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Published in:
Electrochemical Society. Journal

Link to article, DOI:
10.1149/1.2100634

Publication date:
1987

Document Version
Publisher's PDF, also known as Version of record

Citation (APA):
Zachariassen, K., Berg, R. W., Bjerrum, N., & Barner, J. H. V. (1987). Potentiometric Investigation of the Oxide Behavior in NaCl-AlCl3 Melts at 175°C. Electrochemical Society. Journal, 134(5), 1153-1157. DOI: 10.1149/1.2100634

Potentiometric Investigation of the Oxide Behavior in NaCl-AlCl$_3$ Melts at 175°C

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ABSTRACT

By potentiometric measurements in concentration cells with chlorine/chloride or aluminum electrodes, it is shown that the experimental average chloride coordination number of AlO^+ is 1.01 corresponding to the formation of a complex $(AlOCl)_n(AlCl_4^-)_m$ (with $n = 2$ as the most likely value according to recent cryoscopic measurements) in basic, neutral, and weakly acidic NaCl-AlCl$_3$ melts at 175°C ($1.128 < p\text{Cl} < 4.25$). In more acidic melts ($4.25 < p\text{Cl} < 5.0$; $0.503 < X'_{AlCl_3} < 0.516$), the experimental average coordination number decreases. The measurements in this pCl range can, based on a least squares fitting procedure, be explained satisfactorily by the equilibrium

$$(AlOCl)_2(AlCl_4^-)_m \rightleftarrows (AlO^+)_2(AlCl_4^-)_m + 2Cl^-$$

with m = 4, 2, and 0. For these three values of m pK-values between 9.5 and 9.9 are found for the equilibrium. From a statistical point of view solvated (m = 4 and 2) and nonsolvated (m = 0) versions of the equilibrium are equally good. The nonsolvated possibility is not considered to be a realistic one for structural reasons. Proposed structures for a number of solvated oxochloro species of the type $Al_4O_2Cl_8$ and $Al_6O_2Cl_{16}^{2-}$ are given.

The behavior of oxide ions in NaCl-AlCl$_3$ melts has been the subject of several investigations (1-6). The problem is important since oxide contaminations are responsible for oxide coatings on aluminum cathodes and consumption of carbon anodes in electrolytic production of aluminum from melts (7) containing aluminum chloride.

In the field of fundamental chemistry, oxide contaminations can lead to misinterpretations, *e.g.*, in dilute chloroaluminate solutions, since oxochloro complexes rather than chloro complexes are sometimes formed (8).

There has been some dispute as to whether $AlOCl_2^-$ (or solvated forms thereof) exists in basic NaCl-AlCl$_3$ melts, whereas AlOCl has been commonly accepted as the aluminum oxochloro species present in neutral and moderately acidic melts (1-6).

In some previous works (1-3, 5) oxides have been added in such a way that foreign cations were introduced into the NaCl-AlCl$_3$ melts (*e.g.*, $BaCO_3$ and $Ba(OH)_2$ as oxide donors). Also, a nickel electrode was assumed to be an oxide indicator electrode (2). It was later shown that this electrode was in fact a pCl indicator in NaCl-AlCl$_3$ melts containing oxide at 175°C, (3, 5) and that Ba^{2+} ions had acidic properties relative to chloride ions in basic NaCl-AlCl$_3$ melts (9). As a result, Taulelle *et al.* (5) concluded that the only aluminumoxychloro species present in the pCl-range 1.13-4.25 (molar units) was AlOCl. Recently, cryoscopic measurements by Berg *et. al.* (6) have shown that AlOCl is dimeric in nearly neutral NaCl-AlCl$_3$ melts, *i.e.*, exists as $(AlOCl)_2(AlCl_4^-)_m$ where m is an unknown number, probably greater than zero.

We have previously (4) potentiometrically investigated the oxide behavior in NaCl-AlCl$_3$ melts, but at two compositions only. We found that the chloride/oxide exchange number, (*i.e.*, chloride ions liberated for each oxide ion added) was 2.51 for a basic melt ($p\text{Cl} = 1.29$) and for an acidic melt 2.90 ($p\text{Cl} = 4.59$). These measurements were, however, performed with electrode cells equipped with a ceramic material frit (main components: Al_2O_3, SiO_2, and K_2O; 47.4, 45.8, and 2.9 weight percent, respectively), which was not entirely stable towards attack by NaCl-AlCl$_3$ melts (especially when acidic), and the proper composition correction procedure described later in this article was not applied.

