Accepted Manuscript

Novel solvents based on thiocyanate ionic liquids doped with copper(I) with enhanced equilibrium selectivity for carbon monoxide separation from light gases

Gabriel Zarca, Inmaculada Ortiz, Ane Urtiaga

Please cite this article as: G. Zarca, I. Ortiz, A. Urtiaga, Novel solvents based on thiocyanate ionic liquids doped with copper(I) with enhanced equilibrium selectivity for carbon monoxide separation from light gases, *Separation and Purification Technology* (2017), doi: http://dx.doi.org/10.1016/j.seppur.2017.06.069

Novel solvents based on thiocyanate ionic liquids doped with

copper(I) with enhanced equilibrium selectivity for carbon

monoxide separation from light gases

Authors:

Gabriel Zarca, Inmaculada Ortiz, Ane Urtiaga

Dep. Chemical and Biomolecular Engineering, Universidad de Cantabria,

Av. Los Castros s/n, Santander 39005, Spain.

Abstract

This work focuses on the research of novel carbon monoxide (CO) capture solvents to be applied to the separation of CO from other light components contained in gas streams of the process industry, e.g., nitrogen and hydrogen. More specifically, we examine the use of CO-selective capture solutions composed of the ionic liquid 1-ethyl-3-methylimidazolium thiocyanate ($[C_2mim][SCN]$) and the transition metal salt copper(I) thiocyanate (CuSCN) as greener alternatives to the tetrachloroaluminate(III)-aromatic hydrocarbon solutions currently employed for CO separation from gas mixtures. In order to gain insight into the behavior of the selected ionic liquid solutions as chemical solvents for CO, their density and viscosity are characterized with respect to temperature and composition in a wide range of temperatures (273.15-303.15 K), pressures (up to 24 bar) and copper(I) concentrations (0-30 mol%). Moreover, the CO absorption has been assessed and gas-liquid equilibria are successfully described with a thermodynamic model as a function of those variables. The $[C_2mim]_x[Cu]_{1-x}[SCN]$ solutions exhibit favorable properties in terms of competitive CO sorption capacity and high selectivity towards slightly soluble gases, e.g., 996.1 mmol L^{-1} and CO/N_2 selectivity of ~25 at 283.15 K and 23.3 bar, combined with low heat of absorption (-29.5 kJ mol^{-1}) as well as easiness of regeneration and reuse. Consequently, these copper(I)-containing ionic liquids are promising for the development of novel and greener CO/N_2 separation processes alternative to the use of flammable and toxic solvents or energy-intensive cryogenic distillations.

Keywords

2

Introduction

Carbon monoxide (CO) is an industrially relevant gas with a gradually increasing demand [1], either as pure compound or as a component of the synthesis gas, for the large scale manufacturing of a myriad of basic chemicals such as alcohols or aldehydes as well as chemical intermediates produced by carbonylation of organic substrates [2], for which new synthesis routes are being developed [3]. Moreover, it is noteworthy that there is huge amount of research activity in the field of producing liquid hydrocarbons more efficiently via Fischer-Tropsch process using CO as an alternative fuel source [4]. In all cases, either high purity CO (98-99%) or syngas mixtures with carefully adjusted H_2/CO ratios are required to obtain the desired products. In this sense, the main routes to produce CO at industrial level are based on steam reforming, partial oxidation processes and gasification of carbonaceous feedstocks. In addition, strategies directed towards increasing sustainable economic growth, e.g., the recovery of relatively inexpensive and abundant CO from exhaust gases, can be seen as a promising opportunity to further enhance the use of CO as raw material [5]. In any case, CO is always obtained as a constituent of a gas mixture that contains H_2 as well as small amounts of several acidic contaminants, e.g., CO_2, COS, H_2S, and therefore, purification steps are generally involved in its production. In addition, it should be taken into account that, while N_2 is a major component of post-combustion gas streams, the separation of CO from N_2-rich streams is extremely challenging owing to the similar properties of these gases, particularly, boiling point and molecular size, and extremely poor solubility in liquid solvents. Consequently, there is a need of energy efficient separation processes based on novel materials that provide high CO/N_2 selectivity in order to make the recovery of CO from waste gases affordable.

Among the conventional gas separation technologies employed for CO purification, only reactive absorption processes are suitable to produce high purity CO at intermediate scale from N_2-rich industrial gas mixtures. In this context, the most extended process employs a

3

bimetallic cuprous salt, preferably CuAlCl$_4$, dissolved in an excess of an aromatic hydrocarbon solvent, usually toluene [6–10]. This process commonly referred to as the COSORB process was developed in the 1970s and although it allows recovering high purity CO (up to 99.7%) with high yield (95-99%), the complex stability and solvent loses are still serious drawbacks of this process that motivate interest in novel CO-complexing compounds [11]. In fact, it is estimated that processes that employ complexing agents with lifetimes of at least one year would be more competitive than COSORB process [12]. Other technologies such as pressure swing adsorption and membranes are almost exclusively devoted to H$_2$ purification due to the limited availability of CO-selective adsorbents and CO-permselective membranes. Nevertheless, growing interest in separating CO from gas mixtures is bringing into focus novel CO-selective materials based on the ability of *d*-block transition metals to selectively and reversibly bind CO via π-bond complex formation mechanism [13,14]. Recently, π-complexation MOF and zeolite adsorbents with high CO adsorption capacity (2.72-6.04 mmol g^{-1}) [15–18] and copper(I)-containing membranes that provide facilitated transport of CO [19,20] have been reported. Although none of them has been implemented at large-scale, with the exception of a CuCl/zeolite adsorbent with low CO capacity (0.33 mmol g^{-1}) [1], these studies emphasize the importance that transition metals may have as drivers of the CO/N$_2$ separation. A survey of other metals that have been explored as CO-complexing agents includes dissolved palladium and iron macrocyclic complexes [21–23] and selenium [24], which usually exhibit very low solubility in organic solvents and/or very high equilibrium constants of reaction, thus hindering the development of a high capacity and reversible absorption process [22].

In view of that, the reactive absorption technology is now revisited embracing a greener mindset aimed at minimizing the energy requirements of the chemical absorption process and searching advanced materials to replace the volatile organic compounds (VOCs) by solvents with advantageous properties. In this sense, ionic liquids (ILs) are attracting increased

4

attention as engineering fluids owing to their highly desirable properties. Apart from their extremely low vapor pressure, good chemical and thermal stability, non-flammability and wide liquid temperature range [25,26], ILs offer the possibility to dissolve high amounts of transition metal salts, particularly if the salt has a common anion with the IL [27]. In the field of gas separation, ILs can provide several benefits for designing novel processes that avoid solvent evaporation during the regeneration as well as other issues related to the use of conventional molecular solvents such as toxicity, flammability and corrosiveness [28,29]. Most of the progress made for gas separation using ILs thus far is related to the removal of acid gases, mainly CO_2 and SO_2, from combustion gases and natural gas. On the other hand, there is clear evidence that CO and other light gases such as H_2 and N_2 are just sparingly soluble in ILs at low pressures [30–35] and consequently, very high pressures (up to 10 MPa) are required to absorb significant amounts of CO [36–39].

Whereas the physical sorption of gases into pure ILs seems to be limited to high pressure applications, the reactive gas absorption into functionalized ILs has been explored as a way to further increase the absorption capacity at low partial pressures of the target solute. This approach has been mainly proposed for post-combustion CO_2 capture with amino-functionalized ILs [40–42], but also for other applications such as olefin/paraffin separation with reactive ILs containing silver salts [43]. Following the same rationale, pioneering studies by our research group also demonstrated the potential of chlorometalate-based ILs for CO capture and separation from other light gases [44,45]. In particular, the ability of chlorocuprate species to bind CO molecules forming carbonyl complexes [46] was exploited to drive the CO separation from mixed gases in a toluene-free environment. Despite this successful approach, several limitations were identified related to the high viscosity (>4000 mPa s at 293.15 K) of the selected IL solutions [47], $[C_6mim]_{1-x}[Cu]_x[Cl]$, and lower mass transfer rates observed relative to conventional solvents that hampers scaling up of the process [48,49]. Moreover, this high-halogen concentration IL may be corrosive to some materials. Nevertheless, this

5

inspired us to focus on the IL structure-property relationships in the search of more appropriate ILs to perform this separation. In this sense, ILs comprising cyano-based anions are promising candidates that exhibit advantageous properties as solvents. In Table 1, several properties of the IL 1-ethyl-3-methylimidazolium thiocyanate, [C_2mim][SCN], are presented and compared to those of various state-of-the-art materials that have been employed for CO capture. As can be seen, [C_2mim][SCN] possesses remarkably lower viscosity (<30 mPa s at 293.15 K) than the majority of ILs and can be considered safer than toluene owing to its inherent negligible vapor pressure and non-flammability (although the thermal decomposition products of ILs may be flammable) [50]. In addition, [C_2mim][SCN] displays wide liquid range (its degradation temperature is ~125 K above the boiling point of toluene) as well as much lower toxicity to aquatic ecosystems than highly toxic toluene and other ILs used for CO capture such as [C_6mim][Cl] and [C_6mim][NTf$_2$], i.e., the log EC_{50} of [C_2mim][SCN] is much higher than the ecotoxicity of toluene (2.33 μmol L^{-1}). Therefore, in order to take full advantage of the [C_2mim][SCN] properties, in this work we propose the use of this IL together with the transition metal salt copper(I) thiocyanate (CuSCN) as chemical solvent for CO gas absorption. To the best of our knowledge, this is the second example of reactive ILs used for CO capture, although this system has been already proposed as entrainer in vapor + liquid systems, yet with relatively low CuSCN concentrations (0.45 mol kg^{-1}) [51].

