



This is a repository copy of *Infrared spectroscopic study of absorption and separation of CO using copper(I)-containing ionic liquids*.

White Rose Research Online URL for this paper:  
<http://eprints.whiterose.ac.uk/112195/>

Version: Accepted Version

---

**Article:**

Repper, S.E., Haynes, A. [orcid.org/0000-0002-6854-1618](https://orcid.org/0000-0002-6854-1618), Ditzel, E.J. et al. (1 more author) (2017) Infrared spectroscopic study of absorption and separation of CO using copper(I)-containing ionic liquids. Dalton Transactions. ISSN 1477-9226

<https://doi.org/10.1039/C6DT04816A>

---

**Reuse**

Unless indicated otherwise, fulltext items are protected by copyright with all rights reserved. The copyright exception in section 29 of the Copyright, Designs and Patents Act 1988 allows the making of a single copy solely for the purpose of non-commercial research or private study within the limits of fair dealing. The publisher or other rights-holder may allow further reproduction and re-use of this version - refer to the White Rose Research Online record for this item. Where records identify the publisher as the copyright holder, users can verify any specific terms of use on the publisher's website.

**Takedown**

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing [eprints@whiterose.ac.uk](mailto:eprints@whiterose.ac.uk) including the URL of the record and the reason for the withdrawal request.



[eprints@whiterose.ac.uk](mailto:eprints@whiterose.ac.uk)  
<https://eprints.whiterose.ac.uk/>

# Infrared spectroscopic study of absorption and separation of CO using copper(I)-containing ionic liquids

*Stephen E. Repper<sup>a</sup>, Anthony Haynes\*<sup>a</sup>, Evert J. Ditzel<sup>b</sup> and Glenn J. Sunley<sup>b</sup>*

(a) Department of Chemistry, University of Sheffield, Dainton Building, Brook Hill, Sheffield, S3 7HF, UK.

(b) BP Chemicals, Hull Research and Technology Centre, Saltend, Hull, HU12 8DS, UK

## **Abstract**

Absorption of carbon monoxide by copper(I)-containing ionic liquids,  $[C_n\text{mim}][\text{CuX}_2]$  ( $C_n\text{mim}$  = 1-alkyl-3-methylimidazolium,  $n = 2, 4, 6$ ,  $X = \text{Cl, Br, I}$ ) has been investigated using *in-situ* high pressure infrared spectroscopy. For each liquid, observation of a  $\nu(\text{CO})$  band in the region  $2075\text{-}2090\text{ cm}^{-1}$  indicates the formation of copper(I) monocarbonyl complexes, assigned as  $[\text{Cu}(\text{CO})\text{X}_2]$ . The rate of growth and equilibrium intensity of the  $\nu(\text{CO})$  absorption is dependent on applied CO pressure. Binding of CO is reversible such that complete desorption occurs rapidly on heating above  $100\text{ }^\circ\text{C}$  and the liquids are robust over multiple gas absorption/desorption cycles. For the series of  $[C_6\text{mim}][\text{CuX}_2]$  salts the CO absorption ability follows the order  $\text{Cl} \geq \text{Br} \gg \text{I}$ . Selective absorption of CO from  $\text{CO}/\text{H}_2$  and  $\text{CO}/\text{N}_2$  gas mixtures is demonstrated by measuring the changes in headspace CO content upon absorption and desorption of gas. For  $[C_6\text{mim}][\text{CuCl}_2]$ , a single absorb-vent-desorb

cycle yields product gas containing ~95% CO starting from a 1:1 CO/N<sub>2</sub> mixture, increasing to ~98% CO starting from a 4:1 CO/N<sub>2</sub> mixture. This is particularly promising in view of the similar boiling points of CO and N<sub>2</sub> that hinders their separation by cryogenic distillation.

## Introduction

Carbon monoxide is a key feedstock in a number of commercially important industrial processes.<sup>1-3</sup> It is usually generated as synthesis gas (syngas), a CO/H<sub>2</sub> mixture produced from fossil fuel feedstocks, e.g. by steam reforming or partial oxidation of methane.<sup>4</sup> Depending on the application, separation of the components of syngas may be necessary to give CO of high purity. This is most often achieved by cryogenic separation,<sup>5</sup> which allows for the production of high purity CO on a large scale. However, this process is very energy intensive and is also not ideal for gas mixtures with significant nitrogen content due to the similarity in boiling points of CO and N<sub>2</sub>.

Alternative technologies for CO purification are generally based on chemisorption, most often using copper(I) compounds that can bind CO reversibly. The chemistry of Cu(I) carbonyl complexes is well established and the formation, structures and bonding of these species has been discussed extensively elsewhere.<sup>6-19</sup> Strategies for CO-separation that make use of Cu(I) include (i) pressure/temperature swing adsorption (PSA/TSA) using Cu(I) salts on a solid supports (e.g. silica, alumina, carbon, zeolites);<sup>20-23</sup> (ii) an ammoniacal process using CuCl dissolved in aqueous NH<sub>3</sub>;<sup>5</sup> (iii) the COSORB process using CuCl/AlCl<sub>3</sub> dissolved in toluene.<sup>5, 24-27</sup> While these processes have demonstrated considerable potential, some notable drawbacks have prevented their large-scale adoption in industry. The PSA/TSA-type processes are limited by a relatively poor recovered yield of CO, while the ammoniacal process requires the use of a corrosive reaction medium and the COSORB process uses a highly water sensitive absorbent. Both of the solution-based methods also

suffer from potential contamination of the recovered CO by volatiles from the absorbent medium.

An alternative approach is to employ a non-volatile solvent, specifically an ionic liquid, as solvent for the Cu(I) species. Ionic liquids are low melting salts that have received considerable attention over recent years as potential solvents for a range of applications including catalysis and separations.<sup>28-33</sup> Due to electrostatic interactions between the component ions, they exhibit extremely low vapour pressures. Although they are no longer considered completely non-volatile under high vacuum conditions, they can be regarded as having negligible vapour pressure under the conditions of a CO purification process.<sup>34,35</sup>

Low melting copper(I) salts were first reported in 1963 by Tollin *et al* who showed that that a 1:1 melt reaction between [NEt<sub>3</sub>H]Cl and CuCl gives a room temperature liquid.<sup>36</sup> Further studies of this melt, and others containing imidazolium and phosphonium cations, have shown that copper(I) can exist as a number of [Cu<sub>n</sub>Cl<sub>m</sub>]<sup>(m-n)-</sup> anions (e.g. [CuCl<sub>3</sub>]<sup>2-</sup>, [CuCl<sub>2</sub>]<sup>-</sup>, [Cu<sub>2</sub>Cl<sub>3</sub>]<sup>-</sup>).<sup>37-41</sup> For the C<sub>2</sub>mimCl/CuCl system (C<sub>2</sub>mim = 1-ethyl-3-methylimidazolium), a minimum in viscosity and a maximum in ionic conductivity occur at the 1:1 ratio, consistent with [CuCl<sub>2</sub>]<sup>-</sup> as the dominant anionic species. At CuCl mole fractions above or below 0.5 the less mobile species [Cu<sub>2</sub>Cl<sub>3</sub>]<sup>-</sup> and [CuCl<sub>3</sub>]<sup>2-</sup> accumulate. The solid state structure of [C<sub>4</sub>mim]<sub>2</sub>[CuCl<sub>3</sub>] was recently investigated in a low temperature crystallographic study.<sup>42</sup>

