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Article

On the Dissolution of Metals in Ionic Liquids 1. Iron, Cobalt, Nickel, Copper, and Zinc

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Abstract: Ionic liquids are critical reagents for science and technical processes nowadays. Metals are the most used reagents in the industry. It is crucial to have a deeper understanding of how ionic liquids and metals could interact. In this article the interaction of those two families of compounds is accessed. The dissolution (reaction) of metals with ionic liquids is studied, namely the influence of temperature, redox potential, and availability of an oxidant in the process. The final state achieved by the iron metal samples was also addressed by Mössbauer spectroscopy.

Keywords: solubility of metals; ionic liquids; redox potentials

1. Introduction

Ionic liquids are ionic, saltlike materials characterized by having a quite large anion and/or cation, a freezing point below 100 °C, a large liquid range (often larger than 200 °C), a high thermal stability, a room temperature viscosity normally below 100 cP, a moderate polarity, a large electrochemical window (larger than 2 V), being a good solvent for many organic reactions and possessing a negligible vapor pressure [1].

They are used in a variety of applications due to the above-mentioned properties [2,3]. Hydrometallurgy is one of them [4]. Traditional industrial processes produce large aqueous waste volumes and a large source of metal-based emissions into the environment. Those problems lead to studies on the use of ionic liquids for metal dissolution, extraction and recovery [5]. They are also applied in other metal treatment processes as metal finishing, alone or in conjunction with eutectic mixtures [6]. Some research groups try to design ionic liquids specifically for reversible electrochemical deposition/dissolution [7]. Finally, recently Binnemans and coworkers presented the ability of ionic liquids with trichloride anions for oxidative dissolution of metals and alloys [8] and a study about the dissolution of selenium was also published [9]. Another approach, although not entirely equivalent, is to consider some studies made with nanoparticles. In an attempt to prevent or reverse the sintering of transition metal catalyst nanoparticles Banerjee et al. studied the redispersion of nanoparticles sintered in tetraalkylphosphonium halide ionic liquids. Studies by TEM and UV-Vis spectroscopy showed that nanoparticles can be regenerated and their activity recovered by reversing sintering [10]. The same group also showed that Fe nanoparticles in ionic liquids with strongly coordinating anions, e.g., halides, were not particularly stable to oxidation which makes a link to the present study [11]. Another published work shows that stability and catalytic activities were dependent on the nature of the ionic liquids and could be correlated with their ionicity [12]. This study is also in line with previous investigations

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where it was found that the size of the Fe nanoparticles prepared in the presence of different ionic liquids follows the trend: [C_4mim]Cl > [C_4mim]Br > [C_4mim][BF_4] > [C_4mim][PF_6]. The authors suggested that there was an ionic liquid protective layer surrounding the nanoparticle surface, but the most interesting is their proposal of a possible reductive mechanism controlled by ionic liquids [13].

Nevertheless, fundamentals about the dissolution of metals in ionic liquids are still missing. In this work some experiments to shade some light on where the dissolution takes place, how fast it is, which are the main factors that can influence it and some insights about the mechanism are addressed. For that purpose and trying to build a proof of concept that it is possible to study the dissolution of metals in ionic liquids without the use of expensive materials and techniques, an archetypical ionic liquid (1-Butyl-3-Methylimidazolium Chloride), known for its low price and thermal stability [14], and seven p-block and transition metals (Al, Si, Fe, Co, Ni, Cu and Zn) were used.

2. Materials and Methods

2.1. Reagents

1-Butyl-3-Methylimidazolium Chloride (BMIMCl), (Aldrich, Algés, Portugal, >98%); aluminum shot (Johnson Matthey GMBH Alfa Products, Sulzbach (Taunus), Germany >99.9%), silicon single crystal chunks (Advent Research Materials Ltd., Eynsham, United Kingdom, >99.999%), copper lump (GoodFellow, Sant Cugat del Vallès (Catalonia), Spain, >99.9%), iron lump (Johnson Matthey GMBH Alfa Products, >99.9%), cobalt lump (Johnson Matthey GMBH Alfa Products, >99.9%), nickel lump (GoodFellow, >99.9%), zinc sheet (Advent Research Materials Ltd., >99.9%); ethanol 96° (Carlo Erba, Sabadell, Barcelona, Spain).

All compounds and elements were used without further purification.

2.2. Metallic Samples Preparation

The metallic samples used were prepared in the following way. A small piece or foil of metal was pressed or hammered in order to become very thin (<0.1 mm). Then, the surface was polished with sandpaper (180, 600 and 1000 mesh) in order to obtain a flat and smooth area > 1 cm^2. As a result, the side area is negligible when compared with the remaining area of the sample, and consequently the area of contact can be taken as twice the top/bottom area of the thin piece in the dissolution experiments.

