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Potentiometric Study of the Dissociation of the Tetrachloroaluminate Ion in Molten Sodium Chloroaluminates at 175–400°

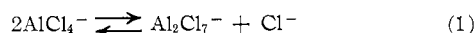
BY G. TORSI¹ AND G. MAMANTOV*

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The equilibrium constant for the dissociation $2\text{AlCl}_4^- \rightleftharpoons \text{Cl}^- + \text{Al}_2\text{Cl}_7^-$ in molten $\text{AlCl}_3\text{-NaCl}$ was determined potentiometrically in the temperature range 175–400°. $\text{p}K$ values, where $K = X_{\text{Cl}^-}X_{\text{Al}_2\text{Cl}_7^-}/X_{\text{AlCl}_4^-}^2$, range from 7.1 (at 175°) to 5.0 (at 400°). The solubility of NaCl in molten NaAlCl_4 as a function of temperature is also reported.

Introduction

The acid-base properties of molten $\text{AlCl}_3\text{-NaCl}$ have been previously studied² at one temperature (175°) and in the composition region near 50:50 mol %. These solvents, however, exhibit more interesting properties at higher AlCl_3 content,^{3–7} such as 63:37 mol %. In this paper the potentiometric determination of the equilibrium constant for the reaction



is reported in the temperature range 175–400°. The measurements at 175° were made in melts that ranged from those saturated with NaCl to melts saturated with AlCl_3 .

Experimental Section

The $\text{AlCl}_3\text{-NaCl}$ melt was prepared from optical grade NaCl (Harshaw Chemical Co.) and AlCl_3 ("anhydrous and free from iron," from Fluka AG). NaCl was heated at ~400° under vacuum for several hours prior to use. The desired quantities of NaCl and AlCl_3 were weighed, sealed in a quartz tube under vacuum with pieces of aluminum wire (m5N grade from Alfa Inorganics), and digested for several days at ~300°. After the impurities had settled, the water-clear melt was cooled slowly, frozen, and stored in a sealed container in a drybox (typical moisture level <2 ppm). In experiments involving additions of AlCl_3 , aluminum chloride, prepared in the laboratory of G. P. Smith at the Oak Ridge National Laboratory, from 99.9999% aluminum and specially prepared⁸ HCl using the procedure given,³ was employed. The purity of melts employed in this work and related studies^{6,7} has been checked voltammetrically. Typical voltammograms for an acidic $\text{AlCl}_3\text{-NaCl}$ (63:37 mol %) melt are shown in ref 7 (see Figure 2).

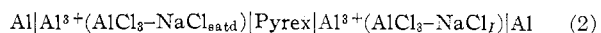
The electrochemical cells employed in potentiometric measurements were made out of Pyrex for measurements in the range 175–250° and out of quartz for measurements at higher temperatures. No attack of cells by the melts has been observed. The reference electrode (see below) was separated from the bulk melt by a Pyrex membrane. Unsheathed aluminum wire (m5N grade from Alfa Inorganics) was the electrode material. Sealed, evacuated cells were employed. A liquid nitrogen trap was used to protect the contents of the cell from pump oil vapors. The cells were dried at ~250° under reduced pressure prior to use. The electrode connections were made with tungsten wire sealed in uranium glass to Pyrex. The reference compartment was always saturated with NaCl. The other compartment was equipped with several side arms which could be broken for additions of either AlCl_3 or NaCl in the drybox. The sensitivity of the torsion balance used in the drybox was 2 mg. After each addition, the cell was evacuated to ~10⁻² Torr and resealed.

This procedure was checked⁷ voltammetrically and shown not to introduce impurities in measurable quantities.

The temperature of the whole cell was controlled to ±2° using an air thermostat. The potentials were measured with a Model 895A dc differential voltmeter (John Fluke Mfg. Co., Inc.). The potentials at equilibrium were found to be independent of the direction from which equilibrium was approached. Potentials were reproducible for each composition to ±3 mV.

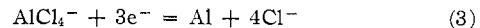
Results and Discussion

The following electrochemical cell was employed for the determination of the equilibrium constant and the measurement of the solubility of NaCl in NaAlCl_4



where I refers to a known composition of the melt.

