color is more stable with PEN^{2-} than with *N*-acetyl-DL-penicillamine.

Conclusions

Manganese(II) has been shown to complex more extensively with sulfur-containing amino acids than simple bidentate or other multidentate amino acids or other non amino acid ligands. Complexation is weak even with cysteine or penicillamine as evidenced by the tendency to form Mn(OH)$_2$(s) during titrations. Mono and bis chelates of cysteine and penicillamine, which are sensitive to O$_2$, can be prepared and isolated. In the presence of O$_2$, both the sulfur-containing ligand and manganese(II) undergo oxidation but the extent of oxidation and products obtained are dependent upon the ligand, the ligand-to-metal ratio, and the pH of the solution.

Acknowledgment. This research was partially supported by NIH Research Grant GM21844-06. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research (R.K.B.). We thank F. Frederick for making magnetic susceptibility measurements on some of the compounds.

Registry No. II, 52-90-4; III, 52-67-5; IV, 616-91-1; V, 1187-84-4; VI, 2485-62-3; Mn(CYS), 84959-60-4; Mn(CYSH)$_2$, 60065-80-7; Na$_2$[Mn(CYS)$_2$], 84944-32-1; Mn(PEN), 84944-33-2; Mn(PENH)$_2$, 84944-34-3; Mn(CYS–SCY), 78264-93-4; Mn(CYS–CH$_3$)$_2$, 84944-35-4.

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Electrochemical Studies of Chloro Complex Formation in Low-Temperature Chloroaluminate Melts. 2. Silver(I)

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A potentiometric titration procedure was used to study the coordination of silver(I) by melt chloride ion in the aluminum chloride–*N*-*n*-butylpyridinium chloride (AlCl$_3$–BPC) and aluminum chloride–1-methyl-2-ethylimidazolium chloride (AlCl$_3$–MEIC) melt systems. Analysis of data resulting from measurements on the cell Al|AlCl$_3$–RCl|fritted disk|AlCl$_3$–RCl,AgCl(dil)|Ag indicated that silver(I) forms very stable, mononuclear complexes of the type AgCl$_p^{1-p}$ ($2 \le p \le 4$) in the chloride ion-rich compositions of these melts. AgCl was insoluble in the equimolar AlCl$_3$–BPC and AlCl$_3$–MEIC melts. Stoichiometric formation constants for silver(I) chloro complexes in basic AlCl$_3$–BPC melt relative to the 66.7 mol % melt are as follows: AgCl$_2^-$, 3.5×10^{19} (40.0 °C), 5.9×10^{18} (60.0 °C); AgCl$_3^{2-}$, 3.2×10^{20} (40.0 °C), 5.2×10^{20} (60.0 °C); AgCl$_4^{3-}$, 1.6×10^{23} (40.0 °C), 4.5×10^{22} (60.0 °C). Stoichiometric formation constants in basic AlCl$_3$–MEIC melt relative to the 66.7 mol % melt are as follows: AgCl$_3^{2-}$, 1.8×10^{20} (40.0 °C); AgCl$_4^{3-}$, 1.5×10^{22} (40.0 °C).

Introduction

The combination of aluminum chloride and certain organic chloride salts results in molten salts that remain liquid well below room temperature. Two classes of these ionic liquids have been recognized and found to be excellent solvents for many organic and inorganic solutes. These ionic liquids are based on *N*-alkylpyridinium chlorides, e.g., the aluminum chloride–*N*-*n*-butylpyridinium chloride (AlCl$_3$–BPC) melt system,[1,2] and dialkylimidazolium chlorides, e.g., the aluminum chloride–1-methyl-2-ethylimidazolium chloride (AlCl$_3$–MEIC) melt system.[3] Concentration cell measurements for both the AlCl$_3$–BPC[4,5] and AlCl$_3$–MEIC[3,6] systems indicate that the predominant chloroaluminate equilibrium reaction existent in these melts is

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

In addition, Raman spectral studies suggest that molecular Al$_2$Cl$_6$ and AlCl$_3$ are absent from melts that are formulated with 66.7 mol % or less AlCl$_3$.[7] Chloroaluminate melts that contain a molar excess of AlCl$_3$ over the organic chloride salt are termed "acidic" while those formulated with an excess of organic salt relative to AlCl$_3$ are denoted as "basic".

