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Density, Viscosity, Surface Tension, and Interfacial Tension in the Systems NaF(KF) + AlF_3

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The temperature dependence of density, viscosity, and surface tension was determined in the system 55 mol % NaF + 45 mol % AlF_3. The interfacial tension between aluminum and the above melt plus the melt 55 mol % KF + 45 mol % AlF_3 was measured at 750 °C. These molten salts are potential low-temperature electrolytes for aluminum electrolysis. It was found that the temperature dependence of density and surface tension could be described by linear equations within the measured temperature ranges. The temperature dependence of viscosity can be described by a quadratic equation.

Introduction

The knowledge of physicochemical properties of a cryolite-based electrolyte for aluminum production is essential for the successful control of the process and for optimization of the computerized process control. Thus, it is desirable to derive empirical equations describing the temperature dependence of the physicochemical properties.

Aluminum is produced electrochemically by the Hall−Heroult process, which is more than 100 years old. This technology uses carbon anodes and a liquid aluminum cathode to decompose alumina dissolved in cryolite, Na_3AlF_6, with different additives, the reaction products being liquid aluminum and CO_2. The process is operated at temperatures of around 960 °C, which is energetically very demanding. Therefore, attempts to develop processes working at lower temperatures are being made in many laboratories around the world. One problem is finding a solvent for alumina with a substantially lower temperature of primary crystallization (700 to 800 °C) and with suitable physicochemical properties.

The temperature of primary crystallization can be lowered by the use of an AlF_3-rich bath. From the phase diagram of the system NaF + AlF_3,[1] it follows that in the subsystem Na_3AlF_6 + AlF_3 the eutectic point is located at 46 mol % AlF_3 and 698 °C.

The density of the molten system NaF + AlF_3 was measured by several authors.[2] The majority of the published density data covers compositions up to 30 mol % AlF_3 in the temperature range of (950 to 1100) °C. Only two studies covered higher contents of aluminum fluoride.[3,4]

The viscosity of the molten system NaF + AlF_3 has been studied in the concentration range of (0 to 35) mol % AlF_3.[5]

The surface tension of molten fluorides and fluoride mixtures containing cryolite has been studied as well.[6] The surface tension in the NaF + AlF_3 system decreases with decreasing content of aluminum fluoride.

The interfacial tension between liquid aluminum and the molten NaF + AlF_3 system was investigated in the temperature range of (1000 to 1100) °C and for different cryolite ratios[7] (molar NaF/AlF_3 ratio).

In the present work, density, viscosity, surface tension, and interfacial tension were measured in melts with high contents of aluminum fluoride and at temperatures below 850 °C. For the KF + AlF_3 system, we have not been aware of any such data until now.

Experimental Section and Results

Chemicals. The following chemicals were used for the preparation of samples: sodium fluoride (Fluka, p.a., dried in a furnace for 2 h at 600 °C); AlF_3 (Lachema, technical, purified by sublimation in a graphite apparatus under argon at atmospheric pressure); KF (Merck, p.a., dried over P_2O_5 for 3 weeks under vacuum at ambient temperature, then for 8 h under vacuum at 180 °C); Al (Aldrich, 99.99%).

Density. The density of the melts was measured using the Archimedean method. A hollow platinum sphere, suspended on a platinum wire 0.3 mm in diameter and attached to an electronic balance unit, was used as the measuring body. The temperature dependence of the volume of the sphere was determined by calibration using molten NaCl, KCl, and $(LiF + NaF + KF)_{eut}$, all of reagent-grade purity. The temperature was measured by a Pt−Pt10Rh thermocouple calibrated at the melting points of KCl, NaCl, and Na_2SO_4. A computer was used to control the device and to collect and evaluate the experimental data. A platinum crucible with a sample (45 g) was placed inside an electric resistance furnace filled with a dry nitrogen atmosphere. The measurements were carried out in a temperature interval of approximately 120 °C starting 10 °C to 20 °C above the temperature of primary crystallization. The heating (cooling) rate was about 2 $K\cdot min^{-1}$. A detailed description of the measuring device and the working procedure is given elsewhere.[8] After the completion of the entire temperature cycle, the initial and final density values did not differ by more than 0.5%. Therefore, it was not necessary to make any correction for composition changes, as was done for the viscosity measurements (see below). The reason was that the density measurements

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Table 1. Temperature Dependence of Density, ρ, for the System of 55 mol % NaF + 45 mol % AlF_3

heating period		cooling period	
t/°C	ρ/g·cm^{-3}	t/°C	ρ/g·cm^{-3}
850	1.8155	730	1.9249
840	1.8251	740	1.9151
830	1.8332	750	1.9064
820	1.842	760	1.897
810	1.8519	770	1.8884
800	1.863	780	1.8788
790	1.8714	790	1.8696
780	1.881	800	1.861
770	1.8904	810	1.8517
760	1.8995	820	1.8418
750	1.9094	830	1.833
740	1.9188	840	1.8243
730	1.9282	850	1.8157

were performed much faster than the viscosity measurements.

