Interfacial Complexation Reactions of Sr^{2+} with Octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine Oxide for Understanding Its Extraction in Reprocessing Spent Nuclear Fuels

Tom J. Stockmann,^[a] Yu Lu,^[b] Jing Zhang,^[a] Hubert H. Girault,^[b] and Zhifeng Ding^{*[a]}

Abstract: The complexation reactions between strontium (Sr^{2+}) and octyl-(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) were studied at the aqueous|1,2-dichloroethane (w|DCE) and aqueous|room-temperature ionic liquid (w|RTIL) microinterfaces, in order to understand its extraction in reprocessing spent nuclear fuels, remediation of environmental contamination, and potential radiological isotope feed stock for ^{90}Y from its isotope ^{90}Sr in fission byproducts. The stoichiometry (or metal to ligand ratios) and overall complexation con-

stant (β) for these reactions at these two interfaces are described herein. Two stoichiometries at the w|DCE interface were discovered, that is, $[\text{Sr}(\text{CMPO})_2]^{2+}$ and $[\text{Sr}(\text{CMPO})_3]^{2+}$ with β values of 4.5×10^{19} and 5.5×10^{25} , respectively. Only one stoichiometry was observed at the w|RTIL interface: $[\text{Sr}(\text{CMPO})_3]^{2+}$ with β equal to 1.5×10^{34} . The larger complexation constant for

$[\text{Sr}(\text{CMPO})_3]^{2+}$ at the w|RTIL interface than those found at the w|DCE interface supported the previous observation of a greater distribution ratio in the aqueous–RTIL metal extraction than that in the aqueous–alkane processing. The kinetics of the reactions at the w|RTIL interface was slow. The stoichiometries at the w|DCE interface were confirmed using biphasic electrospray ionization mass spectrometry (BESI-MS) as well as direct injection of Sr^{2+} and CMPO mixture by means of a “shaking flask” experiment to conventional ESI-MS.

Keywords: extraction • facilitated ion transfer • ionic liquids • strontium • water chemistry

Introduction

The use of radiological isotopes, including ^{131}I , ^{99}Mo , and ^{90}Y , for medical imaging and the treatment of cancers has undergone a rapid change in the last two decades with the advent of radioimmunological treatment (RIT) and the incorporation of radioisotopes within monoclonal antibodies (mAb).^[1] RIT uses the high specificity of mAbs in conjunction with powerful β -emitters to target solid tumours, but reduce the radiological toxicity to other organs and tissue.^[1c,f,2] The most effective isotope for use in RIT is ^{90}Y , since the half-life time of the ^{90}Y is short (64 h), it produces only β - with no γ -emissions, and the energy of these emissions is high (2.2 MeV), resulting in increased penetration into the tumour mass.^[1c] The ^{90}Y isotope can be acquired through neutron-irradiation of yttrium metal oxide^[3] or through the isotopic decay of ^{90}Sr .^[4] Owing to its short half-life and the expense of transporting radioactive material, an in house ^{90}Y generator is deemed preferable with several designs having been proposed to use ^{90}Sr as a perpetual feed

stock.^[4] ^{90}Sr can, in turn, be acquired during nuclear fuel reprocessing, since it is one of many uranium fission byproducts from nuclear power facilities.^[3,5]

Several nuclear fuel reprocessing^[5,6] technologies are currently being implemented around the world on an industrial and laboratory scale, including the transuranic extraction (TRUEX) process.^[3,7] This method makes use of octyl-(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) as a chelating agent in a biphasic solvent extraction procedure between water and an organic solvent, typically *n*-dodecane;^[3,7] this process can be summarized by Equation (1); however, the stoichiometry for this reaction is not clear.

Prompted by the pioneering work of Dai et al.,^[8] recent research towards improving the TRUEX process^[6,7b,c,i] and other metal-extraction techniques^[9] has focused on replacing the organic solvent with a room-temperature ionic liquid (RTIL); RTILs are organic salts with a melting point below 100 °C. In their paper, Dai et al.^[8] showed a 5000 × greater distribution ratio for a dicyclohexyl[18]crown-6-strontium complex using an imidazolium-based RTIL versus a conventional molecular solvent. Beyond this, RTILs also have several properties that make them amiable replacements for organic solvents, including low volatility, good electrical con-

[a] T. J. Stockmann, J. Zhang, Prof. Z. Ding
Department of Chemistry, The University of Western Ontario
1151 Richmond St., London, ON, N6A 5B7 (Canada)
Fax: (+1) 519-661-3022
E-mail: zfding@uwo.ca

[b] Y. Lu, Prof. H. H. Girault
Laboratoire d'Electrochimie Physique et Analytique,
Station 6, École Polytechnique Fédérale de Lausanne,
Lausanne, 1015 (Switzerland)

ductivity, and the ability to tailor the RTIL to meet specific physicochemical requirements.^[10] The techniques used to quantify the distribution ratios between phases have focused on inductively coupled plasma (ICP) measurements of the aqueous phase after extraction,^[7a,8,11] extended X-ray fine structure (EXAFS) measurements,^[7b] or through the use of radioactive tracer isotopes.^[7c,e]

Interestingly, an electrochemical technique employed at the liquid|liquid interface between two immiscible electrolytic solutions (ITIES), typically between water and 1,2-dichloroethane (DCE), is able to acquire sensitive thermodynamic data that can be used to further characterize the metal–ligand extraction process.^[12] Electrochemistry at a liquid|liquid junction has been the subject of numerous excellent reviews^[13] and often involves simple ion transfer (IT) through a push/pull mechanism, whereby the potential is increased linearly within the aqueous phase (w) causing any positive metal ions (i), with charge z , to be ejected into the organic phase (o); this process is summarized below [Eq. (2)]:

When the potential scan is reversed, or proceeds towards negative potentials, the ions are “pulled” back across the ITIES or transferred from o to w. The current can be measured during this process and the current–potential curve obtained is analogous to that obtained in conventional redox electrochemistry. The potential at which IT takes place is called the standard transfer potential and is denoted as $\Delta_o^w \phi^0$; this, in turn, is related to the potential and the activity of species i in each phase through the Nernst equation [Eq. (3)], in which α and β refer generally to the two phases (aqueous and DCE).

$$\begin{aligned} \Delta_o^w \phi_i &= \Delta_o^w \phi_i^0 + \frac{RT}{z_i F} \ln \left(\frac{a_\alpha^i}{a_\beta^i} \right) = \Delta_o^w \phi_i^0 + \frac{RT}{z_i F} \ln \left(\frac{\gamma_\alpha^i}{\gamma_\beta^i} \right) + \frac{RT}{z_i F} \ln \left(\frac{c_\alpha^i}{c_\beta^i} \right) \\ &= \Delta_o^w \phi_i^0 + \frac{RT}{z_i F} \ln \left(\frac{c_\alpha^i}{c_\beta^i} \right) \end{aligned} \quad (3)$$

If concentrations are used to approximate the activities, then the term on the right of Equation (3) is obtained and the formal transfer potential, $\Delta_o^w \phi^0$, is used in place of the standard transfer potential. If the metal species is very hydrophilic, this will result in a high formal transfer potential and thus a greater amount of applied potential required. However, the transfer potential can be reduced through the use of organic ligands and the transfer through interfacial complexation (TIC), which can be generalized by the following reaction [Eq. (4)], in which n is the stoichiometric ratio of the ligand to metal ion.

