It is seen that Boston's (4) and Fannin's (5) data are very near each other below ca. 350 °C and both data sets are slightly higher (ca. 0.2%) than our results in that range.

In the range 350–525 °C, outside the range of validity of any expressions of the literature it is seen that Fannin's (5) equation comes quite close to our measurements and that Boston's (4) and Sato's (7) extrapolated equations give too low and too high densities, respectively. Even around 600 °C Fannin's equation (5) reproduces our measurements within 0.5%.

At high temperatures (where Sato's equation (7) has its validity range) we note that our measurements fall in between Sato's and Fannin's extrapolated data. Sato's equation seems to give results which are 0.6% too high. (The precision of his equation is claimed to be ±0.3%.)

Conclusion

Our expression for the density of molten $NaAlCl_4$ as a function of temperature (model 4) deviates from the best data in the literature by less than 0.3%. Fannin's expression in the $AlCl_3$-rich (acidic) range of the NaCl–$AlCl_3$ system is probably very accurate (within 0.3%) and can presumably be extrapolated safely to higher temperatures (at least this is the case for the equimolar $NaAlCl_4$ composition). Sato's expression seems to give too high densities (0.6%) at least for the equimolar $NaAlCl_4$ composition, perhaps due to the volatility of $AlCl_3$ at high temperatures.

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Registry No. $NaAlCl_4$, 7784-16-9.

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Density of Sodium Tetrachloroaluminate Melts Containing Aluminum Chlorosulfides

Rolf W. Berg,* Hans A. Hjuler, and Niels J. Bjerrum*

The Technical University of Denmark, Chemistry Department A, DK-2800 Lyngby, Denmark

Liquid densities were measured for NaCl–$AlCl_3$ melts into which aluminum and sulfur in the molar ratio 2:3 had been dissolved. The densities were fitted by a polynomial function of temperature (range ca. 175 ≤ t ≤ 350 °C) and composition (ranges ca. 0.48 ≤ X_{NaCl} ≤ 0.52 and 0 ≤ $X_{Al_2S_3}$ ≤ 0.04).

Introduction

Recently it has been shown (1) that aluminum metal and elemental sulfur react in alkali tetrachloroaluminate melts forming aluminum chlorosulfides. These melts are colorless concentrated solutions, possibly containing solute ions like $[Al_nS_{n-1}Cl_{2n+2}]^{n-}$ and $[Al_nS_{n-1}Cl_{2n+2-m}]^{(n-m)-}$ ($n \geq 3$ and $m < n$). Such melts are of considerable interest, as they are formed during discharge of new galvanic cells based on the Al/S couple and a $NaAlCl_4$ electrolyte (2, 3).

The purpose of the present work was to determine an analytical expression for the densities of these melts, which are required for the calculation of solute concentrations and for estimations of battery weights. There are no previous measurements of densities of such solutions. In ref 1 we had to assume that the density of the solutions was approximately that of the NaCl–$AlCl_3$ solvent, which is known quite accurately (4–6).

Experimental Section

The densities were determined by the automated float method (7) (see also preceding paper (6)). NaCl and $AlCl_3$ of high purity were used (6). The aluminum consisted of carefully cleaned thin wires (Baker Analyzed Reagent, containing less than 0.05% Fe, 0.02% Cu, 0.05% Si, and 0.01% Ti, by weight). Sulfur of high purity was distilled before use. The chemicals were added in a dry glovebox to the quartz measuring cells which were sealed under vacuum and preequilibrated in a rocking furnace at ca. 300 °C for several days (until completion of reaction, characterized by the absence of aluminum metal and elemental sulfur).

Results and Discussion

The density as a function of temperature was measured for the nine compositions shown in Table I and in Figure 1. The aluminum and sulfur were weighed such that the molar ratio was as near to 2:3 as possible (the excess of either Al or S is indicated in Table I but ignored in the calculations of the mole fraction $X_{Al_2S_3}$).

