The Phase Transport and Reactions of γ-Irradiated Aqueous-Ionic Liquids

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ABSTRACT

The capability of dissolving a wide range of substrate molecules and the resistance to radiation fields make ionic liquids (ILs) promising media for nuclear fuel reprocessing. If ILs are used in this reprocessing, the stability of the ionic liquid and the phase which it is in contact with in a radiation field is of utmost concern. Biphasic-reactions and transport processes can alter the radiation stability of the IL. ILs, in contact with an aqueous or gas phase, are irradiated in a ^{60}Co γ-irradiation cell and studied using the AC impedance method, Raman spectroscopy, and GC/MSD methods to study the gas and aqueous speciation occurring in radiated samples.

1. Introduction

Due to environmental concerns, there is renewed interest in nuclear power generation. However, this raises the issue of a potential shortage in nuclear fuel. Today, nuclear separation technology uses the liquid-liquid extraction process to separate actinides from fission products. Many difficulties arise in regards to the reprocessing of spent fuel. Spent nuclear fuel contains a large amount of fissile and fertile material. With an appropriate moderator, such materials have the opportunity to spontaneously fission, resulting in a nuclear explosion (criticality). However, although the potential for criticality does exist, if spent fuel has an appropriate amount of neutron poisons the likelihood of such a situation arising is decreased. A second issue arises from the radioactive fission products present in the spent fuel. These products are very radioactive and emit large quantities of radiation. Thus, the solvent in contact with the fuel must be relatively radiation resistant. Thirdly, the separation of actinide elements from lanthanide elements is very difficult due to the wide variety of oxidation states possible.

In regards to separation technologies, the efficiency of liquid-liquid separations is greater than most separation methods [1]. The Plutonium Uranium Extraction (PUREX) process separates the plutonium and uranium from spent nuclear fuel. The process begins by dissolving spent nuclear fuel in nitric acid. Following this dissolution, uranium and plutonium are transferred to an organic phase composed of 30 % tributyl phosphate and kerosene. However, this separation can be problematic in two ways: (1) these fissile nuclides have the potential be used to create nuclear weapons; (2) volatile organic compounds (VOCs) are required for the separation, which are toxic and very flammable [1].

Ideally, a new separation technology could be developed using an alternative solvent. A solvent used in nuclear waste extraction would possess a number of properties: (1) a high intrinsic specificity for trans-U actinides over lanthanides and other fission products, (2) a high yielding synthetic route, (3) thermal, radiation and chemical stability, (4) an efficient switching mechanism (in terms of complexation and decomplexation) and (5) a high immiscibility with aqueous solutions. These characteristics must be maintained in the chemical, radiation and mass transport environments in which the separation process takes place.

As of recent, the use of ionic liquids (ILs) in applications such as synthesis, catalysis, separations, and electrochemistry has grown [2]. ILs are non-flammable, non-explosive liquids that, in comparison to many conventional organic solvents, would be safer to work with [2]. The capability of dissolving a wide range of substrate molecules and the potential for being highly resilient in energy intensive environments (such as radiation fields) make room temperature ionic liquids (RTILs) particularly promising media for the separation and sequestration of metal ion contaminants from radioactive waste effluents in the nuclear fuel cycle.

Room temperature ionic liquids are salts that have a melting point below 100ºC [2]. These liquids typically are composed of a large, organic cation, and variable anions. The cation and anion combinations allow for an almost negligible vapour pressure, high thermal stability, and various rheological properties [1]. By altering the combinations of cation and anion pairs, different "tuned" properties of ILs can be achieved. Such tuneable properties include: hydrophobicity, miscibility with other solvents, polarity, density, viscosity, and the ability to dissolve metal ions [2].

Previous papers have discussed the separation of metal species from aqueous solutions using ILs [3]. Thus, ILs have the potential to separate the actinide elements from the lanthanides and other lower mass elements. An ideal separating agent should incorporate a metal ion-ligating functional group, and act as a hydrophobic solvent and extracting agent [4]. However, if ILs are to be used in the process of nuclear fuel reprocessing, the stability of the IL in a radiation field is of utmost concern.

