MEASUREMENT AND MODELING OF THE ALUMINA SOLUBILITY IN CRYOLITE MELTS AT 1300K

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ABSTRACT

The solubility of alumina was measured experimentally in neutral and basic cryolite melts with a composition range of 3 < cryolite ratio r < 12.5. Thermodynamic activity probes for Al and Na were developed and used to monitor the melt basicity ($\log a_{\text{NaF}}$) and acidity ($\log a_{\text{AlF}_3}$) for the solubility measurements. The alumina solubility in cryolite melts was modeled thermodynamically in terms of three oxyfluoride solutes over the wide composition range of 1.5 < r < 12.5. In an acidic melt, monoxygen Na$_2$Al$_2$O$_7$F$_6$ is the dominant solute. In a less acidic melt, the dioxygen solute Na$_2$Al$_2$O$_2$F$_4$ is dominant. With further increase in melt basicity, another dioxygen solute Na$_4$Al$_2$O$_2$F$_6$ gains importance. The present model describes perfectly the experimentally determined alumina solubility data.

INTRODUCTION

The solubility of Al$_2$O$_3$ in cryolite melts and the melt structure of the NaF-AlF$_3$-Al$_2$O$_3$ system have been active subjects of study for over a century because of the industrial importance of primary aluminum production by the Hall-Heroult process. Although many previous measurements of alumina solubility have been published, and significant progress has been made in understanding the melt structure, further work was necessary to achieve an improved knowledge and correlation in these two contexts.

Skybakmoen, Solheim and Sterten (1) accurately measured the solubility of Al$_2$O$_3$ in cryolite melts for melt compositions in the range of 1.5 < cryolite ratio r < 3 at 1300K. The cryolite ratio r is defined as the ratio of moles NaF to moles AlF$_3$. Solheim and Sterten (2) reported mathematical functions to describe the activities of NaF, AlF$_3$ and Al$_2$O$_3$ in the ternary NaF-AlF$_3$-Al$_2$O$_3$ system for this range of cryolite ratio. As shown in Figure 1, the solubility of Al$_2$O$_3$ in basic cryolite melts (r >3) has been studied several times (3-6), but the data are not consistent. Therefore, in the present study, the solubility of Al$_2$O$_3$ in basic cryolite melts (r >3) was measured experimentally, and (for the first time) described in terms of a quantitative measure of melt basicity.

The published literature for the melt structure of NaF-AlF$_3$-Al$_2$O$_3$ was reviewed in detail in a previous paper (7). It is generally accepted that in acidic (r ≈ 1.5) cryolite melts, Na$_2$Al$_2$OF$_6$ is the dominant solute; in less acidic melts, the neutral solute Na$_2$Al$_2$O$_2$F$_4$ becomes dominant. Some authors (8-10) included another neutral solute Na$_4$Al$_2$OF$_8$ or Na$_3$Al$_2$O$_2$F$_6$ in their models. In basic cryolite melts (r ≥ 3), some basic solute(s) gain in importance. There is controversy concerning the importance of basic
solute entities, with Na$_4$Al$_2$O$_3$F$_6$ (7,11), Na$_6$Al$_2$OF$_{10}$ (8,11) and Na$_3$Al$_5$O$_4$F$_4$ (10,12) having been suggested.

![Graph](image)

**Figure 1.** A collection of the literature data for alumina solubility in neutral and basic cryolite melts

In the current study, the solubility of Al$_2$O$_3$ in basic cryolite melts was measured experimentally for 3 ≤ cryolite ratio $r$ ≤ 12.5 at 1300K. As noted in previous experimental solubility studies, high vapor losses from the melts and attack of the containers are serious experimental problems with basic cryolite melts. Further, the solid phase transition of α-Al$_2$O$_3$ to β-Al$_2$O$_3$ is expected to cause a change in cryolite ratio of the melt. Therefore, all previous measurements based on the original values of melt composition, rather than the equilibrium value of $r$, are subject to error. For this reason, thermodynamic activity probes for Na and Al were developed and used to monitor the melt basicity (or acidity) and thereby relate the equilibrium Al$_2$O$_3$ solubility to the equilibrium melt chemistry. The three-solute model (7) previously proposed for cryolite melts with $r = 1.5$ to 3 was correlated to these alumina solubility data over the wider composition range of 1.5 ≤ $r$ ≤ 12.5. This model provides essentially perfect agreement with the experimentally established alumina solubility data.