Table 1. Properties of several solvents used for CO capture.

Solvent	Density[a] (g cm^{-3})	Viscosity[a] (mPa s)	Flash point (K)	Boiling point[b] (K)	Log EC_{50} (mmol L^{-1})[c]
Toluene	0.87	0.58	277	383.8	2.33
[C_6mim][NTf$_2$]	1.38 [52]	90.1 [53]	N/A	T_{deg} = 701 [54]	2.05
[C_6mim][Cl]	1.04 [47]	14160 [47]	452 [50]	$T_{deg,1}$ < 423; $T_{deg,2}$ > 473 [50]	2.15
[C_2mim][SCN]	1.12 [55]	29.2 [55]	N/A	T_{deg} = 510 [56]	4.15

[a]At 293.15 K. [b]Degradation temperature (T_{deg}) for ILs. [c]Ecotoxicity test: *V. fischeri* [57].

6

Herein, we report the characterization of the thermophysical properties of double salt ILs composed of the IL [C$_2$mim][SCN] and the inorganic salt CuSCN. Particularly, density and viscosity have been measured over a wide temperature range (283.15-353.15 K) in a number of solutions containing up to 30 mol% CuSCN and the composition effect on the phase behavior assessed. Moreover, the thermodynamic study of CO reactive uptake into these capture solutions has been performed assessing the influence of temperature (273.15-303.15 K), pressure (up to 24 bar) and copper(I) concentration (up to 30 mol%) on the total amount of CO absorbed.

Experimental section

Materials. The IL [C$_2$mim][SCN] (>98%) was purchased from IoLiTec. The transition metal salt CuSCN (99%) was purchased from Sigma-Aldrich. Carbon monoxide (99.7%) was supplied by Air Liquid.

Preparation of capture solutions. The general procedure to prepare the CO capture solutions is as follows: the IL [C$_2$mim][SCN] was first heated to 373 K; then, a specific amount of CuSCN was added while stirring the solution and eventually, vacuum (<5 mbar) was applied during 2 h in order to remove any possible traces of VOCs that might be originally present in the pristine IL. The solutions obtained in this way are identified as double salt ILs with compositions [C$_2$mim]$_{1-x}$[Cu]$_x$[SCN], where *x* denotes the mole fraction of CuSCN dissolved in the IL. In this work, solutions with relatively high CuSCN concentrations, up to 30 mol%, were prepared. The average water content of a reference sample (without CuSCN) subjected to the same procedure was determined using Karl Fischer titration to be <20 ppm.

Density measurements. Density data of pure [C$_2$mim][SCN] and several [C$_2$mim]$_{1-x}$[Cu]$_x$[SCN] solutions were measured between 283.15 and 353.15 K at 5 K intervals using an Anton Paar

DMA 5000 densimeter provided with viscosity correction and self-control of temperature. The uncertainty in the density and temperature measurements were $3 \cdot 10^{-5}$ g cm^{-3} and 0.01 K, respectively. The apparatus was calibrated by measuring the density of deionized and degassed water and ambient air.

Viscosity measurements. Viscosity data were measured using a controlled stress rheometer Anton Paar model MCR 102 with cone and plate geometry (49.98 mm diameter, 1.008° cone angle and 102 μm truncation). This configuration is particularly suitable for testing ILs given that very small sample volumes (<2 mL) are required. The viscosities of $[C_2mim]_{1-x}[Cu]_x[SCN]$ solutions at atmospheric pressure were recorded between 293.15 and 353.15 K at temperature intervals of 5 K and at a constant shear rate of 10 s^{-1}. A preliminary test was undertaken to ensure that the ILs solutions possess Newtonian flow at shear rates ranging between 0.1 and 100 s^{-1}. Temperature was registered with a precision of 0.01 K using a Peltier system. The uncertainty in the viscosity measurement was 2%.

Thermal properties. Differential scanning calorimetry (DSC) experiments were run in a TA Instruments Q2000 differential scanning calorimeter, with an uncertainty of ±1 K. Thermograms were recorded during two heating cycles from 183 to 293 K with a heating rate of 1 K min^{-1} after cooling samples at the same rate and keeping them isothermal for 10 min at the lowest temperature. The samples (ca. 15-20 mg) were encapsulated in hermetic aluminum pans with lids of the same material and loaded onto the measuring chamber with an autosampler. An empty pan with its lid was used as the reference, and a 50 mL min^{-1} flow of N_2 (Praxair, 99.999%) was used as sample purge gas. It was ensured that the curves for the first and second cycle were coincident, and the results from the second cycle were used. All DSC thermograms were evaluated using the Universal Analysis 2000 software (Version 4.5.0.5A) by TA Instruments.

Absorption measurements. The experimental procedure employed for measuring the CO reactive uptake is based on the isochoric saturation method which main advantage is that it relies on gas phase measurements, whereas the analysis of the liquid phase is not required. The experimental setup is described in detail in a previous work [48], basically, it consists of a jacketed stirred reactor (Buchi, model Picoclave type 1/100 mL) equipped with a pressure transducer (Aplisens, model PCE-28, 0.2% accuracy) that is connected to a data acquisition device (Endress+Hausser, model Memograph M) which monitors the pressure inside the reactor, and a Pt-100 temperature sensor connected to a cryothermostatic bath (Julabo, model F25-ME), which allows regulating the temperature inside the reactor within ± 0.01 K. Just two minor changes were performed: a jacketed metal vessel was employed this time in order to increase the maximum allowable pressure inside the vessel up to 60 bar and, an intermediate storage cylinder of known volume equipped with an absolute digital manometer (Keller, model Leo 2, 0.1% accuracy at full scale) was incorporated before the reactor inlet.

To obtain the absorption isotherms, first, a known amount of IL solution was poured into the reaction vessel, the temperature set to the desired value and the whole system degassed (<5 mbar) using a vacuum pump (Edwards, model RV5) during 3-4 h. Then, an initial amount of CO was loaded into the intermediate storage cylinder and the pressure recorded. Next, the valve that connects the storage tank and the reactor was opened and the gas absorption proceeded until the system reached equilibrium conditions as determined by pressure changes of no more than 1 mbar for more than 20 min. At that point, the equilibrium pressure was recorded and the intermediate valve was closed. Then, the procedure was repeated loading again the storage cylinder with CO at a higher pressure. Finally, the amount of CO absorbed in each step (n_i) and the accumulated amount of CO absorbed (n_{abs}) at equilibrium conditions were calculated as follows:

$$n_i = \rho_{i,res} \cdot V_{res} + \rho_{i-1,reactor} \cdot \left(V_{reactor} - V_{liq}\right) - \rho_{i,eq} \cdot \left(V_{res} + V_{reactor} - V_{liq}\right) \quad (1)$$

9

$$n_{abs} = n_i + \sum_{n}^{i-1} n_n \qquad (2)$$

where V_{res}, $V_{reactor}$ and V_{liq} stand for the volume of the storage cylinder, the reactor and the liquid sample, respectively, and $\rho_{i,res}$, $\rho_{i-1,reactor}$ and $\rho_{i,eq}$ are the molar densities of gas initially loaded into the storage cylinder, the molar density of gas remaining in the reactor from the previous step and the molar density of gas in the whole system at equilibrium conditions when the intermediate valve is opened, respectively. In this work, the molar densities at given conditions of pressure and temperature were calculated using Peng-Robinson equation of state (PR-EoS) in order to account for deviations from ideality at high pressures and the volume of liquid sample of each solution was determined from the mass of solvent added and its measured density at the corresponding temperature and liquid phase composition. In addition, the partial pressures of the ionic liquid solutions were neglected due to their extremely low volatilities. Eventually, the amount of chemically absorbed CO is reported on a volumetric basis (mol CO per L solvent) to account for any differences in densities between the solvents. Nevertheless, the experimental data are also provided as Supplementary Information expressed both in terms of volume and mole fraction basis. The accuracy of the solubility measurements was checked against CO_2 solubility data in water and in the IL [C$_4$mim][BF$_4$]. The average relative standard deviation between replicated CO reactive absorption experiments was <5%.