The aim of the present investigation was to perform potentiometric measurements in acidic NaCl-AlCl$_3$ melts with pCl higher than 4.25, where no data exist, and with the discussion concerning the possible existence of $AlOCl_2^-$ in mind, we also decided to reinvestigate the basic melts using Na_2O and AlOCl as oxide donors (which contribute no foreign cation).

Experimental

NaCl (analytical grade from Riedel-de Haën) was purified by passing first HCl gas and then dry N_2 through the molten salt, using the procedure described previously (4, 10). AlCl$_3$ was made from molten aluminum metal (99.999%) and dry HCl-gas by the usual method (11). NaAlCl$_4$ was prepared by reacting equal amounts of NaCl and AlCl$_3$ for 24h at 200°C. AlOCl was made according to the method given by Schäfer (12), in which V_2O_5 is reacted with excess AlCl$_3$. As in previous work (4) we used commercial Na_2O from Merck AG. All handling of the chemicals was performed in a nitrogen atmosphere dry box (water content less than 10 ppm). The chemicals were always kept under vacuum in sealed borosilicate ampuls.

The dual-compartment concentration cells used for the potentiometric measurements were of a construction developed by von Barner and Bjerrum (13) modified as described below: The separation of the measuring and reference compartments was made by a sintered borosilicate disk (the ceramic pins from Radiometer used previously (4, 11) corroded in oxide containing melts, especially in the acidic range). Before filling the cells, the porosity of the disk was tested with a 0.10*M* aqueous KCl solution at room temperature in both electrode compartments. A resistance of between 20 and 80 kΩ was considered sufficient. Furthermore, the cells used in this work were without a pressure leveling tube between the two compartments. This was a necessity because of the AlCl$_3$ vapor pressure difference between the two compartments when investigating acidic melts.

The electrodes were either of pure aluminum or of glassy carbon in both compartments (*i.e.*, aluminum or chlorine-chloride cells). The aluminum cells were sealed under vacuum and the chlorine-chloride cells under 1/2 atm 99.9% pure Cl_2 (at room temperature). The furnaces and other types of equipment used have been described previously (13-15).

General Considerations and Definitions

The formality C′ of a component is defined as the initially weighed molar amount divided by the volume of the molten mixture in liters. The pCl and equilibrium constants in this work are given in molar units unless otherwise stated. For the NaCl-AlCl$_3$ solvent, the density expression by Berg, Hjuler, and Bjerrum (16) and a three equilibria model by Fehrmann *et al.* (4) were used to calculate concentrations of the aluminum-chloro species

$$2AlCl_4^- = Al_2Cl_7^- + Cl^- \qquad [1]$$

$$3Al_2Cl_7^- = 2Al_3Cl_{10}^- + Cl^- \qquad [2]$$

$$2Al_3Cl_{10}^- = 3Al_2Cl_6 + 2Cl^- \qquad [3]$$

The equilibrium constants at 175°C were (4): $pK_1 = 7.052$, $pK_2 = 6.9$, $pK_3 = 14.0$. In the calculations on the oxochloro complex equilibria it is of no importance whether a three or two equilibria model are used for the solvent, since they give equally good mathematical descriptions (4). The reference melt ($NaAlCl_4$ saturated with NaCl) was assumed to have a pCl value of 1.128 at 175°C taken from the same work (4).

The experimental average coordination number $\bar{n}_{AlO^+}$ for the AlO^+ unit is defined as

$$\bar{n}_{AlO^+} = \frac{3C'_{AlCl_3} + C'_{NaCl} + C'_{AlOCl} - 4[AlCl_4^-] - 7[Al_2Cl_7^-] - 10[Al_3Cl_{10}^-] - 6[Al_2Cl_6] - [Cl^-]}{C'_{AlOCl}} \qquad [4]$$

where C'_{AlCl_3} and C'_{AlOCl} are corrected for the presence of AlOCl in the $AlCl_3$.

As mentioned previously, it is of utmost importance to know the oxide content of the NaCl-$AlCl_3$ solvent. This was calculated in the following way: Equal molar amounts of NaCl and $AlCl_3$ were reacted as described in the Experimental section. The potentiometric cell was filled with the $NaAlCl_4$ obtained, and the chloride concentration was determined from the Nernst equation (13).