The potential use of copper-containing ionic liquids for gas adsorption has been demonstrated in recent work on alkene/alkyne separation,<sup>43</sup> adsorption of NH<sub>3</sub><sup>44</sup> and PH<sub>3</sub><sup>45</sup> and scrubbing of mercury vapour from natural gas.<sup>46</sup> Desulfurisation of gasoline by complexation of thiophene to Cu(I) in an ionic liquid has also been reported.<sup>47</sup> Most relevant to the present study is the recent work by Urtiaga and co-workers using CuCl dissolved in 1-hexyl-3-methylimidazolium chloride ([C<sub>6</sub>mim]Cl).<sup>48</sup> It was found that the absorption of CO increased

markedly as the CuCl:[C<sub>6</sub>mim]Cl mole ratio was raised over the range 0-0.75:1. The uptake of CO displayed saturation-type pressure dependence, and was consistent with formation of a monocarbonyl copper(I) species. The equilibrium constant for binding of CO to Cu(I) was found to decrease with increasing temperature, and the enthalpy of complexation was determined to be exothermic (-13.4 kJ mol<sup>-1</sup>). In further work on the [C<sub>6</sub>mim]Cl/CuCl system, Urriaga and co-workers have reported the kinetics of CO uptake,<sup>49</sup> mass transport and rheological properties,<sup>50-52</sup> and the use of supported ionic liquid membranes (SILMs) to facilitate separation of CO/N<sub>2</sub> gas mixtures.<sup>53-55</sup>

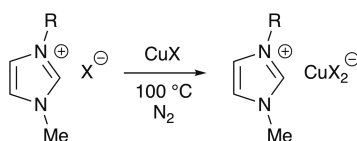
Here we report an investigation of the copper carbonyl species formed by reaction of CO with room temperature ionic liquids based on mixtures of 1-alkyl-3-methylimidazolium halides and copper(I) halides. *In situ* high pressure infrared (HPIR) spectroscopy enables the reversible formation of Cu(I) carbonyl complexes to be observed directly by monitoring their  $\nu(\text{CO})$  absorptions. This represents the first spectroscopic detection of the metal carbonyl species responsible for CO binding in these systems. The ability of these solutions to absorb CO selectively from CO/H<sub>2</sub> and CO/N<sub>2</sub> gas mixtures is also demonstrated using IR spectroscopy to quantify the headspace CO content.

## Results and Discussion

### Synthesis of [1-alkyl-3-methylimidazolium][CuX<sub>2</sub>] salts and low pressure CO reactions

The 1-alkyl-3-methylimidazolium halide salts, [C<sub>n</sub>mim]X (n = 2, 4, 6, denoting the length of the alkyl chain), were prepared by reaction of 1-methylimidazole with the requisite 1-haloalkane (see ESI). In order to generate the copper-containing ionic liquids, equimolar quantities of [C<sub>n</sub>mim]X and the corresponding copper(I) halide were mixed and heated to 80-100 °C under N<sub>2</sub> to form a homogeneous melt (Scheme 1). On cooling to room temperature, an appreciable increase in viscosity was observed, but in all cases the products remained as

fluids. ES-MS analysis of the 1:1 melts showed the expected signals for the  $C_n\text{mim}^+$  cation and a single anionic species corresponding to  $[\text{CuX}_2]^-$ .



**Scheme 1.** Synthesis of  $[\text{C}_n\text{mim}][\text{CuX}_2]$  salts (R = Et,  $^n\text{Bu}$ ,  $^n\text{C}_6\text{H}_{13}$ ; X = Cl, Br, I).

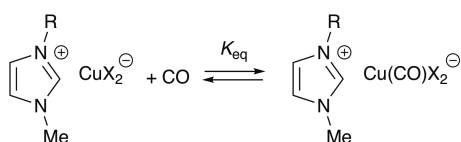
UV/visible spectroscopy was used to assess the presence of any Cu(II) arising from oxidation. For a Cu(II) salt generated deliberately by mixing  $[\text{C}_6\text{mim}]\text{Br}$  and  $\text{CuBr}_2$ , the spectrum of a 1.0 mM solution in  $\text{MeNO}_2$  exhibited strong absorptions with  $\lambda_{\text{max}}$  at 642 and 435 nm (see ESI). A 10 mM solution of the 1:1  $[\text{C}_6\text{mim}]\text{Br}/\text{CuBr}$  melt in  $\text{MeCN}$  only showed very weak absorptions at corresponding wavelengths from which the concentration of Cu(II) was estimated to be  $\sim 0.1\%$  of the total  $[\text{Cu}]$ , showing that oxidation is minimal. Similar observations were made for the  $[\text{C}_6\text{mim}]\text{Cl}/\text{CuCl}$  system.

**Table 1.** IR and  $^{13}\text{C}$  NMR spectroscopic data for Cu(CO) species formed on reaction of  $[\text{C}_6\text{mim}]\text{X}/\text{CuX}$  ionic liquids with CO.

Ionic Liquid	$\nu(\text{CO})/\text{cm}^{-1}$	$\delta\ ^{13}\text{C}/\text{ppm}$
$[\text{C}_6\text{mim}][\text{CuCl}_2]$	2076	172.5
$[\text{C}_2\text{mim}][\text{CuBr}_2]$	2080	-
$[\text{C}_4\text{mim}][\text{CuBr}_2]$	2080	-
$[\text{C}_6\text{mim}][\text{CuBr}_2]$	2081	172.0
$[\text{C}_6\text{mim}][\text{CuI}_2]$	2092	-
$[\text{C}_6\text{mim}]_2[\text{CuCl}_3]$	2051	173.6
$[\text{C}_6\text{mim}]_2[\text{CuBr}_3]$	2058	-

The reactivity of the  $[\text{C}_n\text{mim}][\text{CuX}_2]$  ionic liquids toward CO was initially tested by passing a stream of CO gas through the liquid for ca. 2 min. In each case IR spectroscopy

(thin-film) revealed the appearance of a single  $\nu(\text{CO})$  absorption (Table 1) consistent with formation of  $\text{Cu}(\text{CO})$  species. Subsequent passage of a stream of  $\text{N}_2$  through the liquid, or exposure to high vacuum for a few minutes, caused complete decay of the  $\nu(\text{CO})$  band, indicating that the Cu carbonyl species is labile under mild conditions. Repetition of this sequence using the same sample of ionic liquid resulted in identical observations, confirming that CO uptake is reversible. The simplest interpretation of the infrared data is that CO binds to the dominant  $[\text{CuX}_2]^-$  anions to give 3-coordinate  $[\text{Cu}(\text{CO})\text{X}_2]^-$  complexes. The  $\nu(\text{CO})$  band at  $2076\text{ cm}^{-1}$  observed for the reaction of  $[\text{C}_6\text{mim}][\text{CuCl}_2]$  with CO can be compared with those reported for carbonyl species formed from solutions of  $\text{CuCl}$  in THF ( $2085\text{ cm}^{-1}$ ),<sup>56</sup> hydrochloric acid ( $2100\text{ cm}^{-1}$ )<sup>57</sup> and with “ $\text{Cu}(\text{CO})\text{Cl}$ ” in the solid state ( $2120\text{ cm}^{-1}$ ).<sup>56</sup> The lower frequency observed here is consistent with a more electron rich species, although frequency shifts due to medium effects also likely contribute. The data do not rule out centrosymmetric halide bridged dimers of formula  $[\text{Cu}_2(\text{CO})_2\text{X}_4]$ , but in the absence of direct evidence for such species we assign the carbonyl species as monomeric  $[\text{Cu}(\text{CO})\text{X}_2]^-$  (Scheme 2).



