constrained to be 0.7, a value which would admit some covalency in the chromium–carborane bonds. The resulting best fit, which yielded a value for the distortion parameter Δ of 555 cm^{-1}, is shown in Figure 6, where it may be seen that the fit is not good, even qualitatively. These data suggest that the chromium(II) carborane complex and chromocene have comparable electronic ground states, but it is clear that a structural study of the former is needed before a definitive answer can be had for this problem.

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Appendix

The magnetic susceptibility expression for the $^3\Delta$ state of the d^4 electronic configuration under the influence of a C_{2v} distortion is as follows:

$$\chi_{\parallel} = 3T\{(1 + 2k'ab)^2e^{-\alpha/2} + (1 - 2k'ab)^2e^{\alpha/2} + k'^2[2(a^2 - b^2)^2(e^{\alpha/2} - e^{-\alpha/2})\alpha^{-1} + (e^{\delta x/2} - e^{-\delta x/2})(\delta x)^{-1}]\}/ \{2(e^{\alpha/2} + e^{-\alpha/2}) + e^{\delta x/2} + e^{-x/2}\}$$

$$\chi_{\perp} = 6T\{a^2(e^{\alpha/2} - e^{-\alpha/2} - e^{\delta x/2} + e^{-\delta x/2}) \times (\alpha - \delta x)^{-1} + b^2(e^{\alpha/2} - e^{-\alpha/2} + e^{\delta x/2} - e^{-\delta x/2})(\alpha - \delta x)^{-1}\}/ \{2(e^{\alpha/2} + e^{-\alpha/2}) + e^{\delta x/2} + e^{-\delta x/2}\}$$

$$\chi = {}^1\!/_3(\chi_{\parallel} + 2\chi_{\perp})$$

where $x = -\xi/kT$, $\delta = \Delta/\xi$, $a = {}^1/_2[\delta + (4 + \delta^2)^{1/2}]\{{}^1/_4[\delta + (4 + \delta^2)^{1/2}]^2 + 1\}^{-1/2}$, $b = \{{}^1/_4[\delta + (4 + \delta^2)^{1/2}]^2 + 1\}^{-1/2}$, and $\alpha = x(4 + \delta^2)^{1/2}$.

Registry No. $[(C_2H_5)_4N]_2[Cr(C_2B_{10}H_{12})_2]$, 60270-25-9; $Cs[Cr(1,2\text{-}C_2B_9H_{11})_2]$, 12373-83-0.

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Potentiometric Investigation of Dialuminum Heptachloride Formation in Aluminum Chloride–1-Butylpyridinium Chloride Mixtures

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The solvent acid–base properties of AlCl$_3$:1-butylpyridinium chloride melts from 2.2:1.0 to 0.6:1.0 molar ratios have been investigated by potentiometry. An equilibrium constant, K_3, for the dissociation reaction $2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$ was determined to be $<3.8 \times 10^{-13}$ at 30 °C. The 1-butylpyridinium cation is spontaneously reduced by elemental aluminum in the basic composition range.

Introduction

Considerable interest has been shown recently in molten-salt mixtures that are liquid at ambient temperatures, in view of the possibilities for their use as novel matrix solvents or electrolytes. The fused aluminum halide–alkylpyridinium halide systems are low melting, relatively easy to synthesize, and miscible with organic solvents such as benzene.[1-4] An investigation of the ionic species equilibria in AlCl$_3$–1-butylpyridinium chloride mixtures, by Raman spectroscopy,[5] has indicated that association reaction 1 is virtually complete and

$$2AlCl_4^- + Al_2Cl_6 \rightleftarrows 2Al_2Cl_7^- \qquad (1)$$

that no molecular aluminum chloride could be detected in the 2:1 molar ratio mixture at room temperature.

Equilibria 2–6 have been commonly used to relate the major

$$Al^{3+} + 4Cl^- \rightleftarrows AlCl_4^- \qquad (2)$$

$$2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^- \qquad (3)$$

$$Al_2Cl_6 + Cl^- \rightleftarrows Al_2Cl_7^- \qquad (4)$$

$$2AlCl_3 \rightleftarrows Al_2Cl_6 \qquad (5)$$

$$AlCl_4^- + Al_2Cl_6 \rightleftarrows Al_3Cl_{10}^- \qquad (6)$$

solvent species in AlCl$_3$–MCl systems, M usually being an alkali metal cation.[6-11] If an aluminum reference electrode behaves as a reversible indicator electrode, model equilibria may be applied to potentiometric titration data by using the Nernst equation (7) which, incorporated with the association

$$E = E^\circ + (RT/3F)\ln(a_{Al(III)}/a_{Al(0)}) \qquad (7)$$

constants for reaction 2, gives eq 8 for a reference state

$$\Delta E = (RT/3F)\ln(a^\circ_{AlCl_4^-}/a^i_{AlCl_4^-}) + (4RT/3F)\ln(a^i_{Cl^-}/a^\circ_{Cl^-}) \qquad (8)$$