2.3. Dissolution Procedure for Visualization of the Dissolution

For the optical microscopy observations, the surface of copper and iron metallic foils was additionally polished with 2500 mesh sandpaper in order to acquire a metallic mirror characteristic. In a first step the copper foil was immersed in 1-Butyl-3-Methylimidazolium Chloride (BMIMCl) ionic liquid at 100 °C for 5 h 30 min, removed, cleaned and observed by optical microscopy. In a second step, the copper and iron foils were submerged in the ionic liquid at 150 °C for 40 h, and again removed, cleaned, and examined by optical microscopy.

2.4. Dissolution Procedure for Rate Determination

The ionic liquid BMIMCl was weighed inside a graduated glass beaker using a KERN model ABT 120-5DM analytical balance with a 10^{-5} precision. Then, the beaker glass with the liquid inside was inserted into an oven (Nahita—model 655) already set at the temperature desired for each experiment, controlled to ±1 °C. After the temperature stabilization, the metal piece (previously weighed) was put inside the ionic liquid and the time counting started. After the desired period the beaker glass was removed from the oven and allowed to cool down inside a desiccator with silica gel. When 25 °C was reached, the metallic piece was carefully removed from the ionic liquid (with a minimum ionic liquid quantity), washed with ethanol, dried, and weighed. The glass with the remaining ionic liquid was weighed again (to consider the liquid lost when taking the metal out) and the process was repeated as long as the metal piece kept its shape. This procedure was repeated with the iron, copper, cobalt, nickel, and zinc pieces (aluminum and silicon were not tested at all temperatures since they didn't dissolve), at 120, 140, 160 and 180 °C and for periods of time up to >1000 h. The amount of ionic liquid used in each experiment varies from 5 to 10 g. The amount of metal used varies from 0.2 to 0.5 g. Thus, the ratio of ionic liquid to metal used in the several experiments varies from a minimum of 10 to a maximum of around 50. No difference was noted with the change of IL/M ratio (in the studied range) for the several experiments performed using the same metal and temperature.

Dissolution experiments were also performed in oxygen-free atmosphere. The ionic liquid was first subject to vacuum inside a Schlenk tube to remove the dissolved gases. The Schlenk tube was then inserted into a glovebox with a content of oxygen and water lower than 5 ppm. Zinc and iron metal pieces, together with a glass beaker, were also introduced into the glovebox. A measured amount of ionic liquid (similar to the one used in the experiments conducted in air atmosphere) was dropped in the glass beaker together with the metallic piece. Finally, the glass beaker was inserted in a sealed metallic cylinder container with a screwed lid. The entire ensemble was taken out from the glovebox and put inside the oven at the desired temperature. After a certain period, the container was taken out from the oven, cooled down to room temperature, transferred into the glovebox and finally opened inside it. During all the process until the container was opened inside the glovebox the ionic liquid and the metal piece never made contact with the atmosphere. The metal piece was removed from the ionic liquid, cleaned, and weighed as previously described, to calculate how much of it dissolved in the ionic liquid. The iron solutions produced in this experiment were used in Mössbauer spectroscopy studies.

2.5. Mössbauer Spectrometry

Mössbauer spectroscopy was used in the case of the iron dissolution to characterize the oxidation state of the iron in solution. The spectra were collected in transmission mode using a conventional constant-acceleration spectrometer and a 25 mCi ^{57}Co source in a Rh matrix. The velocity scale was calibrated using α-Fe foil. Isomer shifts are given relative to metallic α-Fe at room temperature. Spectra were collected below the freezing point of the sample using a bath cryostat with the samples immersed in liquid He for measurements at 4 K or in He exchange gas at 20 K. The spectra were fitted to a quadrupole doublet of Lorentzian lines using a nonlinear least-squares method [15].

3. Results and Discussion

Dissolution of Metals in Imidazolium Chloride

The optical microscopy observation of the copper foil after immersing in the ionic liquid for 5 h 30 min at 100 °C revealed no substantial changes when compared with the original material, which led us to test higher temperatures and immersion times. The copper foil treated at 150 °C for 40 h already shows significant signals of dissolution, as can be seen in Figure 1a,b. This effect is more evident in the case of the iron foil, where some fractures were present in the original material (Figure 1c): the attack started from those regions through the grain limits (Figure 1d), the place in the surface with the higher energy, and large cavities can be seen.

