The Surface Tension of Molten Mixtures Containing Cryolite. I. The Binary Systems Cryolite—Alumina and Cryolite—Calcium Fluoride

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Surface tension has been measured in the two molten systems:
(1) Na₃AlF₆—Al₂O₃ (0.4—12wt%Al₂O₃) and (2) Na₃AlF₆—CaF₂ (0—15wt%CaF₂) in the temperature range 1000—1100 °C. The results may be expressed by:

\[ \gamma_1 (\text{mN m}^{-1}) = 264.3 - 0.1318 \text{ t}^\circ \text{C} - 4.6 \log(C_{\text{Al}_2\text{O}_3/\text{wt} \%}) - (3.29 - 0.00329 \text{ t}^\circ \text{C}) \cdot C_{\text{Al}_2\text{O}_3/\text{wt} \%} \]

and

\[ \gamma_2 (\text{mN m}^{-1}) = 274.8 - 0.1392 \text{ t}^\circ \text{C} - (0.19 - 0.00056 \text{ t}^\circ \text{C}) C_{\text{CaF}_2/\text{wt} \%} \]

The relative standard deviation is 0.2 %.

Molten cryolite is the basic electrolyte in the electrowinning of aluminium. The degree of wetting of carbon materials (anode carbon, carbon particles in the bath) by cryolite-based melts depends, partly, on the surface tension of the electrolyte.¹ Knowledge of surface tension data for cryolite systems, therefore, is important for gaining a deeper insight into the process.

In this work the surface tension in some molten salt mixtures containing cryolite has been measured by means of the pin detachment method. This method was first described by Janz and Lorenz,² and was later used by Lillebuen and co-workers at this laboratory.³ It involves a metal sinker with a pin (Fig. 1), dipping into the melt. When the sinker is lifted out of the melt, the apparent weight of the sinker will decrease abruptly the moment it is detached from the melt surface. This weight change is the detachment force, equal to the weight of the liquid column lifted by the pin just before detachment. Lillebuen showed that the surface tension of the liquid may be calculated when the detachment force,

Fig. 1. Platinum sinker for measurement of surface tension in molten salts. 1, Sinker, Pt-10%Rh; 2, Pin for surface tension measurements; 3, Tungsten wire.
the radius of the pin and the specific gravity of the liquid is known.\(^4\)

The specific gravity data were taken from the work by Edwards et al.\(^5\)

**EXPERIMENTAL**

**Apparatus.** The essential features of the thermobalance and the vacuum system have been described elsewhere,\(^3,6\) although the design has been somewhat altered. In the previous design the crucible supporter could be moved vertically relative to the furnace and the suspended sinker. Now the supporter is fixed to the furnace, and the furnace with the supporter can be moved. A bellow connects the furnace to the balance housing. The original balance is replaced by a Mettler electronic weighing cell.

The sinker was made from platinum–10% rhodium alloy and was suspended by a 0.3 mm diameter tungsten wire, previously annealed from an electronic balance into a furnace. The pin diameter (approximately 2.2 mm) was measured at room temperature before each experiment with a precision of a thousandth of one millimeter, and extrapolated to the working temperature using data for thermal expansion of the alloy.

**Chemicals.** Hand-picked cryolite, calcined alumina and analytical grade calcium fluoride were stored and handled in a glove-box containing nitrogen with less than 5 ppm moisture.

**Procedure.** The salts were premelted in a platinum crucible under high purity nitrogen atmosphere and stirred for 30 min with a platinum stirrer. Then the covered crucible with contents was quenched in cold water, and the salt crushed before the experiment. The crushing would ensure a thorough mixing of the components. It was very important to avoid carbon in the system as carbon particles floating on the melt surface would dramatically alter the wetting properties of the liquid.

**Table 1.** Surface tension (mN m\(^{-1}\)) and temperature coefficient d\(\gamma/dT\) (mN m\(^{-1}\) degree\(^{-1}\)) for pure supercooled liquid cryolite, Na\(_3\)AlF\(_6\), at 1000 C.

<table>
<thead>
<tr>
<th>Method of investigation</th>
<th>Ref.</th>
<th>(\gamma(\pm SD))</th>
<th>d(\gamma/dT) ((\pm SD))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pin detachment</td>
<td>This work</td>
<td>135.6 (0.3)</td>
<td>-0.137 (0.003)</td>
</tr>
<tr>
<td>Ring detachment</td>
<td>7</td>
<td>148.3</td>
<td>-0.135</td>
</tr>
<tr>
<td>Max. bubble press.</td>
<td>8</td>
<td>134.0</td>
<td>-0.128</td>
</tr>
<tr>
<td>Capillary</td>
<td>9</td>
<td>145.5</td>
<td>-0.130</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>145.4</td>
<td>-0.124</td>
</tr>
</tbody>
</table>

With the salt mixture in a platinum crucible in place inside the furnace, the whole system was evacuated to 10\(^{-4}\) mbar. The salt was heated to 200\(^\circ\)C and kept at that temperature for a few hours. The apparatus was then back-filled with high purity nitrogen. For the remainder of the experiment nitrogen flowed through the system at a rate of 50 cm\(^3\) min\(^{-1}\).

