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A POTENTIOMETRIC STUDY OF CHLOROALUMINATE EQUILIBRIA IN 1/1
THE ALUMINUM CHLO. (U) FRANK J SEILER RESEARCH LAB
UNITED STATES AIR FORCE ACADEMY C. L. HUSSEY ET AL.

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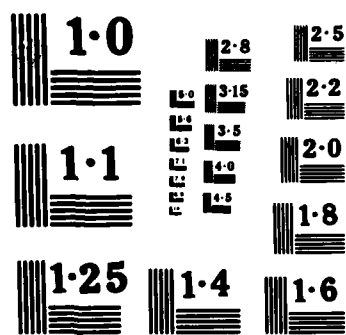
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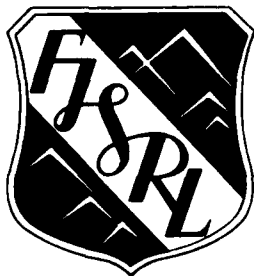


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FRANK J. SEILER RESEARCH LABORATORY

FJSRL-TR-83-0007

JUNE 1984

**A POTENTIOMETRIC STUDY OF
CHLOROALUMINATE EQUILIBRIA IN THE
ALUMINUM CHLORIDE - 1-METHYL-2-
ETHYLIMIDAZOLIUM CHLORIDE
IONIC LIQUID**

**Charles L. Hussey
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John S. Wilkes
Armand A. Fannin, Jr.**

AUG 21 1984

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PROJECT 2303

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UNITED STATES AIR FORCE**

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Project Scientist



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A Potentiometric Study of Chloroaluminate Equilibria in the
Aluminum Chloride-1-Methyl-2-Ethylimidazolium
Chloride Ionic Liquid

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Dr. John S. Wilkes
Lt. Col. Armand A. Fannin, Jr.

June 1984



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Directorate of Chemical Sciences
The Frank J. Seiler Research Laboratory
Air Force Systems Command
United States Air Force Academy
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SUMMARY

→ The upper limit on the stoichiometric equilibrium constant for the tetrachloroaluminate dissociation reaction, $2\text{RAlCl}_4 \rightleftharpoons \text{RAl}_2\text{Cl}_7 + \text{RCl}$, was investigated in the room temperature ionic liquid aluminum chloride-1-methyl-3-ethylimidazolium chloride by means of a potentiometric titration procedure.

2 The values obtained at 40, 50, and 60°C were $5.1 \pm 1.4 \times 10^{-17}$, $1.8 \pm 1.6 \times 10^{-16}$, and $3.8 \pm 1.1 \times 10^{-16}$, respectively. A curve fitting procedure for locating the equivalence point in these titrations is also described.

PREFACE

This report describes work performed under FJSRL Work Unit 2303-F2-10, Organic and Inorganic Electrochemical Measurements. Portions of the experimental part of this study were carried out in the Department of Chemistry at the University of Mississippi. Capt. Hussey is a reservist assigned to the Air Force Office of Scientific Research and attached to FJSRL. Dr. Scheffler is a National Research Council research associate at FJSRL. Dr. Wilkes and Lt. Col. Fannin are permanent staff members at FJSRL.

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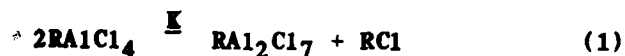
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I. Introduction

Aluminum chloride can be combined with certain organic salts to produce ionic liquids that are molten at room temperature. Familiar examples of such liquids are mixtures of aluminum chloride with N-(n-butyl)pyridinium chloride (BPC) (1,2). However, a new class of room temperature chloroaluminate melts, based on dialkylimidazolium chloride salts, was described recently (3). Mixtures of aluminum chloride, with one of these salts, 1-methyl-3-ethylimidazolium chloride (MEIC), exhibit both a wider electrochemical window and higher electrical conductivity, and are liquid over a larger composition range than corresponding systems based on N-alkylpyridinium halides.

The Lewis acid-base properties of room temperature chloroaluminate melts are governed essentially by the single equilibrium (3-5):



Melts that contain a molar excess of aluminum chloride to organic salt are Lewis acidic by virtue of the coordinately unsaturated Al_2Cl_7^- ion. Conversely, mixtures that contain an excess of the organic salt relative to aluminum chloride are Lewis basic due to uncomplexed chloride ion.