Equation (4) is the electrochemical equivalent of Equa-

tion (1) when $L = \text{CMPO}$ and $i = \text{Sr}^{2+}$. This type of electrochemical reaction is referred to as facilitated ion transfer (FIT), and the thermodynamics have been thoroughly described by Homolka et al.,^[14] Kakiuchi et al.,^[12f] and Girault et al.^[12g,h] In this context, the stoichiometry (n) and complexation constant (β) for Equation (4) can be discerned through the use of cyclic voltammetry (CV). Additionally, it has been discovered that sensitive data, without the use of iR compensation, can be obtained using micro-ITIES typically held at the tip of a pulled micropipette,^[9a,b,12c,d,j,15] while also reducing the amount of sample required.

Mirroring the developments in solvent extraction research, recent work surrounding liquid|liquid electrochemistry has focused on the aqueous|RTIL (w|RTIL) interface,^[9,12j,15a,16] whereby IT and FIT have both been observed.

Thus, using the theory of FIT,^[12f–h,14] described herein is the thermodynamics of strontium transfer through the use of CMPO at the w|DCE and w|RTIL micro-ITIES. In order to verify the ligand stoichiometries, biphasic electrospray ionization mass spectrometry (BESI-MS) and conventional electrospray ionization mass spectrometry (ESI-MS) have also been employed.

Recent tragic events in Japan, with the devastation of the Fukushima nuclear power plant by a tsunami, prompt us to point out that this type of electrochemical technology has also the potential to be employed in environmental remediation and the detection of specific toxic metals.

Experimental Section

Chemicals: Strontium nitrate ($\text{Sr}(\text{NO}_3)_2$), dichloromethane, tetradodecylammonium tetrakis(4-chlorophenyl)borate (TDATPBCl), and 1,2-dichloroethane were purchased from Fluka/Sigma Aldrich (Sigma–Aldrich Canada Ltd., Oakville, ON (Canada)). Octyl(phenyl)- N,N -diisobutylcarbamoylmethylphosphine oxide (CMPO) and trihexyltetradecylphosphonium chloride were obtained from Strem (Strem Chemicals Inc., Newburyport, MA (USA)). Potassium tetrakis(pentafluorophenyl)borate was bought from Boulder Scientific (Boulder Scientific Co., Longmont, CO (USA)). Trihexyltetradecylphosphonium tetrakis(pentafluorophenyl)borate was prepared through a facile metathesis reaction of the their constituent chloride and potassium salts respectively at a 1:1 ratio in dichloromethane as described elsewhere.^[15a]

Micropipettes: The interface between two immiscible electrolytic solutions (ITIES) was maintained at the tip orifice of a specially fabricated borosilicate glass capillary (Figure 1). The capillary fabrication procedure was described elsewhere.^[12j,15] In brief, a borosilicate glass tubing (1.0/2.0 mm internal/external diameter, Sutter Instrument, Novato, CA (USA)) was pulled at its center using an electric puller (Narishige, Model PP-83 (Japan)) generating two capillaries with tapered tips. The tips of the pulled capillaries were then flame annealed and a 0.5 to 1.0 cm length of platinum wire (25 μm in diameter, Goodfellow Cambridge Ltd. (UK)) was inserted into the back (open end) of each capillary. The Pt wire was then annealed in place using the heating coil of the puller while under vacuum suction. The tip of the capillary was then polished by using diamond and alumina grinding pads (Buehler Canada, Markham, ON (Canada)) until a cross-section of Pt wire was exposed. The glass and Pt surfaces were polished, and the ratio of the outer glass radius (r) to Pt disc radius (a), R_g ($R_g = r/a$) was greater than 50. The capillaries were then immersed in a strong acid solution of 3:1 HCl to HNO_3 (Aqua regia) for seven days or until the Pt wire was etched out. What remains is

Figure 1. Modified HEKA capillary holder with pulled capillary containing the aqueous phase and a silver electrode attached to the WE lead of the potentiostat through a BNC connector. The capillary is immersed into the DCE or RTIL phase held in a 1.8 mL glass vial, which also contains a silver electrode connected to the RE/CE leads of the potentiostat.

a uniform, 25 μm diameter microcapillary convenient for maintaining the ITIES at the orifice.

The prepared capillary was held in a HEKA capillary holder (HEKA Electronics, Mahone Bay, NS (Canada)), specially modified by the Electronics Shop at the University of Western Ontario, and equipped with a syringe which was used to maintain the aqueous phase at the tip of the capillary; a Moticam 2000 CCD camera (Motic, Richmond, BC (Canada)) attached to a Navitar 12 $\times$ magnification lens assembly (Navitar, Rochester, NY (USA)) was used to monitor the interface. The holder also possessed an integrated silver wire attached to a BNC connector connected to the working electrode lead of the potentiostat. A second silver wire, placed in the DCE or RTIL phase, was connected to the counter and reference leads of the potentiostat. These silver wires functioned as quasi-reference electrodes. The assembled micro-ITIES apparatus is shown in Figure 1. The following electrochemical cells were used:

Electrochemistry: All electrochemical experiments were performed using the Modulab potentiostat system (Ametek Advanced Measurement Technology, Farnborough, Hampshire (UK)) equipped with a femto-ammeter. The vial containing the DCE or RTIL phase was placed in a vial holder with a jacket for flow of temperature controlled water to/from a heating circulator (VWR, Mississauga, ON (Canada)), which maintained the system at (25 ± 1) and (60 ± 1) $^\circ\text{C}$ for DCE and RTIL experiments, respectively, unless otherwise stated.

Biphasic electrospray ionization mass spectrometry (BESI-MS): The mass spectrometric interface for the measurement of the complexes has been superbly described in previous reports.^[17] In brief, a LTQ (velos) linear ion trap mass spectrometer (Thermo Fisher Scientific, San Jose, CA), operating in the positive ionization mode, was used with an excellently fabricated polyimide (PI) dual-sprayer microchip (DiagnoSwiss SA, Monthey (Switzerland)) fixed on a plate mounted opposite to the spray cone intake; this assembly was situated in place of the commercial ion source housing as shown in Figure 2. The aqueous and 1,2-dichloroethane (DCE) phase was infused separately through two ports in the

Figure 2. Top: Picture of the BESI-MS set-up with the microchip assembly (top left) and the LCT intake (top right). Bottom: Front view of the microchip ejection ports under a microscope.

microchip which was held inside a microchip holder, fabricated in-house. Two syringes (100 μL , Hamilton Co., Reno, NV (USA)) held by syringe pumps (KdScientific, Holliston, MA (USA)) regulating the flow rate of each line at $2 \mu\text{L min}^{-1}$; thus the final flow rate at the electrospray was $4 \mu\text{L min}^{-1}$. These two immiscible phases in separated microchannels ($125 \mu\text{m} \times 50 \mu\text{m} \times \approx 1.5 \text{ cm}$ each) were mixed right after ejection, inside the Taylor cone (the ionized aerosol jet or plume), during electrospray. The tip of the dual sprayer microchip is displayed in the image of a front view at the bottom of Figure 2, which was obtained using a VK-8710 color 3D laser scanning microscope (Keyence Corp. (Japan)). For operation, after MS power supply onset ($U=4\text{--}4.5 \text{ kV}$), the microchip was moved close to the entrance of MS (the use of high voltage should be handled under extreme caution). The current, set between 20 and 200 nA by adjusting the distance between the dual-spray emitter and the entrance to the MS, was monitored by a custom-made nano-ammeter. The temperature of the transfer capillary was set at 200°C . The ion optics parameters were kept constant for each experiment.

