Effect of Phosphonium-based Ionic Liquids on the Corrosion of Carbon Steel under Gamma Radiation

R.P. Morco, J.M. Joseph, A.Y. Musa and J.C. Wren
Department of Chemistry, Western University, 1151 Richmond Street
London, Ontario, Canada N6A 5B7
(rmorco@uwo.ca)

Abstract

The interactions of two ionic liquids with carbon steel surfaces were studied in absence and presence of γ-radiation. Both studied ionic liquids were found to corrode the carbon steel. One of the ionic liquids (labelled $[P_{66614}]^+$ $[Br]^-$) was found to produce corrosion products both with and without radiation present. The second ionic liquid (labelled $[P_{66614}]^+$ $[NTf_2]^-$) did not corrode the steel in absence of γ-radiation, but did corrode it in the presence of γ-radiation.

1. Introduction

Room temperature ionic liquids (RTILs) are composed of distinct ion pairs that remain in the liquid state below 100°C. Ionic liquids usually contain a bulky, long-chained organic cation that is weakly coordinated to a smaller organic or inorganic anion. Recently, interest in RTILs has grown due to their many desirable physical and chemical properties. These include: good conductivity, negligible vapour pressure, high chemical and thermal stability, and wide electrochemical windows [1, 2]. These desirable properties make this class of liquids particularly interesting to study as potential replacements for traditional volatile organic solvents. The ionic liquids can also be tailored to bind with other ions, making them potential agents for separation techniques. They possess unique solvation properties for coordination and extraction of metal ions from aqueous solutions. Studies have demonstrated that RTILs can be used for extraction of metal species from aqueous media [3].

The stability of ionic liquids and their extraction capabilities make them an attractive alternative for use in separation processes in the nuclear industry (such as spent fuel reprocessing). Currently such nuclear separations are mostly done using organic phases such as kerosene and dodecane (e.g., in the PUREX process for spent nuclear fuel) [4]. For use in nuclear applications, the radiation stability of the ionic liquids must be understood and also the materials compatibility of the ionic liquids. There are a few studies on the radiation stability on ionic liquids. There are also separate studies on the interactions of ionic liquids with metal surfaces for applications such as lubricants and corrosion inhibitors [5]. However, there are no studies that combine irradiation of an ionic liquid with its corrosiveness to metal surfaces. Such studies are necessary because it is well known that ionizing radiation can produce reactive radical fragments and these can affect the corrosivity of an irradiated solution.

In this work the interactions of two ionic liquids with carbon steel were investigated in absence and presence of γ-radiation. The techniques used to examine the steel surfaces were Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy. The two ionic liquids were trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl) imide (labelled as $[P_{66614}]^+$ $[NTf_2]^-$) and trihexyltetradecylphosphonium bromide (labelled as $[P_{66614}]^+$ $[Br]^-$).

2. Experimental

The two ionic liquids were purchased from Sigma-Aldrich (>95% pure) and were used without further purification. Round carbon steel coupons with exposed area of 0.785 cm^2 were prepared for each test by abrasion with different grades of polishing paper, followed by diamond polishing, and then sonication for 5 minutes with an acetone/methanol mixture to remove abrasion debris. The desired ionic liquid was added drop wise onto the carbon steel surface until it was fully covered. Reference coupons were allowed to stand in air for 14 h, while other coupons were exposed to 14 h of γ-radiation in a ^{60}Co gamma cell (MDS Nordion) with a uniform dose rate of 5.5 kGy/h. Polished coupons without any ionic liquid present were also irradiated to isolate the effect of radiation in presence of ionic liquid. After irradiation, the coupons were rinsed with acetone to remove the ionic liquid and analyses of the coupon surfaces were performed using FTIR and Raman spectroscopy. All experiments were conducted at room temperature in an ambient environment.

The FTIR measurements were performed using a Bruker IR spectrophotometer with Fourier transformation in the 4000 to 200 cm^{-1} frequency range by reflectance-absorbance mode. Raman spectroscopy was carried out using a Renishaw model 2000 Raman Spectrometer with a laser excitation wavelength of 633 nm.

3. Results and discussion

Figure 1 shows the optical images of the carbon steel coupons upon treatment with ionic liquids (a) $[P_{66614}]^+$ $[NTf_2]^-$ and (b) $[P_{66614}]^+$ $[Br]^-$ without (top two photos of each quadrant) and with exposure to gamma radiation (bottom two photos of each quadrant). The photos show the coupon surfaces before and after rinsing off the ionic liquid with acetone. For $[P_{66614}]^+$ $[NTf_2]^-$, corrosion products can be seen on the surface of irradiated carbon steel coupon, but the non-irradiated coupon is clean and corrosion products are visibly absent. For $[P_{66614}]^+$ $[Br]^-$, both the irradiated and non-irradiated coupons show clear evidence of corrosion.

