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Potentiometric Studies of the Chlorine Electrode in Ambient-Temperature Chloroaluminate Ionic Liquids: Determination of Equilibrium Constants for Tetrachloroaluminate Ion Dissociation

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The potentiometric behavior of the chlorine electrode has been investigated at 40 °C in aluminum chloride–*N*-1-butylpyridinium chloride and in aluminum chloride–1-methyl-3-ethylimidazolium chloride ionic liquids. In basic (excess organic chloride) melts the Nernstian behavior of a tungsten electrode in solutions containing $Cl_2(g)$ indicates two electrode reaction stoichiometries: $Cl_3^- + 2e^- = 3Cl^-$, when chloride ion is in excess over chlorine, and $3Cl_2 + 2e^- = 2Cl_3^-$, when there is an excess of chlorine. Formal potentials of the Cl_2/Cl_3^-, Cl_3^-/Cl^-, and Cl_2/Cl^- couples have been determined in both ionic solvents, and the stability constant of the Cl_3^- ion has been obtained ($\beta_{Cl_3} = 64$ and 30 $dm^3\ mol^{-1}$ in butylpyridinium and imidazolium chloroaluminates, respectively). The difference between $E^{\circ\prime}_{Cl_2/Cl^-}$ values in these two solvents reflects the difference between ionic association constants for the two organic chlorides. In acidic (excess $AlCl_3$) melt compositions, slow equilibria and reactions of chlorine with the organic cations impede potentiometric measurements with the chlorine electrode. The reversible chlorine electrode potential could be measured only in acidic $AlCl_3$–BuPyCl melts, and the tetrachloroaluminate ion dissociation constant $\log K^{BuPyCl} = -17.0 \pm 0.5$ has been obtained. In the acidic 1.1:1 $AlCl_3$–ImCl system the half-life of chlorine is ca. 1 min; thus, the chlorine electrode cannot be used in this system. The tetrachloroaluminate ion dissociation constant in the latter system ($\log K^{ImCl} = -17.1 \pm 0.5$) was calculated from the difference of the aluminum electrode potentials in acidic $AlCl_3$–BuPyCl and $AlCl_3$–ImCl ionic liquids.

Introduction

Mixtures of aluminum chloride and chlorides of large organic cations form ambient-temperature ionic liquids,[1–5] which exhibit interesting acid–base properties.[6,7] The major equilibrium describing acid–base properties of these liquids is the dissociation of tetrachloroaluminate ion:[4,5,8–12]

$$2AlCl_4^- = Al_2Cl_7^- + Cl^- \qquad (1)$$

For a determination of the equilibrium constant of reaction 1, chloride ion activities on both sides of an equivalence point at the neutral (1:1 $AlCl_3$:RCl mole ratio, where R^+ is an alkali metal or an organic cation) melt composition need to be measured. As we have recently found,[13] the aluminum electrode cannot be used for potentiometric measurements in basic ($AlCl_3$:RCl < 1) compositions of either $AlCl_3$–BuPyCl (BuPyCl = *N*-1-butylpyridinium chloride) or $AlCl_3$–ImCl (ImCl = 1-methyl-3-ethylimidazolium chloride) ionic liquids. On the other hand, voltammetric measurements indicated the possibility of the determination of chloride ion activities in these systems in potentiometric experiments with a chlorine electrode. The chlorine electrode has been used previously for potentiometric studies in high-temperature alkali-metal chloroaluminates.[8,14–16]

In this study, potentiometric investigations of the chlorine electrode behavior in ambient-temperature ionic liquids—$AlCl_3$–BuPyCl and $AlCl_3$–ImCl—are described and the equilibrium constant for reaction 1 in these two systems is determined.

Experimental Section

Methods used for synthesis of *N*-1-butylpyridinium chloride and of 1-methyl-3-ethylimidazolium chloride, for purification of $AlCl_3$ (Fluka) and preparation of melts were similar to those described previously.[3,5] Chlorine gas (Matheson) in lecture bottles was used as received.

All experiments were carried out under a purified argon atmosphere in a Vacuum Atmospheres drybox with an HE 493 Dri-Train. Constant temperature (40 ± 1 °C) was maintained witha Selectrol (Thermo Electric) proportional temperature controller.

Tungsten (TE) and glassy-carbon (GCE) electrodes, sealed in glass ($A = 0.0784$ and 0.196 cm^2, respectively), were used as indicator electrodes. The reference electrode was a Ag^+/Ag electrode (0.01 mol dm^{-3} Ag^+ in 1.5:1 $AlCl_3$–RCl melts), whose potential is more stable and reproducible than the aluminum reference electrode usually used in chloroaluminate melts.[17] Rotating-disk experiments were performed with an EG&G PARC 174A polarographic analyzer and HP 7046A X-Y recorder. In potentiometric experiments a Keithley 168 digital voltmeter was used. Absorption spectra were obtained with a Perkin-Elmer Model Coleman 750 spectrophotometer using 0.1-cm matched quartz cells (Wilmad).