Today, studies indicating how radiation will affect the water/ionic liquid biphasic systems, and the chemical and physical parameters affecting the phase separation are rare. Although pulse radiolysis techniques have been previously used [5] to study these ionic liquid systems, they are not effective for studies with slow interfacial reactions. When in contact with fission products from spent fuel, liquids will be exposed to a continuous source of radiation. Under continuous irradiation conditions radiolytic decomposition products of water and ILs will be continuously produced. However, these products will also undergo various reactions with each other as well as solvent molecules. Quickly the chemical speciation in each phase will reach a pseudo-steady state. The pseudo-steady state speciation will dictate the slow interfacial reactions occurring.

For these applications, we are developing a novel separation technology based on the transfer of chemical species through complexation at water/IL interfaces. The separation efficiency of the biphasic system will depend on many parameters including the aqueous oxidation state of the targeted metal ion, its interfacial transport, and metal-ligand complex formation at the water/IL interface or in the IL phase. The facilitated ion transfer across the interface (driven by interfacial complexation) is being studied using microdimensional interfaces to determine ion transfer potentials and kinetic parameters due to interfacial complexation. The most uncertain and unstudied area for these applications is the effect of ionizing radiation on the stability and separation efficiency of biphasic systems.

There have been no studies on the radiation stability of phosphonium-based ionic liquids which are known to have good thermal stability [6]. This study examines the radiation-induced physical and chemical changes of gas-ionic liquid and water-ionic liquid systems that are exposed to steady-state (gamma) irradiation. The phosponium based IL trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide was examined, and will be referred to as the imide IL hereafter. The chemical structure is shown in Figure 1. IL in contact with the gas phase (either argon or air) or with the aqueous phase (argon or air purged) was exposed to γ-irradiation over various lengths of time at a dose rate of 6.4 $kGy \cdot h^{-1}$. The gaseous samples were analyzed by Gas Chromatography – Mass Selective Detector (GC-MSD) for airborne radiolytic decomposition products whereas the radiation induced changes in the ionic liquid phase or water phase were followed using conductivity and Raman spectroscopy.

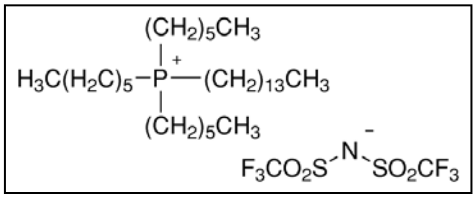

Figure 1 The structure of the IL trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide.

2. Experimental

The phosphonium IL sample trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl) imide, purchased from Sigma-Aldrich, was of the highest purity (>95%). The purity of the samples and the presence of any moisture content were verified using electrospray ionization mass spectrometry (ESI-MS) and differential scanning calorimetry (DSC) analysis. The water samples in contact with ILs were prepared with water purified from a NANOpure Diamond UV ultrapure water system (Barnstead International) with a consistent resistivity of 18.2 $M\Omega \cdot cm$. Samples were placed inside 10 mL headspace vials (Agilent Technologies) and sealed with aluminum crimp caps with PTFE/silicone septa. The deaerated samples were purged with ultra high purity argon (Praxair, 99.99% purity), whereas aerated samples were purged with hydrocarbon free air for 20 minutes prior to irradiation.

Irradiation was conducted in a ^{60}Co gamma cell (MDS Nordion), with a uniform dose rate of 6.4 $kGy \cdot h^{-1}$. At set time intervals samples were removed from the irradiation chamber for analysis. The gas phase was analyzed for volatile decomposition products using GC-MSD, and the aqueous phase and IL layer were analysed using conductivity measurements and Raman spectroscopy.

The conductivity of IL or water was measured using the complex impedance method (BioLogic Science Instruments MCS 200). This method involves measurements of the cell impedance as a function of AC potential frequency ranging from 1 Hz to 200 kHz.
Raman scattering measurements were performed using the Renishaw model 2000 Raman Spectrometer with a laser excitation wavelength of 633 nm. Spectra were recorded for the IL layer and the water layer for non-irradiated and irradiated samples with the laser focused perpendicular to the side of the sample vial.