For the 50:50 mol % composition of $\text{AlCl}_3\text{-NaCl}$ the principal anion is AlCl_4^- ,^{2a,8,9} and the electrode reaction of interest is^{2a}



Therefore, the voltage of this concentration cell ΔE is given by the expression

$$\Delta E = \frac{4RT}{3F} \ln \frac{(a_{\text{Cl}^-})_{\text{satd}}}{(a_{\text{Cl}^-})_I} + \frac{RT}{3F} \ln \frac{(a_{\text{AlCl}_4^-})_I}{(a_{\text{AlCl}_4^-})_{\text{satd}}} + \Delta E_M \quad (4)$$

where ΔE_M is the difference of potential across the Pyrex membrane. Assuming that the selectivity constant for aluminum is zero,¹⁰ ΔE_M consists of the asymmetry potential of the membrane and a term involving the ratio of sodium ion activities on the two sides of the membrane, $(RT/F) \ln (a_{\text{Na}^+(I)}/a_{\text{Na}^+(\text{satd})})$. The asymmetry potential of the membrane was evaluated and corrected for by using the same composition in both compartments. This was usually done by saturating the second compartment with NaCl at the end of each experiment. This asymmetry potential was generally small (≤ 10 mV) and independent of the temperature.

The term $(RT/F) \ln (a_{\text{Na}^+(I)}/a_{\text{Na}^+(\text{satd})})$ was neglected. This approximation may be justified for compositions near 50:50 mol %, since in going to more acidic melts (from AlCl_4^- to AlCl_4^- plus some Al_2Cl_7^-)^{8,9} the ion fraction of Na^+ remains constant. In addition, the activity coefficient of NaCl in these melts is not known.

Therefore, it is assumed that the voltage of cell 2 is given by

$$\Delta E = \frac{4RT}{3F} \ln \frac{(X_{\text{Cl}^-})_{\text{satd}}}{(X_{\text{Cl}^-})_I} + \frac{RT}{3F} \ln \frac{(X_{\text{AlCl}_4^-})_I}{(X_{\text{AlCl}_4^-})_{\text{satd}}} \quad (5)$$

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(2) (a) B. Tremillon and G. Letisse, *J. Electroanal. Chem.*, **17**, 371 (1968);
(b) B. Tremillon and G. Letisse, *ibid.*, **17**, 387 (1968).
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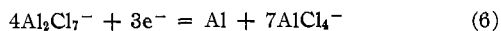
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X_{Cl^-} and $X_{\text{AlCl}_4^-}$ are the mole fractions of Cl^- and AlCl_4^- in the respective melts.

In acidic melts the electrode reaction may be written as^{2a}



and the expression for the voltage of the cell is

$$\Delta E = \frac{4RT}{3F} \ln \frac{(X_{\text{Al}_2\text{Cl}_7^-})_I}{(X_{\text{Al}_2\text{Cl}_7^-})_{\text{satd}}} + \frac{7RT}{3F} \ln \frac{(X_{\text{AlCl}_4^-})_{\text{satd}}}{(X_{\text{AlCl}_4^-})_I} \quad (7)$$

Equation 7, however, is equivalent to eq 5 as may be seen by substituting $KX_{\text{AlCl}_4^-}^2/X_{\text{Cl}^-}$ for $X_{\text{Al}_2\text{Cl}_7^-}$ (see eq 9 below).

In the composition region 50.0 ± 0.2 mol % AlCl_3 , the second term in eq 5 is negligible and ΔE for the cell is given by

$$\Delta E = \frac{4RT}{3F} \ln \frac{(X_{\text{Cl}^-})_{\text{satd}}}{(X_{\text{Cl}^-})_I} \quad (8)$$

Figure 1 illustrates the variation of cell voltage with

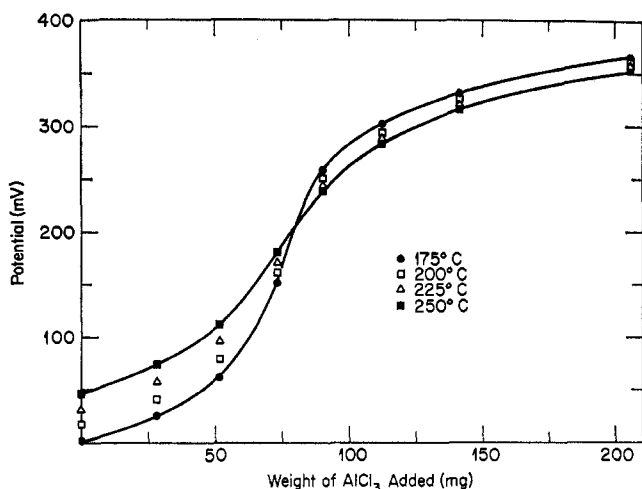


Figure 1.—Potentiometric titration curve for AlCl_3 - NaCl (49.8–50.2 mol %) melt with AlCl_3 . Initial weight of melt, 15.0 g. Addition of 200 mg of AlCl_3 changes the melt composition to AlCl_3 - NaCl (50.3–49.7 mol %).