The acid-base properties of ionic liquids based on AlCl_3 -BPC have been investigated and estimates of the upper limit on the equilibrium constant for Eq. (1) are available for this liquid (4,5). Karpinski and Osteryoung (6) have demonstrated that it is not possible to measure an exact value of K for Eq. (1) if aluminum electrodes are used for the measurements. This is because an aluminum electrode immersed in basic melt experiences a mixed potential that is

less negative than the true potential of the Al(III)/Al redox couple. Two sources of this mixed potential have been advanced (6): corrosion of aluminum by the organic cation (this phenomenon is well-known in the AlCl_3 -BPC melt (7)) and corrosion of aluminum by adventitious hydrogen ion. In place of aluminum electrodes, Karpinski and Osteryoung suggested the use of the Cl_2/Cl^- couple for determining chloride ion activity. Unfortunately, it has been found that Cl_2 reacts with the organic cation in AlCl_3 -MEIC melts, eventually chlorinating all available sites on the cation (8). Thus, the chlorine electrode is not the catholicon for these measurements, either.

This technical report describes a study of the acid-base properties of the AlCl_3 -MEIC melt. Potentiometric measurements were undertaken at aluminum electrodes in order to estimate the upper limit on K for Eq. (1).

II. Experimental

Instrumentation. Experiments were conducted in a dry, oxygen-free nitrogen atmosphere inside a Kewaunee Scientific Engineering Corp. dry box system equipped with a Model 2C2500 30-cfm inert-gas purifier. The procedure for estimating the moisture and oxygen content of this dry box using a 25 W light bulb has been described (9). Instrumentation used to perform cyclic voltammetry and to make potentiometric measurements was identical to that used previously (10). Pulse polarographic experiments were undertaken with a PARC Model 174 polarographic analyzer.

Cells and Electrodes. The cell and furnace used were described previously (9). Aluminum electrodes were fashioned from 1.0-mm diameter aluminum wire (Alfa Products, m5N purity). These electrodes were immersed briefly in a

aqueous solution that was 5% (v/v) in HF and 15% (v/v) in HNO_3 , rinsed with distilled water, and dried under vacuum before use.

Chemicals. Aluminum chloride (Fluka, A.G.) was triply sublimed under vacuum inside the dry box. The synthesis and purification of 1-methyl-3-ethylimidazolium chloride was identical to that described by Wilkes et al. This salt was carefully purified using airless techniques; it was recrystallized three times from mixtures of acetonitrile and ethyl acetate. The oxide content of the AlCl_3 -MEIC melt was determined with TiCl_4 using a pulse polarographic method (11). Melts that contained more than 5 ppm oxide were discarded.

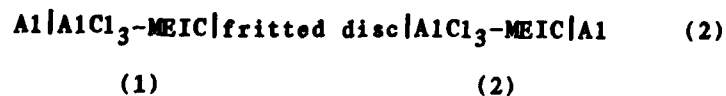
When AlCl_3 is mixed with MEIC, a violent exothermic reaction takes place which results in sublimation loss of AlCl_3 and decomposition of small amounts of MEIC. Consequently, it is very difficult to prepare a large amount of melt of an accurately known composition by combining preweighted quantities of the components. Therefore, it was necessary to determine the initial melt composition directly from titration data. Two procedures were used. The first was based on an approximation of Grans method and is similar to that described by Schoebrechts and Gilbert (5). The second method is described in Appendix A. For brevity, AlCl_3 -MEIC melt compositions specified in this paper are given in terms of the formal mole fraction, N , or mole percent, mole/o, of AlCl_3 in the mixture.