**Scheme 2.** Reaction of  $[\text{C}_n\text{mim}][\text{CuX}_2]$  salts with CO.

Similar experiments using melts generated from 2:1 mixtures of  $[\text{C}_6\text{mim}]\text{X}$  and  $\text{CuX}$  (represented as  $[\text{C}_6\text{mim}]_2[\text{CuX}_3]$  in Table 1) gave  $\nu(\text{CO})$  bands ca.  $25\text{ cm}^{-1}$  lower in frequency than for the 1:1 melts. This suggests the formation of more electron rich carbonyl species, tentatively assigned as dianions,  $[\text{Cu}(\text{CO})\text{X}_3]^{2-}$ . Although we haven't pursued this observation further, it is relevant to the copper speciation in ionic liquids with higher  $[\text{C}_6\text{mim}]\text{Cl}:\text{CuCl}$  ratios, as studied by Urtiaga and co-workers.<sup>48</sup>

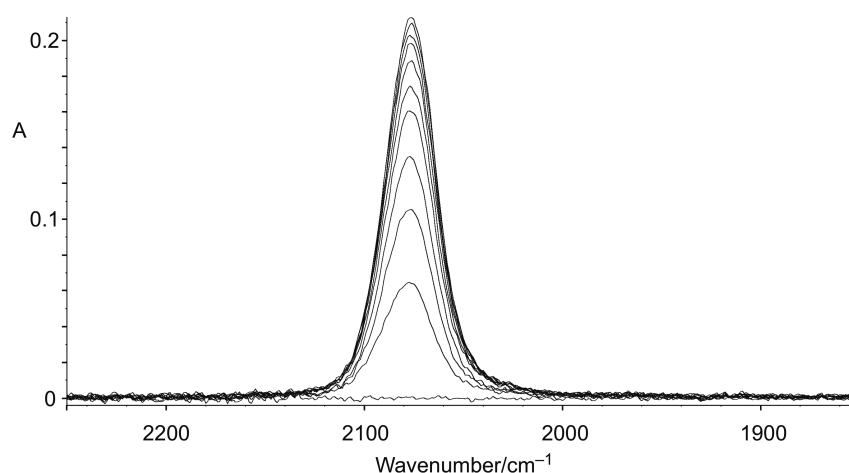
For the series of  $[\text{C}_6\text{mim}][\text{CuX}_2]$  salts, the  $\nu(\text{CO})$  values increase in the order  $\text{Cl} < \text{Br} < \text{I}$ . This is counter to expectation based on the electronegativities of Cl, Br and I, but is reminiscent of the trend observed for Ir(I) Vaska-type complexes,  $[\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{X}]$ .<sup>58</sup> In that case the lower  $\nu(\text{CO})$  values for smaller halide ligands are thought to arise from stronger “filled-filled” repulsive interactions between halogen lone pairs and occupied metal *d*-orbitals, leading to enhanced back donation to the CO ligand. A similar effect may be responsible for the observed trend in  $\nu(\text{CO})$  for the  $[\text{Cu}(\text{CO})\text{X}_2]^-$  species. Changing the alkyl chain length on the imidazolium cation has little effect on  $\nu(\text{CO})$  for the  $[\text{C}_n\text{mim}][\text{CuBr}_2]$  series. In analogous experiments using Cu(II)-containing ionic liquids, generated from 1:1  $[\text{C}_6\text{mim}]\text{X}/\text{CuX}_2$  mixtures ( $\text{X} = \text{Cl}, \text{Br}$ ), there was no evidence for formation of Cu carbonyl complexes. Only a weak, broad absorption was observed at  $\sim 2125 \text{ cm}^{-1}$  due to free (dissolved) CO.

For the  $[\text{C}_6\text{mim}][\text{CuCl}_2]$  and  $[\text{C}_6\text{mim}][\text{CuBr}_2]$  liquids the formation of Cu carbonyl species was also confirmed using  $^{13}\text{C}$  NMR spectroscopy. In each case a single new  $^{13}\text{C}$  resonance was observed near  $\delta$  170 (Table 1) after passing a stream of  $^{13}\text{CO}$  gas through the neat liquid for ca. 30 s. No appreciable changes to any of the  $^{13}\text{C}$  resonances of the imidazolium cation were observed on reaction with CO. Again, passage of a stream of  $\text{N}_2$  through the liquid for ca. 5 min was sufficient to cause the signal due to the  $\text{Cu}(\text{CO})$  complex to disappear. For  $[\text{C}_6\text{mim}]_2[\text{CuCl}_3]$  a single resonance was generated at marginally higher chemical shift than for  $[\text{C}_6\text{mim}][\text{CuCl}_2]$ , presumably indicating formation of  $[\text{Cu}(\text{CO})\text{Cl}_3]^{2-}$ . It was thought that a mixed-halide system (prepared from a 1:1 melt reaction of  $[\text{C}_6\text{mim}]\text{Cl}$  with  $\text{CuBr}$ ) might show separate  $^{13}\text{C}$  signals for  $[\text{Cu}(\text{CO})\text{Cl}_2]^-$ ,  $[\text{Cu}(\text{CO})\text{Br}_2]^-$  and  $[\text{Cu}(\text{CO})\text{ClBr}]^-$  after reaction with  $^{13}\text{CO}$ , but only one  $^{13}\text{C}$  resonance was observed at  $\delta$  171.7, probably due to rapid halide scrambling.



### ***In situ* high pressure infrared studies**

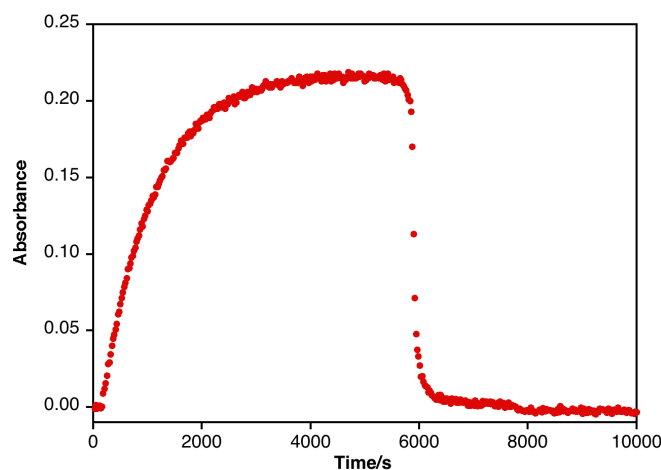
Absorption of CO by the copper(I)-containing ionic liquids at elevated pressure was monitored by in-situ high pressure infrared (HPIR) spectroscopy using a cylindrical internal reflectance (CIR) cell,<sup>59, 60</sup> allowing the effects of CO pressure, temperature, and the rate of gas/liquid mixing to be probed. The observations for the [C<sub>6</sub>mim][CuCl<sub>2</sub>] system are first discussed in detail, followed by comparisons with the other liquids.