Table I. Dependence of Diffusion Coefficient and Stokes–Einstein Product of Chlorine on the Melt Compositions

N_A/N_B[a]	$10^6 D_{Cl_2}$, $cm^2\ s^{-1}$	$10^9 D_{Cl_2}\eta/T$, $g\ cm\ s^{-2}\ K^{-1}$	N_A/N_B[a]	$10^6 D_{Cl_2}$, $cm^2\ s^{-1}$	$10^9 D_{Cl_2}\eta/T$, $g\ cm\ s^{-2}\ K^{-1}$
		$AlCl_3$–BuPyCl			
0.75	0.32	0.52	1.3	4.5	2.73
0.85	0.50	0.53	1.5	5.5	3.07
0.9	0.52	0.47	1.8	4.7	2.4
0.95	0.61	0.50	1.99	5.5	2.55
1.1	3.6	2.35			
		$AlCl_3$–ImCl			
0.72	0.55	0.48	0.95	1.2	0.52
0.85	0.82	0.52			

[a] In this and subsequent tables N_A = number of moles of $AlCl_3$ and N_B = number of moles of RCl.

Concentrations of solvent ions as well as solutes are expressed in mol dm^{-3}. Solvent ion concentrations were calculated from the stoichiometry at the melt preparation by mixing accurately weighed quantities of $AlCl_3$ and an organic salt. Since chlorine reacts with organic cations of these

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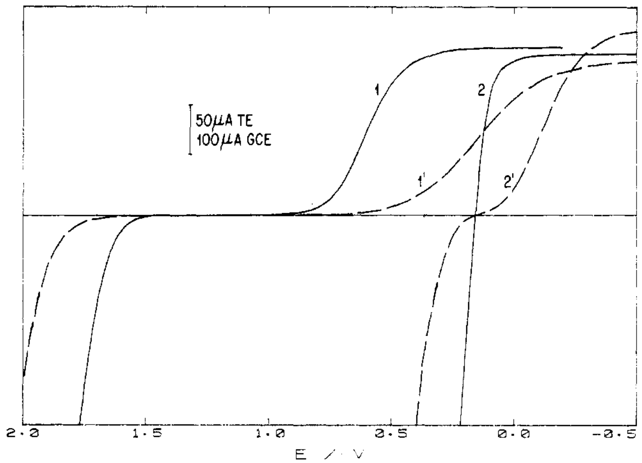

Figure 1. RDE voltammograms (rotation rate 900 rpm) at tungsten (plots 1 and 2) and glassy-carbon (plots 1′ and 2′) electrodes for chlorine solutions in $AlCl_3$–BuPyCl melts: (plots 1 and 1′) 1.3:1 $AlCl_3$:BuPyCl, 5 mM Cl_2; (plots 2 and 2′) 0.9:1 $AlCl_3$:BuPyCl, 20 mM Cl_2.

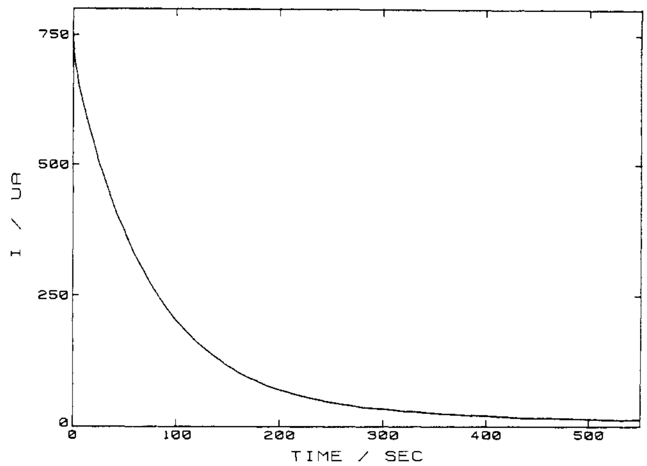

Figure 2. Time dependence of the RDE limiting current of chlorine reduction in a 1.1:1 $AlCl_3$–ImCl melt (E = –0.5 V, tungsten electrode, rotation rate 900 rpm).

low-temperature chloroaluminate melts (vide infra), a sealed cell could not be used. Instead, the chlorine gas was bubbled through the melt in an open cell and the actual concentration of dissolved chlorine was determined by RDE voltammetry immediately after the potential measurements. A diffusion coefficient for chlorine was calculated from RDE experiments performed immediately after the chlorine concentration was determined from the difference in the weight of the melt sample measured before and after chlorine had been bubbled through the melt.