III. Results and Discussion

Stability of aluminum in basic AlCl_3 -MEIC melt. As previously noted, the instability of aluminum in basic melt can complicate the study of chloroaluminate equilibria. For example, aluminum behaves as a reducing agent

toward the 1-(n-butyl)pyridinium cation in basic AlCl_3 -BPC melt. The addition of aluminum to this melt produces the highly colored 4,4'-dibutyl-1,1'-bipyridinium monocation radical (9). MNDO calculations suggest that the 1-methyl-3-ethylimidazolium cation is substantially more difficult to reduce than the 1-(n-butyl)pyridinium cation (3). In fact, the latter species can be electrochemically reduced in basic AlCl_3 -MEIC melt prior to the negative limit of the solvent. Figure 1 shows a cyclic voltammogram for the reduction of 1-(n-butyl)pyridinium cation at a glassy carbon electrode in basic AlCl_3 -MEIC. The reduction peak potential for this solute, -1.43 V versus aluminum in 66.7 mole/o AlCl_3 -MEIC, is considerably positive of the negative limit of the 44.4 mole/o AlCl_3 -MEIC melt at -2.20 V. Thus, aluminum should be more stable thermodynamically with regard to oxidation in basic AlCl_3 -MEIC relative to basic AlCl_3 -BPC. Immersion of small pieces of aluminum foil in basic AlCl_3 -MEIC for several weeks did not result in discernable changes in the aluminum or the melt, while similar experiments with basic AlCl_3 -BPC indicated reduction of the 1-(n-butyl)pyridinium cation within a few days. However, it was not possible to electrochemically deposit aluminum at aluminum or glassy carbon electrodes in basic AlCl_3 -MEIC melt; prolonged electrolysis produced an orange-colored solution in the cathode compartment of the cell.

Potentiometric titration experiments. The concentration cell with transference shown below was used to study chloroaluminate equilibria in AlCl_3 -MEIC melt:



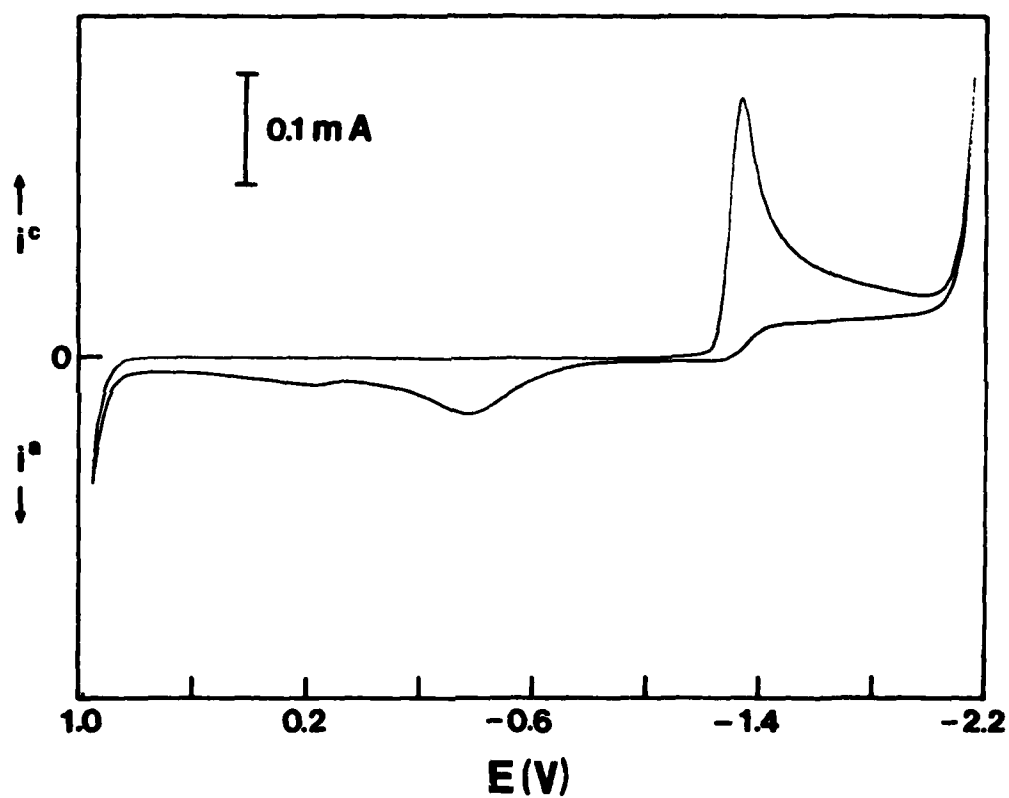


Figure 1. Cyclic voltammogram for the reduction of the 1-(*n*-butyl)pyridinium cation at a glassy electrode in 44 mole/o AlCl_3 -MBIC melt at 40.0°C . Sweep rate was 50 mV/sec.

