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Preparation and Characterization of a Substituted Alkylpyridinium Chloroaluminate Molten Salt System

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A low-temperature molten salt has been prepared from aluminum chloride and 1-*n*-butyl-4-(dimethylamino)pyridinium chloride ((BuDMAP)Cl). The system was liquid at 40 °C. At this temperature it is possible to vary the composition from approximately 0.95:1 to 2:1 (BuDMAP)Cl:$AlCl_3$, the 1:1 system being considered neutral. The cathodic limit of the basic system (excess (BuDMAP)Cl) was about 700 mV more negative than that of the previously studied aluminum chloride–*n*-butylpyridinium chloride (BupyCl) system. However, the anodic limit of the acidic system was about 700 mV more cathodic than the limit in the BupyCl–$AlCl_3$ system; thus the (BuDMAP)Cl cation is more difficult to reduce but easier to oxidize than the corresponding BupyCl cation. A potentiometric titration was performed, and the equilibrium constant for the solvent acid–base reaction, $2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$, was determined to be $(8.4 \pm 0.2) \times 10^{-11}$. It was found that Pb(II) could be reduced in the basic solvent as a result of the increased cathodic limit.

Introduction

In the past several years, low-temperature molten salt systems composed of aluminum chloride and alkylpyridinium salts have been found to be useful solvents for electrochemical and spectroscopic investigations of both organic and inorganic species.[1-7] The attractiveness of these solvents is due both to their low liquidus temperature compared with those of other molten salt systems and to the almost total absence of water, this latter aspect enhancing the stability of radical species in the melt.[4] The aluminum chloride–*n*-butylpyridinium chloride ($AlCl_3$–BupyCl) system, which has evolved as the most widely used $AlCl_3$–alkylpyridinium molten salt system, it characterized by a rather low negative potential limit (−1.1 V vs. Al/2:1 $AlCl_3$:BupyCl reference electrode, or −1.16 V vs. SCE[4]) in the basic region (molar excess of BupyCl), thereby restricting electrochemical studies to species electroactive at less negative potentials. Since many species (for example, ketones, chlorinated organics, and various metal ions) undergo electrochemical reduction at considerably more negative potentials in other solvents,[8] it was thought desirable to attempt to extend this potential limit by modification of one of the melt components. This approach has recently been followed by Wilkes et al.[9] in the development of a group of dialkylimidazolium chloroaluminate melts having a wider cathodic limit than the butylpyridinium chloroaluminates. The cathodic process responsible for the potential limit in the $AlCl_3$–BupyCl basic melt has been found to be reduction of the pyridinium ion; therefore, an approach involving ring substitution of the pyridinium ion was adopted. From studies of substituent effects upon electrochemical reactivity in many systems, it is apparent that an electron-donating substituent is needed, the increased electron density in the pyridinium ring causing reduction to occur at a more negative potential than that characteristic of the unsubstituted pyridinium ion.[10] Finally, the commercial availability of 4-(dimethylamino)pyridine (DMAP) suggested the logical choice of this compound for use in preparation of the desired pyridinium salt. The electrochemical and spectroscopic properties of the low-temperature molten salt system $AlCl_3$–1-*n*-butyl-4-(dimethylamino)pyridinium chloride ((BuDMAP)Cl) are presented herein.

Experimental Section

4-(Dimethylamino)pyridine (DMAP, Reilly Chemical Co.) was purified by twofold vacuum sublimation at 90–100 °C. Preparation of the *n*-butyl chloride salt was similar to that of Jerchel et al.[11] for the methyl iodide salt. The synthesis involved dissolving 50 g of purified DMAP in 700 mL of warm ethyl acetate, with subsequent addition of 400 mL of *n*-butyl chloride (Fisher Chemical Co.). The solution was then refluxed for 2 days, crystals of the pyridinium salt appearing soon after refluxing was begun. After 2 days, the product was filtered from solution through a medium-porosity fritted-glass funnel, giving approximately half of the expected theoretical yield. Continued refluxing and filtering produced additional amounts of the product. After filtration, the combined portions were washed with ethyl acetate and recrystallized from acetonitrile at least twice according to the procedure given previously for the BupyCl salt.[4] The resulting solid was dried in a vacuum oven at 60–70 °C and then again evacuated on a vacuum line in a flask equipped with a stopcock to prevent exposure to air upon transfer to a drybox (Vacuum Atmospheres Corp.) in which all subsequent operations were carried out.