melt composition for one run at different temperatures. As in ref 2a, we have taken the reference electrode potential to be zero. The results, within the limit of the experimental error, were the same if the starting melt was AlCl_3 rich and NaCl was added or if the initial melt was nearly saturated with NaCl , as in Figure 1. To calculate the equilibrium constant, the following procedure was employed. The number of moles of AlCl_3 added to reach the midpoint of the titration curve (Figure 1) was taken to be equal to the number of moles of free Cl^- initially ($\text{AlCl}_3 + \text{Cl}^- \rightarrow \text{AlCl}_4^-$). With this information, using eq 8, the Cl^- concentration at the equivalence point was calculated. At the equivalence point $X_{\text{Cl}^-} = X_{\text{Al}_2\text{Cl}_7^-}$ (see eq 1). Since $X_{\text{AlCl}_4^-}$ is known (at the equivalence point from the number of moles of NaAlCl_4 per kilogram of melt), the constant

$$K = X_{\text{Cl}^-} X_{\text{Al}_2\text{Cl}_7^-} / X_{\text{AlCl}_4^-}^2 \quad (9)$$

is readily calculated (note that K expressed as above is numerically the same on other concentration scales). pK in the temperature range 175–400° is given in Table I. The value of $K' = [\text{Cl}^-][\text{Al}_2\text{Cl}_7^-]$ at 175°

TABLE I
VARIATION OF pK WITH TEMPERATURE

Temp, °C	pK	Temp, °C	pK
175	7.1 ± 0.1	350	5.3 ± 0.2
250	6.3 ± 0.1	400	5.0 ± 0.2
300	5.7 ± 0.2		

expressed on the molality scale is $(2.0 \pm 0.3) \times 10^{-6} \text{ mol}^2 \text{ kg}^{-2}$ (result of three measurements), in reasonable agreement with the value of $(3.4 \pm 0.4) \times 10^{-6}$ obtained by Tremillon and Letisse.^{2a}

The concentration of Cl^- in NaAlCl_4 solutions saturated with NaCl (solubility of NaCl), as a function of temperature, is shown in Figure 2.

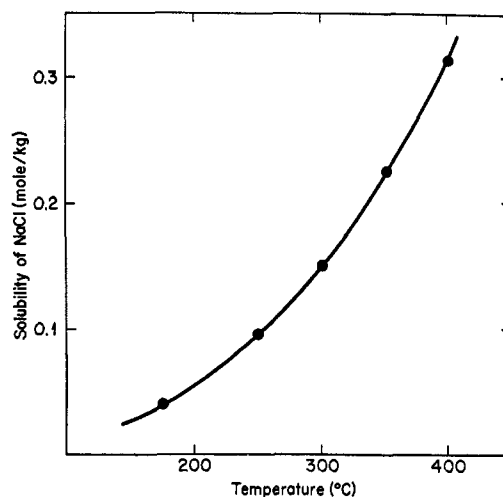


Figure 2.—Solubility of NaCl in NaAlCl_4 melt as a function of temperature.

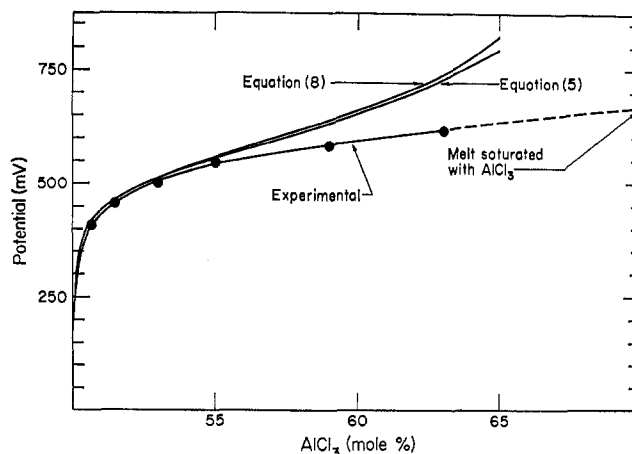
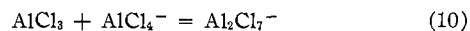


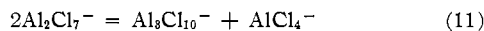
Figure 3.—Comparison of experimental and predicted potentials as a function of melt composition. The approximate composition of the melt saturated with AlCl_3 is 70–80 mol %.

In Figure 3, the experimentally obtained voltages of cell 2 at 175° as the function of melt composition are compared with values calculated from eq 5 and 8 assuming that in the acidic melts the reaction



is quantitative and that the activity coefficients of Na^+ , AlCl_4^- , and Al_2Cl_7^- remain the same. The deviations at compositions beyond 55 mol % AlCl_3 show that the above assumptions are not justified.