Thermodynamic model

The aim of this section is to provide a simple thermodynamic model that can be employed to quantitatively describe the equilibria of CO reactive absorption into the [C$_2$mim]$_{1-x}$[Cu]$_x$[SCN] capture solutions at given conditions of pressure, temperature and composition. However, a

10

molecular-based theoretical model has also been developed for this type of reactive systems within the framework of soft-SAFT equation of state [58]. Considering that the physical solubility of CO in these ILs is expected to be several orders of magnitude lower than the chemical solubility and the fact that its measurement is susceptible to generate large experimental errors [30], we opt to consider an heterogeneous model of reaction between CO and the copper(I) species in solution that avoids the use of gas-liquid equilibrium relationships, such as the Henry law, and should provide an accurate quantitative approximation at low and moderate pressures for this system. Although the coordination between CO and copper(I) in this system is a priori unknown, it is speculated, based on previous works with $[C_6mim]_{1-x}[Cu]_x[Cl]$, that monocarbonyl species are formed [44,59]:

$$CO_{(g)} + Cu(I)^+_{(l)} \leftrightarrow Cu(I)^+(CO)_{(l)} \qquad (3)$$
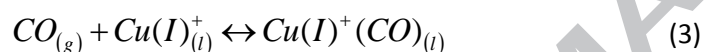
Although a non-ideal behavior of the liquid phase ionic species might be expected for this type of systems, in order to keep the model simple, it has been assumed as an initial approach that the ratio of the solute activity coefficients keeps constant within the range of variables. In addition, the fugacity of the gas species was not included given that deviations from ideal behavior calculated with PR-EoS at the range of experimental conditions are relatively small. Therefore, the equilibrium concentration constant of the complexation reaction can be defined as:

$$K_{eq} = \frac{\left[Cu(I)^+(CO)\right]_{eq}}{P_{CO}^{eq} \cdot \left[Cu(I)^+\right]_{eq}} \qquad (4)$$

where K_{eq} is the equilibrium concentration constant of reaction (bar^{-1}), P_{CO}^{eq} is the equilibrium partial pressure of CO (bar) and $\left[Cu(I)^+(CO)\right]_{eq}$ and $\left[Cu(I)^+\right]_{eq}$ are the equilibrium concentrations (mol L^{-1}) of the carbonyl complex and free copper(I) species, respectively. A mass balance is performed to calculate the concentration of copper(I) cations

11

at equilibrium as the difference between the initial copper(I) concentration, $\left[Cu(I)^+\right]_0$, and

the equilibrium concentration of the complexed species:

$$\left[Cu(I)^+\right]_{eq} = \left[Cu(I)^+\right]_0 - \left[Cu(I)^+(CO)\right]_{eq} \qquad (5)$$

Finally, the chemically absorbed CO at equilibrium conditions is obtained combining Eqs. (4)

and (5):

$$\left[Cu(I)^+(CO)\right]_{eq} = \left(\frac{P_{CO}^{eq} \cdot K_{eq}}{1 + P_{CO}^{eq} \cdot K_{eq}}\right) \cdot \left[Cu(I)^+\right]_0 \qquad (6)$$

In addition, the temperature dependence of the equilibrium constant on the complexation

reaction can be described by means of the van't Hoff equation:

$$\frac{d \ln K_{eq}}{d(1/T)} = -\frac{\Delta H}{R} \qquad (7)$$

where T is the temperature (K), ΔH is the enthalpy of absorption due to the complexation

reaction (kJ mol^{-1}) and R is the gas constant (kJ mol^{-1} K^{-1}).

Results and discussion

Physical and thermal properties. In this section, we report density and viscosity data of the CO

capture solutions as a function of temperature and composition, which are very relevant

thermophysical and transport properties of fluid systems for process design. The measured

densities of pure [C$_2$mim][SCN] and several [C$_2$mim]$_{1-x}$[Cu]$_x$[SCN] solutions from 283.15 to

353.15 K are plotted in Figure 1a and collected in Table S1 of the supplementary Information.

As can be observed, the density of the IL solutions decreased with temperature and increased

with the concentration of CuSCN. In addition, density data of [C$_2$mim][SCN] are in very good

12

agreement with available data reported by other research groups [51,55,60,61].The following linear relationship was employed to describe the temperature dependence of density:

$$\rho\left(\frac{g}{cm^3}\right) = a + b \cdot T \quad (8)$$

where a and b are adjustable parameters provided in Table 2 along with the corresponding relative standard deviations (RSD), which were obtained as:

$$RSD = \left[\frac{1}{N-v}\sum_{i}^{N}\left(\frac{z_{i,\exp} - z_{i,calc}}{z_{i,\exp}}\right)^2\right]^{0.5} \quad (9)$$

where $z_{i,\exp}$ and $z_{i,calc}$ are the experimental and calculated physical property, respectively, N is the number of experimental data points and v is the number of fitted parameters of the equation. The influence of the complex concentration on the density of $[C_2mim]_{1-x}[Cu]_x[SCN]$ solutions is compared in Figure 1b with other solutions that have been employed to capture CO, in particular, with that of $[C_6mim]_x[Cu]_{1-x}[Cl]$ solutions used in our previous works and the $CuAlCl_4$-toluene solutions of the conventional process, revealing that they possess very similar densities in the high concentration end.
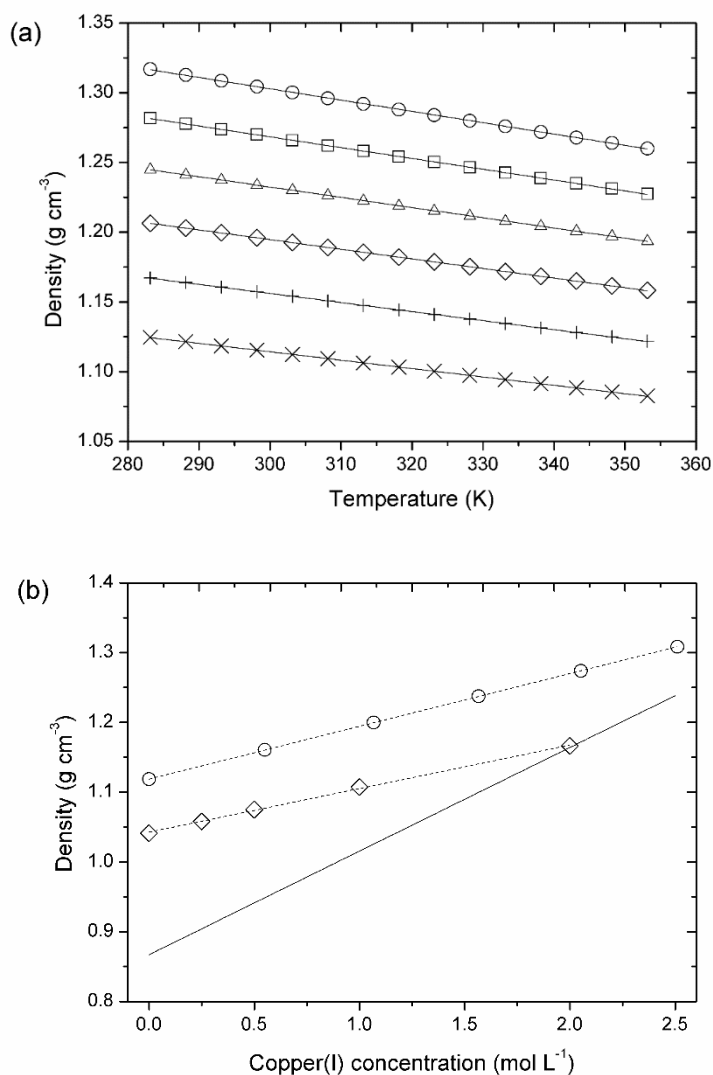
Figure 1. a) Density of $[C_2mim]_{1-x}[Cu]_x[SCN]$ solutions at atmospheric pressure as a function of temperature and CuSCN mole fractions: 0 (x), 0.08 (+), 0.14 ($\diamond$), 0.20 (Δ), 0.25 ($\square$) and 0.30 (O). Symbols are experimental data and solid lines are the values calculated with Eq. (8). b) Influence of copper(I) concentration on the solvent density of several solutions at 293.15 K: $[C_2mim]_{1-x}[Cu]_x[SCN]$ (O), $[C_6mim]_x[Cu]_{1-x}[Cl]$ ($\diamond$) [47] and CuAlCl$_4$-toluene (solid line) [6]. Dotted lines are the linear least-squares regression ($R^2 < 0.9990$).

Table 2. Adjustable parameters of the linear fits ($R^2 > 0.9999$) for density of $[C_2mim]_{1-x}[Cu]_x[SCN]$ IL solutions ($\rho = a+b\cdot T$) and calculated relative standard deviation (RSD).

