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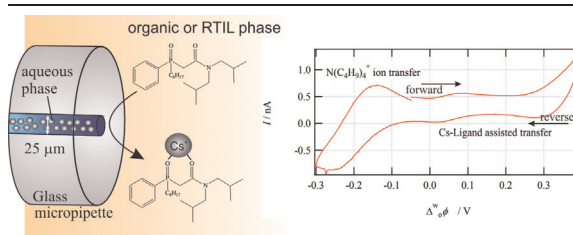
Electrochemical assessment of water|ionic liquid biphasic systems towards cesium extraction from nuclear waste

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HIGHLIGHTS

- Electroanalytical chemistry was employed to assess cesium ion extraction in biphasic systems.
- Water|ionic liquid systems are much more efficient than traditional water|organic ones.
- The metal ion to ligand stoichiometry and overall complexation constant were determined.
- The stoichiometry was confirmed by mass spectrometry.
- The ligand CMPO used in TRUEX processes was found to be effective for the FIT.

GRAPHICAL ABSTRACT



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ABSTRACT

A room temperature ionic liquid (IL) composed of a quaternary tetrabutylphosphonium (trihexyltetradecylphosphonium, P_{66614}^{+}) and tetrakis(pentafluorophenyl)borate anion (TB^{-}) was employed within a water| $P_{66614}TB$ (w| $P_{66614}TB$ or w|IL) biphasic system to evaluate cesium ion extraction in comparison to that with a traditional water|organic solvent (w|o) combination. ^{137}Cs is a major contributor to the radioactivity of spent nuclear fuel as it leaves the reactor, and its extraction efficiency is therefore of considerable importance. The extraction was facilitated by the ligand octyl(phenyl)- N,N' -diisobutylcarbamoylphosphine oxide (CMPO) used in TRans-Uranium EXtraction processes and investigated through well established liquid|liquid electrochemistry. This study gave access to the metal ion to ligand (1: n) stoichiometry and overall complexation constant, β , of the interfacial complexation reaction which were determined to be 1:3 and 1.6×10^{11} at the w| $P_{66614}TB$ interface while the study at w|o elicited an n equal to 1 with β equal to 86.5. Through a straightforward relationship, these complexation constant values were converted to distribution coefficients, δ_{ex} , with the ligand concentrations studied for comparison to other studies present in the literature; the w|o and w|IL systems gave δ_{ex} of 2 and 8.2×10^7 , respectively, indicating a higher overall extraction efficiency for the latter. For the w|o system, the metal ion-ligand

Abbreviations: CE, counter electrode; CV, cyclic voltammograms; ESI-MS, electrospray ionization mass spectroscopy; FIT, facilitated ion transfer; IL, ionic liquid; IT, ion transfer; ACT, ligand transfer to the aqueous phase followed by complexation and transfer to the organic phase; TOC, (metal) transfers to the organic phase with subsequent complexation; micro-ITIES, micro-interface between two immiscible electrolytic solutions; CMPO, octyl(phenyl)- N,N' -diisobutylcarbamoylphosphine oxide; PPW, polarizable potential window; RE, reference electrode; SNF, spent nuclear fuel; TB^{-} , tetrakis(pentafluorophenyl) borate anion; TATB, tetraphenylarsonium tetraphenylborate; TIC, transfer through interfacial complexation; TID, transfer through interfacial decomplexation; TRUEX, TRans-Uranium EXtraction; P_{66614}^{+} , trihexyltetradecylphosphonium; w|DCE, water|1,2-dichloroethane; w|o, water|organic solvent; w| $P_{66614}TB$ or w|IL, water| $P_{66614}TB$; WE, working electrode.

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stoichiometries were confirmed through isotopic distribution analysis of mass spectra obtained by the direct injection of an emulsified water–organic solvent mixture into an electron spray ionization mass spectrometer.

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1. Introduction

Room temperature ionic liquids (ILs), large organic salts with melting points below 100 °C, have attracted a great deal of attention over the past decade with the development of air and water stable versions. The increased interest is due in no small part to their unique properties including a high electrochemical stability that gives rise to large potential windows [1–3], but with a distinct interfacial structure [4–8]. This, in conjunction with ILs low volatility, non-flammability, and high thermal stability make them desirable solvents for a variety of applications including sensors [9], lithium batteries [10,11], and in biphasic metal extraction [12–18]. ILs have shown marked improvement over conventional molecular solvents in many of these areas [13].