The optical observation of copper and iron dissolution in BMIMCl suggested a deeper study on the factors that can influence this dissolution and its mechanism. This study is presented below.

Under the conditions described in the Experimental Section, the copper, iron, cobalt, nickel, and zinc metals were studied and some of the results obtained for 160 °C are presented in Figure 2. Aluminum and silicon were also tested but no signs of dissolution were observed in both cases. For each temperature and metal, the rate of dissolution was found to be constant in the time range studied in this work. The slopes for the several regression lines in Figure 2, as well as regression factors, are as follows: $y = 0.798\ x$ with $R^2 = 0.995$ (iron); $y = 0.697\ x$ with $R^2 = 0.996$ (cobalt); $y = 0.652\ x$ with $R^2 = 0.999$ (nickel); $y = 0.386\ x$ with $R^2 = 0.993$ (copper); and $y = 1.071\ x$ with $R^2 = 0.998$ (zinc).

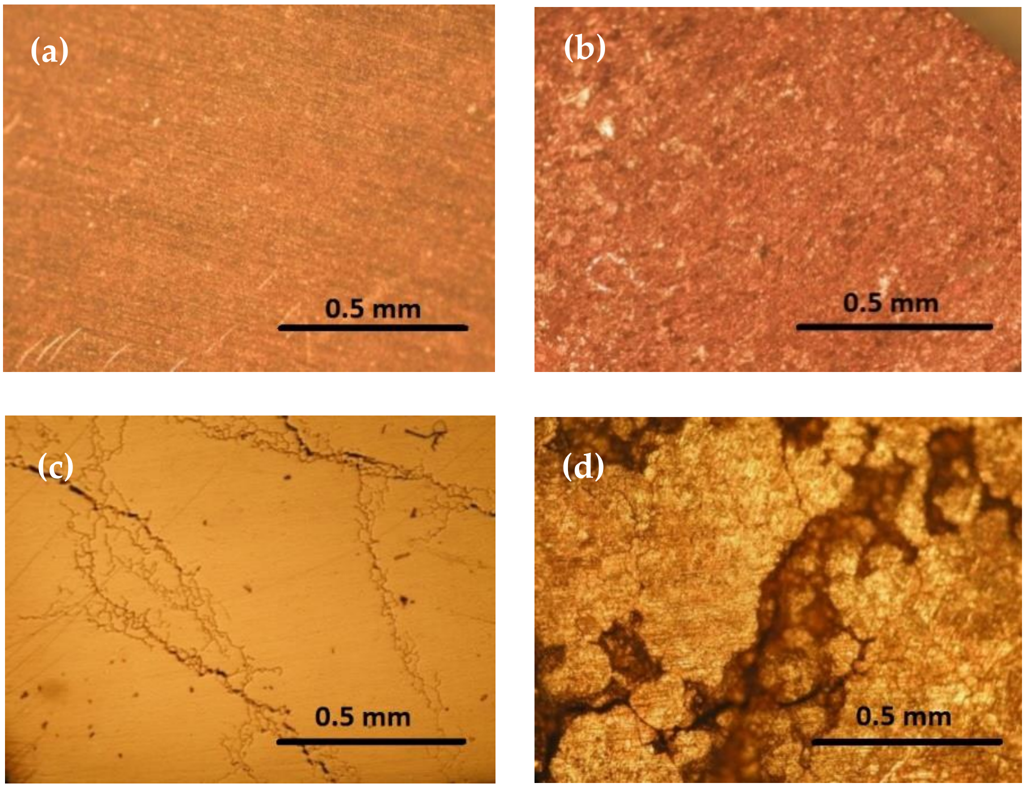

Figure 1. Optical micrographs of the copper, (**a**,**b**), and iron, (**c**,**d**), before and after the immersion in BMIMCl at 150 °C for 40 h, respectively.