**EXPERIMENTAL PROCEDURE**

To achieve an improved knowledge of Al$_2$O$_3$ solubility over a wider composition range of cryolite melts, the solubility of Al$_2$O$_3$ was measured in basic cryolite melts in the composition range of 3 ≤ $r$ ≤ 12.5. Powder and rod segments of α-Al$_2$O$_3$ were used for the
solubility measurements in melts with $r = 3$ and 3.5 while in the more basic melts, $\beta$-$\text{Al}_2\text{O}_3$ powder with a composition of $\text{Na}_2\text{O} \cdot 8\text{Al}_2\text{O}_3$ was used as the $\text{Al}_2\text{O}_3$ source, because $\beta$-$\text{Al}_2\text{O}_3$ (not $\alpha$-$\text{Al}_2\text{O}_3$) is stable in this basic composition range. Large size (> 0.1 mm diameter) powders for both types of $\text{Al}_2\text{O}_3$ were chosen so that rapid settling occurred before sampling. In each experiment for melts with $r = 3$ and 3.5, 30–35g $\text{Na}_3\text{AlF}_6$-$\text{NaF}$ mixed salt was charged into an alumina crucible with an excess amount of $\text{Al}_2\text{O}_3$ powder. The loaded crucible was preheated slowly to 800°C and kept there overnight to remove moisture, and then heated to 1300K. Air bubbles were introduced to stir the melt for 8 hours. Individual thermodynamic activity probes for Na and Al were used to monitor the equilibrium melt chemistry at the times of sample withdrawal. The basic component of the melt, NaF, reacts with $\alpha$-$\text{Al}_2\text{O}_3$ and converts it to $\beta$-$\text{Al}_2\text{O}_3$ when $r$ is greater than $\sim$ 3.7 (13):

$$2\text{NaF}(l) + \frac{3x+1}{3} \text{Al}_2\text{O}_3(\alpha) = \text{Na}_2\text{O} \cdot x\text{Al}_2\text{O}_3(\beta) + \frac{2}{3} \text{AlF}_3(s)$$  \[1\]

Since this solid phase transition causes cracking of $\alpha$-$\text{Al}_2\text{O}_3$ crucibles, a graphite crucible served as the container for the more basic cryolite melts, and $\beta$-$\text{Al}_2\text{O}_3$ powder was used as the alumina source. To prevent oxidation of the graphite crucible, the crucible loaded with 30–35g $\text{Na}_3\text{AlF}_6$-$\text{NaF}$ mixed salt and excess $\beta$-$\text{Al}_2\text{O}_3$ powder was positioned in a mullite reaction chamber with a gas-tight flange, and Ar gas was kept flowing through the reaction chamber during the experiment. The melt was stirred with a platinum rod every 20 minutes to enhance dissolution of solutes in the melt. The melt chemistry was measured using the two reference probes only immediately after sampling, and these measurements required only a few minutes. Extended contact between the melt and the $\alpha$-$\text{Al}_2\text{O}_3$ tubes of the probes would lead to a change in melt chemistry. Samples were taken by quenching a small amount of salt on to an alumina rod. These salt samples were analyzed by inductively coupled plasma emission for total Al content, and the $\text{Al}_2\text{O}_3$ solubility values were calculated.