Electrospray ionization, time-of-flight mass spectrometry (ESI-MS). Conventional ESI-MS data was collected using a Micromass LCT Mass Spectrometer (Waters, Milford, MA (USA)) in the positive ion mode. The ca-

pillary, sample cone, and extraction cone voltages were 5000, 50, and 15 V, respectively, while the acquisition and interscan delay time were set to 4.0 and 0.1 s. A 250 μL syringe (Hamilton Co.), placed inside a syringe pump operating at $10 \mu\text{L min}^{-1}$, was used to perform these injections.

Results and Discussion

Facilitated ion transfer (FIT) of Sr^{2+} at the w|DCE micro-ITIES: Figure 3A shows the cyclic voltammogram (CV) obtained at the aqueous|DCE interface using Cell 1, with no

Figure 3. Cyclic voltammograms of A) Cell 1 at a scan rate of 0.020 V s^{-1} in which the two sections were scanned with initial, upper, and lower potentials of 0.271, 0.718, and -0.139 V for the first section and -0.086 , -0.086 , and -0.402 V for the second section, respectively; and B) Cell 2 (---) with an initial potential of -0.106 V , a scan rate of 0.020 V s^{-1} , and a potential range of 0.442 to -0.283 V , and Cell 3 (—) with an initial, upper, and lower potential of 0.131, 0.427, and -0.270 V , respectively, at a scan rate of 0.020 V s^{-1} .

CMPO present and a scan rate of 0.020 V s^{-1} . The CV was acquired in two sections. In the first section, the cell was initially scanned in the positive direction from 0.271 V. At 0.718 V the limit of the polarizable potential window is reached and is marked by the sudden increase in current brought about by the transfer of the supporting electrolytes; in this instance both Sr^{2+} transfer from $w \rightarrow o$ and tetrakis(pentafluorophenyl)borate (TB^-) transfer from $o \rightarrow w$ are possible. The potential was then scanned in the reverse direction, towards more negative potentials, from 0.718 to -0.139 V . Finally the potential was scanned in the forward direction again from -0.139 to 0.271 V. The last two scan segments show no distinct features, indicating no detectable adsorption or ion transfer (IT).

Cell 1 was then scanned from -0.086 V towards more negative potentials, until -0.402 V , in the second section. A wave can be observed with a peak potential at -0.342 V and this is indicative of nitrate transfer from $w \rightarrow o$. The potential was then scanned towards more positive potentials, from -0.402 to -0.086 V , and a sigmoidal or “s” shaped wave can be observed with a steady-state current from -0.086 V ; this is indicative of nitrate transfer back across the ITIES from $o \rightarrow w$.

The IT and current response are in good agreement with established IT voltammetry at a micro-ITIES hosted by a pipette.^[12c,d,j] The CV was broken down into the two sections in order to limit the number of ions transferring, thus fostering a greater interface stability and improved reproducibility. This is not so integral in the case of Cell 1, that is in the absence of CMPO, but becomes so after its introduction to the system. Figure 4A illustrates the CV obtained with the

Figure 4. Cyclic voltammograms with instrument parameters similar to those described for Figure 3A and by using Cell 1 in the presences of CMPO with $y = 33, 65, 82, 106$, and 142 mm for curves A–E, respectively. This in turn demonstrates that strontium is a hydrophilic metal species.

addition of the 33 mm of CMPO to the DCE phase. Analogous to the blank experiment the CV was split into two regions. The first scan was initiated at a calibrated potential of -0.100 V in the forward direction towards more positive potentials until the switching potential at 0.500 V was reached. During this first segment two peaks can be observed with

current maximums at 0.266 and 0.410 V; these are indicative of the ion transfer through interfacial complexation of Sr^{2+} from the aqueous to organic phase assisted by CMPO. As the potential was scanned from 0.500 to -0.100 V, two sigmoidal shaped waves can be observed with half-wave potentials at approximately 0.166 and 0.369 V; this is indicative of the transfer of metal ions through interfacial decomplexation (TID) reactions at the ITIES. Similar to the blank curve in Figure 3A, the IT of nitrate was then observed while scanning the potential from -0.086 to -0.402 V and back. All CVs acquired at the w|DCE interface were calibrated using the NO_3^- formal transfer potential, $\Delta_o^w \phi_{\text{NO}_3^-}^{o'}$ as -0.314 V,^[12c] based on the TATB^[12a,13a] assumption (TATB = tetraphenylarsoniumtetraphenylborate).

As the concentration of CMPO is increased in the DCE phase from the 33 mM shown in Figure 4A to 65, 82, 106, and 142 mM in Figure 4B–E, respectively, the peak potentials of the multiple peaks shift towards less positive potentials such that peak 1 is observed at 0.388, 0.378, 0.374, and 0.374 V, respectively. The shift in peak 2 is more dramatic eliciting changes of 0.266 to 0.248, 0.237, 0.231, and 0.206 V for Figure 4A–E, respectively. Shifting peak potentials with increasing ligand concentration is in good agreement with established theory concerning facilitated ion transfer (FIT).^[12f–h] The potential shift of the two peaks shown in Figure 4 were examined individually using the theory of FIT described by Girault et al.,^[12g] whereby the stoichiometry (n) and overall complexation constant (β) are related to the initial ligand concentration ($c_{\text{L,initial}}$) in the organic phase by Equation (5), in which z , F , R , and T are the charge of the free metal species, Faraday's constant, the universal gas constant, and the temperature of the system in Kelvin, respectively.

$$-\frac{zF}{RT} \left(\Delta_o^w \phi_{\text{ML}_n^{2+}}^{o'} - \Delta_o^w \phi_{\text{M}^{2+}}^{o'} \right) = n \ln(c_{\text{L,initial}}) + \ln(\beta_n) + \ln(\xi) \quad (5)$$

$\Delta_o^w \phi_{\text{M}^{2+}}^{o'}$ is the formal transfer potential of free strontium metal ion, Sr^{2+} , and was taken to be 0.900 V;^[18] this was determined from a microhole experiment described recently.^[19] $\Delta_o^w \phi_{\text{ML}_n^{2+}}^{o'}$ is the formal transfer potential of the metal–ligand complex, at a given ligand concentration, and was considered equivalent to the calibrated half-wave potential of the metal–ligand complex, $\Delta_o^w \phi_{1/2, \text{ML}_n^{2+}}^{o'}$. The half-wave potential was obtained from the CVs shown in Figure 4 using their peak potentials, $\Delta_o^w \phi_p$, and the following equation from Bard and Faulkner [Eq. (6)]:^[20]

$$\Delta_o^w \phi_{1/2, \text{ML}_n^{2+}}^{o'} = \Delta_o^w \phi_p \pm \frac{0.028}{z} \quad (6)$$