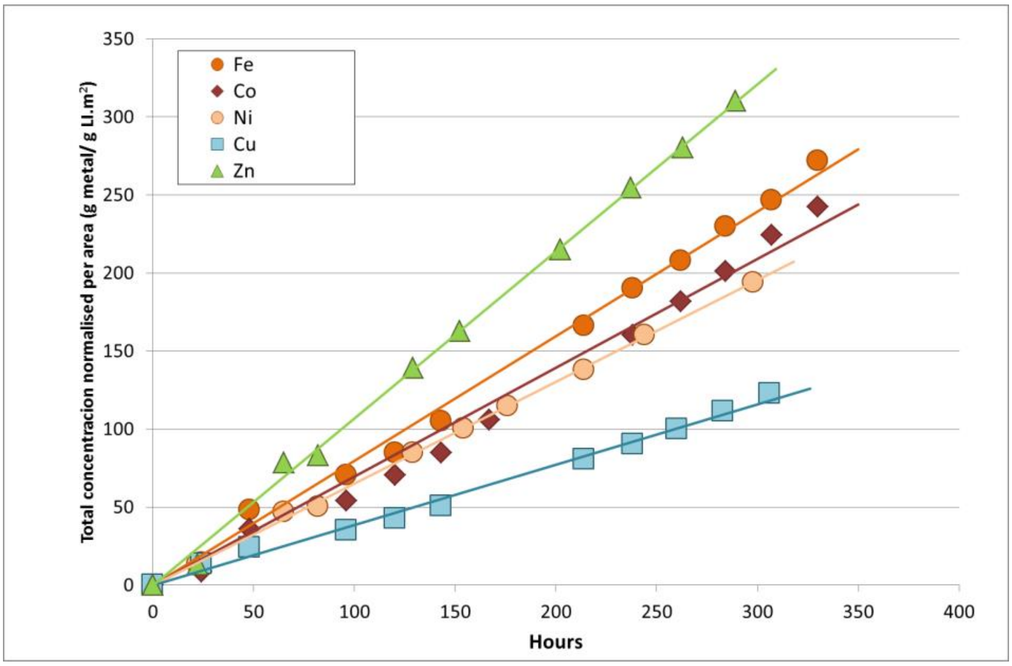

Figure 2. Concentration of dissolved metal in 1-Butyl-3-Methylimidazolium Chloride normalized for a unit area of metal as a function of time for 160 °C experiments. The points are experimental values (orange circles—iron; red diamonds—cobalt; tan circles—nickel; blue Squares—copper; green triangles—Zn).

All values are normalized for a unit area of metal to be comparable. In Table 1 the values for these experiments, as well as equivalent values obtained for other temperatures, are compiled.

Table 1. Metals used, temperatures studied, rates and normalized rates.

Metal	Temperature (°C)	Area of Metal in Contact (m^2)	Rate ($g_{metal}/(g_{IL} \cdot h)$)	Normalized Rate [a] ($g_{metal}/(g_{IL} \cdot h \cdot m^2)$)
Fe	140	2.38×10^{-5}	4.710×10^{-6}	0.198
	160	1.07×10^{-4}	8.560×10^{-5}	0.798
	160	8.86×10^{-5}	6.885×10^{-5}	0.777
	160	7.15×10^{-5}	4.536×10^{-5}	0.634
	160	6.00×10^{-6}	4.329×10^{-6}	0.722
	180	1.88×10^{-5}	6.256×10^{-5}	3.335
Co	160	3.68×10^{-5}	2.506×10^{-5}	0.681
	160	1.86×10^{-5}	1.164×10^{-5}	0.626
Ni	160	1.49×10^{-4}	9.679×10^{-5}	0.651
Cu	140	2.88×10^{-5}	5.319×10^{-6}	0.185
	160	1.40×10^{-5}	6.534×10^{-6}	0.467
	160	2.28×10^{-4}	8.644×10^{-5}	0.379
	180	2.80×10^{-5}	3.160×10^{-5}	1.129
Zn	120	9.50×10^{-5}	5.286×10^{-6}	0.056
	120	8.61×10^{-5}	4.174×10^{-6}	0.048
	140	3.32×10^{-4}	1.236×10^{-4}	0.372
	160	1.39×10^{-4}	1.482×10^{-4}	1.069
	180	2.98×10^{-4}	1.149×10^{-3}	3.854

[a] normalized for a unitary area of metal.

A first comment goes to the good reproducibility achieved (see e.g., the values obtained for four different iron samples at 160 °C). A second comment goes to the clear dependence from temperature, with the normalized rate (last column of Table 1) strongly increasing with temperature, and indicating an endothermic dissolution. Finally, a third comment goes to the fact that the slope remains constant even after hundreds of hours. It must be noted that in a conventional process the dissolution rate decreases with time until it reaches a null value, where an equilibrium between dissolution and deposition is achieved, which corresponds to the solubility (saturation) of the solute in the solvent.