**Figure 1.** Series of IR spectra showing growth of  $\nu(\text{CO})$  band at  $2076 \text{ cm}^{-1}$  on exposure of [C<sub>6</sub>mim][CuCl<sub>2</sub>] to CO (initially 18 bar) at 25 °C.

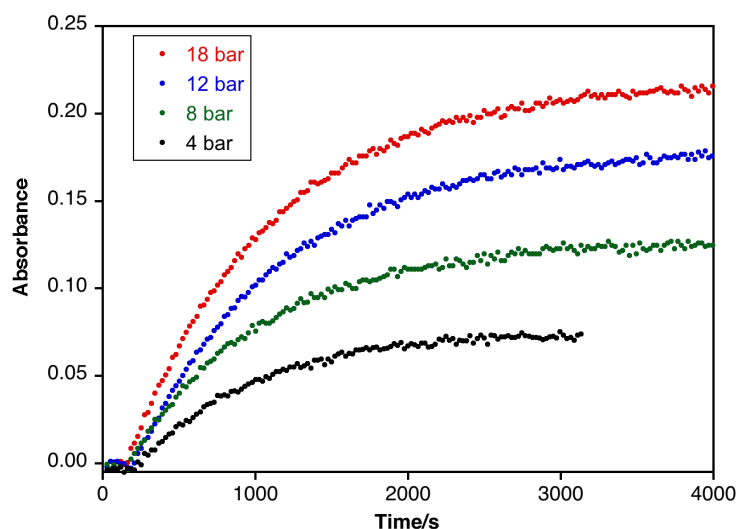
Figure 1 shows a set of *in situ* IR spectra obtained when a stirred sample of [C<sub>6</sub>mim][CuCl<sub>2</sub>] was exposed to a pressure of CO at 25 °C. A single  $\nu(\text{CO})$  band grew at  $2076 \text{ cm}^{-1}$ , the same frequency as observed using 1 atm CO. A plot of absorbance against time for this band (Figure 2) shows that equilibrium is reached after ca. 1 h. With the system at equilibrium, the cell was purged with a flow of N<sub>2</sub>, and heated to 110 °C, resulting in the complete decay of the  $\nu(\text{CO})$  band within ca. 5 minutes, as shown by the trace in Figure 2. After cooling back to 25 °C under N<sub>2</sub>, re-pressurisation of the cell with CO resulted in re-growth of the  $\nu(\text{CO})$  band at  $2076 \text{ cm}^{-1}$ . This sequence could be repeated many times, with no apparent change in behavior. Inspection of the ionic liquid after a series of CO absorption/desorption cycles showed that there was no change in its appearance and no

metallic deposits were present. Analysis by ES-MS indicated the same species (i.e.  $[\text{C}_6\text{mim}]^+$  and  $[\text{CuCl}_2]^-$ ) as observed prior to the CO absorption study. A sample of ionic liquid could be used for multiple experiments conducted over many days without deterioration in behaviour, provided that an atmosphere of  $\text{N}_2$  or CO was maintained in the HPIR cell. This indicated that any oxidation to Cu(II) under these conditions was minimal.



**Figure 2.** Plot of absorbance vs time for  $\nu(\text{CO})$  band at  $2076\text{ cm}^{-1}$ , on exposure of  $[\text{C}_6\text{mim}][\text{CuCl}_2]$  to CO (initially 18 bar) at  $25\text{ }^\circ\text{C}$  (stirrer speed 428 rpm). After ca. 6000 s, the over-pressure of CO was released and the cell heated to  $110\text{ }^\circ\text{C}$ .

Figure 3 shows absorbance vs. time traces for CO uptake by  $[\text{C}_6\text{mim}][\text{CuCl}_2]$  at initial CO pressures from 4-18 bar. It is clear that a higher initial  $p_{\text{CO}}$  results in an increase in the intensity of the  $\nu(\text{CO})$  band attained at equilibrium, indicating that the equilibrium for CO binding (Scheme 2) is pushed further to the right. The rate of CO uptake increases with pressure, as judged from the initial gradient of each plot. Increasing the stirrer speed was also found to enhance the rate of CO uptake (see ESI) but it did not affect the equilibrium  $\nu(\text{CO})$  intensity attained at a given pressure. At higher temperatures, the  $\nu(\text{CO})$  absorption at a particular pressure was weaker. For example, at  $55\text{ }^\circ\text{C}$  the  $\nu(\text{CO})$  intensity at equilibrium was ca. half of that observed at  $25\text{ }^\circ\text{C}$ , consistent with the previously reported temperature dependence and exothermic reaction enthalpy for CO complexation.<sup>48</sup>

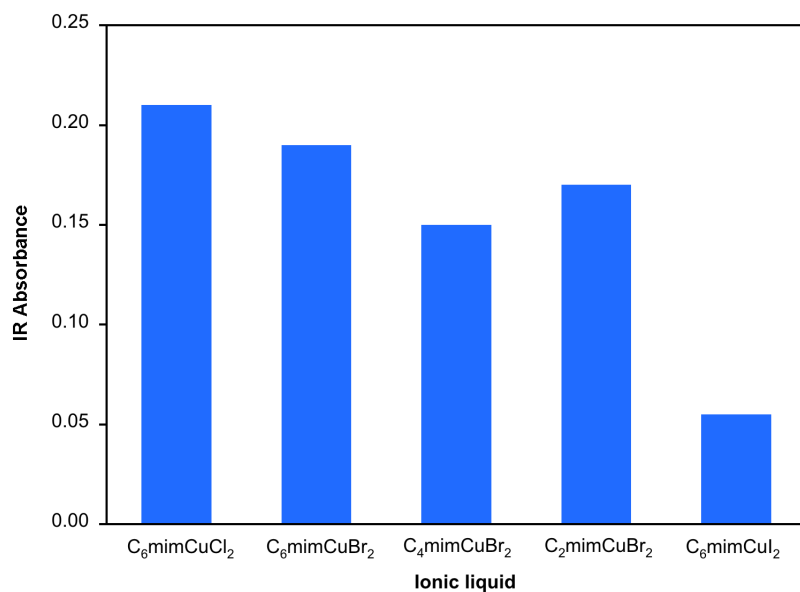


**Figure 3.** Plots of absorbance vs. time for the  $\nu(\text{CO})$  band at  $2076\text{ cm}^{-1}$  during uptake of CO by  $[\text{C}_6\text{mim}][\text{CuCl}_2]$  at different initial CO pressures ( $25\text{ }^\circ\text{C}$ , stirrer speed 428 rpm).