For an equimolar melt free of oxide, $[Cl^-]$ should be equal to $[Al_2Cl_7^-]$ (due to Eq. [1]). By the potentiometric measurements on actual melts of equimolar composition (according to the weighings) it was normally found that $[Cl^-]$ was greater than $[Al_2Cl_7^-]$. A value of $[Cl^-] - [Al_2Cl_7^-]$ greater than zero would arise from an AlOCl contamination of the $AlCl_3$. As we shall see later, AlOCl does not react with chloride in the basic region and the region around the neutral point ($1.28 < pCl < 4.25$). Therefore, the difference $[Cl^-] - [Al_2Cl_7^-]$ corresponds to the fraction of the originally weighed $AlCl_3$ that was actually AlOCl. The amount of AlOCl, W_{AlOCl}, can be calculated as

$$W_{AlOCl} = ([Cl^-] - [Al_2Cl_7^-])/ \times V \times M_{AlCl_3} \qquad [5]$$

where V is the volume of the melt and M_{AlCl_3} is the molar weight of aluminum chloride. Typically, $[Cl^-] - [Al_2Cl_7^-]$ was around 0.03*M*. Hence, nearly half of the AlOCl present in the samples originated from the $NaAlCl_4$ solvent, whereas the rest of the oxide was added as AlOCl or Na_2O. In the evaluation of the measurements it is assumed that the reaction

$$Na_2O + AlCl_3 \rightarrow 2NaCl + AlOCl \qquad [6]$$

proceeds quantitatively [in the CsCl-$AlCl_3$ system it has been shown spectroscopically that the kind of oxide source is unimportant (17)].

Two kinds of mole fractions are of use: X_i (i = $AlCl_3$, NaCl, AlOCl) is the usual mole fraction, whereas X'_i is the binary mole fraction within the NaCl-$AlCl_3$ solvent only (i = NaCl, $AlCl_3$). The latter mole fraction is useful when comparing to cryoscopic results (6).

Results and Discussion

The measured equilibrium voltages of the cells are listed in Table I as a function of the compositions. From these values the pCl and the experimental average coordination numbers for AlO^+ were calculated (Eq. [4]). The calculated results are given as circles in Fig. 1. It is obvious that the experimental average coordination number $\bar{n}_{AlO^+}$ is one in the pCl range from 1.128 to 4.25, which excludes the formation of $AlOCl_2^-$ even in the most basic range in accordance also with conclusions reached by Taulelle *et al.* (5). From the ten first compositions in Table I the experimental value can be calculated to be 1.01 ± 0.05 assuming that $\bar{n}_{AlO^+}$ is constant in that pCl range. The experimental variance of $\bar{n}_{AlO^+}$ was $2.59 \cdot 10^{-3}$.

As reported previously (6), the results obtained were quite independent of whether chlorine/chloride electrodes ($Cl_2 + 2e^- \rightleftarrows 2Cl^-$) or aluminum electrodes ($AlCl_4^- + 3e^- \rightleftarrows Al + 4Cl^-$) were used. The fact that the average experimental AlO^+ chloride coordination number is one reflects the occurrence in the melt of species of the general formula $(AlOCl)_n \cdot (AlCl_4^-)_m$, where n and m are unknown integers. Previously, Berg *et al.* (6) found that one cryoscopically active "particle" was formed for each two AlOCl "particles" added to near neutral NaCl-$AlCl_3$ melts. They concluded that the most likely value of n was 2 in this pCl range. The $(AlOCl)_2$ species thus found is probably solvated by $AlCl_4^-$ forming $(AlOCl)_2(AlCl_4^-)_m$. A value of m = 1 corresponding to the species (I, Fig. 2) has previously been suggested (6), and recently two salts, containing the ion $Al_4O_2Cl_{10}^{2-}$ corresponding to m = 2 have been characterized by x-ray crystal structure determinations (18, 19). The structure of this ion is shown as (II). These two kinds of oxide species are closely related via uptake/release of an $AlCl_4^-$-ion, see (III).

Unfortunately, the cryoscopic method offers no possibility for distinguishing between nonsolvated (m = 0) or solvated forms (m > 0) of $(AlOCl)_2(AlCl_4^-)_m$. Furthermore, no conclusion can be drawn from the potentiometric measurements in the pCl range 1.128-4.25 regarding the solvation problem because of the low solubility of AlOCl in the NaCl-$AlCl_3$ melts. Nevertheless, we think that solvation is probable and that (I) and /or (II) are very likely structures. However, other possibilities exist, *e.g.*, for $Al_3O_2Cl_6^-$ and $Al_4O_2Cl_{10}^{2-}$ three and seven isomeric forms, respectively, can be imagined, etc.