3. Results

3.1 Ionic liquid in contact with gas phase

3.1.1 GC-MSD

The airborne products in the gas phase formed by the radiolytic decomposition of the ILs were analyzed as a function of irradiation time using GC-MSD. The complete analysis of all the peaks was not performed at this stage, but some of the key products were identified, including ethane (C_2H_6), hexafluoroethane (C_2F_6), fluoroform, (CHF_3), and hexane (C_6H_{14}). These fragments were detected independent of irradiation time.

There was no noticeable trend or time dependence of these products as a function of irradiation time, suggesting that the system reaches steady state very quickly. Furthermore, similar decomposition products were identified under argon or air saturation conditions, indicating that O_2 in the gas phase is not effective in controlling the radical reactions at the interface.

3.1.2 Conductivity

The change in the conductivity of ionic liquid due to exposure to γ-irradiation, with a dose rate of 6.4 $kGy \cdot hr^{-1}$, while in contact with the gas phase was monitored as a function of irradiation time, Figure 2. The conductivity of the IL decreased gradually in the first few hours of irradiation before levelling off.

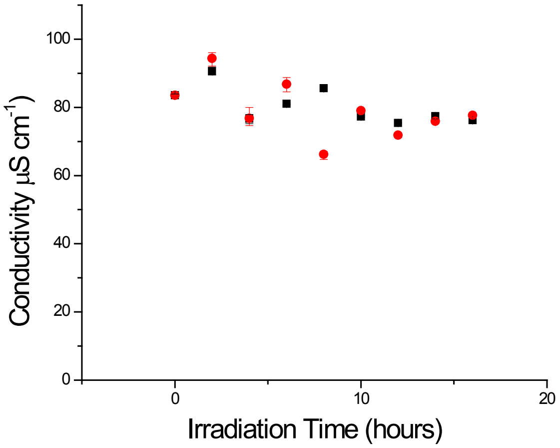

Figure 2 Conductivity of the imide when in contact with the gas phase as a function of irradiation time; ■ imide in contact with air, ● imide in contact with argon.

The change in conductivity due to irradiation was independent of cover gas, indicating that the reactions at the interface and the IL-gas interfacial transfer do not significantly affect the bulk phase property, consistent with the airborne decomposition products observed by the GC-MSD analysis.

3.1.3 Raman spectroscopy

The Raman spectra of the IL taken prior to and after 8 hours of irradiation are compared in Figure 3. The spectra also show negligible changes in the IL phase due to irradiation. Both the aerated and deaerated spectra (not shown) illustrate similar results.

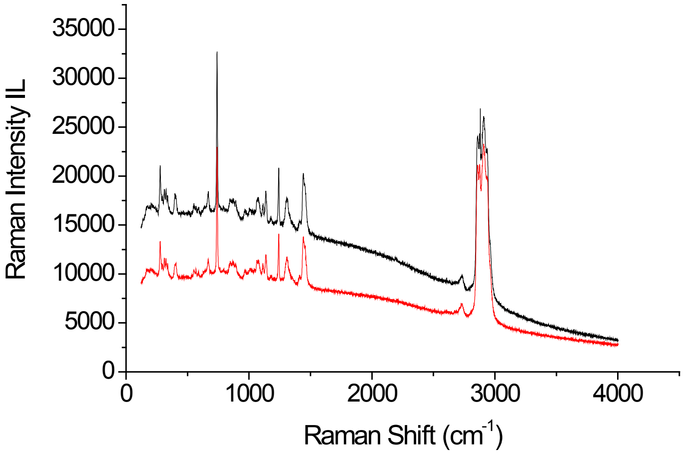

Figure 3 Raman spectra of aerated non-irradiated (-) and aerated irradiated (-) imide samples.