In each experiment the headspace pressure of the cell fell appreciably during the uptake of CO. For example, with an initial  $p_{\text{CO}}$  of 18 bar, the observed pressure drop (8.5 bar) is consistent with absorption of sufficient CO to occupy approximately half of the Cu sites in the ionic liquid (assuming only monocarbonyl species).<sup>61</sup> This allows an estimate for the equilibrium constant for CO binding to Cu (Scheme 2) to be made as  $K_{\text{eq}} \sim 0.02\text{ m}^3\text{ mol}^{-1}$  (or  $25\text{ kg mol}^{-1}$ ), assuming that the physical solubility of CO in the  $[\text{C}_6\text{mim}]\text{Cl}:\text{CuCl}$  liquid is similar to that for  $\text{N}_2$  measured by Urtiaga and co-workers (Henry's law constant  $4.7 \times 10^{-3}\text{ mol kg}^{-1}\text{ bar}^{-1}$  at  $20\text{ }^\circ\text{C}$ ).<sup>48</sup> The value of  $K_{\text{eq}}$  that we obtain is of a similar magnitude to that reported by Urtiaga ( $K_{\text{eq}} = 12.05\text{ kg mol}^{-1}$ ) for the 2:1  $[\text{C}_6\text{mim}]\text{Cl}:\text{CuCl}$  system at  $20\text{ }^\circ\text{C}$ .

Experiments of the sort described above were also performed for some other  $[\text{C}_n\text{mim}][\text{CuX}_2]$  ionic liquids. Figure 4 shows a comparison of the equilibrium  $\nu(\text{CO})$  intensities attained using an initial pressure of 16 bar CO at  $25\text{ }^\circ\text{C}$ . The three  $[\text{C}_n\text{mim}][\text{CuBr}_2]$  salts all gave absorptions a little weaker than that for  $[\text{C}_6\text{mim}][\text{CuCl}_2]$  whereas the band for  $[\text{C}_6\text{mim}][\text{CuI}_2]$  was substantially weaker. If the extinction coefficients for the  $\nu(\text{CO})$  bands of the  $[\text{Cu}(\text{CO})\text{X}_2]$  species are assumed to be similar, these data suggest that the concentration

of Cu(CO) complex generated at equilibrium decreases in the order  $\text{Cl} \geq \text{Br} \gg \text{I}$ .<sup>62</sup> This is consistent with the relative strength of Cu-CO binding ( $\text{Cl} < \text{Br} < \text{I}$ ) indicated by the  $\nu(\text{CO})$  frequencies for  $[\text{CuX}_2(\text{CO})]^-$  in Table 1. However, quantification of the equilibrium constants for CO complexation in these systems would require physical solubility data for CO in the different liquids, which is not available.



**Figure 4.** Equilibrium  $\nu(\text{CO})$  intensity attained for reaction of  $[\text{C}_n\text{mim}][\text{CuX}_2]$  salts with CO (initial  $p_{\text{CO}}$  16 bar) at 25 °C.

### Selective absorption of CO from gas mixtures

Having established that the Cu(I) carbonyl species formed by  $[\text{C}_n\text{mim}][\text{CuX}_2]$  liquids can be probed by *in situ* HPIR spectroscopy, the study was extended to investigate selective binding of CO from gas mixtures. In a typical experiment, a stirred sample of the ionic liquid in the CIR cell was allowed to equilibrate with a known initial pressure of a 1:1 CO:H<sub>2</sub> or CO:N<sub>2</sub> mixture. Once equilibrium was attained (established by *in situ* IR spectroscopy showing formation of Cu(CO) complex, as above) the headspace gas was vented and a sample of the vent-gas was admitted to a gas-cell for analysis by FTIR spectroscopy. The CIR cell was then resealed and heated with stirring to 110 °C to drive the absorbed gases from the liquid phase into the headspace. This was confirmed by the decay of the  $\nu(\text{CO})$  band

due to the Cu(CO) species (as observed in the experiments using pure CO). Once desorption was complete, stirring was ceased to minimise any gas transfer back into the liquid phase while the cell was cooled to 25 °C. A new sample of the headspace gas was admitted into a gas cell for FTIR analysis. The % CO content of each gas sample was assessed by measuring the integrated intensity of the  $\nu(\text{CO})$  ro-vibrational band between 2250 and 1975  $\text{cm}^{-1}$ , by comparison to Beer-Lambert plots of 100% and 50% CO gas samples over a range of pressures in the same gas cell (see ESI).

**Table 2.** Carbon monoxide content of gas samples taken from cell headspace at equilibrium and after gas desorption of gases from ionic liquids using 1:1 CO/H<sub>2</sub> and CO/N<sub>2</sub> mixtures. For each experiment the initial total pressure was 8 bar at 25 °C. Samples of the cell headspace (at 25 °C) were transferred into a gas-cell for quantification of CO content by FTIR spectroscopy. %CO values given are averages of several measurements.

Ionic Liquid	X <sub>2</sub>	%CO	
		At equilibrium	After desorption
[C <sub>6</sub> mim]Cl	H <sub>2</sub>	-	41
[C <sub>6</sub> mim][CuCl <sub>2</sub> ]	H <sub>2</sub>	36	81
	N <sub>2</sub>	30	95
[C <sub>2</sub> mim][CuBr <sub>2</sub> ]	H <sub>2</sub>	42	72
	N <sub>2</sub>	38	90
[C <sub>4</sub> mim][CuBr <sub>2</sub> ]	H <sub>2</sub>	38	73
	N <sub>2</sub>	36	96
[C <sub>6</sub> mim][CuBr <sub>2</sub> ]	H <sub>2</sub>	37	89
	N <sub>2</sub>	33	95

Table 2 shows the %CO (by volume) of headspace samples before and after desorption of gases from the ionic liquid. In a control experiment using 1:1 CO:H<sub>2</sub> with [C<sub>6</sub>mim]Cl in the

absence of CuCl, the gas sampled from the cell headspace after an absorb-vent-desorb cycle was found to be depleted in CO. This arises from the higher physical solubility of H<sub>2</sub> in [C<sub>6</sub>mim]Cl, as noted for other ionic liquids.<sup>63</sup> By contrast, for all the Cu-containing liquids, the headspace gas sampled at equilibrium was depleted in CO relative to the initial gas mixture, demonstrating selective absorption of CO.

Furthermore, the gas sampled *after* desorption was enriched in CO, in some cases to >95%.<sup>64</sup> Starting from a 1:1 CO:N<sub>2</sub> mixture, a single absorb-vent-desorb cycle resulted in ≥90% CO in the cell headspace. For each ionic liquid investigated, the selectivity for absorption of CO from a CO/N<sub>2</sub> mixture was significantly higher than from a CO/H<sub>2</sub> mixture. This is due the physical solubilities of the three gases (H<sub>2</sub> > CO ≈ N<sub>2</sub>)<sup>48, 63, 65-70</sup> so that less N<sub>2</sub> than H<sub>2</sub> will be taken up from a gas mixture under equivalent conditions. In additional experiments with [C<sub>6</sub>mim][CuCl<sub>2</sub>] using gas mixtures initially containing 80% CO, the CO content of the desorbed gas was measured as 96% from CO/H<sub>2</sub> and 98% from CO/N<sub>2</sub>. It can therefore be envisaged that sequential absorption/desorption cycles under appropriate conditions can accomplish effective separation of CO from H<sub>2</sub> and N<sub>2</sub>.