In acidic melts, for pCl values > 4.25 or $X'_{AlCl_3} > 0.503$, the average experimental coordination number $\bar{n}_{AlO^+}$ drops below one (Fig. 1). Hence, at least one new species must be formed in that range. It is likely that this species contains the AlO^+ unit. The AlO^+ unit is known from the ion $Al_3OCl_8^-$, *i.e.*, $(AlO^+)(AlCl_4^-)_2$, see (IV), which has recently been identified in a crystal structure (19).

We have previously (15) developed a computer program which by means of a nonlinear regression procedure (see Appendix) and from initially guessed *pK* values is able to find optimized equilibrium constants for different sets of equilibria.

Table I. Values of cell potentials[a] and mole fractions[b] for NaCl-$AlCl_3$-AlOCl melts at 175°C

$-\Delta E$ (mV)	Oxide source	X_{NaCl}	X_{AlCl_3}	X_{AlOCl}
6.70	Na_2O	0.4979_9	0.4948_8	0.0071_3
9.26	Na_2O	0.4994_4	0.4961_5	0.0044_2
14.31	Na_2O	0.4988_5	0.4958_3	0.0053_2
18.11	Na_2O	0.5001_7	0.4976_4	0.0021_8
22.63	Na_2O	0.4985_8	0.4961_0	0.0053_1
36.20[c]	Na_2O	0.4989_8	0.4973_7	0.0036_5
80.90[c]	AlOCl	0.4997_1	0.4991_2	0.0011_7
116.03	Na_2O	0.4970_7	0.4972_3	0.0057_0
249.20	Na_2O	0.4967_0	0.4999_0	0.0034_0
260.45	Na_2O	0.4957_2	0.4998_5	0.0043_8
290.93	Na_2O	0.4933_0	0.5033_2	0.0033_7
292.00	Na_2O	0.4942_2	0.5043_0	0.0014_9
297.79	AlOCl	0.4934_3	0.5052_9	0.0012_8
311.43	Na_2O	0.4909_1	0.5076_2	0.0014_8
315.64	AlOCl	0.4901_2	0.5086_1	0.0012_7
326.68	AlOCl	0.4865_6	0.5114_2	0.0020_2
344.53	AlOCl	0.4799_5	0.5180_6	0.0019_9

[a] Reference electrode $NaAlCl_4$ melt saturated with NaCl.

[b] Corrected mole fractions. X_{AlCl_3} and X_{AlOCl} are corrected for AlOCl present in the weighed $AlCl_3$.

[c] Measured in Al electrode cell. The value has been multiplied with 3/4 to compare with chlorine/chloride cell values.

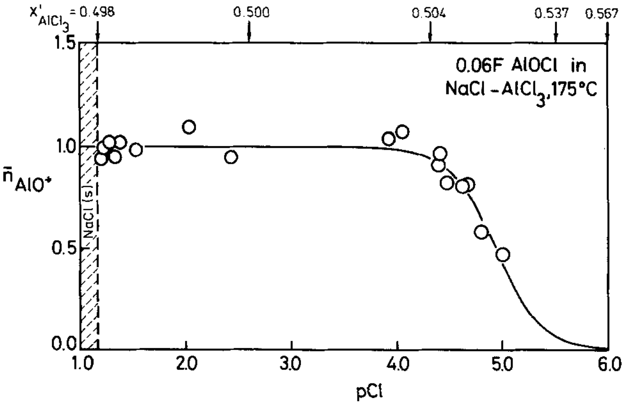

Fig. 1. Average experimental chloride coordination number n for AlO^+ in NaCl-AlCl$_3$ solutions at 175°C as a function of chloroacidity (pCl, molar scale) or mole fraction (X'_{AlCl_3}, nonlinear scale), compared with calculated curve for the reaction

$$(AlOCl)_2 \rightleftarrows (AlO^+)_2 + 2Cl^-$$

0.06 *F* AlOCl (total oxide level including the background oxide contamination). The vertical dashed line shows the limit due to saturation with NaCl.