Interestingly, ILs incorporating quaternary phosphonium cations, such as trihexyltetradecylphosphonium (P_{66614}^+) and tetrabutylphosphonium (P_{8888}^+), have been found to possess higher electrochemical stability over ammonium- or imidazolium-based ILs [3], while they also demonstrate greater hydrophobicity [19,20]. Additionally, the tetrakis(pentafluorophenyl)borate anion (TB^-) has been shown to have good electrochemical stability [21], excellent hydrophobicity [19,20,22], and, critically, low ion-pair interactions [21–23]. Combining these cations and anions generates ILs with excellent physicochemical and electrochemical properties to make them ideally suited, not only in the role of conventional supporting electrolytes, but also as alternative solvents in biphasic metal ion extractions [13] for spent nuclear fuel (SNF) reprocessing.

Recently, ILs combining quaternary alkyl phosphonium cations with TB^- have been prepared to explore their implications in biphasic separations towards SNF reclamation [19,20]. Typically, metal ion extractions are characterized by first mechanically mixing the two phases and then determining the amount of metal ions distributed between the two phases [13,24]. Where these methods differ is in the analysis of metal ion distribution between the phases. Some techniques employ radioisotopes and absorption spectroscopy [25] or inductively coupled plasma (ICP) spectroscopy [18], which can be expensive and require a specialized laboratory or handling procedures.

Electrochemistry at a micro-interface between two immiscible electrolytic solutions (micro-ITIES) offers a cost-effective technique for studying metal ion transfer (IT) and ligand assisted, or facilitated ion transfer (FIT) [12,14,26–28], which are analogous to ion partitioning and interfacial complexation, respectively. These respective processes are shown in Eqs. (1) and (2) for the general case of an ion, i , of charge z transferring from water, w , to an organic, o , phase:



Whereas for FIT, a ligand, L , is added to the organic (or IL) phase and coordinates to the metal ion center interfacially with a metal to ligand stoichiometry of 1: n . The mechanism described in Eq. (2) is commonly referred to as transfer through interfacial complexation (TIC) with the return process termed transfer through interfacial decomplexation (TID); however, two other mechanisms are possible [29]. In one scenario the metal transfers to the organic

phase with subsequent complexation (TOC), while another pathway is through ligand transfer to the aqueous phase followed by complexation and transfer to the organic phase, often abbreviated as ACT [29].

ITIES or biphasic electrochemistry has been the subject of many reviews [30–33]. The so-called soft interface is a vital electrochemical technique, which has been used for biomimetic studies of oxygen reduction catalyzed by metalloporphyrins [34] and metal-free porphyrins [35], IT and ion absorption studies at microhole arrays utilizing a liquid|organo-gel interface with possible sensor applications [36–38], kinetic investigations of pharmaceutical micro-extraction/transfer [39,40], along with nano-pore investigations [41]. These examples simply serve to demonstrate the far-reaching implications and impact of this methodology.

Herein, octyl(phenyl)- N,N' -diisobutylcarbamoylphosphine oxide (CMPO), a ligand employed industrially in the TRans-Uranium EXtraction (TRUEX) processes [25], has been used, along with the ionic liquid, $P_{66614}TB$, as a model system to demonstrate the use of ILs in metal extraction at electrified biphasic interfaces. Owing to the hydrophobic character of CMPO, only the TIC/TID mechanism has been considered.

FIT can be characterized by electrochemistry such that the overall complexation constant, β , and metal to ligand ratio, 1: n can be determined [28]. This technique was pioneered by Samec, Mareček et al. [42], Kakiuchi and Senda [43], and Girault et al. [28] for water|organic (w|o) interfaces and recently for water|IL (w|IL) interfaces [12,14,16,44].

Cesium was chosen as ^{137}Cs is a common fission byproduct that contributes greatly to the radioactivity and thermal heat of SNF (in conjunction with ^{90}Sr) [45], while also having well established free metal ion transfer characteristics studied at w|1,2-dichloroethane (w|DCE), w|nitrobenzene, and w| $P_{66614}TB$ [22,46–49]. These two factors should elicit interest from the nuclear community [50].