## Conclusions

Copper(I) carbonyl complexes generated upon CO absorption by copper-containing ionic liquids have been directly observed for the first time using *in-situ* high pressure IR spectroscopy. The growth and decay of characteristic ν(CO) absorptions demonstrates that [C<sub>n</sub>mim][CuX<sub>2</sub>] salts bind CO reversibly to give monocarbonyl complexes, assigned as [Cu(CO)X<sub>2</sub>]. Desorption of CO is facile at elevated temperature and the liquids are robust over the course of 15-20 CO absorption/desorption cycles with no apparent degradation in their CO absorption capacity. For the [C<sub>6</sub>mim][CuX<sub>2</sub>] series, the CO absorption ability decreases in the order X = Cl ≥ Br >> I, based on comparison of equilibrium ν(CO)

intensities. Experiments using CO/H<sub>2</sub> and CO/N<sub>2</sub> gas mixtures show that the [C<sub>n</sub>mim][CuX<sub>2</sub>] liquids absorb CO selectively. Desorption at elevated temperature yields gas that is greatly enriched in CO, demonstrating the potential applicability of these systems for separation of CO from other gaseous components. The separation of CO from N<sub>2</sub> is particularly effective (e.g. ~98% CO from a 4:1 CO/N<sub>2</sub> mixture after a single absorb-vent-desorb cycle).

## **Experimental**

### *Instrumentation*

Thin film IR spectra (NaCl plates) were recorded on a Nicolet Magna 560 FTIR instrument using OMNIC software. High pressure IR spectra were recorded on a Perkin Elmer Spectrum GX FTIR spectrometer fitted with a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector, using Timebase software. For these spectra a cylindrical internal reflectance cell (CIR) was used, as described previously.<sup>60</sup> Gas phase spectra were recorded on the Nicolet Magna 560 instrument using a 10 cm path length gas cell fitted with NaCl windows. The cell was connected to an Edwards pressure gauge and evacuated prior to being filled with the relevant gas sample to a known pressure. <sup>1</sup>H NMR and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded using either a Bruker AC400 or AC250 instrument in pulsed Fourier transform mode, fitted with a Bruker B ACS-60 sample changer and using solvent as the internal standard. Electrospray mass spectra were recorded using a Waters LCT time-of-flight (TOF) instrument. Elemental analyses were performed using a Perkin Elmer 2400 Elemental Analyser.

### *Materials*

Reagents (1-methylimidazole, 1-chlorohexane, 1-bromoethane, 1-bromobutane, 1-bromohexane, 1-iodohexane, copper(I) halides) were purchased from Sigma Aldrich and

used without further purification. Hydrogen (99.9995% HP grade) and carbon monoxide (99.9% CP grade) were supplied by BOC. Gas mixtures containing CO:H<sub>2</sub> and CO:N<sub>2</sub> (each 50:50 (±2)) were supplied by BOC. N<sub>2</sub> gas for inert atmosphere work, and for use in high pressure reactions was supplied by an in-house generator. <sup>13</sup>CO (< 5% <sup>18</sup>O, 99% <sup>13</sup>C) was purchased from Sigma Aldrich and used directly from the cylinder. The 1-alkyl-3-methylimidazolium halide [C<sub>n</sub>mim]X salts were prepared by the reaction of 1-methylimidazole with the requisite alkyl halide according to published procedures (see ESI).<sup>71-73</sup> The hygroscopic salts were stored under nitrogen.

### ***Copper-containing ionic liquids [C<sub>n</sub>mim][CuX<sub>2</sub>]***

In a typical procedure, a sample of [C<sub>n</sub>mim]X was weighed directly into a dried round bottom flask under N<sub>2</sub>, and to this was added the corresponding copper(I) halide (1 mol equiv.). The mixture was heated to 80-100 °C under N<sub>2</sub> for ca. 1 h to form a homogenous melt. On cooling to room temperature the products became appreciably more viscous, but remained liquid, and were used in the CO absorption studies without further purification. The [C<sub>n</sub>mim][CuX<sub>2</sub>] salts were typically prepared freshly on a 1 g scale for low pressure CO experiments or a 10-15 g scale for HPIR experiments (for which the CIR cell required 8 ml of liquid). <sup>1</sup>H NMR (250 MHz, CD<sub>3</sub>NO<sub>2</sub>) and TOF ES MS data for the salts are listed below. In all cases the ES-MS showed both the [C<sub>n</sub>mim]<sup>+</sup> cation and the [CuX<sub>2</sub>]<sup>-</sup> anion. The isotopic distribution observed for the ES- signal was consistent with [CuX<sub>2</sub>]<sup>-</sup> (values stated below are for the strongest peak).

**[C<sub>6</sub>mim][CuCl<sub>2</sub>]:** δ <sup>1</sup>H, 0.89 (t, 6.5 Hz, 3H), 1.25-1.45 (m, 6H), 1.85-2.05 (m, 2H), 4.01 (s, 3H), 4.29 (t, 7.3 Hz, 2H), 7.48 (s, 1H), 7.51 (s, 1H), 8.81 (s, 1H); m/z 167 ([C<sub>6</sub>mim]<sup>+</sup>), 133 ([CuCl<sub>2</sub>]<sup>-</sup>)

**[C<sub>2</sub>mim][CuBr<sub>2</sub>]:** δ <sup>1</sup>H, 1.58 (t, 7.3 Hz, 3H), 4.00 (s, 3H), 4.33 (q, 7.4 Hz, 2H), 7.46 (s, 1H), 7.51 (s, 1H), 8.58 (s, 1H); m/z 111 ([C<sub>2</sub>mim]<sup>+</sup>), 223 ([CuBr<sub>2</sub>]<sup>-</sup>)



**[C<sub>4</sub>mim][CuBr<sub>2</sub>]:**  $\delta$  <sup>1</sup>H, 0.98 (t, 7.3 Hz, 3H), 1.41 (dq, 14.6 Hz, 7.3 Hz, 2H), 1.95 (dq, 14.9, 7.3 Hz, 2H), 4.01 (s, 3H), 4.29 (t, 7.4 Hz, 2H), 7.47 (s, 1H), 7.51 (s, 1H), 8.60 (s, 1H); m/z 139 ([C<sub>4</sub>mim]<sup>+</sup>), 223 ([CuBr<sub>2</sub>]<sup>-</sup>)

**[C<sub>6</sub>mim][CuBr<sub>2</sub>]:**  $\delta$  <sup>1</sup>H, 0.90 (3H, t, 6.8 Hz), 1.25-1.45 (6H, m), 1.85-2.05 (2H, m), 4.01 (3H, s), 4.28 (2H, t, 7.3 Hz), 7.46 (1H, s), 7.52 (1H, s), 8.60 (1H, s); m/z 167 ([C<sub>6</sub>mim]<sup>+</sup>), 223 ([CuBr<sub>2</sub>]<sup>-</sup>)

**[C<sub>6</sub>mim][CuI<sub>2</sub>]:**  $\delta$  <sup>1</sup>H, 0.9 (3H, t, 6.9 Hz), 1.30-1.45 (6H, m), 2.0 (2H, m), 4.04 (3H, s), 4.32 (2H, t, 7.4 Hz), 7.50 (1H, d, 1.6 Hz), 7.53 (1H, d, 1.6 Hz), 8.77 (1H, s); m/z 167 ([C<sub>6</sub>mim]<sup>+</sup>), 317 ([CuI<sub>2</sub>]<sup>-</sup>)

### ***Low pressure CO studies***

A stream of CO gas was passed for ca. 2 min through the [C<sub>n</sub>mim][CuX<sub>2</sub>] liquid (1 g) via a pipette inserted through a quickfit adaptor fitted with a gas-tight rubber seal attached to a Schlenk line. A sample of the liquid was quickly removed for analysis by IR spectroscopy (thin-film) using the un-treated [C<sub>n</sub>mim][CuX<sub>2</sub>] as background reference. Similarly, for <sup>13</sup>C NMR studies a stream of <sup>13</sup>CO was passed through a sample the [C<sub>n</sub>mim][CuX<sub>2</sub>] liquid in an NMR tube for ca 30 s before spectroscopic analysis.

