

# Corrosion of Stainless Steels in Ionic Liquids

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## Abstract

A number of electrochemical methods were used to determine the corrosion of stainless steels immersed in three different room temperature ionic liquids (RTILs). A three electrode cell was used to study the open circuit potential (ocp) and general corrosion. Cyclic voltammetry was used with the Tafel and Stern methods of analysis and also to detect pitting corrosion. Finally, electrochemical impedance spectroscopy (EIS) was employed to attempt to quantify the corrosion mechanisms.

The overall corrosion rates measured were low, ranging from 0.001 to 0.678mm Y<sup>-1</sup>. The simple ocp analysis gave a reasonably accurate evaluation of the relative corrosion resistance of these systems. Cyclic voltammetry gave erratic results with the Stern method. The Tafel plots exhibited conventional kinetic controlled behaviour only with the cathodic branch. The anodic plot exhibited diffusion control and could not be used for analysis of corrosion. No pitting was found. The EIS was not reliable as the analysis showed non-ideal behaviour. The response was consistent with overlapping time constants at higher frequencies and slow diffusion at low frequencies.

**Keywords:** stainless steels, corrosion, ionic liquids.

## Introduction

Room Temperature Ionic Liquids (RTILs) are a class of non-aqueous solvents that are electrically conducting [1]. Also they have been viewed as a type of molten salt with a glass transition point or melting point typically below 100°C. In chemical reactions there are advantages with the use of RTILs such as zero emissions, recyclable solvents of negligible vapour pressure, high reactivity and electrocatalytic capability. As such they have the potential to give cheaper production of chemicals and the ability to meet tighter environmental controls. However, the density and viscosity of RTILs are greater than those of the normal molecular solvents used in production of chemicals. The use of RTILs can be expected to advance into large scale production of chemicals and therefore their corrosive properties, particularly towards steels, need to be quantified.

In this work, the corrosive properties of seven stainless steels are reported for RTILs based on 1-butyl-3-methylimidazolium (Bmim) cation formulation. Three different anions were used, hexafluorophosphate [PF<sub>6</sub>], bis(trifluoromethane sulfonyl)imide [NTf<sub>2</sub>] which are water insoluble and the water-soluble nitrate [NO<sub>3</sub>]. Details of the (Bmim) cation reactions and structure can be found elsewhere (2–4).

## Experimental Procedure

### RTILs preparations

[Bmim] [Cl] (Fischer) was dissolved into ice-cooled distilled water and the anionic reagent added drop-wise into the stirred solution over a 2–3 hour period. The ionic liquid layer was extracted using dichloromethane and separated from the aqueous phase. After water washing the dichloromethane was removed. The water washing continued until no chloride ions were detectable using silver nitrate. The RTIL was dried at 55°C under vacuum for 12 hours. Purity of product was checked by NMR spectroscopy. The anionic reagents used were hexafluorophosphoric acid (Sigma), lithium bis(trifluoromethane sulfonyl)imide (Fluorochem) and silver nitrate (Aldrich) for the RTILs [Bmim] [PF<sub>6</sub>], [Bmim][NTf<sub>2</sub>] and [Bmim][NO<sub>3</sub>] respectively.

### Corrosion tests and experimental set-up

A three-electrode cell immersed in the RTIL was used and the corrosion monitored by a Voltalab 40 potentiostat. The working electrodes (WE) were 1.2cm-diameter stainless steel (SS) discs (Goodfellow), the quasi-reference electrode (RE) which was developed for ionic liquids [7] was a polished silver wire and the counter electrode (CE) was a platinum wire set

perpendicular to the WE. Quasi-reference electrodes are without liquid junctions avoiding any capacitance effects between the ionic liquid and the aqueous medium present in the conventional frit-based RE.

The SS disc was cleaned and washed in ethyl acetate then dried and stored under vacuum. The silver wire was washed in water then acetone, sonically cleaned and dried at 200°C. The platinum wire was washed in water, ethanol, then dried and flamed before use.

The composition of SSs used are given in Table 1 as wt%. Four examples of each SS type were tested in each RTIL and the results averaged.

