for solvation in an aqueous environment. This hydrophobic property of the water-soluble porphyrins, in turn, can facilitate a solubilization through hydrophobic interactions.

Acknowledgment. The support of the National Science Foundation (Grants CHE-8515411 and INT-8413696) is gratefully acknowledged.

Registry No. (TPPS)H_2, 39050-26-5; (TPPS)Cu, 67204-03-9; (TPPS)Zn, 42712-11-8; TPPS(VO), 93410-57-2.

Contribution from the Department of Chemistry,
University of Mississippi, University, Mississippi 38677

Electrochemistry of Niobium Chloride and Oxide Chloride Complexes in the Basic Aluminum Chloride–1-Methyl-3-ethylimidazolium Chloride Room-Temperature Ionic Liquid

I-Wen Sun and Charles L. Hussey*

Received November 21, 1988

Niobium(V) is complexed as $[NbCl_6]^-$ in the basic aluminum chloride–1-methyl-3-ethylimidazolium chloride ionic liquid, and it can be reduced to $[NbCl_6]^{2-}$ and $[NbCl_6]^{3-}$ in successive, one-electron, reversible redox reactions at a glassy-carbon electrode with voltammetric half-wave potentials of 0.17 and –0.93 V, respectively, in the 44.4/55.6 mol % melt at 40 °C, referenced to aluminum in the 66.7/33.3 mol % melt. The average Stokes–Einstein products for $[NbCl_6]^-$ and $[NbCl_6]^{2-}$ in the ionic liquid are 3.5×10^{-10} and 2.1×10^{-10} cm s^{-2} K^{-1}, respectively. The addition of oxide ion to solutions of $[NbCl_6]^-$ in basic melt produces $[NbOCl_5]^{2-}$. This species can be electrochemically reduced to a strongly paramagnetic monomeric niobium(IV) species, which is associated with a single oxide ion, possibly $[NbOCl_4]^{2-}$ or $[NbOCl_5]^{3-}$. The niobium(V)/niobium(IV) oxide chloride electrode reaction exhibits quasireversible behavior with a standard heterogeneous rate constant of 9.0×10^{-7} cm s^{-1} and a cathodic transfer coefficient of ca. 0.8. The formal electrode potential of the niobium(V)/niobium(IV) oxide chloride redox couple is –0.521 V in the 44.4/55.6 mol % melt. The Stokes–Einstein products of $[NbOCl_5]^{2-}$ and the related niobium(IV) oxide chloride complex are 1.9×10^{-10} and 1.4×10^{-10} cm s^{-2} K^{-1}, respectively. The overall electrochemical scheme for niobium complexes in the $AlCl_3$–MeEtimCl ionic liquid is summarized as follows:

$$\begin{tikzcd}
{[NbCl_6]^- + e^-} & \rightleftharpoons & {[NbCl_6]^{2-} + e^-} & \rightleftharpoons & {[NbCl_6]^{3-}} \\
\text{bright yellow} \arrow[d, shift right, "{``O^{2-}\text{''}}"'] & & \text{pale yellow} \arrow[d, shift right, "{``O^{2-}\text{''}}"'] & & \text{pale green?} \\
{[NbOCl_5]^{2-} + e^-} \arrow[u, shift right, "COCl_2"'] & \overset{\text{slow}}{\rightleftharpoons} & {[NbOCl_y]^{2-y} + (5-y)Cl^-} \arrow[u, shift right, "COCl_2"'] & & \\
\text{colorless} & & \text{violet} & &
\end{tikzcd}$$

Introduction

Room-temperature chloroaluminate ionic liquids are obtained when anhydrous aluminum chloride is combined with certain organic chloride salts, which are normally solids at room temperature. Two examples of these organic salts are 1-(1-butyl)pyridinium chloride (BupyCl) and 1-methyl-3-ethylimidazolium chloride (MeEtimCl).[1] The latter salt is more resistant to reduction than the former, and basic melts[2] containing this salt are superior for dynamic electrochemical measurements at very negative potentials.[3]

Basic room-temperature chloroaluminate melts have been shown to be excellent solvents for stabilizing anionic transition-metal chloride complexes. Some of the factors that are believed to contribute to the unusual stability of these species in these ionic liquids relative to other solvents have been discussed;[4] they include the absence of both the solvation and solvolysis reactions encountered in molecular solvents and the thermally promoted dissociation and disproportionation reactions associated with high-temperature molten salts. A comprehensive list of the various transition-metal complexes that have been investigated in room-temperature chloroaluminate melts has been published.[5]

There is a paucity of information about the electrochemistry and solution chemistry of niobium chloride complexes. These elusive species are very difficult to study in solution because they react with the trace quantities of moisture that are often present in rigorously purified molecular solvents and with the unavoidable, difficult to remove, oxide-containing contaminants that are found in some molten salts. Recently, we reported an effective procedure for removing oxide impurities from $AlCl_3$–MeEtimCl ionic liquids.[6] This procedure, which employs phosgene, can also be used to convert some oxide-containing transition-metal complexes, including niobium oxide chloride complexes, to their respective chloride complexes in situ. By employing this procedure, it should be possible to study transition-metal solutes that are very reactive toward oxide, e.g., high-oxidation-state niobium and tantalum complexes, in these ionic liquids.

The electrochemistry of niobium complexes has not been studied previously in room-temperature chloroaluminate ionic liquids with the exception of an initial investigation that was conducted in this laboratory to test the efficacy of phosgene as an agent for eliminating oxide. However, some limited electrochemical studies involving niobium have been conducted in alkali metal chloride

---

(1) For reviews see: (a) Chum, H. L.; Osteryoung, R. A. In *Ionic Liquids*; Inman, D., Lovering, D. G., Eds.; Plenum: New York, 1981; pp 407–423. (b) Hussey, C. L. *Adv. Molten Salt Chem.* **1983**, *5*, 185–230. (c) Gale, R. J.; Osteryoung, R. A. In *Molten Salt Techniques*; Lovering, D. G., Gale, R. J., Eds.; Plenum: New York, 1983; Vol. 1, pp 55–78.

(2) Basic room-temperature chloroaluminate ionic liquids contain a molar excess of the organic salt component relative to $AlCl_3$, while the acidic ionic liquids contain a molar excess of $AlCl_3$ relative to the organic salt; the excess chloride ion in the former can act as a Lewis base (cf. ref 1).

(3) Lipsztajn, M.; Osteryoung, R. A. *Electrochim. Acta* **1984**, *29*, 1349.

(4) Appleby, D.; Hussey, C. L.; Seddon, K. R.; Turp, J. E. *Nature* **1986**, *323*, 614.

(5) Hussey, C. L. *Pure Appl. Chem.* **1988**, *60*, 1763.

(6) Sun, I.-W.; Ward, E. H.; Hussey, C. L. *Inorg. Chem.* **1987**, *26*, 4309.

