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Compatibility of Imidazolium-Based Ionic Liquids for CO_2 Capture with Steel Alloys: a Corrosion Perspective

Maria Vittoria Diamanti*, Ursenna Vittoria Velardi, Andrea Brenna, Andrea Mele, MariaPia Pedeferri, Marco Ormellese

Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Via Mancinelli 7, 20131 Milan, Italy

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ABSTRACT

Ionic Liquids (ILs) could find applications in CO_2 stripping, where their use could reduce energy consumptions compared to current technologies based on amine absorption. Although preliminary studies showed potential compatibility between metallic alloys and a limited number ILs, their corrosiveness still needs to be fully assessed. This work analyzes the corrosion behavior of steel alloys in contact with several imidazolium-based ILs, changing alternatively cation and anion to highlight possible dependences of corrosion behavior on relevant groups. Potentiodynamic polarization tests were performed in all ILs considered and in water as reference. Different ILs preparation conditions were considered: after purging in nitrogen, i.e., with reduced content of oxygen and water, and after exposure to the atmosphere to restore their natural humidity and oxygen content. Results showed a reduction in the protective character of stainless steel passive film, with no clear trend related to anion composition or cation chain length. Conversely, carbon steel corrosion rate decreased compared to aqueous solutions, and a passivation effect was observed in presence of long chain cations, which was ascribed to a steric effect of adsorbed molecules.

1. Introduction

CO_2 is one of the most important greenhouse gases, representing 77% of total greenhouse gas emissions [1], and is therefore responsible for the majority of infrared energy absorption that increases the temperature of the troposphere – the phenomenon known as global warming. Several CO_2 capture and storage (CCS) or conversion processes have been developed: among them, currently the most used is the post-combustion CO_2 absorption with alkanolamine solvents such as monoethanolamine (MEA), diethanolamine (DEA) and N-methyldiethanolamine (MDEA) [2–4]. This process still presents some drawbacks, such as high energy consumption for solvent regeneration, limited cyclic CO_2 loading capacity and especially corrosiveness towards metallic alloys in contact with the solvent, which limits their industrial use [5,6]. As a matter of fact, the best performing solvents in CO_2 recovery are MEA and primary amine-based ones, but they are also the most corrosive towards steels as compared with other amine solvents, since they react with CO_2 to produce carbamates – which in turn hinder the formation of a protective $FeCO_3$ layer on steel alloys. Moreover, diamines, resulting from degradation of primary and secondary amines, can be strong chelators of iron and thus promote corrosion by acid gases [7–9].

In this frame, the use of ionic liquids (ILs) is proposed as a valid alternative to the current amine-based technology [10]. The interest in ILs as fluids for CO_2 capture and for important applications such as natural gas sweetening relies upon the capability of some ILs of retaining significant amounts of CO_2 while showing limited absorption properties towards hydrocarbons, methane in particular [11]. Moreover, these solvents would provide high efficiency and cyclic loading capacity thanks to a low vapour pressure, which allows full regeneration and reuse without losses in gas streams, and high temperature and chemical stability; regeneration itself would require less energy, due to a different absorption mechanism compared with amines [12,13]. The latter point is of pivotal importance in view of possible applications of ILs technology on the industrial scale. As recently stressed, one of the major issues against the use of ILs is their high cost. However, Papatryfon et al. [14] pointed out that the capability of ILs based absorption units of undergoing sequential duty cycles without need to replenish should

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* Corresponding author. Tel.: +39 0223993137; fax: +39 0223993180.
E-mail address: mariavittoria.diamanti@polimi.it (M.V. Diamanti).

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be accounted for in the economic comparison with the currently used amine based processes that, conversely, require frequent shut down steps. A careful evaluation of the costs associated to ILs use on industrial scale is thus mandatory before discarding ILs as alternative materials for CO_2 sorption.

The direct contact of ILs based sorbents to the metallic components of a plant – pipes, reactors, heat exchangers, desorption chambers etc. – calls for a deep understanding of the compatibility between ILs and metallic materials. Some studies have been performed, mostly focusing on the use of ILs as corrosion inhibitors [15–19], or on the development of new protection solutions for highly reactive metals, such as magnesium or aluminium: this is based on the formation of conversion coatings some tens or hundreds of nanometres thick, rich in phosphates and other ions that show passivating behavior towards such metals [20–22]. On the other hand, fewer studies deal with their corrosiveness towards metals and other materials, from steel alloys to copper and magnesium, to carbon [23–31]. In this respect, common examples of ILs tested include chloride-rich ones, which are clearly unsuitable for the purpose and induce harsh corrosion conditions, being chlorides extremely aggressive towards active-passive metals [27,28]. In the present paper we start a systematic study of the corrosion properties of some alkyl-methylimidazolium ILs [C_nC_1Im] with fluorinated anions on steel alloys. As a starting step of a long term project, we report here on the role played by different alkyl chain lengths bound to the imidazolium ring, and by three different anions, bis(trifluoromethylsulfonyl) imide ([TFSI]), tetrafluoroborate ([BF_4]) and hexafluorophosphate ([PF_6]). This class of ILs showed potential capability of CO_2 capture with good performances [32–34]. The main purpose of this work is to provide some paradigmatic examples and testing protocols of the corrosion profile of pure ILs with CO_2 capture capabilities on steel alloys, as simple systems mimicking the conditions of an industrial plant. Although these systems have been thoroughly investigated from the structural and physicochemical point of view, they have received only marginal attention in the evaluation of their potential corrosiveness towards metallic facilities [35–38]. On account of their potential industrial importance, a systematic study over the corrosion resistance of the typical metals used in existing plants is required to fill this gap. Previous studies on carbon steel pointed out limited corrosiveness of 1-butyl-3-methylimidazolium and 1-ethyl-3-methylimidazolium tetrafluoroborate, also in co-presence of amines and CO_2 [35]; some imidazolium-based ILs are even considered for applications as corrosion inhibitors, due to their adsorption and consequent formation of a protective film on the steel surface [15–18]. More specific and wider spectrum studies showed a correlation between an increase in alkyl chain length and inhibitive properties of 1-alkyl-3-methylimidazolium tricyanomethanide, and associated localized corrosion events with the dissolution of manganese sulfide impurities [36,37]. Yet, such studies are far from completing the picture of ILs corrosiveness, concerning both potential ILs compositions and preparation conditions – e.g., water content, oxygen content, CO_2 content, understanding of the corrosion mechanisms on different metallic alloys.