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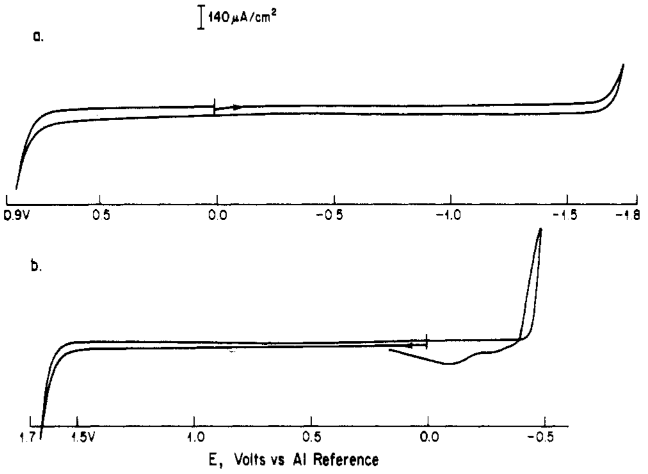

Figure 1. (a) Background cyclic voltammetric scan of the 0.95:1.00 $AlCl_3$:(BuDMAP)Cl melt (scan rate 200 mV/s). (b) Background cyclic voltammetric scan of the 2.00:1.00 $AlCl_3$:(BuDMAP)Cl melt (scan rate 200 mV/s).

Melt preparation involved gradual addition of small pieces of $AlCl_3$ to the pyridinium salt (BuDMAP)Cl. In this manner, it was possible to prepare clear, colorless melts of composition ranging from 0.95:1.00 to 2.00:1.00 in $AlCl_3$:(BuDMAP)Cl at 40 °C. The solubility limit for the basic melt (0.95:1.00), below which excess (BuDMAP)Cl is present, appears to be much smaller than that (0.60:1.00) found for the $AlCl_3$–BupyCl system.[4] A small cathodic peak at −1.4 V (vs. reference electrode described in next paragraph) was observed in background cyclic voltammetric scans of the basic melt if the reagents involved in (BuDMAP)Cl synthesis were not rigorously purified.

The electrochemical cell and electrodes used in this work have been previously described.[4] The reference electrode employed is analogous to that used in the $AlCl_3$–BupyCl system; that is, the electrode consists of an aluminum wire immersed in a 2.00:1.00 $AlCl_3$:(BuDMAP)Cl melt contained in a reference compartment with a porous ceramic junction (Fisher Scientific Co.). The potential of this reference electrode with respect to the 2.00:1.00 $AlCl_3$:BupyCl reference electrode was found to be +50 mV, by direct measurement vs. the 2.00:1.00 $AlCl_3$:BupyCl reference electrode. Electrochemical instrumentation included a PARC 175 universal programmer connected to either a PARC 173 potentiostat/galvanostat with PARC 179 digital coulometer or a Wenking 68 FR 0.5 potentiostat for cyclic voltammetric scans. Potential measurements were carried out with an Analog Devces 311J electrometer connected to a Fluke 8000A digital voltmeter. All electrochemical measurements were performed at 40 ± 1 °C, with use of a proportional temperature controller (Thermoelectric 400).

^{13}C NMR data were acquired on a Varian XL 100 FT NMR spectrometer. An acetone internal reference, contained in a concentric tube inside a 10-mm sample tube, was used in this work.

A potentiometric study of the $AlCl_3$–(BuDMAP)Cl system was carried out by monitoring the potential between an aluminum wire immersed in a melt of variable composition and the reference electrode described above and neglecting any liquid junction potential. The melt composition was varied both by addition of small amounts of $AlCl_3$ to an initially basic melt and by addition of (BuDMAP)Cl to a 2.00:1.00 $AlCl_3$:(BuDMAP)Cl acidic melt.

