The Radiation Stability of Organic Ionic Liquids in Biphasic Systems

S.E. Howett, J.J. Noël and J.C. Wren
University of Western Ontario, London, Ontario, Canada
(jjnoel@uwo.ca)

Abstract

Theinfluence of γ-radiation on the stability of biphasic water/ionic liquid (IL) and gas/IL systems was studied. The behaviours of two phosphonium-based ionic liquids with the same cation and differing anions were compared. Exposure to γ-radiation did not significantly impact ILstability, but it did speed up processes that occurred even in the absence of radiation. The two most significant effects of irradiation were the promotion of faster emulsion layer formation and the precipitation of a fine white solid. Precipitate formation could be deleterious,whereas emulsion layer formation could be either beneficial or detrimental,inan IL-basedseparations process.

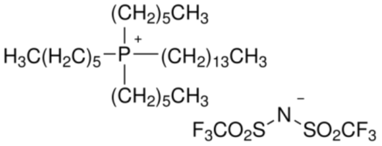
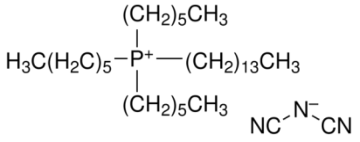
1. Introduction

Though not particularly new, ionic liquids (ILs) are gaining increased recognition as media suitable for use in syntheses, electrochemical applications including solar cells, batteries, sensors, as well as separations [1-5]. With their "tunable" properties, ionic liquids can be considered'designer solvents'. They are liquid at room temperature, making them solvents of choice for use in place of conventional organic solvents in many applications [6-8]. In particular, the ability of ILs to dissolve a wide range of molecules, and their high resilience in energy-intensive environments (such as high-energy radiation fields), make ILs promising media for the separation and sequestration of metal ion contaminants from radioactive waste effluents in nuclear fuel cycles.

A separations process that works through the complexation and transfer of metal ions across an aqueous-IL interface is being considered for nuclear fuel reprocessing and treatmentof waste streams containing heavy metal ions. In a nuclear fuel reprocessing application, the separation fluids would be exposed to a continuous ionizing radiation field. It is important to understand how this ionizing radiation can affect the stability of the ionic liquids present and the ability of the biphasic system to extract metal ionseffectively.

This work examines the effect of γ-radiation on the physical and chemical changes in two gas/IL and water-/IL systems. Two phosphonium-based ILs were studied: trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)amide (hereafter referred to as the amide-IL) and trihexyltetradecylphosphonium dicyanamide (hereafter referred to as the dicyanamide-IL). Despite containing the same cation, the two ILs have considerably different physical properties. Their chemical structures can be found in Table 1.

Table 1 The chemical structures of the ionic liquids and their respective radiolytic decomposition products detected in the gas phase.

Ionic Liquid	amide-IL	dicyanamide-IL
Structure		
Gaseous Products Detected After Radiation Exposure	Ethane (C_2H_6) Hexane (C_6H_{14}) Hexafluoroethane (C_2F_6) Fluoroform (CHF_3)	Dichloromethane (CH_2Cl_2)

Of the different forms of ionizing radiation, γ-radiation should generate the most important effects. The effects of electron or β-radiation should be very similar to those of γ-radiation, except that the penetration through the condensed medium will be lower. The production of molecular products is favoured by α-radiation due to the small interaction volume, so recombination leaving unchanged ILs should dominate in this case. Finally, neutrons do not interact with electrons and should have little radiolytic influence on ILs.

2. Experimental

The ionic liquids were purchased from Sigma-Aldrich (purity ≥ 95%). Purified water from a NANOpure® Diamond UV ultrapure water system (Barnstead International) with a resistivity of 18.2 MΩ·cm was used in the tests. Test vials were prepared by placing 2 mL of water and 2 mL of an ionic liquid inside a 10 mL pyrex vial (Agilent Technologies) and sealing the vial with an aluminum crimp cap containing a PTFE/silicone septum. Sealed vials were de-aerated by purging with ultra-high purity argon (Praxair, 99.99% purity) using syringes. The purging was done immediately before irradiating the vials.