Results

Voltammetric Studies of Chlorine Solutions. Rotating-disk voltammograms recorded in chlorine solutions in acidic and basic $AlCl_3$–BuPyCl mixtures at tungsten and glassy-carbon electrodes are shown in Figure 1. The cathodic chlorine reduction waves exhibit well-defined plateaus, and the cathodic limting currents are linearly dependent on the square root of the electrode rotation rate, showing that these currents are convective diffusion controlled. Since the chlorine concentration was known from the weighings (see Experimental Section), the diffusion coefficient of chlorine in various melt compositions could be calculated from the Levich equation. The values obtained are shown in Table I. Despite the low accuracy of these measurements, resulting from a lack of precision in determining chlorine concentration, the Stokes–Einstein products shown in Table I indicate a reasonable constancy of the chlorine solvolytic radii for basic compositions of $AlCl_3$–ImCl and $AlCl_3$–BuPyCl and also throughout acidic compositions of $AlCl_3$–BuPyCl mixtures. The $D\eta/T$ values for acidic chlorine solutions were, however, distinctly larger than for basic solutions, indicating the formation of different chlorine species in acidic and basic melts (vide infra). The mean values of the Stokes–Einstein products thus obtained were used to determine the actual concentration of dissolved chlorine during the course of experiments by use of RDE voltammetry results. It was found that chlorine concentration in the melts decreased in time; apparently the chlorine solutions in the organic chloroaluminate melts were unstable. The chlorination of imidazolium cation in $AlCl_3$–ImCl melts has been previously observed,[18] and indeed the reaction of chlorine with 1.1:1 $AlCl_3$–ImCl melt was fast. The decrease of the height of the cathodic wave (Figure 2), reflecting the diminution of the chlorine concentration, followed first-order kinetics with a pseudo-first-order rate constant of ca. 5×10^{-3} s^{-1} and a chlorine half-life in this solution of about 1 min. This reaction of chlorine with imidazolium cation hindered potentiometric measurements for chlorine solutions in acidic $AlCl_3$–ImCl mixtures. Fortunately, however, chlorine solutions in acidic $AlCl_3$–BuPyCl melts were more stable. The decrease in the chlorine concentration in the latter solutions did not follow first-order kinetics; the chlorine concentration dropped to half the initial value within ca. 45 min. Chlorine reacted much less rapidly with basic chloroaluminate melts. Its concentration decreased by less than 30% per hour, and chlorine volatilization probably accounted for most of this decrease.

In contrast to the diffusion-controlled cathodic waves, large anodic currents were observed for RDE voltammograms recorded for chlorine solutions in acidic as well as basic melts (Figure 1). Cyclic voltammetric experiments showed that these anodic currents arise from chlorine evolution reactions and reflect the positive potential limits in both $AlCl_3$–BuPyCl and $AlCl_3$–ImCl systems:[13] a well-defined plateau for the chlorine evolution wave from Cl^- oxidation can be obtained only in nearly "neutral" chloroaluminate melts that contain millimolar amounts of Cl^-.[19,20]

The shapes of the RDE voltammograms obtained at tungsten and glassy-carbon electrodes indicate that the electrode reaction rates are much faster at the TE at all melt compositions. A lack of an inflection point at zero current on the voltammogram recorded with a TE in the basic chlorine-containing solution (Figure 1, plot 2) shows that chlorine evolution and reduction processes proceed with low overpotentials. At the GCE these reactions are irreversible (Figure 1, plot 2′). In acidic melt compositions the potential difference between the anodic and the cathodic portions of the RDE voltammogram was also distinctly larger at the GCE (Figure 1, plot 1′) than at the TE (Figure 1, plot 1), thus showing that the electrode reactions are slower at the former electrode.

Potentiometry. The differences of electrode reaction rates in the Cl_2/Cl^- system at different melt compositions and/or different indicator electrodes, observed in voltammetric studies, were also evident in potentiometric experiments. The potential of the TE in chlorine solutions in basic melts was stable, reproducible within ±1 mV, and independent of the electrode rotation rate. The potential of the GCE in the same solution was also quite stable, with a reproducibility of ±2 mV, and its dependence on the electrode rotation rate was also ca. ±2 mV. On the other hand, in acidic melts containing chlorine the potential of a rotating TE was stable after ca. 5-min equilibration, its reproducibility was ca. ±10 mV, and the potential value was dependent, to some extent, on the electrode rotation rate. The difference between the potentials measured in a given solution when the TE was stationary and when this electrode was rotated at 3600 rpm was about 20 mV. The potential of the GCE in the same solution was even more dependent on the electrode rotation rate; the potential of the rotating GCE was about 50 mV more positive than the potential of the stationary electrode. These effects of slow electrode reaction rates in acidic chlorine solutions limited the accuracy of equilibrium potential measurements in acidic $AlCl_3$–BuPyCl mixtures.

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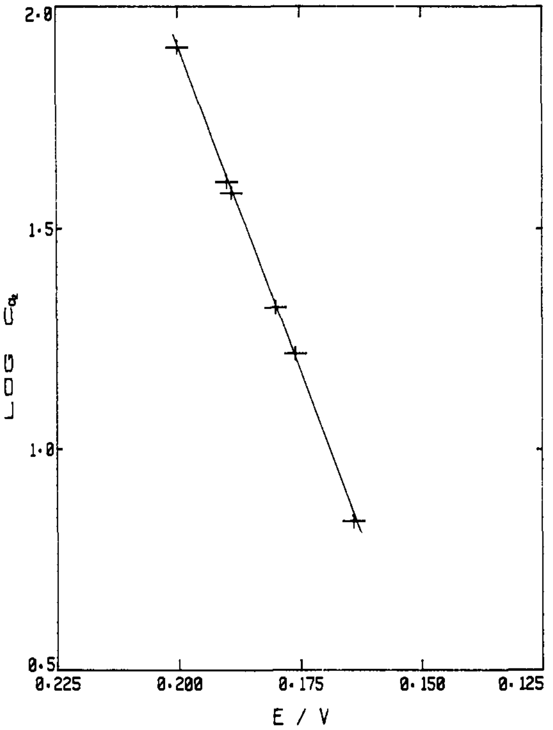

Figure 3. Dependence of the potential of a chlorine electrode in basic (0.9:1 $AlCl_3$:BuPyCl) melt on chlorine concentration. The ordinate has units of mmol dm^{-3}.