In the final term in Equation (5), ξ is equivalent to the square root of the ratio of diffusion coefficients between each phase, $\xi = \sqrt{D_o/D_w}$.^[12g,h] In the case of the aqueous|DCE interface and for the purposes of simplification, the diffusion coefficients for each phase were considered equiv-

alent and thus, $\xi = 1$, and the final term in Equation (5) reduces to zero. In this way the change in potential versus the change in ligand concentration can be graphed as a linear relationship with the slope and y intercept providing the stoichiometry and complexation constant of the interfacial complexation reaction. Figure 5 shows the linear graphs of $-\frac{zF}{RT} \left(\Delta_o^w \phi_{\text{ML}_n^{2+}}^{o'} - \Delta_o^w \phi_{\text{M}^{2+}}^{o'} \right)$ versus $\ln(c_{\text{L,initial}})$, and Table 1 sum-

Figure 5. Plot of $-\frac{zF}{RT} \left(\Delta_o^w \phi_{\text{ML}_n^{2+}}^{o'} - \Delta_o^w \phi_{\text{M}^{2+}}^{o'} \right)$ versus $\ln(c_{\text{L,initial}})$ with data obtained from the curves shown in Figure 4.

Table 1. Thermodynamic data obtained from the linear fitting generated in Figure 4 for peaks 1 and 2, including the metal to ligand ratio (1: n), the overall complexation constant (β). The success of the linear fitting was described using the R^2 value as shown.

	n	β	R^2
peak 1	2	4.5×10^{19}	0.9615
peak 2	3	5.5×10^{25}	0.9647

marizes the data obtained after linear regression analysis. The R^2 values shown in Table 1, 0.9615 and 0.9674 for peaks 1 and 2 respectively, illustrate the good linear fitting obtained. The stoichiometry for peaks 1 and 2 were determined to be 2 and 3, whilst the complexation constants were 4.5×10^{19} and 5.5×10^{25} , respectively. The two electrochemically induced complexation reactions can be described for peaks 1 and 2 using Equations (7) and (8), respectively:

The presence of two stoichiometries agrees well with the extraction data obtained by Makrlík et al.^[7g,h] during their recent work concerning Sr^{2+} from an aqueous solution to nitrobenzene; in these reports they described strontium complexes such as $[\text{Sr}(\text{CMPO})_2]^{2+}$, $[\text{Sr}(\text{CMPO})_3]^{2+}$, and even $[\text{Sr}(\text{CMPO})_4]^{2+}$ in the nitrobenzene phase. In their publication, Makrlík et al.^[7g] used the radioisotope of strontium, ^{85}Sr , determining the distribution ratios of the radioactive species between the aqueous and nitrobenzene phases by means of γ emission and then portraying the result as a function of ligand concentration in the organic phase. This

report^[7g] is evidence towards the stoichiometries observed; however, it should be noted, in the present report no radioactive species were used and this certainly points to a benefit of this as a diagnostic technique, although radioactive isotopes can certainly be used should there be a need.

The appearance of two or more metal-to-ligand stoichiometries has been observed previously using cyclic voltammetry at a liquid|liquid interface.^[9b,12b,f,i,15b] The first time was by Homolka et al.^[12b] for transfer of Fe^{II} , Fe^{III} , Ni^{II} , and Zn^{II} complexes with bipyridine and phenanthroline from water to nitrobenzene; in that paper, however, the complexes were introduced as a methanolic/aqueous mixture to the aqueous phase, followed by ion transfer through the use of an applied electric field. The next series of reports surrounded the cesium FIT using crown ethers as the ligand and were studied by Kakiuchi et al.^[9b,12f] and Dassie et al.^[12j] at w|RTIL and w|DCE interfaces, respectively. Finally, the emergence of multiple peaks within a CV, indicative of multiple FIT stoichiometries, was demonstrated recently by our group^[15b] for dioxouranium and CMPO at w|DCE interfaces. Thus, the appearance and analysis of multiple peaks are in good agreement with previously published voltammetric results.^[9b,12b,f,i,15b]

Mass spectrometry: To further verify the presence of these two Sr–CMPO complexes, the w|DCE solvent system was studied by BESI-MS by means of in-situ mixing of Sr^{2+} in water and CMPO in DCE, along with conventional ESI-MS by means of a “shaking flask” mixing and direct injection.

Figure 6. A) BESI-MS of interfacial reactions using $15\ \mu\text{M}$ CMPO in DCE and $100\ \mu\text{M}$ $\text{Sr}(\text{NO}_3)_2$ in aqueous solution; B) ESI-MS obtained from direct injection after “shake flask” experiment, that is by mixing $100\ \mu\text{L}$ each of a $2.1\ \text{mM}$ $\text{Sr}(\text{NO}_3)_2$ aqueous phase and $100\ \text{mM}$ CMPO DCE phase to form an emulsion. Close-ups of the $[\text{Sr}^{\text{II}}(\text{CMPO})_2]^{2+}$ and $[\text{Sr}^{\text{II}}(\text{CMPO})_3]^{2+}$ peaks are shown inset in each spectrum with calculated isotopic profiles shown in B).

Shown in Figure 6A is the mass spectrum obtained by using BESI-MS, with $15\ \mu\text{M}$ CMPO in DCE and $100\ \mu\text{M}$ $\text{Sr}(\text{NO}_3)_2$ in the aqueous phase for which four main peaks were obtained; doubly charged complexes were observed at $m/z = 451.3$ and 654.9 and they were identified as $[\text{Sr}^{\text{II}}(\text{CMPO})_2]^{2+}$ and $[\text{Sr}^{\text{II}}(\text{CMPO})_3]^{2+}$, respectively. The isotope distribution patterns of these two peaks are an excellent match for the characteristic isotopes of strontium and other elements in these two complexes towards the theoretically calculated $m/z = 451.25$ and 654.90 . Two other peaks were observed and attributed to $[\text{CMPO} + \text{H}]^+$ and $[\text{Na}^{\text{I}}\text{CMPO}_2]^+$. The BESI-MS spectrum confirms the formation of the Sr^{2+} –CMPO complexes observed by the above electrochemical methods at the w|DCE interface.

Tandem MS, or MS/MS, was performed on these two complexes to further explore the coordination strength. MS/MS involves the linear combination of quadrupole mass analyzers; the mass spectrum is first scanned, the ion stream undergoes collision with an inert gas, and finally the fragments are analyzed with the second MS. According to tandem MS spectra, $[\text{Sr}^{\text{II}}(\text{CMPO})_3]^{2+}$ easily lost one CMPO during collision-induced dissociation with very low collision energy, while the other two CMPO complexes, including $[\text{Sr}^{\text{II}}(\text{CMPO})_2]^{2+}$, displayed much stronger binding force and continued binding even with the introduction of a $2\times$ higher collision energy than in the previous case of $[\text{Sr}^{\text{II}}(\text{CMPO})_3]^{2+}$.