**THERMODYNAMIC ACTIVITY PROBES**

The two thermodynamic activity probes for Na and Al are shown schematically in Figure 2. These two probes had “hole-in-tube” configurations, and contained either pure Al or a Sn-0.5 wt% Na alloy ($a_{\text{Na}} = 3.7 \times 10^{-6}$ for 1300K, as measured against an Al-0.1 wt% Na alloy as the reference) in the bottom of the alumina tubes. The composition of the melts over the pure Al and the Na-Sn alloy in the alumina tubes was exactly the same as that for the bulk melt in the alumina crucible because of melt entry and mass transport through the holes (~ 1 mm diameter). Tungsten wires contacting the pure Al or the Na-Sn alloy served as the electrical leads for the reference probes. Another tungsten wire touching the melt in the alumina or graphite crucible was used as the working electrode for both reference probes. The lengths of these tungsten wires exposed to air were minimized by their sealed enclosure in alumina tubes, with only the tips of the wires touching the melt or the liquid metal.
For any given state of the molten salt, this dual sensor arrangement provided values for the Al activity and for the Na activity in the cryolite-base melt. For the NaF-AlF$_3$-Al$_2$O$_3$ ternary system, then these activity values for Al and Na were converted by calculation to provide activities for the NaF and AlF$_3$ components in these melts. For ternary NaF-AlF$_3$-Al$_2$O$_3$ melts, the following reaction was considered:

$$3\text{Na}(l) + \text{AlF}_3(s) = 3\text{NaF}(l) + \text{Al}(l)$$

for which we have

$$\Delta G^0(2) = 3\Delta G_f^0(\text{NaF}) - \Delta G_f^0(\text{AlF}_3) = RT \ln \frac{a_{\text{Na}}^3 a_{\text{AlF}_3}}{a_{\text{NaF}}^3 a_{\text{Al}}}$$

$$\ln a_{\text{AlF}_3} - 3\ln a_{\text{NaF}} = \frac{3\Delta G_f^0(\text{NaF}) - \Delta G_f^0(\text{AlF}_3)}{RT} - 3\ln a_{\text{Na}} + \ln a_{\text{Al}}$$

**Figure 2.** Schematic illustration of the two reference probes to monitor melt chemistry

The thermodynamic data in JANAF tables (14) were used to calculate the first term on the right side of Eq. [4], and the expressions of Sterten and Maeland (15) for
activities of NaF and AlF$_3$ as a function of cryolite ratio $r$ were used to evaluate the two terms on the left side of Eq. [4]. With known values of activities for Al and Na obtained from measurements by the two thermodynamic activity probes, the equilibrium cryolite ratio $r$ value was calculated using the equation:

$$
\frac{F}{RT} [1.361 \ln \left( \frac{3 + r}{0.3 + 0.9r} \right) - 1.493] - 3.029 - 3 \left( \frac{F}{RT} [3.63 \ln r + 0.454 \ln (3 + r) \right. \\
- 4.084 \ln (0.3 + 0.9r) - 0.423] - 0.106 = -11.225 - 3 \ln a_{Na} + \ln a_{Al} \tag{5}
$$

where $r$ is the equilibrium cryolite ratio, and $F$, $R$ and $T$ have their usual meaning. Substitution of the equilibrium $r$ into the equations of Sterten and Maeland (15) gave the activity values for NaF and AlF$_3$ in the melt.

**EXPERIMENTAL RESULTS**

The salt samples were analyzed for total Al by the inductively coupled plasma emission technique and the solubility of Al$_2$O$_3$ was then calculated. The measured solubility results are given in Table 1, with the melt chemistry data recorded by the individual thermodynamic activity probes for Al and Na. Each datum in Table 1 is the average of results from two separate samples. The deviations for the alumina solubility data from the average value were within 0.4 wt% for each datum point.

