Imidazolium ionic liquids: A simple anion exchange protocol†‡

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An efficient and simple protocol was developed to obtain quantitative iodide or bromide exchange for a broad range of anions in imidazolium ionic liquids. Selected anions were loaded in an anion exchange resin using two different procedures and were then used to provide a pure convenient ion pair.

Over the last few years, imidazolium-based frameworks have been developed as room-temperature ionic liquids (RTILs)[2] and there have been advances in anion recognition chemistry[1,3] as well as in N-heterocyclic carbenes (NHCs)[4,5] and their applications. Designed as greener solvents, the room-temperature ionic liquids (RTILs) have been attracting increasing interest as a potential alternative to conventional volatile organic solvents.[2] They are composed of bulky organic cations and a variety of anions whose characteristics can be tailored and tuned by a suitable choice of the cation/anion combination. The basicity, geometry and polarizability of anions are crucial not only for ion pair-formation but also for their role as technicophores, because they exhibit a high potential for tuning technological properties (*e.g.* solubility, viscosity, *etc.*).[6] Moreover, the anion as a toxicophore/ecotoxicophore of an ionic liquid can influence biological effects.[7] On the other hand, chiral anions such as (S)-lactate[8] or (S)-canphorsulfonate[9] in [bmim] salt have been used to induce diastereoselectivity.[10]

Ionic liquids have also recently attracted interest as benign solvent systems for the synthesis of nanomaterials[11] and they are emerging as alternative liquid templates for the generation of a plethora of size- and shape-controlled nanostructures. The morphologies of the metal products are more sensitive to the nature of the anions compared to the cations of the RTILs.[11c,d]

Considering these facts, the possibility of being able to systematically vary the anion constitutes an important factor in reaching the goal of sustainable design of 'task specific ionic liquids'.

The most popular RTILs are the widely employed N,N′-dialkylimidazolium salts, even though they could be considered as non-innocent solvents[12] due to the acidity of C(2)-H. A typical preparation of these salts is the quaternization of N-alkylimidazole with haloalcanes followed by anion exchange.

Over the past few years an enormous variety of halide exchange reactions have been reported. Common methods are based on either double-displacement (treatment with metal or ammonium salts) or acid–base neutralization reactions, and the resulting halide-containing by-product salts are subsequently removed by extraction or precipitation followed by filtration.[2,13] However, the purity as well as the final yield of the process continues being a motive of interest for improvement. Acids remain the ideal source of the desired anions to minimize inorganic contamination. Since an anion exchange cannot be efficiently done with the imidazolium halide and an acid weaker than a hydrohalic acid, the route to a wider range of conjugate bases must pass through a different intermediate. Based on the acidity of the C(2)-H in the imidazolium unit,[14] Earle and Seddon[15] proposed the use of strong bases to provide the formation of NHCs, which are then reprotonated with acid and consequently could potentially incorporate a large number of anions. However, it is necessary to take care with this procedure, given the stability and reactivity of the carbene intermediate.

On the other hand, ion exchange resins have been employed as an efficient tool to perform the anion exchange and their application has been extended to a variety of chemical reactions. Our research group have long used anion exchange resins and described protocols to obtain imidazolium azolate inner salts[16] or to perform halide exchange to PF_6^- through the betaine[17a] or the OH^- salt[17b,c] using Amberlite (OH form).

In the field of ionic liquids, Amberlite (OH form) is used to exchange halides by OH^-, and then acid compounds are added to the solution obtained, the hydroxide being displaced by the new anion through an acid–base reaction. This procedure is useful whenever the intermediate hydroxide salt is stable. Thus, applying this protocol, Ohno and coworkers prepared bio-RTILs when organic acids or natural aminoacids were added to the solution.[18] However, to the best of our knowledge, there are only a few examples in the open literature describing the anion incorporation in the resin before the anion exchange is carried out in a RTIL. In this way, a strong base anion-exchange resin (OH form) was loaded with camphorate, acetate, mesylate, tosylate or lactate from the corresponding acid, and [OTs],[9a] $[SO_4]$,[9b] [I][19a] or [Cl][19b] were substituted by the organic anion.

As a part of our ongoing research into imidazolium-based frameworks,[1] we herein report an efficient and practical procedure using anion-exchange resins to obtain ionic liquids based on imidazolium salts with the selected anion counterpart in quantitative yield. (see Fig. 1)

Seeking a more efficient means of halide removal, we decided to explore the use of an anion exchange resin (AER) conveniently loaded with the new desired anion to afford the expected ion pair.