The experimental "float" densities and the corresponding temperatures are given in Table II. After experiment 4-2 the floats were checked for etching by the melt during the five experimental runs, 3-0–4-2. On the average the densities of the floats decreased by 0.04%. This means that the accuracy

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Table I. Composition of the Nine Experimental Melts Used for the Density Determinations

	initial composition, mmol[a]				mole fraction[b]			
expt no.	NaCl	$AlCl_3$	"Al_2S_3"	total	X_{NaCl}	X_{AlCl_3}	$X_{Al_2S_3}$	excess of
1-0	145.96_2	145.97_5	0	291.93_7	0.5000	0.5000	0	
1-1[c]	169.88_9	145.97_5	11.967	327.83_2	0.5182	0.4453	0.0365	0.021 mmol of S
1-2	169.88_9	165.98_4	11.967	347.84_0	0.4884	0.4772	0.0344	0.021 mmol of S
3-0	91.65_9	91.65_9	0	183.31_8	0.5000	0.5000	0	
3-1	92.40_3	91.65_9	0.384	184.44_6	0.5010	0.4969	0.0021	0.015 mmol of Al
4-0	102.82_7	99.30_6	2.605	204.73_8	0.5022	0.4851	0.0127	0.002 mmol of Al
4-1	107.51_5	99.30_6	5.156	211.97_7	0.5072	0.4685	0.0243	0.018 mmol of S
4-2	111.97_2	99.30_6	7.809	219.08_7	0.5111	0.4533	0.0356	0.483 mmol of S
5-0	125.46_1	136.06_5	0	261.52_6	0.4797	0.5203	0	

[a] 1 mmol = 10^{-3} mol. [b] X_{NaCl} = mol of NaCl/(mol of NaCl + $AlCl_3$ + Al_2S_3), etc. [c] I.e., cell no. 1, with addition no. 1.

Table II. Experimental Densities and Temperatures[a] of the Molten $NaCl-AlCl_3-Al_2S_3$ System and for Comparison Densities Predicted from Table IV, Model 1

				density of floats, g cm^{-3}		predicted density
expt no.	X_{NaCl}	$X_{Al_2S_3}$	measd temp (SD),[b] °C	at 20 °C	at measd temp	(model 1), g cm^{-3}
1-0	0.5000	0.0000	165.6 (10)[c]	1.7096	1.7091	1.6998
1-0	0.5000	0.0000	299.8 (9)	1.6004	1.5996	1.6008
1-0	0.5000	0.0000	409.0 (10)	1.5181	1.5171	1.5202
1-0	0.5000	0.0000	511.5 (13)	1.4411	1.4399	1.4445
1-0	0.5000	0.0000	594.2 (15)	1.3823	1.3810	1.3834
1-1	0.5182	0.0365	220.8 (8)	1.7096	1.7090	1.7121
1-1	0.5182	0.0365	377.1 (8)	1.6004	1.5995	1.5968
1-1	0.5182	0.0365	500.6 (9)	1.5181	1.5169	1.5056
1-2	0.4884	0.0344	205.7 (11)	1.7906	1.7090	1.7068
1-2	0.4884	0.0344	350.6 (14)	1.6004	1.5995	1.5999
1-2	0.4884	0.0344	472.2 (20)	1.5181	1.5169	1.5101
3-0	0.5000	0.0000	195.4 (8)	1.6810	1.6805	1.6778
3-0	0.5000	0.0000	231.6 (9)	1.6538	1.6532	1.6511
3-0	0.5000	0.0000	245.3 (11)	1.6420	1.6413	1.6410
3-0	0.5000	0.0000	266.4 (10)	1.6257	1.6250	1.6254
3-1	0.5010	0.0021	198.6 (8)	1.6810	1.6805	1.6784
3-1	0.5010	0.0021	234.8 (9)	1.6538	1.6532	1.6517
3-1	0.5010	0.0021	249.2 (11)	1.6420	1.6413	1.6410
3-1	0.5010	0.0021	270.2 (10)	1.6257	1.6250	1.6255
4-0	0.5022	0.0127	175.6 (7)	1.7124	1.7120	1.7083
4-0	0.5022	0.0127	214.5 (10)	1.6810	1.6805	1.6796
4-0	0.5022	0.0127	251.0 (10)	1.6538	1.6531	1.6527
4-0	0.5022	0.0127	265.4 (12)	1.6420	1.6413	1.6420
4-0	0.5022	0.0127	287.4 (11)	1.6257	1.6250	1.6258
4-1	0.5072	0.0243	192.5 (7)	1.7124	1.7119	1.7119
4-1	0.5072	0.0243	232.6 (11)	1.6810	1.6804	1.6823
4-1	0.5072	0.0243	270.6 (12)	1.6538	1.6531	1.6543
4-1	0.5072	0.0243	285.2 (13)	1.6420	1.6412	1.6435
4-1	0.5072	0.0243	308.1 (12)	1.6257	1.6249	1.6266
4-2	0.5111	0.0356	209.2 (8)	1.7124[d]	1.7119[d]	1.7150
4-2	0.5111	0.0356	249.8 (11)	1.6810[d]	1.6804[d]	1.6851
4-2	0.5111	0.0356	289.5 (12)	1.6538[d]	1.6530[d]	1.6558
4-2	0.5111	0.0356	304.8 (14)	1.6420[d]	1.6411[d]	1.6445
4-2	0.5111	0.0356	328.2 (12)	1.6257	1.6249	1.6272
5-0	0.4797	0.0000	183.8 (8)	1.6827	1.6823	1.6812
5-0	0.4797	0.0000	193.8 (9)	1.6750	1.6745	1.6738
5-0	0.4797	0.0000	219.0 (10)	1.6529	1.6524	1.6552
5-0	0.4797	0.0000	258.8 (11)	1.6214	1.6208	1.6258