Consequently, using the seven last acidic compositions in Table I, we tested, as described in detail in the Appendix, the simple nonsolvated models involving $(AlOCl)_n$ and $(AlO^+)_p$, *i.e.*, the equilibria models in Eq. [7]

$$q(AlOCl)_n \rightleftarrows \frac{q \cdot n}{p}(AlO^+)_p + q \cdot nCl^- \qquad [7]$$

Since we have fairly dilute solutions of AlOCl, it is unlikely that we are dealing with complexes with more than two AlO^+-units linked together. This restriction gives the four models shown in Table II.

The discrimination between these four nonsolvated models is performed by means of an F-test in which the minimum variance for each model is compared to the experimental variance (see Appendix). Models 2 and 3 have a significance of more than 90% and may thus be considered acceptable explanations of our seven measurements in the most acidic range. The following consideration may help when it comes to distinguishing between these two models. Since AlOCl will probably also be dimeric in the acidic range, it seems as if model 3 is more likely than model 2. Hence, having left out solvation, the conclusion is that the best way to account for the behavior of oxide in quite acidic NaCl-AlCl$_3$ melts ($4.25 < pCl < 5.0$) probably will be by the equilibrium

$$(AlOCl)_2 \rightleftarrows (AlO^+)_2 + 2Cl^- \qquad [8]$$

The pK-value in molar units was found to be 9.88 at 175°C.

As for $(AlOCl)_n$ in the near neutral range, it is from a structural point of view not likely that the $(AlO^+)_p$ species exist in nonsolvated forms in the acidic ($pCl > 4.25$) melts. It is more likely, we think, that species of the general formula $(AlO^+)_p(AlCl_4^-)_s$ occur in this range; p and s are integers.

Table II. *pK*-values and variances for different nonsolvated models for the oxochloro complex formation of Al(III) in acidic NaCl-AlCl$_3$ melts at 175°C[a]

Model number	Equilibrium	pK	Variances	F_{model}[b]
1	$AlOCl \rightleftarrows AlO^+ + Cl^-$	5.14(8)	$8.5 \cdot 10^{-3}$	3.3
2	$2AlOCl \rightleftarrows (AlO^+)_2 + 2Cl^-$	8.50(7)	$3.2 \cdot 10^{-3}$	1.2
3	$(AlOCl)_2 \rightleftarrows (AlO^+)_2 + 2Cl^-$	9.88(6)	$2.8 \cdot 10^{-3}$	1.1
4	$(AlOCl)_2 \rightleftarrows 2AlO^+ + 2Cl^-$	13.60(13)	$11.3 \cdot 10^{-3}$	4.4

[a] $pK = -\log K$, where K is the molar concentration equilibrium constant with the standard error on last digit indicated inside parentheses.

[b] F_{model} = variance of model (7 points) divided by the estimated experimental variance $2.59 \cdot 10^{-3}$ (10 points). The 90% significance level value of F, $F_{0.10}(6.9)$, is 2.55.