Sample vials were irradiated in a ^{60}Co gamma cell (MDS Nordion, model 220) at a fixed dose rate of 5.5 ± 0.5 kGy·h^{-1}, as determined using Fricke dosimetry.Samples were placed inside the gamma cell sample chamber and then lowered into the gamma cell irradiation zone, which consists of 11 tubular pencils containing ^{60}Co and provides a very homogeneous radiation field. Irradiated sample vials were removed from the gamma cell after exposure times ranging from 1 h to 168 h and analyzed immediately. Control samples were also prepared, treated and analyzed in the same way, except that they were held without exposure to gamma-radiation.To ensure that observed differences between irradiated and unirradiated control samples were the consequences of irradiation, we attempted to minimize the period during which the IL and water were in contact with each other outside of the radiation field. For irradiated samples, this contact time was ~25 min pre-irradiation and ~5 min post-irradiation, which in total was much less than the typical irradiation time.

Immediately after irradiation, gas phase analysis was performed by extracting an aliquot of gas from theheadspace above the liquids in the test vial using a gas-tight Luer lock syringe (Agilent

Technologies). These gas samples were injected into a gas chromatograph with a mass spectrometer detector (GC/MSD, Agilent Technologies 6890 N Network GC System with 5973 Network Mass Selective Detector). A 60 m long GS-GASPRO column with an internal diameter of 0.36 mm, with helium as the carrier gas,was used for the separation.

A frequency response analyzer (Solartron, model 1260), operated as a stand-alone instrument, was used to make conductivity measurements on the liquid components of the samples. ZPlot® software (Scribner Associates) was used for experimental control. The conductivities of the aqueous and IL phases of our samples were determined from electrochemical impedance spectroscopy (EIS)measurements, performed over a frequency range of 1 Hz to 1 MHz in a specialized conductivity cell. This consisted of a quartz cuvette with two parallel electrodes made of glassy carbon. The conductivity cell constant was determined prior to each set of experiments using KCl solutions of known conductivity [9], and was experimentally determined to be 10.6 cm^{-1} at the time of experiments with the amide-IL, and 11.0 cm^{-1} at the time of experiments with the dicyanamide-IL.Previous studies examining the effect of γ-radiation on water alone have shown that γ-radiation causes no measurable increase in the conductivity [10].

Infrared spectroscopy was performed on IL samples extracted during the experiments using a Fourier transform infrared spectrometer (FTIR,Bruker). Samples were prepared for FTIR analysisby mixing liquid aliquots or solid precipitate with spectroscopy grade KBrand using a press to form pellets.

As the duration of the tests lengthened, some interesting behaviourwas observed. This included the development of an emulsion layer between the two phases (in the case of the amide-IL tests) and the appearance of a fine white precipitate (in the case of the dicyanamide-IL). To further investigate the identity of these phases, samples from the aqueous phase were collected and imaged using a transmission electron microscope (TEM,Philips EM 200) operating at 100 keV. Sample preparation involved placing aliquots of the aqueous phase on carbon-coated copper grids and allowing them to air dry at room temperature. ImageJ software was used for the size measurement of any particles observed.