	Mole fraction of CuSCN					
	0.0	0.08	0.14	0.20	0.25	0.30
a (g cm^{-3})	1.29463	1.35064	1.40175	1.45288	1.50117	1.54631

b (x10^4 g cm^{-3} K^{-1})	-6.01	-6.49	-6.90	-7.35	-7.76	-8.12
RSD·10^4	1.14	0.92	0.61	0.87	1.23	1.48

The viscosity of [C$_2$mim]$_{1-x}$[Cu]$_x$[SCN] solutions measured between 293.15 and 353.15 K at 5 K intervals is depicted in Figure 2 and compiled in Table S2 of the Supplementary Information. The measured viscosity of pure [C$_2$mim][SCN] is also in good agreement with available data reported elsewhere [51,55,62,63]. As can be seen, both variables, temperature and composition, have a strong influence on the IL viscosity. Among the equations typically employed to quantitatively describe the temperature dependence of viscosity [64], it was found that Litovitz equation performed much better ($R^2 > 0.9970$) than Andrade equation ($R^2 < 0.9828$), both with just two adjustable parameters, in the whole temperature range. Therefore, Litovitz equation was employed to correlate the viscosity data according to:

$$\eta \left(mPa \ s\right) = A \cdot \exp\left(\frac{B}{T^3}\right) \quad (10)$$

where A and B correspond to fitting parameters also provided in Table 3 along with the corresponding relative standard deviations (RSD). If one compares the viscosity of [C$_2$mim]$_{1-x}$[Cu]$_x$[SCN] with that of the [C$_6$mim]$_{1-x}$[Cu]$_x$[Cl] solutions employed in our previous works, which were between ~500 (pure IL) and 16 times (concentrated solutions in copper salt) more viscous [47], a significant enhancement of the CO mass transfer rates should be expected in these new media.
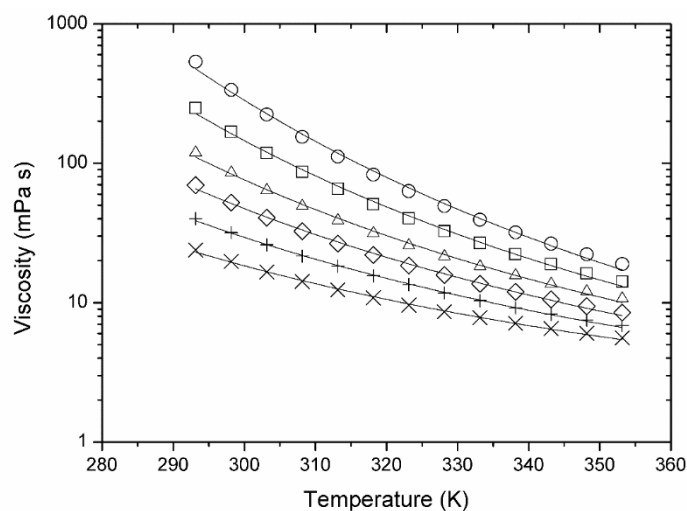
Figure 2. Viscosity of $[C_2mim]_{1-x}[Cu]_x[SCN]$ solutions at atmospheric pressure as a function of temperature and CuSCN mole fractions: 0 (x), 0.08 (+), 0.14 ($\diamond$), 0.20 (Δ), 0.25 ($\square$) and 0.30 (O). Symbols are experimental data and solid lines are the values calculated with Eq. (10).

Table 3. Adjustable parameters of the Litovitz equation ($R^2 > 0.9970$) for viscosity of $[C_2mim]_{1-x}[Cu]_x[SCN]$ IL solutions and calculated relative standard deviation (RSD).

	Mole fraction of CuSCN					
	0.0	0.08	0.14	0.20	0.25	0.30
A (mPa s)	0.7842	0.6268	0.4928	0.4070	0.2896	0.2037
B (x10^{-8} K^3)	0.852	1.039	1.232	1.412	1.679	1.954
RSD	0.02	0.02	0.03	0.04	0.05	0.06

In addition, DSC analyses were undertaken to identify the phase transitions in the pure $[C_2mim][SCN]$ and in the solution containing 30 mol% CuSCN. In the thermograms, the portion of the curve below 200 K was omitted due to lack of stability of the baseline observed in that region. The cooling ramps of the DSC thermograms were in both cases completely featureless, i.e., the samples did not crystallize on cooling; however, a small exothermic peak followed by an endothermic peak were observed in the heating ramp only when low heating rates were applied as can be seen in Figure 3. From these facts, it is speculated that these ILs showed cold crystallization and subsequent melting upon heating, a behavior that is not unusual for other

16

ILs [65]. However, after the incorporation of CuSCN to the IL, this feature is even less pronounced. Considering that the decomposition temperature attributed to $[C_2mim][SCN]$ is 510 K, these ILs will remain in liquid state over a wide temperature range, which is an extremely important feature regarding both sorption and desorption stages. In fact, the boiling point of toluene (383.8 K) is close to temperatures typically employed in desorption units and consequently, it will evaporate during solvent regeneration. In contrast, ILs may offer improved energy efficiency of the process as they will not evaporate under such conditions.
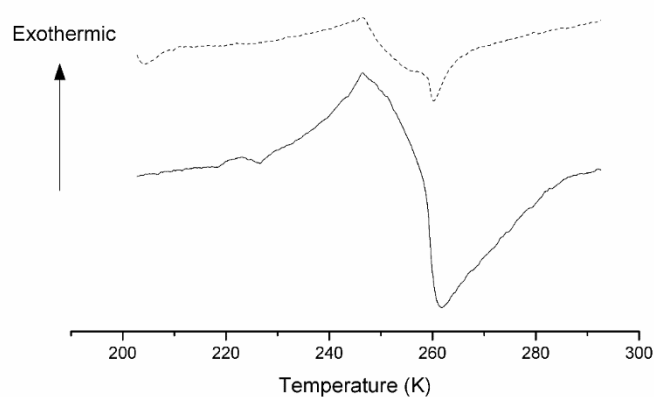

Figure 3. DSC thermograms of pure $[C_2mim][SCN]$ (solid line) and a solution containing 30 mol% CuSCN (dashed line). Heating rate: 1 K min^{-1}.

Chemical absorption of carbon monoxide. In this section, we present the thermodynamic properties for CO reactive absorption into $[C_2mim]_{1-x}[Cu]_x[SCN]$ ILs. First, the influence of the IL composition was assessed to prove that these solutions can be successfully applied to capture CO and separate it from other light gases, particularly from N_2 which is taken as a reference in this work. The experimentally measured solubilities of CO in several ionic liquid solutions containing up to 30 mol% of CuSCN with respect to the equilibrium pressure of CO, up to 8 bar, are depicted in Figure 4 at 293.15 K. As can be seen, the amount of absorbed CO significantly increased with the concentration of copper(I) ions in solution as a consequence of the carbonyl complex formation. The maximum solubility obtained in the most concentrated IL solution (30 mol%) was 287.1 mmol L^{-1} at 7.79 bar and 293.15 K. In addition, data predicted with the

17

thermodynamic model developed in this work, which is described later on in this section, are also plotted.

Once proved that CO is successfully absorbed into the $[C_2mim]_{1-x}[Cu]_x[SCN]$ ILs, the influence of temperature on the absorption process was assessed between 273.15 and 303.15 K in the most concentrated solution, containing 30 mol% of CuSCN, over a wider pressure range, up to 24 bar. Results plotted in Figure 5 show that temperature has a strong influence on the chemisorption process, which is significantly enhanced at low temperature, e.g., the concentration of CO absorbed increased from 502 mmol L^{-1} at 303.15 K and 23.0 bar to 1279 mmol L^{-1} at 273.15 K and 23.9 bar. In addition, the assessment of the amount of complexing agent that is bound to the absorbed CO is presented in Table 4 at several pressures, temperatures and IL compositions. As can be observed, the maximum value of complexed copper(I) cations achieved in this work was ~50% in the most favorable conditions, i.e., lowest temperature and highest pressure and CuSCN concentration, revealing the feasibility of further increasing the amount of CO absorbed in high pressure applications. Furthermore, a comparison is made with the N_2 solubility measured at 283.15 K. As shown in Figure 5, these IL solutions not only provide high sorption capacity towards CO but also a remarkably high equilibrium selectivity against other light gases with poor solubilities in IL media, e.g., the CO/N_2 solubility selectivity of the 30 mol% CuSCN solution is ~25 at 283.15 K.
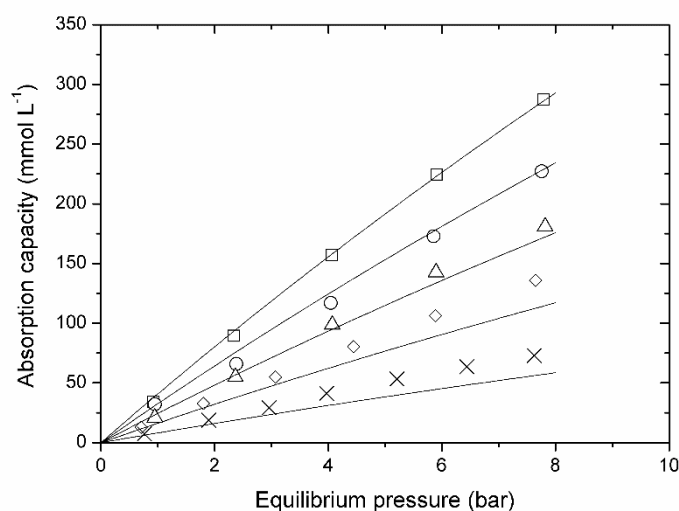
Figure 4. Carbon monoxide absorption isotherms into $[C_2mim]_{1-x}[Cu]_x[SCN]$ ILs at 293.15 K and several CuSCN mole fractions (0.08 (x), 0.14 (◇), 0.20 (Δ), 0.25 (○) and 0.30 (□)). Solid lines are model predictions for CO chemisorption. Experimental data are provided in Table S3.
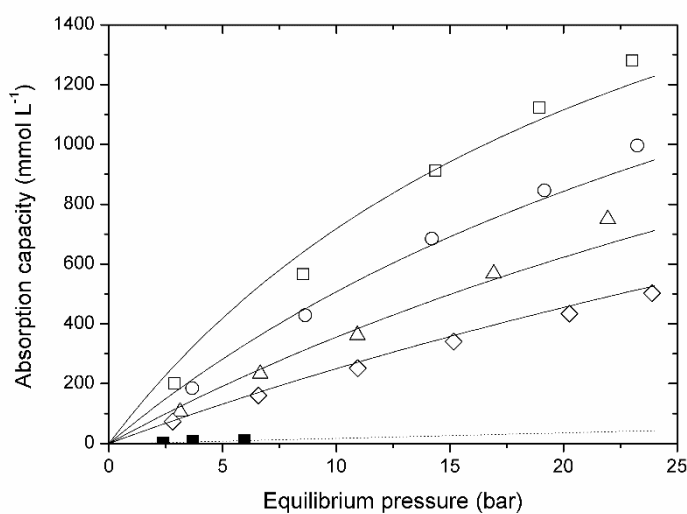