The “shake flask” experiment consisted of combining $100\ \mu\text{L}$ of an aqueous solution of $\text{Sr}(\text{NO}_3)_2$ ($2.1\ \text{mM}$) with a solution of CMPO in DCE ($100\ \text{mM}$) into a small vial and shaking. The emulsified solution was then drawn up into a $250\ \mu\text{L}$ syringe and injected into the ESI-MS. The complete mass spectrum obtained is shown in Figure 6B. Four major mass peaks can be observed at m/z of 408.1 , 430.0 , 450.9 , and 654.6 ; these peaks have been identified as $[\text{CMPO} + \text{H}]^+$, $[\text{Na}^{\text{I}}(\text{CMPO}) + \text{H}]^+$, $[\text{Sr}^{\text{II}}(\text{CMPO})_2]^{2+}$, and $[\text{Sr}^{\text{II}}(\text{CMPO})_3]^{2+}$, respectively. The peak at $408.1\ m/z$ is in very good agreement with the CMPO peak observed in the BESI-MS measurements, while the peak at $430.0\ m/z$ is proposed to be a sodium–CMPO complex. Sodium is often a contaminant in metal salts with the manufacturer indicating a $0.05\ \%$ Na content and this is in good agreement with the result obtained for the BESI-MS experiment, in which a similar Na–CMPO complex, $[\text{Na}^{\text{I}}(\text{CMPO})_2]^+$, was observed. The observed peaks at $m/z = 450.9$ and 654.6 were isolated, as shown inset in Figure 6B, along with their respective calculated isotopic distribution profiles (shown above each inset spectrum) for the proposed strontium–CMPO complexes: $[\text{Sr}^{\text{II}}(\text{CMPO})_2]^{2+}$, and $[\text{Sr}^{\text{II}}(\text{CMPO})_3]^{2+}$. There is a small difference (0.3) between the BESI-MS and ESI-MS spectra and this is most likely the result of a variation in calibration.

The experimental and calculated mass peak profiles are in excellent agreement and are characteristic of the stable strontium isotopes ^{86}Sr , ^{87}Sr , and ^{88}Sr which have an abundance of 9.86 , 7.00 , and $82.58\ \%$,^[21] respectively. Since only one strontium atom is found each complex, these isotopic ratios result in two short peaks, preceding a large main

peak; these were faithfully reproduced in the calculated and experimental profiles. The trailing peaks are common MS features associated with hydrocarbon species.

Therefore, the BESI-MS/ESI-MS data are in good agreement with each other and have confirmed the stoichiometry of the Sr^{2+} -CMPO complexes observed electrochemically at the w|DCE interface.

Facilitated ion transfer (FIT) of Sr^{2+} using CMPO at the micro w|RTIL interface: Next the FIT of strontium was investigated at the w|RTIL interface using our newly discovered ionic liquid, trihexyltetradecylphosphonium tetrakis(pentafluorophenyl)borate ($\text{P}_{66614}\text{TB}$). Figure 3B shows the CV obtained by using Cell 2, in the absence of CMPO ($y=0$), and constituted a “blank” CV; this is overlaid with a CV taken using Cell 3 in which 2 mM of tetramethylammonium nitrate ($\text{TMA}(\text{NO}_3)$) were added to the aqueous phase.

The blank curve in Figure 3B was initiated at 0.131 V, a point at which the current was almost zero, and scanned in the forward direction toward more positive potentials at a scan rate of 0.020 V s^{-1} . The potential was scanned to a switching potential of 0.427 V, at which point the scan direction was reversed and scanned to the lower potential limit of -0.270 V . The final scan segment was from the lower limit, -0.270 V , back to the initial potential of 0.131 V. This blank curve shows an increase in the current response during the forward scan at 0.427 V and a decrease in the current response at -0.270 V during the reverse scan; this is indicative of supporting electrolyte ion transfer, specifically Sr^{2+} from $w \rightarrow o$ and TB^- from $o \rightarrow w$ for the former current response and NO_3^- from $w \rightarrow o$ and P_{66614} from $o \rightarrow w$ for the latter. Aside from these two features the blank curve is devoid of any peaks and this is an excellent indication of the purity of the prepared ionic liquid. Noticeably, the potential window spanned more than 0.8 V. It should be noted that the polarized potential window (PPW) is limited predominantly by TB^- at the positive end and NO_3^- at the negative end^[19a] and since the estimated RTIL bulk concentration of the potential-limiting TB^- is 1.0 M, this is a good indication considering the PPWs size.

The CV of Cell 3 in Figure 3B used similar parameters as those chosen for the blank; the initial potential was -0.106 V with the upper and lower potential range set at 0.442 and -0.283 V . During the initial forward scan an anodic wave with a peak at 0.321 V can be observed and this is indicative of TMA^+ transfer from $w \rightarrow o$, while a cathodic peak is shown with at current maximum 0.179 V during the reverse scan; this is TMA^+ transferring from the ionic liquid phase back to the aqueous phase. This description concerning the transfer of TMA^+ across the ITIES formed at the tip of a micropipette agrees well with our previous results^[15a] and with the results of Kakiuchi et al.^[9a,16a] The peak-to-peak separation between the forward and reverse peak-shaped waves was 0.142 V. This large peak separation was observed previously at the w|RTIL micro-ITIES^[9c,15a,16a] and in homogeneous RTIL electrochemistry;^[22] it has been explained as owing to either uncompen-

sated resistance or slow IT/electron-transfer kinetics. TMA^+ IT was used to calibrate the potential scale at the w| $\text{P}_{66614}\text{TB}$ ITIES by using the TATB assumption;^[12a,13a] with $\Delta_{\text{RTIL}}^w \phi_{\text{o}'}^{\text{TMA}^+} = 0.293 \text{ V}$.^[15a] The half-wave potential was determined by using Equation (6) and the peak potential of the forward scan, that is, TMA^+ transfer from $w \rightarrow o$.

Figure 7 illustrates the CVs obtained using Cell 2 with $y=35, 50, 62, 85$, and 111 mm for curves A, B, C, D, and E, respectively. In Figure 7A, the CV was initiated at -0.083 V

Figure 7. Cyclic voltammograms obtained by using Cell 2 with similar instrument parameters as described for Figure 3B, in the presence of CMPO with $y=35, 50, 62, 85$, and 111 mm for curves A–E, respectively.

and scanned in the forward direction towards positive potentials at a rate of 0.020 V s^{-1} . A peak-shaped wave showed a maximum current at 0.099 V and this is indicative of the transfer through interfacial complexation (TIC) of Sr^{2+} from $w \rightarrow o$ with CMPO. The scan continued until 0.356 V at which point the scan direction was reversed and headed towards negative potentials until -0.190 V . During this scan segment a peak-shaped wave was observed with a peak potential at -0.080 V and this has been attributed to the transfer of Sr^{2+} back across the ITIES through interfacial decomplexation of the Sr^{2+} -CMPO complex. Interestingly, only one pair of peaks was observed in contrast to two at the w|DCE interface.