The large variation in chloride ion activity that can be achieved in these anhydrous, ionic liquids prompts them to be interesting solvents in which to study transition-metal coordination. In previous papers[8,9] we examined the coordination of cobalt(II), iron(II), iron(III), and nickel(II) by melt chloride ion in the AlCl$_3$–BPC system. Although a number of authors have discussed various aspects of silver(I) electrochemistry in molten chloroaluminates,[10–15] there is a paucity of data regarding the coordination of this metal species in these melts. The study reported herein concerns a potentiometric investigation of silver(I) chloro complex formation that was undertaken in both the AlCl$_3$–BPC and AlCl$_3$–MEIC systems.

Experimental Section

Instrumentation. Melt preparation and subsequent titration experiments were conducted in a dry, oxygen-free nitrogen atmosphere

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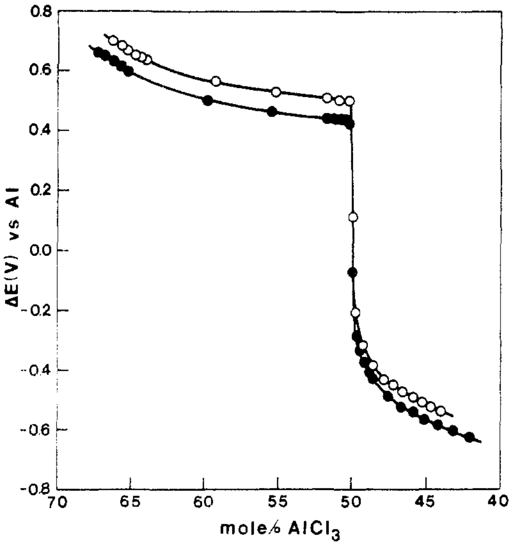

Figure 1. Potentiometric titration curves for Ag(I) in $AlCl_3$–BPC at 40.0 °C (○) and 60.0 °C (●). The initial Ag(I) concentrations were 7.52×10^{-3} *M* (40.0 °C) and 6.88×10^{-3} *M* (60.0 °C).

inside a Kewaunee Scientific Engineering Corp. drybox system equipped with a Model 2C2500 30-cfm inert-gas purifier. The procedure for monitoring the moisture and oxygen content of this drybox has been described.[9] The instrumentation used to carry out controlled potential coulometry was identical with that used in past studies.[8,9] Pulse polarographic experiments were performed with a PARC Model 174 polarographic analyzer.

Cell and Electrodes. The cells, furnace, and glassy carbon electrodes used were described previously.[9] Silver indicator electrodes were made from 0.5-mm diameter silver wire (Alfa Products, m3N purity). The electrodes were polished with emery cloth, rinsed with acetone, and dried with Kimwipes before use.

Chemicals. The procedures used for purification of $AlCl_3$, synthesis of BPC and MEIC, and preparation of the $AlCl_3$–BPC and $AlCl_3$–MEIC melts were similar to those detailed in previous publications.[2,3,8,9] The oxide content of both of the chloroaluminate melts employed in this study was determined by using the pulse polarographic procedure developed by Osteryoung and co-workers.[16,17] Melts that contained more than 5 ppm oxide were discarded. For conciseness, the melt compositions specified throughout this paper are expressed in terms of the apparent mole percent (mol %) of $AlCl_3$ in each $AlCl_3$–BPC or $AlCl_3$–MEIC melt.

Potentiometric Measurements. Poteniometric titration measurements involving the Ag(I)/Ag half-cell in both $AlCl_3$–BPC and $AlCl_3$–MEIC were conducted by using the cell arrangement formally depicted in (I). The left-hand cell compartment contained melt that

$$\mathrm{Al|AlCl_3{-}RCl|fritted\ disk|AlCl_3{-}RCl,AgCl(dil)|Ag} \qquad \text{(I)}$$

was 66.7 mol % in $AlCl_3$. The melt composition in this compartment was kept constant, since it served as the reference electrode. The technique for performing titrations was described previously.[9] Cell potentials were stable to ±0.001 V during the titration. As noted previously,[9] the precision of an individual experiment exceeded the reproducibility of the system. However, the maximum deviation between otherwise identical titration curves was ca. ±0.025 V.

