ON THE IMPROVED ABSORPTION OF CARBON MONOXIDE IN THE IONIC LIQUID 1-HEXYL-3-METHYLIMIDAZOLIUM CHLOROCUPRATE

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Abstract

This study is focused on the design of a liquid phase system to be used in facilitated transport-supported ionic liquid membranes (SILMs) for the recovery of carbon monoxide from gaseous streams based on the ability of CO molecules to form π complexation bounds with Cu^+ ion. As liquid phase we propose the use of the ionic liquid 1-hexyl-3-methyl-imidazolium chlorocuprate prepared by the direct mixture of copper(I) chloride (CuCl) with 1-hexyl-3-methylimidazolium chloride ([hmim][Cl]).

A comprehensive look at the reaction mechanism and the equilibrium parameters obtained from the experimental characterization of the physical and chemical solubility of carbon monoxide in pure [hmim][Cl], and in mixtures CuCl/[hmim][Cl] is presented. The gas equilibrium solubility experimental work was carried out in the CuCl/[hmim][Cl] molar ratio range from 0 to 0.75, temperature from 273.15 K to 303.15 K and pressures up to 20 bar. The values of the Henry's law constant for the physical solubility of CO in [hmim][Cl] changed from 15.3 x 10^{-3} mol kg^{-1} bar^{-1} to 2.7 x 10^{-3} mol kg^{-1} bar^{-1} as the temperature increased from 273.15 to 293.15 K. The chemical solubility of CO in the reactive ionic liquid media increased with the increase of the concentration of CuCl, with the increase of pressure and as temperature decreases. In the operation range of variables the maximum absorption of CO was of 2.26 mol kg^{-1} that was reached working at 20 bar, at CuCl/[hmim][Cl] molar ratio of 0.75 and 273.15 K.

Keywords:

Carbon monoxide, reactive absorption, ionic liquid, complexation reaction, 1-hexyl-3-methylimidazolium chloride

1. Introduction

Carbon monoxide is a key raw material in the synthetic routes for a variety of major chemical products including methanol, formaldehyde, acetic acid, isocyanates, aldehydes, formic acid, pesticides, and herbicides. It has an increased importance as raw material for liquid hydrocarbon fuels in the Fischer-Tropsch process where CO molecules are coupled to C-C bond formation [1]. All sources of carbon monoxide are essentially gas mixtures, most common being the synthesis gas, coke-oven gas and blast furnace gases [2]. We propose the flue gases from carbon black manufacturing as a new source for carbon monoxide separation and recovery. The exhaust flue gases generated in the reactor are used for power generation when they are converted to carbon dioxide, water and heat. The final released gas is CO_2 and therefore carbon black industry still leaves an environmental footprint contributing to the global warming effect. The recovery of CO from the flue gases would represent an abundant and relatively inexpensive source of CO that would greatly enhance further growth of CO as a raw material for the chemical industry. Such growth could result in the CO-based chemical industries approaching the same level of importance as the ethylene-based chemical industries [3]. The recovery of CO from the flue gases would also contribute to the reduction in the process emissions approaching the zero discharge goal. In order to obtain pure CO, it has to be separated from these mixtures which may contain other components, e.g. H_2, N_2, CO_2, CH_4 and H_2O. The typical composition in major components of the flue gas stream from carbon black manufacturing is: 60% N_2, 20% CO, 15% H_2 and 5% CO_2 (vol. % on a dry basis).