For some of the metals (iron, copper and zinc) several temperatures were studied, so it is possible to see how temperature influences the solution rate. The obtained results are depicted in Figure 3 and show a logarithmic behavior which is expected for a process that possesses some activation energy. However, some caution is needed since the used ionic liquid can suffer decomposition with long term treatments at high temperatures. Despite the fact that this ionic liquid is stable [14] and its decomposition temperature in the short term is above 250 °C [16], in the long run the same reference states that the loss of 1% mass per 10 h occurs somewhere around 140 °C [16]. In addition, another reference [17] indicates that at 180 °C isothermal TGA studies with 15–18 milligrams with argon purge of 150 mL/min could lead, for this ionic liquid, to a loss of about 25% of the mass in about 15 h. We checked and, in our conditions (a static oven and circa 10 g of ionic liquid in a glass beaker), after 24 h a loss of only ~1%, at most, was detected. Nevertheless, if some loss of ionic liquid occurs due to temperature, and considering the methodology used, the concentration in solution would be even higher and the process even faster.

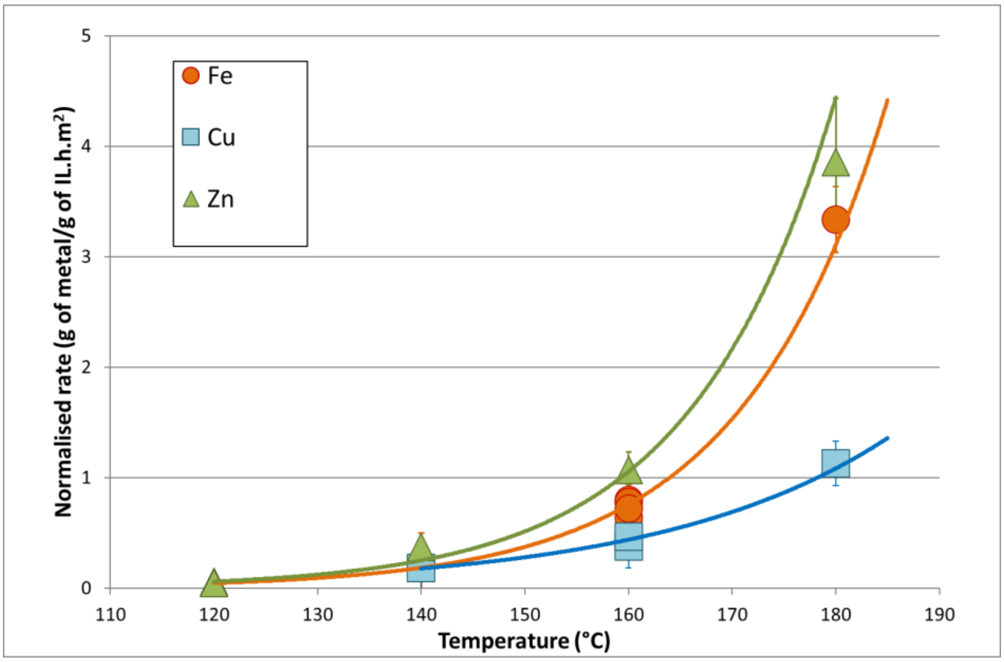

Figure 3. Normalized rate as a function of temperature (orange circles—iron; blue Squares—copper; green triangles—Zn). The lines are exponential curves with the following equations: $y = 9.38 \times 10^{-6} e^{7.06 \times 10^{-2} x}$; $R^2 = 0.988$ (iron); $y = 3.14 \times 10^{-4} e^{4.53 \times 10^{-2} x}$; $R^2 = 0.983$ (copper); $y = 1.06 \times 10^{-5} e^{7.19 \times 10^{-2} x}$; $R^2 = 0.984$ (zinc).

Mössbauer spectroscopy was used to study the Fe solutions in order to shed some light on the dissolution mechanism. The spectrum of Fe dissolved in the ionic liquid consists of a single quadrupole doublet (Figure 4). The estimated isomer shift relative to metallic α-Fe at room temperature and quadrupole splitting (Table 2) are typical of high-spin Fe^{2+}, spin state S = 4 [18]. No traces of metallic Fe or Fe^{3+} are observed. The results therefore show that all the iron present in solution is present as Fe^{2+}. Thus, an oxidation process is involved in the dissolution of metals in ionic liquid. If the metal oxidizes an oxidant should be present. Our first guess is molecular oxygen dissolved in the ionic liquid. Another possibility could be that the organic cation of the ionic liquid (1-Butyl-3-Methylimidazolium) will reduce to 1-Butyl-3-Methylimidazole. These two possibilities were tested, and the obtained results are presented below.