Table I. Absorption Spectroscopic Data for Niobium Chloride Complexes

species	solvent	λ, nm (ε, M^{-1} cm^{-1})	ref
$[NbCl_6]^-$	CH_3CN	205 (1.2×10^4),[a] 241 (1.0×10^4), 292 (4.0×10^4), 316 (1.6×10^4),[a] 355 (4.0×10^3)[a]	16
	CH_3CN	242 (8.1×10^3), 294 (3.4×10^4), 318 ($\sim 1.4 \times 10^4$),[a] 355 ($\sim 2.5 \times 10^3$)[a]	17
	44.4/55.6 mol % $AlCl_3$–MeEtimCl	291 (3.3×10^4), 317 (1.7×10^4),[a] 354 (3.8×10^3)[a]	this work
	49.0/51.0 mol % $AlCl_3$–MeEtimCl	291 (3.2×10^4), 316 (1.7×10^4),[a] 360 (4.1×10^3)[a]	this work
$[NbCl_6]^{2-}$	CH_3CN	249 (9.0×10^3), 287 (9.6×10^3), 314 ($<2.4 \times 10^3$),[a] 350 ($<4.2 \times 10^2$),[a] 410 ($<10^2$)[a]	18
	CH_3CN + $[(C_2H_5)_4N]Cl$	247, 287, 316,[a] ~357,[a] ~408,[a] ~515[a]	18
	DR[b]	223, 263,[a] 282, 318,[a] 420, ~610[a]	18
	KCl pellet	230, 250, 287, 328,[a] 391,[a] 490	19
	44.4/55.6 mol % $AlCl_3$–MeEtimCl	249,[c] 285 (1.4×10^4), ~320 (2.0×10^3),[a] 432 (13), ~480 (10)	this work

[a] Shoulder. [b] Diffuse reflectance. [c] Proximate to solvent UV cutoff.

based chloroaluminates. For example, Verdieck and Yntema[7] attempted to deposit niobium metal from solutions of niobium(V) in molten $AlCl_3$–NaCl–KCl (66/20/14 mol %), and Gut[8] observed two reduction waves at a mercury electrode in solutions of niobium(V) chloride in $AlCl_3$–MCl (50/50 mol %, M = Na or K) and attributed these waves to the Nb(V)/Nb(IV) and Nb(IV)/Nb(III) redox couples. Raman spectroscopic studies indicated that $[NbCl_6]^-$ is the predominant niobium chloride complex in very basic $AlCl_3$–NaCl and $AlCl_3$–KCl at temperatures above 200 °C while $NbCl_5$ is the predominant species in less basic melts.[9] Niobium solutes have also been studied in molten alkali-metal chlorides at high temperatures (>450 °C).[10] However, it is difficult to extrapolate the electrochemical results that were observed in these ionic liquids to room temperature.

The electrochemistry of several niobium chloride complexes has been investigated in molecular solvents like methylene chloride[11] and acetonitrile.[12] Voltammetric half-wave potentials were presented for both the $[NbCl_6]^{-/2-}$ and $[NbCl_6]^{2-/3-}$ redox couples in these two solvents. However, studies conducted in the latter solvent were mainly concerned with ligand-exchange reactions in which acetonitrile participated as a ligand; extreme measures were necessary to prevent hydrolysis of the niobium complexes in acetonitrile.[12]

In this paper, we report a systematic investigation of the electrochemistry of niobium chloride complexes in oxidation states three, four, and five in the basic $AlCl_3$–MeEtimCl ionic liquid. In addition, we have generated and characterized two high-oxidation-state oxide-containing niobium complexes by precisely controlling the oxide level in the melt with a known oxide source, Li_2CO_3,[13] and phosgene.

Experimental Section

Apparatus. All experiments were conducted inside a Kewaunee Scientific Equipment Corp. glovebox that was equipped with a Model 2C2500 30 ft^3 min^{-1} inert-gas purifier. The oxygen and moisture content of the nitrogen-filled glovebox were monitored by observing the lifetime of a 25-W clear, incandescent light bulb whose filament was exposed to the glovebox atmosphere. A filament lifetime of approximately 10 days was associated with an atmosphere of acceptable quality. Electrochemical experiments were performed with an EG&G Princeton Applied Research Corp. Model 173 potentiostat, equipped with a Model 179 digital coulometer plug-in module, and an EG&G PARC Model 175 universal programmer. The EG&G PARC Model 178 reference electrode probe was placed inside the glovebox and connected to the reference electrode in the experimental cell (vide infra) by a short lead. Resistance compensation was employed during all electrochemical experiments, except controlled-potential electrolysis. Data were displayed on either a Houston Instruments Model 100 X-Y/Y-t recorder or a Nicolet Explorer I digital oscilloscope.

Electrochemical experiments were carried out in a cell that was fabricated by closing the open end of a 125-mL Erlenmeyer flask and then attaching four 14/20 ground-glass joints to the bottom of the flask. The cell was also fitted with a side arm made from a Rotaflo PTFE stopcock that terminated with the ball of a ball and socket joint. The cell could be rendered vacuum tight by stoppering the ground-glass joints through which the electrodes normally passed and then closing the stopcock. The cell was open to the glovebox atmosphere during electrochemical experiments, but it could be sealed, removed from the glovebox, and attached to an external vacuum line when it was necessary to add phosgene gas to the liquid contained within.

The glassy-carbon rotating-disk electrode (GCRDE) that was used for voltammetric measurements (geometrical area 0.071 cm^2) has been described.[14] The counter and reference electrode compartments were constructed from 14/35 male ground-glass joints and were terminated with ACE Glass porosity E fritted-glass tips. Aluminum wires (Alfa, m5N) served as the counter and reference electrodes. All potentials are reported versus aluminum immersed in the nominal 66.7/33.3 mol % $AlCl_3$–MeEtimCl ionic liquid. Controlled-potential electrolysis experiments were conducted in the vacuum cell described above with a large surface area platinum-gauze working electrode or in a cell constructed from a glassy-carbon cup.

Absorption spectra were recorded with the use of either a Perkin-Elmer Hitachi Model 200 UV–vis spectrophotometer or a Perkin-Elmer Model 3840 Lambda Array spectrophotometer. The solutions for study were examined in 10-mm and 1-mm path length fused silica cells fitted with airtight Teflon caps.

Chemicals. The procedures that were used for the purification of $AlCl_3$ by vacuum sublimation, the synthesis and purification of MeEtimCl, and the preparation of the $AlCl_3$–MeEtimCl ionic liquid were described previously.[15] Niobium(V) chloride (Alfa, 99%+, resublimed) was used as received since attempts to purify this material by sublimation in a sealed quartz tube inside the glovebox did not result in a product of higher quality than the commercial starting material. Phosgene was used as obtained from the manufacturer (Van De Mark Chemical Co., Lockport, NY) and was added directly to the melt in the electrochemical cell described above on a vacuum line at slightly less than 1 atm of pressure. (*Safety caution*: phosgene is an insidiously poisonous gas, and it should be handled only with a vacuum line in a well-ventilated fume hood.)

Results and Discussion

Chloride Complexes. Niobium(V). The addition of niobium(V) chloride to the basic $AlCl_3$–MeEtimCl ionic liquid resulted in a bright yellow solution. In order to ensure that all of the added niobium(V) was present only as its chloride complex, the melt was treated with phosgene before and after dissolution of the niobium(V) chloride. It was especially difficult to avoid oxide contamination of the very dilute solutions that were used for spectroscopic measurements since the niobium(V) appeared to react with moisture bound to the surface of the rigorously dried

---

(7) Verdieck, R. G.; Yntema, L. F. *J. Phys. Chem.* **1944**, *48*, 268.
(8) Gut, R. *Helv. Chim. Acta* **1960**, *43*, 830.
(9) (a) von Barner, J. H.; Bjerrum, N. J.; Smith, G. P. *Acta Chem. Scand.* **1978**, *A32*, 837. (b) Huglen, R.; Mamantov, G.; Smith, G. P.; Begun, G. M. *J. Raman Spectrosc.* **1979**, *8*, 326.
(10) For a review of this area, see: Plambeck, J. A. In *Encyclopedia of Electrochemistry of the Elements*; Bard, A. J., Ed.; Dekker: New York, 1976; Vol. 10.
(11) Heath, G. A.; Moock, K. A.; Sharp, D. W. A.; Yellowlees, L. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1503.
(12) (a) Bursten, B. E.; Green, M. R.; Katović, V.; Kirk, J. R.; Lightner, D. *Inorg. Chem.* **1986**, *25*, 831. (b) Kirk, J. R.; Page, D.; Prazak, M.; Katović, V. *Inorg. Chem.* **1988**, *27*, 1956.
(13) Linga, H.; Stojek, Z.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 3754.
(14) Scheffler, T. B.; Hussey, C. L. *Inorg. Chem.* **1984**, *23*, 1926.
(15) Sun, I.-W.; Ward, E. H.; Hussey, C. L.; Seddon, K. R.; Turp, J. E. *Inorg. Chem.* **1987**, *26*, 2140.