The results obtained are shown in Table 1. The density results fit the linear equation

$$\frac{\rho}{\text{g·cm}^{-3}} = 2.6033 - 9.2738 \times 10^{-4}\frac{t}{°\text{C}} \qquad (1)$$

with a standard deviation of approximation $sd_\rho = 0.0017$ g·cm^{-3}.

Viscosity. The viscosity was measured using a precision computerized absolute torsional viscometer. The viscosity was determined from the damping of an oscillating cylinder. The damped harmonic curve was reconstructed from the time intervals obtained by passing a reflected light beam by a mirror attached to a pendulum over fixed stationary phototransistors. In the calculation procedure, some necessary corrections were applied.[9,10]

A sample of 25-cm^3 volume was prepared by mixing NaF with the appropriate quantity of AlF_3. The sample was prepared in a glovebox and then quickly transferred to the furnace, where it was held under an atmosphere of dried nitrogen. One Pt−Pt10Rh thermocouple was placed inside the crucible in order to measure the temperature of the melt, and a second one was located outside the crucible for temperature control. The temperature in the furnace was increased to a preset value of 750 °C. The thermocouple inside the crucible was also used to indicate when the sample was melted. About 15 min after melting, when the temperature was stabilized at 750 °C, the measuring procedure was initiated.

Several recordings of the viscosity were made at this constant temperature; subsequently, a temperature increase with a slope of about 1 K·min^{-1} was initiated. The measuring period was 275.5 s. When the temperature reached 820 °C, the temperature slope was switched to a negative value, and the measurements were continued until the lower temperature limit of 720 °C was reached. Here again, the temperature slope was switched to a positive value and increased until the final value of 750 °C (identical to the initial one) was reached. The apparatus used in this work has been described in detail elsewhere.[9,10]

Because this melt with a high content of AlF_3 has a relatively high vapor pressure,[2] the composition and thus the viscosity change with time. To eliminate any error caused by this effect, the first six values, measured at a constant temperature of 750 °C, were plotted versus time. Time "zero" was set at about 5 min after melting. The rate of viscosity change with time was evaluated and used later to correct the viscosity data with respect to changes in composition. Based on the first six data points, the linear dependence of the composition change was assumed to be valid, although the rate of composition change is probably more complicated. The effect of the composition change on viscosity versus time can be described by the linear equation

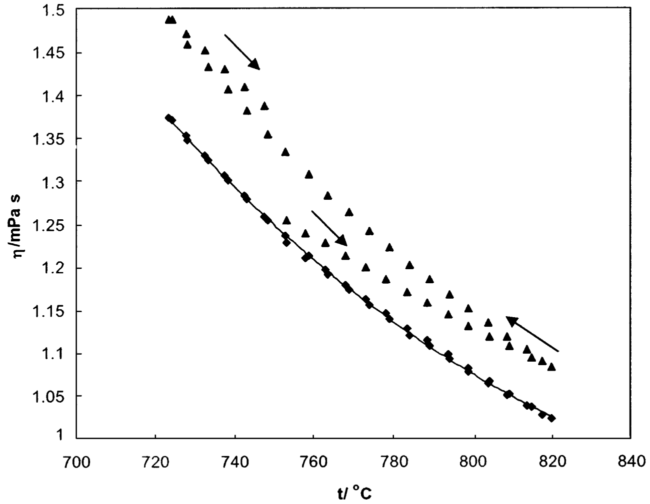

Figure 1. Temperature dependence of viscosity. ▲, Experimental data; ◆, corrected data. Arrows indicate the directions of the thermal treatment.

$$\frac{\eta(\text{comp})}{\text{mPa·s}} = 1.2416 + 9.568 \times 10^{-6}\frac{\tau}{\text{s}} \qquad (2)$$

with a standard deviation of approximation sd = 5.69 × 10^{-7} mPa·s.