Stainless Steel	%Fe	%Cr	%Ni	%Mo	%Nb	%Ti
310	55	25	20	–	–	–
304	72	18	10	–	–	–
17-7PH	76	17	7	–	–	–
15-7PH	75.7	15	7	2.3	–	–
316	69	18	10	3	–	–
347	71	18	10	–	1	–
321	72	18	9	–	–	1

*Table 1: Percentage composition (wt%) of Stainless steels*

The electrochemical corrosion tests conducted at 20°C were in order of performance:

- Open current potential (ocp) measured in 0.75s periods against the RE for 10 minutes
- Cyclic voltammetry (CV) using a scan rate of 0.25mVs<sup>-1</sup> commencing at the ocp and going back and forwards by  $\pm 200$ mV along the cathodic and then the anionic paths over several cycles. Corrosion data were subjected to Tafel and the 2<sup>nd</sup> Stern analyses.

- (c) Electrochemical impedance spectroscopy (EIS). The applied potential was split into a DC signal imposed on the WE for 120s before a sine wave AC signal of 5mV amplitude at 20 frequencies per decade was imposed between a frequency range of 100kHz to 100mHz. Z-view software was used to model the equivalent circuit.
- (d) Pitting corrosion (PC). The WE was initially polarized to  $-10\text{mV}$  against the ocp and scanned anodically at  $1\text{mVs}^{-1}$  until a current of  $10\mu\text{A}$  was obtained. After a minute's pause the process was reversed.
- (e) General Corrosion (GC). An anodic overvoltage of  $40\text{mV}$  above the ocp was achieved by scanning at  $+10\text{mVs}^{-1}$  and then reversing the process to  $-40\text{mV}$ . Six voltammograms were run with a minute's pause between each. The resistance polarization  $R_p$  was then calculated.
- (f) Surface analysis was obtained using a Joel 6300 Scanning Electron Microscope on the steels before and after testing.

## Results and Discussion

### Open circuit analysis

Data are given in Table 2. For all tests there was a variation with time that required at the most 5 minutes before a consistent pattern emerged. The stability of the steels to corrosion was indicated by a positive potential.

For the  $[\text{Bmim}][\text{NO}_3]$  ionic liquid the best corrosion resistance was obtained with the high Cr/Ni alloy and the performance dropped away as first the Cr and then the Ni concentrations were reduced. Taking notice of the spread of the data the doped steels gave poorer corrosion resistance particularly the 347 SS with Nb addition. Replacement of Cr with Mo in the 15-7PH steel gave a significant reduction in performance. A similar effect was noted with Mo in the 316 SS.

The  $[\text{Bmim}][\text{PF}_6]$  ionic liquid did not give a consistent fall in corrosion resistance with a drop in Cr/Ni content. In fact the 304 SS shows a result which appeared to be well out-of-line and perhaps would have been expected to be closer to the performance of the 316 SS alloy, bringing the ocp results more in line with the pattern given by the  $[\text{Bmim}][\text{NO}_3]$  data. The corrosion resistance appeared to be marginally better than for the  $[\text{Bmim}][\text{NO}_3]$  ionic liquid a fact which cannot solely be attributed to the non-aqueous nature of the medium since the  $[\text{Bmim}][\text{NTf}_2]$  ionic liquid gave the poorest corrosion resistance. It is possible that the

presence of lithium ions not removed in the final washing of the [Bmim][PF<sub>6</sub>] ionic liquid led to improved corrosion resistance.