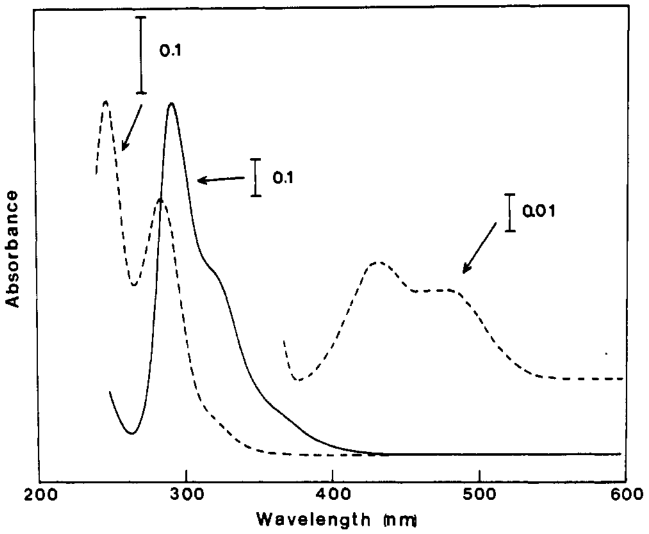

Figure 1. Absorption spectra of niobium(V) and -(IV) chloride complexes in the 44.4/55.6 mol % $AlCl_3$–MeEtimCl ionic liquid: (—) 2.88 × 10^{-4} M niobium(V); (---) 2.47 × 10^{-4} M niobium(IV); (inset) 2.48 × 10^{-2} M niobium(IV) (cell path lengths 1.00 mm).

Pyrex glass containers in which the solutions were prepared. Fortunately, the presence of even small amounts of niobium oxide impurities could be detected readily by using cyclic voltammetry.[6] An absorption spectrum of a dilute, oxide-free solution of niobium(V) in 44.4/55.6 mol % $AlCl_3$–MeEtimCl is shown in Figure 1, and data taken from this spectrum and a similar spectrum of niobium(V) that was recorded in the 49.0/51.0 mol % melt are summarized in Table I. No absorption maxima were detected in this solution other than those reported, even when the solution was made very concentrated (>25 mM) in niobium(V). The spectroscopic data for niobium(V) in basic $AlCl_3$–MeEtimCl are in good agreement with data reported in the literature for the $[NbCl_6]^-$ ion. The absorption spectrum of this species is relatively simple and consists entirely of ligand to metal charge-transfer (LMCT) bands because niobium(V) is a $4d^0$ ion; spectral assignments for the electronic transitions associated with this complex ion have been discussed at length by several research groups.[16,17,20]

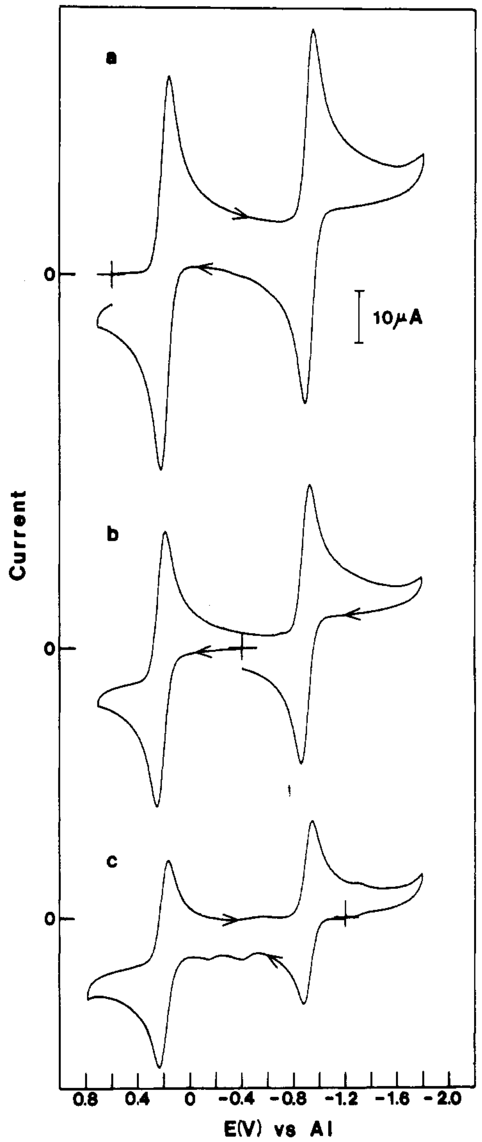

Figure 2. Cyclic voltammograms of niobium(V), -(IV), and -(III) chloride complexes at a glassy-carbon electrode in the 49.0/51.0 mol % $AlCl_3$–MeEtimCl ionic liquid at 40.0 °C: (a) 9.95 × 10^{-3} M niobium(V) chloride; (b) solution in (a) after reduction at −0.50 V; (c) solution in (b) after reduction at −1.2 V. The sweep rates were 0.050 V s^{-1}.

A cyclic voltammogram of a solution of $[NbCl_6]^-$ in the 49.0/51.0 mol % ionic liquid at a glassy-carbon electrode is shown in Figure 2a. Two reduction waves with peak potentials, E_p, of approximately 0.15 and −0.96 V, respectively, are apparent. Since the rest potential of the solution was positive of the first wave, the second wave must be due to further reduction in the electrode diffusion layer of the product that resulted from the first reduction process. The cyclic voltammetric peak potential separation for the first wave, which was measured after reversing the scan at −0.10 V, was constant with a value of ca. 0.063 V over the range of scan rates from 0.01 to 0.20 V s^{-1}. This value is in excellent agreement with the theoretical value of approximately 0.062 V expected for a one-electron, reversible electrode reaction at 40 °C.[21] The peak current ratio, i_p^a/i_p^c, which was calculated by using Nicholson's empirical procedure,[22] was constant with a value of 1.0, and the peak current function, $i_p^c/v^{1/2}$, where v is the scan rate, was essentially constant for a series of cyclic voltammograms that were recorded over this same range of scan rates. The first reduction wave was also investigated with the GCRDE; a plot of the limiting current versus the square root of the angular velocity of the GCRDE was linear over the range of velocities that were investigated, i.e., from 105 to 209 rad s^{-1}. Electrochemical data for the Nb(V)/Nb(IV) redox reaction in both the 49.0/51.0 and 44.4/55.6 mol % melts are summarized in Table II. The shift in $E_{1/2}$ with pCl[23] that can be calculated for the Nb(V)/Nb(IV) system from the data in this table (0.015 V/pCl unit) is less than the shifts that were observed for other redox couples in $AlCl_3$–MeEtimCl in which both the oxidized and reduced forms of the couple are known to exhibit the same chloride coordination number, e.g., $[IrCl_6]^{2-/3-}$ (0.022 V/pCl unit)[15] and $[WCl_6]^{-/2-}$ (0.018 V/pCl unit).[14] This suggests that the potential of the Nb(V)/Nb(IV) redox couple is essentially independent of pCl, i.e., $[NbCl_6]^-$ retains the same chloride coordination after reduction. Taken together, the results presented above indicate that