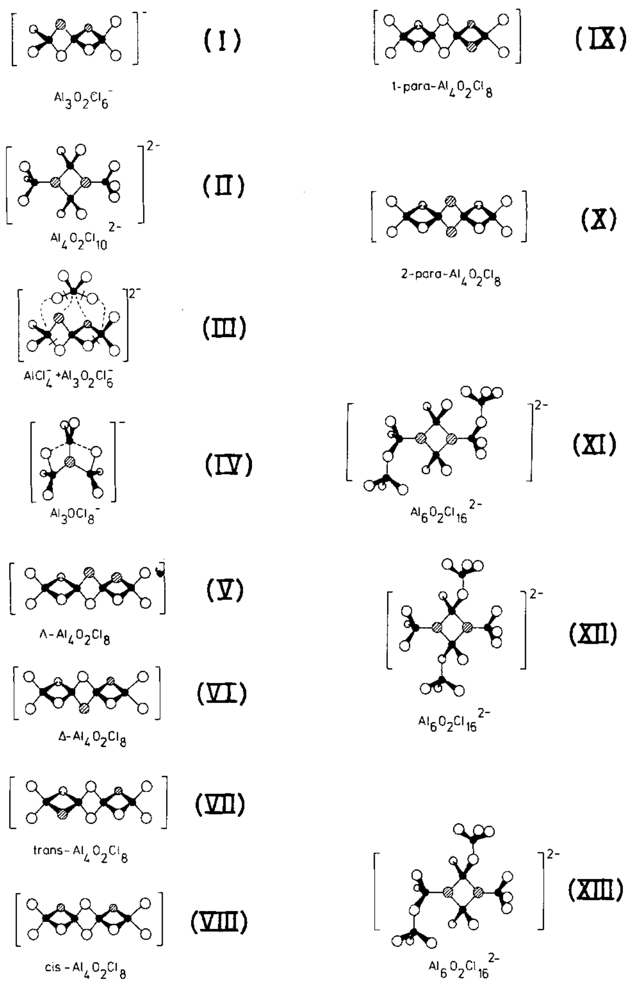

Fig. 2

This leads to equilibria of the general type

$$q(AlOCl)_n(AlCl_4^-)_m + \frac{q}{p}(n \cdot s - p \cdot m)AlCl_4^- \rightleftarrows \frac{q \cdot n}{p}(AlO^+)_p(AlCl_4^-)_s + q \cdot nCl^- \qquad [9]$$

Our present computer program is only capable of calculating equilibria with $n \cdot s = p \cdot m$, *i.e.*, equilibria in which the number of $AlCl_4^-$ solvent ions bound to oxochloro species is restricted to be the same on both sides of the equilibrium arrows. Of course, models with a different number of bound solvent ions will be possible as well, but these cannot be treated in the available program.

The results of the computations on the solvated models are shown in Table III. In order to be able to compare with the nonsolvated models investigated above (Table II), only solvated models with n and p being 1 or 2 were taken into consideration.

The F-tests show that a number of models are not able to explain the measurements on a 90% significance level. This is the case for models 1a, b, 4a, and b, for which the corresponding nonsolvated models (1 and 4 in Table II) also gave poor fits. Among the models 2a, b, 3a, b, and c, only models 2a, 3b, and c are able to explain the measurements on a 90% significance level.

However, model 2a, involving an oxomonomeric species in the near neutral pCl range where $(AlOCl)_n$ is stable (*i.e.*, when Eq. [9] is displaced to the left), is not able to explain the previous $n = 2$ cryoscopic evidence (6). Models 3b and c, on the other hand, are both perfectly fit to do this. Model 3b has the lowest variance of all models taken into account in this work. The pK-value for this

Table III. *pK*-values and variances for different solvated[a] models for the oxochloro complex formation of Al(III) in acidic NaCl-$AlCl_3$ melts at 175°C

Model number	Equilibrium	*pK*	Variance	F_{model}[b]
1a	$(AlOCl)(AlCl_4^-) \rightleftarrows (AlO^+)(AlCl_4^-) + Cl^-$	4.99(9)	$13 \cdot 10^{-3}$	5.0
1b	$(AlOCl)(AlCl_4^-)_2 \rightleftarrows (AlO^+)(AlCl_4^-)_2 + Cl^-$	4.85(10)	$17 \cdot 10^{-3}$	6.7
2a	$2(AlOCl)(AlCl_4^-) \rightleftarrows (AlO^+)_2(AlCl_4^-)_2 + 2Cl^-$	8.28(9)	$5.4 \cdot 10^{-3}$	2.0
2b	$2(AlOCl)(AlCl_4^-)_2 \rightleftarrows (AlO^+)_2(AlCl_4^-)_4 + 2Cl^-$	8.08(11)	$9.6 \cdot 10^{-3}$	3.7
3a	$(AlOCl)_2(AlCl_4^-) \rightleftarrows (AlO^+)_2(AlCl_4^-) + 2Cl^-$	9.75(5)	$9.8 \cdot 10^{-3}$	3.8
3b	$(AlOCl)_2(AlCl_4^-)_2 \rightleftarrows (AlO^+)_2(AlCl_4^-)_2 + 2Cl^-$	9.69(5)	$2.46 \cdot 10^{-3}$	0.95
3c	$(AlOCl)_2(AlCl_4^-)_4 \rightleftarrows (AlO^+)_2(AlCl_4^-)_4 + 2Cl^-$	9.52(5)	$3.3 \cdot 10^{-3}$	1.3
4a	$(AlOCl)_2(AlCl_4^-)_2 \rightleftarrows 2(AlO^+)(AlCl_4^-) + 2Cl^-$	13.17(12)	$15 \cdot 10^{-3}$	5.6
4b	$(AlOCl)_2(AlCl_4^-)_4 \rightleftarrows 2(AlO^+)(AlCl_4^-)_2 + 2Cl^-$	13.25(10)	$16 \cdot 10^{-3}$	6.3

[a] Solvated with $AlCl_4^-$.

