Electrochemistry of Hg(II) Salts in Room-Temperature Ionic Liquids

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Supporting Information

ABSTRACT: The electrochemistry of HgCl₂ and [Hg(NTf₂)₂] ([NTf₂]⁻ = bis-{[(trifluoromethyl)sulfonyl]imide} has been studied in room temperature ionic liquids. It has been found that the cyclic voltammetry of Hg(II) is strongly dependent on a number of factors (e.g., concentration, anions present in the mixture, and nature of the working electrode) and differs from that found in other media. Depending on conditions, the cyclic voltammetry of Hg(II) can give rise to one, two, or four reduction peaks, whereas the reverse oxidative scans show two to four peaks. Diffuse reflectance UV−vis spectroscopy and X-ray powder diffraction have been used to aid the assignment of the voltammetric waves.

INTRODUCTION

Mercury is a neurotoxic metal which causes damage to the environment and to health, making it a high priority in environmental legislation. Mercury enters the environment through a variety of sources, both natural (e.g., volcanoes) and related to human activity (e.g., emissions from fossil fuel combustion, mining, or solid waste combustion), and it can be found in different chemical forms (e.g., elemental mercury, Hg(II) salts, organomercurials). There is, therefore, increasing demand not only for the reduction of mercury released into the environment but also for better detection and removal methods.

Ionic liquids (ILs) have recently been investigated as a means of sequestering mercury from both liquid and gas streams. However, the speciation of the mercury in the ionic liquids is largely unknown. Ionic liquids are essentially molten salts that are liquid at or near room temperature; among their many useful properties are their high inherent conductivity, wide electrochemical stability, negligible volatility, tunable miscibility, and unique solvating characteristics. These properties make the ILs an alternative media for the remediation of mercury. The low vapor pressure prevents significant vaporization of the ionic liquid and with it the mercury and the tenability allows efficient design of sequestering moieties to be added to the cation/anion. Recovery of the ionic liquid is vital due to their cost and, therefore, due to the high conductivity of the media, electrochemistry presents an attractive method of IL remediation once they have become saturated with Hg. Furthermore, Hg is an attractive electrode material for fundamental electrochemical studies. However, before such goals can be adequately realized, fundamental studies into the electrochemical behavior of Hg in ILs are required.

Studies on the electrochemistry of mercury in room temperature ILs are very limited, with only one work published, to date, and which focuses in the water- and anion-sensitive AlCl₃−[C₃mim]Cl ([C₃mim]⁺ = 1-ethyl-3-methylimidazolium). Therein, in acidic AlCl₃−[C₃mim]Cl (66.7−33.3 mol %) mixtures, cyclic voltammetry at glassy carbon or tungsten working electrodes shows that HgCl₂ is reduced in two steps to Hg₂⁺ and mercury metal (eqs 1 and 2). However, in basic 44.4−55.6 mol % AlCl₃−[C₃mim]Cl, a chloride Hg(II) complex forms which is then reduced in a single step to Hg(0) (eq 3). It was also found that Hg₂Cl₂ rapidly disproportionates in the Lewis basic mixture (eq 4). Both in acidic and basic mixtures, a single oxidative stripping peak is observed in the reverse scans. Related studies on molten salts at high temperature showed analogous results. Thus, HgCl₂ shows one single reduction from Hg(II) to Hg(0) at Pt working electrodes in molten LiCl−KCl (450 °C)5,5 or ZnCl₂−KCl (300 °C),6 with Hg(I) species not observed in these systems. It should be noted that at high scan rates, i.e., between 3.7 and 45.8 V s⁻¹, the cyclic voltammetry of HgCl₂ in ZnCl₂−KCl contains a prewave preceding the bulk reduction of Hg(II) to Hg(0) which is related to the adsorption of mercury. Accordingly, the reverse scans also show two oxidation peaks. In addition, it has also been shown that the Hg(II)/Hg(0) reduction is reversible at high scan rates, but at low scan rates the metal deposits onto the electrode and reacts to form PtHg₄.6

\[
\begin{align*}
2\text{Hg}^{2+} + 2e^- &\rightarrow \text{Hg}_2^{2+} \\
\text{Hg}_2^{2+} + 2e^- &\rightarrow 2\text{Hg} \\
[\text{HgCl}_2 + x\text{Cl}^-]^{x-} + 2e^- &\rightarrow \text{Hg} + (2 + x)\text{Cl}^- \\
\text{Hg}_2\text{Cl}_2 + x\text{Cl}^- &\rightarrow [\text{HgCl}_2 + x\text{Cl}^-]^{x-} + \text{Hg}
\end{align*}
\]