---

(16) Furlani, C.; Zinato, E. *Z. Anorg. Allg. Chem.* **1967**, *351*, 210.
(17) Brisdon, B. J.; Fowles, G. W. A.; Tidmarsh, D. J.; Walton, R. A. *Spectrochim. Acta* **1969**, *25A*, 999.
(18) Fowles, G. W. A.; Tidmarsh, D. J.; Walton, R. A. *Inorg. Chem.* **1969**, *8*, 631.
(19) Horner, S. M.; Clark, R. J. H.; Crociani, B.; Copley, D. B.; Horner, W. W.; Collier, F. N.; Tyree, S. Y. *Inorg. Chem.* **1968**, *7*, 1859.
(20) Valloton, M.; Merbach, A. E. *Helv. Chim. Acta* **1974**, *57*, 2345.
(21) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; p 230.
(22) Nicholson, R. S. *Anal. Chem.* **1966**, *38*, 1406.
(23) For an electrochemical reaction of the type $[MCl_x]^{n-x} + ze^- \rightleftharpoons [MCl_y]^{n-z-y} + (x-y)Cl^-$, a negative shift in $E_{1/2}$ of approximately $2.3(x-y)RT/zF$ V/unit decrease in pCl is expected, e.g., a negative shift of approximately 0.062 V/pCl unit for $z = x - y = 1$ at 40 °C. In practice, we find that this method is not especially reliable for estimating $x - y$ since small negative shifts in $E_{1/2}$ with decreasing pCl are almost always observed for redox systems involving highly charged complex ions in room-temperature chloroaluminates, even when $x - y = 0$. One possible explanation for these shifts has been advanced; cf. ref 15.

Table II. Summary of Electrochemical Data for Niobium Complexes in Basic $AlCl_3$–MeEtimCl at 40 °C

redox syst	solute	mol % $AlCl_3$	E_p,[a] V	$E_{1/2}$,[b] V	10^7D,[c] $cm^2\ s^{-1}$	$E°'$, V	$10^{10}\eta D/T$, $g\ cm\ s^{-2}\ K^{-1}$
Nb(V)/Nb(IV)	$[NbCl_6]^-$	49.0	0.153	0.183	8.21	0.191[d]	3.5 ± 0.3
Nb(IV)/Nb(V)	$[NbCl_6]^{2-}$[e]	49.0	0.215	0.181	4.92		2.1 ± 0.3
Nb(IV)/Nb(III)	$[NbCl_6]^{2-}$[e]	49.0	−0.958	−0.923	4.91		2.1 ± 0.3
Nb(III)/Nb(IV)	$[NbCl_6]^{3-}$[f]	49.0	−0.889	−0.920	>2.59		>1.1
Nb(V)/Nb(IV)	$[NbCl_6]^-$	44.4	0.143	0.172	4.98	0.182[d]	3.4 ± 0.2
Nb(IV)/Nb(V)	$[NbCl_6]^{2-}$[e]	44.4	0.205	0.174	3.02		2.1 ± 0.2
Nb(IV)/Nb(III)	$[NbCl_6]^{2-}$[e]	44.4	−0.978	−0.935[g]	3.26		2.2 ± 0.2
Nb(III)/Nb(IV)	$[NbCl_6]^{3-}$[e]	44.4	−0.905	−0.933[g]	>1.50		>1.0
Nb(V)/Nb(IV)	$[NbOCl_5]^{2-}$	44.4	−0.712	−0.535[g]	2.82[h]	−0.521[i] (−0.488)[j]	1.9 ± 0.2
Nb(IV)/Nb(V)	$[NbOCl_y]^{2-y}$	44.4	−0.369	−0.559[g]	2.01[h]		1.4 ± 0.1

[a] Average voltammetric peak potential over the range of sweep rates from 0.01 to 0.20 V s^{-1}. All potentials are referenced to Al in the 66.7/33.3 mol % melt. $E_{1/2}$ for the oxidation of ferrocene was observed at 0.25 and 0.22 V versus this reference electrode in the 44.4/55.6 and 49.0/51.0 mol % ionic liquids, respectively. [b] Average GCRDE value over the range of angular velocities from 105 to 209 rad s^{-1}. [c] Average value from stationary- and rotating-electrode voltammetry and chronoamperometry. [d] Formal potential estimated from $E_{1/2}$, D_R, and D_O by using $E°' = E_{1/2} + 0.027 \ln (D_O/D_R)^{2/3}$. [e] Produced by electrolytic reduction of $[NbCl_6]^-$. [f] Produced by electrolytic reduction of $[NbCl_6]^{2-}$. [g] Estimated from cyclic voltammetric peak potentials by using $(E_p^a + E_p^c)/2$. [h] Rotating-disk-electrode voltammetric and chronoamperometric data only. [i] 44.4/55.6 mol % ionic liquid. [j] 49.0/51.0 mol % ionic liquid.

the first cyclic voltammetric wave corresponds to the reversible, uncomplicated, one-electron reaction

$$[NbCl_6]^- + e^- \rightleftharpoons [NbCl_6]^{2-} \qquad (1)$$

Similar results were found in "super dry" CH_3CN.[12] The Stokes–Einstein product, $\eta D/T$, where η is the absolute viscosity of the melt, D is the diffusion coefficient of the electroactive species, and T is the absolute temperature, for $[NbCl_6]^-$ is the largest that we have observed for a hexachlorometalate complex in basic $AlCl_3$–MeEtimCl (Table II).

Niobium(IV). Exhaustive controlled-potential electrolysis experiments were performed with bulk solutions of $[NbCl_6]^-$ at an applied potential of −0.50 V. Plots of log i versus t,[24] which were constructed from the experimental electrolysis current–time data, gave n values of 0.92 and 0.97. The solutions that resulted from these experiments were pale yellow-brown in color. A cyclic voltammogram of the solution in Figure 2a that was recorded after exhaustive reduction at −0.50 V is shown in Figure 2b. It is apparent from this voltammogram that the same redox couples that were accessible in the $[NbCl_6]^-$ solution are still accessible in this solution. However, the one-electron reduction product of $[NbCl_6]^-$ is now the principal electroactive species present in solution. Since the value of $E_{1/2}$ for the oxidation of this niobium(IV) species was within 0.002 V of that for the reduction of $[NbCl_6]^-$ (Table II), the niobium species present in this solution must be $[NbCl_6]^{2-}$. The values of $\eta D/T$ for $[NbCl_6]^{2-}$ (Table II) are comparable in size to those of some other octahedral transition-metal hexachlorometalate complexes with the same overall charge and metal oxidation state, notably $[IrCl_6]^{2-}$ (1.8×10^{-10} g cm s^{-2} K^{-1}),[15] $[MoCl_6]^{2-}$ (1.8×10^{-10} g cm s^{-2} K^{-1}),[25] and $[OsCl_6]^{2-}$ (2.1×10^{-10} g cm s^{-2} K^{-1}).[26]