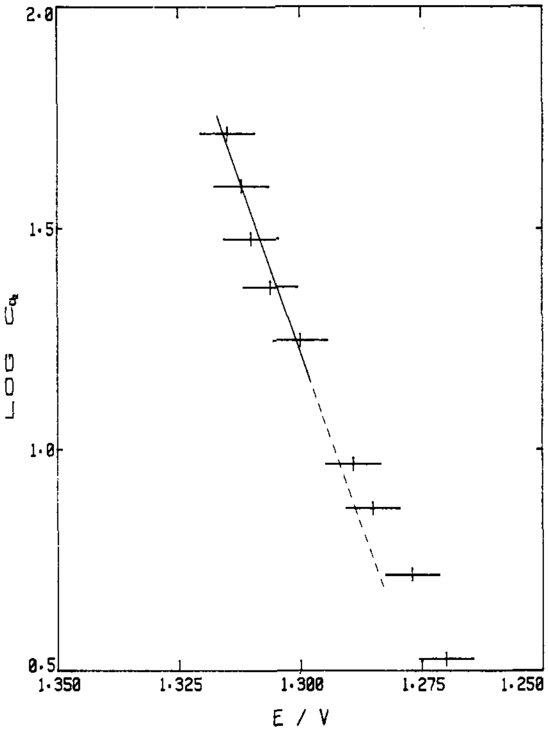

Figure 4. Dependence of the potential of a chlorine electrode in acidic (1.8:1 $AlCl_3$:BuPyCl) melt on chlorine concentration. The ordinate has units of mmol dm^{-3}.

Table II. Potentiometric Results for Chlorine Solutions in Basic Melts

N_A/N_B	C_{Cl},[a] mol dm^{-3}	$10^3C_{Cl_2}$, mol dm^{-3}	E_{eq}, V	$E°'_{Cl_3^-/Cl^-}$, V
		$AlCl_3$–BuPyCl		
0.75	1.1	109	0.161	0.195
		71	0.154	0.194
		22	0.138	0.194
0.85	0.645	111	0.184	0.196
		52	0.172	0.194
		7	0.145	0.194
0.9	0.42	82	0.200	0.198
		41	0.190	0.198
		38	0.189	0.198
		21	0.180	0.197
		16	0.176	0.196
		7	0.163	0.195
0.95	0.21	52	0.226	0.202
		12	0.202	0.198
		$AlCl_3$–ImCl		
0.72	1.404	140	0.169	0.209
		48	0.153	0.208
		14	0.136	0.208
0.85	0.60	107	0.202	0.211
		94	0.199	0.210
		38	0.186	0.209
		31	0.183	0.209
0.95	0.232	81	0.258	0.233
		43	0.246	0.229
		20	0.230	0.224

[a] Concentration of Cl^- calculated from measured or interpolated density data of ref 33 and 34.

However, the potential measured with a rotating TE at chlorine concentration greater than 20 mM followed the Nernst equation; a plot of E vs. log C_{Cl_2} had the slope 0.032 V (the theoretical value at 40 °C is 0.031 V) (Figure 3). This result and also the fact that potentials measured with a TE in acidic chlorine solutions were 20–30 mV more positive than the values measured in the same solutions with a GCE show that the equilibrium potential of the Cl_2/Cl^- couple was not significantly affected by the possible reaction of chlorine with tungsten, since any contribution of the latter reaction would shift the potential to less positive values. The accuracy of equilbrium potential measurements for the chlorine electrode in basic melts was much better than in acidic melt compositions. In solutions with excess chloride over chlorine the dependence of the equilibrium potential on chlorine concentration followed the Nernst equation, with a 0.031–0.034-V slope, over the concentration range 7–100 mM (Figure 4). At high chloride concentrations, changes of the equilibrium potential with concentration of dissolved chlorine and/or chloride ion followed eq 2. The formal potential of the Cl_3^-/Cl^- couple, calculated from

$$E = E°'_{Cl_3^-/Cl^-} + \frac{RT}{2F} \ln [Cl_3^-] - \frac{3RT}{2F} \ln [Cl^-] \qquad (2)$$

the latter equation, was constant at the most basic compositions of $AlCl_3$–BuPyCl and $AlCl_3$–ImCl melts (Table II), and the mean values were 0.195 and 0.214 V, respectively. This indicates the stoichiometry of the redox reaction determining the potential of the indicator electrode is

$$Cl_3^- + 2e^- = 3Cl^- \qquad (3)$$

The formation of Cl_3^- ion in chlorine solutions in the basic melts was also indicated by the difference in the Stokes–Einstein products of chlorine in acidic and basic melt compositions (Table I). This was additionally confirmed by UV spectra recorded for chlorine solutions in acidic and basic $AlCl_3$–BuPyCl melts (Figure 5). The molar absorptivity of chlorine with increasing chloride ion activity has been observed for molten alkali-metal chlorides[21] and for $AlCl_3$–CsCl melts[22] and was assigned to Cl_3^- formation. At lower chloride concentrations $E°'_{Cl_3^-/Cl^-}$ was not, however, constant, especially in $AlCl_3$–ImCl mixtures, where the formal potential shifted to more positive values (Table II). This indicates that Cl_3^- stability in basic low-temperature chloroaluminates is