3.2 Ionic liquid in contact with water

3.2.1 Conductivity

The radiation stability of IL in contact with water was studied. Figure 4 shows the changes in conductivities of the imide IL and water phases due to γ-irradiation, where the irradiation was conducted on the imide IL in contact with water under air or argon saturated conditions. Also shown in the figure are the conductivities of the non-irradiated samples of both phases as a function of contact time. The imide IL is hydrophobic when in contact with water, it forms and remains as a distinctive layer below the water layer over an extensive period.

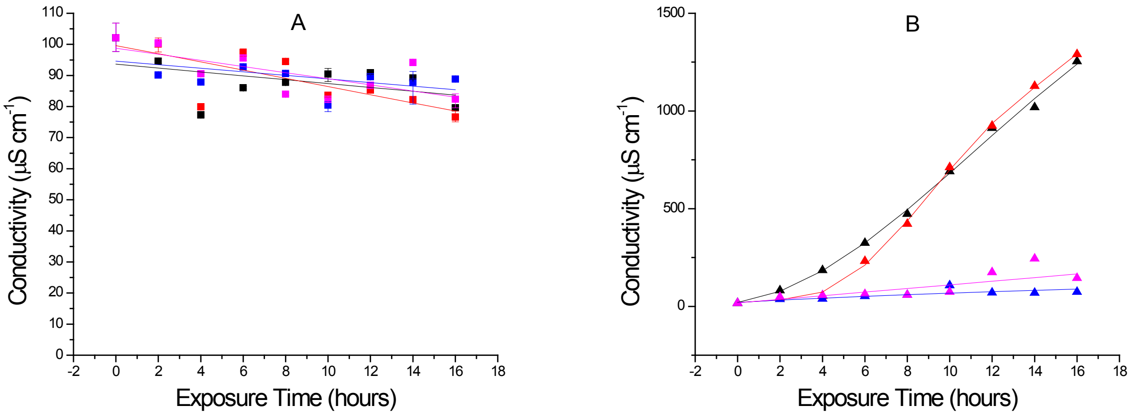

Figure 4 Conductivity as a function of reading number of (a) the imide ionic liquid layer and (b) the water layer in contact with the imide; ■/▲aerated and irradiated, ■/▲ deaerated and irradiated, ■/▲aerated only blank, ■/▲ deaerated only blank.

The conductivity of the imide IL layer in contact with water gradually decreased with time even in the absence of irradiation, possibly due to some mixing of the IL and the water phases. The additional change in conductivity due to irradiation was difficult to quantify due to large scattering in the data. The comparison of Figure 2 with Figure 4a suggests that there is no significant difference in the IL-phase conductivity between the imide samples irradiated while in contact with the gas and water phases. The effect of radiation can be better appreciated from the conductivity of the water layer, Figure 4b. The conductivity of the water layer of the irradiated imide-water samples also shows a significant increase with time, compared to a much smaller increase observed for the non-irradiated samples.

3.2.2 Raman spectroscopy

The Raman spectra of the IL and the water layers of the irradiated samples are compared with those of non-irradiated samples in Figure 5. The Raman spectra of the imide IL phase shows no significant changes in the positions or the shapes of the well-defined peaks, except the difference in the background observed. The development of a broad peak with irradiation can be clearly seen in the Raman spectra of the water phase shown in Figure 5b. The intensity of the broad band increased with irradiation time, similarly as the increase observed for the conductivity of the water phase with irradiation time.

What contributes to the broad peak has not been clearly established. However, the aggregates formed in the water layer are considered to be responsible.