FTIR reflectance absorption measurements were utilized to determine the type of corrosion products formed on the carbon steel surfaces. The FTIR spectra of iron oxides and hydroxides are well established. The low wavenumber region has been attributed to the lattice vibration of Fe-O while the high wavenumber region is due to the absorption band of OH stretching [6]. An FTIR spectrum obtained from a carbon steel coupon treated with $[P_{66614}]^+$ $[NTf_2]^-$ (Figure 2) has a close resemblance to the spectrum for γ-FeOOH.

For the $[P_{66614}]^+$ $[Br]^-$ a signature IR band at 420 cm^{-1} of γ -Fe_2O_3 (maghemite) was observed (Figure 3) for the irradiated coupons. No significant maghemite peaks were observed for the non-irradiated coupons, but noticeable peaks at 1110, 920, 800 and 650 cm^{-1} were observed. These correspond to δ-FeOOH (feroxyhyte).

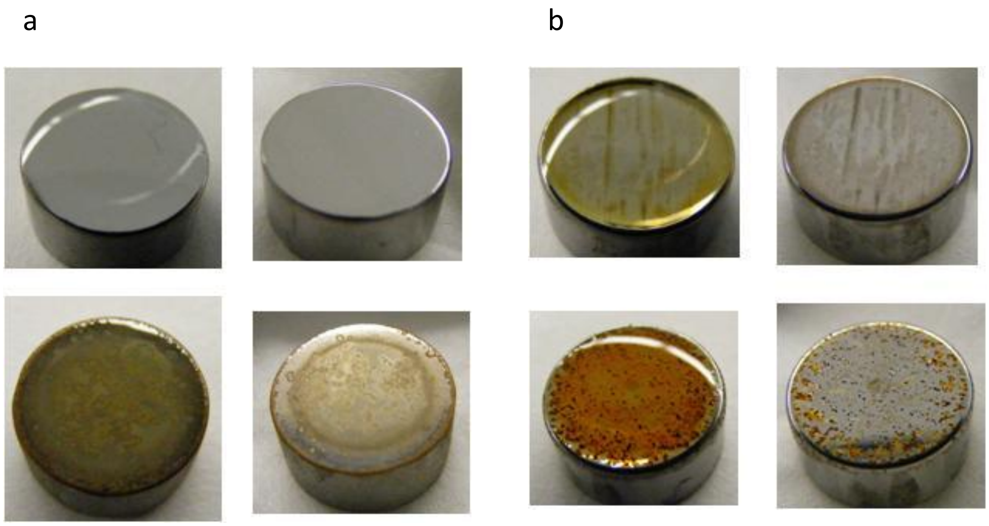

Figure 1: Photographs of carbon steel coupons after interaction with (a) $[P_{66614}]^+$ $[NTf_2]^-$ and (b) $[P_{66614}]^+$ $[Br]^-$. The photos on the left and right of each quadrant were taken before and after, respectively, rinsing with acetone. The two photos at the top of each quadrant were show coupons that were not irradiated, while the bottom two photos show 14 h irradiated coupons.

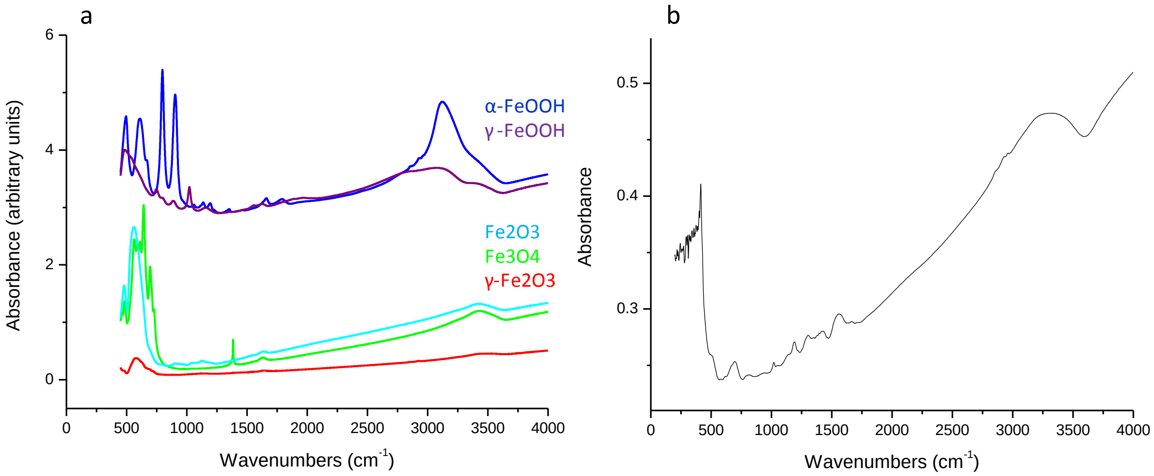

Figure 2 IR spectra of (a) different iron oxide and oxyhydroxide reference standards and (b) spectrum of an irradiated carbon steel coupon treated with $[P_{66614}]^+$ $[NTf_2]^-$.