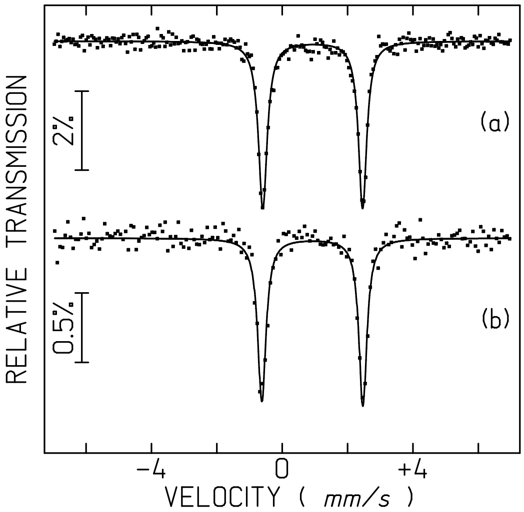

Figure 4. Mössbauer spectra taken at 4 K of Fe dissolved in the ionic liquid in air (**a**) and in nonoxidizing atmosphere (**b**).

Table 2. Estimated parameters from the Mössbauer spectra.

Sample	T	IS	QS
Fe dissolved in the ionic liquid in air	20 K	1.05	3.05
	4 K	1.05	3.09
Fe dissolved in the ionic liquid in nonoxidizing atmosphere	4 K	1.04	3.09

IS (mm/s) isomer shift relative to metallic α-Fe at 295 K; QS (mm/s) quadrupole splitting. Estimated errors $\leq$ 0.02 mm/s.

An experience was designed in order to mimic those already done, but in the absence of oxygen. The ionic liquid was subject to vacuum inside a Schlenk tube to remove all the dissolved gas. The tube was then inserted in a glovebox with a content of oxygen and water lower than 5 ppm. Metal pieces (zinc and iron were used in this experiment) and glasses were put inside the glovebox. Measured amounts of ionic liquid were introduced in the glasses with the metallic pieces. Finally, the glasses were inserted in a stanch sealed metallic cylinder container with a screwed lid. The ensemble was taken out from the glovebox and put inside the oven at 160 °C as in the other experiments described above. After 120 h the container was taken out of the oven, cooled down to room temperature, transferred into the glovebox and finally opened inside it. The metal pieces were taken from the ionic liquid and cleaned as previously described. Then, they were weighed to calculate how much of it dissolved in the ionic liquid. Almost no metal dissolves (less than 1% when compared with the other experiments) which support that the oxidant of the process is the dissolved molecular oxygen.

The Mössbauer spectrum of Fe dissolved in BMIMCl following the nonoxidizing procedure described above show a much lower relative absorption than the spectrum of the sample obtained in air (Figure 4), consistent with a significantly lower dissolution of the metal under these conditions. The estimated (mm/s) isomer shift relative to metallic α-Fe at 295 K (IS) and (mm/s) quadrupole splitting (QS) (Table 2) of the doublet observed are the same as those of the sample obtained in air, showing that the very low amount of Fe that was dissolved is present as Fe^{2+} in the same form in both samples.

The other possibility for explaining the very small amount of Fe dissolved in the experiment in the absence of air could be the reduction of the organic cation to 1-Butyl-3-Methylimidazole. In this case it should be possible to detect the signature of the imidazole in the infrared spectra. The infrared spectra of several final solutions of the ionic liquid were obtained. Some bands that can be attributed to the imidazole were detected, but the result is not clear since they are indistinguishable from those of imidazoliumn. All this, points to residual dissolved oxygen being the most probable reason for the observed residual dissolution.

The results obtained indicate that the dissolution process involves the oxidation of the metal via the dissolved molecular oxygen and suggests that the metallic cation replaces the organic cation of the ionic liquid. This process can explain why the rate of dissolution remains constant even after hundreds of hours: as long as there are organic cations to be replaced by the metallic cations the process could keep going on at a steady pace. Probably, when approaching the total substitution of the organic cation some decrease in the slope would be noticed. However, after around 300 h at 160 °C for iron and Zn, respectively, only 18.2% and 19.6% of the total organic cations were replaced by metal ones, showing that the full substitution is still quite far away.

Since the process involves the oxidation of the metals under study the obtained rates are expected to correlate with the redox potentials of those metals. Taking into account that iron oxidizes to the +2 state (as showed by the Mössbauer experiments) it will be considered that all the metals will oxidize to the same oxidation state. The redox potentials for the $M^{2+} + 2e^- \rightleftharpoons M(s)$ equation are -0.76 V for zinc, -0.44 V for iron, -0.28 V for cobalt, -0.25 V for nickel and +0.34 V for copper [19–21]. The obtained results for this correlation are presented in a graphical form in Figure 5. A linear fit is achieved for each temperature, in agreement with the oxidation of the metals as the main cause for dissolution.