To verify that only one stoichiometry is present at the w|RTIL interface, differential pulse voltammetry (DPV) was

applied to Cell 2 with [CMPO] = 111 mM using the following parameters: step potential, pulse amplitude, pulse period, pulse width, initial and final potentials equal to 0.010 V, 0.050 V, 0.5 s, 0.1 s, −0.090 and 0.400 V, respectively; a reverse scan was also obtained with initial and final potentials of 0.400 and −0.090 V. The DPV obtained is shown in Figure 8 with only one peak potential at 0.157 V during the

Figure 8. DPV using Cell 2, in the presence of CMPO with $\gamma = 111$ mM, with an initial and final potential of −0.090 and 0.400 V; step, pulse amplitude, pulse period, and pulse width of 0.010 V, 0.050 V, 0.5 s, and 0.1 s, respectively. For the reverse scan the initial and final potentials have simply been switched.

forward scan, thus indicating that only a single ion transfer has taken place. It should be noted, however, that this peak is broad and may be the result of two stoichiometries having effectively merged; that is to say, the difference in the nominal, overall complexation constant between the complexes with $n=2$ and $n=3$ may be small. Additionally, a CV was taken using Cell 2 and [CMPO] = 111 mM but at a scan rate of 0.001 V s^{-1} (data not shown). In this CV a single ion transfer was observed with one peak on the forward scan, indicative of TIC, and another on the reverse scan, typical of TID. However, the peak-to-peak separation becomes very large ($>0.300 \text{ V}$), and this may be indicative of the system transition from one controlled by diffusion of the ligand in the RTIL phase to one in which it is controlled by the consumption of species at the interface, that is, a system that generates a steady-state current response. Both of these experiments point to a scenario in which the kinetics of the interfacial reactions is slow although the Gibbs energy is favorable. Moving forward, as the concentration of the ligand increases, in Figure 7 the peak potential of the forward wave shifts to less positive potentials; $\Delta_{\text{RTIL}}^w \phi_p$ equal to 0.088, 0.085, 0.065, and 0.050 V for curves B–E, respectively. Analogous to strontium FIT at the w|DCE interface, the series of CVs obtained at the w|P₆₆₆₁₄TB interface were analyzed by using Equation (5). Two critical points concerning the analysis of the present case must be made initially.

First, the ξ term in Equation (5) cannot be neglected, therefore the diffusion coefficient for the ionic liquid was estimated based on our recent publication,^[15a] concerning diffusion in RTILs using the ferrocene/ferrocenium redox

couple as a probe. In this previous work, ferrocene was oxidized to ferrocenium and the diffusion coefficient was obtained through two electrochemical techniques: cyclic voltammetry, by altering the scan rate, and chronoamperometry in conjunction with two curve fitting methods described by Shoup and Szabo^[23] and Aoki and Osteryoung,^[24] ferrocene is a relatively large organic molecule which we considered analogous to CMPO and the Sr–CMPO complex. In this way the diffusion coefficient for the RTIL phase was estimated to be $3.5 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$.^[15a] The diffusion coefficient for strontium in the aqueous phase was obtained from the literature,^[25] $1.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. Secondly, the formal free-metal transfer potential of Sr^{2+} at the w|P₆₆₆₁₄TB ITIES could not be measured, therefore, the formal transfer potential at the w|DCE interface^[19b] was used to approximate its value. It was noted that the formal transfer potential of TMA^+ at the w|P₆₆₆₁₄TB interface was shifted positively by 0.133 V relative to its transfer at the w|DCE interface, therefore, considering this a general trend, it was incorporated such that: $\Delta_{\text{DCE}}^w \phi_{\text{Sr}^{2+}}^{\circ} + 0.133 \text{ V} \approx \Delta_{\text{RTIL}}^w \phi_{\text{Sr}^{2+}}^{\circ} \approx 1.033 \text{ V}$.

This assumption was based on three factors. First, the recent work by Samec et al.^[9c] and Kakiuchi et al.^[16a] showed a correlation between the trends in formal transfer potentials of ions at the w|DCE and w|RTIL interfaces; each ion showed distinct transfer potentials, but the trends in hydrophilicity between w|DCE and w|RTIL paralleled each other. Secondly, our recent work^[15b] surrounding UO_2^{2+} FIT and IT, in conjunction with Sr^{2+} IT at the w|DCE, point to the extreme hydrophilicity of these ions and thus a large formal transfer potential is expected. Finally, the size and position of the calibrated PPW suggests that this value is a good approximation. Therefore, continuing with the analysis, the plot of $-\frac{zF}{RT} \left(\Delta_{\text{RTIL}}^w \phi_{\text{ML}_2^{2+}}^{\circ} - \Delta_{\text{RTIL}}^w \phi_{\text{M}^{2+}}^{\circ} \right)$ versus $\ln(c_{\text{L,initial}})$ is shown in Figure 9 with a linear fit giving a slope equal to 3 and a y intercept of 75; the linear plot shows good correlation to the FIT theory with an $R^2 = 0.9777$. It is interesting to note, looking at Equation (5), the slope of the line is independent of the formal transfer coefficient and ξ , therefore, it is also independent of the assumptions made surrounding the diffusion coefficients and formal

Figure 9. Plot of $-\frac{zF}{RT} \left(\Delta_{\text{RTIL}}^w \phi_{\text{ML}_2^{2+}}^{\circ} - \Delta_{\text{RTIL}}^w \phi_{\text{M}^{2+}}^{\circ} \right)$ versus $\ln(c_{\text{L,initial}})$ with data obtained from the curves shown in Figure 7.

transfer potential of the free strontium metal species. Using these estimations, however, the accumulated complexation constant was calculated to be 1.5×10^{34} .

Figure 10A and B show proposed structures of $[\text{Sr}(\text{CMPO})_2(\text{H}_2\text{O})_2]^{2+}$ and $[\text{Sr}(\text{CMPO})_3]^{2+}$, respectively, with an octahedral geometry; solvent molecules in the case of

Figure 10. Proposed structures for A) $[\text{Sr}(\text{CMPO})_2(\text{H}_2\text{O})_2]^{2+}$ and B) $[\text{Sr}(\text{CMPO})_3]^{2+}$.

$[\text{Sr}(\text{CMPO})_3]^{2+}$ have been neglected for simplicity. In a recent publication by Cole et al.,^[26] they described the crystal structures of several strontium complexes with a maximum coordination number to the strontium center of seven. The octahedral geometry shown in Figure 10B has a coordination number of six; while this geometry minimizes steric hindrance, a trigonal bipyramidal geometry may also be possible with two CMPOs in a bidentate configuration and one monodentate. In this case, the monodentate CMPO would most likely coordinate through the oxygen of the phosphine oxide.^[7d,27] Junk and Steed^[28] recrystallized the strontium nitrate salt from an aqueous solution of [18]crown-6 (18C6) and obtained the complex $[\text{Sr}(\text{NO}_3)_2(18\text{C}6)]$ with strontium

held within the ring of the crown ether, coordinated to the six ring oxygen atoms, and the two nitrates located on opposite sides of the ring plane with O, O' -bidentate coordination; therefore the total coordination number of their crystal structure was ten.