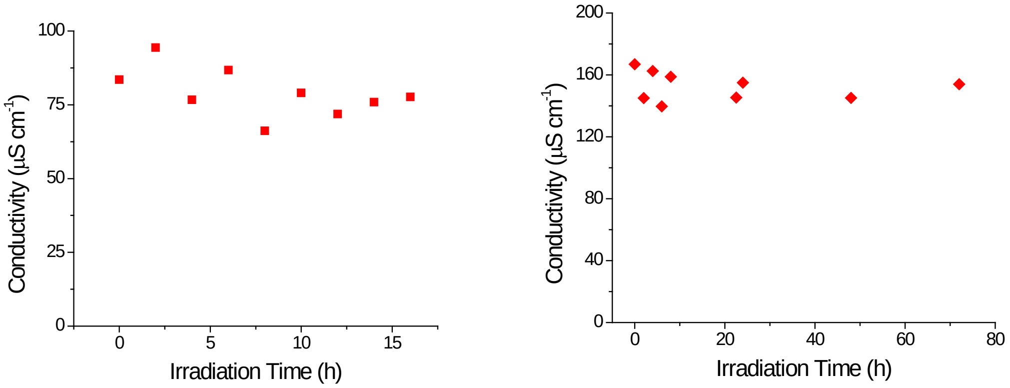
3. Results

3.1 Ionic Liquids in Contact with Argon Gas

Gaseous species presentin the headspace of test vials initially containing only an ionic liquid sample, after irradiation, were identified using the GC/MSD and are listed in Table 1. Previous experiments have indicated that similar radiolytic decomposition products are produced, regardless of whetherthe gaseous environment is aerated or deaerated [10]. The absence of oxygenated organic gaseous species indicates that reactions at the gas/IL interface contributelittle to the radiolytic degradation. For this reason, only deaerated samples were investigated.In the case of the amide-IL, the gas phase products identified include ethane (C_2H_6), hexafluoroethane (C_2F_6), fluoroform (CHF_3), and hexane (C_6H_{14}). The presence of these species can be attributed to radiolytic decomposition of the IL, and their volatility accounts for their transfer into the gas phase. Only one gaseous organic species,dichloromethane (CH_2Cl_2), was identified in the gas in contact with the dicyanamide-IL.

Dichloromethane was a somewhat surprising find, since the dicyanamide-IL does not contain chlorine atoms and therefore cannot yield dichloromethane as a radiolysis product. However, the dichloromethane is likely residual from the synthesis of the dicyanamide-IL;in the synthetic process, the dicyanamide-IL is washed with dichloromethane on a column, and even the best ILs from chemical suppliers invariably contain traces of impurities. The volatility of this organic solvent allows it to transfer easily into the gas phase above the IL, and its amount is consistent with the grade of chemical available (95% purity).

Changes in the IL phase during irradiation were monitored using electrochemical impedance spectroscopy (EIS) measurements to determine the conductivity, Figure 1. Of the two ILs studied, the amide-IL had the lower conductivity. In contrast, the dicyanamide-IL had a higher conductivity, ~150 μS·cm^{-1}, a value that is consistent with the findings of Vaughan et al. [11]. Although there was some scatter in the conductivity values for both ILs, neither showed a significant change in conductivity with irradiation time. This finding is in accordance with other studies of ILs irradiated and in contact with a gas phase [12, 13].


(a)

(b)

Figure 1 Conductivity as a function of irradiation time for(a) amide-IL and (b) dicyanamide-IL samples.

3.2 Ionic Liquids in Contact with Water

The stability of bothILsin contact with an aqueous phase was studied. Of the two ILs, the dicyanamide-IL is the more conductive and slightly less viscous [14, 15]. Furthermore, the dicyanamide-IL is less dense than water, allowing it to floatatop the water layer in the two-phase system. In contrast, the amide-IL is denser than water and forms a layer below the water layer.

3.2.1 Trihexyltetradecylphosphonium dicyanamide

Contact with water induced the same conductivity changes in the IL layer of both irradiated and un-irradiated systems,as seen in Figure 2a. The initial conductivity of ~150 μS·cm^{-1} increased sharply with increasing time of exposure to water, leveling off at 300 – 350 μS·cm^{-1}. This steady state was establishedafter ~25 hours of contact.

In contrast, irradiation had a clear impact on the conductivity of the aqueous phase, Figure 2b. The water layer conductivity was initially very low(~10 $\mu S \cdot cm^{-1}$) and, in the absence of irradiation, it increased slowly and continuously over the entire duration of our tests. However, in the presence of radiation, the conductivity of the water layer increaseddramaticallyat an approximately linear rate, rising to ~900 $\mu S \cdot cm^{-1}$ after 100 h of radiation exposure. From previous studies we know that this increase in conductivity cannot be attributed to the irradiation of water alone [10]. Rather, the increase is mostly certainly a consequence of the transfer of ions fromthe IL phase to the aqueous phase.

