ELECTRICAL CONDUCTIVITY AND DENSITY OF CHLORIDE MELTS

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Abstract

The electrical conductivity and density of chloride melts containing LiCl, KCl, CaCl\textsubscript{2}, MgCl\textsubscript{2}, NaCl, and AlCl\textsubscript{3} are determined as a function of temperature between 700-750°C. All of the melts deviate negatively from the additive electrical conductivity law. The conductivity of melts can be predicted by assuming the complexes: LiCl-AlCl\textsubscript{3}, NaCl-AlCl\textsubscript{3}, NaCl-KCl, KCl-AlCl\textsubscript{3}, NaCl-LiCl, and KCl-LiCl. For most of the melts the predicted values agree with the measured values within two percent. Densities of the mixtures agree well with the additivity law.

Introduction

Commercial interest in chloride based fused salt electrolysis has increased over the last several years, particularly with the announcement of the Alcoa Smelting Process. The low liquidus temperatures and the ability to use an inert anode in molten chloride electrolytes permit operation of electrolytic cells at low temperatures with energy saving electrode designs. Reported here are two important physical properties—electrical conductivity and density—measured over a wide range of compositions of sodium chloride (NaCl), potassium chloride (KCl), lithium chloride (LiCl), calcium chloride (CaCl\textsubscript{2}), magnesium chloride (MgCl\textsubscript{2}) and aluminum chloride (AlCl\textsubscript{3}). A method for calculating conductivity and density in the chloride melts is presented.

Materials

The electrolyte components were Culinox-Morton Grade 999 NaCl; Lithium Corporation of America anhydrous cell grade LiCl; Baker and Adamson anhydrous, reagent grade, 8-mesh CaCl\textsubscript{2}; Baker and Adamson reagent grade, crystal KCl; Oregon Metallurgical Corporation anhydrous MgCl\textsubscript{2}. The
AlCl₃ was produced by the chlorination of Al₂O₃ in the Alcoa Smelting Process.

**Procedure**

The required composition, with AlCl₃ omitted, was melted under argon in a Vycor test tube. AlCl₃ was added to each melt (.5 g AlCl₃/100 g bath) to remove water, and the Al₂O₃ formed was allowed to settle to the bottom of the test tube. Additional AlCl₃ was added by introducing AlCl₃ vapor into the melt.

Compositions were determined by sampling the melt at the same time conductivity and density measurements were made. Melt samples were taken in 7 mm closed bottom Vycor tubes with a slot cut approximately 4 cm from the bottom. The preheated sample tube was purged with argon while being positioned with the slot at the required sampling level. The purge was stopped allowing the sample to fill the tube, then restarted and the sample withdrawn.

Melt samples were dissolved in deionized water. In concentrations less than 20%, AlCl₃ was determined by titration with sodium hydroxide to a phenolphthalein end point in the presence of sodium gluconate. When AlCl₃ concentrations were greater than 20%, AlCl₃ was determined by dissolving the sample in water, adjusting the pH to 10 with KOH, adding KF to precipitate K₃AlF₆, and titrating the released OH⁻ with HCl. Calcium ion interference was eliminated by precipitation as an oxalate.

CaCl₂ was determined by complexometric titration with EDTA at pH 12.5 using hydroxy naphthol blue indicator.

MgCl₂ was determined by complexometric titration with EDTA at pH 10 using Erio Black T as an indicator.

NaCl, KCl, and LiCl were determined by atomic absorption spectroscopy.

**Density**

Density was measured with a Fisher Chain Gravitometer using a 3.80 cc nickel bob. When bath depth was insufficient for this size of bob, a less accurate 0.922 cc pancake-shaped nickel bob was used. The bobs were suspended by a 28-ga nichrome wire. They were calibrated to Janz values in molten NaCl at 810°C and molten LiCl at 700 and 376.
750°C. The calibrations agreed after correcting for the thermal expansion of nickel. No correction was required for the surface tension effect on the 28-ga wire.

Electrical Conductivity

Electrical conductivity was determined with a quartz capillary conductivity cell using an AC Wheatstone bridge operated at 500, 1000, 2000, and 5000 Hz. Polarization effects were removed by extrapolating to infinite frequency, the zero intercept of a linear least square line of measured resistance vs. frequency to -0.5 power. The conductivity cell was of the dip cell type, made by welding a 50 mm long, 1.5 mm bore quartz capillary onto a 9 mm OD, 3 mm ID quartz tube. A nickel sheathed thermocouple measured the temperature and served as the internal electrode. A 3/8-inch diameter graphite rod served as the external electrode for the dip cell. Rapid balancing of the bridge was facilitated by an oscilloscope. The bridge error signal passed through an isolating, narrow band filter to the oscilloscope's high gain vertical input. A reference signal from the bridge input was applied to the horizontal input producing an elliptical pattern. Capacitive balance closed the ellipse and resistive balance rotated the ellipse or line to horizontal.