S.S. Alloy	R.T.I.L.					
	[Bmim] [NO <sub>3</sub> ]		[Bmim] [PF <sub>6</sub> ]		[Bmim] [NTf <sub>2</sub> ]	
	Ocp (V)	(Vs <sup>-1</sup> )	Ocp (V)	(Vs <sup>-1</sup> )	Ocp (V)	(Vs <sup>-1</sup> )
<b>310</b>	0.208 ± 0.009	-0.004	0.222 ± 0.007	0	0.003 ± 0.001	-3×10 <sup>-5</sup>
<b>304</b>	0.124 ± 0.004	-4×10 <sup>-5</sup>	-0.007 ± 0.002	-2×10 <sup>-5</sup>	-0.003 ± 0.001	-2×10 <sup>-4</sup>
<b>17-7PH</b>	0.061 ± 0.018	-6×10 <sup>-6</sup>	0.052 ± 0.033	0	-0.015 ± 0.003	-2×10 <sup>-5</sup>
<b>15-7PH</b>	-0.038 ± 0.015	0.001	-0.020 ± 0.005	3×10 <sup>-5</sup>	-0.012 ± 0.009	-1×10 <sup>-5</sup>
<b>316</b>	0.058 ± 0.025	-9×10 <sup>-5</sup>	0.079 ± 0.002	0.02	0.005 ± 0.002	-2×10 <sup>-5</sup>
<b>347</b>	0.044 ± 0.004	-1×10 <sup>-5</sup>	0.051 ± 0.003	6×10 <sup>-6</sup>	-0.005 ± 0.001	-2×10 <sup>-5</sup>
<b>321</b>	0.059 ± 0.012	-3×10 <sup>-5</sup>	0.058 ± 0.018	6×10 <sup>-6</sup>	-0.026 ± 0.010	-2×10 <sup>-5</sup>

*Table 2: Open circuit potential [V] and Rate of change [Vs<sup>-1</sup>] at 600s*

The [Bmim][NTf<sub>2</sub>] ionic liquid gave the poorest corrosion resistance. The corrosion resistance fell as the Cr/Ni content of the steels were reduced, but doping with Mo led to an improvement in performance as evidenced by the results of the 15-7PH and 316 SS. Doping with Nb acted in a similar way in contrast to Ti addition where corrosion was shown to increase. The overall increase in corrosion of the [Bmim][NTf<sub>2</sub>] may be due to the presence of chloride ions which was not washed out during preparation of the ionic liquid.

In general the corrosion resistance of these ionic liquids appear to be greater than with 316 L SS in Hanks' solution used to simulate body conditions [8]. The higher composition of Cr/Ni in the steels gave the best corrosion resistance to RTILs. Doping of the steels at the expense of the Cr/Ni content tended to improve the corrosion resistance for non-aqueous ionic liquids but had the opposite effect for the aqueous RTIL.

## Cyclic Voltammetric Analysis

A Tafel analysis was performed [9] which displayed typical behaviour only in the cathodic region where the current increased logarithmically with over potential. In the anodic region the current rapidly reached a steady state at low voltages possibly due to diffusion control or to passivation limitation. Hence only the cathodic region could be analysed. The results are given in Table 3.

S.S. Alloy	R.T.I.L.		
	[Bmim][NO <sub>3</sub> ] K <sub>corr</sub> (mmY <sup>-1</sup> )	[Bmim][PF <sub>6</sub> ] K <sub>corr</sub> (mmY <sup>-1</sup> )	[Bmim][NTf <sub>2</sub> ] K <sub>corr</sub> (mmY <sup>-1</sup> )
310	0.0018 ± 0.0005	0.001	0.0088 ± 0.004
304	0.0023 ± 0.0005	0.001	0.0117 ± 0.008
17-7PH	0.0825 ± 0.003	0.175 ± 0.002	0.0155 ± 0.004
15-7PH	0.0043 ± 0.001	0.678 ± 0.2	0.0043 ± 0.001
316	0.0035 ± 0.001	0.002 ± 0.001	0.0053 ± 0.001
347	0.0050 ± 0.002	0.002	0.0075 ± 0.001
321	0.0043 ± 0.003	0.002 ± 0.001	0.0088 ± 0.004

*Table 3: Tafel cathodic corrosion values [mmY<sup>-1</sup>]*

For the [Bmim][NO<sub>3</sub>] ionic liquid the corrosion increased as the Cr/Ni content of the steel fell. Doping, particularly with Mo in the 15-7PH SS increased the corrosion resistance. Otherwise, doping increased the corrosion but the data spread precluded further comment.