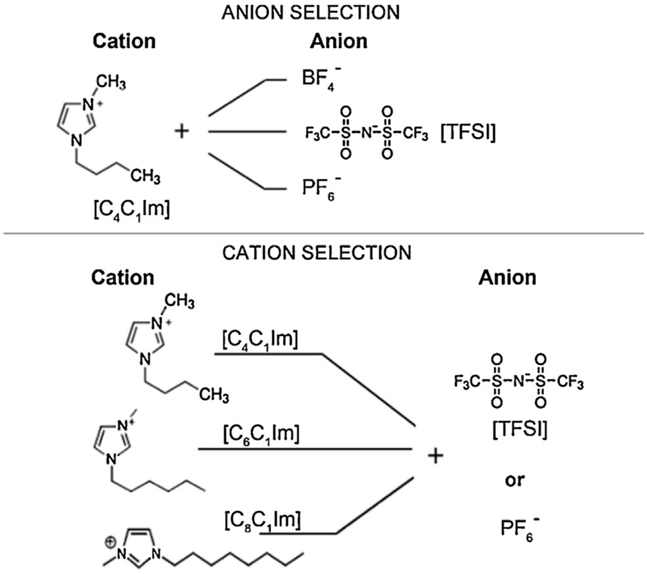

Fig. 1. Molecular structures of ILs investigated; the variation of anions on a common cation and of cations on a common anion is highlighted.

2. Experimental methods

Imidazolium-based ILs were purchased from IOLITEC GmbH, with declared purity higher than 99%. Different formulations were chosen, in order to observe the possible influence of either anion composition or cation alkyl chain length. The following ILs were selected: 1-butyl-3-methylimidazolium tetrafluoroborate [C_4C_1Im][BF_4], 1-butyl-3-methylimidazolium hexafluorophosphate [C_4C_1Im][PF_6], 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide [C_4C_1Im][TFSI] to test the effect of anion composition; 1-butyl-3-methylimidazolium [C_4C_1Im], 1-hexyl-3-methylimidazolium [C_6C_1Im], and 1-methyl-3-octylimidazolium [C_8C_1Im], all combined with [TFSI] anion or with [PF_6] anion to test the effect of alkyl chain. Molecular structures are summarized in Fig. 1; the main physical properties are reported in Table 1.

All ILs were preliminarily treated in vacuum at 70 °C for five hours in order to minimize water content, which was then measured by Karl Fischer titration. ILs were stored under nitrogen atmosphere in a drybox in order to keep water and oxygen content as low as possible. Initial water contents resulted to be between 100 and 1000 ppm, being lower in [TFSI] based ILs; this demonstrates a hydrophilic character of the selected ILs, which tend to absorb water by simple contact with the atmosphere, as happened when preparing them for the measurements. Corrosion tests were performed on the dehydrated and purged ILs: water values measured before and after potentiodynamic polarization tests were very similar, indicating that the corrosion tests were performed in homogeneous conditions.

Corrosion tests were then repeated on ILs after aeration by exposure to the atmosphere for 48 hours, in order to restore their natural oxygen content and humidity, which increased by 20% in [TFSI] based liquids, by 100% in [PF_6] ones and by 1 order of

Table 1
Physical data of ILs investigated, as provided by the producer.

IL	[C_4C_1Im][TFSI]	[C_6C_1Im][TFSI]	[C_8C_1Im][TFSI]	[C_4C_1Im][BF_4]	[C_4C_1Im][PF_6]	[C_6C_1Im][PF_6]	[C_8C_1Im][PF_6]
purity	>99%	>99%	>99%	>99%	>99%	>99%	>99%
density (g/ml)	1.43	1.36	1.32	1.17	1.37	>1.26	1.20
viscosity (cP)	61.41	68	104	108	285	>707	1052
water (ppm)	50	100	40	150	120	>190	180