2. Experimental

2.1. Chemicals

All chemicals were purchased as reagent grade or higher and used as received without further purification. Cesium nitrate ($CsNO_3$), cesium chloride ($CsCl$), tetrabutylammonium chloride ($TBACl$), 1,2-dichloroethane (DCE), and dichloromethane were obtained from Sigma-Aldrich Canada Ltd. (Mississauga, ON). Trihexyltetradecylphosphonium chloride ($P_{66614}Cl$) was bought from Strem Chemical Inc. (Newburyport, MA) while potassium tetrakis(pentafluorophenyl) borate (KTB) was ordered from Boulder Scientific Company (Mead, CO). $P_{66614}TB$ was prepared through the metathesis of $P_{66614}Cl$ with KTB in dichloromethane; this procedure, along with purification steps, has been described in detail elsewhere [19,20].

2.2. Micropipette fabrication

A few of our recent publications describe the micropipette fabrication [19,20,46]; however, a brief outline follows. A borosilicate glass capillary (1.0 mm/2.0 mm internal/external diameter, Sutter Instrument Co., Novato, CA, USA) was fixed inside a Narishige electric puller (Model #PP-83, Japan) with the capillary centered around the pullers heating coil. Upon heating and pulling,

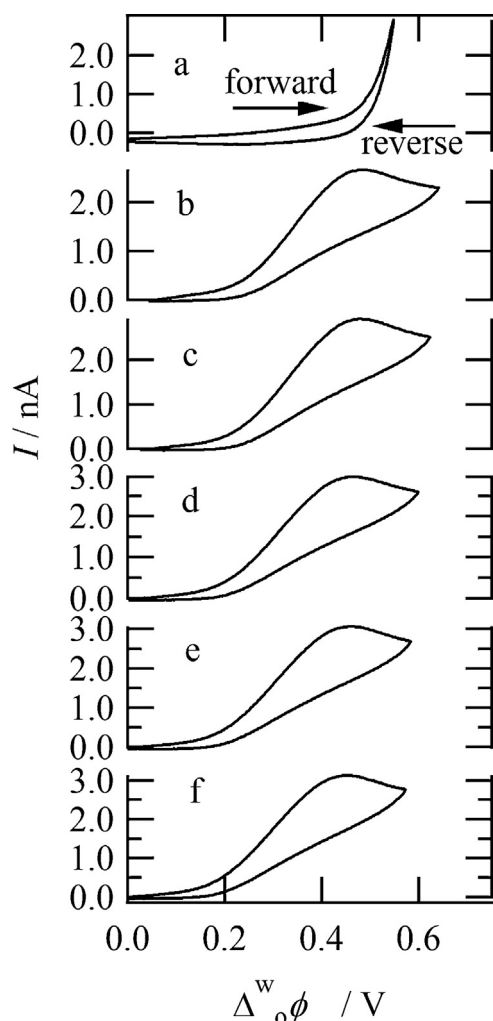


Fig. 1. Cyclic voltammograms acquired using Cell 1 with a CMPO concentration (y) equal to 0, 22, 43, 62, 80, and 96 mM, for curves a, b, c, d, e, and f, respectively, at a scan rate of 0.025 V s^{-1} .

potential required to elicit ion transfer. Thus, the CVs overlaid in Fig. 1 agree well with the theory of FIT [28]. This can be further elucidated through the following equation [28].

$$-\frac{zF}{RT}(\Delta_o^w \phi_{il_n^{z+}}^{\sigma'} - \Delta_o^w \phi_{i^{z+}}^{\sigma'}) = n \ln(c_{\text{init.}}) + \ln(\beta) + \ln(\xi) \quad (4)$$

The formal IT potential of the metal ion–ligand complex, $\Delta_o^w \phi_{il_n^{z+}}^{\sigma'}$, was obtained directly from its CV. $\Delta_o^w \phi_{i^{z+}}^{\sigma'}$ is the formal IT potential of the free metal ion, which is a constant unique to each metal ion and biphasic system; this was taken to be 0.480 V [22]. The variables n , $c_{L,o}^*$, and β , are the metal to ligand stoichiometry (1: n), initial ligand concentration, and overall complexation constant, respectively. Please note that CMPO is quite hydrophobic and thus its partitioning to the aqueous phase should be low. In this way, by varying the initial concentration of the ligand and plotting the potential differences vs. $\ln(c_{L,o}^*)$, a linear relationship can be developed such that the slope is the metal to ligand stoichiometry whilst the y-intercept can be used to elucidate the overall complexation constant. The final term in Eq. (4), ξ , is equal to $\sqrt{D_{i,o}/D_{i,w}}$; for the w|DCE case, the diffusion coefficients in each phase were considered equal and thus the term was reduced to 0.

