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Aluminium-Oxygen Containing Species in Fluoride Melts

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Cryoscopic measurements on the sodium fluoride rich side in the reciprocal salt system $NaF-AlF_3-Na_2O-Al_2O_3$ are presented. The amounts of cryolite and oxide added to NaF are so small that ideal behaviour of the solution can be expected. The results indicate complex formation, with the $Al_2OF_x^{4-x}$ complex as a dominating species when the ionic ratio Al^{3+}/O^{2-} is larger than five.

The aluminium-oxygen containing species in molten mixtures of aluminium oxide and cryolite have been of great interest over a long period of time, mainly because of the industrial importance of this kind of systems in connection with aluminium production. Grjotheim *et al.*[1] have made a list of some of the suggestions of structural entities in the melt. Summarizing some of the latest works,[1–3] one finds that the following points seem to be accepted.

1. In the dilute range, the number of oxygen atoms per complex is one. This is based on the cryoscopic measurements by Holm [2] in cryolite systems. Al_2O_3 creates three and $NaAlO_2$ two foreign particles at infinite dilution in cryolite.

2. From entropy considerations the number of aluminium atoms per complex is assumed to be one in the dilute range.[3] No measurements give this number explicitely.

3. In the more concentrated range it seems to be difficult to fit experimental data to theoretical models. Suggestions like AlO_2^-, $Al_2OF_x^{4-x}$, $Al_2O_2F_y^{2-y}$, $Al_3O_2F_z^{5-z}$ are made.

A possible way of testing these theories is to work in a ternary system where both cryolite (Na_3AlF_6) and oxide (Al_2O_3, $NaAlO_2$) are solutes. Cryoscopic measurements in these systems will give an average value of the number of aluminium- and oxygen-atoms in the complex in the ranges where ideal behaviour of the melt can be expected. Structural informations of oxygen-aluminium-containing complexes in melts with small content of cryolite, may contribute to the understanding of melts with higher cryolite content.

When sodium fluoride is used as a solvent, this component will form the first solid phase in the region of high sodium fluoride content.[5] Solid solubility of the other components in sodium fluoride is extremely small.[2,4] In the system

$NaF-Na_3AlF_6$ ideal Temkin behaviour of the melt can be expected for $x_{Na_3AlF_6} \leq 0.07$ [4]. When we neglect the differences in specific heat of solid and liquid phaces, the liquids-line of the system is given by:

$$\Delta\bar{S}_{NaF} = \Delta H_f\left(\frac{1}{T} - \frac{1}{T_f}\right) + \frac{\Delta\bar{H}_{NaF}}{T} \quad (1)$$

Calculations of the partial differential heat of mixing, $\Delta\bar{H}_{NaF}$, using data from Holm [6] will give a contribution of -0.03 e.u. with $x_{Na_3AlF_6} = 0.05$. The error limits of the measured heats of mixing are, however, so large (giving ± 0.2 e.u. at this point) that no definite conclusions can be drawn from the calculation. Since the two anions of the mixture have different charge and size, one may expect deviations from the ideal Temkin entropy of mixing. A rough estimate of the partial entropy of mixing $\Delta\bar{S}_{NaF}$ may be obtained using the equation derived by Flory for the entropy of mixing for an athermal solution of polymers and monomers. This was done for the mixture of the anions AlF_6^{3-} and F^- for the composition $x_{NA_3AlF_6} = 0.05$. In this calculation it is assumed that threevalent anions will occupy three sites, and the monovalent anion will occupy one site. The partial entropy of mixing for sodium fluoride calculated on this base from Flory's equation is 10 % higher than the value obtained from the simpler Temkin model for an ideal ionic mixture. We therefore find it unnecessary to use the Flory equation or other refined method for the calculation of the partial entropy of mixing for sodium fluoride and we will use the simple equation $\Delta\bar{S}_{NaF} = -R \ln X_{F^-}$. Neglecting the small partial heat of mixing and using the Temkin model in the entropy calculation, one obtains

$$-R \ln X_{F^-} \simeq \Delta H_f\left(\frac{T_f - T}{T_f T}\right)$$

and finally the well known cryoscopic relation:

$$\Delta T \simeq Kx \quad (2)$$

where $\Delta T = T_f - T$ and x is the fraction of anions different from F^-. Na^+ is the only cation present in the system.