(superscript °) and any other state i (superscript i). Hence, an electrochemical cell of the type

$$Al|RCl,\ AlCl_3(ref)\vdots fritted\ disk\vdots AlCl_3(c),\ RCl|Al$$

where R represents an alkylpyridinium cation, may be used as a pCl$^-$ electrode. The purpose of the present investigation is twofold: (i) to quantitatively assess the association constants for the major ionic equilibria and (ii) to examine the effects that the nature of the cationic moiety of the halide salt has on the solvent equilibria.

Experimental Section

Melts were prepared by mixing accurately weighed quantities of purified aluminum chloride and 1-butylpyridinium chloride. The purification procedures for these compounds are described elsewhere.[5] In order to avoid discoloration and thermal decomposition, we added

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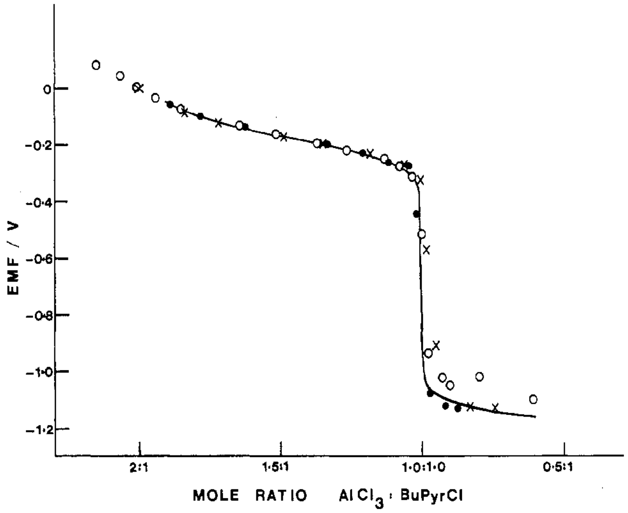

Figure 1. Potentiometric data for $AlCl_3$–1-butylpyridinium chloride vs. Al(0) [2:1 mixture:reference mole ratio]: ×, 30 °C; ○, 60 °C; ●, 120 °C; —, theory (30 °C).

the pieces of aluminum chloride slowly, with stirring, to the 1-butylpyridinium chloride crystals in the cell. The colorless solvents can be titrated either by weighed additions of 1-butylpyridinium chloride to an acidic melt or by anodization of an aluminum electrode to a basic melt, which is tantamount to the addition of $AlCl_3$. The former procedure was finally adopted because of a spontaneous reaction of aluminum with the solvent in melts which contain an excess of free chloride ions; vide infra.

The electrochemical cell employed for the potentiometric titrations was made of Pyrex, and the reference electrode compartment, containing coiled aluminum wire (m 5N, Alfa Products), was isolated with a fritted Pyrex disk. The electrolyte level in the reference electrode compartment was maintained very slightly higher than that of the bulk solution. A proportional thermoelectric controller was used to control the temperature of the melt to ±1 °C by use of a Pyrex-sheathed chromel–alumel thermocouple (Thermo Electric 400). All operations were made under a drybox atmosphere of purified argon.

Results

Figure 1 illustrates the results of experimental titrations from approximately 2.0:1.0 to 0.6:1.0 molar ratio $AlCl_3$:1-butylpyridinium chloride at 30, 60, and 120 °C, respectively. The overall features of the sigmoidal curve are distinct in several respects from those obtained for the $AlCl_3$–NaCl melt at 175 °C.[6] First, the potential difference between the plateau regions in Figure 1 is larger by a factor of approximately 2–3 than that of the $AlCl_3$–NaCl melt, resulting in a greater pCl^- range. Second, the data for the basic portion of the curve were less reproducible than those for the acidic regions, and a blue coloration appearing at the aluminum electrode is an indication that secondary reaction occurs. Finally, unlike the potential data for the high-temperature $AlCl_3$–NaCl systems, the curve changes slope again in the region of the 2:1 molar ratio melt composition.