The salt was kept at constant temperature (\(\pm 0.2^\circ\)C) for one hour before each set of measurements.

The crucible was raised or lowered by means of a reversible electric motor connected to a gear box from which a shaft moved the furnace at an adjustable speed, maximum 0.4 mm min\(^{-1}\). When the pin touched the surface the weight of the sinker increased abruptly. By slowly lowering the
furnace from this position, the weight increased steadily and passed through a well-defined maximum before a stable minimum was attained after detachment. The latter is the weight of the sinker in nitrogen atmosphere. The accuracy of the weighing was ±0.1 mg. The measurements at each temperature were reproducible within 0.1%. The weight change was recorded on a strip chart recorder.

Fig. 2 shows a typical weight–time record.

After detachment the weight of the sinker includes the weight of a melt droplet attached to the tip of the pin. As a consequence, a difference is observed in the base line recorded before the very first contact between pin and melt and after the first detachment. A correction must be made for this discrepancy. The weight of the droplet so determined may be compared after the experiment with the weight of the easily removable frozen droplet attached to the tip of the pin. It may well amount to 2% of the detachment force, and consequently introduce a substantial systematic error.

RESULTS

In Table 1 the surface tension data for the pure supercooled fused cryolite at 1000 °C from this work are compared with available literature data. The overall standard deviation of our surface tension measurements was ±0.2%.

The present results for pure molten cryolite were obtained in three separate runs, and the data are given in Fig. 3 where the surface tension is plotted versus temperature. The whole temperature region was covered by making 5 measurements in each run; a total of 15 measurements.

Results for the two binary mixtures of Na3AlF6 with Al2O3 and CaF2, respectively, are given in Fig. 3 and Fig. 4. In Fig. 5 the surface tension is plotted versus solute concentration for the two binary mixtures at 1000 °C. As can be observed from Fig. 5, the surface tension appears to reach

**Fig. 3.** Surface tension in Na3AlF6–Al2O3 melts. □, Na3AlF6; ●, 0.4 wt% Al2O3; △, 1 wt% Al2O3; ◊, 2 wt% Al2O3; ○, 5 wt% Al2O3; ■, 8 wt% Al2O3; ▲, 10 wt% Al2O3.


**Fig. 4.** Surface tension in Na3AlF6–CaF2 melts. —, Na3AlF6; □, 3 wt% CaF2; ■, 5 wt% CaF2; ○, 8 wt% CaF2; △, 10 wt% CaF2; ●, 15 wt% CaF2.

**Fig. 5.** Surface tension in Na3AlF6–Al2O3 and Na3AlF6–CaF2 melts at 1000 °C. ●, Present work, CaF2; ○, Present work, Al2O3; ——, Bloom and Burrows,8 Al2O3; ——, Vajna,7 Al2O3.
Table 2. Constants in eqn. (1). Temp. range: 1000–1100 °C. Concentration ranges: 0.4 ≤ wt% Al₂O₃ < 12, 0 ≤ wt% CaF₂ < 15.

<table>
<thead>
<tr>
<th>System</th>
<th>a₀</th>
<th>a₁</th>
<th>a₂</th>
<th>a₃</th>
<th>a₄</th>
<th>SD_{rel}%</th>
</tr>
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<tbody>
<tr>
<td>Na₃AlF₆</td>
<td>272.5</td>
<td>-0.1369</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>±0.19</td>
</tr>
<tr>
<td>Na₃AlF₆–Al₂O₃</td>
<td>264.3</td>
<td>-0.1318</td>
<td>-3.29</td>
<td>-4.6</td>
<td>0.00329</td>
<td>±0.18</td>
</tr>
<tr>
<td>Na₃AlF₆–CaF₂</td>
<td>274.8</td>
<td>-0.1392</td>
<td>-0.19</td>
<td>0</td>
<td>0.00056</td>
<td>±0.21</td>
</tr>
</tbody>
</table>

a constant value in the Na₃AlF₆–Al₂O₃ melt when the concentration of Al₂O₃ approaches saturation (12.5 %).¹¹

The surface tension values in the cryolite systems investigated have been fitted to an equation of the form (1).

\[
\gamma / \text{mN m}^{-1} = a_0 + a_1 t ^{\circ} \text{C} + a_2 (C_{\text{solute}}/\text{wt%}) + a_3 \log (C_{\text{solute}}/\text{wt%}) + a_4 t ^{\circ} \text{C}(C_{\text{solute}}/\text{wt%})
\]  

(1)

In Table 2 the constants in this equation are given together with the relative standard deviation in per cent.