Results and Discussion

As seen in Figure 1a, the dimethylamino substituent in the para position of the pyridinium ring produces the desired negative shift of the cathodic background potential limit in the basic melt, this limit being approximately 700 mV more negative than that for the cathodic limit of the $AlCl_3$–BupyCl basic melt. Similar substituent effects are well-known in the electrochemistry of organic compounds, although the magnitude of the effects quoted for dimethylamino substitution in most cases is somewhat less than that in the present case.[10] At such a negative potential as is involved in the cathodic background process, the possibility of aluminum deposition should also be considered; however, upon a scan into the cathodic background and subsequent reversal of the scan, only broad oxidation peaks at −0.64 and −0.50 V were noted, the absence of a well-defined stripping peak indicating that aluminum deposition is probably not involved in the cathodic background process. The fate of the reduced *n*-butyl-4-(dimethylamino)pyridinium ion has not been established at present, but it is possible that the dimethylamino substituent in the para position would block coupling of any pyridinyl radicals produced, preventing a mechanism for the reduction process analogous to that observed for the *n*-butylpyridinium ion in the $AlCl_3$–BupyCl basic melt.[11] This assumption is supported by the observation that reduction of the present basic melt, either by electrochemical means or by addition of aluminum wire to the melt, does not result in the formation of highly colored products, whereas similar treatment of the basic $AlCl_3$–BupyCl melt produces an intense blue color due to the highly conjugated 4,4′-butylviologen formed by 4,4′, coupling of pyridinyl radicals followed by H_2 elimination. Finally, it should be noted that the anodic process responsible for the positive potential limit in the basic melt is apparently due to chloride oxidation, occurring at approximately the same potential as for the $AlCl_3$–BupyCl basic melt.

Figure 1b shows a background scan obtained for a 1.03:1.00 acidic melt, in which it is apparent that the cathodic background limit corresponds closely to that for a 1.05:1.00 $AlCl_3$:BupyCl melt.[13] Both processes involve aluminum deposition, as was demonstrated in the present case by the observation of a stripping peak upon scan reversal after a brief excursion into the cathodic background.[13] The most striking aspect of this background curve, however, is the negative shift, amounting to approximately 700 mV, of the anodic potential limit compared to that observed for the 1.05:1.00 $AlCl_3$:BupyCl acidic melt. That this shift in potential for the acidic melt anodic background processes in the two melt systems is approximately the same as the shift observed for the two basic melt cathodic background processes suggests that the anodic background process in the acidic pyridinium melts corresponds to oxidation of the pyridinium ion, since the altered electron density in the substituted pyridinium ring should cause reduction to be more difficult, and oxidation to be less difficult, in the substituted ring than in the unsubstituted ring. Evidence for this assignment in the present melt was obtained by addition of (BuDMAP)Cl to a 2.00:1.00 $AlCl_3$:BupyCl melt (91 mM), the cyclic voltammogram of this melt showing an oxidation peak at −1.95 V. At the much higher concentrations of (BuDMAP)Cl ion present in the $AlCl_3$–(BuDMAP)Cl acidic melt, the onset of butyl(dimethylamino)pyridinium ion oxidation would account for the anodic background limit at −1.6 V. The involvement of pyridinium ion in the $AlCl_3$–BupyCl anodic process, however, remains less certain, being based solely on the similarity in background potential shifts between corresponding acidic and basic melts in the two systems. Another process such as oxidation of a chloride-containing species ($AlCl_4^-$ or $Al_2Cl_7^-$) could be responsible for the anodic background limit for the acidic $AlCl_3$–BupyCl system.

