more soluble (see Figure 4) than the anhydrous one; also, its solubility/pH slope is much more pronounced. This last feature comes out, in part, from the lowering of the pK_{1A} value at increasing temperatures. Therefore, the higher occurrence in human stones (*3-5*, *8*) of the anhydrous crystals can be a consequence not only of their thermodynamic stability but also of the higher solubility of the hydrated ones. On the contrary, the nonpolar structure of UA, as well as the thermodynamic parameter values, clearly shows that a very minor role is played by solute-solvent interactions.

Registry No. Uric acid, 69-93-2.

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Density of Molten $NaAlCl_4$. A Reinvestigation

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The automated "float" method was used over a temperature range of 160–600 °C to measure liquid densities of $NaCl-AlCl_3$ mixtures containing 50 mol % $AlCl_3$. Linear and quadratic expressions in temperature were fitted to the data, which compare satisfactorily with the literature.

Introduction

Molten $NaCl-AlCl_3$ mixtures are important solvents and their densities have been often studied (*1-10*). The results of these studies are not entirely consistent. Most recently two extensive papers appeared (*5*, *7*) which seem to be quite reliable.

Fannin et al. (*5*), using dilatometric tubes, studied densities in the acidic range of the phase diagram (i.e., $AlCl_3$ mol % from 50 to 75) at low temperatures (from the melting points up to ca. 350 °C) and reported their results as a quadratic equation in temperature as well as mole fraction (nine parameters). Their results were in good agreement (within 1%) with Boston's (*4*) and Midorikawa's (*3*) older data.

Sato et al. (*7*), on the other hand, using a manometric method, studied the density of the $LiCl-NaCl-AlCl_3$ system in the basic range (i.e., less than 50 mol % $AlCl_3$) at high temperatures (from ca. 527 to ca. 927 °C). Their density data were reported as a linear function of temperature and quadratic function of composition (12 parameters).

By comparing these two equations and their ranges of validity, we see that the temperature range from ca. 350 to ca. 527 °C is excluded and both equations cover the equimolar $NaAlCl_4$ melt density only at their boundary of validity. Of more importance, quantitative calculations for $NaAlCl_4$ (see later) show that Fannin's equation (*5*) gives too low densities when extrapolated upward in temperature and that Sato's equation (*7*) gives too low densities when extrapolated downward in temperature, relative to each other. This means that the curvature of the density dependence on temperature is not properly accounted for, or it means that one or another of the two equations is not correct for the $NaAlCl_4$ melt.

The present investigation was performed in order to find a single temperature expression for the density of the equimolar $NaCl-AlCl_3$ melt and at the same time to test the validity of the equations of Fannin (*5*) and Sato (*7*).

Table I. Experimental Densities and Temperatures of $NaAlCl_4$ Melts

densities of floats, g cm^{-3}		measd temp at the indicated mole fraction, °C	
at 25 °C	at measd temp	$X_{NaCl} = 0.4999_8$ [b]	$X_{NaCl} = 0.5000_2$ [c]
1.709 60	1.709 14	165.6 (10)[a]	
1.681 04	1.680 51		195.4 (8)
1.653 82	1.653 20		231.6 (9)
1.641 96	1.641 30		245.3 (11)
1.625 75	1.625 05		266.4 (10)
1.600 40	1.599 62	299.8 (9)	
1.518 10	1.517 09	409.0 (10)	
1.441 07	1.439 87	511.5 (13)	
1.382 30	1.380 96	594.2 (15)	

[a] I.e., 165.6 ± 1.0 °C. [b] Scan rate = 50 °C h^{-1}. [c] Scan rate = 12 °C h^{-1}.

Experimental Section

The densities were measured by the automated float method (*11*, *12*) with a new microprocessor controlling/registering unit constructed in our laboratory. The method is based on magnetic detection of quartz floats with iron cores as they pass a differential transformer. The idea is that the temperature and hence the density of the melt (placed in a long tube together with the floats) are increased or decreased gradually. The density of the quartz floats does not change much with temperature, and, if the difference in density between floats and melt originally is small, the floats will consequently either sink or float at a given temperature. Floats of different densities were made by sealing small weights of iron (50–300 mg) into small pieces of quartz tubes (outside diameter 6 mm and length 20–30 mm). The densities at 20 °C of these floats were obtained by the Archimedian method by weighing the floats in air and in water and correcting for the buoyancy of the air.