Figure 5. Influence of temperature on carbon monoxide absorption reactive uptake into $[C_2mim]_{1-x}[Cu]_x[SCN]$ IL containing 30 mol% CuSCN: 303.15 (◇), 293.15 (Δ), 283.15 (○) and 273.15 K (□). N_2 physical solubility (■) measured at 283.15 K is also shown. Solid lines are model predictions for CO chemisorption and dotted line represents the N_2 solubility fitted to

19

the Henry's law and extrapolated over the whole pressure range. Experimental data are provided in Table S4.

Table 4. Amount of complexed copper(I) cations at several temperatures, IL compositions and pressures.

T (K)	x_{CuSCN}	P (bar)	Complexed Cu$^+$ (%)	T (K)	x_{CuSCN}	P (bar)	Complexed Cu$^+$ (%)
303.15	0.08	7.5	7.1	283.15	0.08	7.3	21.7
	0.14	7.4	5.9		0.14	7.6	20.1
	0.20	7.6	7.4		0.20	7.7	18.2
	0.25	7.8	7.5		0.25	7.6	17.7
	0.30	7.8	7.6		0.30	7.8	14.5
		23.9	20.2			23.3	39.5
293.15	0.08	7.6	13.3	273.15	0.08	7.7	32.6
	0.14	7.6	12.7		0.14	7.7	27.4
	0.20	7.8	11.5		0.20	6.6	22.6
	0.25	7.8	11.1		0.25	7.7	24.5
	0.30	7.8	11.4		0.30	7.7	20.6
		22.0	29.9			23.0	50.4

Standard uncertainty for solubility measurements: u(T) = 0.01 K, u(P) <0.2% and u(S$_{CO}$) <5%.

As for the thermodynamic model, the equilibrium constant of the complexation reaction and the heat of absorption were determined by fitting all the experimental data to the equations derived in a previous section. Figure 6 depicts the influence of temperature on the equilibrium constant of reaction, which can be satisfactorily described by the van't Hoff equation with heat of absorption of -29.53 kJ mol^{-1}. Moreover, as can be observed in Figure 7, the model developed in this work successfully provides a quantitative description of the absorption process in a wide range of temperature (273.15-303.15 K), pressure (up to 24 bar) and composition of the CO capture solutions (8-30 mol% CuSCN), the larger deviations being systematically observed under the least favorable conditions, i.e., low pressure, temperature and CuSCN concentration.
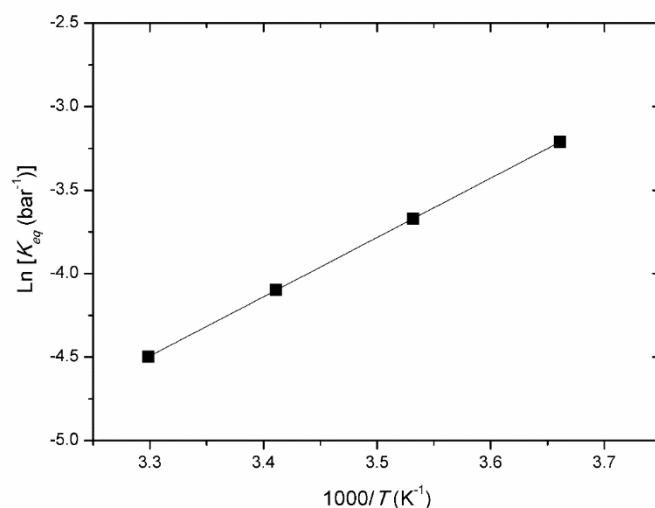
Figure 6. Temperature influence on the equilibrium constant of the complexation reaction between CO and copper(I) in the $[C_2mim]_{1-x}[Cu]_x[SCN]$ IL solutions described by the van't Hoff equation (T_{ref} = 298.15 K). Solid line represents the linear least-squares regression (R^2 = 1).
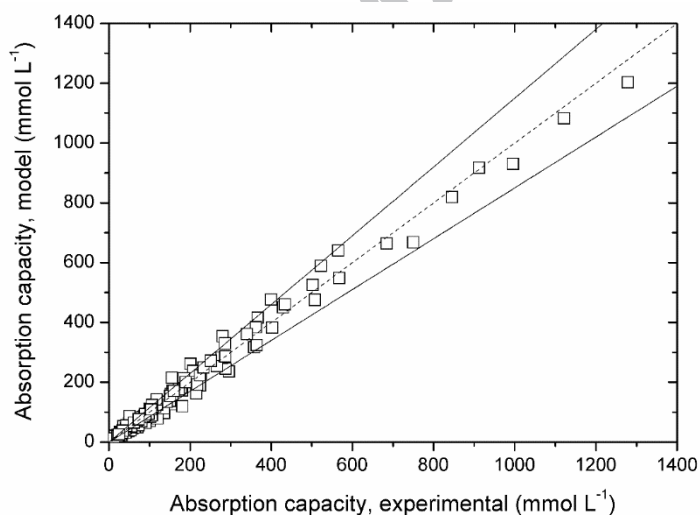

Figure 7. Parity plot between experimental and modeled data of CO reactive uptake into $[C_2mim]_{1-x}[Cu]_x[SCN]$ ILs. Data obtained in solutions containing 8-30 mol% CuSCN at temperatures between 273.15 and 303.15 K and pressures up to 24 bar. Solid lines represent ±15% deviations.

In Table 5, a comparison is made between the performance of the CO sorption process in the molecular and ionic solutions presented in Table 1. As can be seen, the CO uptake in pure ILs such as $[C_6mim][NTf_2]$ is much lower than the sorption capacities achieved by selectively

21

binding CO with a complexing agent, namely, copper(I) salts. On the other hand, although the chemical sorption of CO in toluene-based solutions [6–8] seems to be favored over the CO uptake into ILs, there is, however, a noticeable reduction of the absorption enthalpy in IL-based solvents relative to that typically found in organic molecular solvents. For instance, the heat of absorption between CO and $CuAlCl_4$ in toluene [7] is more than 2-fold the value found in this work between CO and CuSCN in $[C_2mim][SCN]$. Similarly, very large heats of absorption are common for CO_2 capture into aqueous amines solutions [66], whereas it has been shown that ILs can be tuned to provide lower enthalpies of reaction [67]. Consequently, the recovery of the absorbed gases and the regeneration of the IL-based capture solutions will be performed at the expense of much lower energy requirements.

Table 5. Physical and chemical uptake of CO in several molecular and IL media.

Solvent	H_{CO} (x10^{-3} bar)[a]	Complexing agent	Sorption capacity (mmol L^{-1})	Heat of absorption (kJ mol^{-1})
Toluene	1.29 [33]	$CuAlCl_4$ (1.0 mol L^{-1})	1023 at 7.8 bar and 313.15 K	-67 [7]
$[C_6mim][NTf_2]$	0.76 [33]		95.4[b] at 31.2 bar and 293.15 K	-1.29 [38]
$[C_6mim][Cl]$	N/A	CuCl (2.0 mol L^{-1})	595.0[b] at 7.6 bar and 293.15 K	-13.4 [44]
$[C_2mim][SCN]$	N/A	CuSCN (2.5 mol L^{-1})	750.6 at 22.0 bar and 293.15 K	-29.5

[a]Henry constant of CO at 295.15 K. [b]Solubility in mmol kg^{-1}.