Estimation of Equilibria Constants

An approximate conditional equilibrium constant for the potentiometric data of Figure 1, in terms of the major equilibrium reaction (1), may be obtained by using eq 8 for the acidic range (state *i*) and a reference state at the equivalence midpoint of the potential break in the potentiometric titration when $a_{Cl^-} = a_{Al_2Cl_7^-}$. The activities of any free Al(III) ions, $Al_3Cl_{10}^-$ ions, or molecular Al_2Cl_6 or $AlCl_3$ are disregarded for the purpose of this calculation with respect to the major ionic constituents of the melt, namely, $AlCl_4^-$, $Al_2Cl_7^-$, and Cl^-. The liquid junction potential at the Pyrex frit reference was neglected.[6,7] Then, at 30 °C

$$K_3 = [Al_2Cl_7^-][Cl^-]/[AlCl_4^-]^2 = 3.8 \times 10^{-13}$$

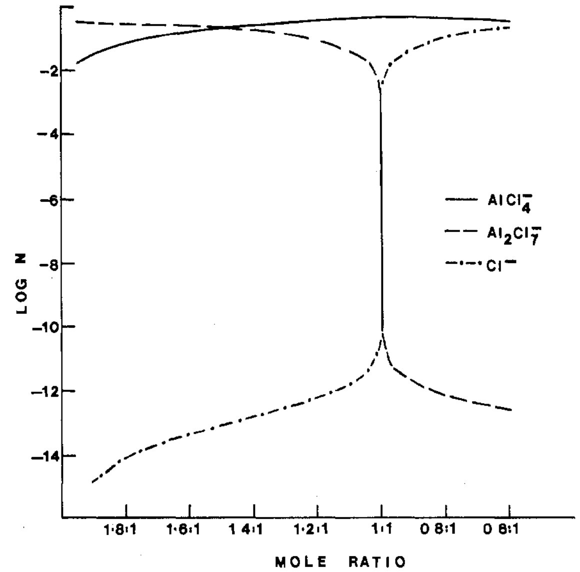

Figure 2. Mole fraction, *N*, of the major species in the melt at 30 °C as a function of the net $AlCl_3$:RCl mole ratio.

The potential function represented by eq 8 is shown in Figure 1 as a solid line for this value of K_3. Compared to that of the $AlCl_3$–NaCl system at 175 °C,[6,7] the experimental change in potential with molar composition steepens between the 1.6:1 and 2.2:1 molar ratios and more closely follows the form of eq 8. Thus, the replacement of activities by concentrations appears justified in this system. Obviously, this model is inappropriate for aluminum chloride:1-butylpyridinium chloride ratios in excess of 2:1. In addition, the estimation of the equilibrium constant in this manner assumes that the positive shift due to the mixed potential arising from the spontaneous reduction of the 1-butylpyridinium cation by elemental aluminum is not significant (<1.0:1.0 mole ratio range). This will be true if the exchange reaction for the aluminum couple is large relative to the cathodic reduction currents; however, the magnitude of K_3 should be regarded as a minimum value. Figure 2 illustrates the changes in the species composition calculated for the K_3 value of 3.8×10^{-13}. The chloride ion mole fraction almost spans the range found in the proton–hydroxyl equilibrium in water.

Potentiometric curves were obtained at 30, 60, 120, and 175 °C but did not reveal any significant differences in the potential span. This is unlike the $AlCl_3$–NaCl system at higher temperatures which has a 25% reduction in the potential span at 250 °C compared to that at 175 °C.[7]

Discussion

The results of this potentiometric study are consistent with the Raman spectral data and indicate that the formation of $Al_2Cl_7^-$ ion proceeds to a greater extent in the $AlCl_3$–1-butylpyridinium chloride system than in the previously studied alkali metal halide systems (Table I). Unfortunately, it is difficult to compare directly the absolute values for the equilibrium constant K_3. Different model systems have been used, and in certain cases there are restrictions in the accessible stability of liquidus temperature ranges. Torsi and Mamantov[11] have reported an increase in K_3 through the cation series $Li^+ < Na^+ < K^+ < Cs^+$, at 400 °C. This finding essentially agrees with the interpretations by Ikeuchi and Krohn[12] or Schulze et al.,[8] who use a three-parameter model and report a decrease in the equilibrium constants for reaction 4 at 450 °C; Na^+ (2×10^{-6}) < Rb^+ (1.1×10^{-8}) < Cs^+ (1×10^{-9}); K_3 for this model remains relatively constant (Table I). The direct correlation between the cationic radii and the extent of $Al_2Cl_7^-$ ion formation may relate to the inverse ionic field strength as one might expect anionic complexes to be