In Table 1, the solubility maximum for alumina in the cryolite melt system at 1300K occurs close to the cryolite ratio $r = 4$, and the solubility decreases somewhat with further increase in the melt basicity. Foster (3) and Roberts et al. (12) also found the maximum alumina solubility in cryolite melts at around $r = 4$ at similar temperatures. The equilibrium cryolite ratios for basic melts in Table 1 were found to be systematically higher than the initial (weighed out) values.

| Initial cryolite ratio $r$ | Equil. cryolite ratio $r$ | Melt chemistry | Alumina solubility |
|---------------------------|--------------------------|----------------|---------------------|
|                           |                          | $a_{NaF}$      | $a_{AlF_3}$  wt %  | mol %    |
| 3.0                       | 2.98                     | 0.353          | 4.43 x 10^-4      | 13.7     | 7.6     |
| 3.5                       | 3.58                     | 0.459          | 1.56 x 10^-4      | 14.7     | 8.0     |
| 4.0                       | 4.10                     | 0.536          | 8.64 x 10^-3      | 15.2     | 8.1     |
| 4.5                       | 4.65                     | 0.606          | 5.17 x 10^-3      | 15.1     | 7.9     |
| 5.0                       | 5.25                     | 0.664          | 3.25 x 10^-3      | 14.8     | 7.7     |
| 6.0                       | 6.42                     | 0.731          | 1.61 x 10^-3      | 14.5     | 7.3     |
| 8.0                       | 8.44                     | 0.802          | 7.11 x 10^-6      | 12.7     | 6.2     |
| 12.0                      | 12.5                     | 0.879          | 2.80 x 10^-6      | 10.2     | 4.8     |
MODELING OF THE Al₂O₃ SOLUBILITY IN THE NaF-AlF₃ SYSTEM AT 1300K

As described in a previous paper (7), acidic, neutral and basic solutes Na₂Al₂OF₆, Na₂Al₂O₂F₄ and Na₄Al₂O₂F₆ (denoted as A, N and B, respectively) were interpreted to be the oxyfluoride complexes in the cryolite melt for 1.5 ≤ r ≤ 3. In addition to these oxygen-containing solutes, Na₃AlF₆, Na₂AlF₅ and NaAlF₄ (denoted as C, D and E, respectively) were accepted to be oxygen-free solutes existing in the melt (16-18). The equilibrium constants for the formation of these solutes were derived and are shown in Table 2. The modeled results can be applied to the whole stability range for α-Al₂O₃, that is, cryolite ratio r ≤ 3.7.

| Table 2. Equilibrium constants for the formation of solutes in cryolite melts for r ≤ 3 (7) |
|-----------------------------------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| Equilibrium constant                         | K_A               | K_N               | K_B               | K_C               | K_D               | K_E               |
| Derived value                                 | 17640             | 374               | 348               | 7442              | 3711              | 335               |
| Estimated ΔG°, KJ/mol                         | -2952.2           | -2549.7           | -3411.4           | -2562.5           | -2123.8           | -1666.5           |

In the β-Al₂O₃ stability range with r ≥ 3.7, the same three oxyfluoride solutes, with stabilities described by the values of Gibbs energies of formation (ΔG°) of Table 2, were assumed to be responsible for the dissolution of β-Al₂O₃. The composition of β-Al₂O₃ powder used in the present study was Na₂O·8Al₂O₃, and therefore its dissolution reactions are described as follows:

\[ \text{Na}_2\text{O} \cdot 8\text{Al}_2\text{O}_3(\beta) + 48\text{NaF} + 34\text{AlF}_3 = 25\text{Na}_2\text{Al}_2\text{OF}_6 \text{ (solute A)} \]  \[6\]

\[ \text{Na}_2\text{O} \cdot 8\text{Al}_2\text{O}_3(\beta) + 23\text{NaF} + 9\text{AlF}_3 = \frac{25}{2}\text{Na}_2\text{Al}_2\text{O}_2\text{F}_4 \text{ (solute N)} \]  \[7\]

\[ \text{Na}_2\text{O} \cdot 8\text{Al}_2\text{O}_3(\beta) + 48\text{NaF} + 9\text{AlF}_3 = \frac{25}{2}\text{Na}_4\text{Al}_2\text{O}_2\text{F}_6 \text{ (solute B)} \]  \[8\]

The molar fractions of these fluoroxyanion solutes were related to the thermodynamic activity of NaF (denoted as \(a_1\)), the activity of AlF₃ (denoted as \(a_2\)) and the equilibrium constants for their formation reactions (called \(K_A', K_N'\) and \(K_B'\), respectively):

\[ 25\log[A] = \log K_A' - 48\log a_1 - 34\log a_2 \]  \[9\]

\[ \frac{25}{2}\log[N] = \log K_N' - 23\log a_1 - 9\log a_2 \]  \[10\]
The substitution of molar fractions for the activities of these solute complexes infers the assumption of an ideal solution, or at least constant (concentration-independent) Raoultian activity coefficients.