Finally, recovering the absorbed CO and regenerating the absorbent are very important issues concerning the technical feasibility of capture solutions in industrial applications that should be borne in mind when assessing new solvent alternatives. Moreover, although it is well known that the main problems found in using a liquid absorbent for CO absorption, particularly an aqueous solvent, are the low solubility of cuprous salts in liquid media and the instability of copper(I) ions due to oxidation and disproportionation [46], it has been reported

that copper(I) can be stabilized in ionic liquid media [68]. In this work, all the IL solutions employed can be completely regenerated and reuse in a new absorption cycle by simple means: after completing an absorption cycle, temperature was increased to 333.15 K and pressure reduced below 5 mbar. Those conditions were applied during at least 2 h to ensure complete desorption, however, shorter times may also prove feasible. Figure 8 shows all the CO absorption/desorption cycles performed into the same solution at several temperatures. As can be seen, the first and second absorption isotherms are almost coincident at every temperature thus demonstrating that the absorption capacity of the solvent is completely recovered over 8 cycles.
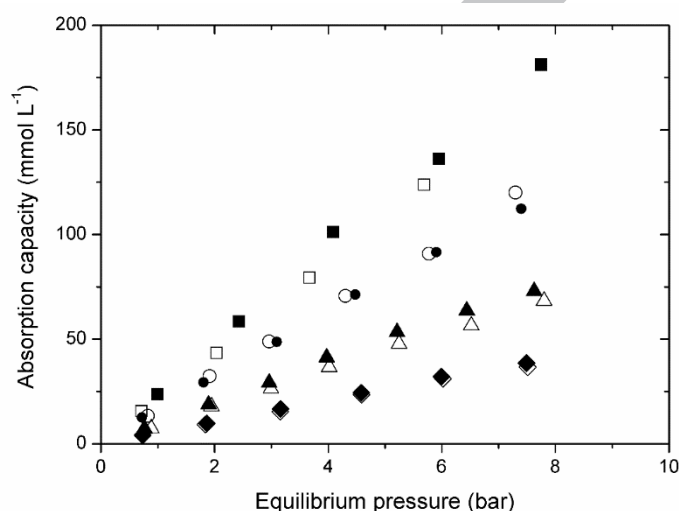

Figure 8. Series of absorption/desorption cycles performed using the same $[C_2mim]_{1-x}[Cu]_x[SCN]$ IL solution containing 8 mol% CuSCN: 303.15 (diamonds), 293.15 (triangles), 283.15 (circles) and 273.15 K (squares). Hollow and filled symbols are the first and second loading cycles, respectively. Experimental data are provided in Table S5.

As concluding remarks, ILs solutions containing transition metal salts offer great potential as alternative solvents to aromatic hydrocarbons for the development of safer and less energy intensive CO-selective separation processes dealing with non-condensable gas mixtures of the chemical and petrochemical industry in applications such as the removal of CO from flue gases of the process industry with a high content of nitrogen or prized inert gases like argon, the

purification of H_2 and the H_2/CO ratio adjustment, among others. The use of these solutions may improve the energy efficiency and process safety in terms of exposure risks because of the negligible vapor pressure, non-flammability and low ecotoxicity of the thiocyanate-based IL solvent; besides, the studied solutions show more advantageous properties in relation to the kinetic phenomena involved in the separation processes, i.e., much lower viscosity, than the IL solutions employed in our previous works. Moreover, the utilization of greener solvents such as ILs coupled with the development of intensified separation processes based on membrane technology can provide an excellent opportunity for achieving enhanced efficiencies compared to traditional gas separation processes [69].

Conclusions

This work focuses on the great potential of cyano-based ILs, which can be tailored by incorporating a transition metal salt with a common anion, to provide safer and more energy efficient alternatives to the separation of CO from non-condensable gas mixtures in applications that report high economic interest such as the adjustment of H_2/CO syngas ratio and the removal of CO from flue gases of the process industry for its further reuse. Therefore, double salt IL solutions with composition $[C_2mim]_{1-x}[Cu]_x[SCN]$ have been prepared in this work as selective CO chemical absorbents for the development of greener separation processes for CO recovery from industrial gas streams. In order to gain insight on the fundamentals of this innovative separation, the thermophysical properties of the IL solutions have been characterized, paying special attention to the composition effect on the resulting viscosity so as to overcome one of the main limitations that hinders the implementation of ILs as engineering fluids. In this sense, the properties displayed by $[C_2mim]_{1-x}[Cu]_x[SCN]$ solutions represent a clear improvement over previous IL-based capture solutions, particularly, those

containing halogen anions, which are impractical for separation purposes owing to their extremely high viscosities.

The $[C_2mim]_{1-x}[Cu]_x[SCN]$ IL solutions used in this work exhibit high CO sorption capacity as a result of the formation of complexes with available copper(I) cations in the IL media. The highest CO sorption capacity attained in this work with IL solutions containing 30 mol% CuSCN is 1279.2 mmol L^{-1} at 273.15 K and 23 bar. Consequently, considerably high equilibrium selectivities can be achieved in this way towards light gases that are just sparingly soluble into ILs such as N_2 and H_2 among others, e.g., CO/N_2 selectivities around 25-30 can be achieved at 283.15 K in solutions concentrated in CuSCN. Moreover, these IL-based solvents represent a promising alternative to the conventional technology that employs $CuAlCl_4$-toluene solutions as they may provide improved energy efficiencies due to their inherent negligible vapor pressures, wider liquid range and much lower heat of absorption. In addition, $[C_2mim][SCN]$ can be considered safer than the conventional solvent used (i.e., toluene) in terms of exposure risks, flammability and ecotoxicity. Although the most concentrated solution used in this work still has a viscosity of ~500 mPa s at room-temperature, these absorption solvents warrant consideration for the development of novel separation processes since further improvements may come as a result of modifying the chemical structure of the IL or blending with high boiling point molecular solvents.

Acknowledgements

25

References

[1]   Y. Chen, P. Ning, Y. Xie, Y. Chen, H. Sun, Z. Liu, Pilot-scale experiment for purification of CO from industrial tail gases by pressure swing adsorption, Chinese J. Chem. Eng. 16 (2008) 715–721. doi:10.1016/S1004-9541(08)60145-7.

[2]   W. Bertleff, Carbonylation, Ullmann's Encycl. Ind. Chem. (2000) 1–19. doi:10.1002/14356007.a05_217.

[3]   Y. Wang, J. Zhang, H. Chen, Z. Zhang, C. Zhang, M. Li, F. Wang, Ru/ceria-catalyzed direct formylation of amines and CO to produce formamides, Green Chem. 19 (2017) 88–92. doi:10.1039/C6GC02603F.

[4]   K. Liu, Z. Cui, W. Chen, L. Zhang, Coal and Syngas to Liquids, in: K. Liu, C. Song, V. Subramani (Eds.), Hydrog. Syngas Prod. Purif. Technol., John Wiley & Sons, Inc., Hoboken, NJ, USA, 2009: pp. 486–521. doi:10.1002/9780470561256.ch12.

[5]   G.S. Patil, S. Baruah, N.N. Dutta, Facilitated transport of carbon monoxide: A review, Gas Sep. Purif. 5 (1991) 2–8. doi:10.1016/0950-4214(91)80040-C.

[6]   J. Koschel, A. Pfennig, M. Henschke, H. Hartmann, Absorption of carbon monoxide, hydrogen, and methane in toluene and copper(I) tetrachloroaluminate-toluene solutions at elevated pressures, Energy & Fuels. 5 (1991) 729–733. doi:10.1021/ef00029a018.

[7]   R. V Gholap, R. V Chaudhari, Absorption of carbon monoxide with reversible reaction in cualcl4-toluene-complex solutions, Can. J. Chem. Eng. 70 (2009) 505–510. doi:10.1002/cjce.5450700313.

[8]   J.A. Hogendoorn, W.P.M. van Swaaij, G.F. Versteeg, The absorption of carbon monoxide in COSORB solutions: absorption rate and capacity, Chem. Eng. J. Biochem. Eng. J. 59 (1995) 243–252. doi:10.1016/0923-0467(94)02959-8.

[9]   T. Sato, I. Toyoda, Y. Yamamori, T. Yonemoto, H. Kato, T. Tadaki, Chemical Reaction of Carbon Monoxide With Copper(I)-Tetrachloroaluminate(III)-Aromatic Hydrocarbon Solutions - Equilibrium and Kinetics., J. Chem. Eng. Japan. 21 (1988) 192–198. doi:10.1252/jcej.21.192.

[10]   G.B. McVicker, Heats of dissociation of 2:1 and 1:1 molecular complexes formed between toluene and copper(I) tetrachloroaluminate, Inorg. Chem. 11 (1972) 2485–2488. doi:10.1021/ic50116a038.

[11]   F.A. Caruso, R.J. De Feo, R.B. Long, D.G. Walker, Bimetallic salts and derivatives thereof their preparation and use in the complexing of ligands, US 3651159 A, 1972.