With the [Bmim][PF<sub>6</sub>] ionic liquid the corrosion fell with increase in Cr/Ni content of the steels. The drop in Cr content with the 15-7PH steel led to a dramatic increase in corrosion which was not mitigated by the inclusion of Mo in the formulation; this result was in contrast to the [Bmim][NO<sub>3</sub>] ionic liquid data. However, doping of the 304SS by Mo (along with Nb and Ti) led to only a slight drop in performance.

By comparison the results for the [Bmim][NTf<sub>2</sub>] ionic liquid showed the 15–7PH SS had the lowest corrosion rate indicating along with the 316 SS that for this RTIL Mo had a significant effect in reducing corrosion. The corrosion rate also increased progressively with Nb and then Ti doping. The usual increase in corrosion with drop in the Cr/Ni content was observed to occur.

The results from the 2<sup>nd</sup> Stern analysis are detailed in Table 4

S.S. Alloy	R.T.I.L.		
	[Bmim][NO <sub>3</sub> ] kΩ cm <sup>2</sup>	[Bmim][PF <sub>6</sub> ] kΩ cm <sup>2</sup>	[Bmim][NTf <sub>2</sub> ] kΩ cm <sup>2</sup>
310	123.3 ± 61.3	355.3 ± 60.7	12.2 ± 5.2
304	132.0 ± 15.6	441.0 ± 74.6	20.5 ± 5.2
17–7PH	45.6 ± 18.0	152.0 ± 32.0	53.5 ± 12.0
15–7PH	120.3 ± 19.0	345.2 ± 74.6	53.9 ± 8.5
316	81.1 ± 26.0	94.1 ± 21.5	15.3 ± 5.5
347	65.2 ± 13.0	206.6 ± 72.9	21.8 ± 5.3
321	97.1 ± 20.0	97.4 ± 15.2	27.4 ± 7.8

*Table 4: Polarisation resistance (Rp) measurements obtained by the 2<sup>nd</sup> Stern Analysis*

Considering the wide spread of some of the data, the resistance to corrosion followed a similar pattern to that already observed with the [Bmim][NO<sub>3</sub>] ionic liquid with resistance rising with Cr/Ni content. There was a dramatic improvement with the 15–7PH SS which was due to the Mo addition. The doped steels gave slightly reduced performance but the spread of data precluded any further analysis. It was noticeable that the results of predictions using the E<sub>corr</sub> values were often at variance with those obtained with the R<sub>p</sub> data no doubt attributable to difficulties in determination of the parameters accurately from the voltage–current curve. Also the 2<sup>nd</sup> Stern method often resulted in a wider spread to the data and therefore appeared to be less reliable than the Tafel method of analysis.



For the [Bmim][PF<sub>6</sub>] ionic liquid the corrosion resistance was greater than in the [Bmim][NO<sub>3</sub>] environment. Although on average the lower Cr/Ni content of the 304 SS gave a superior performance to the high content 310 SS, the error spread indicated that the corrosion increased as the Cr/Ni content was reduced. The performance of the 15-7PH steel was abnormally good and stands in variance to both the ocp and Tafel analyses. Also the Nb-doped 347 SS appears to give abnormally better corrosion results.

Of the three ionic liquids, the [Bmim][NTf<sub>2</sub>] compound gave the poorest results for all SS grades. In addition, the higher Cr/Ni steels gave the poorest performance. In addition, the 7PH steels gave the highest corrosion resistance, and the 15-7PH grade showed no effect of Mo addition. The result shows no parallels with either the ocp or Tafel analyses, and therefore the conclusion must be made that the 2<sup>nd</sup> Stern analysis was not as reliable as other methods of corrosion estimation such as the Tafel plot.

The general corrosion (GC) tests showed a consistent pattern where the Rp value rose with time to a plateau value, after about 10 minutes, giving the data of Table 5.