The furnace and its regulation have been described in detail previously in connection with the introduction of the "automated float method" (*11*). Passage temperatures were detected by

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Table II. Results of Least-Squares Regression Fitting of a General Equation $\rho = A - (B \times 10^{-4})(t - t_0) + (C \times 10^{-8})(t - t_0)^2$ to the Data in Table I[a]

	constraints	A, g cm^{-3}	B, g cm^{-3} °C^{-1}	C, g cm^{-3} °C^{-2}	SD, g cm^{-3}	r^2 [b]
model 1	$t_0 = 0$, $C = 0$	1.8294 (23)[c]	7.59 (7)		0.0028	0.999 46
model 2	$t_0 = 0$	1.8463 (41)	8.66 (25)	14 (3)	0.0015	0.999 87
model 3	$t_0 = 175$ °C, $C = 0$	1.6964 (14)	7.60 (7)		0.0028	0.999 46
model 4	$t_0 = 175$ °C	1.6991 (10)	8.17 (14)	14 (3)	0.0015	0.999 87

[a] ρ is the density of molten NaAlCl$_4$ in g cm^{-3} and t is the temperature in °C. [b] Coefficient of determination $r^2 = [\Sigma(t - \bar{t})(\rho - \bar{\rho})]^2 / [\Sigma(t - \bar{t})^2 \Sigma(\rho - \bar{\rho})^2]$; $\bar{x} = \Sigma x/n$; n = number of points $(t,\rho) = 9$. [c] I.e., 1.8294 ± 0.0023.

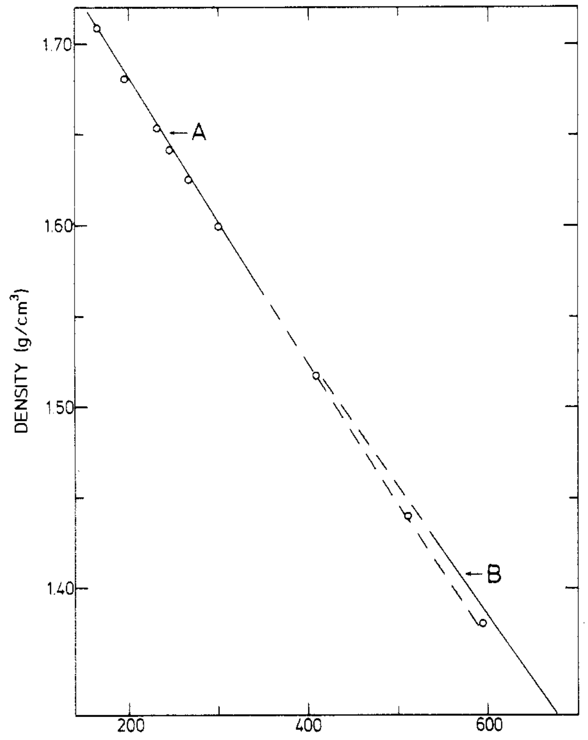

Figure 1. Density of the NaAlCl$_4$ melt vs. temperature: (O) this work. The low/high temperature curves (full lines) are due to (A) Fannin et al. (*5*) and (B) Sato et al. (*7*). The dashed lines show extrapolated values.

Table III. Density of Molten NaAlCl$_4$ as a Function of Temperature

temp, °C	density of the equimolar NaAlCl$_4$ melt, g cm^{-3}				
	measd (this work)	calcd			
		model 4 (this work)	ref *4*[a]	ref *5*[b]	ref *7*[c]
165.6	1.7091	1.7068	1.7102	1.7095	1.6940
175.0		1.6991	1.7025	1.7019	1.6873
195.4	1.6805	1.6825	1.6858	1.6853	1.6728
200.0	1.675[d]	1.6787	1.6820	1.6816	1.6696
231.6	1.6532	1.6533	1.6561	1.6562	1.6471
245.3	1.6413	1.6424	1.6449	1.6452	1.6374
250.0		1.6386	1.6410	1.6414	1.6341
266.4	1.6251	1.6256	1.6276	1.6283	1.6224
299.8	1.5996	1.5993	1.6002	1.6017	1.5987
300.0		1.5992	1.6000	1.6016	1.5986
350.0		1.5604	1.5590	1.5621	1.5631
400.0		1.5224	1.5180	1.5231	1.5276
409.0	1.5171	1.5156	1.5106	1.5161	1.5212
450.0		1.4850	1.4770	1.4844	1.4921
500.0		1.4484	1.4360	1.4462	1.4566
511.5	1.4399	1.4401	1.4266	1.4374	1.4485
550.0		1.4124	1.3950	1.4083	1.4211
594.2	1.3810	1.3813	1.3588	1.3751	1.3898
600.0		1.3772	1.3540	1.3708	1.3857
650		1.3426	1.3130	1.3337	1.3502
700.0	1.335[e]	1.3088	1.2720	1.2970	1.3147