Results and Discussion

Potentiometric Titration Curves. Representative potentiometric titration curves for silver(I) in $AlCl_3$–BPC are shown in Figure 1. Titration curves for silver(I) in $AlCl_3$–MEIC melt were very similar in appearance. The silver(I) species precipitated during titration experiments when these melts were ca. 50.0 mol % in $AlCl_3$. However, the precipitate redissolved when the $AlCl_3$ content was adjusted slightly above or below this value. The precipitate was collected, washed, and analyzed by using X-ray diffraction methods and found to be AgCl. Solutions of silver(I) in the $AlCl_3$–BPC and $AlCl_3$–MEIC systems were colorless in both the acidic and basic composition regions of these melts. The UV cutoff of these melts, which was observed at ca. 350 nm, precluded the acquisition of useful spectroscopic data concerning silver(I).

The substantial negative departure in cell potential, ΔE, for basic data points relative to acidic data points (Figure 1) and the tendency for precipitated AgCl to redissolve in melt containing excess chloride ion suggest that silver(I) forms very stable chloro complex ions in basic melt. Similar behavior has been observed for cobalt(II), iron(II), iron(III), and nickel(II)[8,9,18,19] in basic $AlCl_3$–BPC. The formation of mononuclear silver(I) chloro complex species of the type $AgCl_p^{1-p}$, complexed by $p \leq 4$ chloride ions, is well-known in nitrate hydrate melts[20,21] and aprotic molecular solvents[22] containing excess chloride ion at temperatures and silver(I) concentrations comparable to those used in the present study.

Inspection of Figure 1 also reveals that ΔE decreased in acidic melts as the $AlCl_3$ mol % was decreased. However, this decrease in ΔE was larger than expected on the basis of simple dilution of the silver(I) species. One explanation for this behavior involves changes in the anionic solvation environment of silver(I). In very acidic melt, e.g., 66.7 mol % $AlCl_3$, the principal anionic constituent is $Al_2Cl_7^-$ ion; this is progressively changed to $AlCl_4^-$ ion as the melt is titrated with RCl. Close to the 50 mol % composition, the melt anions are almost entirely $AlCl_4^-$ ion. Changes in ΔE for the Ag(I)/Ag half-cell in acidic melt are most likely related to this large variation in anion speciation.

Chloro Complex Models. The formation of *m* types of mononuclear chloro complex ions of the type $AgCl_p^{1-p}$ was considered in both $AlCl_3$–BPC and $AlCl_3$–MEIC melts. Information concerning the identity and stability of these complex ions can be obtained by curve fitting basic melt titration data to the expression

$$\Delta E = E^{\circ\prime}{}_{\mathrm{Ag(I)/Ag}} + 2.3\frac{RT}{F}\log X_{\mathrm{Ag(I)}}{}^{\mathrm{T}} - 2.3\frac{RT}{F}\log \sum_{p=1}^{m}[\beta'_p(X_{\mathrm{Cl^-}})^p] + E_{\mathrm{j}} \qquad (2)$$

In eq 2, $E^{\circ\prime}{}_{\mathrm{Ag(I)/Ag}}$ is the apparent standard potential of the Ag(I)/Ag couple in melt with negligible chloride ion activity, E_j is the cell liquid-junction potential, $X_{\mathrm{Ag(I)}}{}^{\mathrm{T}}$ and $X_{\mathrm{Cl^-}}$ are the mole fractions of silver(I) and chloride ion, respectively, in basic melt, and β'_p is the mole fraction based, stoichiometric formation constant for the *p*th complex ion. It should be noted that the magnitude of β', calculated by using eq 2, depends on the value of $E^{\circ\prime}{}_{\mathrm{Ag(I)/Ag}}$ chosen. Inspection of Figure 1 indicates that the latter will vary in acidic melt with the melt composition. In accord with previous investigations,[8,9] $E^{\circ\prime}{}_{\mathrm{Ag(I)/Ag}}$ was measured in melts that were 66.7 mol % in $AlCl_3$. Quantitative studies of the autosolvolysis reaction represented in eq 1 have determined that the chloride ion activity in these melts is vanishingly small.[3-6] The stability constants for silver chloro complex ions reported herein are relative to silver(I) in the 66.7 mol % melt. Values of $E^{\circ\prime}{}_{\mathrm{Ag(I)/Ag}}$ for silver(I) in this melt were obtained from the intercepts of Nernst plots constructed with data generated by coulometric introduction of silver(I) into the melt. Standard