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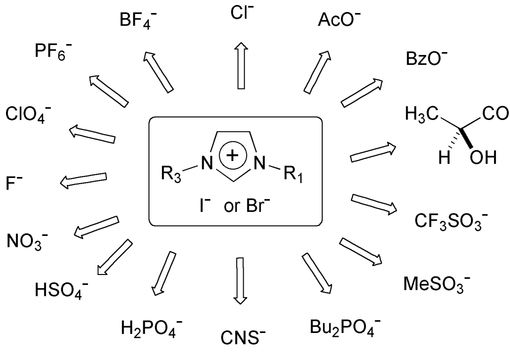

Fig. 1 Selected anions investigated to perform the halide exchange in imidazolium ionic liquids.

The initial targets of exchange were carboxylate anions, and [bmim][I] was used for carrying out the conversion. The strongly basic anion exchange resin Amberlist A-26 (OH form) was selected, given that it allows the use of aqueous mixtures and non-aqueous solvents, which facilitates the use of acids with low solubility in water. A packed column was treated with a carboxylic acid hydro-methanolic solution. The process involves the acid–base reaction with OH^-, resulting in the retention of the carboxylate anion in the resin and the displacement of the formed water together with the eluted solution (see Fig. 2).

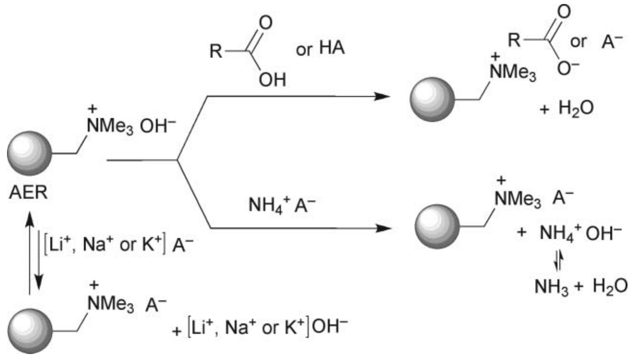

Fig. 2 Chemical processes involved when anion exchange resin OH^- form was treated with acids (organic or inorganic), ammonium salts, or alkaline salts.

A methanolic [bmim][I] solution was passed through a column packed with the A-26 ($R\text{-}CO_2^-$ form) and [bmim][AcO], [bmim][BzO] or [bmim][(*S*)-lactate] were quantitatively obtained after solvent elimination, confirmed by ^1H NMR. Remarkably, no evidence of NHC formation was observed, despite the basic media.

In order to expand the range of introducible counterions, the resin was charged with oxoanions derived from sulfonate ($MeSO_3^-$) or phosphate ($Bu_2PO_4^-$) together with inorganic anions such as Cl^-, NO_3^-, ClO_4^- or BF_4^- by treatment with the corresponding diluted acidic solutions. When the [bmim][I] solution was passed through the conveniently packed column, the exchange was carried out in quantitative form. The integration of the signal corresponding to the organic substituent in ^1H NMR showed the total exchange of I^- anion by $MeSO_3^-$ or $Bu_2PO_4^-$, whereas the C(2)-H chemical shift value in the imidazolium moiety indicated the substitution by inorganic anions.[20] Moreover, ESI(−)-MS experiments qualitatively confirmed that I^- was not present in the samples from the inorganic anion exchange,[21] according to the silver chromate test[19b] (< 20 ppm) (see ESI‡). This simple procedure allowed us to quickly and cleanly exchange the I^- anion, which was retained in the column, obtaining the pure new ion pair after the in vacuum solvent elimination. On the other hand, AER was recycled to the OH form, by treatment with a 10% NaOH aqueous solution, being available for re-use in another exchange process.

Encouraged by these results, our focus shifted toward the introduction of a new set of weakly basic anions. However, the treatment of the resin with strong acids can denaturalize the polymeric matrix by overheating during the loading, due to the high exothermic acid–base reaction. To circumvent this problem we developed a novel method to exchange hydroxide anions based on the use of ammonium salts, directly loading the anions by the reaction of the acidic cation with the basic OH^- of the resin. The aim of this procedure was to exchange OH^- for the new anion, which led to the formation of ammonium hydroxide. In aqueous solution most of this weak base remained dissociated in ammonia and water, so it did not displace the loaded anion (see Fig. 2).