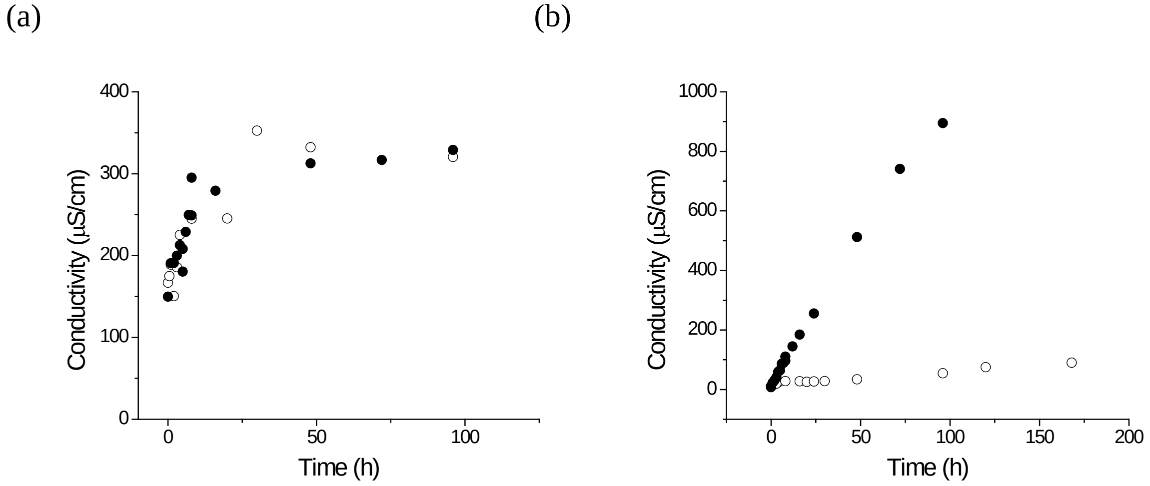

(a) (b)

Figure 2 Conductivity as a function of contact time for the water/dicyanamide-ILsamples: (a) IL layer and (b) aqueous layer. Symbols differentiatedata from ● irradiated and○ unirradiated samples.

After more than 8 h of irradiation,a white precipitate could be seen accumulating in the water/dicyanamide-IL sample. The precipitate settled quickly at the bottom of the vial in theaqueous layer (Figure 3) and neither the water nor IL layers appeared cloudy.

In an effort to determine the identity of the white precipitate, we collected it by taking aliquots containing the white precipitate from the water phase and placing them on glass slides. The water was allowed to evaporate from the slides, then the white precipitate was gentlyscraped from the slides and analyzed with FTIR. The FTIR spectrumof the precipitate and that of the pure dicyanamide IL havesimilarities in the main peaks of dicyanamide-IL (Figure 4), but the precipitate also has additional sharp peaks in the region 1000-1800 cm^{-1} and a broad band centred on ~3300 cm^{-1}. The FTIR peaks indicate that the dicyanamide anion is a main component of the precipitate, while the other peaks are consistent with incorporation of OH^- or water into the precipitate.