The $AlCl_3$–(BuDMAP)Cl molten salt system was further characterized by ^{13}C NMR spectrometry. Since a similar study for the $AlCl_3$–BupyCl system has been carried out,[14] the results are particularly interesting. The values for the carbon resonances observed for the basic and acidic melts of both the $AlCl_3$–(BuDMAP)Cl and the $AlCl_3$–BupyCl systems are presented in Table I. Eight resonances were observed for both the 2.00:1.00 and the 0.95:1.00 $AlCl_3$:(BuDMAP)Cl melts, consistent with the existence of only one isomer of the bu-

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Table I. ^{13}C NMR Data for Pyridinium Ions in $AlCl_3$–BupyCl and $AlCl_3$–(BuDMAP)Cl Molten Salts

melt system	C-2, C-6	C-3, C-5	C-4	C-7	C-8	C-9	C-10	C-11
2.0:1.0 $AlCl_3$:BupyCl[a]	144.5	128.6	143.1	62.3	32.7	19.0	13.2	
0.8:1.0 $AlCl_3$:BupyCl[a]	145.2	128.1	144.0	61.4	33.5	18.9	13.2	
2.0:1.0 $AlCl_3$:(BuDMAP)Cl[b]	143.1	110.6	158.1	61.0	35.4	22.2	16.6	43.3
0.8:1.0 $AlCl_3$:(BuDMAP)Cl[b]	143.3	110.3	157.9	60.6	35.4	22.1	22.1	43.2

[a] Relative to internal Me_4Si. [b] Measured vs. internal acetone reference; corrected to Me_4Si reference by using acetone carbonyl resonance as 205.2 ppm.

tyl(dimethylamino)pyridinium ion formed by reaction of DMAP with butyl chloride. The chemical shift for the carbon attached to the dimethylamino substituent (158 ppm) appears to be closer to that for the corresponding carbon in aniline (147 ppm) than for that in the anilinium ion (129 ppm),[15] supporting the assumption of butyl substitution at the pyridine nitrogen rather than at the dimethylamino nitrogen. Comparison of the chemical shifts for the dimethylamino carbons in the 0.95:1.00 and 2.00:1.00 $AlCl_3$:(BuDMAP)Cl melts indicates that the amino nitrogen is apparently not bound to $Al_2Cl_7^-$ even in very acidic conditions. This observation may be explained by the electron-withdrawing effect of the pyridinium ring on the amino nitrogen, which deactivates this site to attack by Lewis acids such as $Al_2Cl_7^-$. Finally, having established that the butyl substituent is attached to the pyridinium nitrogen and that the dimethylamino substituent remains uncomplexed in the acidic melt, we made the assignments for the ring carbons by employing known substituent shifts for aromatic systems.[15]

Calculation of Equilibrium Constant

As in the $AlCl_3$–BupyCl system,[7] a quantitative evaluation of the equilibrium among the anionic species was carried out. Since the dimethylamino substituent of the pyridinium ion apparently does not undergo complexation by $Al_2Cl_7^-$ even in very acidic melts, the anionic species considered in this treatment are the same as those involved in the $AlCl_3$–BupyCl system. The equilibrium of interest is, then

$$2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^- \tag{1}$$

for which an equilibrium constant K_{eq} is desired. The experimental evaluation of this constant is identical with that used in the previous study of the $AlCl_3$–BupyCl system[7] and is presented in some detail in the following paragraphs.

It has been shown[7] that an electrochemical cell of the general type

$$\mathrm{Al/RCl,\ AlCl_3(reference)|junction|AlCl_3(c),\ RCl/Al} \tag{I}$$

where R denotes an alkylpyridinium ion, can be used as a chloride electrode according to the equation

$$\Delta E = (RT/3F)\ln(a^{\circ}_{AlCl_4^-}/a^{i}_{AlCl_4^-}) + (4RT/3F)\ln(a^{i}_{Cl^-}/a^{\circ}_{Cl^-}) \tag{2}$$

the superscripts ° and i denoting reference and other states, respectively. As seen in Figure 2, a plot of the potential of an aluminum wire in a melt of variable composition vs. melt composition is characterized by a large potential break at the neutral point and an increase in slope of the curve past the 1.7:1.0 $AlCl_3$:(BuDMAP)Cl point, as observed for the $AlCl_3$–BupyCl melt.[7] The magnitude of the potential break at the neutral point, however, is somewhat less than that for the $AlCl_3$–BupyCl system, indicating that the equilibrium constant for reaction 1 is correspondingly larger in the present case.