[b] F_{model} = variance of model divided by the estimated experimental variance, $2.59 \cdot 10^{-3}$, obtained for the nonsolvated AlOCl form. The experimental variances for the solvated forms of AlOCl do not differ markedly from this value. The 90% significance level value of F, $F_{0.10}(6.9)$ is 2.55.

model is 9.69 which is hardly different from the 9.88 value of the corresponding nonsolvated equilibrium (Eq. [8]). The "acidic" species of model 3b $(AlO^+)_2(AlCl_4^-)_2 = Al_4O_2Cl_8$ can be visualized in the 6 isomers shown as (V)-(X). Acidic species corresponding to the one of model 3c ($Al_6O_2Cl_{16}^{2-}$) has been proposed by Rytter (21), see XI, but other isomers can be imagined, *e.g.*, XII and XIII.

Support for the formation of $Al_4O_2Cl_8$ molecules should be obtainable from mass spectroscopy of the gas phase over the melts. Indeed, an $Al_4O_2Cl_7^+$ fraction has been identified previously by mass spectroscopy (20).

As mentioned, our program unfortunately is not capable of calculating on models with differences in numbers of associated solvent ions on the two sides of the equilibria.

To do this a new algorithm is needed. This would enable us to study equilibria like

$$Al_3O_2Cl_6^- + 3AlCl_4^- \rightleftarrows 2Al_3OCl_8^- + 2Cl^- \qquad [10]$$

and

$$Al_4O_2Cl_{10}^{2-} + 2AlCl_4^- \rightleftarrows 2Al_3OCl_8^- + 2Cl^- \qquad [11]$$

that involve simple known ions. In addition to a new computer program, which is able to calculate such models, more measurements of high precision are needed to obtain a significant discrimination between all the likely equilibria, at least on the basis of potentiometric measurements alone.

The cryoscopic measurements of Berg *et al.* (6) only covered the near neutral melts ($X'_{AlCl_3} < 0.504$; $p\text{Cl}^- < 4.3$) which means that no data is available in the acidic *p*Cl range where $\bar{n}_{AlO^+}$ drops below one.

From cryoscopic measurements in the more acidic range where the species $(AlO^+)_p(AlCl_4^-)_s$ are the major aluminum oxochloro complexes formed, it should however also be possible to determine the degree of polymerization of these species.

From such measurements, ν_{AlOCl} can be evaluated and the number p, occurring in the general equation

$$pAlOCl + pAl_2Cl_7^- \rightarrow (AlO^+)_p(AlCl_4^-)_s + (2p - s)AlCl_4^- \qquad [12]$$

can be obtained since $\nu_{AlOCl} = (1 - p)/p$.

According to Fig. 1 more than 90% of the AlOCl added should react to give $(AlO^+)_p(AlCl_4^-)_s$ species in the *p*Cl region 5.4-6.0. In this area, two preliminary cryoscopic measurements have been performed so far (22), yielding ν_{AlOCl} values near −1/2. According to these preliminary results, a *p*-value of two is obtained, *i.e.*, a dimeric species should be formed. When this result is combined with the model calculations on the potentiometric measurements, it seems very likely that $(AlO^+)_2(AlCl_4^-)_s$ is the acidic oxochloro species in Eq. [9].

In conclusion, it can be said that only $(AlOCl)_2(AlCl_4^-)_m$ exists in basic and weakly acidic NaCl-$AlCl_3$ melts. ($1.128 < p\text{Cl} < 4.25$) at 175°C. This is in agreement with the results of Taulelle *et al.* (5). In more acidic melts, probably dimeric species of the kind $(AlO^+)_2(AlCl_4^-)_s$ starts forming. A value of two for both m and s seems a reasonable guess taking into consideration the model discriminations based on the potentiometric measurements in this work and previous structural determinations on aluminum oxochloro compounds (18-20).

From a strictly statistical point of view the potentiometric measurements are explained equally well by the best solvated and nonsolvated models, but it remains that dimeric species are significant, that is, Eq. [8] or solvated forms hereof.

Acknowledgments

The authors are grateful for support from The Danish Council for Scientific and Industrial Research, Julie Damm's Foundation, Director Ib Henriksens Foundation, and The Ministry of Energy.

Manuscript submitted July 8, 1985; revised manuscript received Dec. 2, 1986.