S.S. Alloy	R.T.I.L.		
	[Bmim][NO <sub>3</sub> ] kΩ cm <sup>2</sup>	[Bmim][PF <sub>6</sub> ] kΩ cm <sup>2</sup>	[Bmim][NTf <sub>2</sub> ] kΩ cm <sup>2</sup>
<b>310</b>	125 ± 62.2	155 ± 17.1	76.9 ± 3.0
<b>304</b>	208 ± 62.1	112 ± 10.1	116.3 ± 22.1
<b>17-7PH</b>	145 ± 51.2	251 ± 84.2	103.5 ± 9.3
<b>15-7PH</b>	243 ± 58.3	147 ± 11.8	242 ± 50.1
<b>316</b>	246 ± 71.3	69.5 ± 4.7	121 ± 3.6
<b>347</b>	155 ± 48.0	54.0 ± 8.6	108 ± 19.4
<b>321</b>	223 ± 64.8	39.7 ± 4.8	97.8 ± 5.9

*Table 5: Polarisation resistance (Rp) measurements obtained by the general corrosion method.*



For the [Bmim][NO<sub>3</sub>] ionic liquid the initial values of  $R_p$  were below those obtained by cyclic voltammetry given in Table 4, but rose well above those values. Thus the stability of all the steels increased to a maximum suggesting that a passive protective layer was being formed. The doped steels had better long-term corrosive resistance than the straight Cr/Ni alloys with the possible exception of the 347 SS Nb alloy.

The [Bmim][PF<sub>6</sub>] ionic liquid exhibited a significant variation in that both the initial and final  $R_p$  values were below those in Table 4 from the cyclic voltammetry tests with the exception of the 17-7PH alloy. The implication was that the majority of the steels became less resistant to corrosion with prolonged exposure to this ionic liquid. There was the possibility that contaminating water-generated HF was present which would destabilise the protective layer [10, 11]. In this case the straight Cr/Ni alloys possessed a better long-term corrosive resistance than the doped steels, with the possible exception of the 15-7PH alloy.

With the [Bmim][NTf<sub>2</sub>] ionic liquid the initial (and final)  $R_p$  values were significantly higher than the corresponding values from cyclic voltammetry suggesting that a more stable system was evolving with time as a passive surface layer was forming on the steel surfaces which was not dissolved by the ionic liquid medium. Both the straight Cr/Ni alloys and the doped steels gave approximately the same result with again the 15-7PH alloy being a possible exception.

## Pitting Corrosion

A characteristic current/voltage pattern was observed at a specific potential  $E_{trans}$  where the reverse sweep in the voltammetry was higher than the forward sweep due to the pitting process. At scans to this extreme potential transpassive behaviour occurred as electron transfer reactions took place across or within the passivating layer leading to a steep rise in current. The larger the  $E_{trans}$  potential, the more stable the material was to pitting corrosion. Data obtained are given in Table 6.

For all systems studied, no evidence of a hysteresis loop was found that would indicate pitting corrosion. However, transpassive behaviour was observed in every case. The high values of potential, mainly above 1V, were indicative of the protective nature of the surface oxide on the steels. The [Bmim][NTf<sub>2</sub>] medium gave the lowest  $E_{trans}$  values and the curves obtained indicated that an oxidation process occurred which was reminiscent of the presence of a halide impurity such as LiCl due to the preparation procedure. There also were indications with the sweeps in the [Bmim][PF<sub>6</sub>] medium that some type of oxidation/reduction occurred during the process.

For the ionic liquids the  $E_{trans}$  was greatest for the [Bmim][PF<sub>6</sub>] medium and lowest in the [Bmim][NTf<sub>2</sub>] liquid. For each of the ionic liquids the doped steels gave a similar reading with the highest value always obtained with the 304 SS. The low value obtained for the 310 SS in [Bmim][NTf<sub>2</sub>] stands out as unusual.

S.S. Alloy	R.T.I.L.		
	[Bmim][NO <sub>3</sub> ] $E_{trans}$ (V)	[Bmim][PF <sub>6</sub> ] $E_{trans}$ (V)	[Bmim][NTf <sub>2</sub> ] $E_{trans}$ (V)
310	1.06	1.66	0.33
304	1.25	1.76	1.11
17-7PH	1.05	1.60	0.95
15-7PH	1.13	1.58	1.09
316	1.17	1.55	1.07
347	1.19	1.60	1.04
321	1.18	1.61	1.07

*Table 6: Pitting corrosion analysis*

## SEM analysis

The electron micrographs indicated the ionic liquid was a very mild corrosive environment with slight etching of the surface of the steels, particularly at the grain boundaries.

