Room temperature haloaluminate ionic liquids. Novel solvents for transition metal solution chemistry

Charles L. Hussey

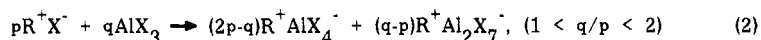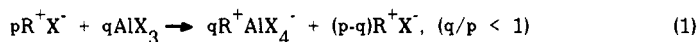Department of Chemistry, University of Mississippi, University, MS 38677 USA

Abstract · Room temperature haloaluminate ionic liquids like aluminum chloride-1-(1-butyl)pyridinium chloride, aluminum chloride-1-methyl-3-ethylimidazolium chloride, and aluminum bromide-1-methyl-3-ethylimidazolium bromide have been found to be excellent solvents in which to study the solution chemistry of transition metal halide complexes and related species. Both monomeric and polymeric complexes have been investigated in these solvents. The anhydrous, nominally aprotic nature of these ionic liquids precludes the solvation and solvolysis phenomena that often corrupt these species in molecular solvents like water and acetonitrile. As a result, these ionic liquids stabilize a number of species that ordinarily exhibit only transient existence in most molecular solvents at room temperature. In addition, the recent finding that phosgene can be used both to remove adventitious oxide impurities from neat ionic liquids and to effect the in situ conversion of transition metal oxide halide complexes to halide complexes opens new pathways for investigating the solution chemistry of the former species.

INTRODUCTION

Room temperature haloaluminate ionic liquids constitute an interesting and relatively unexplored class of versatile solvents (for reviews see refs. 1-3). Familiar examples of these two component ionic liquids are $AlCl_3$-1-(1-butyl)pyridinium chloride ($AlCl_3$-BupyCl), $AlCl_3$-1-methyl-3-ethylimidazolium chloride ($AlCl_3$-MeEtimCl), and $AlBr_3$-1-methyl-3-ethylimidazolium bromide ($AlBr_3$-MeEtimBr). As ionic liquids, i.e., molten salts, these nonaqueous, nominally aprotic materials possess several very attractive properties including low melting points (as low as -90 °C in some cases), excellent chemical and thermal stabilities, negligible vapor pressure at elevated temperatures, and high intrinsic electrical conductivity. They are miscible in significant proportions with molecular solvents that, as a group, exhibit a wide range of dielectric constants. Among these solvents are acetonitrile, benzene, propionitrile, toluene, and methylene chloride.

A novel aspect of these ionic solvents is their adjustable Lewis acidity; substantial variations in acidity can be effected simply by varying the molar ratio of the two components. These variations in acidity can be used to induce substantial changes in the coordination of complex solutes present in the melt. The acid-base properties of these ionic liquids are dictated by the species present at a given molar ratio. For example, when an aluminum halide, AlX_3, is combined with an organic salt, R^+X^-, the constituents of the resulting ionic liquid are determined by the molar ratio of these components, q/p,

according to the following reactions, which proceed essentially to completion:

$$pR^+X^- + qAlX_3 \longrightarrow qR^+AlX_4^- + (p\text{-}q)R^+X^-, \ (q/p < 1) \qquad (1)$$

$$pR^+X^- + qAlX_3 \longrightarrow (2p\text{-}q)R^+AlX_4^- + (q\text{-}p)R^+Al_2X_7^-, \ (1 < q/p < 2) \qquad (2)$$

If q/p is less than 1, these melts consist of essentially R^+X^- and $R^+AlX_4^-$ (refs. 4-6); they are "basic" because they contain halide ions that are not bound to aluminum. When q/p is greater than 1 but less than 2, $R^+AlX_4^-$ and $R^+Al_2X_7^-$ (refs. 4-6) are the principle constituents of the system, and these molten salts are "acidic" due to the presence of the latter species, which is a halide ion acceptor. Those ionic liquids for which $q/p = 1$ are considered "neutral" because they contain only $R^+AlX_4^-$. However, finite concentrations of X^- and $Al_2X_7^-$ are always present in neutral melts as a consequence of the following autosolvolysis reaction:

$$2R^+AlX_4^- \rightleftharpoons R^+Al_2X_7^- \ + \ R^+X^- \qquad (3)$$
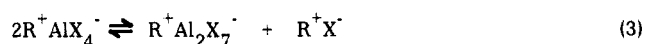
Likewise, very small amounts of X^- and $Al_2X_7^-$ are always present in acidic and basic ionic liquids, respectively, for the same reason. The equilibrium constant for Eq. 3 has been estimated to be on the order of 10^{-16} to 10^{-18} for the $AlCl_3$-MeEtimCl and $AlCl_3$-BupyCl systems at 40 °C (refs. 7,8).

Room temperature haloaluminate ionic liquids are excellent solvents for absorption spectroscopy. However, as is the case for any solvent, the useful spectral range of these liquids is dependent upon purity. Colorless $AlCl_3$-BupyCl, $AlCl_3$-MeEtimCl, and $AlBr_3$-MeEtimBr exhibit a UV cutoff of approximately 280 nm. Both of the imidazolium based systems have been employed as solvents for studies in the near infrared at wavelengths up to 2,200 nm.