The equilibrium constants $K_a'$, $K_n'$ and $K_b'$ were related to the Gibbs energy changes for reactions [6] through [8], including unknown $\Delta G^0_f(Na_2O\cdot8Al_2O_3)$. The $\Delta G^0_f$'s for $\alpha-Al_2O_3$, NaF and AlF$_3$ were taken from the JANAF Tables (14), and the $\Delta G^0_f$'s for Na$_2$Al$_2$OF$_6$, Na$_2$Al$_2$O$_2$F$_4$ and Na$_4$Al$_2$O$_2$F$_6$ were calculated from the equilibrium constants $K_a$, $K_n$ and $K_b$ (in Table 2) to be -2952.2, -2549.7 and -3411.4 KJ/mol, respectively.

In this basic melt range, Na$_3$AlF$_6$, Na$_2$AlF$_5$ and NaAlF$_4$ were again considered as the oxygen-free solutes:

$$3NaF + AlF_3 = Na_3AlF_6(C)$$ [12]

$$2NaF + AlF_3 = Na_2AlF_5(D)$$ [13]

$$NaF + AlF_3 = NaAlF_4(E)$$ [14]

The molar fractions of these oxygen-free solutes can be calculated using Eqs. [15-17].

$$[C] = K_c a_1^3 a_2$$ [15]

$$[D] = K_d a_1^2 a_2$$ [16]

$$[E] = K_e a_1 a_2$$ [17]

This procedure again implies the assumption of an ideal solution or a constant Raoultian activity coefficient for each species. The equilibrium constants for the reactions [12-14] for the cryolite melts with $r \geq 3.7$ were chosen to be those as shown in Table 2.

In addition to these solutes mentioned above, some NaF, but no AlF$_3$, would remain in the basic melt, as discussed in the previous paper (7). Therefore, the basic cryolite melt should include the oxygen-containing solutes Na$_2$Al$_2$OF$_6$, Na$_2$Al$_2$O$_2$F$_4$ and
Na$_4$Al$_2$O$_2$F$_6$ from the dissolution of β-Al$_2$O$_3$, as well as the oxygen-free solutes Na$_3$AlF$_6$, Na$_2$AlF$_5$ and NaAlF$_4$, and NaF that remain in the melt.

Sets of equations that include the unknown Gibbs energy of formation for Na$_2$O·8Al$_2$O$_3$ (β-Al$_2$O$_3$) can be established for the several elemental balances. For oxygen:

$$([A] + 2[N] + 2[B])n_t = 3x_3$$ \[18\]

where $x_3$ is the molar fraction of dissolved Al$_2$O$_3$ in a ternary system of NaF-AlF$_3$- Al$_2$O$_3$, as listed in the last column in Table 1, and $n_t$ the total moles of all the species in the melt. The six groups of solubility and melt chemistry data obtained experimentally for this basic composition range of β-Al$_2$O$_3$ stability, as listed in Table 1, lead to six equations. Other equations can be similarly established by this element balance approach.