The potential scale has been calibrated using the tetraphenylammonium tetraphenylborate (TATB) [56], or Parker's [57] assumption which use well established IT potentials of simple ions, such as

tetramethylammonium (TMA^+ ; 0.160 V [58]) or nitrate (NO_3^- ; -0.380 V [46]), as internal standards. The half-wave potentials were determined from the peak potential, $\Delta_o^w \phi_p$, and the relation, $\Delta_o^w \phi_{1/2,il_n^{z+}} = \Delta_o^w \phi_p \pm 0.028 \text{ V}/z$, as described in Bard and Faulkner [53,54].

Applying this methodology to the CV data illustrated in Fig. 1, one can arrive at the linear graph displayed in Fig. 2A. The linear regression results are listed as an inset in Fig. 2A such that the slope is 1, the y-intercept is 4.46, and the R^2 is 0.971. If the diffusion coefficients in the organic and aqueous phases are assumed to be approximately equivalent, then Eq. (4) can be simplified and $\ln \beta_n$ directly extrapolated; in this case β_n is 86.5. The relatively high R^2 value, 0.971, shows a satisfactory linear trend.

A proposed structure of CsCMPO^+ with three water molecules is drawn in Fig. 2B demonstrating a possible octahedral geometry. CMPO coordinates predominantly to the metal ions through the oxygens on the carbamoyl or phosphine oxide groups, while the latter is the most preferred [15,59]. Alkali ligand coordination chemistry is presented extensively in the literature, with the state of research being reviewed annually [60]. Cesium coordination numbers (c.n.) can be high when considering the ubiquitous dibenzo-crown-ether series of ligands, generating c.n. equal to 6 or, in the case of sandwich compounds, 12 or higher [61,62]. Comparatively, the electrochemistry detailed herein points to only one CMPO and, therefore a maximum c.n. of 2. Recent studies of dioxouranium, strontium, and rubidium FIT describe the coordination of these metals with w|DCE ligand stoichiometries [12,14,27] of 2 or 3; therefore, the result for Cs^+ was highly feasible. In fact the low Cs:CMPO ratio is a result of the decreased hydrophilicity of cesium, relative to other alkali and alkali earth metals, rather than its poor coordination [46,51]. Owing to the relatively high hydrophilicity of rubidium and strontium, they would require a higher number of ligands to elicit IT while cesium does not. Indeed, until recently cesium was one of the few alkali metal ions whose IT could be observed at the w|DCE interface [58,63].

3.2. Stoichiometry confirmation using electrospray ionization mass spectroscopy

Fig. 3 illustrates the mass spectrum obtained through direct injection of an emulsified water-DCE biphasic mixture containing 20 mM CsNO_3 and 100 mM CMPO , respectively, into the electrospray ionization mass spectrometer (ESI-MS). In this experiment, $100 \mu\text{L}$ of the cesium nitrate aqueous solution, along with $100 \mu\text{L}$ of the DCE ligand solution, were placed in a small flask and shaken. Fig. 3 shows the four mass peaks of interest occurring at 132.9, 408.3, 540.2, and 947.5 m/z corresponding to Cs^+ , $[\text{CMPO} + \text{H}]^+$, $[\text{CsCMPO}]^+$, and $[\text{CsCMPO}_2]^+$, respectively. $^{132.9}\text{Cs}$ is the 100% abundant isotope of cesium [64] and thus its peak at 132.9 m/z shows no perceivable distribution pattern. This also greatly simplifies the isotopic distribution analysis for the remaining peaks, which possess the typical descending mass pattern common to most hydrocarbons. This can be seen in the $[\text{CMPO} + \text{H}]^+$ mass peak, but more notably for the $[\text{CsCMPO}]^+$ and $[\text{CsCMPO}_2]^+$, which are shown as magnified insets with their respective calculated distribution profiles displayed below. The experimental and calculated profiles are in excellent agreement.

These data generating a 1:1 metal ion to ligand stoichiometry, are in good agreement with that observed electrochemically, along with previous reports for rubidium [14] and strontium [12].

3.3. Investigation of Cs-FIT at the w|P₆₆₆₁₄TB interface

Trace a in Fig. 4 illustrates the CV obtained at a w|IL micro-interface using Cell 2 with no ligand added to the IL phase ($y = 0$).