[12]   N.N. Dutta, G.S. Patil, Developments in CO separation, Gas Sep. Purif. 9 (1995) 277–283. doi:10.1016/0950-4214(95)00011-Y.

[13]   R. Yang, π-Complexation Sorbents and Applications, in: R. Yang (Ed.), Adsorbents Fundam. Appl., John Wiley & Sons, Inc., Hoboken, NJ, USA, 2003: pp. 191–230. doi:10.1002/047144409X.ch8.

[14]   C.J. King, Separation processes based on reversible chemical complexation, in: R.T. Rousseau (Ed.), Handb. Sep. Process Technol., John Wiley & Sons, Inc., New Jersey,

26

1987: pp. 760–774.

[15]   J. Peng, S. Xian, J. Xiao, Y. Huang, Q. Xia, H. Wang, Z. Li, A supported Cu(I)@MIL-100(Fe) adsorbent with high CO adsorption capacity and CO/N2 selectivity, Chem. Eng. J. 270 (2015) 282–289. doi:10.1016/j.cej.2015.01.126.

[16]   F. Gao, Y. Wang, S. Wang, Selective adsorption of CO on CuCl/Y adsorbent prepared using CuCl2 as precursor: Equilibrium and thermodynamics, Chem. Eng. J. 290 (2016) 418–427. doi:10.1016/j.cej.2016.01.054.

[17]   E.D. Bloch, M.R. Hudson, J.A. Mason, S. Chavan, V. Crocellà, J.D. Howe, K. Lee, A.L. Dzubak, W.L. Queen, J.M. Zadrozny, S.J. Geier, L.C. Lin, L. Gagliardi, B. Smit, J.B. Neaton, S. Bordiga, C.M. Brown, J.R. Long, Reversible CO binding enables tunable CO/H2 and CO/N2 separations in metal-organic frameworks with exposed divalent metal cations, J. Am. Chem. Soc. 136 (2014) 10752–10761. doi:10.1021/ja505318p.

[18]   F. Gao, Y. Wang, X. Wang, S. Wang, Selective CO adsorbent CuCl/AC prepared using CuCl 2 as a precursor by a facile method, RSC Adv. 6 (2016) 34439–34446. doi:10.1039/C6RA03116A.

[19]   G. Zarca, W.J. Horne, I. Ortiz, A. Urtiaga, J.E. Bara, Synthesis and gas separation properties of poly(ionic liquid)-ionic liquid composite membranes containing a copper salt, J. Memb. Sci. 515 (2016). doi:10.1016/j.memsci.2016.05.045.

[20]   G. Zarca, I. Ortiz, A. Urtiaga, Copper(I)-containing supported ionic liquid membranes for carbon monoxide/nitrogen separation, J. Memb. Sci. 438 (2013). doi:10.1016/j.memsci.2013.03.025.

[21]   S.E. Lyke, M.A. Lilga, D.A. Nelson, B.R. James, C.L. Lee, Separation of syngas components using a dissolved palladium complex, Ind. Eng. Chem. Prod. Res. Dev. 25 (1986) 517–521. doi:10.1021/i300024a003.

[22]   C.A. Koval, R.D. Noble, J.D. Way, B. Louie, Z.E. Reyes, B.R. Bateman, G.M. Horn, D.L. Reed, Selective transport of gaseous carbon monoxide through liquid membranes using an iron(II) macrocyclic complex, Inorg. Chem. 24 (1985) 1147–1152. doi:10.1021/ic00202a007.

[23]   C.S. Sharma, P.K. Goswami, N.N. Dutta, Studies on facilitated transport of carbon monoxide using a novel iron(II) complex, Sep. Sci. Technol. 28 (1993) 1789–1797. doi:10.1080/01496399308019043.

[24]   N. Sonoda, N. Mtyoshi, S. Tsunoi, A. Ogawa, N. Kambe, A new and convenient process for separation of carbon monoxide, Chem. Lett. 19 (1990) 1873–1876. doi:10.1246/cl.1990.1873.

[25]   K.R. Seddon, Ionic Liquids for Clean Technology, J. Chem. Technol. Biotechnol. 68 (1997) 351–356. doi:10.1002/(SICI)1097-4660(199704)68:4<351::AID-JCTB613>3.0.CO;2-4.

[26]   H. Zhao, Innovative Applications of Ionic Liquids As "Green" Engineering Liquids, Chem. Eng. Commun. 193 (2006) 1660–1677. doi:10.1080/00986440600586537.

[27]   T. Vainikka, D. Lloyd, L. Murtomäki, J.A. Manzanares, K. Kontturi, Electrochemical study of copper chloride complexes in the RTIL 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, Electrochim. Acta. 87 (2013) 739–748. doi:10.1016/j.electacta.2012.09.062.

[28]   J.E. Bara, T.K. Carlisle, C.J. Gabriel, D. Camper, A. Finotello, D.L. Gin, R.D. Noble, Guide to CO2 separations in imidazolium-based room-temperature ionic liquids, Ind. Eng. Chem. Res. 48 (2009) 2739–2751. doi:10.1021/ie8016237.

[29]   M.S. Shannon, J.E. Bara, Reactive and reversible ionic liquids for CO2 capture and acid gas removal, Sep. Sci. Technol. 47 (2012) 178–188. doi:10.1080/01496395.2011.630055.

[30]   Z. Lei, C. Dai, B. Chen, Gas solubility in ionic liquids, Chem. Rev. 114 (2014) 1289–1326. doi:10.1021/cr300497a.

[31]   J. Jacquemin, P. Husson, V. Majer, M.F.C. Gomes, Low-pressure solubilities and thermodynamics of solvation of eight gases in 1-butyl-3-methylimidazolium hexafluorophosphate, Fluid Phase Equilib. 240 (2006) 87–95. doi:10.1016/j.fluid.2005.12.003.

[32]   J. Jacquemin, M.F. Costa Gomes, P. Husson, V. Majer, Solubility of carbon dioxide, ethane, methane, oxygen, nitrogen, hydrogen, argon, and carbon monoxide in 1-butyl-3-methylimidazolium tetrafluoroborate between temperatures 283 K and 343 K and at pressures close to atmospheric, J. Chem. Thermodyn. 38 (2006) 490–502. doi:10.1016/j.jct.2005.07.002.

[33]   C.A. Ohlin, P.J. Dyson, G. Laurenczy, Carbon monoxide solubility in ionic liquids: determination, prediction and relevance to hydroformylation., Chem. Commun. (Camb). (2004) 1070–1. doi:10.1039/b401537a.

[34]   J. Blath, M. Christ, N. Deubler, T. Hirth, T. Schiestel, Gas solubilities in room temperature ionic liquids - Correlation between RTiL-molar mass and Henry's law constant, Chem. Eng. J. 172 (2011) 167–176. doi:10.1016/j.cej.2011.05.084.

[35]   Q. Gan, Y. Zou, D. Rooney, P. Nancarrow, J. Thompson, L. Liang, M. Lewis, Theoretical and experimental correlations of gas dissolution, diffusion, and thermodynamic properties in determination of gas permeability and selectivity in supported ionic liquid membranes, Adv. Colloid Interface Sci. 164 (2011) 45–55. doi:10.1016/j.cis.2011.01.005.

[36]   J. Kumełan, Á.P.S. Kamps, D. Tuma, G. Maurer, Solubility of CO in the ionic liquid [bmim][PF6], Fluid Phase Equilib. 228–229 (2005) 207–211. doi:10.1016/j.fluid.2004.07.015.

[37]   J. Kumełan, Á. Pérez-Salado Kamps, D. Tuma, G. Maurer, Solubility of the single gases H2 and CO in the ionic liquid [bmim][CH3SO4], Fluid Phase Equilib. 260 (2007) 3–8. doi:10.1016/j.fluid.2006.06.010.

[38]   J. Kumelan, Á.P.S. Kamps, D. Tuma, G. Maurer, Solubility of the single gases carbon monoxide and oxygen in the ionic liquid [hmim][Tf2N], J. Chem. Eng. Data. 54 (2009) 966–971. doi:10.1021/je8007556.

[39]   L.J. Florusse, S. Raeissi, C.J. Peters, An IUPAC Task Group Study: The Solubility of Carbon Monoxide in [hmim][Tf2N] at High Pressures, J. Chem. Eng. Data. 56 (2011) 4797–4799. doi:10.1021/je200764g.

[40]   L.M. Galán Sánchez, G.W. Meindersma, A.B. de Haan, Kinetics of absorption of CO2 in amino-functionalized ionic liquids, Chem. Eng. J. 166 (2011) 1104–1115. doi:10.1016/j.cej.2010.12.016.

[41] H. Guo, Z. Zhou, G. Jing, Kinetics of carbon dioxide absorption into aqueous [Hmim][Gly] solution, Int. J. Greenh. Gas Control. 16 (2013) 197–205. doi:10.1016/j.ijggc.2013.03.024.