[a] Temperature scan rates: 10–50 °C h^{-1}. [b] SD = standard deviation. [c] I.e., 165.6 ± 1.0. [d] After the experiment 4-2, the densities of four floats were remeasured; at 20 °C they gave 1.7118, 1.6806, 1.6530, and 1.6410 g cm^{-3} and after correction for expansion at the measured temperatures 1.7112, 1.6799, 1.6523, and 1.6402 g cm^{-3}.

of the densities must be taken to be not better than ±0.001 g cm^{-3}. The etching probably occurred on all floats and also on the inside surfaces of the quartz cells. Hence, the melts must contain small amounts of dissolved SiO_2, presumably of the order of 0.05% by weight, assuming uniform etching of all internal quartz surfaces. In experiments 1-1 and 1-2 the etching was probably worse since these cells have been heated to higher temperatures. These cells probably were saturated with oxides according to the reactions (*8–10*) $SiO_2(s) \rightleftarrows SiO_2(dissolved)$, $SiO_2(s) + {}^4/_3AlCl_3(l) \rightleftarrows {}^2/_3Al_2O_3(dissolved) + SiCl_4(g)$, $Al_2O_3(s) \rightleftarrows Al_2O_3(dissolved)$, but the solubility of silica and alumina is believed to be rather small so that the density data obtained should still be close to the data valid for the pure $NaCl-AlCl_3-Al_2S_3$ system.

The density as a function of temperature for each experiment is plotted in Figure 2. As can be seen, there is in all cases a largely linear dependence. In Table III the obtained densities for each composition are given by the equation

$$\rho = A(X_{NaCl}, X_{Al_2S_3}) - B(X_{NaCl}, X_{Al_2S_3})(t - 175) \qquad (1)$$

where ρ is the density in g cm^{-3}, A and B are fitting parameters which depend on composition, and t is the temperature in °C. The uncertainty in the A parameter is smaller when the temperature dependence is based on 175 °C than when developed

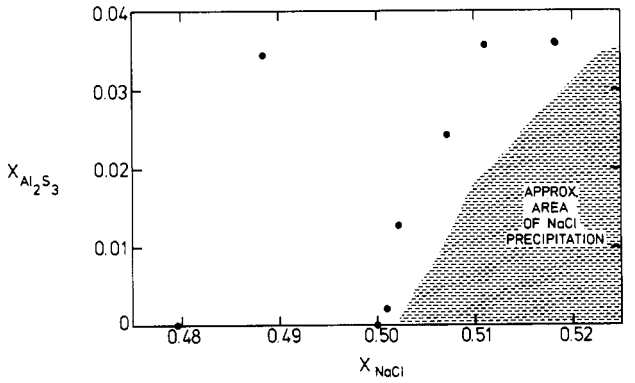

Figure 1. Graphical representation of the experimental compositions covered in this work.

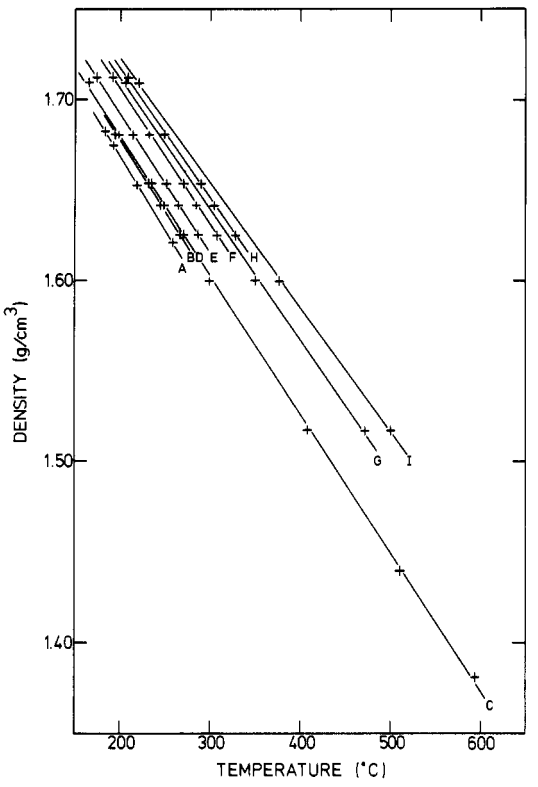

Figure 2. Densties of the nine compositions of the $NaCl-AlCl_3-Al_2S_3$ system as function of temperature: experiments (A) 5-0, (B) 3-0, (C) 1-0, (D) 3-1, (E) 4-0, (F) 4-1, (G) 1-2, (H) 4-2, and (I) 1-1.

from the usual 0 °C. This is, of course, of importance when the dependence on composition is being investigated.