A micrograph image of a $[P_{66614}]^+$ $[Br]^-$ treated coupon (Figure 4a) shows brownish cracked scales on the surface. A Raman spectrum of the scales (Figure 4b) has a close resemblance to a maghemite (γ-Fe_2O_3) reference spectrum. An FTIR spectrum also shows formation of maghemite on the metal surface. The dependence of the corrosivity of $[P_{66614}]^+$ $[NTf_2]^-$ can be explained by its radiation chemistry. It has been reported that the $[NTf_2]$- anion is decomposed by γ-radiation to produce a number of fragment radiolysis products (e.g., $•CF_3$, F•, $CF_3SO_2•$, H•, and $•CH_3$). These can then recombine to form stable fluorinated species (e.g., CF_3-CF_3, HCF_3, CH_3-CF_3 and HF) [7, 8]. The fluorinated radiolysis radicals and HF could induce localized corrosion. This could explain the observation of carbon steel corrosion only after radiation exposure in the case of $[P_{66614}]^+ [NTf_2]^-$.

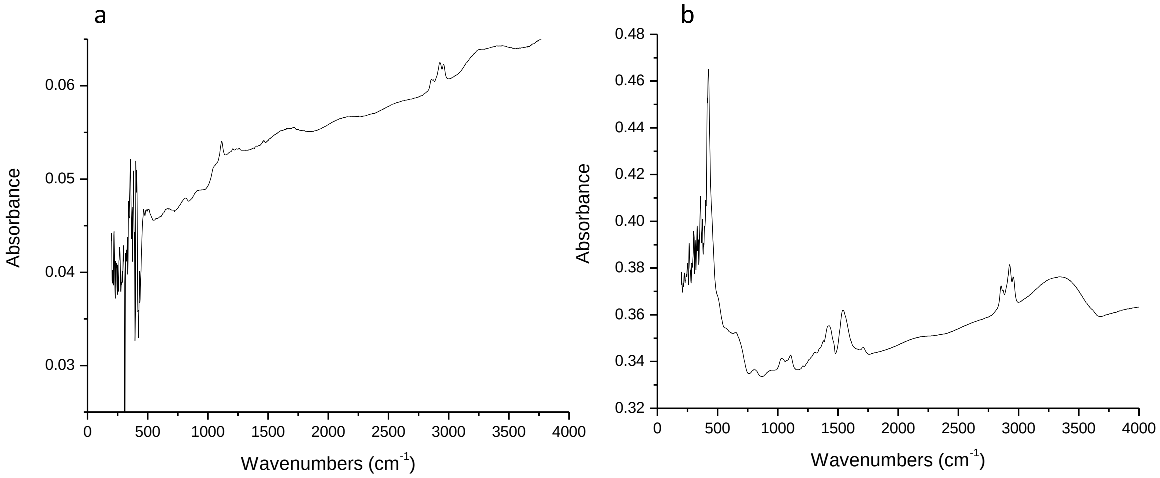

Figure 3: IR spectra of (a) non-irradiated and (b) irradiated coupon treated with $[P_{66614}]^+ [Br]^-$.