As can be observed from Table 1, there is a considerable disagreement between the present results for pure cryolite and previously published data. An exception is the data of Bloom and Burrows.⁸ This is also reflected in Fig. 5 where the present data in the Na₃AlF₆–Al₂O₃ system are compared with the data of Vajna ⁷ and Bloom and Burrows.⁸

DISCUSSION

We believe that the discrepancy between the surface tension data reported by us and those given in the literature must be due to experimental uncertainties in the literature data.

As can be observed from the data of Vajna ⁷ and Bloom and Burrows ⁸ given in Fig. 5, the limiting slopes of \( \gamma \) plotted versus wt% Al₂O₃ do not approach zero at saturation. Moreover, a variation in the surface tension can be observed even for Al₂O₃ concentrations above the saturation limit.

As mentioned previously, it is very important to have a clean melt with no insoluble particles floating on the melt surface. The melting point of the cryolite used in the present work was 1010 °C which is equal to that reported by Holm ¹² and slightly above the value given by Foster ¹³ (1009 °C). Bloom and Burrows report an approximate melting point of 1004 °C and indicated a 99.6 % purity of their cryolite, while Vajna does not give any data for the cryolite used. The experimental set-up of Vajna indicates that he must have had large temperature gradients across his cell. This makes his temperatures uncertain and therefore also his surface tension values since \( \gamma \) has a significant temperature coefficient. Bloom and Burrows report severe corrosion on their stainless steel tube. It is not clear, however, if this corrosion influenced the purity of their melts.

Gibbs surface tension equation ¹⁴ [eqn. (2)] gives a relation between the surface concentration \( \Gamma_1 \) of component 1 and the activity of this component. Accordingly, the surface concentration of Al₂O₃ or Al–O containing species must be positive since \( \gamma \) decreases when the Al₂O₃ content of the melt is increasing (Fig. 5).

\[
\Gamma_1 = - \frac{d \gamma}{RT \ln a_1}
\]  

(2)

When Al₂O₃ dissolves in a cryolite melt, ionic species are formed. The most plausible species are Al₂O₂F³⁻ and Al₂OF⁵⁻.¹⁵–¹⁷ These ionic

![Fig. 6. Surface tension in Na₃AlF₆–Al₂O₃ melts at 1000 °C plotted versus the natural logarithm of the Al₂O₃ activity in the melt.](image)

species will thus be enriched in the surface until surface-phase saturation.

In Fig. 6 $y$ is plotted versus $\ln a_{\text{Al}_2\text{O}_3}$. A straight line is obtained down to 0.4 wt% $\text{Al}_2\text{O}_3$. This shows that surface saturation occurs at very low bulk concentration of $\text{Al}_2\text{O}_3$ (eqn. 2). From the slope of the line the surface-phase concentration of $\text{Al}_2\text{O}_3$ is calculated to be $\Gamma_{\text{Al}_2\text{O}_3} = 7.2 \times 10^{-8}$ mol/m$^2$. If we, as a first approximation, assume that a monolayer of the solute species covers the surface, this surface concentration gives an area per formula unit $\text{Al}_2\text{O}_3$ on the surface $1/\Gamma_{\text{Al}_2\text{O}_3} = 2.3 \times 10^{-9}$ $\text{nm}^2/\text{Al}_2\text{O}_3$. This area is too large to match any possible oxygen–containing ionic species in the $\text{Na}_3\text{AlF}_6–\text{Al}_2\text{O}_3$ system. It does, however, show that the oxygen–containing complex ions are far apart from each other on the surface of the melt. This is consistent with the long range coulomb repulsion between the ions.

The conductivity of liquid cryolite is reduced when alumina is added. This reflects an increase in the covalency of the liquid cryolite structure, and thus formation of species with lower surface tension, in agreement with observations. When CaF$_2$ is added to cryolite, the melt becomes more ionic and the surface tension increases accordingly.

Acknowledgements. This work has been financially supported by \textit{Norges teknisk-naturvitenskapelige forskningsråd} (NTNF.), grant 0511.00581. Dr. Carlos Ferro expresses his appreciation to NTNF for a research grant which made his stay in Norway possible.

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