APPENDIX

The program for testing the different model equilibria is based on the following equations for the nonsolvated aluminum oxochloro complexes. The formality C'_i, where i represents NaCl, $AlCl_3$ (corrected for AlOCl content), or total AlOCl, respectively, is calculated from [A-1]

$$C'_i = W_i/(M_i \cdot V) = W_i \cdot \rho \Big/ \left(M_i \cdot \sum_i W_i \right) \qquad [A\text{-}1]$$

(W_i, M_i, V, and ρ are weights, molar weights, volume, and density (16), respectively.) The problem is then for each experimental composition to solve eight equations [A2-A9]

$$K_1 = [Al_2Cl_7^-][Cl^-]/[AlCl_4^-]^2 \qquad [A\text{-}2]$$

$$K_2 = [Al_3Cl_{10}^-]^2[Cl^-]/[Al_2Cl_7^-]^3 \qquad [A\text{-}3]$$

$$K_3 = [Al_2Cl_6]^3[Cl^-]^2/[Al_3Cl_{10}^-]^2 \qquad [A\text{-}4]$$

$$K = [(AlO^+)_p]^{qn/p}[Cl^-]^{qn}/[(AlOCl)_n]^q \qquad [A\text{-}5]$$

$$[Na^+] + n[(AlO^+)_n] = [AlCl_4^-] + [Al_2Cl_7^-] + [Al_3Cl_{10}^-] + [Cl^-] \qquad [A\text{-}6]$$

$$C'_{NaCl} = [Na^+] \qquad [A\text{-}7]$$

$$C'_{AlCl_3} = [AlCl_4^-] + 2[Al_2Cl_7^-] + 3[Al_3Cl_{10}^-] + 2[Al_2Cl_6] \qquad [A\text{-}8]$$

$$C'_{AlOCl} = n[(AlOCl)_n] + p[(AlO^+)_p] \qquad [A\text{-}9]$$

The above equations [A2-A9] are four mass action expressions corresponding to equilibria [1], [2], [3], and [7], the charge balance and two independent mass balances. These equations in the unknown concentrations $[AlCl_4^-]$, $[Al_2Cl_7^-]$, $[Al_3Cl_{10}^-]$, $[Al_2Cl_6]$, $[(AlOCl)_n]$, $[(AlO^+)_p]$, $[Cl^-]$, and $[Na^+]$ can be solved for fixed values of K using a standard computer routine. Next, for each composition the coordination number corresponding to the chosen model and K-value, $\bar{n}_{model}(K)$, is calculated using Eq. [4]. Finally, the sum of squared deviations

$$S.S. = \sum_{j=1}^{N} (\bar{n}_{model,\,j} - \bar{n}_{experimental,\,j})^2 \qquad [A\text{-}10]$$

(where N is the number of measurements, here the seven most acidic points) is minimized allowing K to change, using the Marquardt iterative principle. The final optimized value of K for a given model is then obtained and the whole procedure is repeated for the next model (see Table II).

The final variance of $\bar{n}$ for each model is

$$\sigma^2_{\min} = S.S./(j - 1) \qquad [A\text{-}11]$$

This variance forms one part of the basis for a statistical evaluation (F-test) of the different models. The other part is the experimentally determined variance, which can be calculated from

$$\sigma^2_{\exp} = \sum_{k=1}^{M} (\bar{n}_a - \bar{n}_{\exp,k})^2/(k - 1) \qquad [A\text{-}12]$$

where the summation over $k = 1, 2, \ldots\ldots M$ does not include the data used in [A10-A11] and where $\bar{n}_a$ is the average value of $\bar{n}$ for the M measurements, assumed to be an estimate of the true $\bar{n}$. (For the present case a $\sigma^2_{\exp}$ value of $2.59 \cdot 10^{-3}$ was calculated from that part of the measurements, where $\bar{n}$ was assumed to be constant and found as 1.01 assuming further that the experimental precision does not vary with pCl).

For each model, F_{model} can now be found from

$$F_{\text{model}} = \sigma^2_{\min}/\sigma^2_{\exp} \qquad [A\text{-}13]$$

and compared with the statistical table value of $F(N - 1, M - 1)$ corresponding to the chosen significance level. For a model to be considered as acceptable, the F_{model} value should be less than F.

For the case of solvated aluminum oxochloro complexes the equations [A-5], [A-6], [A-8], and [A-9] must be changed, but the procedure is in principle the same.

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