Both compartments of this cell were filled with melt that was ca. 60 mole/o in AlCl_3 prior to the start of an experiment. Weighed portions of MEIC were added to compartment 2 of the cell during an experiment and the potential of the cell was recorded after dissolution of the MEIC. The aluminum electrodes were carefully wiped with abrasive tissue (Kimwipes) before each data point was recorded. The melt composition in the left-hand cell compartment was kept constant. Figure 2 shows representative titration curves obtained at 40.0, 50.0, and 60.0°C, using this cell. Several experiments were conducted at each temperature. Cell potentials were stable and reproducible throughout each titration experiment.

Analysis of chloroaluminate concentration cells. Øye and King (12) reported that the potential of a chloroaluminate concentration cell with transference, similar to that shown in Eq. (2), is given formally by the expression

$$\underline{FE} = \int_1^2 \frac{1}{3} d\mu_{\text{AlCl}_3} - \frac{t_{\text{Al}}}{3} d\mu_{\text{AlCl}_3} - t_{\text{R}} d\mu_{\text{RCl}} \quad (3)$$

In Eq. (3), RCl represents MEIC, and t_{Al} and t_{R} are the formal transport numbers of the aluminum ion and the melt cation, respectively. Hussey and Øye (13) have measured transport numbers in the AlCl_3 -MEIC melt. The internal transport number of the organic cation relative to chloride is 1.00 in this melt. In this event Eq. (3) simplifies to

$$\underline{FE} = \int_1^2 \frac{1}{3} d\mu_{\text{AlCl}_3} - d\mu_{\text{RCl}} \quad (4)$$

Equation (4) may also be written in terms of the activities of the major chloroaluminate species in basic melt

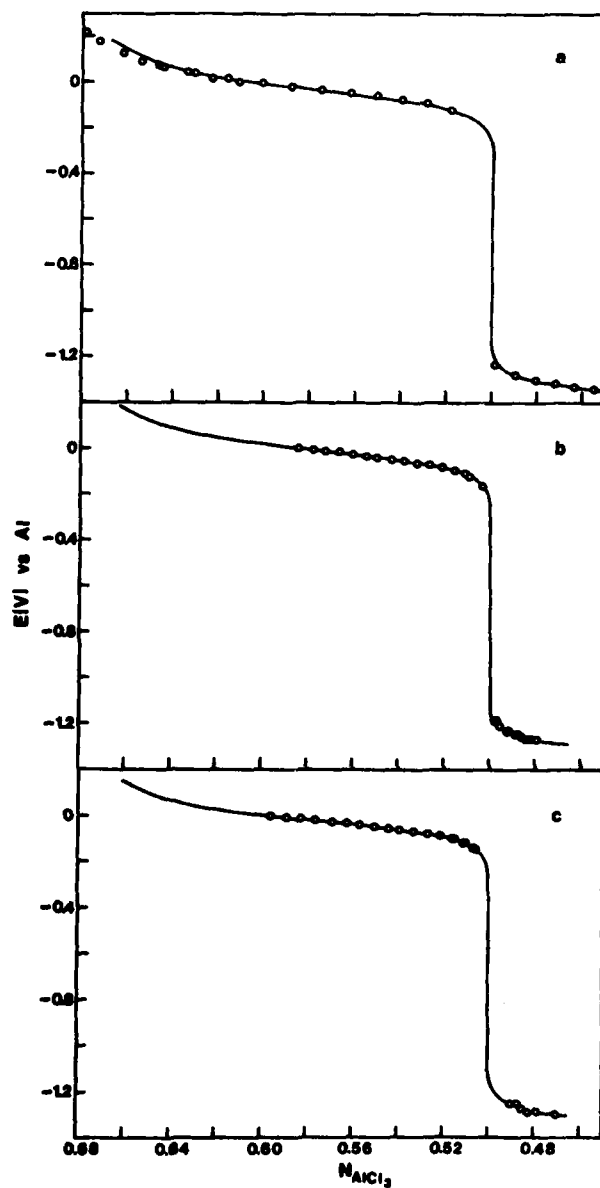


Figure 2. Potentiometric titration curves for the AlCl_3 -MEIC system; a) 60.0°C , b) 50.0°C , and c) 40.0°C . Solid lines were calculated from the estimated equilibrium constants for Eq. (1) that were determined from the experimental data in each figure.