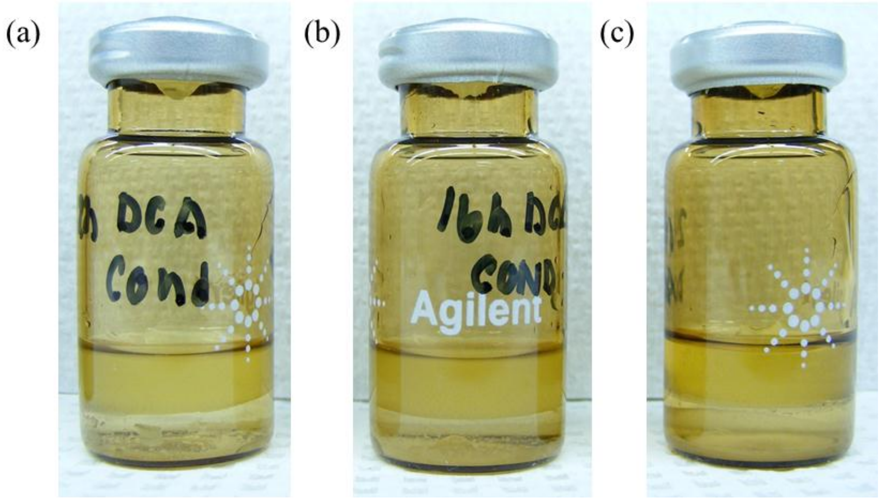


Figure 3   Photographs of vials containingwater/dicyanamide-ILafter irradiation for (a) 12 h, (b) 16 h, and (c) 24 h. The upper layer in the vial is the IL phase and the lower layer is the aqueous phase. A white precipitate can be observed at the bottom of eachvial. The initially colourless glass of the vials has been darkened by radiation exposure.

Particles suspended in the aqueous phase were captured on a TEM grid andimaged with TEM(Figure 5). The TEM micrographs showed a fine particulate, with particles in the nanometer size range (hence their suspension in the aqueous phase).

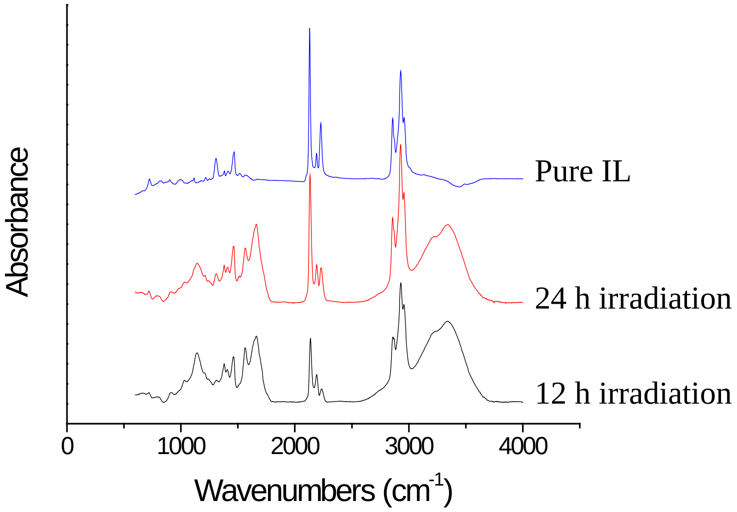


Figure 4 FTIR spectra of pure dicyanamide-ILand of the precipitates formed after irradiation of awater/dicyanamide-IL sample for 12 h and for 24 h.

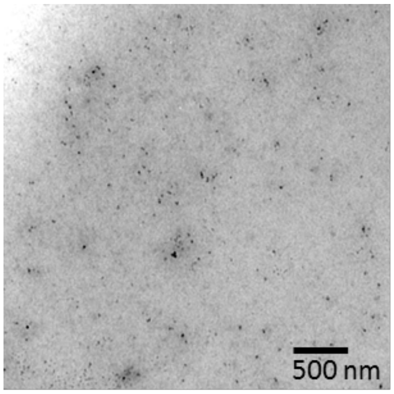


Figure 5 TEM images of particulates in the aqueous phase of the water/dicyanamide-IL systemfollowing 16 h of irradiation.

