Viscosity of the NaCl + $AlCl_3$ Melt System, Including the Effect of Added Oxide

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The viscosity of the NaCl + $AlCl_3$ melt system has been measured in the composition range 48.5–59 mol % $AlCl_3$ and temperature range 200–400 °C. The viscosity of the system is expressed as a function of temperature and composition. The effect of dissolved sodium oxide on the viscosity of the system was also measured up to a nominal oxide concentration of 0.5 mol kg^{-1}, as a function of temperature, Na:Al ratio, and oxide content.

Two papers have been published on the viscosity of the NaCl + $AlCl_3$ system. Kryagova (*1*) measured the viscosity in the temperature range $200 < t < 300$ °C and composition range $0.5 < x_{AlCl_3} < 0.66$. She used a capillary-flow viscometer and reported a viscosity minimum at about 52 mol % $AlCl_3$. Brockner, Tørklep, and Øye (*2*) measured the viscosity in the range $160 < t < 300$ °C and $0.50 < x_{AlCl_3} < 0.80$, using an oscillating cup viscometer. They did not report a viscosity minimum, but they did report a viscosity maximum at about 66 mol % $AlCl_3$. The viscosity values quoted by Brockner, Tørklep, and Øye are about 10–20% lower than those according to Kryagova. No previous measurements of the effect of oxide contamination on the viscosity have been published.

The present set of measurements was made to resolve this difference, and also to measure the effect, on the viscosity of the melt, of replacing some of the sodium chloride by sodium oxide. Chloroaluminate melts react rapidly with atmospheric water vapor to give oxygen-containing species in solution in the melt. This makes the preparation of oxide-free chloroaluminate melts very difficult. Thus, most melts contain significant concentrations of oxygen-containing species in solution.

The viscosity of the system was measured using an Ostwald capillary-flow viscometer. The melt was drawn up into the upper bulb by a diaphragm pump, and was then allowed to flow back under gravity. The time taken for the melt level to drop between two marks above and below the upper bulb (outflow time) was measured using a Gallenkamp TKM-475-S quartz stopwatch. The outflow time (t) for such a viscometer is related to the viscosity by the expression

$$\eta/\varrho t = \alpha + \beta\varrho/t^2 + \gamma V \qquad (1)$$

as the "calibration value" $\eta/\varrho t$ is a function of the kinetic energy of the liquid in the tube (proportional to ϱ/t^2) and the volume of liquid in the viscometer (V). The viscometer capillary tube was approximately 750 μm in diameter, with a length of 10 cm. The viscometer developed thermal stress cracks several times during the measurements, necessitating the replacement of the capillary tube. Thus, it was necessary to recalibrate the viscometer a number of times. The viscometer required about 20 cm^3 of melt, and the values of $\eta/\varrho t$ were in the range $(5-10) \times 10^{-9}$ m^2·s^{-2}.

The melts were prepared by slowly heating a mixture of $AlCl_3$, NaCl, and Na_2CO_3 (as a source of sodium oxide) in the viscometer until the mixture melted completely. This usually gave a water-clear melt; if any solid particles were observed, the melt was discarded. Mixing of the materials inside the viscometer was achieved by drawing the melt up into the upper bulb and then allowing it to flow back a number of times. Fisons AR NaCl (99.5%) and AnalaR sodium carbonate (BDH 99.5%) were dried at 300 °C for 24 h before use. AnalaR $AlCl_3$ (BDH, assay ex Cl$^-$, 97%) was sublimed under vacuum from an acidic $NaAlCl_4$ melt. The materials were loaded into the viscometer in a glovebox filled with dry nitrogen, and the viscometer, viscometer head, and diaphragm pump were connected in the glovebox and removed as a single unit. Melts containing oxide were prepared by using a mixture of NaCl and Na_2CO_3 in place of the NaCl. The Na_2CO_3 decomposes in the melt to give CO_2 and Na_2O, which then dissolves in the melt. The $AlCl_3$ mole fraction was calculated from the amount of $AlCl_3$ and Na^+ (from NaCl and Na_2O) present.

The composition of the melt was determined by mass. The masses of NaCl, Na_2CO_3 (where used), and $AlCl_3$ loaded into the viscometer were recorded. As the viscometer head was cold, a small amount of $AlCl_3$ would sublime out of the melt onto the head while the viscometer was in use. Therefore, the viscometer, minus the head, was weighed approximately every 2 h while the measurements were being made; in no case did sublimation lead to a change of over 0.05 mol % in x_{AlCl_3}.