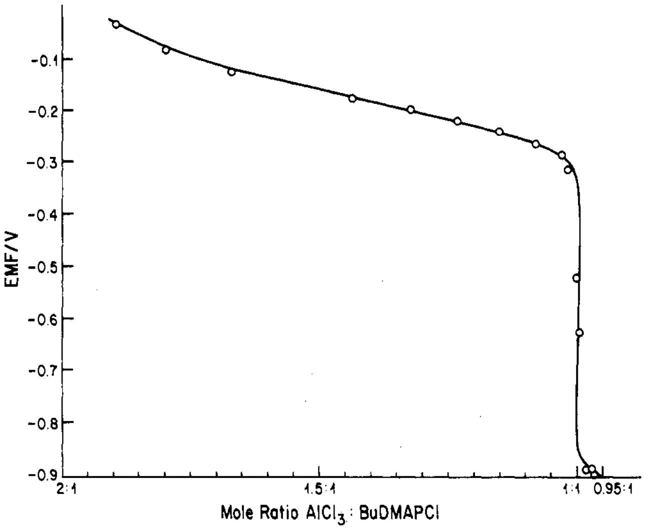

Figure 2. Data for potentiometric titration of the $AlCl_3$–(BuDMAP)Cl system: open circles, experimental values at 40 °C; solid line, calculated values.

In calculating a value for the equilibrium constant from experimental data, it is convenient to define an anionic mole fraction X_a = moles of a/total moles of anions, where a represents $Al_2Cl_7^-$, $AlCl_4^-$, or Cl^-, for use in eq 2 as a measure of the activities of these species, since the equilibrium expression (1) involves only anions. The reference state is taken to be the neutral 1.00:1.00 $AlCl_3$:(BuDMAP)Cl melt, which corresponds to a position at the midpoint of the potential break in Figure 2 at which $X_{Al_2Cl_7^-} = X_{Cl^-}$ and $X_{AlCl_4^-}$ is essentially unity. Since the composition of the melt is varied in a known fashion in the $AlCl_3$:(BuDMAP)Cl region of 1.00:1.00 to 2.00:1.00, the values of $X_{AlCl_4^-}$ and $X_{Al_2Cl_7^-}$ are known with a great deal of certainty. For melt compositions in the acidic region, the corresponding cell potentials, when referenced to that of the reference state to give ΔE, may be used in eq 2 to arrive at an experimental value for $X^{i}_{Cl^-}/X^{\circ}_{Cl^-}$. Denoting this ratio by y, and realizing that $X^{\circ}_{Cl^-} = K_{eq}^{1/2}$ at the reference state, we find that $X^{i}_{Cl^-} = K_{eq}^{1/2}y$. Substituting this value for $X^{i}_{Cl^-}$ in the equilibrium constant expression gives

$$K_{eq} = \frac{K_{eq}^{1/2}yX^{i}_{Al_2Cl_7^-}}{(X^{i}_{AlCl_4^-})^2} \tag{3}$$

or

$$K_{eq} = \frac{(yX^{i}_{Al_2Cl_7^-})^2}{(X^{i}_{AlCl_4^-})^4} \tag{4}$$

where it is assumed that $X^{\circ}_{AlCl_4^-} = 1$. The data in Figure 2 (open circles) were used to calculate an average value for K_{eq} of $(8.4 \pm 0.2) \times 10^{-11}$. The solid curve in Figure 2 was constructed by using this K_{eq} value.

It is somewhat surprising that the K_{eq} value for equilibrium 1 in the two molten salt systems $AlCl_3$–BupyCl and $AlCl_3$–(BuDMAP)Cl (3.8×10^{-13} at 30 °C and 8.4×10^{-11} at 40 °C, respectively) should be so different, considering that both systems involve rather large cations of approximately similar dimensions and the same system of anions. This large difference in K_{eq} values can probably be attributed to either