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In Lewis acidic chloroaluminate melts, it has been possible to detect stable Hg(I) species. For example, Hames and Plambeck reported that the reduction of HgCl$_2$ in AlCl$_3$--NaCl--KCl eutectic at 150 °C at tungsten electrodes occurs in two steps (eqs 1 and 2). These studies also showed that Hg(0) deposited at the electrode reacts with diffusing Hg$^{2+}$ thus decreasing the amount of mercury metal available for electrochemical oxidation. In AlCl$_3$--NaCl melts (175 °C), using a Pt working electrode, Torsi et al. observed three 2-electron-reduction steps for Hg(II): first to Hg$^{2+}$ (eq 1), then to Hg$_2$ (detected for the first time; eq 5) and finally to Hg(0) (eq 6).

$$3\text{Hg}_2^{2+} + 2\text{e}^- \rightarrow 2\text{Hg}_3^{2+} \quad (5)$$

$$\text{Hg}_3^{2+} + 2\text{e}^- \rightarrow 3\text{Hg} \quad (6)$$

In the present paper, the electrochemistry of HgCl$_2$ has been studied in a series of room temperature ionic liquids. The effect of varying the concentration of the solution, the nature of the working electrode, and the cation/anion of the ionic liquid has been analyzed. Solutions with added chloride at various concentrations have also been studied. For comparison, the cyclic voltammetry of [Hg(NTf$_2$)$_2$] has been carried out in [C$_4$mim]-[NTf$_2$]. Specific mechanistic insights include the observation that the reduction of Hg$^{2+}$ to Hg(0) takes place in three steps via the formation of intermediate species Hg$_2$ and Hg$_3$. In addition, during the reoxidation of Hg four species are observed related to Hg$_2$, Hg$^{2+}$, and the oxidation of Cl$^-$ bound mercury complexes, including [HgCl$_3$]$^-$ and [HgCl$_4$]$^{2-}$, even in mixtures in the absence of added chloride.

### Experimental Section

The ionic liquids [C$_4$mim][NTf$_2$] ([C$_4$mim]$^+ = \text{1-butyl-3-methylimidazolium}$) and [C$_4$mim][NO$_3$] were prepared following published procedures. The ionic liquids [C$_4$mim][Cl], [C$_4$mim][PF$_6$] and [C$_4$mim][BF$_4$] were supplied by Merck KGaA and [C$_4$mim][NTf$_2$] were prepared in a similar way using an excess of HgCl$_2$ and tartaric acid. The ionic liquids [C$_4$mim][NTf$_2$] were prepared in a similar way using an excess of HgCl$_2$ and tartaric acid. The ionic liquids [C$_4$mim][NTf$_2$] were prepared in a similar way using an excess of HgCl$_2$ and tartaric acid. The ionic liquids [C$_4$mim][NTf$_2$] were prepared in a similar way using an excess of HgCl$_2$ and tartaric acid. The ionic liquids [C$_4$mim][NTf$_2$] were prepared in a similar way using an excess of HgCl$_2$ and tartaric acid.

$$[\text{Hg}^{2+}]_{\text{NTf}_2} + 2\text{e}^- \rightarrow \text{Hg} \quad (7a)$$

### Results and Discussion

A summary of the proposed reactions and peak assignments for the CVs of Hg(II) in ILs is shown in Table 1. Electrochemistry of [Hg(NTf$_2$)$_2$] in [C$_4$mim][NTf$_2$]. The cyclic voltammetry of a ca. 20 mM solution of [Hg(NTf$_2$)$_2$] was performed in [C$_4$mim][NTf$_2$] at GC and Pt electrodes (Figure 1). In both cases, one broad reduction peak was observed at -0.03 V (GC), 0.11 V (Pt), with a symmetrical stripping wave appearing in the reverse scans [O$_{1a} = 0.83$ V (GC), 0.72 V (Pt)]. These peaks are assigned to the two-electron reduction of Hg(II), presumably in the form of bis{[trifluoroethyl]sulfonfyl} imide-containing species, to Hg(0), as shown in eq 7a, and the corresponding inverse oxidation reaction.

$$[\text{Hg}^{2+}]_{\text{NTf}_2} + 2\text{e}^- \rightarrow \text{Hg} \quad (7a)$$