$$\underline{E} = \frac{RT}{3F} \int_1^2 d \ln a_{\text{RA1Cl}_4} - 4 d \ln a_{\text{RC1}} \quad (5)$$

or in acidic melt

$$\underline{E} = \frac{RT}{3F} \int_1^2 4 d \ln a_{\text{RA1}_2\text{Cl}_7} - 7 d \ln a_{\text{RA1Cl}_4} \quad (6)$$

Autosolvolytic equilibrium constant. - The stoichiometric equilibrium constant for the reaction depicted in Eq. (1) is defined as

$$\underline{K}' = \frac{(\underline{X}_{\text{RC1}})(\underline{X}_{\text{RA1}_2\text{Cl}_7})}{(\underline{X}_{\text{RA1Cl}_4})^2} \quad (7)$$

where $\underline{X}_{\text{RC1}}$, $\underline{X}_{\text{RA1Cl}_4}$, and $\underline{X}_{\text{RA1}_2\text{Cl}_7}$ represent the mole fractions of RC1, RA1Cl₄, and RA1₂Cl₇. Values of $\underline{K}'$ for the AlCl₃-MEIC system were obtained by curve fitting data in the vicinity of the 50 mole/o composition to the equation

$$\underline{E} = \frac{4RT}{3F} \ln \frac{\underline{K}'(\underline{X}_{\text{RA1Cl}_4})^2_A}{(\underline{X}_{\text{RC1}})_B(\underline{X}_{\text{RA1}_2\text{Cl}_7})_A} + \frac{RT}{3F} \ln \frac{(\underline{X}_{\text{RA1Cl}_4})_B}{(\underline{X}_{\text{RA1Cl}_4})_A} \quad (8a)$$

where A and B denote acidic and basic compartments, and $\underline{E} = \underline{E}_B - \underline{E}_A$. The details of this procedure are given in Appendix B. Average values of the upper limit of $\underline{K}'$, resulting from several experiments, are listed in Table I and are compared with other chloroaluminate systems. The approximate distribution of ionic species in AlCl₃-MEIC melt, calculated by using the $\underline{K}'$ value at 40°C given in Table I, is shown in Figure 3. The equilibrium constants for Eq. (1) are several orders of magnitude smaller in AlCl₃-MEIC than those determined for the AlCl₃-BPC system. This suggests that the value of $\underline{K}'$ obtained in the present study is probably much closer to the true value of $\underline{K}'$ than estimates propounded by other workers (4,5). In fact, Karpinski and Osteryoung (6) predict that the

Table I. Chloroaluminate autosolvolysis equilibrium constants.

Melt System	t(°C)	K'	ref.
$AlCl_3$ - MEIC	40.0	$(5.1 \pm 1.4^a) \times 10^{-17}$	this work
$AlCl_3$ - MEIC	50.0	$(1.8 \pm 1.6^a) \times 10^{-16}$	this work
$AlCl_3$ - MEIC	60.0	$(3.8 \pm 1.1^a) \times 10^{-16}$	this work
$AlCl_3$ - BPC	40.0	$(1.2 \pm 0.2) \times 10^{-13}$	(5)
$AlCl_3$ - BPC	49.0	$(4.5 \pm 0.4) \times 10^{-13}$	(5)
$AlCl_3$ - BPC	60.0	1.5×10^{-12}	(5)
$AlCl_3$ - BDMAPC ^b	40.0	$(8.4 \pm 0.2) \times 10^{-11}$	(14)
$AlCl_3$ - NaCl	175.0	$(1.06 \pm 0.02) \times 10^{-7}$	(15)
$AlCl_3$ - LiCl	175.0	5×10^{-5}	(16)
$AlCl_3$ - LiCl	400.0	1.6×10^{-4}	(16)
$AlCl_3$ - NaCl	400.00	1.0×10^{-5}	(16)
$AlCl_3$ - KCl	400.00	1.6×10^{-6}	(16)
$AlCl_3$ - CsCl	400.00	4.0×10^{-8}	(16)