A convenient way to represent the results is to combine the data obtained at different temperatures and compositions into one empirical equation which fits the observations as closely as possible.

Using standard least-squares regression methods (*11*), we tried general polynomial expressions like

$$\rho = a + bt + ct^2 + dX_{NaCl} + eX_{NaCl}^2 + fX_{Al_2S_3} + gX_{Al_2S_3}^2 \quad (2)$$

Analysis of regression models using different analytical equations like eq 2 to fit the data of Table II showed that terms in t^2 and $X_{Al_2S_3}^2$ were of no significance. The two most satisfactory analytical expressions and the corresponding parameters are shown in Table IV. The best expression, model 1, gives a slightly better fit but also has one parameter (D) more than model 2. The significance of D may be questioned but parameters A, B, C, and E are indispensable.

In order to test the validity of the expressions in Table IV, we compared predicted densities with the measurements on acidic and basic $NaCl-AlCl_3$ melts by Fannin et al. (*4*) and Sato et al. (*5*) ($X_{Al_2S_3} = 0$). The predicted densities show variations in temperature and composition similar to the observations and are generally accurate to within 0.01 g cm^{-3} or better, inside the range of validity of our equation.

Table III. Linear Density Equations of the Molten $NaCl-AlCl_3-Al_2S_3$ Experiments[a] Obtained by Least-Squares Regression Analysis

expt no.	A,[b] g cm^{-3}	B,[b] g cm^{-3} °C^{-1}	r^2 [c]	SD, g cm^{-3}
1-0	1.6984 (29)[d]	7.65 (10)	0.9994	0.0036
1-1	1.7398 (20)	6.87 (9)	0.9998	0.0017
1-2	1.7296 (43)	7.22 (21)	0.9991	0.0004
3-0	1.6968 (8)	7.83 (12)	0.9995	0.0006
3-1	1.6990 (6)	7.76 (9)	0.9997	0.0005
4-0	1.7120 (5)	7.77 (7)	0.9997	0.0006
4-1	1.7245 (7)	7.52 (8)	0.9997	0.0007
4-2	1.7361 (10)	7.29 (9)	0.9995	0.0009
5-0	1.6895 (6)	8.24 (12)	0.9995	0.0007

[a] For the measured temperature ranges. [b] $\rho = A(X_{NaCl}, X_{Al_2S_3}) - [B(X_{NaCl}, X_{Al_2S_3}) \times 10^{-4}](t - 175)$. [c] r^2 = coefficient of regression, defined as in ref *6*. [d] I.e., 1.6984 ± 0.0029.

Table IV. Coefficients in the Empirical Polynomial[a] for the Density of the Molten $NaCl-AlCl_3-Al_2S_3$ System[b]

	model 1	model 2
A	1.693 (1)	1.693 (1)
B	7.38 (6)	7.38 (6)
C	0.42 (8)	0.35 (7)
D	7.9 (5.0)	
E	1.17 (5)	1.21 (5)
SD, g cm^{-3}	0.0037	0.0038
r^2	0.9977	0.9975

[a] $\rho = A - (B \times 10^{-4})(t - 175) + C(X_{NaCl} - 0.5) + D(X_{NaCl} - 0.5)^2 + EX_{Al_2S_3}$ in g cm^{-3}, t in °C. [b] Temperature range 175-350 °C, X_{NaCl} range 0.48-0.52 and $X_{Al_2S_3}$ range 0-0.04.

In order to test the validity of the expressions in Table IV, we compared predicted densities with the measurements on acidic and basic $NaCl-AlCl_3$ melts by Fannin et al. (*4*) and Sato et al. (*5*) ($X_{Al_2S_3} = 0$). The predicted densities show variations in temperature and composition similar to the observations and are generally accurate to within 0.01 g cm^{-3} or better, inside the range of validity of our equation.

Registry No. $NaAlCl_4$, 7784-16-9; Al, 7429-90-5; S, 7704-34-9.

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