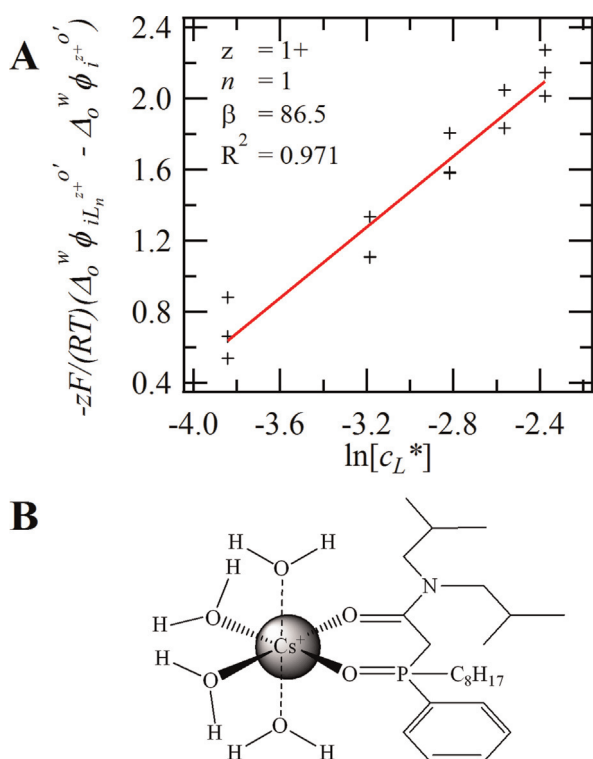


Fig. 2. (A) Graph of $-\frac{zF}{RT}(\Delta_0^w \phi_{iL_n}^{z+} - \Delta_0^w \phi_{iL_n}^{z+})$ versus $\ln[c_L^*]$ with, inset, linear regression data for the slope ($n = 1$) and $R^2 = 0.971$. (B) Proposed structure of CsCMPO⁺ with possible hydration sphere including 3 H₂O molecules creating an octahedral geometry.

The scan was initiated at approximately -0.180 V and was swept at a rate of 0.020 V s⁻¹ with a potential range from -0.250 to 0.575 V. During the forward scan, a peak-shaped wave can be observed with a peak potential at -0.018 V; this is indicative of TBA⁺ transfer from w to IL. The edge of the PPW was reached at 0.522 V, upon which the scan direction was switched and proceeded towards negative potentials until -0.256 V. Within the reverse scan another peak-shaped wave can be observed and is owing to the transfer of TBA⁺ back from the IL to w.

The w|IL interface is distinct from the w|DCE interface as the increased viscosity within the IL phase translates into a lower diffusion coefficient. Diffusion within the IL phase is slow enough

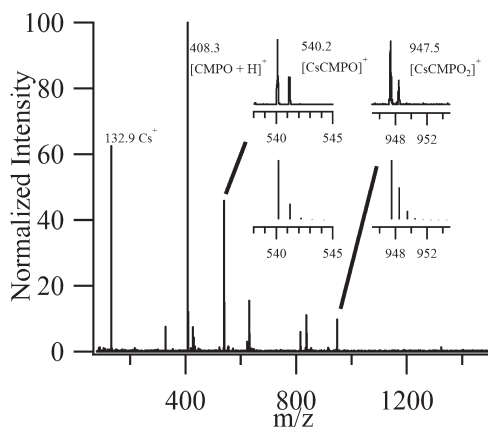


Fig. 3. Mass spectrum recorded through direct injection of an emulsified biphasic solution containing 100 mM of CMPO in the DCE phase and 20 mM of CsNO₃ in the aqueous phase. Inset, above are magnified sections of the mass spectrum whilst below are calculated isotopic distributions for [CsCMPO]⁺ (540.2 m/z) and [CsCMPO₂]⁺ (947.5 m/z).

that the mechanism of IT changes from hemispherical, or diffusion controlled, to linear, or consumption controlled; this is the primary reason that the reverse wave is peak-shaped and not sigmoidal as in the case of the w|DCE interface.