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Table I. Results of Least-Squares Fit to Eq 2

melt system	t/°C	model	log β'_1	log β'_2	log β'_3	log β'_4	variance[a]
$AlCl_3$-BPC	40.0	1-2			*b*		
		1-3			*b*		
		1-4	17.0	...	...	23.3	4.31×10^{-5}
		2-3			*b*		
		2-4	...	19.6	...	23.2	6.73×10^{-6}
		3-4			*b*		
		1-2-3			*b*		
		1-2-3			*b*		
		1-3-4			*b*		
		2-3-4	...	19.5	20.5	23.2	6.64×10^{-6}
		1-2-3-4			*b*		
$AlCl_3$-BPC	60.0	1-2			*b*		
		1-3			*b*		
		1-4	16.7	...	...	22.8	1.50×10^{-5}
		2-3			*b*		
		2-4	...	19.0	...	22.7	1.06×10^{-6}
		3-4	...	...	21.2	22.5	3.81×10^{-6}
		1-2-3			*b*		
		1-2-4			*b*		
		1-3-4			*b*		
		2-3-4	...	18.8	20.7	22.7	3.71×10^{-7}
		1-2-3-4			*b*		
		1-2			*b*		
		1-3			*b*		
		1-4	16.5	...	...	22.3	8.00×10^{-6}
		2-3			*b*		
		2-4	...	18.5	...	22.2	5.90×10^{-6}
		3-4	...	...	20.2	22.2	5.66×10^{-6}
		1-2-3			*b*		
		1-2-4			*b*		
		1-3-4			*b*		
		2-3-4	...	18.0	20.1	22.2	5.62×10^{-6}
		1-2-3-4			*b*		

[a] Variance of the fit based on the relative error and number of model parameters. [b] Program would not converge or the attempted fit resulted in a negative β' value.

potential values in $AlCl_3$–BPC were found to be 0.880 ± 0.005 and 0.874 ± 0.013 V at 40.0 and 60.0 °C, respectively, and 0.854 ± 0.001 V in $AlCl_3$–MEIC melt at 40.0 °C.

The liquid-junction potential for cell I was assumed small and neglected. Rationalization for the neglect of E_j is based on the fact that cell I can be considered to be a series combination of cells II–IV. Thus, the liquid-junction potential

$$Cl_2|AlCl_3\text{–}RCl,AgCl(dil)|Ag \tag{II}$$

$$Al|AlCl_3\text{–}RCl|Cl_2 \tag{III}$$

$$Al|AlCl_3\text{–}RCl|\text{fritted disk}|AlCl_3\text{–}RCl|Al \tag{IV}$$

for cell I is actually that for cell IV. Previous studies involving concentration cells with transference similar to cell IV indicated that the liquid-junction potential of these cells was small.[5,6]

Potentiometric titration data for silver(I) in basic melts were fit to several versions of eq 2 by using a Taylor series linearized least-squares procedure.[23] Models for silver(I) in basic melt were tested in which various combinations of AgCl, $AgCl_2^-$, $AgCl_3^{2-}$, and $AgCl_4^{3-}$ were included. The formation of AgCl ($p = 1$) can be excluded from consideration on the basis of its insolubility (vide supra). However, this species was included in the models tested to see whether such models could be eliminated from consideration on the basis of the quality of the fit obtained. Cationic, polynuclear species of the type Ag_qCl^{q-1} were neglected in this study, since their formation is unlikely in solvents that contain excess chloride ion relative to silver(I).[24] During each cycle of this fitting routine, experimental values of X_{Cl^-} were corrected for the amount of chloride ion complexed by silver(I) by using estimates of the formation constants obtained during that cycle. The fitting process was repeated with the corrected values of X_{Cl^-}. The overall procedure was cycled until no significant refinement of the variance of the fit was noted. Ultimately, correction of raw X_{Cl^-} values was small since the formal silver(I) concentration was kept below 1.0×10^{-2} M.