The structure in Figure 10A was proposed with the work of Junk and Steed^[28] in mind, as the CMPO molecules lie in a plane around the strontium metal with two solvent water molecules on opposite sides; thus, an octahedral geometry is formed. While no water molecules were observed during either the BESI-MS or ESI-MS experiment, it is possible they are only weakly coordinated and easily removed during the harsh ionization conditions. The total number of ligands participating in the interfacial complexation reaction is in agreement with the results shown by Makrlík et al.^[7g,h] and these previous structural reports^[26,28] are also in evidence towards two or three CMPO molecules participating in the interfacial complexation.

Interestingly, the complexation constant at the w|RTIL interface is nine magnitudes greater than that observed at the w|DCE interface. This large equilibrium constant further explains why $[\text{Sr}(\text{CMPO})_3]^{2+}$ can be formed at the interface at which the reaction kinetics are very slow; thermodynamics, in this case, is dominant. This is in agreement with the large increase in distribution ratios observed using RTILs versus molecular solvents in conventional solvent extractions.^[7b,c,8]

Conclusion

The FIT of Sr^{2+} assisted by the CMPO ligand at the w|DCE and w|RTIL interface was investigated for the first time. At the w|DCE interface two metal:ligand stoichiometries of 2 and 3 for the interfacial complexation reactions were observed with accumulated equilibrium constants (β) of 4.5×10^{19} and 5.5×10^{25} , respectively. These stoichiometries have been confirmed through the use of BESI-MS and ESI-MS by means of a “shake flask” experiment; mass peaks observed at 451.3 and 654.9 have an isotopic finger print that suggests they belong to $[\text{Sr}(\text{CMPO})_2]^{2+}$ and $[\text{Sr}(\text{CMPO})_3]^{2+}$ complexes, respectively. Comparing these two MS experiments, BESI-MS is valuable for short-lived chemical species; however, the “shake flask” technique, while not experimentally sophisticated, was able to obtain similar data and this is most likely owing to the strength of the metal–ligand complexes.

Only one stoichiometry was observed at the w|RTIL interface, with $n=3$ and $\beta=1.5 \times 10^{34}$. Interestingly the complexation constant is 273 million times greater than that observed using molecular solvent, but it should be noted that, because of the assumptions made concerning the diffusion coefficients in the aqueous and RTIL phases, along with $\Delta^w_{\text{RTIL}} \phi_{\text{Sr}^{2+}}$, that this is an estimation. The high β value, however, may be an additional explanation as to why the reported distribution constants for RTIL extractions are higher than those of conventional organic solvents.

The above studies will provide guidelines in reprocessing spent nuclear fuels to obtain Sr to be used in radioimmunology. As well it should be noted that, while a non-radiogenic, stable form of strontium (^{88}Sr) was used, this was only for convenience of handling and is shown here as a model system; these data are assumed to be transferrable to any isotopic form of strontium.

Acknowledgements

We would like to thank J. Clara Wren, Jamie Noël, David W. Shoesmith, Paul J. Ragogna, Manuel A. Méndez, Astrid J. Olaya, Fernando Cortes-Salazar, Dmitry Momotenko, Ken Simpson, Jonathan Dube, Fanguo Deng, Susan Howett, Pam Yakabuskie, Jiju Joesph, Kalen Swanick, John Vanstone, Jon Aukima, Justin Smith, Doug Hairsine, Valérie Devaud, Maria Szuman, Sherrie McPhee, and Marylou Hart for their helpful discussions and technical support. T.J.S. would like to acknowledge the Department of Chemistry at the University of Western Ontario (UWO) for "A Special International Research Experience" (ASPIRE) travel award and Prof. Hubert Girault at the Swiss Federal Institute of Technology in Lausanne (EPFL) for graciously accommodating a research exchange. Z.D. is grateful to UWO for offering him a sabbatical year (2010–2011) and EPFL for accommodating one month stay in Prof. Girault's lab. This work was supported by the Ontario Research Foundation, Natural Sciences and Engineering Research Council of Canada (NSERC), Canada Foundation for Innovation, Ontario Innovation Trust, the Premier's Research Excellence Award, l'École Polytechnique Fédérale de Lausanne, and the University of Western Ontario.