Once the cryoscopic constant K is known the fraction of anions different from F^- can be found from measurements. In this case the K-value taken from experiments with Na_3AlF_6 in NaF is (430 ± 10) deg.

It is reasonable to assume that the deviation from ideal behaviour due to interaction between anions is not very different for systems containing the AlF_6^{3-} complex and systems where oxygen containing complexes are present, as long as the solutions are dilute.

Oxygen ions can be introduced into melts of $NaF-Na_3AlF_6$ by adding Na_2CO_3 to the system. The carbonate will decompose completely to oxide which is built into a complex ion. The complete decomposition of the carbonate can be verified by introducing the oxygen ions by addition of $NaAlO_2$ instead of carbonate. The addition of oxygen in the form of carbonate is chosen for reasons of convenience. The carbonate is easily obtained in high purity and it dissolves quickly. As will be shown later, addition of oxygen in the form of carbonate also gives better accuracy in the determination of solubility limits.

When a small amount of Na_3AlF_6 is added to fused NaF, the freezing point of NaF is depressed according to the fraction of anions different from F^-, the fraction of foreign particles as given by eqn. (2). If one then adds carbonate (or oxygen ions) to this mixture, one can imagine that the freezing point may continue depressing, remain constant, or be elevated. If the oxygen ions did not combine with the AlF_6^{3-} anions, the fraction of foreign particles would increase giving a depression in the freezing point. If the oxygen ions combined with AlF_6^{3-} in such a way that all complexes continued containing one aluminium, the fraction of foreign particles would not change significantly. The freezing point would be practically unaltered. Finally, if the oxygen ions formed complexes with AlF_6^{3-} containing more than one aluminium, the fraction of foreign particles would decrease and thus the freezing point would be elevated by the carbonate addition.

Theoretically we can expect the following dependence of the freezing point depression, ΔT, on the oxide addition, depending on the complex formed.

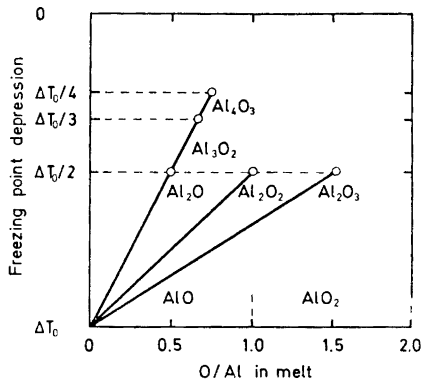

Fig. 1. Expected variation in the freezing point depression of NaF as a function of the O/Al-ratio (keeping the Al-content constant) for different structural entities in the melt. The number of fluoride ions in the complex is not considered. Dashed lines indicate theoretical limits of complex formation.

Fig. 1 illustrates that:

1. Formation of complexes of the type $AlO_kF_l^{3-k-l}$ should give no change in the number of foreign particles in the melt, irrespective of the values of k and l. The ΔT provided by the cryolite anions before adding oxide should remain constant up to the point where the solubility limit is reached.

2. Formation of complex ions with more than one Al per complex should give an increase in the freezing point of the $NaF-Na_3AlF_6$ mixture. ΔT at the solubility limit will indicate the kind of complex present if many types are possible.

If $NaAlO_2$ or Al_2O_3 are used as oxide sources instead of Na_2CO_3, the picture will be the same except for rotation of the curves around the ΔT_0-point, due to the simultaneous addition of Al.

EXPERIMENTAL

The equipment used was similar to that used by Grjotheim.[4] Temperature gradients over the system were less than 0.1°C/cm. Accuracy in temperature measurements was ±0.2°C. The Pt/Pt 10 % Rh thermocouple was annealed and calibrated before use.