^a95% confidence interval

^b1-*n*-butyl-4-(dimethylamino)pyridinium chloride

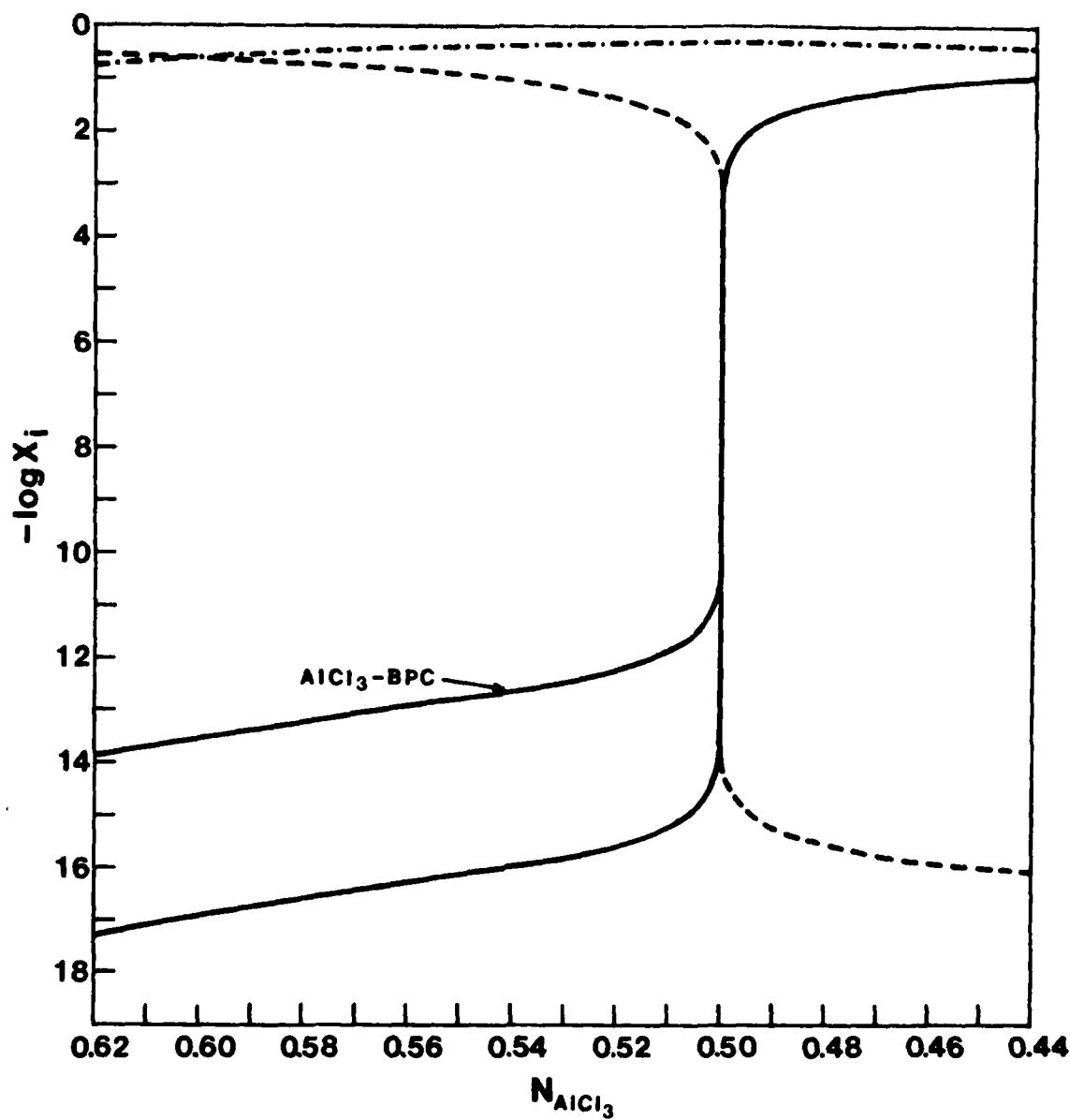


Figure 3. Distribution of species in the AlCl_3 -NEIC melt at 40.0°C , —, $\log X_{\text{RCl}}$; - · -, $\log X_{\text{RA1Cl}_4}$; - -, $\log X_{\text{RA1Cl}_7}$. The upper limit on $\log X_{\text{RCl}}$, attainable in the AlCl_3 -BPC melt, is shown for comparison. Values of $\log X_{\text{RCl}}$ for the AlCl_3 -BPC system were calculated from the estimates of $\underline{K}$ given in reference 5.

actual value of $\underline{K}'$ for both the AlCl_3 -BPC and AlCl_3 -MEIC melts may lie in the interval from 10^{-19} to 10^{-15} . Nevertheless, the estimates of $\underline{K}'$ reported herein should be considered to be the upper limit on $\underline{K}'$ due to the various side reactions which complicate the aluminum electrode reaction in basic melt.

IV. Conclusion

The solid lines that appear in Fig. 1 were calculated by using estimates of $\underline{K}'$ that were determined directly from the experimental data shown in each figure. These lines were calculated by using the integrated forms of Eqs. (5) and (6). It is interesting to note that in every case (Fig. 1) these calculated lines represent the experimental data precisely, except in very acid melt where the AlCl_3 content exceeds ca. 63 mole/o. It should be noted that recent ^{27}Al NMR studies suggest the presence of $\text{Al}_3\text{Cl}_{10}^-$ in very acid AlCl_3 -MEIC melt (17). Therefore, it may be necessary to consider other equilibria in addition to Eq. (1) in very acidic melt.

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VI. Appendix A:

The initial composition of the melt in the cell (Eq. (2)) and each new composition arising in compartment 2 of the cell after the addition of a known amount of MEIC were determined by the curve fitting technique described below. When RAI_2Cl_7 and RAICl_4 in the equation

$$E = \frac{4RT}{3F} \ln \frac{(\bar{x}_{\text{RAI}_2\text{Cl}_7})_2}{(\bar{x}_{\text{RAI}_2\text{Cl}_7})_1} + \frac{7RT}{3F} \ln \frac{(\bar{x}_{\text{RAICl}_4})_1}{(\bar{x}_{\text{RAICl}_4})_2} \quad (\text{A-1})$$

are represented in terms of the apparent mole fractions of AlCl_3 in compartments 1 and 2 of the cell N_1 and N_2 , respectively, Eq. (A-2) results:

$$E = \frac{4RT}{3F} \ln \left[\frac{2N_2-1}{2N_1-1} \right] \left[\frac{1-N_2}{1-N_1} \right] + \frac{7RT}{3F} \ln \left[\frac{2-3N_1}{2-3N_2} \right] \left[\frac{1-N_2}{1-N_1} \right] \quad (\text{A-2})$$

Furthermore, N_1 and N_2 can be expressed in terms of the initial weight of melt, $\bar{W}_m$, and the initial weight of salt, $\bar{W}_s^i$, and the cumulative weight of salt added at each point, $\bar{W}_s$, in compartment 2, according to Eqs. (A-3) and (A-4):

$$N_1 = \frac{\bar{W}_m - \bar{W}_s^i}{\bar{W}_m - \bar{W}_s^i(1-R)} \quad (\text{A-3})$$

$$N_2 = \frac{\bar{W}_m - \bar{W}_s^i}{\bar{W}_m - \bar{W}_s^i(1-R) + \bar{W}_s R} \quad (\text{A-4})$$

R represents the ratio of the formula weight of AlCl_3 to that of the organic salt. Substitution of Eqs. (A-3) and (A-4) into (A-2) results in a complex equation that can be computer fitted to measurements of E at each $\bar{W}_s$ in acidic melt. This equation can be used to calculate $\bar{W}_s^i$ if $\bar{W}_m$ is known.