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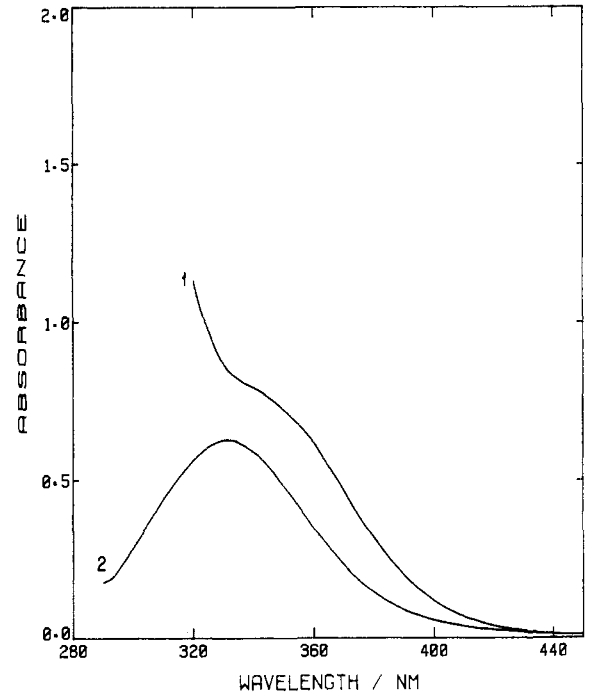

Figure 5. Absorption spectra of chlorine solutions in acidic and basic $AlCl_3$–BuPyCl melts: (1) 9 mM Cl_2, 0.9:1 $AlCl_3$:BuPyClf (2) 50 mM Cl_2, 1.3:1 $AlCl_3$:BuPyCl.

Table III. Potentiometric Results for Nearly "Neutral" Melts

$10^3C_{Cl_3^-}$, mol dm^{-3}	$10^3C_{Cl_3}$, mol dm^{-3}	E_{eq}, V	$E°'_{Cl_2/Cl_3^-}$, V
	$AlCl_3$–BuPyCl		
6	49	0.373	0.357
4.9	53	0.388	0.364
3.8	74	0.402	0.357
2.9	46	0.399	0.366
2.1	92	0.437	0.367
	$AlCl_3$–ImCl		
4.4	94	0.397	0.346
3.6	66	0.391	0.349
2.5	120	0.432	0.356
2.5	45	0.390	0.354
1.7	60	0.415	0.357

not high, and at low chloride concentration another electrode reaction affects the potential of the indicator electrode. Such behavior, with the equilibrium potential showing nonlinear dependence on log C_{Cl_2}, was observed for solutions with no marked excess of chlorine or chloride ion. However, in solutions with more than a 10-fold excess of chlorine over chloride ion, in nearly "neutral" melts, the potential of the indicator electrode followed the Nernst equation written for reaction 4. The values of the

$$3Cl_2 + 2e^- = 2Cl_3^- \qquad (4)$$

formal potential of the Cl_2/Cl_3^- couple calculated from eq 5 are

$$E = E°'_{Cl_2/Cl_3^-} + \frac{3RT}{2F}\ln\,[Cl_2] - \frac{RT}{F}\ln\,[Cl_3^-] \qquad (5)$$

shown in Table III. The accuracy of these measurements was less than at higher chloride concentrations. Because of difficulties in the "neutral" melt preparation,[19,20,23,24] concentrations of both chlorine and chloride ion were calculated from RDE voltammetry results, C_{Cl_2} from the height of the cathodic wave and $C_{Cl_3^-}$ from the anodic limiting current (Figure 6). The mean values of the Cl_2/Cl_3^- formal potential are 0.362 and 0.352 V for $AlCl_3$–BuPyCl and $AlCl_3$–ImCl systems, respectively.

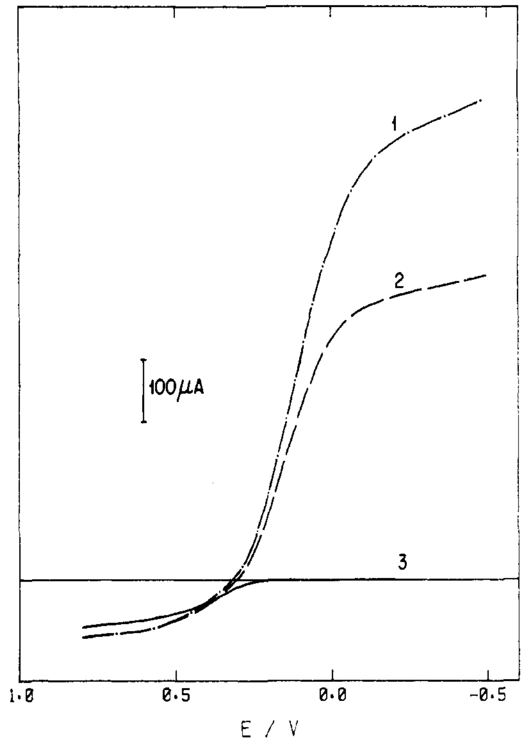

Figure 6. RDE voltammograms for chlorine solutions in nearly "neutral" $AlCl_3$–BuPyCl melt, C_{Cl_2} = (1) 35, (2) 25, and (3) 0 mM (tungsten electrode, rotation rate 900 rpm). Excess BuPyCl over $AlCl_3$ is 13 mM for all curves.