The useful electrochemical potential range of each of the aforementioned ionic liquids is a function of q/p. The $AlCl_3$-MeEtimCl system exhibits the largest electrochemical window of these ionic liquids. The useful potential range of the acidic chloroaluminate melts ($q/p > 1$) extends from approximately 0 to 2.0 V versus a reference electrode consisting of aluminum metal immersed in the $q/p = 2$ ionic liquid. The positive potential limit of these ionic solvents is determined by oxidation of chloroaluminate ions while the negative limit is determined by aluminum metal deposition. The potential window of the basic chloroaluminate melts extends from approximately -2.0 to 0.8 V in the case of the $AlCl_3$-MeEtimCl system and from -1.2 to 0.8 V for $AlCl_3$-BupyCl . The positive potential limit of basic melt is governed by the oxidation of Cl^- to Cl_2 while the negative limit is determined by reduction of the organic cation. Neutral $AlCl_3$-MeEtimCl has a very large potential window that extends from ca. -2.0 to 2.0 V. This potential window is comparable to that for acetonitrile. Not surprisingly, the electrochemical window of the $AlBr_3$-MeEtimBr system is somewhat smaller than that exhibited by its chloride analogs. Acidic bromoaluminates can be used over the range of potentials extending from 0 to 1.8 V (versus Al immersed in $q/p = 2$ melt) while the useful potential range of basic melts extends from about -2.0 to 0.6 V.
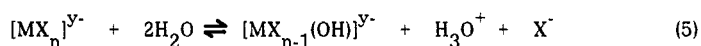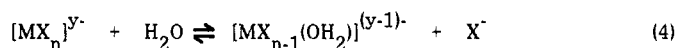
Compared to most conventional molecular solvents, room temperature haloaluminate ionic liquids are difficult to purify and must be protected from the atmosphere in order to avoid degradation by atmospheric moisture, which is believed to react with the aluminum halide species to produce aluminum oxide halide complexes and protonic impurities. Acidic ionic liquids can be purified for electrochemistry by electrolysis between aluminum electrodes in an undivided cell, but there is evidence that this may introduce oxide impurities (ref. 9). Basic ionic liquids can not be purified in this fashion, and, until recently, high quality melts could be obtained only through repeated vacuum sublimation of the aluminum halide and

diligent recrystallization of the organic salt in the absence of moisture. However, procedures for removing both protonic and oxide impurities from the chloride based ionic liquids are now available. The former procedure is based on the reaction of ethylaluminum dichloride, $C_2H_5AlCl_2$, with protonic impurities to produce $AlCl_3$ and C_2H_6 (ref. 10); the latter procedure is based on the reaction of phosgene, $COCl_2$, with any species containing oxide and produces CO_2 and Cl^- (refs. 11,12). Additional aspects of this reaction will be discussed in greater detail in a succeeding section.

In this article the properties of room temperature haloaluminate ionic liquids that contribute to their usefulness as solvents for transition metal and related complexes are described, and a list of the complexes that have been investigated in these solvents to date is provided. In addition, specialized techniques that have been used to study the chemistry of complexes in these ionic liquids are discussed along with recent results concerning the chemistry of transition metal oxide halide complexes and metal-metal bonded polynuclear halide complexes.

RATIONALE FOR USING ROOM TEMPERATURE HALOALUMINATE IONIC LIQUIDS

Historically, many studies of the solution chemistry of actinide, lanthanide, and transition metal halide complexes have been conducted in molecular solvents like water, acetonitrile, and methylene chloride. Recently, it was pointed out that solvation, solvolysis, and dissociative side reactions often corrupt transition metal halide complexes and related species in molecular solvents (ref. 13). If undetected, the products resulting from these side reactions often lead to erroneous conclusions about the solution chemistry of these complexes. Among other things, they give rise to distortions in the electronic spectra of some species and to ambiguous electrochemical results. For example, some transition metal halide complexes undergo the following hydration and hydrolysis reactions in aqueous solution even when high concentrations of halide ion are present in these solutions (ref. 13):

$$[MX_n]^{y-} + H_2O \rightleftharpoons [MX_{n-1}(OH_2)]^{(y-1)-} + X^- \qquad (4)$$

$$[MX_n]^{y-} + 2H_2O \rightleftharpoons [MX_{n-1}(OH)]^{y-} + H_3O^+ + X^- \qquad (5)$$

Conventional nonaqueous molecular solvents, like acetonitrile, can be employed in place of water in order to avoid hydrolysis reactions, but solvation reactions are still possible:

$$[MX_n]^{y-} + 2CH_3CN \rightleftharpoons [MX_{n-2}(NCCH_3)_2]^{(y-2)-} + 2X^- \qquad (6)$$
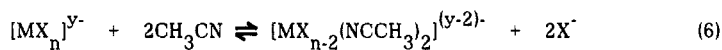
Solvation reactions are unlikely in nonaqueous solvents with low dielectric constants like methylene chloride, but solubility limitations are frequently encountered.