Electrochemistry of HgCl$_2$ at GC Electrode. Electrochemistry of HgCl$_2$ in [C$_4$mim][NTf$_2$]. The cyclic voltammetries at a 5 mM and a saturated solution of HgCl$_2$ in [C$_4$mim][NTf$_2$] were measured in a 1 cm$^2$ glovebox and leaving the mixture to stir for 24 h before analysis. Saturated solutions HgCl$_2$ in [C$_4$mim]-[NTf$_2$] were prepared in a similar way using an excess of HgCl$_2$ (ca. 0.025 g). The concentration of the saturated solution was estimated using a Milestone DMA-80 Direct Mercury Analyzer wherein 0.01 cm$^2$ of the saturated solution was diluted by a factor of 100 in ethanol and analyzed. After three readings, the average concentration of the solution was determined to be 28 mM. Solutions of HgCl$_2$ (20 mM) in [C$_4$mim][NTf$_2$] in the presence of chloride were prepared in a similar manner as described above by adding [C$_4$mim][Cl] (40 mM, 0.0139 g; 60 mM, 0.0210 g; 80 mM, 0.0279 g) at the same time as HgCl$_2$.
Table 1. Summary of the Proposed Reactions and Peak Assignments

<table>
<thead>
<tr>
<th>peak</th>
<th>reaction</th>
</tr>
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<tbody>
<tr>
<td>R_1</td>
<td>[Hg^{2+}][NTf_2] + 2e^- \rightarrow Hg         (7a)</td>
</tr>
<tr>
<td>R_2</td>
<td>[Hg^{2+}][NTf_2/Cl] + 2e^- \rightarrow Hg       (7b)</td>
</tr>
<tr>
<td>O_1a</td>
<td>[HgCl_2]^- + 2e^- \rightarrow Hg + (2+x)Cl^-  (3)</td>
</tr>
<tr>
<td>R_3</td>
<td>2[Hg^{2+}][NTf_2] + 2e^- \rightarrow 2Hg^{2+} (5)</td>
</tr>
<tr>
<td>R_2c</td>
<td>Hg^{2+} + 2e^- \rightarrow 3Hg                  (6)</td>
</tr>
<tr>
<td>R_4</td>
<td>[HgCl_2]_x^- + xe^- \rightarrow Hg + (2+x)Cl^- (3)</td>
</tr>
<tr>
<td>O_3</td>
<td>Cl^- + 2e^- \rightarrow 2Cl^-                  (13)</td>
</tr>
<tr>
<td>O_3/O_3a</td>
<td>Hg \rightarrow [Hg^{2+}][NTf_2] + 2e^-  (7a)</td>
</tr>
<tr>
<td>O_4</td>
<td>2Cl^- \rightarrow Hg^{2+} + 2Cl^-              (12)</td>
</tr>
<tr>
<td>O_5</td>
<td>Hg + (2+x)Cl^- \rightarrow [HgCl_2]_x^- + xe^- (3)</td>
</tr>
</tbody>
</table>

studied at GC. The concentration of the saturated solution was estimated to be 28 mM (see Experimental Section). The 5 mM solution showed two reduction peaks, i.e., a small peak at 0.27 V (R_1) and a larger peak at -0.64 V (R_2). The reverse scan displayed three oxidation peaks at -0.35 V (O_1), -0.04 V (O_2), and 1.49 V (O_3) (Figure 2a, solid line). Peaks R_2 and O_2 have the characteristic sharp shape of a deposition and stripping process, respectively. When the sweep is reversed after R_1 (Figure 2a, dashed line) the anodic scan shows initially some cathodic current but no clear peaks. Analogous results were obtained from a saturated solution (Figure 2b, solid line); however, in this case, the two reduction peaks R_1 (-0.35 V) and R_3 (-0.72 V) are of similar intensity. In addition, the third oxidation peak appears split, with a maximum at 1.54 V (O_3) and a shoulder at ca. 1.42 V (O_3a).