- [1] a) D. Neri, H. Petrucci, G. Winter, Y. Light, R. Marais, K. E. Britton, A. M. Creighton, *Nat. Biotechnol.* **1996**, *14*, 485–490; b) G. P. Adams, R. Schier, *J. Immunol. Methods* **1999**, *231*, 249–260; c) P. Chinn, G. Braslawsky, C. White, N. Hanna, *Cancer Immunol. Immunother.* **2003**, *52*, 257–280; d) D. M. Goldenberg, *Cancer Immunol. Immunother.* **2003**, *52*, 281–296; e) C. Ebbinghaus, J. Scheuermann, D. Neri, G. Elia, *Curr. Pharm. Des.* **2004**, *10*, 1537–1549; f) P. J. Hudson, C. Souriau, *Nat. Med.* **2003**, *9*, 129–134.
- [2] D. Ciavardelli, G. D'Anniballe, G. Nano, F. Martin, G. Federici, P. Sacchetta, I. C. Di, A. Urbani, *Rapid Commun. Mass Spectrom.* **2007**, *21*, 2343–2350.
- [3] P. S. Dhami, P. W. Naik, N. L. Dudwadkar, R. Kannan, P. V. Achuthan, A. D. Moorthy, U. Jambunathan, S. K. Munshi, P. K. Dey, U. Pandey, M. Venkatesh, *Sep. Sci. Technol.* **2007**, *42*, 1107–1121.
- [4] a) D. W. Wester, R. T. Steele, D. E. Rinehart, J. R. DesChane, K. J. Carson, B. M. Rapko, T. S. Tenforde, *Appl. Radiat. Isot.* **2003**, *59*, 35–41; b) Patent: M. J. O'Hara, B. M. Rapko, M. K. Edwards, D. W. Wester, Medical Isotope Generator Systems, Battelle Memorial Institute (USA), **2008**, US20080258076; c) M. L. Bonardi, L. Martano, F. Groppi, M. Chinol, *Appl. Radiat. Isot.* **2009**, *67*, 1874–1877.
- [5] A. P. Paiva, P. Malik, *J. Radioanal. Nucl. Chem.* **2004**, *261*, 485–496.
- [6] K. L. Nash, *ACS Symp. Ser.* **2006**, *933*, 22–40.
- [7] a) M. W. Peters, E. J. Werner, M. J. Scott, *Inorg. Chem.* **2002**, *41*, 1707–1716; b) A. E. Visser, M. P. Jensen, I. Laszak, K. L. Nash, G. R. Choppin, R. D. Rogers, *Inorg. Chem.* **2003**, *42*, 2197–2199; c) A. E. Visser, R. D. Rogers, *J. Solid State Chem.* **2003**, *171*, 109–113; d) E. S. Stoyanov, T. Vorob'yova, I. V. Smirnov, *J. Struct. Chem.* **2005**, *46*, 829–838; e) T. Fujii, K. Aoki, H. Yamana, *Solvent Extr. Ion Exch.* **2006**, *24*, 347–357; f) C. Lamouroux, S. Rateau, C. Moulin, *Rapid Commun. Mass Spectrom.* **2006**, *20*, 2041–2052; g) E. Makrlík, P. Vanura, P. Selucky, *Z. Phys. Chem. (Muenchen Ger.)* **2009**, *223*, 253–261; h) E. Makrlík, P. Vaňura, P. Selucky, *Acta Chim. Slov.* **2010**, *57*, 485–490; i) M. P. Antony, R. Kumaresan, A. S. Suneesh, S. Rajeswari, B. Robertselvan, V. Sukumaran, R. Manivannan, K. V. Syamala, K. A. Venkatesan, T. G. Srinivasan, P. R. Vasudeva Rao, *Radiochim. Acta* **2011**, *99*, 207–215.
- [8] S. Dai, Y. H. Ju, C. E. Barnes, *J. Chem. Soc. Dalton Trans.* **1999**, 1201–1202.
- [9] a) N. Nishi, T. Kawakami, F. Shigematsu, M. Yamamoto, T. Kakiuchi, *Green Chem.* **2006**, *8*, 349–355; b) N. Nishi, H. Murakami, S. Imakura, T. Kakiuchi, *Anal. Chem.* **2006**, *78*, 5805–5812; c) J. Langmaier, A. Trojanek, Z. Samec, *Electroanalysis* **2009**, *21*, 1977–1983.
- [10] J. D. Holbrey, R. D. Rogers, R. A. Mantz, P. C. Trulove, V. A. Cocalia, A. E. Visser, J. L. Anderson, J. L. Anthony, J. F. Brennecke, E. J. Maginn, T. Welton, R. A. Mantz, in *Ionic Liquids in Synthesis*, Wiley-VCH, Weinheim, **2008**, Chapter 3.
- [11] S. A. Ansari, P. K. Mohapatra, D. R. Raut, M. Kumar, B. Rajeswari, V. K. Manchanda, *J. Membr. Sci.* **2009**, *337*, 304–309.
- [12] a) A. J. Parker, *Electrochim. Acta* **1976**, *21*, 671–679; b) D. Homolka, H. Wendt, *Ber. Bunsen-Ges. Phys. Chem.* **1985**, *89*, 1075–1082; c) G. Taylor, H. H. J. Girault, *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *208*, 179–183; d) J. A. Campbell, H. H. Girault, *J. Electroanal. Chem. Interfacial Electrochem.* **1989**, *266*, 465–469; e) T. Wandlowski, V. Marecek, Z. Samec, *Electrochim. Acta* **1990**, *35*, 1173–1175; f) T. Kakiuchi, M. Senda, *J. Electroanal. Chem.* **1991**, *300*, 431–445; g) F. Reymond, P.-A. Carrupt, H. H. Girault, *J. Electroanal. Chem.* **1998**, *449*, 49–65; h) F. Reymond, G. Lager, P.-A. Carrupt, H. H. Girault, *J. Electroanal. Chem.* **1998**, *451*, 59–76; i) S. A. Dassié, L. M. Yudi, A. M. Baruzzi, *J. Electroanal. Chem.* **1999**, *464*, 54–60; j) T. J. Stockmann, Z. Ding, *J. Electroanal. Chem.* **2010**, *649*, 23–31.
- [13] a) Z. Samec, J. Langmaier, T. Kakiuchi, *Pure Appl. Chem.* **2009**, *81*, 1473–1488; b) R. A. W. Dryfe, *Adv. Chem. Phys.* **2009**, *141*, 153–215; c) H. H. J. Girault, D. J. Schiffrin, *Electroanal. Chem.* **1989**, *15*, 1–141; d) H. Girault, *Electroanal. Chem.* **2010**, *23*, 1–104.
- [14] D. Homolka, K. Holub, V. Marecek, *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *138*, 29–36.
- [15] a) T. J. Stockmann, J. Zhang, J. C. Wren, Z. Ding, unpublished results; b) T. J. Stockmann, Z. Ding, *Anal. Chem.* **2011**, *83*, 7542–7549.
- [16] a) T. Kakiuchi, N. Tsujioka, *Electrochem. Commun.* **2003**, *5*, 253–256; b) J. Langmaier, Z. Samec, *Anal. Chem.* **2009**, *81*, 6382–6389; c) J. Langmaier, Z. Samec, *Electrochem. Commun.* **2007**, *9*, 2633–2638.
- [17] a) M. A. Méndez, M. Prudent, B. Su, H. H. Girault, *Anal. Chem.* **2008**, *80*, 9499–9507; b) M. Prudent, Eacute, M. A. Ndez, H. H. Girault, *Anal. Sci.* **2008**, *24*, 1399–1404; c) M. Prudent, H. H. Girault, *J. Am. Soc. Mass Spectrom.* **2008**, *19*, 560–568; d) R. A. Hartvig, M. A. Me'ndez, M. V. Weert, L. Jorgensen, J. Østergaard, H. H. Girault, H. Jensen, *Anal. Chem.* **2010**, *82*, 7699–7705; e) Y. Lu, M. Prudent, L. Qiao, M. A. Mendez, H. H. Girault, *Metallomics* **2010**, *2*, 474–479.
- [18] T. J. Stockmann, Z. Ding, unpublished results.
- [19] a) A. J. Olaya, M. A. Méndez, F. Cortes-Salazar, H. H. Girault, *J. Electroanal. Chem.* **2010**, *644*, 60–66; b) T. J. Stockmann, A. J. Olaya, M. A. Méndez, H. H. Girault, Z. Ding, *Electroanalysis* **2011**, DOI: 10.1002/elan.201100401.
- [20] A. J. Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd ed., John Wiley & Sons, New York, **2001**.
- [21] N. E. Holden in *CRC Handbook of Chemistry and Physics*, Vol. 91 (Ed.: W. M. Haynes) CRC, Boca Raton, FL (USA), **2011**, pp. 11–82.
- [22] a) K. R. J. Lovelock, F. N. Cowling, A. W. Taylor, P. Licence, D. A. Walsh, *J. Phys. Chem. B* **2010**, *114*, 4442–4450; b) E. I. Rogers, D. S. Silvester, D. L. Poole, L. Aldous, C. Hardacre, R. G. Compton, *J. Phys. Chem. C* **2008**, *112*, 2729–2735.
- [23] D. Shoup, A. Szabo, *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *140*, 237–245.
- [24] K. Aoki, J. Osteryoung, *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *160*, 335–339.
- [25] H. S. Harned, F. M. Polestra, *J. Am. Chem. Soc.* **1953**, *75*, 4168–4169.
- [26] M. L. Cole, G. B. Deacon, C. M. Forsyth, K. Konstas, P. C. Junk, *Dalton Trans.* **2006**, 3360–3367.
- [27] a) E. P. Horwitz, W. W. Schulz in *New Separation Chemistry Techniques for Radioactive Waste and Other Specific Applications*, Elsevier

er, New York, **1991**, pp. 21–29; b) F. Arnaud-Neu, J. K. Browne, D. Byrne, D. J. Marrs, M. A. McKervey, P. O'Hagan, M. J. Schwing-Weill, A. Walker, *Chem. Eur. J.* **1999**, 5, 175–186.

[28] P. C. Junk, W. S. Jonathan, *J. Chem. Soc. Dalton Trans.* **1999**, 407–414.

Received: August 11, 2011
Published online: October 24, 2011