[a] $\rho = \alpha - \beta t$; $\alpha \simeq 1.846$ and $\beta \simeq 8.2 \times 10^{-4}$. t = temperature in °C. Parameters obtained by extrapolation to 50 mol % AlCl$_3$ (*4*). [b] $\rho = \alpha - \beta t + \gamma t^2$; $\alpha = 1.84635$; $\beta = 8.3925 \times 10^{-4}$ and $\gamma = 7.775 \times 10^{-8}$. t = temperature in °C. α, β, and γ calculated by using a 50 mol % AlCl$_3$ composition and formulas in ref *5*. [c] $\rho = \alpha - \beta t$; $\alpha = 1.81151$ and $\beta = 7.0975 \times 10^{-4}$. t = temperature in °C. α and β calculated by using 50 mol % AlCl$_3$ and no LiCl and converting to °C by using $t = T - 273.15$; T = temperature in Kelvin (*7*). [d] Value from ref *9*. [e] Value obtained from ref *6* and *8*, by calculation or extrapolation. Probably inaccurate due to loss of AlCl$_3$.

Table IV. Comparison of the Density vs. Temperature Expressions $\rho = A - (B \times 10^{-4})t + (C \times 10^{-8})t^2$

	A, g cm^{-3}	B, g cm^{-3} °C^{-1}	C, g cm^{-3} °C^{-2}
our model 2	1.846 29	8.657	13.98
ref *3*	1.848	8.12	
ref *4*	1.846	8.2	
ref *5*	1.846 35	8.3925	7.75
ref *7*	1.811 51	7.0975	

platinum resistance thermometers (from Degussa) which were calibrated at the freezing points of pure tin and water within ±0.5 °C. The measured temperatures are probably correct to within ±0.7 °C (the regulation of the furnace is approximately ±0.1 °C). NaCl (analytical reagent from Riedel-de Haën) was purified by passing HCl gas first over the solid and then through the melt, flushing with pure N$_2$, and finally filtering the melt. AlCl$_3$ was made from pure metal (99.999%) and HCl gas (made by reaction between hydrochloric acid and sulfuric acid) and further purified by distillation over Al foil and a NaCl-AlCl$_3$ phase at 200 °C. Handling of the solid salts was performed as described earlier (*13*).

Results and Discussion

The experimental densities and temperatures of the NaCl-AlCl$_3$ system are given in Table I. The densities of the floats used were calculated on the basis of eight determinations at room temperature and corrected for the thermal expansion of quartz at the measured temperature. The standard deviations of the measured temperatures are calculated in accordance with the procedure described previously (*11*).

The data in Table I were then used to fix the parameters A, B, and C in the density expression $\rho = A + B(t - t_0) + C(t - t_0)^2$; ρ = density and t = temperature. The parameters A, B, C, and t_0 are shown in Table II (models 1-4). In two of the models C and t_0 were fixed to zero in order to compare with the literature equations. The standard deviations of A, B, and C were calculated without taking into account the precision of ρ and t. Hence, the precision in A, B, and C is overestimated in Table II. It can be seen that the parameters A and B are much better determined when t_0 = 175 °C is used. Furthermore, inclusion of the parameter C in a model gives a better fit (the coefficient of determination r^2 is closer to 1), and the conclusion is that model 4 is the best one to use, at least among these four models.

Comparison with Literature

The density expressions from the literature and our results are compared in Tables III and IV and in Figure 1.

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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

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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. $175 \leq t \leq 350$ °C) and composition (ranges ca. $0.48 \leq X_{NaCl} \leq 0.52$ and $0 \leq X_{Al_2S_3} \leq 0.04$).

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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