The IT of TBA⁺ was used as the internal reference, with $\Delta_{IL}^w \phi_{TBA^+}^0 = -0.173$ V, according to the TATB assumption [56,57]. The formal IT potential of TBA⁺ at the w|P₆₆₆₁₄TB interface was determined relative to the IT of tetramethylammonium [19]. The TBA cation was chosen as it transfers towards the negative end of the PPW and, therefore allows for better observation of the possible Cs⁺-FIT peaks. Nitrate ion transfer has been used previously [14] for the study of rubidium FIT; however, employing only CsNO₃ in the aqueous phase resulted in a physical instability in the ITIES when scanning to more negative potentials. Additionally, CsCl afforded a wider PPW as Cl⁻ transfer is more negative.

Utilizing the same strategy employed at the w|DCE interface, the initial ligand concentration was then altered from 27 mM to 48, 62, and 82 mM for traces b, c, d, and e in Fig. 4 and, after the addition of the CMPO, a new peak appears with half-wave potentials at 0.243, 0.203, 0.166, and 0.131 V, respectively. Analogous to the w|DCE case, increasing the ligand concentration lowers the amount of applied potential required to elicit charge transfer. Using Eq. (4), with $\Delta_{IL}^w \phi_{Cs^+}^0$ equal to 0.518 V [47], the effect of $-\frac{zF}{RT}(\Delta_{IL}^w \phi_{CsCMPO^+}^0 - \Delta_{IL}^w \phi_{Cs^+}^0)$ versus $\ln(c_{CMPO}^*)$ was developed and illustrated in Fig. 5. Linear regression analysis revealed a satisfactory fitting with an R^2 of 0.9196, a slope of 3, and a y -intercept of 21.65.

This is interesting as it indicates 3 CMPO molecules participated in the interfacial complexation reaction, which translates to a higher overall complexation constant. Unfortunately, the high

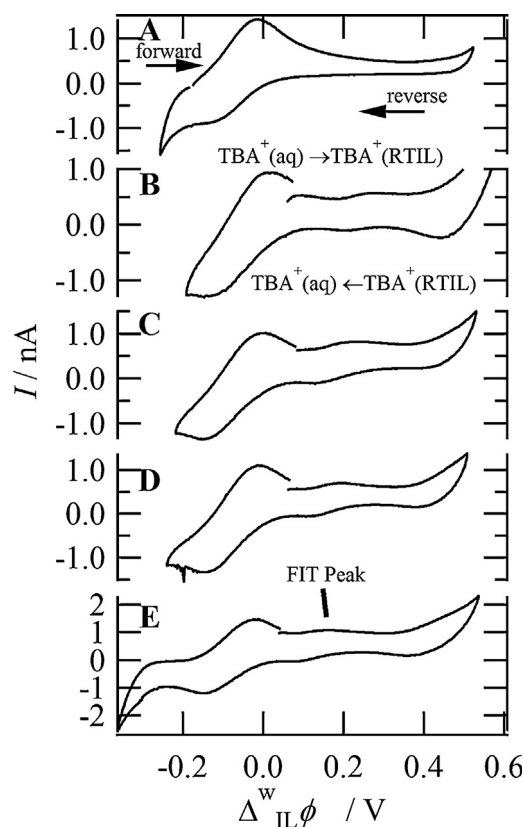


Fig. 4. Cyclic voltammograms (CV) obtained using Cell 2 with CMPO concentrations (y) of 0, 27, 48, 62, and 82 mM for traces a, b, c, d, and e, respectively. Instrument parameters included a scan rate of 0.020 V s⁻¹, an initial potential of ~ 0.000 V, and a potential range from approximately -0.250 to 0.575 V. All CVs have been calibrated using the TATB assumption and the simple IT of TBA⁺; $\Delta_{IL}^w \phi_{TBA^+}^0 = -0.173$ V.

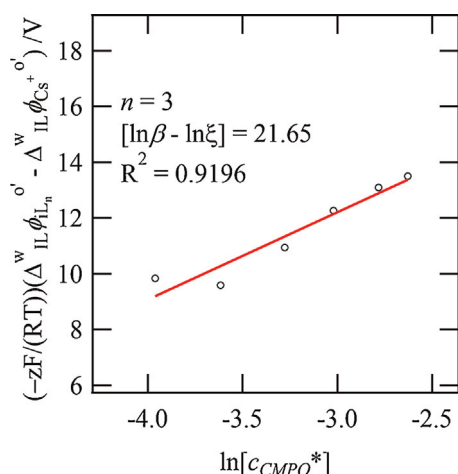


Fig. 5. Plot of $-zF/(RT)(\Delta_{IL}^w \phi_{IL_n}^{o'} - \Delta_{IL}^w \phi_{Cs^+}^{o'})$ versus $\ln[C_{CMPO*}]$ with, inset, linear regression data for the slope (i.e., metal to ligand, 1:n ratio, $n=3$), y-intercept relationship $[\ln\beta + \ln\xi] = 21.65$, and $R^2 = 0.9196$.