This means that each experimental viscosity value must be lowered by a factor of $9.568 \times 10^{-6}\tau$/s. Consequently,

$$\frac{\eta(\text{corr})}{\text{mPa·s}} = \eta(\text{exp}) - 9.568 \times 10^{-6}\frac{\tau}{\text{s}} \qquad (3)$$

where τ is the time from the beginning of the measurement. A good proof that this correction procedure is valid and that the assumption of linear composition change is applicable in this case is the fact that the first and the last viscosity data points measured at the same temperature are almost identical, as shown in Figure 1.

All numerical data obtained in the measurements and in the treatment of the data are presented in Table 2. A polynomial equation of the second degree describing the dependence of viscosity on temperature was derived in the form

$$\frac{\eta(\text{poly})}{\text{mPa·s}} = 12.731 - 0.02639\frac{t}{°\text{C}} + 1.4775 \times 10^{-5}\left(\frac{t}{°\text{C}}\right)^2 \qquad (4)$$

with a standard deviation of approximation of $sd_\eta = 0.004$ mPa·s. The overall uncertainty was estimated to be below 1%.

Surface Tension. The surface tension was determined from the maximum pressure in a bubble formed on the tip of a capillary. The capillary was immersed in the molten salt to an exactly known depth at a given temperature. The maximum bubble pressure was reached when the bubble formed a hemisphere with a radius equal to the radius of

Table 2. Temperature Dependence of Viscosity, η, Data for the System of 55 mol % NaF + 45 mol % A1F$_3$

t/°C	time/s	η(exp)/mPa·s	η(corr)/mPa·s	$\frac{100(\eta(\text{corr}) - \eta(\text{poly}))}{\eta(\text{corr})}$
748.5	600	1.2469		
749.2	1860	1.2603		
749.1	1980	1.2608		
749.2	2100	1.2622		
749.4	2340	1.2642		
749.4	2520	1.2645		
749.4	2795	1.2665	1.2397	−0.7985
753.2	3070.5	1.2553	1.2259	−0.6391
757.9	3346	1.2402	1.2081	−0.5359
762.8	3621.5	1.2294	1.1947	−0.0598
767.9	3897	1.214	1.1767	0.0433
772.9	4172.5	1.2008	1.1608	0.2428
778.0	4448	1.1865	1.1439	0.3170
783.3	4723.5	1.1718	1.1265	0.3474
788.3	4999	1.1596	1.1117	0.4451
793.6	5274.5	1.1457	1.0952	0.4032
798.9	5550	1.1321	1.0789	0.3105
804.0	5825.5	1.1194	1.0636	0.1719
809.3	6101	1.108	1.0496	0.1276
814.7	6376.5	1.0952	1.0341	−0.1107
819.8	6652	1.0838	1.0201	−0.3655
817.6	6927.5	1.0902	1.0239	−0.4685
813.6	7203	1.1042	1.0352	−0.2528
808.6	7478.5	1.1197	1.0481	−0.1796
803.8	7754	1.1361	1.0618	−0.0430
798.8	8029.5	1.1525	1.0756	−0.0248
794.0	8305	1.1693	1.0898	0.0157
788.9	8580.5	1.1873	1.1051	0.0186
783.9	8856	1.2032	1.1184	−0.2056
779.0	9131.5	1.2243	1.1369	−0.0015
773.8	9407	1.2429	1.1528	−0.1728
768.9	9682.5	1.2647	1.1720	−0.0401
763.6	9958	1.2842	1.1889	−0.2921
758.6	10233.5	1.3088	1.2108	−0.0852
752.9	10509	1.3354	1.2348	−0.0173
748.3	10784.5	1.3551	1.2518	−0.2016
743.1	11060	1.3831	1.2772	0.0136
738.2	11335.5	1.4081	1.2996	0.0349
733.2	11611	1.4338	1.3226	0.0191
727.9	11886.5	1.4595	1.3457	−0.1596
723.2	12162	1.489	1.3726	0.1044
724	12437.5	1.4886	1.3695	0.1758
727.7	12713	1.4727	1.3510	0.1602
732.4	12988.5	1.4528	1.3285	0.1718
737.3	13264	1.4315	1.3045	0.0971
742.4	13539.5	1.4105	1.2809	0.0571
747.5	13815	1.3889	1.2566	−0.0926