3.2.2 Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)amide

In the water/amide-IL system, the conductivity of the IL phase showed littlechange from its initial value, regardless of irradiation or contact time; only a very slight decreasing trend over time was observed (Figure 6).Again, as was the case for the water dicyanamide-IL system, the conductivity of the aqueous phaseincreased with time and exposure to radiation.The magnitudes of the changes in the water conductivity were similar for both ILs and the time dependence was similar, although there is a suggestion of an incubation period for the amide-IL before the water conductivity starts to rise sharply with irradiation. The amide-IL tests were run for longer irradiation periods than the dicyanimide-IL tests (more than 150 h) and the increase in the water conductivity continued at a rate that was approximately constant with time.

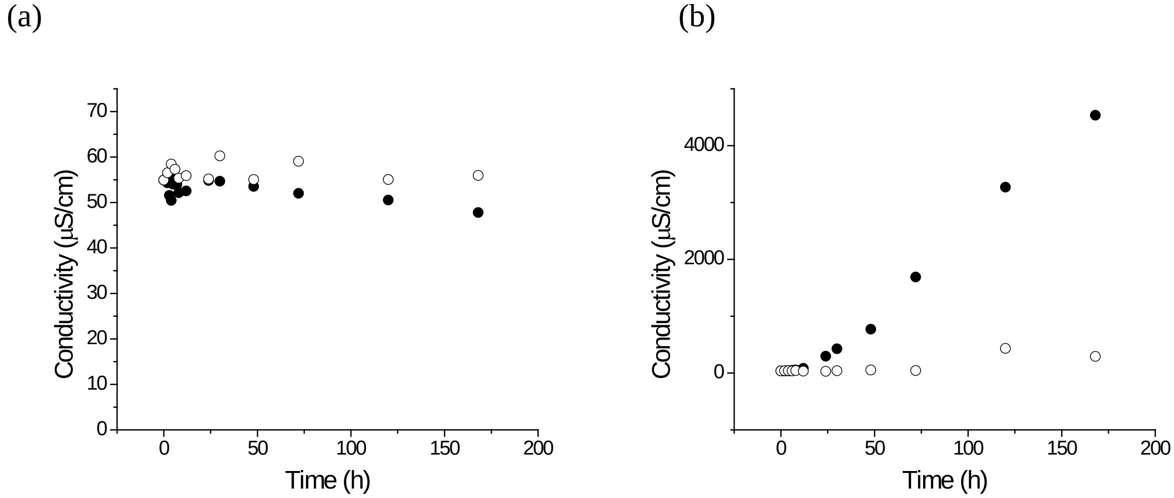


Figure 6 Conductivity as a function of contact time for the water/amide-IL system: (a) IL layer and (b) water layer. Symbols differentiatedata from ● irradiated and○ unirradiated samples.

In contrast to the dicyanimide-IL tests, at longer times a cloudy region indicative of emulsification began to develop in the IL layer near the water interface (growth of such an emulsion has been observed previously)[10]. This cloudy region expanded downwardsfrom the water/IL interfaceover time. The emulsion was observed in both the presence and absence of irradiation, but irradiation accelerated the development of the emulsion. As a result of the development of this emulsion at the water/IL interface, the shape of the interface changed and became less distinct.

4. Discussion

Upon irradiation very little to no change is observed in the conductivity of the pure ILs; which is consistent with headspace gas analysis where few volatile radiolysis products were detected. The net radiolytic degradation of the ILs was expected to be very small due to theirlow dielectric constant. The probability of an excited or charged species formed by absorption of ionizing radiation and then escaping recombination in a liquid is proportional to the dielectric constant of the medium [10, 16]. The dielectric constants of ionic liquids are comparable to those of organic solvents, and this favours recombination, as opposed to charged species separation and the consequently observed radiolytic degradation.

However, when placed in contact with a water phase the ILs then display differences in their conductivities. The conductivity of the dicyanamide-IL increasedover time whereas the amide-IL maintained a constant conductivity when exposed to water; atrend that was retained upon irradiation of the ILs. Analysis of the precipitate isolated from the aqueous phase in contact with the dicyanamide-IL identified the dicyanamide anion. If dicyanamide anions are transferred from the IL phase to the aqueous phase, then anions from the water must likewise transfer to the IL phase in order to avoid excessive electrical charge differences between the two phases, this confirming our conductivity observations. The water can provide only hydroxide (OH^-)anions. The entry of OH^-ions into the IL would be expected to increase the IL layer conductivity as the decrease in IL purity would decrease the IL viscosity (thereby increasing ionic mobility) and OH^- is more mobile than the IL ions.