Like $[NbCl_6]^-$, $[NbCl_6]^{2-}$ is an extremely efficient oxide scavenger. Small voltammetric waves due to niobium oxide complexes (vide infra) could be found in $[NbCl_6]^{2-}$ solutions after approximately 24–36 h, even when the solutions were stored in carefully dried, vacuum-tight glass vessels in the glovebox. However, any $[NbCl_6]^{2-}$ that was inadvertently converted to an oxide-containing species in solution could be recovered by treatment of the solution with phosgene.[6]

Absorption spectra, recorded for $[NbCl_6]^{2-}$ under oxide-free conditions in the melt, are shown in Figure 1. Data taken from these spectra are collected in Table I along with literature data for the $[NbCl_6]^{2-}$ complex ion. Unfortunately, we were able to locate only a single uncorroborated report of the solution UV–vis absorption spectrum of $[NbCl_6]^{2-}$ for comparison. While the wavelengths of the more intense bands that were recorded in the melt agree well with those that were recorded for this complex ion in CH_3CN, the less intense bands, which have been assigned to d–d transitions,[18] do not agree with respect to either position or intensity. However, there is reasonable agreement between the positions of the maxima found in basic $AlCl_3$–MeEtimCl and the literature values recorded both for $Cs_2[NbCl_6]$ in solid KCl and for solid $[(C_2H_5)_4N]_2[NbCl_6]$. A simple NMR experiment in which the ^1H NMR spectrum of the melt was recorded both with and without added $[NbCl_6]^{2-}$ revealed that solutions of $[NbCl_6]^{2-}$ in basic $AlCl_3$–MeEtimCl are not significantly paramagnetic at room temperature. This observation is in accordance with the prediction of Johnson and Bereman.[27]

As shown in Figure 2b, the $[NbCl_6]^{2-}$ complex ion can be reduced voltammetrically at $E_p = -0.98$ V; the average peak potential separation for a series of cyclic voltammograms that were recorded by scanning from −0.60 to −1.2 V and then back to −0.60 V was 0.064 V over the range of scan rates from 0.01 to 0.20 V s^{-1}. In addition, the value of i_p^a/i_p^c was close to 1.0 and $i_p^c/v^{1/2}$ was essentially constant over this same range of scan rates. A plot of the GCRDE limiting current as a function of the square root of the angular velocity was linear over the range of velocities from 105 to 209 rad s^{-1}. As noted for the $[NbCl_6]^{-/2-}$ redox reaction, the pCl dependence of $E_{1/2}$ for the Nb(IV)/Nb(III) reaction, calculated from the data in Table II (0.016 V/pCl unit), is less than that observed for other redox couples in basic $AlCl_3$–MeEtimCl in which the chloride coordination number is known to be the same for both the oxidized and reduced forms of the couple. Thus, the second reduction wave in Figure 2 appears to arise from the following reversible, uncomplicated reaction

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

in which $[NbCl_6]^{3-}$ is stable on the voltammetric time scale.

Niobium(III). Several exhaustive controlled-potential electrolysis experiments were conducted at −1.2 V with solutions containing $[NbCl_6]^{2-}$. A plot of log i versus t, which was created from the current–time data resulting from one of these experiments, gave an n value of 1.02, suggesting that a niobium(III) species was produced. A notable feature in the absorption spectrum of these green niobium(III) solutions is a broad absorption band centered at 646 nm with a molar absorptivity of approximately 50 M^{-1} cm^{-1}.

A cyclic voltammogram of the solution in Figure 2b after exhaustive reduction at −1.2 V is illustrated in Figure 2c. This voltammogram, which was initiated from the solution rest potential, exhibits the same waves as the voltammograms of the solutions containing $[NbCl_6]^-$ and $[NbCl_6]^{2-}$, Figure 2a,b, respectively. However, small amounts of one or more additional electroactive species are also present. The value of $E_{1/2}$ for the oxidation of the major niobium(III) product was within 0.003 V

---

(24) MacNevin, W. M.; Baker, B. B. *Anal. Chem.* **1952**, *24*, 986.

(25) Scheffler, T. B.; Hussey, C. L.; Seddon, K. R.; Kear, C. M.; Armitage, P. D. *Inorg. Chem.* **1983**, *22*, 2099.

(26) Sun, I.-W.; Ward, E. H.; Hussey, C. L. *J. Electrochem. Soc.* **1988**, *135*, 3035.

(27) Johnson, D. P.; Bereman, R. D. *J. Inorg. Nucl. Chem.* **1972**, *34*, 679.

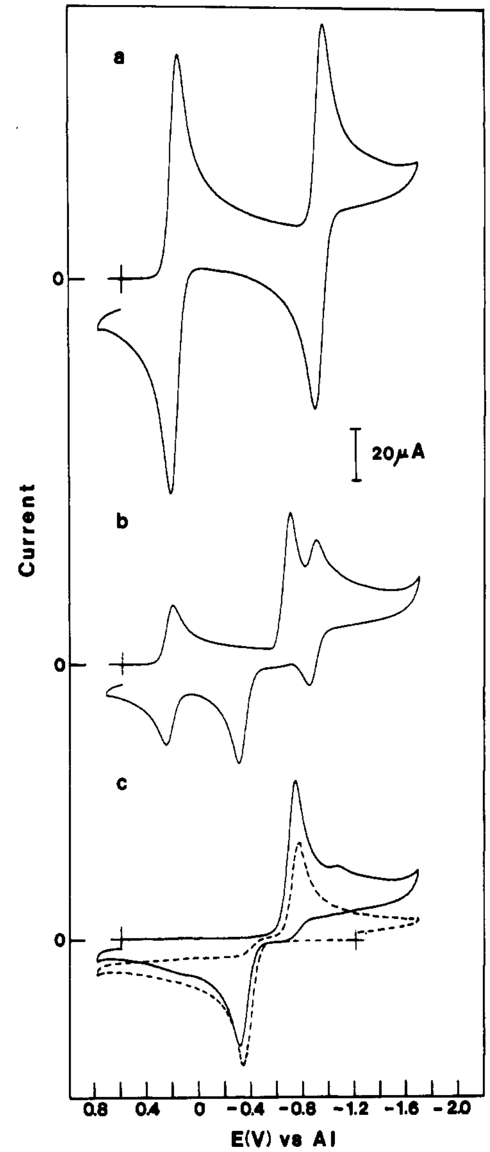

Figure 3. Cyclic voltammograms of niobium(V) and -(IV) at a glassy-carbon electrode in the 44.4/55.6 mol % $AlCl_3$–MeEtimCl ionic liquid at 40.0 °C: (a) 29.3 × 10^{-3} M niobium(V) chloride; (b) solution in (a) after the addition of "O^{2-}" (the moles of O^{2-} added were equivalent to 74% of the total moles of niobium); (c) (—) solution in (a) after the addition of 1 mol of O^{2-}/mol of niobium and (---) solution in (b) after reduction at −1.2 V. The sweep rates were 0.050 V s^{-1}.

of the value of $E_{1/2}$ for the reduction of $[NbCl_6]^{2-}$ (Table II). Based on these results and those presented above, it is reasonable to conclude that $[NbCl_6]^{3-}$ is the principal niobium(III) species present in the reduced solution.

