



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



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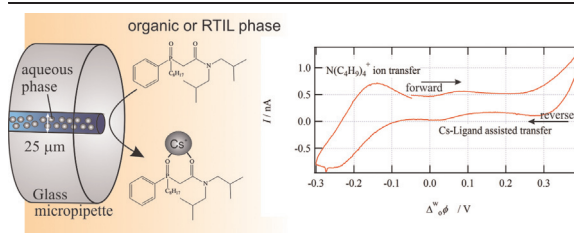
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HIGHLIGHTS

- 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 alkyldiisobutylphosphonium (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,

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