Table 3. Temperature Dependence of Surface Tension, σ, Data for the System of 55 mol % NaF + 45 mol % A1F$_3$

t/°C	h/mm	p/Pa	σ/mN m^{-1}	t/°C	h/mm	p/Pa	σ/mN m^{-1}
813	1	344	78.79	769	1	376	86.62
813	2	363	78.95	769	2	396	87.46
813	3	383	79.62	769	3	417	87.79
813	4	402	79.53	769	4	435	87.61
802	1	354	81.33	760	1	380	87.87
802	2	373	81.46	760	2	400	88.18
802	3	393	81.86	760	3	420	88.49
802	4	412	82.00	760	4	438	88.29
790	1	362	83.35	749	1	384	88.86
790	2	384	84.23	749	2	403	88.88
790	3	404	84.61	749	3	424	89.43
790	4	424	84.98	749	4	443	89.47
779	1	371	85.63	740	1	388	89.85
779	2	392	86.23	740	2	407	89.86
779	3	411	86.32	740	3	427	90.13
779	4	430	86.42	740	4	446	90.15

the capillary. The surface tension can be calculated according to the following equation,[11]

$$\sigma = \frac{r}{2}(P_{\max} - ghd) \tag{5}$$

where r is the capillary radius, $P_{\max}$ is the maximum bubble pressure, g is the gravitational constant, h is the depth of immersion of the capillary, and d is the density of the melt.

A mixture with a volume of approximately 10 cm^3 was prepared by mixing NaF with the appropriate amount of AlF$_3$. The sample was prepared in a glovebox, weighed in the platinum crucible, and then quickly transferred to the furnace, where it was held under an atmosphere of dry nitrogen. The measuring device consisted of an electric resistance furnace provided with an adjustable head to secure the position of a platinum capillary, a Pt−Pt10Rh thermocouple, and a platinum wire. The platinum wire served as the electrical contact for monitoring the exact point of contact of the capillary with the liquid surface.

The platinum capillary had an outer diameter of 3 mm. A metallographic microscope (JENAPOL) was used to measure the diameter of the capillary orifice, which was found to be 1.033 mm. The actual radius of the capillary at a given temperature was calculated using thermal expansion data for platinum. The immersion depth was adjusted with an accuracy of 0.01 mm. A digital micromanometer (COMMET LB/ST 1000) was used to determine the pressure of the bubbles with an accuracy of ±1 Pa. Nitrogen was used to generate the bubbles and to maintain an inert atmosphere above the sample. The gas was slowly passed through the capillary during the experiment to avoid condensation in the upper part of the capillary. The nitrogen flow was adjusted using a needle valve. The rate of bubble formation was approximately 1 bubble per (20 to 30) s.

Within 15 min after the preset temperature was reached, the measuring procedure was started, and the capillary was slowly immersed in the molten salt. Several recordings of the surface tension were made at this constant temperature at different immersion depths (1, 2, 3, and 4 mm). The average value was used as the final value of the surface tension at a given temperature. The temperature was lowered at a rate of approximately 1 K·min^{-1}. The surface tension was measured at 10 K temperature intervals. The overall uncertainty of the surface tension determination was estimated to be less than ±1.5%.

All the numerical data obtained in these measurements are presented in Table 3. The linear dependence of surface tension on temperature in the present system is as follows:

$$\frac{\sigma}{\text{mN·m}^{-1}} = 198.02 - 0.1448\frac{t}{°\text{C}} \tag{6}$$

with a standard deviation of approximation sd$_\sigma$ = 0.754 mN·m^{-1}.

The obtained temperature slope for the surface tension is higher (−0.14 mN·m^{-1}·K^{-1}) compared to a temperature slope of −0.06 mN·m^{-1}·K^{-1} extrapolated from data given by Perez.[4]

Interfacial Tension. The method used for interfacial tension measurements in this work was based on the capillary depression phenomenon, which takes place when a tube that is not wetted by the metal is moved through the aluminum/melt interface. This method has been used by Dewing and Desclaux[12] to measure the interfacial tension of aluminum/cryolite. The method was based on monitoring the position of the metal/salt interface inside a tube. By connecting the capillary tube to a horizontal glass tube in which there is a liquid meniscus, the position of the salt/metal interface can be determined on the basis of the movement of this meniscus.