The chemical nature of room temperature haloaluminate ionic liquids precludes the reactions discussed above. Water can not exist in these ionic liquids because it is destroyed through reaction with the haloaluminate anions. Furthermore, since these melts are completely ionic, they are, like many other molten salts, superb solvents for highly charged complex ions. It should be noted that the deleterious side reactions described above also can be avoided by using high temperature (> 150 °C) inorganic ionic liquids like alkali halides or alkali halide-based haloaluminates. However, the chemistry that is observed for a given solute in these high temperature systems is frequently quite different from that observed for the same solute at room temperature as a consequence of thermally induced dissociation and disproportionation reactions. In addition, these inorganic ionic solvents are less convenient because they must be maintained at elevated temperatures.

COMPLEX CHEMISTRY IN ROOM TEMPERATURE HALOALUMINATES

A large number of actinide, lanthanide, and transition metal ions have been studied in the basic composition region of room temperature haloaluminate ionic liquids while a rather limited number of species have been investigated in acidic ionic liquids. In basic melts, well defined anionic complexes have been found without exception. Although many of the higher oxidation state actinide, lanthanide, and transition metal ions are quite stable in acidic ionic liquids and exhibit well-defined electrochemistry, the nature of the soluble entities is equivocal. Some workers have proposed the existence of cationic halide complexes that are solvated by haloaluminate anions. The various species that have been studied are collected in Table 1 along with references to the original literature. The bromide-containing species that are listed in this table were studied in the $AlBr_3$-MeEtimBr ionic liquid while chloride-containing complexes were investigated in either $AlCl_3$-BupyCl or $AlCl_3$-MeEtimCl.

TABLE 1. Actinide, lanthanide, and transition metal complexes in room temperature haloaluminate ionic liquids.

Basic ionic liquids (q/p < 1)

$[AgCl_2]^-$, $[AgCl_3]^{2-}$?, $[AgCl_4]^{3-}$ (ref. 14)

$[CoCl_4]^{2-}$ (ref. 15)

$[CuCl_2]^-$, $[CuCl_3]^{2-}$?, $[CuCl_4]^{3-}$, $[CuCl_4]^{2-}$ (ref. 16)

$[CrCl_6]^{3-}$ (ref. 17)

$[FeBr_4]^-$ (ref. 18)

$[Fe(cp)_2]$ (cp = cyclopentadiene) (ref. 19)

$[FeCl_4]^{2-}$, $[FeCl_4]^-$ (refs. 20-22)

$[IrCl_6]^{3-}$, $[IrCl_6]^{2-}$ (ref. 23)

$[MoCl_6]^{3-}$, $[MoCl_6]^{2-}$, $[MoOCl_4]^{2-}$? (ref. 24)

$[Mo_6Cl_{14}]^{2-}$ (ref. 25)

$[NbCl_6]^{3-}$, $[NbCl_6]^{2-}$, $[NbCl_6]^-$, $[Nb_2O_2Cl_x]^{6-x}$, $[Nb_2O_2Cl_y]^{4-y}$ (ref. 26)

$[NiCl_4]^{2-}$ (refs. 21,27)

$[NdCl_6]^{3-}$ (ref. 28)

$[NpCl_6]^{3-}$, $[NpCl_6]^{2-}$ (ref. 29)

$[OsCl_6]^{3-}$, $[OsCl_6]^{2-}$ (ref. 30)

$[Re_2Cl_8]^{2-}$, $[Re_3Cl_{12}]^{3-}$, $[ReCl_6]^{2-}$ (ref. 31)

$[Ru_2Br_9]^{3-}$, $[Ru_2Br_9]^{4-}$ (ref. 32)

$[RuCl_6]^{3-}$, $[RuCl_6]^{2-}$ (refs. 33,34)

$[Ru_2OCl_{10}]^{4-}$ (ref. 32)

$[RuO_2Cl_4]^{2-}$ (ref. 35)

$[TaCl_6]^{2-}$, $[TaCl_6]^-$ (ref. 26)

$[TiBr_6]^{2-}$ (ref. 18)

$[TiCl_6]^{3-}$, $[TiCl_6]^{2-}$, $[TiOCl_4]^{2-}$ (ref. 36)

$[UBr_6]^{3-}$, $[UBr_6]^{2-}$, $[UO_2Br_4]^{2-}$ (ref. 37)

$[UCl_6]^{3-}$, $[UCl_6]^{2-}$, $[UO_2Cl_4]^{2-}$ (ref. 38),

$[WCl_6]^{3-}$, $[W_2Cl_9]^{3-}$, $[W_2Cl_9]^{2-}$, $[WCl_6]^{2-}$, $[WCl_6]^-$ (ref. 39)

Acidic ionic liquids (q/p > 2)

$[NpCl_x]^{(4-x)+}$ ($3 \geq x \geq 1$) (ref. 29)

$[Ru(bipy)_3]^{3+}$, $[Ru(bipy)_3]^{2+}$ (bipy = bipyridine) (refs. 40,41)

$[SmCl]^{2+}$ (ref. 42)

$[TmCl_2]^+$, $[TmCl]^{2+}$ (ref. 43)

$[UCl_x]^{(4-x)+}$ ($3 \geq x \geq 1$) (refs. 44,45)

$[YbCl]^{2+}$, $[YbCl_2]^+$, $[YbCl]^+$ (ref. 42)