The first reduction peak is slightly shifted with respect to that observed in the [Hg(NTf_2)_2] solution at GC (Figure 1); but a good match between the first reduction peak of [Hg(NTf_2)_2] and HgCl_2 in [C_mim][NTf_2] is found at Pt electrodes (see below). It is, therefore, suggested that a small amount of a Hg(II) bis[(trifluoromethyl)sulfonyl]imide complex and/or a mixed [NTf_2^-][Cl^-] species forms in the HgCl_2/[C_mim][NTf_2] mixtures which is reduced to Hg(0) (eqs 7a and 7b, Table 1) at a more positive potential than the main Hg(II) species present in the HgCl_2 solution, [Hg^{2+}][Cl^-]. The second reduction peak, R_5, is assigned to the reduction of [Hg^{2+}][Cl^-] to Hg(0) (eq 8).

 bulk electrochemistry is carried out at the two reduction peaks for the saturated solution at GC plates. In both cases, a white paste was observed at the GC surface. The deposits were analyzed using X-ray powder diffraction (see Supporting Information) and showed similar patterns which corresponded well to that of HgCl_2.** The formation of HgCl_2 during bulk electrolysis is mainly attributed to the reaction of electrogenerated Hg(0) with excess Hg^{2+}, as shown in eq 9.** In addition, direct reduction of Hg^{2+} to HgCl_2(s) may occur to some extent at R_3 during the cyclic voltammetry.

\[ \text{Hg} + \text{Hg}^{2+} + 2\text{Cl}^- \rightarrow \text{HgCl}_2(s) \]  (9)

The presence of a cathodic current in the anodic scans when the sweep is reversed after R_1 (Figure 2a, solid line) indicates nucleation of Hg at the electrode surface. The small shift observed in R_2 when the scan is first run toward positive potential (Figure 2a, dotted line) may be attributed to passivation of the electrode surface, for example, by chloride formed at high potential from traces of chloride present as an impurity in the ionic liquid.

The occurrence of several oxidation peaks in the reverse scans (Figure 2) contrasts with that observed in [Hg(NTf_2)_2]/[C_mim][NTf_2] solutions (Figure 1) and for HgCl_2 in AlCl_3/[C_mim][Cl], where only one stripping peak is found. A comparison between Figures 1 and 2 indicates that none of the peaks O_1 - O_3 correspond to the formation of a Hg(II) bis[(trifluoromethyl)sulfonyl]imide species. In addition, there is no evidence of free chloride remaining in the solution after O_1 (i.e., the oxidation of free Cl^- to Cl_2 at GC in [C_mim][NTf_2] should appear as a peak at 1.1 V;** see below). Taking the above into account, the first oxidation wave, O_1, may be assigned to the formation of Hg^{2+}, probably as Hg_{2+}(s), at the electrode surface, either by direct oxidation of Hg to Hg_{2+}(s) (eq 10) and/or by oxidation of Hg^{2+} to Hg_{2+} (eq 11) followed by reaction 9. The second oxidation peak, O_2, would then correspond to the stripping of HgCl_{2+}(s) to form Hg^{2+} (eq 12). Finally, the peaks at ca. 1.5 V (O_3 and O_3a) are initially attributed to the oxidation of mercury chloride species formed during the electrochemical cycle. This is discussed further in the next section.

\[ 2\text{Hg} + 2\text{Cl}^- \rightarrow \text{Hg}_2\text{Cl}_2(s) + 2\text{e}^- \]  (10)

\[ \text{Hg} \rightarrow \text{Hg}^{2+} + 2\text{e}^- \]  (11)

\[ \text{Hg}_2\text{Cl}_2(s) \rightarrow 2\text{Hg}^{2+} + 2\text{Cl}^- + 2\text{e}^- \]  (12)

**Electrochemistry of HgCl_2 in [C_mim][NTf_2] in the Presence of [C_mim][Cl].** In order to provide a more detailed understanding of the electrochemical behavior of HgCl_2 in [C_mim][NTf_2], the effect of adding chloride to a 20 mM solution of HgCl_2 was analyzed at GC (Figure 3). Chloride was added as [C_mim][Cl] at...
three different concentrations: 40 mM (Figure 3a), 80 mM (Figure 3b), and 120 mM (Figure 3c). The DR UV−vis spectra of the solutions were also carried out.