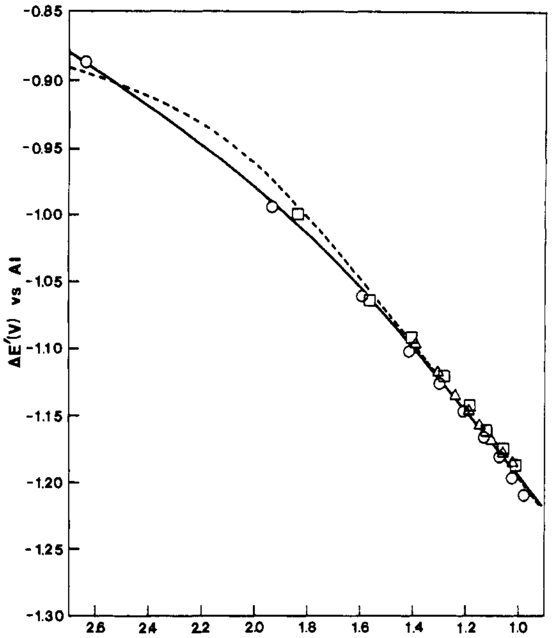

Figure 2. Variation of the corrected cell potential, $\Delta E'$, with the ion mole fraction of chloride in basic $AlCl_3$–BPC melt at 40.0 °C: $AgCl_2^-$–$AgCl_3^{2-}$–$AgCl_4^{3-}$ model; ---, AgCl–$AgCl_4^{3-}$ model. The initial Ag(I) concentrations were 7.52×10^{-3} *M* (○), 9.27×10^{-3} *M* (□), and 9.25×10^{-3} *M* (△).

The results obtained by fitting different models to the experimental data are listed in Table I. Consideration of the variance of each of the completed fits, listed therein, suggests that the best model for silver(I) chloro complexes in basic $AlCl_3$–BPC is the one that takes into account $AgCl_2^-$, $AgCl_3^{2-}$, and $AgCl_4^{3-}$. The superiority of this model over the one that takes into account only AgCl–$AgCl_4^{3-}$ is shown in Figures 2 and 3. These figures show plots of the cell potential corrected for dilution of silver(I), $\Delta E'$, vs. log X_{Cl^-}, where $\Delta E'$ is related to ΔE by eq 3. The lines that appear in these figures were

$$\Delta E' = \Delta E - E^{\circ\prime}{}_{Ag(I)/Ag} - 2.3\frac{RT}{F}\log X^{T}{}_{Ag(I)} \tag{3}$$

calculated by using the formation constants obtained from the fit for each model.

A clear decision as to whether the $AgCl_3^{2-}$–$AgCl_4^{3-}$ model or the $AgCl_2^-$–$AgCl_3^{2-}$–$AgCl_4^{3-}$ model best represent silver(I) in basic $AlCl_3$–MEIC cannot be made on the basis of the quality of the fits obtained, since the variance for these fits is almost the same. The lack of uniqueness between these models is most likely a result of the limited range of low X_{CL^-} examined in this system compared to the range in the $AlCl_3$–BPC melt, rather than a reflection of gross differences in complex formation in the two melt systems. On this presumption the three-parameter model was considered applicable to the $AlCl_3$–MEIC melt, also. However, it should be noted that the accuracy of β'_2 obtained from the three-parameter fit is uncertain in this case. The line shown in Figure 4 was

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(23) These calculations were performed in double precision on a Digital Equipment Corp. PDP-11/45 computer system.