Techniques used to study complex chemistry

The methods that have been used to study complex species in room temperature haloaluminates are essentially the same as those used for similar investigations in conventional solvents. These techniques include cyclic and rotating disk electrode voltammetry, chronoamperometry, controlled potential coulometry, potentiometry, and ultraviolet-visible-IR absorption spectroscopy. Numerous examples in which these techniques have been applied to the study of complexes in these ionic liquids can be found by consulting the references listed in Table 1. Therefore, further discussions of these techniques will be omitted. Coupled optical-electrochemical or spectroelectrochemical techniques also have been adapted for investigations of complex ions in room temperature haloaluminate ionic liquids. In particular, a fiber optic based, microprocessor controlled spectroelectrochemistry system was constructed especially for the acquisition of transmission spectroelectrochemical data in these molten salts (refs. 33,41). This system employs a reticulated vitreous carbon optically transparent electrode (RVC-OTE) and is completely controlled by two linked microprocessors that simultaneously collect both electrochemical and spectroscopic data. This spectroelectrochemistry system can be used to conduct thin layer cyclic voltammetric, cyclic voltabsorptometric, chronocoulometric, chronoabsorptometric, and spectropotentiostatic experiments. It has been used for studies of the $[IrCl_6]^{2-/3-}$ and $[RuCl_6]^{2-/3-}$ redox couples in basic $AlCl_3$-MeEtimCl (refs. 23,33), and the $[Ru(bipy)_3]^{3+/2+}$ system in acidic $AlCl_3$-MeEtimCl (ref. 41). Figure 1 shows absorption spectra for the $[RuCl_6]^{2-/3-}$ system in basic $AlCl_3$-MeEtimCl that were obtained with this system
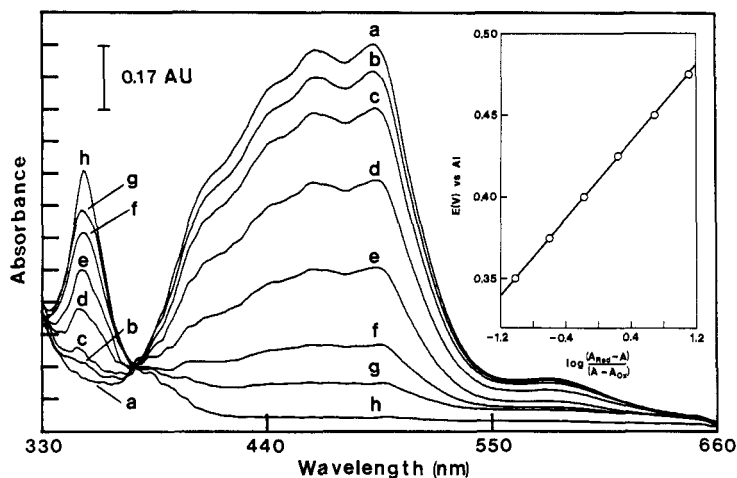

Fig. 1. Absorption spectra of 2.09 mM $[RuCl_6]^{2-}$ in the 49.0/51.0 mol % $AlCl_3$-MeEtimCl ionic liquid at 40 °C at various applied potentials: (a) 0.600, (b) 0.475, (c) 0.450, (d) 0.425, (e) 0.400, (f) 0.375, (g) 0.350, and (h) 0 V. Inset: Nernst plot constructed from the spectropotentiostatic data. The potentials in this and succeeding figures are referenced to Al in 66.7/33.3 mol % $AlCl_3$-MeEtimCl.

at various applied potentials in the RVC-OTE and a Nernst plot that was constructed from these spectra. Since each spectrum in this figure was recorded after Nernstian equilibrium was established in the cell, i.e., when the current decreased essentially to zero, the formal potential that is obtained with this method is essentially free from effects due to uncompensated cell resistance. This potential value is of higher quality than values obtained with conventional voltammetric methods because these methods involve potential measurement during current flow. Figure 2 illustrates a cyclic voltammogram and its optical counterpart, a differential cyclic voltabsorptammogram, that were acquired simultaneously for the $[Ru(bipy)_3]^{3+/2+}$ couple in acidic $AlCl_3$-MeEtimCl with the spectroelectrochemistry system and RVC-OTE cell discussed above. These experiments differ from similar experiments conducted in bulk solutions of electroactive species in that they were carried out in a cell with a fixed volume, and they result from the complete oxidation or reduction of all of the solute entrained in that volume of solvent.
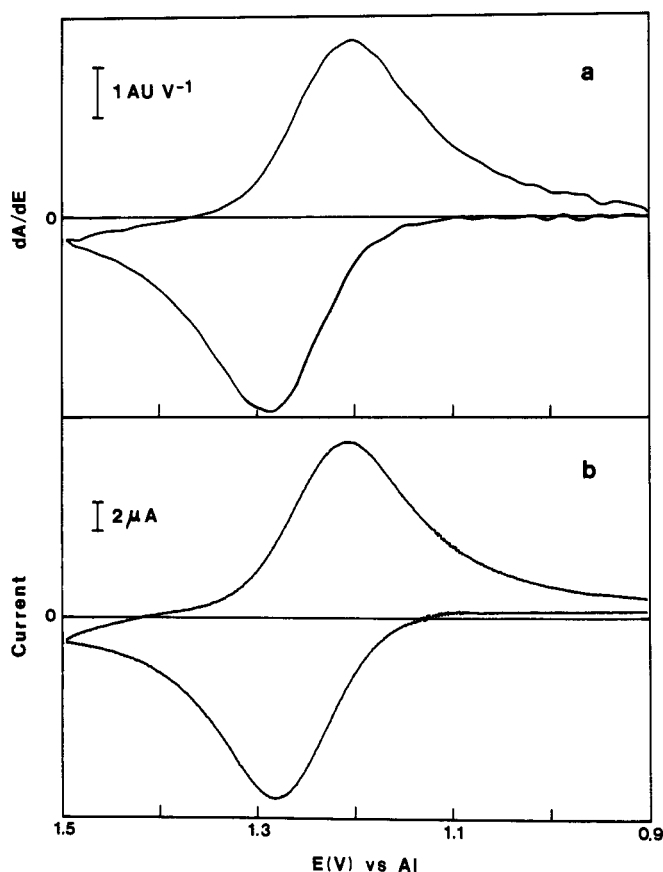
Fig. 2.   (a) Differential cyclic voltabsorptammogram and (b) cyclic voltammogram of
a 0.60 mM solution of $[Ru(bipy)_3]^{2+}$ in 60.0/40.0 mol % $AlCl_3$-MeEtimCl at 40 $^{\circ}$C in
the RVC-OTE cell. The sweep rate was 0.20 mV s^{-1}.

