calculations refer to zero temperature and make no allowance for entropic contributions. Applications of the present ionic model in classical simulation runs on these melts will be necessary for this purpose.

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