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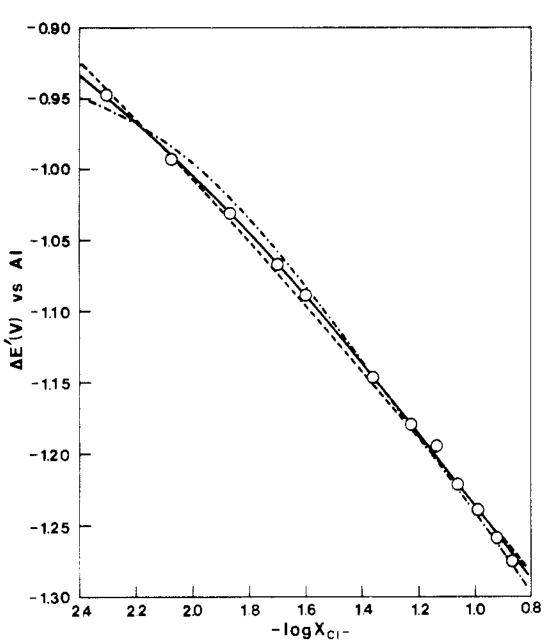

Figure 3. Variation of the corrected cell potential, $\Delta E'$, with the ion mole fraction of chloride in basic $AlCl_3$–BPC melt at 60.0 °C: —, $AgCl_2^-$–$AgCl_3^{2-}$–$AgCl_4^{3-}$ model; ---, AgCl–$AgCl_4^{3-}$ model; ····, $AgCl_2^-$–$AgCl_4^{3-}$ model. The initial Ag(I) concentration was 6.88 × 10^{-3} *M*.

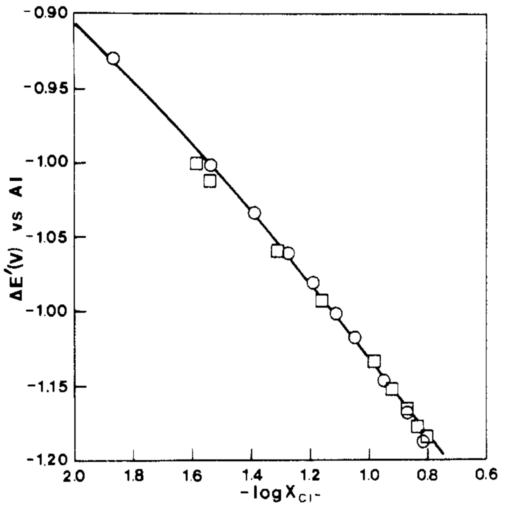

Figure 4. Variation of the corrected cell potential, $\Delta E'$, with the ion mole fraction of chloride in basic $AlCl_3$–MEIC at 40.0 °C ($AgCl_2^-$–$AgCl_3^{2-}$–$AgCl_4^{3-}$ model). The initial Ag(I) concentrations were 3.61 × 10^{-3} *M* (○) and 3.60 × 10^{-3} *M* (□).

calculated by using the formation constants resulting from the three-parameter fit. However, a line calculated by using the $AgCl_3^{2-}$–$AgCl_4^{3-}$ model represents the data equally well.

Formation Curves and Chloro Complex Stability. Formation curves for silver(I) chloro complexes in the basic $AlCl_3$–BPC melt at 40.0 and 60.0 °C, calculated by using the three-parameter formation constants listed in Table I, are shown in Figure 5. These curves suggest that the tetrahedral $AgCl_4^{3-}$ ion is the principal species existent in the melt, since it comprises more than 90% of the silver(I) chloro complex species in melt that is less than 45.5 mol % in $AlCl_3$. Only a small fraction of silver(I) appears to be complexed as $AgCl_3^{2-}$ at 40.0 °C. In fact, a model that accounts only for the existence of $AgCl_2^-$ and $AgCl_4^{3-}$, albeit physically unrealistic, represents the data almost as well as the three-parameter model (Table I). The fraction of $AgCl_3^{2-}$, relative to the others, increases as the temperature is raised to 60.0 °C. Figure 5 suggests that the increase in the fraction of $AgCl_3^{2-}$ occurs at the expense of $AgCl_2^-$ and $AgCl_4^{3-}$. This is most likely due to a small shift in the equilibrium