The dip cells were calibrated in 30.39% (maximum conductivity) \( \text{H}_2\text{SO}_4 \) solution at room temperature to obtain cell constants. Calibrations of several cells were checked by measuring conductivities of melts of LiCl and NaCl. Good agreement was obtained with the conductivity values given by Janz (1) after adding a small amount of Al or Mg to remove residual moisture or hydroxide ion.

Results

Electrical conductivity and density measurements were made over a range of compositions of NaCl, KCl, LiCl, CaCl\(_2\), MgCl\(_2\), and AlCl\(_3\). Some of the melts formed two immiscible liquid phases.

A melt of 25%*NaCl, 25% LiCl, 25% KCl, and 25% CaCl\(_2\) (Figure 1) at 700°C separated into two immiscible liquid phases with the addition of 3% AlCl\(_3\). Further additions of AlCl\(_3\) to 28% increased the amount of the top phase with the AlCl\(_3\) content of the bottom phase remaining nearly constant at 3.0-3.2%. At 28% AlCl\(_3\), the top phase was 45% of the

*Compositions are given in weight percent.
total volume. Electrical conductivity at 700°C was 2.55 ohm$^{-1}$cm$^{-1}$ before AlCl$_3$ addition and decreased to 2.12 ohm$^{-1}$cm$^{-1}$ at 3% AlCl$_3$. The density decreased from 1.700 g/cc to 1.620 g/cc as AlCl$_3$ increased from 0-3%. When the second phase formed, KCl was extracted from the bottom phase and the conductivity of the bottom phase increased. The temperature coefficient $\Delta K/\Delta T$ from 700 to 750°C was 0.0012 ohm$^{-1}$cm$^{-1}$deg$^{-1}$ for the bottom phase.

A melt of 33.3% NaCl, 33.3% KCl, and 33.3% LiCl had a conductivity of 3.10 ohm$^{-1}$cm$^{-1}$ at 700°C and a density of 1.533 g/cc. Addition of 7.4% AlCl$_3$ decreased the conductivity to 2.41 ohm$^{-1}$cm$^{-1}$ and density to 1.500 g/cc. The temperature coefficient was 0.0036 ohm$^{-1}$cm$^{-1}$deg$^{-1}$.

Addition to the above of 16.7% CaCl$_2$ and 17% AlCl$_3$ resulted in the formation of two liquid phases with 4.1% AlCl$_3$ and a conductivity of 2.31 ohm$^{-1}$cm$^{-1}$ in the bottom phase. The conductivity of the top phase was 0.99 ohm$^{-1}$cm$^{-1}$ at 694°C. Densities of the two liquid phases were 1.586 for the bottom phase and 1.498 g/cc for the top phase.

The conductivity of a binary mixture—37% KCl, 63% LiCl—was 3.67 ohm$^{-1}$cm$^{-1}$ and density was 1.453 g/cc at 700°C. The addition of 7.6% AlCl$_3$ formed two liquid phases. Conductivity of the bottom phase dropped to 2.90 ohm$^{-1}$cm$^{-1}$ while the top phase had a conductivity of 0.92 ohm$^{-1}$cm$^{-1}$. Increasing the total AlCl$_3$ to 15.4% increased the conductivity of the bottom phase to 2.99 ohm$^{-1}$cm$^{-1}$. The top phase remained at 0.92 ohm$^{-1}$cm$^{-1}$. The density of the top phase was 1.324 g/cc and the bottom phase 1.428 g/cc. Increasing the temperature decreased the amount of top phase. Addition of NaCl to this ternary mixture both lowered the conductivity of and decreased the amount of top phase. The decrease in top phase was accompanied by an increased amount of AlCl$_3$ in the bottom phase. Adding CaCl$_2$ to the melt increased the amount of top phase by extracting AlCl$_3$ from the bottom phase. The conductivity of the bottom phase also increased.