The voltabsorptometric technique, which was developed by electrochemists working in conventional sol-
vents, promises to be a useful tool for probing homogeneous chemistry coupled to electrode reactions in
these ionic liquids. It also appears valuable for investigating redox systems that are positioned close
to the positive and negative limits of these ionic solvents where large background currents obscure the
small currents arising from electroactive solutes at low concentration. These background currents have
little or no effect on the spectral response of the absorbing species.

Transition metal oxide halide complexes

Room temperature haloaluminate ionic liquids often are contaminated with oxide-containing species that
appear to be produced during the reaction of adventitious water either with the AlX_3 component or with
haloaluminate ions in the ionic liquid (vide supra). The structures of these oxide-containing contami-
nants have not been established, but it appears very likely that they consist of aluminum coordinated to
both oxide and halide (see ref. 12 and references therein). These oxide-containing species are capable
of donating "O^{2-}" to some transition metal systems to produce oxide halide complexes. The behavior
shown in the following reaction has been observed for both titanium(IV) bromide and chloride complexes in
basic melts (refs. 18,36):

$$[TiX_6]^{2-} + "O^{2-}" \rightleftharpoons [TiOX_4]^{2-} + 2X^- \tag{7}$$
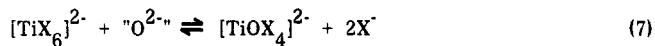
A similar reaction also appears to occur between oxide and $[MoCl_6]^{2-}$ (ref. 24). The equilibrium reaction
shown in Eq. 7 forms the basis of a very useful voltammetric method for determining the oxide level in
basic room temperature chloroaluminate ionic liquids (ref. 9)

Recently, it was demonstrated that $COCl_2$ can be used to remove oxide impurities from room temperature haloaluminate ionic liquids (refs. 11,12). In addition, $COCl_2$ can be used to effect the in situ conversion of transition metal oxide halide species back to their respective halide complexes (ref. 12). For example, Fig. 3 shows cyclic voltammograms of a solution of titanium(IV) in basic $AlCl_3$-MeEtimCl containing "O^{2-}" before and after treatment with $COCl_2$. The voltammogram recorded before treatment exhibits two reduction waves; the first wave at approximately -0.3 V arises from the electrochemically reversible reduction of $[TiCl_6]^{2-}$ to $[TiCl_6]^{3-}$ and the second at -0.7 V corresponds to the reduction of $[TiOCl_4]^{2-}$ (ref. 36). After treatment of the solution with $COCl_2$, the second reduction wave disappears completely and the first wave increases in height, signalling the conversion of $[TiOCl_4]^{2-}$ back to $[TiCl_6]^{2-}$.
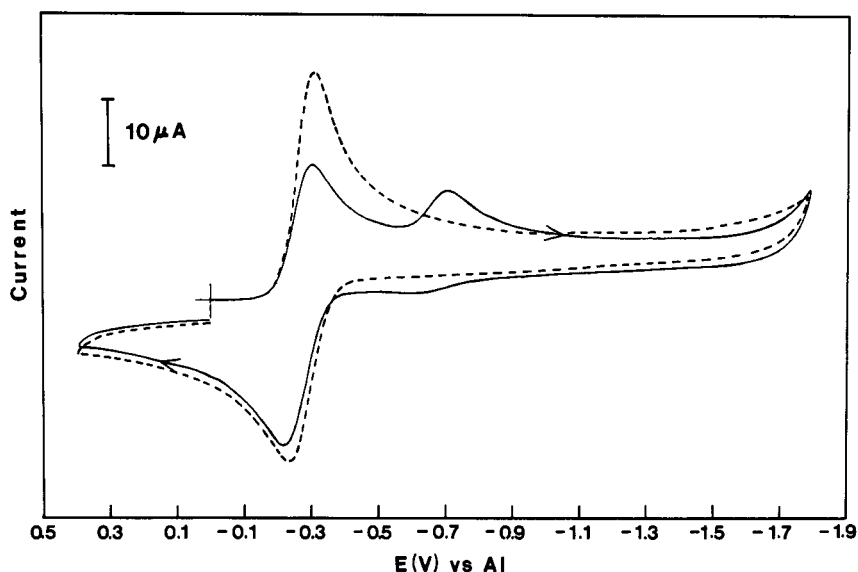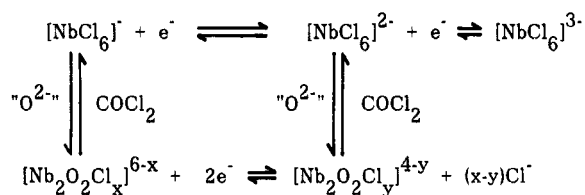