The viscometer was maintained at constant temperature using a well-stirred bath of the ternary eutectic $NaNO_3$ + $NaNO_2$ + KNO_3 in a Pyrex beaker to allow visual observation. Due to the vigorous reaction between the nitrate melt and the chloroaluminate melt, which would have occurred had the viscometer broken in the salt bath, the salt bath assembly was enclosed in a Perspex box. Also, the bath was placed near the fume extractor fan, which would take up the NO_2 formed in such a reaction. The temperature was measured using a type K thermocouple mounted in contact with the capillary tube. The reference junctions were maintained at 0 °C in a water–ice bath, and the voltage was measured using a Thurlby 1504a digital voltmeter. The temperature was kept within 0.5 K of the temperature recorded.

The viscometer was calibrated with various amounts of distilled water and molten sodium nitrate (Fisons AR, 99.5%, filtered when molten). The calibration values obtained using $NaNO_3$ were within ±1% of those obtained using water. From the measured outflow times and the densities and viscosities of sodium nitrate (*3*) and water (*4*), the values of α, β, and γ in eq 1 were calculated.

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Table 1. Values of the Constants in Viscosity Functions 2–6

function	*a*	*b*	*c*	*d*	*e*	*f*	no. of points	R^2
2	−2.67 ± 0.02	1664 ± 14	1.26 ± 0.08				66	0.996
3	−2.90 ± 0.03	1791 ± 15	0.87 ± 0.11	0.35 ± 0.01			162	0.989
4	−2.89 ± 0.03	1788 ± 15	1.00 ± 0.13	0.38 ± 0.02	−0.80 ± 0.46		162	0.989
5	−2.82 ± 0.03	1749 ± 14	0.89 ± 0.09			197 ± 7	162	0.991
6	−2.81 ± 0.03	1740 ± 14	1.07 ± 0.11		−1.10 ± 0.40	223 ± 12	162	0.992

Table 2. Viscosity Data Points

x_{AlCl_3}	$m(O^{2-})$/ $(mol{\cdot}kg^{-1})$	t/°C	η/(mPa·s)	x_{AlCl_3}	$m(O^{2-})$/ $(mol{\cdot}kg^{-1})$	t/°C	η/(mPa·s)	x_{AlCl_3}	$m(O^{2-})$/ $(mol{\cdot}kg^{-1})$	t/°C	η/(mPa·s)
0.502	0	250	1.680	0.4893	0	350	0.980	0.517	0.514	375	1.041
		250	1.672			350	0.980			375	1.041
		250	1.672			350	0.976			350	1.153
		275	1.471			350	0.980			350	1.153
		275	1.454	0.4925	0	300	1.247			300	1.496
		275	1.454			300	1.247			300	1.491
		300	1.265			300	1.238			250	2.042
		300	1.265			300	1.242			250	2.023
		300	1.256	0.4954	0	250	1.631	0.521	0.180	325	1.248
		325	1.111			250	1.631			325	1.256
		325	1.111			250	1.631			325	1.265
		325	1.120			250	1.631			300	1.423
		350	0.986	0.4973	0	200	2.366			300	1.423
		350	0.986			200	2.366	0.577	0.437	250	1.882
		350	0.986			200	2.344			250	1.872
		400	0.858			200	2.354			300	1.367
		400	0.858	0.547	0.555	250	2.209			300	1.377
0.525	0	225	2.081			250	2.200			300	1.367
		225	2.072			250	2.209			350	1.044
		225	2.072			300	1.595			350	1.063
		250	1.726			300	1.586			350	1.063
		250	1.734			300	1.595			400	0.873
		250	1.734	0.570	0.542	400	0.955			400	0.863
0.532	0	200	2.410			400	0.960			400	0.873
		200	2.410			400	0.965	0.512	0.355	325	1.307
		200	2.410			375	1.080			325	1.307
		225	1.986			375	1.065			325	1.307
		225	1.986			350	1.288			325	1.316
		225	1.994			350	1.303			250	2.012
		250	1.676			350	1.279			250	1.994
		250	1.676			325	1.373	0.548	0.144	250	1.850
		250	1.676			325	1.373			250	1.850
0.532	0	275	1.438			300	1.575			250	1.866
		275	1.438			300	1.575			275	1.580
		275	1.446			300	1.575			275	1.571
0.548	0	317	1.250			275	1.852			275	1.571
		317	1.250			275	1.838			325	1.189
		317	1.250			250	2.214			325	1.189
		307	1.316			250	2.199			325	1.198
		307	1.316			220	2.777			350	1.051
0.587	0	225	2.241			220	2.763			350	1.059
		225	2.241			210	3.041			350	1.059
		275	1.580			210	3.055	0.552	0.367	200	3.200
		275	1.580	0.530	0.304	225	2.222			250	2.143
		300	1.395			225	2.230			250	2.133
		300	1.403			225	2.222			250	2.152
		300	1.403			250	1.872			275	1.794
0.4851	0	400	0.803			250	1.864			275	1.803
		400	0.803			275	1.617			275	1.794
		400	0.799			275	1.609			325	1.381
										325	1.381
										325	1.362
										325	1.362