A detailed description of this method is given elsewhere.[13] One advantage of this method is that ceramic capillary tubes such as alumina (sintercorundum) are not

Table 4. Experimental Constants for Interfacial Tension Measurement and Final Results for the Systems of Aluminum/(55 mol % NaF + 45 mol % AlF_3) (A) and Aluminum/(55 mol % KF + 45 mol % AlF_3) (B) Melts

system	A	B
capillary ID/mm	4.96	4.96
temperature/°C	750	750
melt density/$\mathrm{g.cm^{-3}}$	1.91	1.768
capillary OD/mm	8	8
crucible ID/mm	70	65
interfacial tension $\gamma/\mathrm{mN{\cdot}m^{-1}}$	796 ± 5	701 ± 10

wetted by the majority of metals and are nearly inert in the majority of low-temperature molten salts. Another advantage is that the metal and the salt can be kept in contact with each other long enough before the start of the interfacial tension measurements, allowing for chemical equilibrium to be established.

During the computational procedure, several corrections must be made. To reduce the magnitude of these corrections, it is preferable that the diameter of the crucible be as large as possible. For the evaluation of the experimental data, a computer program (IFT) written in Visual Basic was developed. This program allowed us to evaluate concurrently 10 experimental curves, which were taken in 1 measurement cycle. The program allows a fully automatic evaluation of the curve, finds inflection points on the curve, and performs a calculation of the interfacial tension with the appropriate experimental constants.

The results of the interfacial tension measurements of the systems aluminum/55 mol % NaF + 45 mol % AlF_3 and aluminum/55 mol % KF + 45 mol % AlF_3 at 750 °C are given in Table 4. No temperature dependence was evaluated because there is a very minute dependence between these two variables. Over a 100 °C range, the change in interfacial tension is within the experimental error.

For the measurements of interfacial tension in the aluminum/55 mol % NaF + 45 mol % AlF_3 system, a graphite crucible with a 70-mm i.d. was used, and a sinter-corundum crucible with a 65-mm i.d. was used for the latter system because the 55 mol % KF + 45 mol % AlF_3 melt attacks graphite crucibles. The measurements were taken 15 min after the salt had melted and the temperature was equilibrated. No noticeable shift in the measured values due to compositional changes with time was observed within the measuring period of 45 min. Experimental constants for both systems are given in Table 4.

The final result for the 55 mol % NaF + 45 mol % AlF_3 system, after excluding the highest and lowest values from the statistical calculations, based on 10 experimental values was $\gamma = (796 \pm 5)\ \mathrm{mN{\cdot}m^{-1}}$. For the 55 mol % KF + 45 mol % AlF_3 system, 10 measurements were performed, and after excluding the highest and lowest value from the statistical calculation, the final result was $\gamma = (701 \pm 10)\ \mathrm{mN{\cdot}m^{-1}}$.

Conclusions

The temperature dependences of density, viscosity, surface tension, and interfacial tension in the 55 mol % NaF + 45 mol % AlF_3 system were determined.

The density was measured over the temperature range of (730 to 840) °C, yielding the linear equation

$$\frac{\rho}{\mathrm{g{\cdot}cm^{-3}}} = 2.6033 - 9.2738 \times 10^{-4}\frac{t}{^{\circ}\mathrm{C}}$$

with a standard deviation of $\mathrm{sd}_\rho = 0.0017\ \mathrm{g{\cdot}cm^{-3}}$.

Viscosity was measured over the temperature range of (725 to 840) °C, and a quadratic equation was obtained:

$$\frac{\eta(\mathrm{poly})}{\mathrm{mPa{\cdot}s}} = 12.731 - 0.0234\frac{t}{^{\circ}\mathrm{C}} + 1.4775 \times 10^{-5}\left(\frac{t}{^{\circ}\mathrm{C}}\right)^2$$

with a standard deviation of $\mathrm{sd}_\eta = 0.0040\ \mathrm{mPa{\cdot}s}$.

For surface tension, a linear dependence on temperature was observed in the range of (740 to 815) °C (i.e., $(\sigma/\mathrm{mN{\cdot}m^{-1}}) = 198.02 - 0.145(t/^{\circ}\mathrm{C})$ with a standard deviation of $\mathrm{sd}_\sigma = 0.754\ \mathrm{mN{\cdot}m^{-1}}$).

Interfacial tension was measured at one temperature, 750 °C. The value of $\gamma = (796 \pm 5)\ \mathrm{mN{\cdot}m^{-1}}$ was determined for the 55 mol % NaF + 45 mol % AlF_3 system. For the 55 mol % KF + 45 mol % AlF_3 system, the interfacial tension was found to be $\gamma = (701 \pm 10)\ \mathrm{mN{\cdot}m^{-1}}$.

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