viscosity of the IL phase means the diffusion coefficient ratio found in the final term of Eq. (4) cannot be ignored. Previous studies of ferrocene diffusion in conventional electrochemistry [19] provide an estimate for the ξ term with a D_{IL} equal to $5.0 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, while D_w was estimated to be $2.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. Ferrocene, an organo-metallic compound, provides a facile analog for the metal ion–ligand complex and its diffusion coefficient was used as an approximation for the metal ion–ligand complex in the IL phase [19]. In this way, the overall complexation constant, for CsCMPO_3^+ , was calculated to be 1.6×10^{11} . The relatively high stoichiometry, $n=3$, points to a possible octahedral ligand coordination geometry to reduce steric hinderance between ligands. This is a common metal ion:ligand ratio, along with n equal to 2, for alkali, alkali earth, and even heavier lanthanide metals undergoing complexation with CMPO [12,59].

Additionally, the Cs^+ wave is not as high as expected from relative high Cs^+ concentration. Scan rate experiments were then performed in order to determine the diffusion limiting species. For the case of Cs^+ -FIT, these data indicated that diffusion of the ligand to the interface is limiting. Details of these experiments have been provided in the electronic Supplementary Material.

Traditionally, metal ion extraction is evaluated through distribution ratios [17,18,25], for example through the following:

$$\delta_\alpha = \frac{[\text{Cs}_{IL}^+]}{[\text{Cs}_{aq}^+]} \quad (5)$$

where a theoretical δ_α can be determined using the kinetic/thermodynamic parameters described herein and by Eq. (6):

$$K_{n,\alpha} = \frac{c_{IL_n,\alpha}}{c_{IL_{(n-1)},\alpha} c_{L,\alpha}} \text{ or } \beta_\alpha = \frac{c_{IL_n,\alpha}}{c_{L,\alpha}^n} = \prod_{j=0}^n K_j \quad (6)$$

In this way, $(c_{L,\alpha})^n \beta \approx \delta_\alpha$ and a general comparison can be made such that the distribution ratio for the w|DCE is only 2 at the highest ligand concentration, but 8.2×10^7 for the w|IL case.

Interestingly, this result seems to demonstrate that Cs-FIT at the w|P₆₆₆₁₄TB interface using CMPO as a ligand, has some benefits relative to w|DCE complexation. First, a lower applied potential to elicit metal ion complexation is a serious advantage as this means less energy needs to be applied to the system in order to achieve separation. Additionally, the high w|IL complexation constant reveals a substantial theoretical distribution coefficient, that also suggests improved efficiency.

However, 3 equivalents of ligand are required at the w|P₆₆₆₁₄TB interface versus only 1 at w|DCE. This is in contrast to recent

studies surrounding rubidium [14] and strontium [12] which demonstrated a marked improvement for the w|IL versus the w|DCE system. Critically, this points to a possible advantage in selectivity towards Rb^+ and Sr^{2+} versus Cs^+ that could be capitalized upon for SNF reclamation.

4. Conclusions

A model system for biphasic metal ion extraction was developed, comprised of the ionic liquid P₆₆₆₁₄TB. This IL was chosen owing to the excellent electrochemically stable cation/anion pair that have been shown to possess weak ion-pair interactions and extreme hydrophobicity. FIT of Cs^+ with CMPO, a common ligand employed in industrial SNF recycling, was studied at an IL interface electrochemically and compared to the well established w|DCE interface. The former elicited a metal ion to ligand (1:n) stoichiometry of 1:3 with an overall complexation constant, β , estimated to be 1.6×10^{11} , while the latter demonstrated an n equal to 1 with β equal to 86.5. Previous results showed higher complexation constants for strontium and rubidium at the w|P₆₆₆₁₄TB interface. This may suggest a higher selectivity for these ions over cesium using this biphasic system.

The CsCMPO stoichiometry at the w|DCE interface was confirmed through the use of ESI-MS and a ‘shake-flask’ experiment.

5. Supplementary data

Scan rate experiments at the w|IL micro-interface.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.aca.2014.03.012>.

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