A Fortran IV computer program was written for this purpose. This program uses a Taylor series linearized least-squares routine to obtain the value of $\bar{W}_2^i$ that minimized the error between the experimental potential and the calculated potential. Estimates of the melt composition obtained with this procedure are at least as good as those obtained by using Grans method (5), cf., Table A-I. One significant advantage of the procedure described herein over the other method (5) is that it is not necessary to collect a large amount of titration data immediately prior to the equivalence point. This can result in considerable experimental convenience when a good estimate of the initial melt composition is not available.

Table A-I. Results for calculation of initial melt compositions.

t (°C)	Initial melt composition (mole/o AlCl_3)		% relative difference
	this work	Grans method (5)	
40.0	60.73	60.10	1.0
	60.34	59.72	1.0
	59.54	59.45	0.2
50.0	58.83	58.59	0.4
	58.43	58.27	0.3
60.0	60.30	59.45	1.4
	61.07	59.83	2.1
	59.08	59.09	0.0
	59.82	60.16	-0.6

VII. Appendix B:

The values of $\underline{K}'$ that appear in Table I were calculated from potentiometric titration data in the 50.0 ± 4.0 mole/o composition region using this modified version of Eq. (8):

$$\underline{E}_i - \underline{E}_j = \frac{4RT}{3F} \ln \frac{(2-3\underline{N}_i)^2(1-\underline{N}_i) \underline{K}'}{(1-\underline{N}_i)(2\underline{N}_i-1)(1-2\underline{N}_j)} + \frac{RT}{3F} \ln \frac{\underline{N}_i(1-\underline{N}_i)}{(1-\underline{N}_j)(2-3\underline{N}_i)} \quad (B-1)$$

Data, consisting of the potential differences between an acidic reference point, $\underline{N}_i$, and a series of basic data points, $\underline{N}_j$, were fitted to Eq. (B-1) so as to minimize the sum of the errors between calculated and experimental values of $\underline{E}_i - \underline{E}_j$. This procedure was repeated successively for each value of $\underline{N}_i$ that was in the appropriate composition range of the data set. Values of $\underline{K}'$ obtained during each cycle were then averaged to give the best estimate of $\underline{K}'$ for the experiment. A sample of the output obtained during a fitting cycle with the Fortran IV computer program written for this purpose is shown in Table B-I.

Table B-I. Example of a fitting cycle for determination of $\underline{K}'$ from Eq. (B-1).

$\underline{E}_i - \underline{E}_j$ (V)		Error(V)	$\underline{N}_j$
exptl.	calcd.		
-1.1198	-1.1587	3.89×10^{-2}	0.4946
-1.1826	-1.1807	-1.91×10^{-3}	0.4900
-1.1816	-1.1898	8.15×10^{-3}	0.4871
-1.2038	-1.1953	-8.46×10^{-3}	0.4849
-1.2203	-1.2002	-2.01×10^{-2}	0.4827
-1.2183	-1.2077	-1.06×10^{-2}	0.4786
-1.2286	-1.2194	-9.16×10^{-3}	0.4701

temperature = 40.0°C

$\underline{E}_1 = -0.0751$ V

$\underline{N}_1 = 0.5265$

$\underline{K}' = 3.8 \times 10^{-17}$

Standard deviation of the fit = 1.34×10^{-3} (V)

Convergence occurred in 8 iterations

Cycle no. = 2

VIII. Glossary:

- a_i activity of component i, Eqs. (5) and (6).
- E cell potential (V).
- E_1 cell potential (V), acid melt in compartment 2, Eq. (2).
- E_j cell potential (V), basic melt in compartment 2, Eq. (2).
- K' stoichiometric equilibrium constant, Eq. (1).
- N mole fraction of $AlCl_3$.
- N_1 mole fraction of $AlCl_3$ in acidic melt.
- N_j mole fraction of $AlCl_3$ in basic melt.
- N_1 mole fraction of $AlCl_3$ in compartment 1, Eq. (2).
- N_2 mole fraction of $AlCl_3$ in compartment 2, Eq. (2).
- t_i transport number.
- X_i mole fraction.
- W_m initial weight of melt (g).
- W_s cumulative weight of MEIC added (g).
- W_s^i initial weight of MEIC in melt (g).
- μ_i chemical potential.