Fig. 3. Cyclic voltammograms of a 14.2 mM solution of titanium(IV) chloride at a glassy carbon electrode in the 49.0/51.0 mol % $AlCl_3$-MeEtimCl ionic liquid at 28 $^{\circ}$C: (——) 5.1 mM in oxide; (- - -) after the addition of $COCl_2$ followed by removal of the unreacted $COCl_2$ in vacuo. The sweep rates were 50 mV s^{-1}.

Thus, the usefulness of $COCl_2$ extends beyond merely improving the quality of these melts. More importantly, since the oxide concentration can now be controlled precisely either through the addition of Li_2CO_3 (ref. 36) or $COCl_2$, reactions between halide complexes and oxide can be investigated in these ionic liquids that would be difficult to study in other solvent systems. For example, by utilizing both Li_2CO_3 and $COCl_2$, the following scheme has been elucidated for the niobium(V), and -(IV) chloride and oxide chloride complexes in basic $AlCl_3$-MeEtimCl (ref. 26):
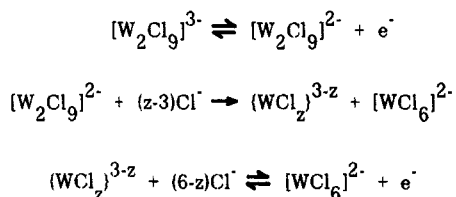
Scheme 1

$$[NbCl_6]^- + e^- \rightleftharpoons [NbCl_6]^{2-} + e^- \rightleftharpoons [NbCl_6]^{3-}$$

$$\text{"}O^{2-}\text{"} \Updownarrow COCl_2 \qquad \text{"}O^{2-}\text{"} \Updownarrow COCl_2$$

$$[Nb_2O_2Cl_x]^{6-x} + 2e^- \rightleftharpoons [Nb_2O_2Cl_y]^{4-y} + (x-y)Cl^-$$

The reactions between $[NbCl_6]^-$ and $[NbCl_6]^{2-}$ and "O^{2-}" in the ionic liquid proceed rapidly to completion, but both reactions can be reversed completely by using $COCl_2$. Without the use of $COCl_2$, it seemed impossible to prepare solutions of the niobium(V) and -(IV) hexachloride complexes that did not contain at least small amounts of the dimeric oxide chloride species.

Transition metal halide cluster complexes

The term "metal cluster" is used to designate polynuclear species with two or more metal atoms in which metal-metal bonding is of sufficient strength to contribute substantially to the heat of formation of the species (ref. 46). These metal-metal bonds differentiate metal cluster species from classical Werner complexes in which metal atoms may share ligands, but do not interact with one another. Metal-metal bonds appear to impart unique properties to transition metal complexes, and such species are of great interest as a consequence of their structure, bonding, and reactivity. Like monomeric complexes, the stability of metal cluster species in molecular solvents is often determined by the reactivity of the solvent.

Not surprisingly, room temperature haloaluminate ionic liquids have been found to be excellent media for stabilizing transition metal halide cluster complexes (Table 1). The dimeric tungsten(III) complex, $[W_2Cl_9]^{3-}$, which exhibits a formal metal-metal triple bond, and $[Ru_2Br_9]^{3-}$, which is believed to exhibit a single bond (ref. 32), were among the first species of this type to be investigated in ionic liquids. Both species are quite stable in basic $AlCl_3$-MeEtimCl; the former complex was found to undergo a reversible one electron oxidation at a glassy carbon electrode on the voltammetric time scale to the mixed oxidation state complex, $[W_2Cl_9]^{2-}$, which possesses a W_2^{7+} metal core. However, $[W_2Cl_9]^{3-}$ exhibits a two electron oxidation at the same potential on the time scale encompassed by controlled potential electrolysis and results in the formation of the tungsten(IV) species, $[WCl_6]^{2-}$. These two very different results were reconciled in terms of the following ECE mechanism in which a very slow homogeneous disproportionation reaction is coupled to the first charge transfer process; the intermediate tungsten(III) species that is produced in this reaction, $(WCl_z)^{3-z}$, is more easily oxidized than the parent species (ref. 39):

Scheme 2

$$[W_2Cl_9]^{3-} \rightleftharpoons [W_2Cl_9]^{2-} + e^-$$

$$[W_2Cl_9]^{2-} + (z-3)Cl^- \longrightarrow (WCl_z)^{3-z} + [WCl_6]^{2-}$$

$$(WCl_z)^{3-z} + (6-z)Cl^- \rightleftharpoons [WCl_6]^{2-} + e^-$$

$[Ru_2Br_9]^{3-}$ was found to undergo a reversible one electron reduction to $[Ru_2Br_9]^{4-}$ at a glassy carbon electrode in basic $AlBr_3$-MeEtimBr (ref. 32). The latter species exhibited considerable stability in the ionic liquid at room temperature. It should be emphasized that comparable stability of this species in molecular solvents can only be achieved at 233 K in dichloromethane (ref. 47).