In the case of the solution with the least amount of added Cl\(^-\) (40 mM, Figure 3a), the scan run first toward positive potential (dashed line) shows an oxidation wave at 1.5 V (O3) to gether with a very small peak at 1.1 V (O4). The latter corresponds to the oxidation of free Cl\(^-\) to Cl2 (eq 13), as previously reported.\(^{17}\) Its very low intensity indicates that effectively all the added chloride is bound to Hg(II), i.e., probably forming the stable chloromercurate anion [HgCl4]\(^{2-}\). A smaller amount of other species, such as [HgCl3]\(^-\), may also be present in the solution, as indicated by DR UV−vis spectroscopy (see below). As expected, the relative intensity of O4 increases with added Cl\(^-\) (Figure 3b,c, dashed lines).

\[ 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^- \quad (13) \]

Peak O3, which is present in the scans run first toward positive potential for all three solutions (Figure 3, dashed lines), and peak O3a (Figure 2) are, therefore, assigned to the oxidation of Cl\(^-\) bound to Hg(II) (eq 14). Given that peaks O3 and O3a are present in the CVs of HgCl2 without added chloride (Figure 2), chloromercurate(II) anions should form in the proximity of the electrode after reaction 12, from the chemical reaction of Hg\(^{2+}\) and excess Cl\(^-\).

\[ 2\text{Cl}^-/\text{C138Hg(II)} \rightarrow \text{Cl}_2 + 2\text{e}^- \quad (14) \]

Generation of Cl2 at peaks O3 and O4 is confirmed by the presence of reduction peak R4 (0.35 V) in the reverse scans (Figure 3), and which corresponds to the reduction of Cl2 to Cl\(^-\).\(^{17}\) For comparison, the cyclic voltammogram of a 40 mM solution of [C4mim][Cl] in [C4mim][NTf2] is included in Figure 3b. This further confirms the origin of peaks O4 and R4.
From the cyclic voltammograms in Figure 3, it can be seen that the stripping peak O₂ decreases with added chloride, with one very broad wave (O₃) emerging as the concentration of Cl⁻ increases. In the presence of excess Cl⁻, Hg₂Cl₄ is not stable (eq 4), and O₃ is, therefore, assigned to the oxidation of Hg(0) directly to anionic species of the type [HgCl₂⁺x]⁻ (x = 1 or 2; eq 3)

\[
\text{Hg} + (2 + x)\text{Cl}^- \rightarrow [\text{HgCl}_2 + x]^x^- + 2e^- \quad (3')
\]

In the scans run toward negative potential first (Figure 3, solid lines), one broad reduction peak (R₃) at ca. −1.1 V was observed for all three solutions. Peak R₃ is assigned to the reduction of [HgCl₂⁺x]⁻ to Hg(0) (eq 3) and it appears at more negative potential than peaks R₁ and R₂ in the solutions with no added chloride (Figure 2). This is consistent with the formation of stable chloromercurate(II) species. Analogous behavior has been found in basic chloroaluminate ionic liquids⁵ and molten alkali metal chlorides,⁴ where, in excess Cl⁻, Hg(I) species are not detected and stable mercury chloride species are reduced in one 2-electron step to Hg(0) (see eqs 3 and 4).

Reduction peak R₂ also appears when the scans are run first toward positive potential (Figure 3, dashed lines); however, a cathodic shift is observed in Figure 2, b and c. This may be due to passivation of the glassy carbon electrode by electrogenerated chlorine at the upper potential limit.¹⁵,¹⁶ For example, it has been shown that chlorine formed at highly positive potentials can attack the glassy carbon surface, rendering it less susceptible to adsorption.¹⁶ This may prevent [HgCl₂⁺x]⁻ for approaching the electrode surface, thus making more difficult its reduction.

All the voltammograms in Figure 3 show current crossover in the scans reversed after R₃, indicating nuclei formation at the electrode surface. The requirement of large nucleation overpotentials for the deposition of Hg from [HgCl₂⁺x]⁻ solutions parallels that observed in basic AlCl₃–[C₄mim][NTf₂] mixtures, where metal deposition was found to occur through instantaneous or progressive nucleation at GC or W electrodes, respectively.³ Herein, chronoamperometric studies on the HgCl₂ solution containing 40 mM of added chloride were carried out to study the nucleation of mercury at the GC electrode. Chronoamperograms were obtained upon stepping the potential from the open-circuit potential (OCP) to potentials (Eₖn) ranging from −0.98 to −2 V. Nucleation peaks were observed only at Eₖn between −0.98 V and −1.3 V (Figure 4; the profiles obtained at −2 V < Eₖn < −1.3 V were similar to that at −2 V and are not included in the figure). Analysis of the nucleation curves according to the Scharifker–Hills model¹⁸ indicated that the process takes place mainly through instantaneous nucleation. However, while very good fittings are obtained for Eₖn = −0.98 or −1.1 V, increasing deviation from the simulated instantaneous nucleation curve is observed as the end potential becomes more negative. Examples of the dimensionless (I/Iₖn)² vs (t/tₖn) plots at both extremes are shown in Figure 5 (see Supporting Information for plots at other Eₖn values). Deviations from the theoretical models are not uncommon and are often attributed to a departure from the hemispherical geometry assumed in the nucleation models.¹⁹ Another possibility is that the deviations may reflect the severe approximations made in the analytical theory used.²⁰