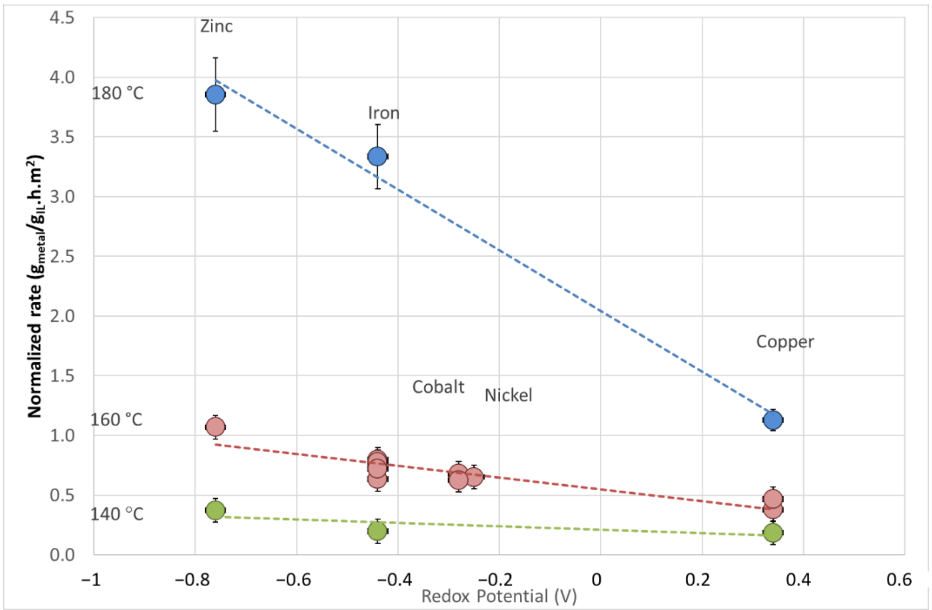

Figure 5. Normalized rate as a function of the Normal Redox potential for the various metals (blue dot—180 °C; red dot—160 °C; green dot—140 °C).

To better understand the dissolution process, fresh solutions of Fe, Cu, Co and Al in the ionic liquids were prepared and the metals were allowed to dissolve at 120, 140 and 160 °C for around 330 h. At that point, the experiment was stopped and the metals were weighed to determine the concentrations in solution and the density of the final solutions (with the metal dissolved) by using a small 5 mL picnometer. The density of the pure ionic liquid was also measured as 1.0865, which is in good agreement with the published value [22]. The data for the densities and the concentration of metal in solution are presented in Table 3. The data for aluminum metal was not presented in the table since, as previously observed, the aluminum does not dissolve, and the densities of all solutions are similar to that of the pure ionic liquid. A correlation between the density of the solutions and the studied temperature can be noticed (Figure 6). It has some similitude with Figure 3. However, far more interesting is a correlation of the metal concentration vs. the density of the solution (Figure 7). It seems that as the metal dissolves and the metal cation replaces the organic cation, the density of the solution grows in the same proportion, which agrees with the replacement of the organic cation by the metal cation.

Table 3. Densities and metal concentration of final solutions.

Temperature (°C)	Metal	Density (g/mL)	Metal in Solution (g_{Metal}/g_{IL})
120	Cu	1.0897	0.00082
	Fe	1.0966	0.00758
	Co	1.0878	0.00041
140	Cu	1.0924	0.00268
	Fe	1.0993	0.00895
	Co	1.0939	0.00234
160	Cu	1.1261	0.02749
	Fe	1.1295	0.02915
	Co	1.1130	0.01890