### ***High pressure CO studies***

A sample of the [C<sub>n</sub>mim][CuX<sub>2</sub>] salt (8 ml) was transferred into the CIR cell and the reactor head screwed securely into place. The cell was then purged with a flow of N<sub>2</sub> for approximately 30 minutes and aligned to the beam path of the FTIR instrument using a tilt table mount to maximise the intensity of the detector signal. The cell was heated to the required temperature and the overhead stirrer motor was attached and set to the desired rotation speed. A background spectrum (256 scans) was then collected. The Timebase software was programmed to collect a series of spectra at prescribed intervals to monitor the progress of the reaction with CO. The cell was flushed by filling to the desired pressure of

CO and venting 5 times, before being filled with CO to the desired pressure and sealed to begin the experiment. Pressure changes that occurred during the absorption of CO were recorded using the gauge fitted to the cell. Once equilibrium was attained (as judged by IR spectroscopy), any excess headspace pressure was vented and the cell purged with a flow of N<sub>2</sub>. The cell was then heated to 110 °C to drive absorbed gas from the liquid. Once desorption was complete, the cell was allowed to cool to 25 °C and sealed under N<sub>2</sub>. For repeat runs using different conditions, the same [C<sub>n</sub>mim][CuX<sub>2</sub>] sample was left in the cell with no apparent deterioration observed.

### ***Gas separation experiments***

The same general procedure was employed as that described above for the high pressure CO absorption experiments, with the following modifications. The CIR cell was pressurised with a CO:X<sub>2</sub> mixture (X<sub>2</sub> = H<sub>2</sub> or N<sub>2</sub>) instead of pure CO. For experiments using a 50:50 CO:X<sub>2</sub> ratio, the gas mixtures were as supplied by BOC. For other ratios, the cell was pressurised with the desired partial pressure of X<sub>2</sub>, before adding an overpressure with CO to produce the desired ratio in-situ. Once CO uptake reached equilibrium (monitored by *in situ* HPIR), stirring was ceased and a sample of the residual headspace gas was transferred into a gas cell to determine its % CO content. The excess pressure in the CIR cell was then vented down to 1 atm, and the cell was re-sealed. Stirring was then recommenced and the cell heated to 110 °C to force desorption of gases absorbed in the liquid phase. Once this was complete, stirring was ceased and the cell allowed to cool before samples of the new headspace gas were collected for analysis by gas phase IR spectroscopy. After each experiment the cell was purged with a flow of N<sub>2</sub> prior to being sealed in preparation for the next reaction run. In all cases, several samples of the final headspace gas were analyzed to allow a mean % CO content to be determined. Each experiment was repeated at least twice to check for reproducibility.

## **Acknowledgements**

We thank the EPSRC and BP Chemicals Ltd. for funding this research (Industrial CASE studentship to SER) and Dr. Sander Gaemers of BP for some preliminary scoping experiments on this system.

## **Supplementary Information**

Plots of initial CO uptake rates and equilibrium  $\nu(\text{CO})$  intensity data from HPIR experiments. UV/visible spectra for assessment of trace [Cu(II)]. Calibration plots for gas phase CO quantification. Synthetic procedures for  $\text{C}_n\text{mimX}$  salts.

## References

1. M. Beller, ed., *Catalytic Carbonylation Reactions, Top. Organomet. Chem.*, vol. 18, Springer, Berlin, 2006.
2. L. Kollár, ed., *Modern Carbonylation Methods*, Wiley-VCH, Weinheim, 2008.
3. A. Haynes, *Adv. Catal.*, 2010, **53**, 1-45.
4. S. P. Goff and S. I. Wang, *Chem. Eng. Prog.*, 1987, **83**, 46-53.
5. N. N. Dutta and G. S. Patil, *Gas Sep. Purif.*, 1995, **9**, 277-283.
6. M. I. Bruce, *J. Organomet. Chem.*, 1972, **44**, 209-226.
7. M. I. Bruce and A. P. P. Ostaszewski, *J. Chem. Soc., Dalton Trans.*, 1973, 2433-2436.
8. Y. Souma, J. Iyoda and H. Sano, *Inorg. Chem.*, 1976, **15**, 968-970.
9. H. V. R. Dias and H. L. Lu, *Inorg. Chem.*, 1995, **34**, 5380-5382.
10. M. Fianchini, T. R. Cundari, N. J. DeYonker and H. V. R. Dias, *Dalton Trans.*, 2009, 2085-2087.
11. C. Dash, A. Das, M. Yousufuddin and H. V. R. Dias, *Inorg. Chem.*, 2013, **52**, 1584-1590.
12. A. S. Goldman and K. Krogh-Jespersen, *J. Am. Chem. Soc.*, 1996, **118**, 12159-12166.
13. J. J. Rack, J. D. Webb and S. H. Strauss, *Inorg. Chem.*, 1996, **35**, 277-278.

14. A. J. Lupinetti, S. Fau, G. Frenking and S. H. Strauss, *J. Phys. Chem. A*, 1997, **101**, 9551-9559.
15. S. H. Strauss, *J. Chem. Soc., Dalton Trans.*, 2000, 1-6.
16. A. J. Lupinetti, V. Jonas, W. Thiel, S. H. Strauss and G. Frenking, *Chem. Eur. J.*, 1999, **5**, 2573-2583.
17. O. G. Polyakov, S. M. Ivanova, C. M. Gaudinski, S. M. Miller, O. P. Anderson and S. H. Strauss, *Organometallics*, 1999, **18**, 3769-3771.
18. A. J. Lupinetti, S. H. Strauss and G. Frenking, *Prog. Inorg. Chem.*, 2001, **49**, 1-112.
19. R. D. Pike, *Organometallics*, 2012, **31**, 7647-7660.
20. Y. C. Xie, J. P. Zhang, J. G. Qiu, X. Z. Tong, J. P. Fu, G. Yang, H. J. Yan and Y. Q. Tang, *Adsorption*, 1996, **3**, 27-32.
21. H. Hirai, K. Wada and M. Komiyama, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 2217-2223.
22. F. Kasuya and T. Tsuji, *Gas Sep. Purif.*, 1991, **5**, 242-246.
23. L.-Q. Zhu, J.-L. Tu and Y.-J. Shi, *Gas Sep. Purif.*, 1991, **5**, 173.
24. D. J. Haase and D. G. Walker, *Chem. Eng. Prog.*, 1974, **70**, 74-77.
25. G. B. McVicker, *Inorg. Chem.*, 1972, **11**, 2485-&.
26. T. Sato, I. Toyoda, Y. Yamamori, T. Yonemoto, H. Kato and T. Tadaki, *J. Chem. Eng. Jpn.*, 1988, **21**, 192-198.
27. J. A. Hogendoorn, W. P. M. Vanswaaij and G. F. Versteeg, *Chem. Eng. J. & Biochem. Eng. J.*, 1995, **59**, 243-252.