The surface of the 15-7PH SS was rougher than the other steels which may have contributed to its behaviour under testing being so different.

X-Ray analysis of the surface of the steels before and after testing showed that the Mo-doped steels 15-7PH and 316 suffered a significant reduction in the surface Mo content in the [Bmim][NO<sub>3</sub>] ionic liquid, and a slight reduction in Mo content in the [Bmim][PF<sub>6</sub>] medium, but no reduction in the [Bmim][NTf<sub>2</sub>] ionic liquid. There was a slight reduction in Ti on the surface of the 321 SS in the [Bmim][NO<sub>3</sub>] medium, and a significant reduction in Nb content of the steel surface of 347 SS in the [Bmim][PF<sub>6</sub>] ionic liquid.

## Electrochemical Impedance Spectroscopy (EIS)

EIS is frequently used in corrosion studies [12–18] because it can determine the magnitude of the individual processes taking place within an electrochemical cell by developing an equivalent electrical circuit that mimics the corrosion process, for example. Firstly, the complex impedance plane was analysed using circular regression resulting in semi-circular sections if the resistive and capacitive reactions are of similar magnitude [19]. Secondly the low frequency range of the Bode diagram was analysed by linear regression with pure resistance and pure capacitance represented by horizontal and sloped lines respectively. The Bode diagram analyses were preferred with complex systems due to the ease of quantifying the different processes involved in comparison with the overcrowded complex plane. An equivalent circuit was then devised allowing estimation of the magnitude of the processes involved.

The complex plane plots for SSs immersed in RTILs were reminiscent of multiple overlaid but slightly displaced time constants at higher frequencies with a Warburg diffusion component giving a 45° line slope at low frequency. Circular regression over 10–10<sup>5</sup> Hz were performed to obtain the solution resistance  $R_s$  and resistance polarisation  $R_p$ . The complex plane plots showed slow diffusion was taking place through a surface layer, possibly an oxide layer [20]. There was no clear separation between the high and low frequency response. Table 7 sets out the results.

S.S. Alloy	R.T.I.L.					
	[Bmim] [NO <sub>3</sub> ]		[Bmim] [PF <sub>6</sub> ]		[Bmim] [NTf <sub>2</sub> ]	
	$R_s$ ( $\Omega$ )	$R_p$ (k $\Omega$ )	$R_s$ ( $\Omega$ )	$R_p$ (k $\Omega$ )	$R_s$ ( $\Omega$ )	$R_p$ (k $\Omega$ )
<b>310</b>	121	55.51	652	20.39	304	27.79
<b>304</b>	387	49.50	914	75.75	283	25.26
<b>17-7PH</b>	61	61.21	424	179.31	295	47.60
<b>15-7PH</b>	72	42.59	498	121.78	283	19.87
<b>316</b>	123	26.77	582	46.93	291	34.46
<b>347</b>	134	13.95	687	30.95	307	61.89
<b>321</b>	130	182.28	652	20.39	291	5.17

*Table 7: Electrochemical Impedance Spectroscopy Results*

The observed variation of  $R_s$  was due to the varying distance between the electrodes during testing but the values are in agreement with the RTILs conductivities [21]. In general,  $R_p$  determined from the high frequency region of the complex plane were lower than those determined by the 2<sup>nd</sup> Stern analysis for [Bmim][NO<sub>3</sub>] and [Bmim][PF<sub>6</sub>] but somewhat higher in the third RTIL. The 7PH SS showed a variation from these general trends. For ideal systems the  $R_p$  values determined by the two different methods should be the same.

Non-ideal behaviour of the analysis was highlighted by the lack of separation between the low and high frequency response in the complex plane. This was caused by overlapping time constants in the simulation. Inhomogeneity of the electrode surfaces and the highly organised H-bonded solid-ionic liquid surfaces may have added to the problems [22]. The impedance detected multiple corrosion processes each with a separate  $R_p$  value making comparison between the two methods impossible.

Linear regression analysis was utilised in the 0.1–10Hz low frequency range of the complex plane, and the Bode diagram. Ideal Warburg behaviour would be indicated if a straight line of slope 1 was detected within the complex plane (or slope –0.5 in the Bode diagram). Table 8 details the results.