The minor side products noted in this reduced solution may be niobium(III) chloride complexes different from $[NbCl_6]^{3-}$, since they disappear from the solution when the $[NbCl_6]^{3-}$ is oxidized back to $[NbCl_6]^{2-}$ and/or $[NbCl_6]^-$. However, we did not undertake a detailed investigation of these species. As a consequence of these side products, we are unable to report a precise value of the diffusion coefficient of $[NbCl_6]^{3-}$ because there did not appear to be any reliable way to measure the concentration of this species in the melt. However, an estimate of the lower limit of $\eta D/T$ for this species is given in Table II. As expected, this estimate is comparable to the values that have been reported for some other transition-metal hexachlorometalates with the same overall charge and metal oxidation state, e.g., $[IrCl_6]^{3-}$ (1.3 × 10^{-10} g cm s^{-2} K^{-1}),[15] $[MoCl_6]^{3-}$ (1.1 × 10^{-10} g cm s^{-2} K^{-1}),[25] and $[OsCl_6]^{3-}$ (1.5 × 10^{-10} g cm s^{-2} K^{-1}).[26]

The enhanced stability of $[NbCl_6]^{3-}$ in basic $AlCl_3$–MeEtimCl is unexpected since $[NbCl_6]^{3-}$ is demonstrably unstable on the voltammetric time scale in "super dry" CH_3CN.[12b] We have been

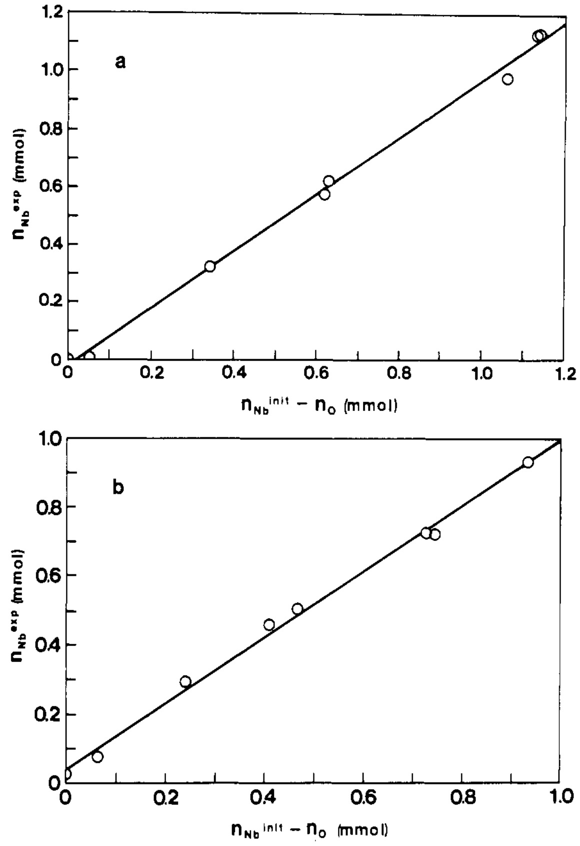

Figure 4. Plots of n_{Nb}^{exp} versus $n_{Nb}^{init} - n_O$ resulting from amperometric titration experiments involving "O^{2-}" and (a) niobium(V) and (b) niobium(IV). The solid lines were calculated from the least-squares slopes and intercepts of the experimental data shown.

unable to locate any reports of studies in which compounds containing $[NbCl_6]^{3-}$ were synthesized or of absorption spectroscopic data for this complex. Kostikova et al.[28] discuss the X-ray spectrum of solid K_3NbCl_6 but give no details about the preparation of this compound. The metal–metal-bonded dimer, $[Nb_2Cl_9]^{3-}$,[29] appears to be the only well-characterized niobium(III) chloride complex. This complex may be one of the side products present in the solutions containing $[NbCl_6]^{3-}$ (vide supra).

Oxide Chloride Complexes. Niobium(V). The addition of oxide, represented for convenience as "O^{2-}",[30] to solutions of $[NbCl_6]^-$ in basic $AlCl_3$–MeEtimCl results in a decrease in the heights of the $[NbCl_6]^{-/2-}$ and $[NbCl_6]^{2-/3-}$ reduction waves and the appearance of a new reduction wave at E_p^c = −0.71 V with an associated oxidation wave at E_p^a = −0.37 V (Figure 3). These voltammetric results suggest that $[NbCl_6]^-$ is converted to a niobium(V) oxide containing species. This species can be converted back to $[NbCl_6]^-$ by using phosgene.[6]

An amperometric titration experiment was conducted in an effort to gain insight into the niobium/oxygen ratio in this oxide-containing complex and to assess the completeness of the reaction between O^{2-} and $[NbCl_6]^-$. In this experiment, small, precisely weighed amounts of Li_2CO_3 were added to a solution containing a known quantity of $[NbCl_6]^-$, and the voltammetric reduction wave of this species was recorded after equilibrium was established. The number of millimoles of $[NbCl_6]^-$ remaining in the solution after each addition, n_{Nb}^{exp}, were calculated from the voltammetric wave height, which reached a constant value within a few minutes following each addition. A plot of n_{Nb}^{exp} versus $n_{Nb}^{init} - n_O$, where n_{Nb}^{init} is the initial millimoles of $[NbCl_6]^-$ and n_O is the number of millimoles of O^{2-} that were added, is

---

(28) Kostikova, G. P.; Kostikov, Yu. P.; Troyanov, S. I.; Korol'kov, D. V. *Inorg. Chem.* **1978**, *17*, 2279.

(29) Maas, E. T.; McCarley, R. E. *Inorg. Chem.* **1973**, *12*, 1096.

(30) At the present time, the chemistry of oxide in room-temperature chloroaluminate ionic liquids is poorly understood (cf. citation 5 of ref 6).

Table III. Absorption Spectroscopic Data for Niobium Oxide Chloride Complexes

species	solvent	λ, nm (ε, M^{-1} cm^{-1})	ref
$[NbOCl_5]^{2-}$	CH_3CN	205 (3.0 × 10^4),[a] 228 (4.0 × 10^3), 278 (1.6 × 10^4) 313 (1.1 × 10^3)[a]	16
	12 M HCl	228 (3.6 × 10^3), 280 (1.1 × 10^4), ~320 (1.3 × 10^3)[a]	this work
	44.4/55.6 mol % $AlCl_3$–MeEtimCl	278 (1.3 × 10^4), ~317 (1.2 × 10^3)[a]	this work
	49.0/51.0 mol % $AlCl_3$–MeEtimCl	280 (1.4 × 10^4), ~320 (1.4 × 10^3)[a]	this work
$[NbOCl_y]^{2-y}$	44.4/55.6 mol % $AlCl_3$–MeEtimCl	~315 (200), 524 (7)	this work

[a] Shoulder.