To avoid undercooling, which is common in cryolite systems, stirring and addition of seeding crystals were essential. The seeding crystals were weighed to reduce uncertainty in composition.

Optimum cooling rate was 1 – 1.5°C/min. The chemicals used were: Na_2CO_3 and NaF, *p.a.* Merck, Darmstadt, and Na_3AlF_6, handpicked cryolite from Ivigtut, Greenland. Before use the $NaCO_3$ was melted in a platinum crucible.

RESULTS

The results are given graphically in Figures 2, 3, 4, 5 and in Table 1. This table gives experimental data from Figs. 2, 4, and 5.

Table 1.

Mol fraction Na_3AlF_6 before adding Na_2CO_3	0.0300	0.0529	0.0700
$\Delta T/\Delta T_0$ at solubility limit	0.55 ± 0.03	0.55 ± 0.03	0.51 ± 0.03
Ratio O/Al in melt solubility limit	0.83 ± 0.05	0.80 ± 0.05	0.80 ± 0.05
Average ratio Al:O in complex, highest and lowest value	1.70→1.50	1.80→1.55	2.00→1.60

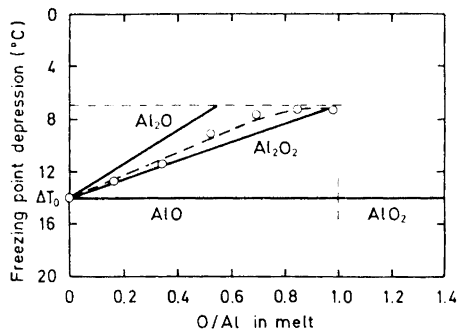

Fig. 2. Observed variation in the freezing point of NaF with addition of Na_2CO_3 to a NaF-$NaAlF_6$ mixture with $X_{Na_3AlF_6} = 0.0300$. Theoretical lines for different kinds of complex formation are indicated. Thin dashed lines show theoretical limits of complex formation.

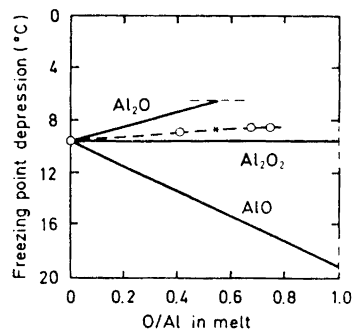

Fig. 3. Observed variation in the freezing point of NaF with addition of $NaAlO_2$ to a mixture of NaF-Na_3AlF_6. The experimental point marked * corresponds to a mixture with mol fraction of Al-atoms equal to 0.0300. Theoretical lines for different kinds of complex formation are indicated. Thin dashed lines show theoretical limits of complex formation.

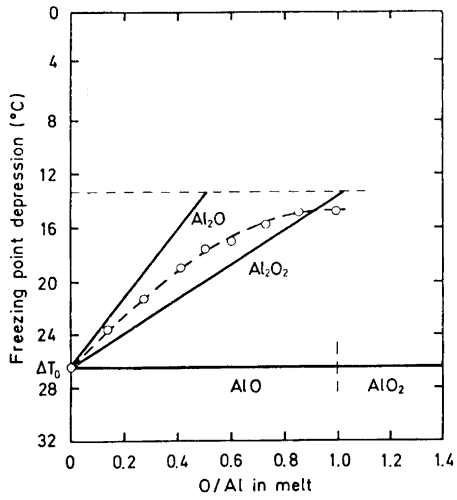

Fig. 4. Observed variation in the freezing point of NaF with addition of Na_2CO_3 to a NaF-Na_3AlF_6 mixture with $X_{Na_3AlF_6} = 0.0529$. Theoretical lines for different kinds of complex formation are indicated. Thin dashed lines show theoretical limits of complex formation.