S.S. Alloy	R.T.I.L.					
	[Bmim] [NO <sub>3</sub> ]		[Bmim] [PF <sub>6</sub> ]		[Bmim] [NTf <sub>2</sub> ]	
	Plane	Bode	Plane	Bode	Plane	Bode
<b>310</b>	-1.60	-0.682	-0.95	-0.555	-1.81	-0.656
<b>304</b>	-1.26	-0.730	-1.25	-0.646	-1.64	-0.687
<b>17-7PH</b>	-1.49	-0.721	-0.56	-0.574	-1.24	-0.618
<b>15-7PH</b>	-0.75	-0.603	-0.55	-0.500	-1.20	-0.645
<b>316</b>	-0.84	-1.362	-1.35	-0.563	-1.52	-0.682
<b>347</b>	-1.21	-0.641	-0.77	-0.563	-1.29	-0.673
<b>321</b>	-0.92	-0.682	-0.56	-0.364	-1.08	-0.589

*Table 8: Slopes in the Complex Plane and the Bode Diagram data*

The complex plane gradient was not –1 nor the corresponding gradient of the Bode diagram –0.5, both being generally higher than the ideal value. Such deviation was

observed by Zeng et al [16] for molten salt corrosion and was attributed to tangential diffusion. The same mechanism was possible in this work as an oxide layer was formed on the surface of the metals, giving a pathway for cross-diffusion. It is interesting to note that the [Bmim][PF<sub>6</sub>] results were closest to ideal values where it has been suggested the surface oxide layer was attacked by the ionic liquid. Li and Pickup [23] reported non-ideal Warburg behaviour which was attributed to low-frequency capacitance. In this case the non-ideality could be caused by slow ion diffusion and distributed capacitance at low frequencies.

## Conclusions

As RTILs move into industrial processes their corrosion characteristics need to be quantified. In this work electrochemical techniques are used to determine the corrosion rates of seven stainless steels in three RTIL media. The ocp analysis provided an indication of the relative corrosion resistances of the steels which was directly related to the Cr/Ni content. Doped steels improved the corrosion resistance in non-aqueous media but did the opposite for aqueous ionic liquids. It was important to remove contaminants such as Cl ions from the RTILs during their preparation since such impurities adversely affect the steel corrosion resistance.

The cyclic voltammetric analysis indicated that the cathodic branch of the Tafel plot showed conventional kinetic controlled behaviour and could be used to estimate corrosion rate, However, the anodic branch was diffusion controlled and could not be used. Further, the estimation of conversion current was difficult and resulted in the Stern method yielding results for the polarisation resistance that were well scattered and less reliable. The Tafel plots showed the corrosion rate fell as the Cr/Ni content of the steels rose for all RTILs, in agreement with the ocp findings. Doping of the steels led to a modest change in the corrosion rate but when Cr was replaced by Mo dramatic fluctuation in corrosion took place, going up or down depending on the media. No pitting corrosion was in evidence for these steels.

EIS results were complex and uncharacteristic of the response expected for simple redox systems. The behaviour was typical of slow diffusion with the complex plane plots being compressed while exhibiting a Warburg impedance at low frequencies. The first intercept of the plot gave  $R_s$  values consistent with the known conductivities of RTILs. In the high frequency range where  $R_p$  would be expected to be displayed as a single semi-circular time constant that corresponded to a single charge transfer reaction, a broad AC response was obtained which appeared to be composed of a number of overlapping time constants.

Circular regression analysis led to  $R_p$  values much smaller than those observed using DC voltammetry. Further, the slopes of the ideal plane and Bode diagram indicated non-ideality. The AC response obtained was reminiscent of slow diffusion through surface oxide layers. A number of other processes may be responsible for non-ideal behaviour including distributed capacitance and tangential diffusion. Certainly the presence of the Warburg line at low frequencies was in agreement with the anodic concentration overpotential behaviour observed in the dc measurements. It is likely the corrosion current was controlled by charge compensating ion diffusion within the oxide layer on the surface of the steels.

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