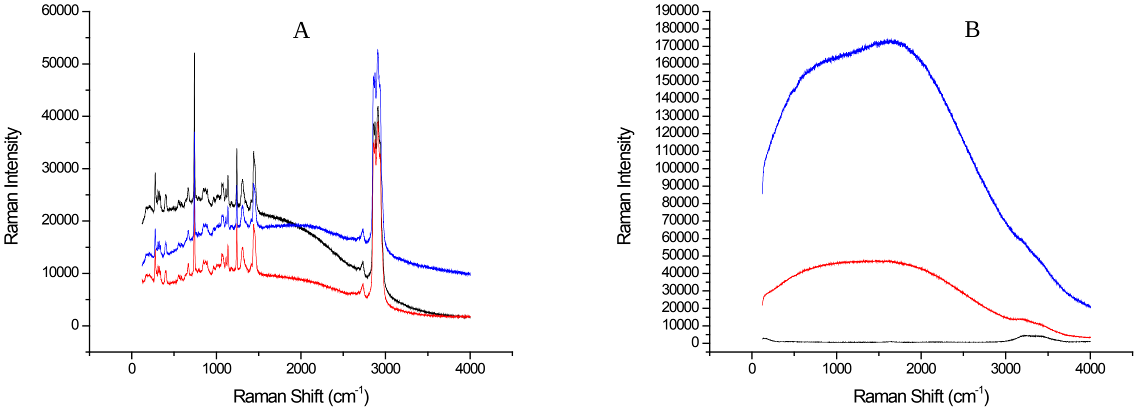

Figure 5 Raman spectra of the imide IL layer in contact with the aqueous layer; (a) imide IL layer and (b) water layer for (—)non-irradiated, (—) 6h irradiated, and (—) 18h irradiated.

4. Discussion

The effects of γ-irradiation of the gas-IL systems observed by the GC-MSD and conductivity measurements are consistent with the expectation from the current understanding of the interaction of ionizing radiation with matter. The radiolytic products detected and identified in the gas phase are the smaller decomposition products of the ILs with higher vapour pressures. For example, the hexane fragments observed can be attributed to radiolytic fragmentation from the alkyl chains on the cation.

The cover gas composition has very little effects on the gas speciation. Being a good radical scavenger, oxygen would quickly react with organic radicals forming ketones and aldehydes. No effect of cover gas on the gas speciation thus strongly suggests that the radiation induced reactions at the gas-IL interface region are negligible. This further supports the claim that the gaseous species are the result of the radiolytic decomposition of the bulk phase IL, which then transfers to the gas phase.

The conductivity and Raman spectroscopy results indicate that the ILs in contact with gas phases are relatively radiation resistant, as expected. The small decrease in the conductivity of the imide IL due to irradiation is attributed to the polymerization and/or crosslinking of the organic ligands. Polymerization or crosslinking of the organic ligands can occur in the IL phase, but their products will not be transferred to the gas phase. In addition to the smaller probability of escaping geminate reactions, the diffusion of free radicals and ions in the bulk IL phase is also more restricted in a more viscous IL, promoting polymerization to the formation of smaller products in a more viscous medium. The formation of a larger anion or cation moiety would decrease the conductivity of the IL, and its effect would be more significant in a more viscous IL. A schematic representation of the potential processes occurring in the ionic liquid in contact with gas phase is shown in Figure 6.

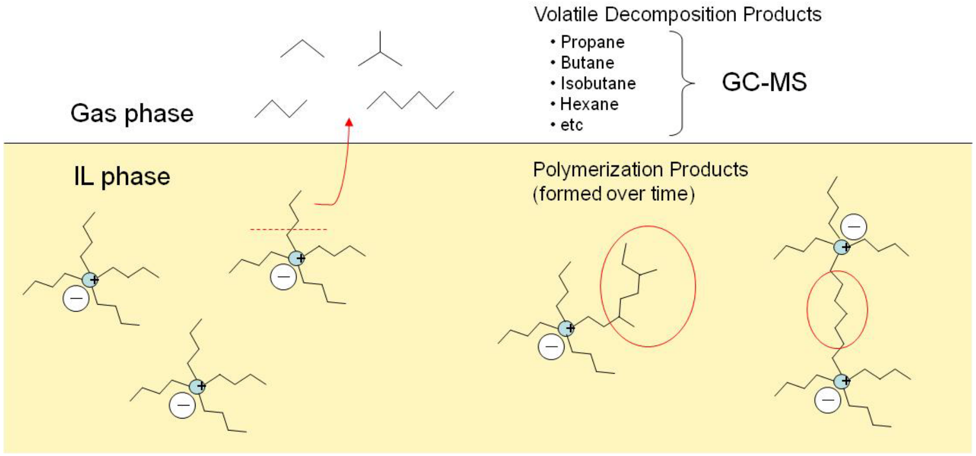

Figure 6 Schematic of the recombination of fragments produced from irradiation of ionic liquid in contact with gas phase.