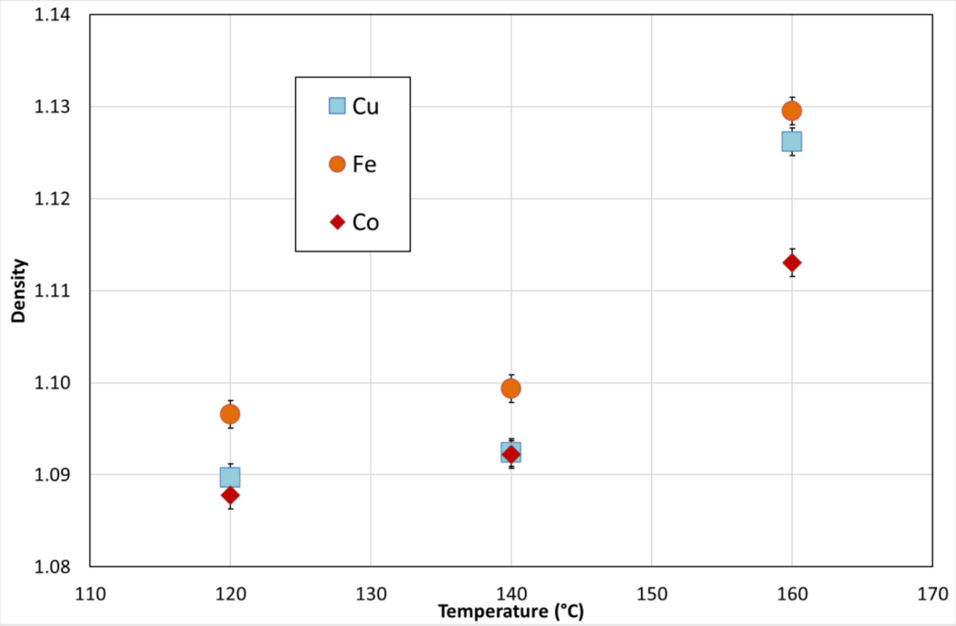

Figure 6. Density of the final IL solutions as a function of the temperature.

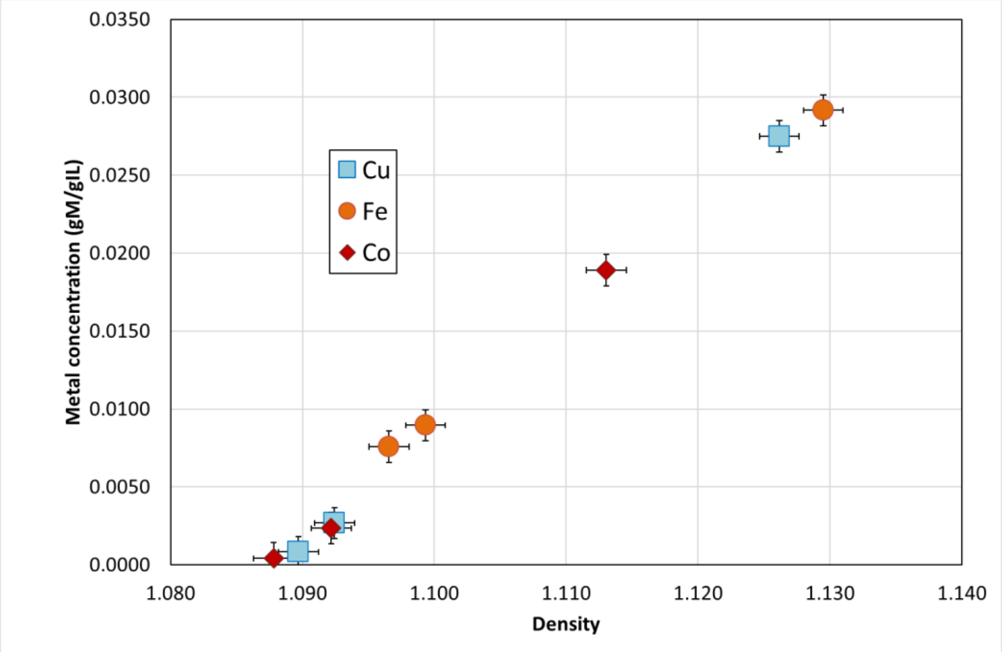

Figure 7. Concentration of metal as function of the density of the final IL solutions.

4. Conclusions

The present study on the interaction between metals and ionic liquids led to several major conclusions. Only transition metals, Fe, Co, Ni, Cu and Zn, are significantly dissolved, while Al and Si (p-elements) are not. The "dissolution" of the transition metals in ionic liquids is in reality a redox oxidation reaction where the metal is oxidized from zero to a divalent oxidation state. Thus, the metal can substitute the organic cation in the ionic liquid structure, resulting in an enormous dissolution capability. Even in the cases where the metal reacts with the ionic liquid for around 300 h at 160 °C, only 18–19% of the organic cations are substituted by the metallic cations. This is probably the reason why the rate of "dissolution" is constant along the time in the studied periods.

A strong effect of temperature was also noticed. Finally, the densities of Fe, Co and Cu solutions were found to follow a common straight line that depends solely on the metal concentration. This is probably a consequence of the similarity between the densities of the studied metals, but agrees with the replacement of the organic cation by the metal cation, as suggested by the Mössbauer data and the experiments in nonoxidizing atmosphere.

These final solutions could be very interesting for applications, since metal concentration obtained is rather high and the metal atoms are quite separated from each other. One of their possible uses is in homogeneous catalysis since a very high availability of the metals should be achieved.

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