Recently, it was determined that the addition of molybdenum(II) chloride (Mo_6Cl_{12}) to basic $AlCl_3$-MeEtimCl produces the $[Mo_6Cl_{14}]^{2-}$ anion (ref. 25), which is known to exhibit single metal-metal bonds. This transition metal chloride cluster complex is very interesting because it has been found to exhibit photoluminescence in acetonitrile when it is irradiated at 436 nm. The luminescence appears to arise from the long-lived excited species, $\{[Mo_6Cl_{14}]^{2-}\}^*$ (ref. 48). It is also appears possible to observe luminescence from this excited species in basic $AlCl_3$-MeEtimCl, and Fig. 4 illustrates absorption and emission spectra recorded for such a solution. Luminescence can also be observed from solutions of Mo_6Cl_{12} in acidic $AlCl_3$-MeEtimCl, but the structure of the luminescent species has not been established. Some additional species that are under study at the present time include $[Re_2Cl_8]^{2-}$ and $[Re_3Cl_{12}]^{3-}$ (ref. 31). The latter complex is obtained when rhenium(III) chloride is dissolved in basic $AlCl_3$-MeEtimCl. In this cluster, each rhenium atom participates in a metal-metal double bond with two other rhenium atoms. This cluster and the quadruply metal-metal bonded $[Re_2Cl_8]^{2-}$ complex appear to be stable indefinitely in the ionic liquid at room temperature, and both species exhibit reversible one electron reduction reactions at a glassy carbon electrode in this solvent (ref. 31).
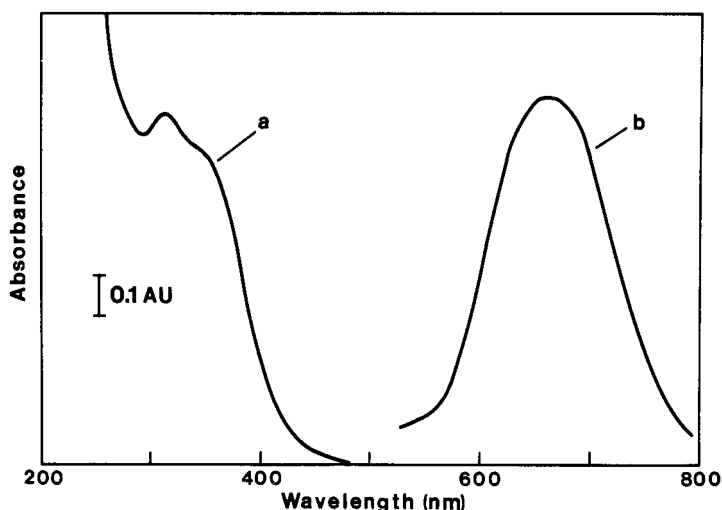
Fig. 4. (a) Absorption and (b) uncorrected emission spectra for a 2.25 mM solution of $[Mo_6Cl_{14}]^{2-}$ in the 49.0/51.0 mol % $AlCl_3$-MeEtimCl ionic liquid at room temperature. The absorption spectrum was recorded versus pure melt in a 1 mm pathlength fused silica cuvette.

REFERENCES

1. H. L. Chum and R. A. Osteryoung in Ionic liquids, D. Inman and D. G. Lovering, Eds., pp. 407-423, Plenum, New York (1981).

2. C. L. Hussey in Advances in Molten Salt Chemistry, Vol. 5, G. Mamantov and C. B. Mamantov, Eds., pp. 185-230, Elsevier, Amsterdam (1983).

3. R. J. Gale and R. A. Osteryoung in Molten Salt Techniques, Vol. 1, D. G. Lovering and R. J. Gale, Eds., pp. 55-78, Plenum Press, New York (1983).

4. R. J. Gale, B. Gilbert, and R. A. Osteryoung, Inorg. Chem. 17, 2728-2729 (1978).

5. T. Matsumoto and K. Ichikawa, J. Am. Chem. Soc. 106, 4316-4320 (1984).

6. S. Takahashi, N. Koura, M. Murase, and H. Ohno, J. Chem. Soc., Faraday Trans. 2 82, 49-60 (1986).

7. Z. J. Karpinski and R. A. Osteryoung, Inorg. Chem. 24, 2259-2264 (1985).

8. C. L. Hussey, T. B. Scheffler, J. S. Wilkes, and A. A. Fannin, Jr., J. Electrochem. Soc. 133, 1389-1391 (1986).

9. Z. Stojek, H. Linga, and R. A. Osteryoung, J. Electroanal. Chem. 119, 365-370 (1981).

10. T. A. Zawodzinski, Jr., R. T. Carlin, and R. A. Osteryoung, Anal. Chem. 59, 2639-2640 (1987).

11. A. K. Abdul-Sada, A. G. Avent, M. J. Parkington, T. A. Ryan, K. R. Seddon, and T. Welton, J. Chem. Soc., Chem. Commun., 1643-1644 (1987).