The effect on the reduction of Hg(II) of varying scan rate was also studied in the case of the HgCl₂ solution containing 40 mM of added chloride. The peak currents for R₃ and O₂ increase linearly with the square root of scan rate, indicating that they correspond to diffusion-controlled processes (see Supporting Information). The number of electrons transferred at R₃ was estimated to be 2, in agreement with eq 3. The diffusion coefficient of [HgCl₂⁺x]⁻ in [C₄mim][NTf₂] was calculated to be 2.5 × 10⁻¹¹ m² s⁻¹ from cyclic voltammetry or chronoamperometry data, respectively. This is similar to the diffusion coefficient reported for [HgCl₂⁺x]⁻ in basic AlCl₃–[C₂mim][Cl] at 40 °C (3 × 10⁻¹¹ m² s⁻¹).³

**Cyclic Voltammetry of HgCl₂ at Pt Electrode.** **Cyclic Voltammetry of HgCl₂ in [C₄mim][NTf₂].** The electrochemistry of a 5 mM and a saturated solution of HgCl₂ in [C₄mim][NTf₂] was also investigated using a Pt working electrode. The 5 mM solution showed similar behavior to that observed at GC, with two reduction (R₁ 0.07 V, R₂ −0.47 V) and two oxidation peaks.

**Figure 4.** Chronoamperometry at a GC electrode of a solution of HgCl₂ (20 mM) and [C₄mim][Cl] (40 mM) in [C₄mim][NTf₂] using Eₖn values between −0.98 and −2 V.

**Figure 5.** Dimensionless plots generated from the nucleation profiles at Eₖn = −1 V (a) and Eₖn = −1.3 V (b), overlaid with the simulated data for progressive (dashed lines) and instantaneous (solid lines) nucleation processes.
Cyclic voltammetry of HgCl₂ in Other Ionic Liquids at GC and Pt. The cyclic voltammetry of HgCl₂ was also examined in other ILs at GC and Pt with both electrodes showing similar behavior (Figure 7 and Supporting Information). The effect of varying the cation was studied using four [NTf₂]⁻ anion based ionic liquids ([C₆mim][NTf₂], [C₄mim][NTf₂], [C₈mim][NTf₂], and [C₄py][NTf₂]). All the HgCl₂ solutions (5 mM) showed similar electrochemical behavior as that found in [C₄mim][NTf₂], with two reduction peaks (R₁ and R₂) and three main oxidation peaks (O₁–O₃) observed in all cases (Figure 7a). The second reduction peak in [C₆mim][NTf₂] appears at −0.93 V and is significantly shifted toward more negative potential compared with the other ionic liquids, where the reduction is seen at ca. −0.6 V. This may be due to the fact that [C₆mim][NTf₂] has the highest viscosity (see Supporting Information for viscosity data) and could also be associated with the formation of solvent multilayers on the electrode surface, presumably related to the long side chain in [C₆mim][NTf₂]. The formation of multilayer architectures on electrode surfaces which are dependent on the nature of the IL ions has been suggested to have a strong influence on electrochemical reactions.²³

The influence of the anion was analyzed in the series [C₄mim][X] (X = DCA, FAP, PF₆). The CV in [C₄mim][PF₆] is similar to that found in [C₄mim][NTf₂] and the peaks are assigned to analogous processes, whereas the voltammetry in [C₄mim][FAP] shows two ill-defined reduction peaks, but no clear oxidation features (see Supporting Information). The different oxidation behavior can be due to different stability of mercury species in the [FAP]⁻ ionic liquid or to the formation of different solvation layers on the electrode surface,²³ possibly related to the larger size and asymmetry of the [FAP]⁻ anion, compared with [PF₆]⁻ and [NTf₂]⁻. The CV in [C₄mim][DCA] (Figure 7b) resembles that of [C₄mim][NTf₂] with excess Cl⁻, with one broad reduction peak observed. The DCA anion behaves as a pseudohalide ligand and it is, therefore, expected that dicyanamide—Hg(II)
species form in the solution, which would then be reduced in a 2-electron step to Hg(0).