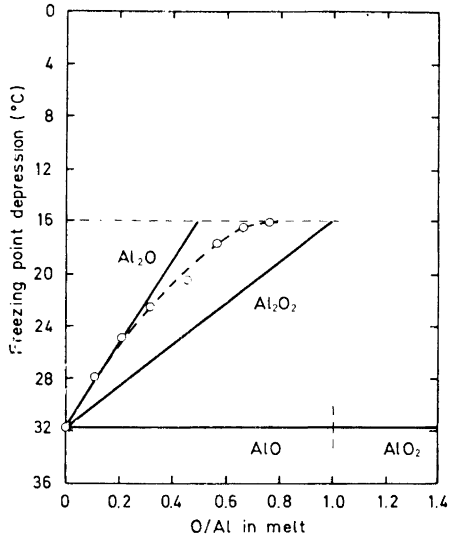

Fig. 5. Observed variation in the freezing point of NaF with addition of Na_2CO_3 to a NaF-Na_3AlF_6 mixture with $X_{Na_3AlF_6} = 0.0700$. Theoretical lines for different kinds of complex formation are indicated. Thin dashed lines show theoretical limits of complex formation.

As can be seen from Figs. 2, 4, 5 the freezing point depression, ΔT, varies with both the ratio O/Al in the melt and with the amount of cryolite initially present. Because of this, results from $NaAlO_2$ addition are not easily compared with the ones from Na_2CO_3-addition. Only one point from the curves on Figs. 2 and 3 should coincide. This is the point marked with a star on Fig. 3 and the point corresponding to the same O/Al-ratio on Fig. 2. Within experimental errors they give complete agreement for the average ratio Al:O in complexes formed in the melt, as calculated from material balance.

It is now obvious why addition of Na_2CO_3 is chosen instead of $NaAlO_2$. The relative decrease in ΔT is smaller when $NaAlO_2$ is used, and this makes the determination of solubility limits more difficult.

DISCUSSION

The following conclusions can be drawn by comparison of theoretical and experimental data:

1. More than one type of aluminium-oxygen containing species is present in the melt over the investigated interval of oxygen addition to the melt. This is concluded from the observation that the experimental curve for ΔT as a function of the O/Al-ratio does not fit any of the theoretical curves.

2. The maximum number of aluminium atoms per complex is probably two, though relatively small quantities of complexes with higher aluminium content cannot be excluded. The reason for this are the two facts: (a) ΔT at the solubility limit is more than half the starting value ΔT_0 before adding Na_2CO_3, (b) The solubility limit is given by a relatively high ratio O/Al ($\simeq 0.8$) in the melt.

Longer chains of Al – O-complexes should reduce the solubility limit and decrease the value of $\Delta T/\Delta T_0$. If these were energetically stable they should have the largest probability at high O^{2-} (in complex) concentration, that is at the solubility limit, and therefore markedly affect the values mentioned. The experimental data therefore indicate that complexs containing three aluminium are unlikely in the concentration range investigated.

3. Complexes with one aluminium cannot be dominating in the melt. Complexes of this kind will not affect the freezing point obtained for the $NaF-Na_3AlF_6$ solution. The rise in temperature is due to the formation of complexes with two Al only (if three Al per complex is excluded). From this fact and from material balances, the ratio between species with one and two Al can be calculated to have a value not higher than 1/4.

4. The existence of a complex with structure Al – O – Al is the only reasonable explanation for a line, steeper than the theoretical line for the Al_2O_2-type complex. This complex should from the above considerations be of importance.

A mixture of the following Al – O-structures is now possible:

1. Al – O
2. O – Al – O
3. Al – O – Al
4. $Al\langle{}^{O}_{O}\rangle Al$
5. Al – O – Al – O
6. O – Al – O – Al – O

As for the species No. 6, this is the neutral molecule Al_2O_3 (possibly with F-ions attached), and previous data [3] seem to exclude this kind of particles.

It should be stated that this method does not differentiate between complexes 4 and 5. But as 5 gives two oxide ions bound in different ways, No. 4 is considered as the most stable of these. In the following, a complex with structure 5 is therefore excluded.