[42] B.E. Gurkan, T.R. Gohndrone, M.J. McCready, J.F. Brennecke, Reaction kinetics of CO2 absorption in to phosphonium based anion-functionalized ionic liquids, Phys. Chem. Chem. Phys. 15 (2013) 7796. doi:10.1039/c3cp51289d.

[43] A. Ortiz, L. María Galán, D. Gorri, A.B. de Haan, I. Ortiz, Reactive Ionic Liquid Media for the Separation of Propylene/Propane Gaseous Mixtures, Ind. Eng. Chem. Res. 49 (2010) 7227–7233. doi:10.1021/ie100576r.

[44] O.C. David, G. Zarca, D. Gorri, A. Urtiaga, I. Ortiz, On the improved absorption of carbon monoxide in the ionic liquid 1-hexyl-3-methylimidazolium chlorocuprate, Sep. Purif. Technol. 97 (2012). doi:10.1016/j.seppur.2012.02.015.

[45] G. Zarca, I. Ortiz, A. Urtiaga, Kinetics of the carbon monoxide reactive uptake by an imidazolium chlorocuprate(I) ionic liquid, Chem. Eng. J. 252 (2014) 298–304. doi:10.1016/j.cej.2014.05.011.

[46] D.R. Smith, J.A. Quinn, The facilitated transport of carbon monoxide through cuprous chloride solution, AIChE J. 26 (1980) 112–120. doi:10.1002/aic.690260118.

[47] G. Zarca, M. Fernández, A. Santamaría, I. Ortiz, A. Urtiaga, Non-Newtonian shear-thinning viscosity of carbon monoxide-selective ionic liquid 1-hexyl-3-methylimidazolium chloride doped with CuCl, Sep. Purif. Technol. 155 (2014). doi:10.1016/j.seppur.2015.07.032.

[48] G. Zarca, I. Ortiz, A. Urtiaga, Recovery of carbon monoxide from flue gases by reactive absorption in ionic liquid imidazolium chlorocuprate(I): Mass transfer coefficients, Chinese J. Chem. Eng. 23 (2015). doi:10.1016/j.cjche.2014.06.040.

[49] G. Zarca, A. Urtiaga, I. Ortiz, P. Cañizares, M.A. Rodrigo, Carbon monoxide reactive separation with basic 1-hexyl-3-methylimidazolium chlorocuprate(I) ionic liquid: Electrochemical determination of mass transport properties, Sep. Purif. Technol. 141 (2015). doi:10.1016/j.seppur.2014.11.027.

[50] H.J. Liaw, C.C. Chen, Y.C. Chen, J.R. Chen, S.K. Huang, S.N. Liu, Relationship between flash point of ionic liquids and their thermal decomposition, Green Chem. 14 (2012) 2001–2008. doi:10.1039/c2gc35449g.

[51] M. Larriba, P. Navarro, J. García, F. Rodríguez, Selective extraction of toluene from n-heptane using [emim][SCN] and [bmim][SCN] ionic liquids as solvents, J. Chem. Thermodyn. 79 (2014) 266–271. doi:10.1016/j.jct.2013.11.005.

[52] M. Tariq, A.P. Serro, J.L. Mata, B. Saramago, J.M.S.S. Esperança, J.N.C. Lopes, L.P.N. Rebelo, High-temperature surface tension and density measurements of 1-alkyl-3-methylimidazolium bistriflamide ionic liquids, Fluid Phase Equilib. 294 (2010) 131–138. doi:10.1016/j.fluid.2010.02.020.

[53] M. Tariq, P.J. Carvalho, J.A.P. Coutinho, I.M. Marrucho, J.N.C. Lopes, L.P.N. Rebelo, Viscosity of (C2–C14) 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ionic liquids in an extended temperature range, Fluid Phase Equilib. 301 (2011) 22–32. doi:10.1016/j.fluid.2010.10.018.

[54]   H. Tokuda, K. Hayamizu, K. Ishii, M.A.B.H. Susan, M. Watanabe, Physicochemical
        Properties and Structures of Room Temperature Ionic Liquids. 2. Variation of Alkyl
        Chain Length in Imidazolium Cation, J. Phys. Chem. B. 109 (2005) 6103–6110.
        doi:10.1021/jp044626d.

[55]   M.G. Freire, A.R.R. Teles, M.A.A. Rocha, B. Schröder, C.M.S.S. Neves, P.J. Carvalho, D. V.
        Evtuguin, L.M.N.B.F. Santos, J.A.P. Coutinho, Thermophysical characterization of ionic
        liquids able to dissolve biomass, J. Chem. Eng. Data. 56 (2011) 4813–4822.
        doi:10.1021/je200790q.

[56]   J.M. Pringle, J. Golding, C.M. Forsyth, G.B. Deacon, M. Forsyth, D.R. Macfarlane,
        Physical trends and structural features in organic salts of the thiocyanate anion, J.
        Mater. Chem. 12 (2002) 3475–3480. doi:10.1039/B208372H.

[57]   M. Alvarez-Guerra, A. Irabien, Design of ionic liquids: an ecotoxicity (Vibrio fischeri)
        discrimination approach, Green Chem. 13 (2011) 1507. doi:10.1039/c0gc00921k.

[58]   G. Zarca, I. Ortiz, A. Urtiaga, F. Llovell, Accurate thermodynamic modeling of ionic
        liquids/metal salt mixtures: Application to carbon monoxide reactive absorption, AIChE
        J. In press (2017). doi:10.1002/aic.15790.

[59]   S.E. Repper, A. Haynes, E.J. Ditzel, G.J. Sunley, Infrared spectroscopic study of
        absorption and separation of CO using copper(I)-containing ionic liquids, Dalt. Trans. 46
        (2017) 2821–2828. doi:10.1039/C6DT04816A.

[60]   S. Seki, S. Tsuzuki, K. Hayamizu, Y. Umebayashi, N. Serizawa, K. Takei, H. Miyashiro,
        Comprehensive refractive index property for room-temperature ionic liquids, J. Chem.
        Eng. Data. 57 (2012) 2211–2216. doi:10.1021/je201289w.

[61]   L.E. Ficke, R.R. Novak, J.F. Brennecke, Thermodynamic and Thermophysical Properties
        of Ionic Liquid + Water Systems, J. Chem. Eng. Data. 55 (2010) 4946–4950.
        doi:10.1021/je100522z.

[62]   Q. Zhang, M. Li, X. Zhang, X. Wu, The Thermodynamic Estimation and Viscosity,
        Electrical Conductivity Characteristics of 1-Alkyl-3-Methylimidazolium Thiocyanate Ionic
        Liquids, Zeitschrift Für Phys. Chemie. 228 (2014) 851–867. doi:10.1515/zpch-2014-
        0536.

[63]   C.M.S.S. Neves, K.A. Kurnia, J.A.P. Coutinho, I.M. Marrucho, J.N.C. Lopes, M.G. Freire,
        L.P.N. Rebelo, Systematic study of the thermophysical properties of imidazolium-based
        ionic liquids with cyano-functionalized anions, J. Phys. Chem. B. 117 (2013) 10271–
        10283. doi:10.1021/jp405913b.

[64]   G. Yu, D. Zhao, L. Wen, S. Yang, X. Chen, Viscosity of ionic liquids: Database,
        observation, and quantitative structure-property relationship analysis, AIChE J. 58
        (2012) 2885–2899. doi:10.1002/aic.12786.

[65]   K. Machanová, Z. Wagner, A. Andresová, J. Rotrekl, A. Boisset, J. Jacquemin, M.
        Bendová, Thermal properties of alkyl-triethylammonium bis{(trifluoromethyl)sulfonyl}
        imide ionic liquids, J. Solution Chem. 44 (2015) 790–810. doi:10.1007/s10953-015-
        0323-3.

[66]   I. Kim, H.F. Svendsen, Heat of absorption of carbon dioxide (CO2) in monoethanolamine
        (MEA) and 2-(aminoethyl)ethanolamine (AEEA) solutions, Ind. Eng. Chem. Res. 46
        (2007) 5803–5809. doi:10.1021/ie0616489.

30

[67] C. Wang, X. Luo, H. Luo, D. Jiang, H. Li, S. Dai, Tuning the basicity of ionic liquids for equimolar CO2 capture, Angew. Chemie Int. Ed. 50 (2011) 4918–4922. doi:10.1002/anie.201008151.

[68] C. Huang, B. Chen, J. Zhang, Z. Liu, Y. Li, Desulfurization of Gasoline by Extraction with New Ionic Liquids, Energy & Fuels. 18 (2004) 1862–1864. doi:10.1021/ef049879k.

[69] L. Gómez-Coma, A. Garea, A. Irabien, Non-dispersive absorption of CO2 in [emim][EtSO4] and [emim][Ac]: Temperature influence, Sep. Purif. Technol. 132 (2014) 120–125. doi:10.1016/j.seppur.2014.05.012.

Highlights

- Low viscosity copper(I)-containing thiocyanate ILs for CO chemisorption.

- High CO sorption capacity and equilibrium selectivity towards light gases.

- Greener alternative than conventional toluene-based CO/N_2 separation.