**UV–Vis Studies.** DR UV–vis spectra of HgCl₂ in [C₄mim][NTf₂] were carried out in the absence and presence of chloride (Figure 8). The spectrum of HgCl₂ shows a maximum at 242 nm, whereas the spectra of the solutions containing [C₄mim][Cl] all show a broad absorption peak with a maximum at 248 nm which increases as the concentration of Cl⁻ increases. The peaks have a shoulder at longer wavelength (ca. 260 nm), which is more accentuated in the solution with 40 mM of added Cl⁻.

These results indicate that HgCl₂ reacts with the added Cl⁻ in the ionic liquid, in agreement with the voltammetric studies discussed above. The maximum at 248 nm is, therefore, assigned to [HgCl₄]²⁻. A red shift in the absorption of [HgCl₄]²⁻ with respect to that of HgCl₂ has also been reported in aqueous and acetonitrile solutions. In these solvents, the λ_max for HgCl₂ and [HgCl₄]²⁻ appears at ca. 200 and 230 nm, respectively. The shoulder at 260 nm is tentatively assigned to [HgCl₃]⁻, expected to be more abundant in the solution with the lowest amount of Cl⁻. In acetonitrile, the absorption maximum of [HgCl₃]⁻ (240 nm) is also observed at longer wavelength than that of [HgCl₂]⁻ (234 nm).  

**CONCLUSIONS**

The electrochemistry of Hg(II) in room temperature ionic liquids is strongly influenced by the nature of the working electrode (GC or Pt), the concentration of the solution, and the ionic liquid composition. In HgCl₂/[C₄mim][NTf₂] solutions, a certain amount of Hg(II) in [NTf₂]⁻ and/or mixed-ligand Hg(II) in [C₄mim][NTf₂]⁻/Cl⁻ species form which are reduced to Hg(0) at a more positive potential than the main Hg(II) species present in the HgCl₂ solution, [Hg₂Cl₄]⁴⁻ as indicated by comparison with the CVs of [Hg[NTf₂]₂] in [C₄mim][NTf₂]. At GC electrode, the reduction of [Hg₂Cl₄]⁴⁻ to Hg(0) occurs in one step, with similar behavior also observed for dilute solutions at Pt electrode. However, in concentrated solutions at Pt electrodes, the reduction of Hg(II) to Hg(0) takes place in three steps, related to the formation of intermediate species Hg₂Cl₄⁻ and Hg₃Cl₄²⁻. The reduction of Hg(II) in other [NTf₂]⁻-based ionic liquids (dilute solutions) is qualitatively the same as that in [C₄mim][NTf₂]. Analogous behavior is also found in ionic liquids containing different anions. Shifting in the reduction potentials with IL composition is related mainly to the different viscosity of the media.

In the presence of an excess of a strongly complexing agent (i.e., in [C₄mim][NTf₂] with added chloride or in [C₄mim][DCA]), anionic species of the type [HgxCl₂₋₋] (X = Cl, DCA) appear to be predominant in solution, and are reduced in a single 2-electron reduction to Hg(0). The scans for these systems depict nucleation loops. Chronoamperometric studies on a 1:2 HgCl₂:Cl⁻ solution in [C₄mim][NTf₂] at GC indicated that the nucleation of mercury takes place through an instantaneous process.

The reoxidation of Hg also showed unusual behavior with two to four peaks observed in the reverse scans (except in [C₄mim][FAP]). The first two peaks are related to the oxidation of Hg to Hg₂Cl₄⁻ and Hg₃Cl₄²⁻, whereas the peaks appearing at more positive potentials correspond to the oxidation of Cl⁻ attached to mercury. Results suggest that various chloromercurate(II) species form during the oxidative scans, including [HgCl₃]⁻ and [HgCl₄]²⁻, even in solutions with no added chloride.

**ASSOCIATED CONTENT**

Supporting Information. X-ray powder diffraction patterns; dimensionless plots generated from the nucleation profiles; cyclic voltammograms; and viscosities of the ionic liquids used in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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**REFERENCES**


**Figure 8.** Diffuse reflectance UV–vis spectra of a 20 mM solution of HgCl₂ in [C₄mim][NTf₂] in the absence (a) and presence of [C₄mim][Cl] (b, 40 mM; c, 80 mM; d, 120 mM).