The Amberlist A-26 (OH form) resin was treated with $AcONH_4$ or $ClNH_4$ aqueous solution in order to check that the loading had been effective. When the [bmim][I] solution was passed through the new charged resin, [bmim][AcO] or [bmim][Cl] were obtained in quantitative form, confirmed by comparison with the same ion pair obtained from the acid charged resin. These results confirm that the anion exchange resin can be conveniently loaded with the desired anion from the corresponding ammonium salt.

Likewise, following this procedure, $CF_3SO_3^-$ and $(CN)S^-$ anions as well as inorganic anions such as F^-, PF_6^-, $H_2PO_4^-$ or HSO_4^- were loaded in the AER (see Table 1). Complete exchange was achieved when [bmim][I] methanolic solution was passed through the column and, in all cases, ESI(−)-MS confirmed the nature of the new ion pair,[22] and the qualitative absence of the iodide anion. Although some anions (only AcO^-, Cl^- and PF_6^- were studied) could be loaded by both protocols, the use of acid was the best procedure for organic anions, and ammonium salts for inorganic anions.

On the other hand, we attempted to load the AER with the $(TfO)_2N^-$ or $MeSO_4^-$ from their commercially available Li^+ or K^+ salt, respectively. Neither of these two anions were exchanged in the resin (OH form),[23] which indicated that cations play an

Table 1 Anion source for loading Amberlist A-26[a]

Anion	Source	Anion	Source
AcO^-	$AcOH$, $NH_4^+AcO^-$	F^-	$NH_4^+F^-$
BzO^-	$BzOH$	Cl^-	$NH_4^+Cl^-$, HCl
(*S*)-Lactate⁻	(*S*)-Lactic acid	PF_6^-	$NH_4^+PF_6^-$, HPF_6
$MeSO_3^-$	$MeSO_3H$	$H_2PO_4^-$	$NH_4^+H_2PO_4^-$
$Bu_2PO_4^-$	Bu_2PO_4H	HSO_4^-	$NH_4^+HSO_4^-$
BF_4^-	HBF_4	$CF_3SO_3^-$	$NH_4^+CF_3SO_3^-$
ClO_4^-	$HClO_4$	$(CN)S^-$	$NH_4^+(CN)S^-$
NO_3^-	HNO_3		

[a] A hydro-alcholic or methanolic acid solution or aqueous ammonium salt solution were used for the loading of selected anions in AER.

important role in successful AER anion loading. When the anion exchange took place within the resin, alkaline salts (LiOH or KOH) were formed. In contrast with ammonium hydroxide, the OH^- anion in these strong bases displaced the new anion, which reversed the process and returned the resin to the OH form (see Fig. 2).[24] This aspect was confirmed when we treated A-26 (OH form) with a NaCl solution and the Cl^- exchange did not take place, although it was successfully loaded with HCl or NH_4Cl (see Table 1).

Having examined the exchange of the iodide anion, the same process was explored from the bromide imidazolium salt. Thus, treatment of [bmim][Br] with the corresponding AER, conveniently loaded with the selected anion, led to the complete exchange of Br^-, as had occurred with the I^- anion.

Regarding other ionic liquids based on imidazolium salts, [bbim][I] and [bbim][Br] were examined as well as [mmim][I], and in all cases I^- or Br^- exchange was obtained. Exceptionally, treatment of [mmim][I] afforded a quantitative exchange, although in some instances the recovery of the new ion pair was only about 90–95%.

In all cases, the purity of the ionic liquids obtained was qualitatively determined using ^{1}H-NMR spectra, and/or ESI(−)-MS experiments, and the original halide was not observed. According to the silver chromate test, most analysis indicated the low halide contents (< 20 ppm). Further quantification of possible halide impurity was restricted by instrumental limitation.

In summary, we have developed an efficient, simple and practical procedure for the exchange of iodide or bromide for a variety of anions in imidazolium ionic liquids, using an anion exchange resin. The preparation of an AER conveniently loaded with a new selected anion by treatment with acid or ammonium salts not only offers an efficient tool to prepare the appropriate ion pair, including task-specific and chiral RTILs, but it is also recyclable and minimizes the formation of toxic by-products, with the corresponding environmental benefits. Our current efforts are being directed to broadening the protocol to an increased number of anions and ionic liquids, using non-aqueous media for the loading and exchange procedures.

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