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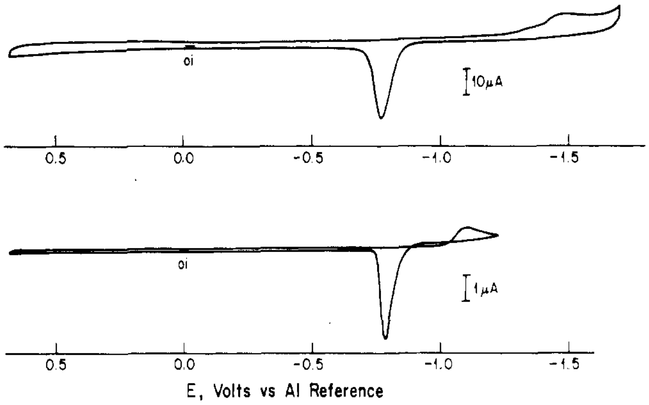

Figure 3. Cyclic voltammograms of millimolal Pb^{2+} (added as $PbCl_2$) in basic 0.95:1.00 $AlCl_3$:(BuDMAP)Cl melt, at 40 °C: upper, vitreous carbon electrode; lower, tungsten electrode.

or both of two phenomena. First, the spontaneous reduction of the butylpyridinium cation by the aluminum indicator electrode observed in the previous study[7] was assumed to give rise to a mixed potential that would, of course, alter the value of the equilibrium constant obtained from the potentiometric analysis. In the $AlCl_3$–(BuDMAP)Cl system, however, this problem seems to be much less severe (see above) and the K_{eq} value obtained would therefore be more accurate. Since the existence of a mixed potential would be expected to cause an increase in the derived equilibrium constant,[7] the larger value obtained for the $AlCl_3$–(BuDMAP)Cl system would seem to argue against the importance of the mixed-potential contribution; however, it is possible that some other process related to the spontaneous reduction occurring in the $AlCl_3$–BupyCl melt (such as formation of a polymeric film on the aluminum electrode) produces a potential difference sufficiently large to cause the observed difference in K_{eq} values for the two systems. A second consideration involves the magnitude of the liquid-junction potential at the reference electrode–solution interface, which depends upon the relative mobilities of the cations and anions in the system.[16] Since both systems involve large cations, however, it is doubtful that the small difference in sizes (and hence mobilities) of these cations would cause the large difference in K_{eq} values found for the two systems. The absolute values of the equilibrium constant in either system may, of course, be affected by any liquid-junction potential, as has been recently pointed out,[17] but by analogy to recent work,[21] it may reasonably be assumed that junction potentials would be small.

Electrochemistry of Pb^{2+} in Basic $AlCl_3$–(BuDMAP)Cl Melt

As mentioned previously, the extended negative potential limit of the basic $AlCl_3$–(BuDMAP)Cl melt allows the electrochemical investigation of species reducible at potentials more negative than that of the $AlCl_3$–BupyCl background reduction process, presenting an opportunity to study these species in a chemically similar medium. Since the reduction of the Pb^{2+} ion has been extensively investigated in other media, it was considered desirable to conduct a brief study of its electrochemical behavior in the present system.[18]

As seen in the upper curve of Figure 3, the reduction of Pb^{2+} at glassy C occurs at −1.43 V as a rather broad process, with subsequent oxidation of the metallic lead film evident as an anodic stripping peak at −0.77 V. The separation in potential between these two processes indicates a rather high degree of irreversibility for the system as a whole, probably due to a substantial overpotential for lead deposition on the glassy-carbon electrode. The reduction process appeared to proceed much more easily at a tungsten electrode (lower curve of Figure 3), occurring at −1.12 V, while the peak potential for the stripping process remained virtually the same (−0.78 V). The irreversible nature of the deposition process appears, then, to be associated primarily with the electrode material employed, although the probable existence of the Pb^{2+} ion in the melt as a chloro complex[19,20] may also be of importance in this regard. Although the basic melt composition range in this system is somewhat limited, it appears to be a useful, low-temperature chloride medium for electrochemical studies.

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Registry No. $AlCl_3$, 7446-70-0; (BuDMAP)Cl, 82522-15-4; Pb^{2+}, 14280-50-3; $AlCl_3$·(BuDMAP)Cl, 82536-76-3.

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