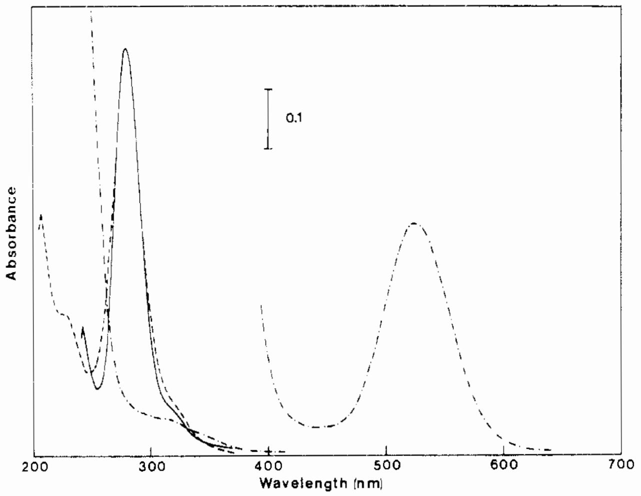

Figure 5. Absorption spectra of niobium(V) and -(IV) oxide chloride complexes: (—) 4.83 × 10^{-4} M niobium(V) in the 49.0/51.0 mol % $AlCl_3$–MeEtimCl ionic liquid (cell path length 1.00 mm); (- - -) 6.27 × 10^{-4} M $[NbOCl_5]^{2-}$ in 12 M aqueous HCl (cell path length 1.00 mm); (-·-) 2.10 × 10^{-3} M niobium(IV) in the 44.4/55.6 mol % $AlCl_3$–MeEtimCl ionic liquid (cell path length 1.00 mm); (inset) 5.69 × 10^{-2} M niobium(IV) in the same solvent (cell path length 1.00 cm).

shown in Figure 4a. Least-squares analysis of the experimental data in this plot gave a slope of 0.997 with a small intercept and a correlation coefficient of 0.996. The linearity of this plot suggests that the reaction between $[NbCl_6]^-$ and O^{2-} proceeds essentially to completion, unlike the reaction between $[TiCl_6]^{2-}$ and O^{2-},[13] while the slope of this plot indicates that the niobium/oxygen ratio of this oxide-containing species is 1.0.

An absorption spectrum of niobium(V) in basic melt in which all of the $[NbCl_6]^-$ was converted to its oxide-containing counterpart is shown in Figure 5. Also shown in this figure is a spectrum of niobium(V) chloride in 12 M aqueous hydrochloric acid; this aqueous solution is known to contain $[NbOCl_5]^{2-}$.[19,31] The spectrum of the niobium(V) oxide containing species in the melt is very similar in appearance to that for $[NbOCl_5]^{2-}$ in the aqueous solution. The essential features of the spectra in Figure 5 are summarized in Table III along with literature data for $[NbOCl_5]^{2-}$ in CH_3CN. These spectroscopic results, when combined with the results of the amperometric titration experiment, strongly suggest that $[NbOCl_5]^{2-}$ is the niobium(V) oxide containing complex in basic $AlCl_3$–MeEtimCl.

However, one troubling aspect of this assignment is the diminutive $\eta D/T$ value for this species (Table III), which is only 55% of that for $[NbCl_6]^-$. This small value led us to prematurely designate the niobium(V) oxide chloride complex as a dimer.[5,6] However, careful examination of the extensive body of $\eta D/T$ values that have been determined for many transition-metal halide complexes in room-temperature haloaluminate melts suggests that, with only a few exceptions, the magnitude of this parameter is more closely related to the overall charge on the complex ion than to the oxidation state of its metal core or to its coordination geometry. The full implications of this apparent correlation will not be discussed here, but it does suggest that at least some or possibly all highly charged anions may diffuse in the melt in association with the melt cations. In this context, the Stokes–Einstein product for $[NbOCl_5]^{2-}$ in the ionic liquid is not unusual. In fact, it is in quite good agreement with that for $[NbCl_6]^{2-}$ and many other octahedral chloride complexes with the same overall charge. The $\eta D/T$ values for some of these species have been listed above.

Niobium(IV). Controlled-potential electrolysis experiments were conducted with solutions of $[NbOCl_5]^{2-}$ in basic melt at an applied potential of −1.2 V. The exhaustively reduced solutions were violet in color. Plots of log i versus t, which were constructed from the current–time data that resulted from these electrolysis experiments, gave an average value of $n = 0.97$ for this reduction process, i.e., 1 mol of electrons is transferred for each 1 mol of niobium atoms. This result was confirmed via an exhaustive coulometry experiment. Cyclic voltammograms of a solution of $[NbOCl_5]^{2-}$ before and after reduction are shown in Figure 3c, and they indicate that the reduced form of $[NbOCl_5]^{2-}$, which is a niobium(IV) oxide chloride complex, is the principal species present in solution following reduction. In addition, voltammograms comparable to those for the reduced $[NbOCl_5]^{2-}$ solution are observed for $[NbCl_6]^{2-}$ solutions containing a molar excess of O^{2-}.

In order to deduce the niobium/oxygen ratio in the niobium(IV) oxide containing species, an amperometric titration experiment similar to that conducted with $[NbCl_6]^-$ was undertaken with $[NbCl_6]^{2-}$. A plot of n_{Nb}^{exp} versus $n_{Nb}^{init} - n_O$ that resulted from this experiment is shown in Figure 4b. The least-squares slope of this plot was 0.955, and the correlation coefficient of the fit was 0.995. These results were very similar to those obtained with O^{2-} and $[NbCl_6]^-$; i.e., the reaction between O^{2-} and $[NbCl_6]^{2-}$ appears to proceed essentially to completion, and the niobium/oxygen ratio in the resulting oxide chloride complex is 1.0. This niobium(IV) oxide containing species was converted back to $[NbCl_6]^{2-}$ when phosgene was added to the ionic liquid. Alternatively, it could be electrochemically oxidized to $[NbOCl_5]^{2-}$. The diffusion coefficient for this complex, which was estimated from rotating-disk-electrode voltammetric and chronoamperometric data, is similar in magnitude to that for $[NbOCl_5]^{2-}$.

An absorption spectrum of a basic melt solution containing only the niobium(IV) oxide chloride complex is shown in Figure 5. A single weak absorption band at ca. 320 nm can be seen prior to the UV cutoff of the melt, while very concentrated solutions of this complex exhibit a weak, symmetrical absorption band at 524 nm, which probably arises from a d–d electronic transition (Figure 5). A simple ^1H NMR experiment, similar to that used to study $[NbCl_6]^{2-}$, indicated that melt solutions containing this niobium(IV) oxide chloride complex were intensely paramagnetic as opposed to solutions containing only $[NbOCl_5]^{2-}$, which, as expected, displayed no paramagnetic properties. Cozzi and Vivarelli[32] report that solutions of niobium(IV) in 13 M HCl, which are believed to contain $[NbOCl_4]^{2-}$ and $[NbCl_6]^{2-}$, exhibit a red-orange color, while similar solutions of niobium(IV) prepared with 10 M HCl, are violet in color. In addition, these solutions exhibit single absorption bands at 478 and 495 nm, respectively, in the wavelength region from 350 to 900 nm. Although these results do not

---

(31) Griffith, W. P.; Wickins, T. D. *J. Chem. Soc. A* **1967**, 675.

(32) Cozzi, D.; Vivarelli, S. *Z. Anorg. Allg. Chem.* **1955**, *279*, 165.

(33) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; p 291.

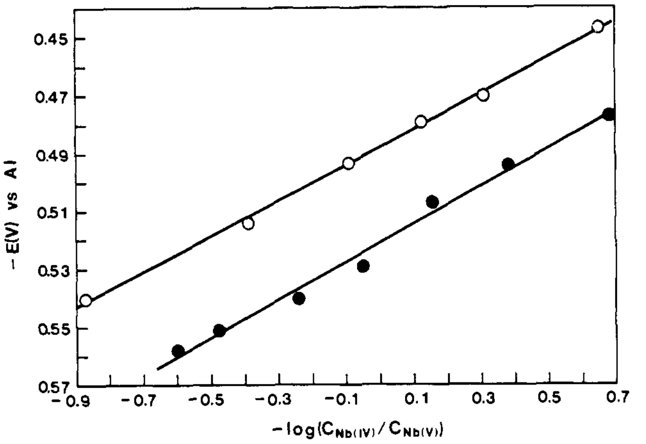

Figure 6. Nernst plots for the niobium(V)/niobium(IV) oxide chloride complex redox reaction at 40 °C: (○) 49.0/51.0 mol % $AlCl_3$–MeEtimCl; (●) 44.4/55.6 mol % $AlCl_3$–MeEtimCl. The solid lines were calculated from the least-squares slopes and intercepts of the experimental data shown.

permit the definitive assignment of $[NbOCl_4]^{2-}$ as the niobium(IV) species in basic $AlCl_3$–MeEtimCl, they do not eliminate this possibility.