The ternary mixture—72.6% LiCl, 13.7% KCl, 13.7% CaCl$_2$ (Figure 2)—had a conductivity of 4.54 ohm$^{-1}$cm$^{-1}$ and a density of 1.507 g/cc at 704°C. Two phases formed with the addition of 1% AlCl$_3$. The AlCl$_3$ concentration in the bottom phase increased from 3% to 6% when AlCl$_3$ in the total melt was raised to 22%. The bottom phase conductivity was 3.89 ohm$^{-1}$cm$^{-1}$ and density was 1.477 g/cc at 20% AlCl$_3$ and 790°C. The top phase conductivity was 1.19 ohm$^{-1}$cm$^{-1}$ and density was 1.290 g/cc. When the bottom phase was electrolyzed to produce Al and Cl$_2$, the top phase continued to feed AlCl$_3$ to the bottom phase until the top phase dis-
Pure molten LiCl had an electrical conductivity of 6.18 ohm$^{-1}$cm$^{-1}$ and a density of 1.463 g/cc at 700°C. This was the highest conductivity of any of the melts measured. Aluminum chloride lowered the conductivity of LiCl much more than would be expected, based on dilution by an inert nonconductive species (Figure 3). From 0-15% AlCl$_3$ each molecule of AlCl$_3$ appeared to block conduction of between one and nine Li$^+$ ions, depending upon the AlCl$_3$ concentration. Density of the mixture deviated only slightly (1%) from additivity. The addition of KCl and/or NaCl lowered the conductivity more than would be expected from substituting Na$^+$ or K$^+$ for Li$^+$. It appears that the KCl and NaCl formed a more stable complex with LiCl than with AlCl$_3$.

In melts of MgCl$_2$ and LiCl at low AlCl$_3$ concentrations, the MgCl$_2$ reduced conductivity by the amount expected from the substitution of the poorer conducting Mg$^{2+}$ for Li$^+$ ion, but at 6-10% AlCl$_3$ the MgCl$_2$ improved conductivity.

Sodium chloride base melts decreased in conductivity with the addition of AlCl$_3$ more rapidly than expected from an inert diluent (Figure 3).

**Discussion**

In all of the molten chlorides measured, the electrical conductivity showed negative deviations from an additive effect. The LiCl-AlCl$_3$ system showed the greatest deviation (54%) at the composition 3LiCl·AlCl$_3$.

One goal of this work was to determine a method of predicting the electrical conductivity of mixtures of NaCl, LiCl, KCl, CaCl$_2$, MgCl$_2$, and AlCl$_3$ over a wide range of compositions and in the temperature range of 700-800°C. Although Van Artsdalen and Yaffe caution against assuming complexes based on conductivity, the method used to obtain good agreement between measured values of conductivity and predicted values of conductivity was to assume a series of complexes formed having conductivities listed in Table I. Many of the complexes have been previously suggested. No effort was made in this work to identify the complexes or in any other way verify their existence. Complexes assumed were KLiCl$_2$(3), NaLiCl$_2$, NaKCl$_2$, LiAlCl$_4$(4), and NaAlCl$_4$(5).

The procedure was to calculate first the number of moles of each salt present in 100 grams of melt. Next, the
distribution of these salts between the above-mentioned assumed complexes was calculated using empirical relationships that were adjusted by trial and error to minimize the standard deviation between the calculated electrical conductivities and measured conductivities in this work and in the literature. This resulted in the following distribution factors:

\[ K_{\text{LiKCl}_2} = 0.9 \frac{\text{Moles LiCl} + \text{Moles KCl}}{S1} \]  (Eq.1)

\[ K_{\text{LiNaCl}_2} = [0.9 - 0.375(\text{wt}\% \text{AlCl}_3 + 2 \text{ wt}\% \text{KCl})] \times \frac{\text{Moles LiCl} + \text{Moles NaCl}}{S1} \]  (Eq.2)

\[ K_{\text{NaKCl}_2} = 0.9 \frac{\text{Moles NaCl} + \text{Moles KCl}}{S1} \]  (Eq.3)

\[ K_{\text{LiCl-xAlCl}_3} = 1 - 0.99 \frac{\text{Moles NaCl} + \text{Moles KCl}}{S1} \]  (Eq.4)

For \( x = 0 \) to \( 1 \)

\*\( S1 = \) Moles NaCl + Moles LiCl + Moles KCl + Moles AlCl\(_3\)

These distribution functions were used in the following manner: First it was determined whether KCl or LiCl was in excess of LiKCl\(_2\). The moles of the salt not in excess multiplied by the distribution function \( K_{\text{LiKCl}_2} \) determined the amount of LiKCl\(_2\). The residuals of LiCl and KCl remaining after removing the calculated LiKCl\(_2\) were carried to the LiNaCl\(_2\) and NaKCl\(_2\) and the same calculation sequence followed.