For the Na elemental balance,

$$2[A] + 2[N] + 4[B] + 3[C] + 2[D] + [E] + [NaF])n_t = \frac{r}{r + 1}(1 - x_3)$$ \[19\]

For the Al elemental balance,

$$(2[A] + 2[N] + 2[B] + [C] + [D] + [E])n_t = \frac{1 + (2r + 1)x_3}{r + 1}$$ \[20\]

For the F elemental balance,

$$(6[A] + 4[N] + 6[B] + 6[C] + 5[D] + 4[E] + [NaF])n_t = \frac{r + 3}{r + 1}(1 - x_3)$$ \[21\]

In addition to these elemental balances, the sum of molar fractions for all the solutes should be unity for each composition of cryolite melt:

$$[A] + [N] + [B] + [C] + [D] + [E] + [NaF] = 1$$ \[22\]

The standard Gibbs energy of formation for Na$_2$O·8Al$_2$O$_3$ (β-Al$_2$O$_3$) was calculated by fitting the experimental data using a computer software program to be $-10511.5$ KJ/mol. The concentrations of solutes were then calculated. This program...
provided minimum errors for all the relations considered above; the largest deviation is within 6%. The calculated (best fit) $\Delta G_f^\circ$ value for $\beta$-Al$_2$O$_3$ with the Na$_2$O·8Al$_2$O$_3$ composition is very close to the value provided by reference 13, which is calculated to be -10552.3 KJ/mol.

The present work, combined with the previously study (7), provides an understanding of the dissolution behavior of alumina ($\alpha$-Al$_2$O$_3$ and $\beta$-Al$_2$O$_3$) in a wide melt composition range of 1.5 $\leq r \leq$12.5. A comparison of the experimentally determined alumina solubility in the NaF-AlF$_3$ system over this wide composition range at 1300K and the solubility calculated using the present model is shown in Figure 3. The vertical dashed line in Figure 3 separates the stability ranges for $\alpha$-Al$_2$O$_3$ and $\beta$-Al$_2$O$_3$ (13). The solubility lines from the experimental measurements and from the modeling overlap each other, and therefore the modeled alumina solubility line is shown as a solid line in Figure 3, with data points indicating the experimentally measured solubility of alumina. The alumina solubility data in the cryolite melt with the composition range of 1.5 $\leq r \leq$3 (open data points) are from reference 1, while those for the composition range of 3 $\leq r \leq$ 12.5 (solid data points) are from the present study. The other three lines in Figure 3 indicate the calculated dissolved alumina contents contributed by the acidic, neutral and basic solutes: Na$_2$Al$_2$OF$_6$, Na$_2$Al$_2$O$_2$F$_4$ and Na$_4$Al$_2$O$_2$F$_6$, respectively. Following references 1 and 2, the concentration of dissolved Al$_2$O$_3$ is expressed in molar fraction, which is based on the three-component system NaF-AlF$_3$-Al$_2$O$_3$, without considering the

![Cryolite ratio r (mole NaF/mole AlF$_3$)](image)

**Figure 3.** Comparison of Al$_2$O$_3$ solubility in NaF-AlF$_3$ system at 1300K as a function of melt basicity from experiments (data points) and calculated from the present model (top line). The top line is the modeled Al$_2$O$_3$ solubility line, and the data points are experimentally determined values. The other three lines represent the individual Al$_2$O$_3$ solubility contributions by acidic (Na$_2$Al$_2$OF$_6$), neutral (Na$_2$Al$_2$O$_2$F$_4$) and basic (Na$_4$Al$_2$O$_2$F$_6$) solutes, respectively.
existence of Na$_3$AlF$_6$, Na$_2$AlF$_5$ or NaAlF$_4$. In Figure 3, the solubility of alumina is plotted as a function of $-\log a_{\text{NaF}}$, with the corresponding values for cryolite ratio $r$ also shown on the plot. From Figure 3, at a low basicity, the acidic solute Na$_2$Al$_2$OF$_6$ is the dominant species. However, as the melt becomes less acidic, even for a cryolite ratio $> 3$, the neutral solute Na$_2$Al$_2$O$_2$F$_4$ is more important than the other two complexes. The neutral solute reaches a maximum concentration in Figure 3 at about $r = 3$, consistent with the coefficients for its formation reaction. The basic solute Na$_4$Al$_2$O$_2$F$_6$ gains importance in the basic melt, and reaches a maximum concentration at $r = 5$ to 6, consistent with the coefficients for its formation reaction of Eq. [8].