28. T. Welton, *Chem. Rev.*, 1999, **99**, 2071-2083.
29. V. I. Parvulescu and C. Hardacre, *Chem. Rev.*, 2007, **107**, 2615-2665.
30. N. V. Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123–150.
31. M. Freemantle, *An Introduction to Ionic Liquids*, RSC Publishing, Cambridge, 2010.
32. R. Giernoth, *Angew. Chem. Int. Ed.*, 2010, **49**, 2834–2839.
33. J. P. Hallett and T. Welton, *Chem. Rev.*, 2011, **111**, 3508-3576.
34. L. P. N. Rebelo, J. N. C. Lopes, J. Esperanca and E. Filipe, *J. Phys. Chem. B*, 2005, **109**, 6040-6043.
35. M. J. Earle, J. Esperanca, M. A. Gilea, J. N. C. Lopes, L. P. N. Rebelo, J. W. Magee, K. R. Seddon and J. A. Widegren, *Nature*, 2006, **439**, 831-834.
36. J. T. Yoke, J. F. Weiss and G. Tollin, *Inorg. Chem.*, 1963, **2**, 1210-1216.
37. D. D. Axtell, B. W. Good, W. W. Porterfield and J. T. Yoke, *J. Am. Chem. Soc.*, 1973, **95**, 4555-4559.
38. S. A. Bolkan and J. T. Yoke, *Inorg. Chem.*, 1986, **25**, 3587-3590.
39. S. A. Bolkan and J. T. Yoke, *J. Chem. Eng. Data*, 1986, **31**, 194-197.
40. S. A. Bolkan and J. T. Yoke, *J. Electrochem. Soc.*, 1987, **134**, 1698-1702.
41. J. Estager, J. D. Holbrey and M. Swadźba-Kwaśny, *Chem. Soc. Rev.*, 2014, **43**, 847–886.
42. P. Zürner, H. Schmidt, S. Bette, J. Wagler and G. Frisch, *Dalton Trans.*, 2016, **45**, 3327-3333.

43. J. H. Kim, J. Palgunadi, D. K. Mukherjee, H. J. Lee, H. Kim, B. S. Ahn, M. Cheong and H. S. Kim, *PCCP*, 2010, **12**, 14196–14202.
44. F. T. U. Kohler, S. Popp, H. Klefer, I. Eckle, C. Schrage, B. Bohringer, D. Roth, M. Haumann and P. Wasserscheid, *Green Chem.*, 2014, **16**, 3560-3568.
45. D. J. Tempel, P. B. Henderson, J. R. Brzozowski, R. M. Pearlstein and H. Cheng, *J. Am. Chem. Soc.*, 2008, **130**, 400–401.
46. M. Abai, M. P. Atkins, A. Hassan, J. D. Holbrey, Y. Kuah, P. Nockemann, A. A. Oliferenko, N. V. Plechkova, S. Rafeen, A. A. Rahman, R. Ramli, S. M. Shariff, K. R. Seddon, G. Srinivasan and Y. Zou, *Dalton Trans.*, 2015, **44**, 8617–8624.
47. C. P. Huang, B. H. Chen, J. Zhang, Z. C. Liu and Y. X. Li, *Energy & Fuels*, 2004, **18**, 1862-1864.
48. O. C. David, G. Zarca, D. Gorri, A. Urtiaga and I. Ortiz, *Sep. Purif. Technol.*, 2012, **97**, 65-72.
49. G. Zarca, I. Ortiz and A. Urtiaga, *Chem. Eng. J.*, 2014, **252**, 298-304.
50. G. Zarca, A. Urtiaga, I. Ortiz, P. Canizares and M. A. Rodrigo, *Sep. Purif. Technol.*, 2015, **141**, 31-37.
51. G. Zarca, I. Ortiz and A. Urtiaga, *Chin. J. Chem. Eng.*, 2015, **23**, 769-774.
52. G. Zarca, M. Fernández, A. Santamaría, I. Ortiz and A. Urtiaga, *Sep. Purif. Technol.*, 2015, **155**, 96–100.
53. G. Zarca, I. Ortiz and A. Urtiaga, *J. Membr. Sci.*, 2013, **438**, 38-45.
54. G. Zarca, I. Ortiz and A. Urtiaga, *Chem. Eng. Res. Des.*, 2014, **92**, 764-768.

55. G. Zarca, W. J. Home, I. Ortiz, A. Urriaga and J. E. Bara, *J. Membr. Sci.*, 2016, **515**, 109-114.
56. M. Pasquali, C. Floriani and A. Gaetani-Manfredotti, *Inorg. Chem.*, 1981, **20**, 3382-3388.
57. M. A. Busch and T. C. Franklin, *Inorg. Chem.*, 1979, **18**, 521-524.
58. F. Abu-Hasanayn, A. S. Goldman and K. Krogh-Jespersen, *Inorg. Chem.*, 1994, **33**, 5122-5130.
59. W. R. Moser, J. E. Cnossen, A. W. Wang and S. A. Krouse, *J. Catal.*, 1985, **95**, 21-32.
60. J. M. Birbeck, A. Haynes, H. Adams, L. Damoense and S. Otto, *ACS Catal.*, 2012, **2**, 2512-2523.
61. Copper concentration is estimated based on a density for [C<sub>6</sub>mim][CuCl<sub>2</sub>] of ~1.3 g cm<sup>-3</sup> (extrapolated from densities reported in ref. 51) giving [Cu] ~ 4.3 mol dm<sup>-3</sup>.
62. It should also be noted that the Cu(I) concentrations of the liquids will differ
63. J. Kumelan, Á. Pérez-Salado Kamps, D. Tuma and G. Maurer, *Fluid Phase Equilib.*, 2007, **260**, 3-8.
64. The levels of enrichment reported in Table 2 underestimate the % CO actually absorbed by the liquid, since the desorbed gas is diluted to a small extent by the residual CO-depleted headspace gas after venting.
65. Z. Lei, C. Dai and B. Chen, *Chem. Rev.*, 2014, **114**, 1289-1326.



66. J. L. Anthony, E. J. Maginn and J. F. Brennecke, *J. Phys. Chem. B*, 2002, **106**, 7315-7320.
67. J. L. Anthony, J. L. Anderson, E. J. Maginn and J. F. Brennecke, *J. Phys. Chem. B*, 2005, **109**, 6366-6374.
68. P. J. Dyson, G. Laurency, C. A. Ohlin, J. Vallance and T. Welton, *Chem. Commun.*, 2003, 2418-2419.
69. J. Kumelan, Á. Pérez-Salado Kamps, D. Tuma and G. Maurer, *Fluid Phase Equilib.*, 2005, **228**, 207-211.
70. J. Kumelan, Á. Pérez-Salado Kamps, D. Tuma and G. Maurer, *J. Chem. Eng. Data*, 2006, **51**, 11-14.
71. S. V. Dzyuba and R. A. Bartsch, *J. Heterocycl. Chem.*, 2001, **38**, 265-268.
72. J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker and R. D. Rogers, *Green Chem.*, 2001, **3**, 156-164.
73. W. Kubo, T. Kitamura, K. Hanabusa, Y. Wada and S. Yanagida, *Chem. Commun.*, 2002, 374-375.