Table IV. Potentiometric Results for Acidic $AlCl_3$–BuPyCl Melts

N_A/N_B	$C_{Al_2Cl_7^-}/C_{AlCl_4^-}$, mol^{-1} dm^3	$10^3C_{Cl_2}$, mol dm^{-3}	$C_{Al_2Cl_7^-}/C_{AlCl_4^-}$, mol^{-1} dm^{-3}	$E°'_{Cl_2/AlCl_4^-}$
1.3	0.164	50	1.218	1.307
		41	1.214	1.305
		33	1.210	1.304
		28	1.208	1.305
1.5	0.572	53	1.241	1.296
		38	1.237	1.296
		30	1.233	1.295
		20	1.220	1.288
1.8	6.24	52	1.315	1.306
		39	1.312	1.306
		31	1.310	1.308
		24	1.306	1.307
		18	1.300	1.305
1.99	3260	68	1.420	1.238
		58	1.410	1.231
		42	1.407	1.232
		30	1.399	1.228

The equilibrium potential of the Cl_2/Cl^- couple in acidic ambient-temperature chloroaluminates could be measured only in $AlCl_3$–BuPyCl mixtures (vide supra). The results are shown in Table IV, and the dependence of the equilibrium potential on the melt acidity and chlorine concentration indicated the stoichiometry of the electrode reaction

$$Cl_2 + 2Al_2Cl_7^- + 2e^- = 4AlCl_4^- \qquad (6)$$

Thus the formal potential of the $Cl_2/AlCl_4^-$ couple was calculated from eq 7 and is also shown in Table IV. The values obtained

$$E = E°'_{Cl_2/AlCl_4^-} + \frac{RT}{2F}\ln\,[Cl_2] + \frac{RT}{F}\ln\frac{[Al_2Cl_7^-]}{[AlCl_4^-]^2} \qquad (7)$$

are approximately constant except for the most acidic melt composition. This deviation does not necessarily indicate a change in the electrode reaction stoichiometry. It may have been caused

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by an inaccuracy in the melt composition; melts with $AlCl_3$:RCl mole ratios close to 2 are poorly buffered, and a small inaccuracy in the melt composition causes a large change in equilibrium chloride concentration. The other reason for the deviation could be a significant decrease of the exchange current for the chlorine evolution and reduction processes caused by a low concentration of $AlCl_4^-$ ion, the reactant in the anodic process. From the values of $E°'_{Cl_2/AlCl_4^-}$ obtained in 1.3:1, 1.5:1, and 1.8:1 $AlCl_3$–BuPyCl mixtures, the mean value of 1.302 V was calculated.

Despite the experimental difficulties limiting the accuracy of the measurements, potentiometric experiments with chlorine electrodes permit the determination of the electrode reaction stoichiometries and the measurements of the formal potentials for Cl_3^-/Cl^-, Cl_2/Cl_3^-, and $Cl_2/AlCl_4^-$ couples in low-temperature chloroaluminate ionic liquids.

Estimation of Equilibrium Constants. From the formal potentials measured in these potentiometric experiments, several equilibria constants could be calculated. The formal potential of the Cl_2/Cl^- system was obtained from the $E°'_{Cl_2/Cl_3^-}$ and $E°'_{Cl_3^-/Cl^-}$ values:

$$E°'_{Cl_2/Cl^-} = \frac{E°'_{Cl_2/Cl_3^-} + 2E°'_{Cl_3^-/Cl^-}}{3} \tag{8}$$

The $E°'_{Cl_2/Cl^-}$ values obtained for $AlCl_3$–BuPyCl and $AlCl_3$–ImCl systems are 0.251 and 0.260 V vs. the Ag^+/Ag reference electrode, respectively. In order to compare these values, the ferrocene/ferrocenium ion system was used as the reference redox couple. The formal potential of the ferrocene/ferrocenium couple is almost independent of the solution acidity throughout the basic, neutral, and slightly acidic melt compositions in $AlCl_3$–BuPyCl mixtures.[17] Therefore, we have assumed that it is about the same in the butylpyridinium and imidazolium tetrachloroaluminates. Thus, intersolvent comparisons can be made with potentials referred to the ferrocene electrode. The Cl_2/Cl^- formal potentials in the $AlCl_3$–BuPyCl and $AlCl_3$–ImCl systems are 0.593 and 0.620 V vs. the potential of the ferrocene/ferrocenium ion couple in the respective "neutral" melts. This small difference between the formal potentials of the Cl_2/Cl^- couple in $AlCl_3$–BuPyCl and $AlCl_3$–ImCl ionic liquids, reflecting mainly the difference in organic cation–chloride ion interactions, may indicate a higher degree of ionic association of imidazolium chloride than of butylpyridinium chloride.