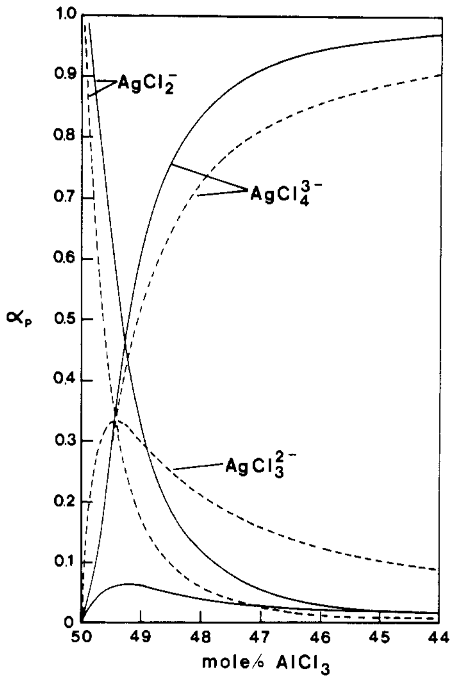

Figure 5. Silver(I) chloro complex formation curves in basic $AlCl_3$–BPC melt: —, 40.0 °C; ---, 60.0 °C.

Table II. Tetrahedral Transition-Metal Chloro Complexes and Stoichiometric Formation Constants in Chloroaluminate Melts

species	melt	t/°C	log β'_4 [a]	ref
$AgCl_4^{3-}$	$AlCl_3$-BPC	40.0	23.2	this work
	$AlCl_3$-BPC	60.0	22.7	this work
	$AlCl_3$-MEIC	40.0	22.2	this work
$CoCl_4^{2-}$	$AlCl_3$-BPC	36.0	46.2	8
$FeCl_4^{2-}$	$AlCl_3$-BPC	40.0	46.6	9
$FeCl_4^-$	$AlCl_3$-BPC	40.0	77.9	9
$NiCl_4^{2-}$	$AlCl_3$-BPC	40.0	49.7	9

[a] Formation constants were calculated relative to the metal ion in the respective 66.7 mol % melt.

$$AgCl_2^- + AgCl_4^{3-} \rightleftharpoons 2AgCl_3^{2-} \qquad (4)$$

toward the right as the temperature of the system is raised. Equilibrium constants for the reaction depicted in eq 4 and calculated from the log β' values for the $AgCl_2^-$–$AgCl_3^{2-}$–$AgCl_4^{3-}$ models in Table I are ca. 2 × 10^{-2} at 40 °C and 0.8 at 60 °C in agreement with this prediction.

Examination of the literature indicates that formation of the coordinately saturated species, $AgCl_4^{3-}$, is rarely observed in aprotic molecular solvents and molten alkali nitrate melts containing excess chloride ion. However, Nicolić and Gal[21] report a value of log β'_4 = 7.8 for $AgCl_4^{3-}$ in molten $NH_4NO_3{\cdot}2H_2O$ at 70.0 °C, but this value indicates much lower stability for $AgCl_4^{3-}$ than is found in $AlCl_3$–BPC or $AlCl_3$–MEIC. In addition, formation curves, calculated by using formation constant data for silver(I) in $NH_4NO_3{\cdot}2H_2O$,[21] indicate that $AgCl_4^{3-}$ is a minor species in this melt at any practically attainable X_{Cl^-}. One implication that can be surmised from the enhanced formation of $AgCl_4^{3-}$ in the low-temperature chloroaluminate melts vs. the $NH_4NO_3{\cdot}2H_2O$ system is that chloride ion is less solvated in basic $AlCl_3$–BPC or $AlCl_3$–MEIC than in $NH_4NO_3{\cdot}2H_2O$. Table II summarizes formation constants for $AgCl_4^{3-}$ and other tetrahedral transition-metal chloro complexes that have been measured in basic $AlCl_3$–BPC. The estimates of log β'_4 for $AgCl_4^{3-}$ obtained in the present study are in good agreement with log

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β'_4 values listed for other species if the relative HSAB acidities[25] of the various ions are taken into account.

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Registry No. Ag, 7440-22-4; $AlCl_3$, 7446-70-0; BPC, 1124-64-7; MEIC, 84927-47-9.