The effect of γ-irradiation on the IL conductivity of the imide IL is not only independent of the cover gas composition, but also independent of whether the IL is in contact with a gas or aqueous phase, consistent with the above claim that the change in the bulk IL phase is relatively small.

Decreases in the conductivity of the IL layer can be attributed to the accumulation of neutral species, which can join together to form large aggregates in solution. Hydrated electrons formed in the water layer as a result of radiolysis could quickly diffuse into the ionic liquid layer and combine with the cations to form neutral species at the IL-water interface. The accumulation of neutral species, containing both hydrophobic and hydrophilic regions, could aggregate in a manner where the hydrophobic areas of the neutral species can escape the proximity of water. This aggregation is similar with that of metal ions following irradiation in water [7].

The observation that the IL conductivity is not significantly affected by irradiation (Figure 4) is consistent with the expectation of the small net radiolytic decomposition. Although the homogeneous reaction kinetics of solvated electrons and other primary radiolytic products in the IL phase have not been studied, the small yield of solvated electrons and the strong coulombic field existing in the IL phase suggests that the net radiolytic products under long-term radiolysis should be small. Irrespective of the type of product formed, the net yields of the radiolytic decomposition products of the studied phosphonium-based ILs was too small to be observed by Raman spectroscopy: no new peaks, or changes in the positions and the relative intensities of the well-defined peaks were detected (Figure 5).

The increase in the conductivity of the water layer under both irradiated and non-irradiated conditions indicates the transfer of species from the IL phase to the water layer. Under the radiation field this transfer in further enhanced. The irradiation performed likely increases the mixing that is occurring between the ionic liquid and the aqueous phase. It is believed that the ionic liquid is not incorporating itself with the aqueous layer because there is no change in peaks in the Raman spectra of the ionic liquid between different irradiation times. From the Raman spectra and the conductivity it is known that there is little breakdown in the ionic liquid layer itself.

The mixing theory is further supported by the size of the particles detected in the aqueous layer. In non-irradiated samples the particle size detected in the aqueous layer is approximately 100 nm to 120 nm. In those samples that were irradiated the particle size is much smaller, ranging between 10 nm to 30 nm on average. This indicates that irradiation is not responsible for the transfer of species between layers because transfer occurs in the absence of radiation. However, radiation is able to produce smaller fragments and radiolytic products which can transfer phases more easily than the larger species observed in the non-irradiated samples.

5. Conclusions

This work has provided insight regarding the radiation stability of ionic liquids in contact with water. The radiation stability of trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide is good under both air and argon conditions. The gas phase analysis of both the air and the argon saturated samples as the cover gas showed similar products. Conductivity measurements illustrated a similar trend showing that O_2 does not play key role in the radiolysis of ILs.

In the case of the system in contact with water, water radiolysis produces reactive species at a greater extent, which can interact with the IL phase. Additional changes occur when the ionic liquid is in contact with water than when it is in contact with gas, as water can be mixed with the ionic liquid layer to a certain extent, which could be accompanied by an increase in the area of contact of the ionic liquid to reactive radiolysis species formed in water. The mixing occurs with and without irradiation of the sample. However, based on conductivity results and Raman spectra, the irradiated samples seem to have an increased rate of mixing, which could be beneficial in the separation process. The mixing may assist in the separations process, allowing for a larger surface area to complete the separations process.

The changes in conductivity and Raman spectra due to irradiation were explained using a theory of aggregates forming. Aggregates may be formed as a result of the migration of hydrated electrons produced by water radiolysis into the ionic liquid layer, which can combine with the IL cation, resulting in neutral species that can form clusters.

As to whether ILs are stable enough under radiation to be properly used as solvent for nuclear waste effluents, further research is required. This project shows that the effect of radiation on ILs depends on the phase that the IL is in contact, and for the application of ILs to biphasic separation, the radiation stability of the IL must be evaluated under irradiation of the biphasic system, and not of the pure IL phase only.

6. References

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