From the difference between the formal potentials of the Cl_3^-/Cl^- and Cl_2/Cl^- couples, the stability constant of Cl_3^- in the two chloroaluminate melts was calculated (eq 9). The values

$$\log \beta_{Cl_3^-} = \frac{E°'_{Cl_2/Cl^-} - E°'_{Cl_3^-/Cl^-}}{2.3\dfrac{RT}{2F}} \tag{9}$$

of the Cl_3^- ion stability constant in $AlCl_3$–BuPyCl and $AlCl_3$–ImCl mixtures are 64 and 30 $mol^{-1}\ dm^3$, respectively. The smaller stability constant of Cl_3^- ion in the $AlCl_3$–ImCl system is another indication of a possible higher degree of association of $Im^+\cdots Cl^-$ than of $BuPy^+\cdots Cl^-$.

The equilibrium constant of the tetrachloroaluminate ion dissociation (eq 1) determines the shift of the $Cl_2/AlCl_4^-$ formal potential with respect to the formal potential of the Cl_2/Cl^- couple:

$$E°'_{Cl_2/Cl^-} = E°'_{Cl_2/AlCl_4^-} + \frac{RI}{F}\ln K \tag{10}$$

Thus, with the accuracy of the formal potential measurements estimated as about ±0.025 V, the value of $\log K^{BuPyCl} = -17.0 \pm 0.5$ is obtained from eq 10 for the equilibrium constant of tetrachloroaluminate ion dissociation in the $AlCl_3$–BuPyCl ionic liquid at 40 °C. In the $AlCl_3$–ImCl system the formal potential of the $Cl_2/AlCl_4^-$ couple could not be obtained (vide supra) and eq 10 could not be used for the estimation of the tetrachloroaluminate ion dissociation constant in this system. Therefore, a chloride ion activity in acidic $AlCl_3$–ImCl and $AlCl_3$–BuPyCl mixtures was measured with an aluminum electrode. The equilibrium potential of the latter electrode cannot be measured in basic ambient-temperature chloroaluminate melts.[13] In acidic composition of these melts the potential of the aluminum electrode was, however, stable, well reproducible, and stirring independent, and as shown in several works on the potentiometry of the aluminum electrode in these systems,[4,5,11,12] its dependence on the melt activity follows the Nernst equation:

$$E = E°'_{Al(III)/Al} + \frac{RT}{3F}\ln [AlCl_4^-] - \frac{4RT}{3F}\ln [Cl^-] \tag{11}$$

The equilibrium potentials of an aluminum electrode in 1.5:1 $AlCl_3$–ImCl and 1.5:1 $AlCl_3$–BuPyCl melts were measured with respect to the potential of the ferrocene/ferrocenium ion couple in the neutral imidazolium and butylpyridinium tetrachloroaluminates and were –0.395 and –0.407 V in $AlCl_3$–ImCl and in $AlCl_3$–BuPyCl melts, respectively. From this potential difference the ratio of the tetrachloroaluminate ion dissociation constant in the two ionic solvents could be calculated. If we substitute $[Cl^-] = K[AlCl_4^-]^2/[Al_2Cl_7^-]$ into eq 1 and remember that in 1.5:1 $AlCl_3$–RCl mixtures $[AlCl_4^-] = [Al_2Cl_7^-]$, the following relationship is obtained:

$$E_{Al(III)/Al}{}^{ImCl} - E_{Al(III)/Al}{}^{BuPyCl} = \frac{RT}{F}\ln\frac{[AlCl_4^-]^{BuPyCl}}{[AlCl_4^-]^{ImCl}} + \frac{4RT}{3F}\ln\frac{K^{BuPyCl}}{K^{ImCl}}$$

Since $[AlCl_4^-]^{BuPyCl} = 1.749\ mol\ dm^{-3}$ and $[AlCl_4^-]^{ImCl} = 1.981\ mol\ dm^{-3}$, $\log \log (K^{BuPyCl}/K^{ImCl}) = 0.175$ so that $\log K^{ImCl} = -17.1 \pm 0.5$. Thus, as indicated previously by voltammetric results,[13] the equilibrium constant of tetrachloroaluminate ion dissociation is of the same order of magnitude in $AlCl_3$–BuPyCl and in $AlCl_3$–ImCl ionic liquids.

Discussion

The stoichiometries of the electrode equilibria in chlorine solutions in organic chloroaluminate ionic liquids as indicated by adherence to different forms of the Nernst equation indicate the formation of different chlorine species at different solution acidities. In acidic and neutral solutions molecular chlorine (Cl_2) is dissolved, and at high chloride concentrations trichloride ion (Cl_3^-) forms. Chloride ion in basic melt compositions forms ionic aggregates with the organic cations. In acidic solutions the equilibrium concentration of chloride ion is very low (vide infra) and the chlorine reduction product is tetrachloroaluminate ion.