Residual LiCl was then combined with AlCl\(_3\). The non-linearity of the conductivity of LiCl + AlCl\(_3\) with AlCl\(_3\) required that the LiCl + AlCl\(_3\) conductivity be represented by three equations covering the ranges (1) 0-7\% AlCl\(_3\), (2) 7-20\% AlCl\(_3\), and (3) 20-30\% AlCl\(_3\). This three region treatment was applied only when the number of moles of AlCl\(_3\) were less than the number of moles of LiCl. When the number of moles of AlCl\(_3\) exceeded the number of moles of LiCl, the LiCl was calculated entirely as LiAlCl\(_4\). Residual AlCl\(_3\) was then combined with NaCl as NaAlCl\(_4\) and any remaining AlCl\(_3\) was treated as inert diluent. Also small amounts of KCl, NaCl, and LiCl depending upon composition may end up not complexed and all of the MgCl\(_2\) and CaCl\(_2\) were considered not complexed.
Once the moles of each salt complex and moles of uncomplexed salts had been determined, they were converted back to weight percents. Next the volume fraction, \( V_i \), of each of the 12 possible components listed in Table I was calculated by Equation 5. The density of each component, \( d_i \), and conductivity, \( K_i \), was calculated by equations in Table I.

\[
V_i = \frac{(W_i/d_i)}{\sum_1^{12} (W_i/d_i)} \quad \text{where:} \quad V_i = \text{volume fraction (Eq.5)} \\
W_i = \text{weight percent of component $i$} \\
d_i = \text{density of component $i$, g/cc}
\]

The conductivity of the melt, \( K \), was then calculated by Equation 6:

\[
K = \sum_1^{12} V_i K_i \quad \text{where:} \quad K_i = \text{specific conductivity of component $i$, ohm}^{-1}\text{cm}^{-1}
\]

Density of the melt, \( D \), was calculated by Equation 7:

\[
D = 100/\sum_1^{12} W_i/d_i \quad (\text{Eq.7})
\]

Calculated conductivities generally agreed within 2% of the measured values in this work. Examples are shown in Table II. Calculated densities generally agreed within 1% of the measured density. Examples are given in Table III. If a melt forms two liquid phases, the composition of each phase must be determined and its conductivity and density calculated separately.

References

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Properties of the melt—25% NaCl, 25% KCl, 25% LiCl, 25% CaCl₂ at 700°C

Figure 1
Properties of the melt—72.6% LiCl, 13.7% KCl, 13.7% CaCl₂

Figure 2
Electrical conductivity of LiCl-AlCl₃ and NaCl-AlCl₃

Figure 3
**TABLE I**
Density and Electrical Conductivity of Melt Components

| Component | Regression Equation |
|-----------|---------------------|
| NaCl      | $D = \frac{(1.611 + 0.001897T)}{(1 + 0.001538T)}$<br>$K = 3.224 + 0.0036\tau$ |
| LiCl      | $D = \frac{(1.463 + 0.002464\tau)}{(1 + 0.002\tau)}$<br>$K = (6.18 + 0.009142\tau)/(1 + 0.0006956\tau)$ |
| KCl       | $D = \frac{(1.568 + 0.001619\tau)}{(1 + 0.001429\tau)}$<br>$K = (1.911 + 0.002372\tau)/(1 - 0.0002703\tau)$ |
| MgCl₂     | $D = \frac{(1.682 + 0.0044628\tau)}{(1 + 0.002857\tau)}$<br>$K = (0.983 + 0.004765\tau)/(1 + 0.002553\tau)$ |
| CaCl₂     | $D = \frac{(2.115 + 0.003768\tau)}{(1 + 0.002\tau)}$<br>$K = (1.68 + 0.00367\tau)/(1 - 0.0003636\tau)$ |
| AlCl₃     | $D = \frac{(1.225 - 0.00060005\tau)}{(1 - 2E-8\tau)}$<br>$K = 0$ |
| LiKCl₂    | $D = \frac{(1.523 + 0.0017615\tau)}{(1 + 0.0015384\tau)}$<br>$K = 2.47 + 0.0046\tau$ |
| LiNaCl₂   | $D = \frac{(1.545 - 0.00048\tau)}{(1 + 2.5E-8\tau)}$<br>$K = 3.46 + 0.005\tau$ |
| NaKCl₂    | $D = \frac{(1.578 - 0.07136\tau)}{(1 + 0.04526\tau)}$<br>$K = (2.317 + 0.005035\tau)/(1 + 0.0008108\tau)$ |
| LiAlCl₄   | $D = 1.2631 - 0.000476\tau$<br>$K = 0.643 + 0.00095\tau$ |
| NaAlCl₄   | $D = 1.26 - 0.0008\tau$<br>$K = (1.475 + 0.00526\tau)/(1 + 0.002\tau)$ |
| LiCl+AlCl₃| $D = 1.4641 - 0.000426\tau - 0.0004637A + (8.032E-5 - 2.037E-7\tau)A^2$<br>$D = 1.405 - 0.0005\tau - (0.002222 + 1.24E-6\tau)A$<br>[for AlCl₃ >19%]<br>$K = 6.182 + 0.00468\tau - 0.04861A - 0.019605A^2 + 0.00077022A^3$<br>[for AlCl₃ 0-7%]<br>$K = 7.4034 + 0.00468\tau - 0.44363A + 0.0195A^2 - 0.00033963A^3$<br>[for AlCl₃ 7-20%]<br>$K = (5.02 - 0.07A)(1 + 0.00015\tau)$<br>[for AlCl₃ 20-30%] |