A total of 162 viscosity determinations were performed. The density of the melt was taken from the density function given by Fannin et al. (*5*). As there are no published data on the effect of oxide ion concentration on the density of the melt, we have assumed that the presence of oxide ions does not affect the density, and that the density is defined only by the temperature and Na:Al ratio. From the density, outflow time, and weight of the melt, the volume, kinetic energy, calibration parameter $\eta/\varrho t$, and viscosity were calculated. Some melts were made salt-saturated, using an excess of NaCl. The composition of salt-saturated melts was taken from refs 6 and 7.

The logarithm of the viscosity was fitted to the following functions of temperature, x_{AlCl_3}, and concentration of oxide ions, $m(O^{2-})$/(mol of Na_2O/kg of melt):

$$\ln(\eta/\mathrm{mPa{\cdot}s}) = a + b/(T/\mathrm{K}) + c(x - 0.5) \text{ (oxide-free only)} \tag{2}$$

$$\ln(\eta/\mathrm{mPa{\cdot}s}) = a + b/(T/\mathrm{K}) + c(x - 0.5) + dm(O^{2-})/(\mathrm{mol{\cdot}kg^{-1}}) \text{ (all points)} \tag{3}$$

$$\ln(\eta/\text{mPa·s}) = a + b/(T/\text{K}) + c(x - 0.5) + dm(\text{O}^{2-})/(\text{mol·kg}^{-1}) + e(m(\text{O}^{2-})/(\text{mol·kg}^{-1}))(x - 0.5) \text{ (all points)} \quad (4)$$

$$\ln(\eta/\text{mPa·s}) = a + b/(T/\text{K}) + c(x - 0.5) + f(m(\text{O}^{2-})/(\text{mol·kg}^{-1}))/(T/\text{K}) \text{ (all points)} \quad (5)$$

$$\ln(\eta/\text{mPa·s}) = a + b/(T/\text{K}) + c(x - 0.5) + e(m(\text{O}^{2-})/(\text{mol·kg}^{-1}))(x - 0.5) + f(m(\text{O}^{2-})/(\text{mol·kg}^{-1}))/(T/\text{K}) \text{ (all points)} \quad (6)$$

x_{AlCl_3} is the nominal mole fraction of AlCl_3 in the melt, on the basis that $x_{\text{AlCl}_3} + x_{\text{NaCl}} + 2x_{\text{Na}_2\text{O}} = 1$. The best-fit values of the constants in the functions, as determined by the Quattro Pro 4.0 spreadsheet program, are given in Table 1.

These functions may be used in the composition range $0.485 < x_{\text{AlCl}_3} < 0.59$, and $0 \le m(\text{O}^{2-}) \le 0.5$. For melts where $x_{\text{Al}} < 0.55$, the functions may be used in the temperature range 200−400 °C; at more acidic compositions, the activation energy appears to increase, and the functions should only be used in the temperature range 250−350 °C. The data points are tabulated in Table 2.

The viscosity of the oxide-free melts is about 2−4% lower than the uncorrected values according to Brockner, Tørklep, and Øye, and about 0−2% higher than their corrected values (they recommend (*2*) that their results be multiplied by a correction factor of 0.963), and about 10−20% lower than those according to Kryagova.

The negative value of e in functions 4 and 6 indicates that the increase in viscosity due to oxide ions is greater in basic than in acidic melts.

The reproducibility (precision) of the data points is about ±1%. The accuracy is mainly limited by two factors. Firstly, it is possible that the melts contained small amounts of oxygen-containing species in addition to the oxide which was deliberately added; this would increase the observed viscosity, but probably by less than 1.5%. Also, we have assumed that the presence of oxide ions does not affect the density; if it does, this will affect the recorded viscosity. However, it is unlikely that the presence of the small amounts of oxide added would have a large effect on the density. It seems reasonable to suggest that this will lead to an error no greater than ±2% at an oxide ion concentration of 0.5 mol·kg^{-1}, and that this error will be proportional to the oxide ion concentration. The uncertainty in the viscosity due to the temperature variation of ±0.5 °C is relatively small.

Throughout this work we have assumed that the melt behaves as a Newtonian liquid over the range of shear rates employed. The structural units present are fairly small discrete ions, and no evidence has previously been presented for non-Newtonian behavior in molten salt systems of this kind (*2*, *3*).

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