Nb(V)/Nb(IV) Electrode Reaction. Nernst plots were constructed for the niobium(V)/niobium(IV) oxide chloride redox reaction in the 49.0/51.0 and 44.4/55.6 mol % melts by using controlled-potential electrolysis to adjust the Nb(V)/Nb(IV) concentration ratio in a solution initially containing only $[NbOCl_5]^{2-}$ (Figure 6). The Nb(V)/Nb(IV) concentration ratios in these solutions were determined with rotating-disk-electrode voltammetry. The least-squares slope and intercept of the plot that was constructed with data taken in the 49.0/51.0 mol % melt were 0.062 and −0.488 V, respectively, while the slope and intercept of the plot that was created with data collected in the 44.4/55.6 mol % ionic liquid were 0.065 and −0.521 V, respectively. Taken with the controlled-potential electrolysis results that are presented above, these slopes indicate that the niobium(V)/niobium(IV) oxide chloride redox reaction is a one-electron process involving monomeric complexes as opposed to a two-electron process involving dimeric species, which would be expected to yield an experimental slope close to 0.031 V at 40 °C. Not surprisingly, this result is quite different than that found in concentrated hydrochloric acid, where the reduction of niobium(V) to niobium(IV) is complicated by disproportionation of the latter into niobium(V) and niobium(III).[34,35]

The intercepts of these Nernst plots, which correspond to the formal redox potential, $E^{\circ\prime}$, of the Nb(V)/Nb(IV) couple in each of these ionic liquids, exhibit a negative shift with melt composition of ca. 0.045 V/pCl unit. This shift in $E^{\circ\prime}$ is only 72% of the 0.062 V/pCl unit shift expected for the loss of a single chloride ion during the reduction process.[23] Thus, it is not possible to state with confidence that the one-electron reduction of $[NbOCl_5]^{2-}$

$$[NbOCl_5]^{2-} + e^- \rightleftharpoons [NbOCl_y]^{2-y} + (5-y)Cl^- \qquad (3)$$

is accompanied by the loss of chloride from the niobium coordination sphere.

The very large peak potential separations exhibited by the voltammograms in Figure 3c suggest that the niobium(V)/niobium(IV) oxide chloride electrode reaction is complicated either by slow heterogeneous kinetics or by a coupled homogeneous following chemical reaction (EC mechanism). For example, the latter pathway could result in the rapid formation of a product such as $[NbOCl_4]^{2-}$ that would be more difficult to oxidize than $[NbOCl_5]^{3-}$, the direct one-electron-reduction product of $[NbOCl_5]^{2-}$. This could also lead to a peak potential separation substantially greater than the 0.062 V anticipated for a one-electron reversible process. However, no coupling wave indicative of an EC mechanism was observed after voltammetric scan reversal at scan rates as high as 20 V s^{-1}, the practical limit of our experimental system. Thus, if such a chemical step is coupled to the reduction of $[NbOCl_5]^{2-}$, this step must be extremely rapid. On the other hand, the $[NbOCl_5]^{2-}$ reduction peak potential was observed to shift negatively at the rate of about 30 mV per order of magnitude increase in scan rate. Figure 7 shows plots of the current for the reduction of this species at a GCRDE as a function of the square root of the angular velocity of the electrode. These plots were constructed from current measurements at selected potentials on the ascending portions of the GCRDE voltammetric waves that were recorded at different angular velocities. They clearly illustrate that the niobium(V) reduction process is controlled by the interfacial charge-transfer rate at more positive potentials (−0.625 V) and by the mass-transfer rate at more negative potentials (−0.875).

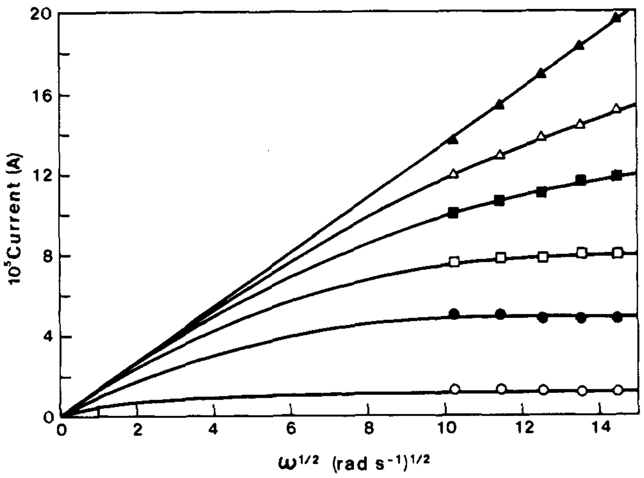

Figure 7. Plots of the current versus the square root of the angular velocity of the GCRDE at selected potentials (V) on the voltammetric waves for the reduction of 5.69 × 10^{-2} M $[NbOCl_5]^{2-}$ in 44.4/55.6 mol % $AlCl_3$–MeEtimCl at 40 °C: (○) −0.625; (●) −0.675; (□) −0.700; (■) −0.725; (△) −0.750; (▲) −0.875.

In order to obtain an estimate of the standard heterogeneous rate constant, k°, and the cathodic transfer coefficient, α, for the Nb(V)/Nb(IV) electrode reaction from this data, it was first necessary to calculate potential-dependent heterogeneous rate constants, $k_f(E)$ for the reduction of niobium(V). These rate constants were calculated from the average values of the rotation-rate-independent currents in the potential range from −0.625 to −0.700 V and from the intercepts of the linear plots of $1/i$ versus $1/\omega^{1/2}$ that were constructed from data recorded in the region of mixed control (−0.725 to −0.775 V) by using the equation[33]

$$i = nFA(k_f(E))C_0^* \qquad (4)$$

Implicit in the use of this equation is the assumption that the back-reaction can be ignored at these potentials. Since the first data point is over 100 mV negative of $E^{\circ\prime}$ for the reaction and the reaction appears to be very sluggish, this assumption seems justified. According to eq 5, the slope of a plot of ln $k_f(E)$ versus $-E$ gives α, while the intercept at $-E^{\circ\prime}$ yields k°. A plot of this

$$k_f(E) = k^\circ \exp(-\alpha nFE/RT) \qquad (5)$$

type, which was constructed from data taken at several different niobium(V) concentrations in the 44.4/55.6 mol % ionic liquid, yields $\alpha = 0.8$ and $k^\circ = 9 \times 10^{-7}$ cm s^{-1}. However, it may be necessary to revise this rate constant if the niobium(V)/niobium(IV) oxide chloride reduction reaction is found ultimately to be complicated by both a very rapid following chemical step and slow heterogeneous kinetics.

Acknowledgment. We wish to acknowledge helpful discussions about this work with Prof. Walter E. Cleland and Dr. Kenneth R. Seddon, University of Sussex. This research was supported by the National Science Foundation (Grant No. CHE-8715464).

---

(34) Cozzi, D.; Vivarelli, S. *Z. Elektrochem.* **1954**, *58*, 177.

(35) McCullough, J. Ph.D. Thesis, Polytechnic Institute of Brooklyn, 1967.