12. I-W. Sun, E. H. Ward, and C. L. Hussey, Inorg. Chem. 26, 4309-4311 (1987).

13. D. Appleby, C. L. Hussey, K. R. Seddon, and J. E. Turp, Nature 323, 614-616 (1986).

14. T. M. Laher and C. L. Hussey, Inorg. Chem. 22, 1279-1283 (1983).

15. C. L. Hussey and T. M. Laher, Inorg. Chem. 20, 4201-4206 (1981).

16. T. M. Laher and C. L. Hussey, Inorg. Chem. 22, 3247-3251 (1983).

17. T. B. Scheffler, Ph.D. Dissertation, University of Mississippi, 1984.

18. I-W. Sun, J. R. Sanders, and C. L. Hussey, J. Electrochem. Soc., submitted.

19. Z. J. Karpinski, C. Nanjundiah, and R. A. Osteryoung, Inorg. Chem. 23, 3358-3364 (1984).

20. C. L. Hussey, L. A. King, and J. S. Wilkes, J. Electroanal. Chem. 102, 321-332 (1979).

21. T. M. Laher and C. L. Hussey, Inorg. Chem. 21, 4079-4083 (1982).

22. C. Nanjundiah, K. Shimizu, and R. A. Osteryoung, J. Electrochem. Soc. 129, 2474-2480 (1982).

23. I-W. Sun, E. H. Ward, C. L. Hussey, K. R. Seddon, and J. E. Turp, Inorg. Chem. 26, 2140-2143 (1987).

24. T. B. Scheffler, C. L. Hussey, K. R. Seddon, C. M. Kear, and P. D. Armitage, Inorg. Chem. 22, 2099-2100 (1983).

25. P. A. Barnard and C. L. Hussey, to be submitted.

26. I-W. Sun and C. L. Hussey, Inorg. Chem., submitted.

27. R. J. Gale, B. Gilbert, and R. A. Osteryoung, Inorg. Chem. 18, 2723-2725 (1979).

28. M. Lipsztajn and R. A. Osteryoung, Inorg. Chem. 24, 716-719 (1985).

29. J. P. Schoebrechts and B. Gilbert, Inorg. Chem. 24, 2105-2110 (1985).

30. I-W. Sun and C. L. Hussey, J. Electrochem. Soc., in press.

31. I-W. Sun and C. L. Hussey, to be submitted.

32. D. Appleby, R. I. Crisp, P. B. Hitchcock, C. L. Hussey, T. A. Ryan, J. R. Sanders, K. R. Seddon, J. E. Turp, and J. A. Zora, J. Chem. Soc., Chem. Commun., 483-485 (1986).

33. E. H. Ward and C. L. Hussey, Anal. Chem. 59, 213-217 (1987).

34. C. L. Hussey, D. Appleby, P. B. Hitchcock, K. R. Seddon, J. A. Zora, and R. I. Crisp, J. Chem. Soc., Dalton Trans., submitted.

35. R. I. Crisp, C. L. Hussey, and K. R. Seddon, J. Chem. Soc., Dalton Trans., submitted.

36. H. Linga, Z. Stojek, and R. A. Osteryoung, J. Am. Chem. Soc. 103, 3754-3760 (1981).

37. T. J. Mohammed, D. Phil. Thesis, University of Sussex, 1987.

38. P. B. Hitchcock, T. J. Mohammed, K. R. Seddon, J. A. Zora, C. L. Hussey, and E. H. Ward, Inorg. Chim. Acta 113, L25-L26 (1986).

39. T. B. Scheffler and C. L. Hussey, Inorg. Chem. 23, 1926-1932 (1984).

40. S. Sahami and R. A. Osteryoung, Inorg. Chem. 23, 2511-2518 (1984).

41. E. H. Ward, P. A. Barnard, I-W. Sun, and C. L. Hussey, Proc. Joint Intl. Symp. Molten Salts 87, 445-457 (1987).

42. J. P. Schoebrechts, B. P. Gilbert, and G. Duyckaerts, J. Electroanal. Chem. 145, 127-138 (1983).

43. J. P. Schoebrechts, B. P. Gilbert, and G. Duyckaerts, J. Electroanal. Chem. 145, 139-146 (1983).

44. R. De Waele, L. Heerman, and W. D'Olieslager, J. Electroanal. Chem. 142, 137-146 (1982).

45. R. De Waele, L. Heerman, and W. D'Olieslager, J. Less-Common Metals 122, 319-327 (1986).

46. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 4th ed., Chap. 26, Wiley, New York (1980).

47. V. T. Coombe, G. A. Heath, T. A. Stephenson, and D. K. Vattis, J. Chem. Soc., Dalton Trans., 2307-2309 (1983).

48. A. W. Maverick and H. B. Gray, J. Am. Chem. Soc. 103, 1298-1300 (1981).