The conductivity of the amide-IL was not affected by water/IL contact; instead the interaction involved micelle formation and emulsification, as previously described [10]. We initially expected that micelles would also be observed on the TEM grid prepared from the aqueous layer in the dicyanamide system. However, in the dicyanamide IL system, no visible emulsion layer formed in either the IL or aqueous phases. Resulting TEM micrographs of the aqueous phase did not show evidence of micelles, but rather detected the nanometer-scale precipitate dispersed throughout the aqueous phase. Precipitate formation has not been observed in our previous IL studies.

The FTIR spectra show the precipitate formed in the dicyanamide-IL system remains identical regardless of irradiation time. Compared to the FTIR spectraof the pure IL (Figure 4) one can see that there are few significant differences between the pure IL and the precipitate product. Although we have not been able to conclusively identify this precipitate, it is likely that it is either a salt compound used in the synthesis of the dicyanamide-IL, or a phosphonium dicyanamide salt formed during our experiments.

In both water/IL systems, the aqueous phase conductivity increased linearly with irradiation time. In the water/amide-IL system there may be signs of an induction period of several hours duration before the aqueous phase conductivity began to rise. Currently we have insufficient information to comment further on the observation of an induction period, but this is an area for further research. The general increase in conductivity of the water layer is not surprising, since we have previously shown that radiation facilitates inter-phase mixing in water/IL systems [10]. Pure water is a rather poor conductor, and so addition of ions from the IL phase should increase its conductivity.

The implications of these observations for applications in separations processes in which ILs are used to extract metal ions from water containing dissolved nuclear fuel are not entirely clear at this stage. Certainly precipitate formation would complicate the process by adding a third phase to the mixture, necessitating that filtration or settling steps be added to the separations process. It also results in the consumption of the ionic liquid, an expensive component of the process that would need to be recycled. The formation of micelles and emulsion layers has beneficial aspects –the interfacial contact area of water and IL would be greatly increased, facilitating much more rapid phase separation of the metal ions- but also detrimental ones –the emulsion may be difficult and time-consuming to coalesce, impeding the removal of metal ions and recycling of the IL in the separations process.

5. Conclusions

Although a variety of previous papers have discussed and compared the physical properties of ionic liquids under various conditions, this is the first work to compare the effects of steady-stateirradiation ontrihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)amide and trihexyltetradecylphosphonium dicyanamide ILs in biphasic (gas/IL and water/IL) systems.

The ILs studied were both relatively radiation resistant; however, γ-radiation influences the rate of micelle (in the case of the amide-IL) and precipitate formation (in the case of the dicyanamide-IL). In the absence of radiationthe transfer of IL ions into the aqueous phase occurs, in spite of the immiscibility of the two phases, though irradiation greatly accelerates and enhances this transfer. The consequencesof this ion transfer differ between the dicyanamide and the amide-ILs. In the latter case, the ion transfer acts to increase the IL ion concentration in the water layer untilthe critical micelle concentration is achieved an emulsion layer is formed. However, in the former case, an emulsion layer does not form. Instead, irradiation acts to promote the generation of a fine precipitate, which is dispersed throughout the IL and aqueous phases. This precipitate has not yet been fully characterized, though it does appear to incorporate the dicyanamide anion of the IL.

In summary, we can conclude that irradiation impacts both the dicyanamide-IL and the amide-IL when they are in contact with an aqueous phase. The implications of emulsion layer and precipitate formation for applications of these ILs in separations and extractions are currently unresolved. It is very probable that the formation of the type of precipitate observed here would not be desirable in a separations process.

6. Acknowledgement

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