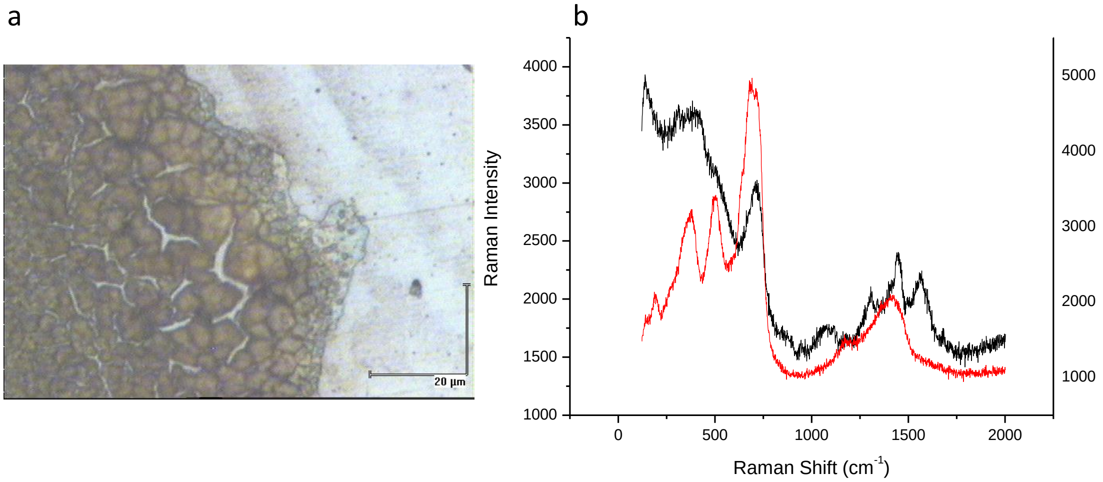

Figure 4: a) Micrograph image of irradiated sample treated with $[P_{66614}]^+ [Br]^-$ and b) Raman spectrum of scaled area (black line) and a maghemite (γ-Fe_2O_3) reference spectrum (red line).

The $[P_{66614}]^+ [Br]^-$ ionic liquid is corrosive even in the absence of irradiation because it is more hydroscopic compared to that of $[P_{66614}]^+ [NTf_2]^-$. This means that this ionic liquid will absorb water vapour from the ambient air and this water will be available to participate in the steel corrosion. As well, the presence of bromide ion makes this ionic liquid more corrosive even without radiation exposure as halides ions can induce corrosion on steel [9]. Based on the nature of the oxide layer formed on the carbon steel coupons it appears that $[P_{66614}]^+$ $[Br]^-$ is more corrosive than $[P_{66614}]^+$ $[NTf_2]^-$ for carbon steel.

4. Conclusions

This study shows that ionic liquids cannot be assumed to be good corrosion inhibitors under all conditions. Carbon steel can be corroded by ionic liquids while exposed to γ-radiation. Some ionic liquids can cause corrosion even in the absence of ionizing radiation. In addition the nature of the corrosion film that is formed on carbon steel depends on the ionic liquid composition.

5. Acknowledgements

This work was funded under the NSERC (Natural Science and Engineering Research Council of Canada) Discovery grant and the Ontario Research Fund Excellence in Research: Nuclear Ontario grant. The authors would like to recognize Ms. Mary Jane Walzak at Surface Science Western for the Raman spectroscopy measurements.

6. References

[1] P. Wasserscheid, T. Welton, “lonic Liquids in Synthesis”, 2nd ed. Wiley-VCH, Weinheim (2008).

[2] T. Welton, “Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis” Chem. Rev. 99 (1999) 2071−2083.

[3] S. Dai, Y.H. Ju, C.E. Barnes, “Solvent extraction of strontium nitrate by a crown ether using room-temperature ionic liquids”, Dalton Trans.,(1999) 1201–1202.

[4] S.H. Ha, Russel N. Menchavez, and Y.M. Koo, “Reprocessing of spent nuclear waste using ionic liquids”, Korean J. Chem. Eng. 27 (2010) 1360-1365

[5] N. V. Likhanova, O. Olivares-Xometl, D. Guzmán-Lucero, M. A. Domínguez-Aguilar, N. Nava, M. Corrales-Luna, M. C. Mendoza, “Corrosion inhibition of carbon steel in acidic environment by imidazolium ionic liquids containing vinyl-hexafluorophosphate as anion”, Int. J. Electrochem. Sci., 6 (2011) 4514 – 4536.

[6] H. Namduri and S. Nasrazadani, “Quantitative analysis of iron oxides using Fourier transform infrared spectrophotometry”, Corr. Sci. 50 (2008) 2493-2497.

[7] G. Le Rouzo, C. Lamouroux, V. Dauvois, A. Dannoux, S. Legand, D. Durand, P. Moisy and G. Moutiers, “Anion effect on radiochemical stability of room-temperature ionic liquids under gamma irradiation”, Dalton Trans. (2009) 6175-6184.

[8] S. E. Howett, J. M. Joseph, J. J. Noël, J. C. Wren, “Effect of gamma irradiation on gas-ionic liquid and water-ionic liquid interfacial stability”, J. Colloid. Int. Sci. 361 (2011) 338-350.

[9] K. Yazdanfar, X. Zhang, P.G. Keech, D.W. Shoesmith, J.C. Wren, “Film conversion and breakdown process on carbon steel in the presence of halides”, Corr. Sci. 52 (2010) 1297-1304