Table I. Mole Fraction Equilibrium Constants for $Al_2Cl_7^-$ Ion Formation in $AlCl_3$-MCl^a Melts from Potentiometric Data

system	$K_3{}^b$	temp, °C	ref
$AlCl_3$-1-BupyCl	$<3.8 \times 10^{-13}$	30	this work
	$<5.7 \times 10^{-12}$	60	this work
	$<3.6 \times 10^{-10}$	120	this work
	$<1.2 \times 10^{-8}$	175	this work
$AlCl_3$-NaCl	1.06×10^{-7}	175	6
	8.00×10^{-8}	175	7
	7.77×10^{-8}	175	10
	1.33×10^{-7}	175	9
$AlCl_3$-LiCl	1.6×10^{-4}	400	11
$AlCl_3$-NaCl	1.0×10^{-5}	400	11
$AlCl_3$-KCl	1.6×10^{-6}	400	11
$AlCl_3$-CsCl	4.0×10^{-8}	400	11
$AlCl_3$-NaCl	5.78×10^{-7}	450	8
$AlCl_3$-RbCl	2.87×10^{-7}	450	8
$AlCl_3$-CsCl	7.58×10^{-7}	450	8

[a] M represents a cationic species. [b] Dissociation constant for $2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$.

more stable with decreasing cationic polarizability.[11] The value of K_3 obtained with the relatively large, organic 1-butylpyridinium cation is consistent with this general trend.

The major effect of temperature variation, from 30 to 175 °C, is consistent with a change in the reaction equilibrium, according to the relation

$$\Delta G^\circ = -RT \ln K_3$$

On the basis of the equilibrium constants obtained from the potentiometric curves for this system (Table I), the free energy remains approximately constant throughout the 145 °C temperature span at $(7.1 \pm 0.3) \times 10^4$ J mol^{-1}. Unfortunately, precise thermodynamic data is precluded because of the corrosion process which occurs in the basic $AlCl_3$–1-butylpyridinium chloride systems. One practical consequence of the increased $Al_2Cl_7^-$ ion formation and the lower activity of free Al_2Cl_6 in these molten mixtures, relative to the $AlCl_3$–NaCl system, is that sublimation losses of Al_2Cl_6 are minimal even at 175 °C. They may be also useful solvent systems for stabilizing unusually low valence metallic ion species.

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Registry No. $AlCl_3$, 7446-70-0; 1-BupyCl, 1124-64-7; $Al_2Cl_7^-$, 27893-52-3.

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Free Metal and Free Ligand Concentrations Determined from Titrations Using Only a pH Electrode. Partial Derivatives in Equilibrium Studies

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In the studies of metal complex equilibria in aqueous solutions, the variation techniques presented by Osterberg, Sarkar, Kruck, and McBryde allow one to calculate free metal and free (unassociated) ligand concentrations from titration experiments using only a pH electrode. The method makes no assumptions about the associated species present in solution and is thus model independent. We present an alternate general derivation of the expressions and attempt to clarify the technique. Although the approach described below is applicable to any number of components (metals, ligands), in a manner analogous to Hedström's treatment of two-component systems we treat the three-component system by introducing six Jacobian unit determinants for the six variables (M, L, H, m, l, h), that is, the three total and three free concentrations of the metal, ligand, and hydrogen respectively:

$$J\left(\frac{M, \ln m, \ln h}{\ln l, L, \ln h}\right) = 1 \qquad J\left(\frac{M, \ln m, H}{\ln l, L, H}\right) = 1$$

$$J\left(\frac{L, \ln l, \ln m}{\ln h, H, \ln m}\right) = 1 \qquad J\left(\frac{L, \ln l, M}{\ln h, H, M}\right) = 1$$

$$J\left(\frac{H, \ln h, \ln l}{\ln m, M, \ln l}\right) = 1 \qquad J\left(\frac{H, \ln h, L}{\ln m, M, L}\right) = 1$$

These Jacobians are very useful in deriving numerous variational expressions. Using computer-generated data, we test the techniques under a variety of conditions. A useful Fortran computer program is discussed. A simple technique for analytically evaluating implicit functions such as $(\partial \mathrm{pH}/\partial M)_L$ or $(\partial \mathrm{pH}/\partial L)_M$ is presented. This enables one to avoid the use of numerical methods in the least-squares refinement of formation constants, thus leading to substantial reduction in the computational effort.

Introduction

Osterberg[1] and, later, Sarkar and Kruck[2] and McBryde[3] introduced an extremely valuable technique for evaluating the free metal and free ligand concentrations in multicomponent equilibria by the use of pH titration data alone. That is, one could indirectly measure pM (−log [M], [M] = free metal concentration) and pL ([L] = free (unassociated) ligand concentration) values by using only a pH electrode. The

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