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Oxidative Electropolymerization of Polypyridyl Complexes of Ruthenium

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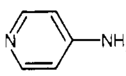
It has been found that polypyridyl complexes of ruthenium that contain aromatic amine groups, e.g., $[(bpy)_2Ru(4\text{-}pyNH_2)_2]^{2+}$ (bpy = 2,2′-bipyridine, 4-pyNH$_2$ = 4-aminopyridine), $[(bpy)_2Ru(3\text{-}pyNH_2)_2]^{2+}$ (3-pyNH$_2$ = 3-aminopyridine), $[(bpy)_2Ru(5\text{-}phenNH_2)]^{2+}$ (5-phenNH$_2$ = 5-amino-1,10-phenanthroline), $[(bpy)Ru(5\text{-}phenNH_2)_2]^{2+}$, and $[Ru(5\text{-}phenNH_2)_3]^{2+}$, undergo electrochemically induced, oxidative polymerization reactions. The resulting polymers form fairly stable, electrochemically active films on the oxidizing electrode, which can be Pt, SnO_2, or vitreous carbon. Complexes containing only one amine substituent are difficult to polymerize but can be copolymerized with $[Ru(5\text{-}phenNH_2)_3]^{2+}$. Evidence is presented to suggest that the polymerization process is ligand based and affected by the addition of base to the polymerization media. Stability studies indicate that the films lose electrochemical activity upon repeated oxidative cycling in the presence of trace H_2O. Visible and IR spectroscopies were employed to probe the nature of the polymer link, and the results are discussed with respect to mechanistic studies of the oxidative electropolymerization of aniline.

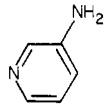
Introduction

Recent work has shown that polypyridyl complexes of ruthenium and osmium containing conjugated olefinic groups form stable, electroactive polymeric films on the electrode following electrochemical reduction of a π^* molecular orbital of one of the polypyridyl ligands.[1,9] This reduction presumably initiates a free-radical, anionic olefin polymerization process, which results in the polymer-coated electrodes.

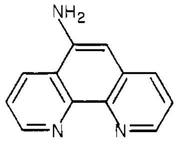
One of our goals has been to invent a broadly based chemistry for the incorporation of metal complex sites into polymers[1b,2] and polymer films. In this paper we introduce a new approach to the preparation of polymer films by electrochemical polymerization. The approach is based on the oxidative polymerization of ruthenium complexes that have an aromatic amine group or groups on the surrounding ligands; the ligands used here are



4-aminopyridine,
4-pyNH$_2$



3-aminopyridine,
3-pyNH$_2$



5-amino-1,10-
phenanthroline, 5-phenNH$_2$

The reasoning for our experiments was based on the known oxidative electropolymerization of aniline and its derivatives;[3] oxidation of aniline and related compounds to their radical cations results in polymeric film growth on the electrode surface. Since oxidation of a complex like $[Ru(5\text{-}phenNH_2)_3]^{2+}$ results in the oxidation of the ligand, we anticipated that analogous polymerization reactions might occur following oxidation of the complexes. In fact, the strategy has proven successful and we have prepared polymeric films on Pt, SnO_2, and vitreous carbon electrodes from $[Ru(5\text{-}phenNH_2)_3]^{2+}$ and similar complexes.

There is an important difference between films prepared by oxidative electropolymerization of $[Ru(5\text{-}phenNH_2)_3]^{2+}$ and those from aniline. Poly(aniline) films prepared by oxidation in pyridine/acetonitrile solution tend to act as electrical insulators.[3a,c] As insulators, they inhibit electron transfer between the electrode and redox couples in the external solution, including the oxidation of additional aniline monomer, which stops film growth. Poly(aniline) films prepared in 0.1 M H_2SO_4[3b] are less readily passivated but still do not have well-defined electrochemical reactivity. In contrast, films of poly-$[Ru(5\text{-}phenNH_2)_3]^{2+}$ display well-defined $Ru^{III/II}$ electrochemical reactivity and continued film growth via film-mediated oxidation of additional monomer, as well as film-mediated oxidation of other redox couples in an external solution.

Experimental Section

Materials. Tetraethylammonium perchlorate (TEAP) was prepared with use of a literature procedure,[4] purified by recrystallization from hot water four times, dried under vacuum at 100 °C for 10 h, and stored in a vacuum desiccator. Acetonitrile (Burdick and Jackson)

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