Previous Raman work⁹ indicated the presence of equilibria such as



and reaction 10 in acidic melts. The existence of Al_2Cl_6 and at least one uncharacterized species in

compositions of high AlCl_3 content (possibly $\text{Al}_3\text{Cl}_{10}^-$) was also demonstrated by the Raman measurements.

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A Spectral and Conductance Study of Gallium Trihalides and Their Complexes in Acetonitrile

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Infrared and conductance measurements of gallium trihalides and their complexes in acetonitrile are reported. Gallium trihalides are found to dissociate in acetonitrile to give solvated dihalogallium ion GaX_2S_2^+ (where X = Cl, Br, or I and S = acetonitrile) and tetrahalogallate ion GaX_4^- . The cation solvation number of 2 was determined from pmr spectral measurements of concentrated solutions of gallium tribromide in acetonitrile at low temperatures. The stability of the tetrahalogallate ion in acetonitrile solutions was established from conductance and infrared measurements of $(\text{C}_2\text{H}_5)_4\text{NGaX}_4$ salts. Single-ion limiting conductance values of 98.0, 103.1, and 106.2 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ were obtained for GaCl_4^- , GaBr_4^- , and GaI_4^- , respectively. The preference of gallium for four-coordination in acetonitrile, in both the anion and the cation, is discussed in terms of the base strength and solvating power of the solvent. The 1:1 adducts of gallium trihalide with the strong basic bidentate ligand 1,10-phenanthroline are ionic salts containing the GaX_4^- as the anion. The cation is six-coordinate $\text{Ga}(\text{phen})_2\text{X}_2^+$. Based upon this formulation, the salts behave as typical 1:1 electrolytes in acetonitrile with low single-ion conductance values of 63.1, 47.8, and 37.5 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ for the dichloro-, dibromo-, and diiodobis(1,10-phenanthroline)-gallium(III) cations, respectively. Addition of AgBF_4 to their acetonitrile solutions results in the formation of salts formulated as $\text{Ga}(\text{phen})_2(\text{BF}_4)_2\text{GaX}_4$. The tendency of gallium to assume a higher coordination number than 4 with strong basic ligands is also shown in the case of the 2:3 gallium trichloride- and gallium tribromide-pyridine complexes in which the cation probably is five-coordinated and the anion is GaX_4^- .

Introduction

This work is part of a continuing effort to define the nature of solute species in acetonitrile. Previously, boron trihalides and their complexes,^{2,3} aluminum chloride, phosphorus pentachloride, antimony pentachloride,⁴ and ionic salts⁵ had been investigated. The growing use of acetonitrile as a solvent for polarographic studies,^{6,7} for ionic reactions,⁸ and for electrosynthesis⁷ encourages continued activity in solute characterization.

Results

Tetraethylammonium Tetrahalogallates.—The measured molar conductances and corresponding concentrations for the tetraethylammonium tetrahalogallate salts in acetonitrile at 25° are shown in Table I. The data indicate that the tetrahalogallate salts are typical 1:1 electrolytes in acetonitrile. Computer analysis of the data by the Fuoss-Onsager conductance equation^{9,10} on a 7040 IBM computer showed that the salts are completely dissociated and have Λ_0 values of 183.0 ±

0.9 $(\text{C}_2\text{H}_5)_4\text{NGaCl}_4$, 188.1 ± 0.7 $(\text{C}_2\text{H}_5)_4\text{NGaBr}_4$, and 191.2 ± 0.8 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ $(\text{C}_2\text{H}_5)_4\text{NGaI}_4$. Values of 98.0, 103.1, and 106.2 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ were obtained for the single-ion limiting conductance of GaCl_4^- , GaBr_4^- , and GaI_4^- , respectively. A value of 85.05¹¹ $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ was used for λ_0 of the tetraethylammonium ion. The relative order of single-ion limiting conductances is that which is expected for the case where the smaller, more polarizing ion interacts more strongly with the polar solvent to produce a large solvodynamic radius and a reduced ion mobility.

The infrared spectrum of crystalline tetraethylammonium tetrabromogallate shows a strong band at 270 cm^{-1} which is assigned to the ν_3 frequency of the tetrahedral GaBr_4^- ion.^{12,13} This band appears at the same position in the infrared spectrum of its acetonitrile solution. The infrared spectrum of crystalline tetraethylammonium tetrachlorogallate shows a very strong band at 372 cm^{-1} (with a shoulder at 357 cm^{-1}), which is characteristic of the ν_3 vibration of GaCl_4^- (T_d).^{12,14,15} In the solution spectrum of the salt, this band cannot be observed because it is buried under the strong acetonitrile absorption band at 375 cm^{-1} . The ν_3 frequency of GaI_4^- (T_d) at 225 cm^{-1} ^{13,15} lies below the experimental limit of our instrument.

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