The equilibrium constants were calculated from the formal potentials measured in potentiometric experiments. The problems involved in the analysis of potentiometric measurements in chloroaluminate melts have been discussed by several authors.[8,9,10,14,24-26] It has usually been assumed that emf's measured in these systems can be described by a simple Nernst equation written in terms of concentrations, thus neglecting liquid-junction potentials and activity coefficients. The results of a number of potentiometric studies in these systems seem to confirm the validity of such simplification; the models based on these assumptions fit the experimental data within limits of experimental uncertainty. In addition, two recent results confirm the relative unimportance of liquid-junction potentials for emf's measured in organic chloroaluminate ionic liquids. The internal transference number of Im^+ in acidic $AlCl_3$–ImCl mixtures has been shown to be 1.[27] Although no transference number measurements have been made in the BuPyCl–$AlCl_3$ system, by analogy, we assume this for the BuPyCl–$AlCl_3$ melts. Also, the formal potential of the ferrocene/ferrocenium ion couple, measured for a cell configuration similar to that in the present work, has been found to be constant throughout most of the accessible range of $AlCl_3$–BuPyCl system

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Table V. Equilibrium Constants for $AlCl_4^-$ Ion Dissociation in $AlCl_3$–RCl[a] Melts

syst	log K^b	temp, °C	ref
$AlCl_3$–BuPyCl	−17.0	40	this work
	−16.9	40	13
	<−12.4	30	11
	−12.9	40	12
$AlCl_3$–ImCl	−17.1	40	this work
	−16.6	40	13
	−18.7	30	5
$AlCl_3$–(BuDMAP)Cl	−10.1	40	4

[a] R = organic cation. [b] $K = [Al_2Cl_7^-][Cl^-]/[AlCl_4^-]^2$.

compositions.[17] Therefore, in the present work liquid-junction potentials and activity coefficient terms were neglected.

The value of the Cl_3^- stability constant in $AlCl_3$–BuPyCl and $AlCl_3$–ImCl ionic liquids indicates the formation of trichloride ion at higher chloride concentrations. The existence of Cl_3^- was also postulated in these melts on the basis of diffusion coefficients obtained from rotating-disk measurements.[20] This agrees with the results obtained for chlorine solutions in basic alkali-metal chloroaluminates.[22] The Cl_3^- ion formation was not observed in the $AlCl_3$–NaCl melt; however, in a similar system containing larger cations ($AlCl_3$–CsCl), UV spectra indicated the formation of Cl_3^- ions. The relative stability of the Cl_3^- ion in $AlCl_3$–BuPyCl and $AlCl_3$–ImCl ionic liquids, much greater than that in aqueous solutions,[28] indicates the characteristic features of the acid–base interactions in these organic chloroaluminates. Strong interactions of solutes with the Lewis base, chloride ion (and also with the Lewis acid, heptachloroaluminate ion), are promoted by relatively weak interactions between solutes and large organic cations and tetrachloroaluminate anions.

The ionic association of butylpyridinium and imidazolium cations with chloride ion in basic chloroaluminates has been indicated by NMR,[29,30] FTIR,[31] and UV absorption[24] spectroscopies and also by the analysis of conductivity measurements.[32] The difference of the formal potentials of the Cl_2/Cl^- couple in $AlCl_3$–BuPyCl and $AlCl_3$–ImCl systems reflects a higher degree of the ionic association for imidazolium chloride than for butylpyridinium chloride, as could be expected from the difference in the sizes of these cations.

The values of the equilibrium constants for reaction 1 in $AlCl_3$–BuPyCl and $AlCl_3$–ImCl ionic liquids obtained in this work are shown in Table V together with the values previously reported for these and similar systems. The results of potentiometric experiments with the chlorine electrode give more accurate values than the preliminary estimates of the tetrachloroaluminate ion dissociation constant based on the formal potentials of the Cl_2/Cl^- couple inferred from CV results.[13] These values allow a quantification of basic properties of $AlCl_3$–BuPyCl and $AlCl_3$–ImCl ionic liquids in terms of "chlorobasicity", with pCl as a numerical measure of basicity.[8] They indicate the very wide range of basicity accessible in these melts; by a change in the $AlCl_3$:RCl mole ratio from 0.75:1 to 1.99:1, pCl can be varied from ca. 0. to 20.

The tetrachloroaluminate ion dissociation constants measured with the chlorine electrode are considerably different from those calculated from results of potentiometric studies with aluminum electrodes. As we have shown previously,[13] the latter electrode cannot be used in basic organic chloroaluminates where aluminum electrode equilibria are very slow and a mixed potential is measured. This factor was also addressed in our initial publication on this matter, where it was specifically indicated that the value of log *K* was <−12.4.[11] Unfortunately, the use of the chlorine electrode in ambient-temperature chloroaluminates is hindered by the slow electrode equilibria in acidic melt compositions and by acid-catalyzed reaction of chlorine with the organic cations. The latter reaction appears to be much slower in basic organic chloroaluminates and requires further investigation, since it may not preclude potentiometric experiments with chlorine solutions in a sealed-off system. The Nernstian behavior of the chlorine electrode in basic chloroaluminates could allow studies of acid–base equilibria involving chloride ion, even in systems with nonelectroactive solutes.

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Registry No. BuPyCl, 1124-64-7; ImCl, 65039-09-0; $AlCl_4^-$, 17611-22-2; $AlCl_3$, 7446-70-0; Cl_2, 7782-50-5.

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