The concentrations of all the assumed solute complexes in the cryolite melts for $1.5 \leq r \leq 12.5$ were calculated according to the present model, and the calculated results are plotted in Figure 4. In this case, the molar fractions refer to the solution comprising seven solutes, which sum to unity.

![Figure 4. Calculated concentrations of all solutes for alumina-saturated cryolite melts at 1300K](image)

From Figure 4, in the acidic melt with the cryolite ratio $r$ close to 1.5, NaAlF$_4$ and Na$_2$Al$_2$OF$_6$ are dominant for oxygen-free and oxygen-containing solutes, respectively. For a less acidic melt or a basic melt, Na$_2$AlF$_5$ and then NaF become the dominant oxygen-free solutes while Na$_2$Al$_2$O$_2$F$_4$ is the most important of the three oxygen-containing solutes up to $r = 6$ where Na$_4$Al$_2$O$_2$F$_6$ becomes dominant.

Generally speaking, the present model is qualitatively in agreement with all the other models (8-12) with respect to the existence of the acidic and neutral solutes.
Na$_2$Al$_2$OF$_6$ and Na$_2$Al$_2$O$_2$F$_4$. However, in his model for the composition range of 1 \( \leq r \leq 12 \), Sterten (11) included a fourth (a basic) solute Al$_2$OF$_{10}^{6-}$ in addition to the three solutes Al$_2$OF$_6^{2-}$ (acidic), Al$_2$O$_2$F$_4^{2-}$ (neutral) and Al$_2$O$_2$F$_6^{4-}$ (basic). As discussed above, the present three-solute model leads to an excellent fit of the calculated results to the experimentally determined solubility of alumina, and therefore, introduction of the fourth solute for 1.5 \( \leq r \leq 12.5 \) seems unnecessary. The basic solutes Al$_2$OF$_{10}^{6-}$ assumed by Kvande (9), and Al$_2$O$_4$F$_4^{3-}$ proposed by Gilbert et al. (12), are replaced by Al$_2$O$_2$F$_6^{4-}$ from the present model.

**CONCLUDING REMARKS**

In the present study, the Al$_2$O$_3$ solubility was measured in basic cryolite melts over a composition range of 3 \( \leq r \leq 12.5 \). Thermodynamic activity probes for Al and Na were used to monitor the melt chemistry (basicity/acidity). The experimentally determined alumina solubility in the basic melts indicates a maximum value in solubility at approximately \( r = 4 \) at 1300K.

The newly measured alumina solubility data, combined with those determined experimentally by Skybakmoen, Solheim and Sterten (1) for the melts with a composition range of 1.5 \( \leq r \leq 3 \), were used to model the melt structure for the NaF-AlF$_3$-Al$_2$O$_3$ system over the wide composition range 1.5 \( \leq r \leq 12.5 \). The present three-solute model leads to a virtually perfect match with the experimentally determined alumina solubility over this cryolite salt composition range at 1300K.

According to the present model, the three solutes Na$_2$Al$_2$OF$_6$, Na$_2$Al$_2$O$_2$F$_4$ and Na$_4$Al$_2$O$_2$F$_6$ describe well the melt structure of NaF-AlF$_3$ system with dissolved alumina. The acidic solute Na$_2$Al$_2$OF$_6$ is the dominant species in an acidic melt with the cryolite ratio \( r \) close to 1.5; with the increase in the melt basicity the neutral solute Na$_2$Al$_2$O$_2$F$_4$ becomes more important than the other two complexes. In basic melts, a significant contribution to alumina solubility is provided from the basic solute Na$_4$Al$_2$O$_2$F$_6$.

The formation of fluoroxyanion solutes and their redistribution with changing melt basicity leads to a constriction in the range of acid-base chemistry. For the entire composition range of Figure 3, the total variation in melt basicity (\( \log a_{NaF} \)) amounts to only approximately one decade. Thus, the melt chemistry can be considered to be highly buffered.

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