$\tau =$ Temp., °C = 700
A = wt % AlCl₃
D = Density, g/cc
K = Conductivity, ohm⁻¹cm⁻¹
E = Exponential, base 10
### TABLE II

**Electrical Conductivity of Chloride Melts**

| Compound, Weight % | NaCl | LiCl | KCl | MgCl₂ | CaCl₂ | AlCl₃ | Temp. °C | Conductivity ohm⁻¹·cm⁻¹ | Calc. | Meas. | Delta |
|---------------------|------|------|-----|-------|-------|-------|----------|--------------------------|-------|-------|-------|
|                     | 43.94| 0.00 | 56.06 | 0.00  | 0.00  | 0.00  | 700      | 2.333                    | 2.334 | 0.00  | 0.00  |
|                     | 0.00 | 36.25| 63.75 | 0.00  | 0.00  | 0.00  | 725      | 2.688                    | 2.695 | -0.007|
|                     | 0.00 | 90.00| 0.00  | 0.00  | 0.00  | 10.00 | 700      | 4.577                    | 4.580 | -0.003|
|                     | 30.47| 0.00 | 0.00  | 0.00  | 0.00  | 69.53 | 750      | 1.580                    | 1.580 | 0.000 |
|                     | 39.00| 58.50| 0.50  | 0.50  | 1.50  | 0.00  | 701      | 4.613                    | 4.540 | 0.073 |
|                     | 49.31| 40.39| 0.46  | 0.46  | 1.38  | 8.00  | 699      | 3.429                    | 3.490 | -0.061|
|                     | 53.42| 33.01| 1.96  | 1.24  | 0.37  | 10.00 | 700      | 3.198                    | 3.170 | 0.028 |
|                     | 50.45| 31.17| 1.85  | 1.17  | 0.35  | 15.00 | 720      | 2.794                    | 2.730 | 0.064 |

### TABLE III

**Density of Chloride Melts**

| Compound, Weight % | NaCl | LiCl | KCl | MgCl₂ | CaCl₂ | AlCl₃ | Temp. °C | Density, g/cc | Calc. | Meas. | Delta |
|---------------------|------|------|-----|-------|-------|-------|----------|----------------|-------|-------|-------|
|                     | 100.00| 0.00 | 0.00| 0.00  | 0.00  | 0.00  | 801      | 1.561          | 1.550 | 0.011 |
|                     | 0.00  | 100.00| 0.00| 0.00  | 0.00  | 0.00  | 700      | 1.464          | 1.463 | 0.001 |
|                     | 0.00  | 90.00 | 0.00| 0.00  | 0.00  | 10.00 | 700      | 1.426          | 1.426 | 0.000 |
|                     | 0.00  | 72.60 | 13.70| 0.00  | 13.70 | 0.00  | 704      | 1.540          | 1.520 | 0.020 |
|                     | 33.33 | 33.33 | 33.33| 0.00  | 0.00  | 0.00  | 700      | 1.542          | 1.533 | 0.009 |
|                     | 30.87 | 30.87 | 30.87| 0.00  | 0.00  | 7.40  | 700      | 1.504          | 1.500 | 0.004 |