The presence of a complex of the type O – Al – O also seems unlikely. This complex would give no change in ΔT by oxide addition. To explain the experimental results it could therefore be present only in minor quantities. Since it contains two oxygen ions it should be favoured at higher oxide additions. But then one would expect the formation of this complex to extend the solubility limit beyond the observed O/Al ratio. Energetically the complex would not be favourable as it gives a low number of Al – O bonds in the system. From entropy consideration it would also be unfavourable to have the two oxygen combined with the aluminium in a system having an excess of aluminium. If we should consider complexes where the oxygen ion has only one aluminium neighbour, the complex Al – O is more likely.

The mixture of oxygen containing species will therefore be considered most likely to be a mixture of Al – O, Al – O – Al, and Al$\langle{}^{O}_{O}\rangle$Al complex types.

To check whether the structure Al$\langle{}^{O}_{O}\rangle$Al was necessary or not for the description of the experimental lines, the following equilibrium reaction, symbolically written, was considered:

$$\mathrm{Al} + \mathrm{Al}-\mathrm{O} \rightleftharpoons \mathrm{Al}-\mathrm{O}-\mathrm{Al}$$

The only complex present giving the rise in T then would be the Al – O – Al type. If n_1 is the initial number of mol of cryolite in the system, n_2 is the number of moles of Na_2CO_3, and n_3 is the number of moles of foreign particles in the melt (calculated from ΔT and K) we will have:

Mol	Al – O – Al :	$n_1 - n_3$	
Mol	Al – O :	$n_2 - (n_1 - n_3)$	(oxygen balance)
Mol	Al (cryolite anions) :	$n_3 - n_2$	(aluminium balance)

The results of these calculations give an "equilibrium constant" varying with concentration and a wrong solubility limit. The bending of the ΔT *versus* O/Al curve cannot be understood. So the conclusion must be: The set of complexes in the above equation is not sufficient to explain the observations.

Now let us assume that the complete picture can be described by the equilibria:

(1)	$\mathrm{Al} + \mathrm{O} \rightarrow \mathrm{Al}-\mathrm{O}$	(completely)
(2)	$\mathrm{Al}-\mathrm{O} + \mathrm{Al} \rightleftharpoons \mathrm{Al}-\mathrm{O}-\mathrm{Al}$	
(3)	$2\,\mathrm{Al}-\mathrm{O} \rightleftharpoons \mathrm{Al}\langle{}^{O}_{O}\rangle\,\mathrm{Al}$	

When the Al/O ratio is large, reaction (2) is dominating. This is demonstrated by the fact that the experimental line approaches the theoretical line for Al_2O-configuration as the starting value of cryolite is increased from mol fraction 0.030 to 0.070.

As the amounts of Na_2CO_3 (O^{2-} in the complex) increases, reaction (3) will give Al$\langle{}^{O}_{O}\rangle$Al configurations because of excess Al – O formed. This will explain the curving of the experimental line.

Since previous measurements give no information about the number of aluminium atoms in oxygen containing species in cryolite, the results from this investigation may be of importance for the understanding of the structure of these species. The present results are not in contradiction to Holm's cryoscopic measurements in pure cryolite mentioned earlier, but they indicate that the number of aluminium atoms in the one-oxygen containing complex is more likely to be two than one at infinite dilution. The results also show that the stability of the AlO_2^- ion in NaF-rich melts are probably not so high as suggested by Foster.[5]

To give more definite statements, further investigations are needed over the whole range of concentrations. It may be valuable to combine the cryoscopic measurements with spectroscopic measurements. Such measurements are in progress.

SUMMARY

1. Oxygen ions form several kinds of stable complexes in sodium fluoride-cryolite mixtures.

2. The number of aluminium atoms in these complexes is probably not higher than two.

3. When the number ratio of cryolite to sodium oxide is larger than five, the dominating part of the complexes are of the type Al – O – Al.

4. With decreasing ratio cryolite/sodium oxide, the average ratio Al:O in complex will decrease, but it is still larger than one at the solubility limit.

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