Proven technologies for separation of CO rely mostly on absorption in ammoniacal cuprous chloride, aromatic $CuAlCl_4$ solution (COSORB), cryogenic fractionation and pressure swing adsorption (PSA) [4]. Generally, conventional absorption processes present the drawback of high energy consumption and operating cost and in particular for CO the main problem is the instability of Cu^+ ion which in a disproportionation reaction gives Cu^0 and Cu^{2+}. Cryogenic distillation apart from being an expensive separation method has the inconvenience that the separation of CO in the presence of N_2 is difficult owing to the similar boiling point. Membrane-based separation technology as applied for syngas ratio adjustment is based on the use of hydrogen permeable membranes using different types of materials: polymeric membranes [5, 6] nanoporous carbon membranes [7] and metallic membranes [8]. The facilitated transport of CO

through supported liquid membranes (SLM) would give a permeate product enriched in CO and in comparison with absorption processes the technology has an improved contact area and uses less solution to achieve the same separation efficiency. Furthermore the use of an ionic liquid as the inmobilized liquid phase can avoid the typical problems related to SLM processes [9, 10] and they can also be excellent solvents for the carrier agent. Therefore, we focus our study on a gas-liquid absorption process having as a goal the design of a carrier agent / solvent system with good characteristics to be used in facilitated transport – SILMs later on.

The proposed process for the separation and recovery of carbon monoxide is based on its ability along with that of olefins, aromatic and thiophenic compounds to form a π complexation bound with *d*- block transition metals and their ions [11]. The bound is constituted of two contributions: the usual σ bound formed by the overlapping of the bounding π electrons of the gas to the unoccupied outermost *s* orbital of the metal and the additional back-donation from the metal *d* orbital to the empty antibonding π orbital of the gas [12-15]. The π-complexation bonds are stronger than those formed by van der Waals interactions, but they are also weak enough to be broken by traditional engineering means such as increasing temperature and/or decreasing pressure [16]. For carbon monoxide complexation the use of Cu^{+}, Fe^{2+}, Pd^{0}, Zn^{2+} and Co^{2+} has been more prevalent in both gas-liquid and gas-solid processes (see table 1).

The key issue in developing a separation process based on reversible complexation is the ability of a carrier to bind selectively to the permeant with appropriate equilibrium and rate constants (K_{eq}). For a system to be efficient enough recommended values of the equilibrium parameters by Noble et al [1] are between 2 x 10^{2} M^{-1} and 2 x 10^{4} M^{-1} for facilitated transport of gases in liquid membranes at solubilities around 5 x 10^{-3} M and partial pressures from 1.01 x 10^{4} Pa to 1.01 x 10^{5} Pa. Table 1 shows the values of the equilibrium constants (K_{eq}) reported in the literature for CO complexation with transition metals and their ions. The magnitude of K_{eq} for copper (I) based systems is within the recommended range and therefore copper (I) can be considered as the optimum carrier in membrane facilitated transport.

The main problem in using a liquid absorbent is the low solubility of cuprous chloride in liquid media and the instability of Cu^{+} due to oxidation and disproportionation. In the industrial process of liquid absorption of CO, the COSORB process, a mixture of CuCl, $AlCl_3$ and toluene is used and therefore the availability of Cu^{+} is lowered. We propose an imidazolium-based ionic

liquid with the chloride anion, [Rmim][Cl], as solvent because it is able to solubilize high amounts of CuCl and at the same time the CuCl/[Rmim][Cl] mixture is stable to oxidation and disproportionation . The mixture of CuCl with [Rmim][Cl] leads to a so called Lewis acid-based ionic liquid [17] where the metal halide CuCl acts as Lewis acid. Depending on the relative proportions of CuCl and [Rmim][Cl] several anionic species are present at equilibrium [18-21] as reported in Table 2. The drawback of these types of ionic liquids is their water sensitivity; they absorb water from the atmosphere leading to their decomposition by hydrolysis [17]. Furthermore, Cu(I) can disproportionate to Cu(II) and Cu^0. To avoid these phenomena, the samples should be stored in vacuum sealed vials or be quickly used after preparation. However these absorption media are by far more stable than aqueous medium.

To conclude, this work studies the reactive absorption of CO in a copper (I) based ionic liquid formed by the mixture of [hmim][Cl] and CuCl salt. The equilibrium parameters, namely the equilibrium constant, K_{eq}, and the enthalpy of reaction, ΔH_r, were evaluated. In addition new data for the physical solubility of CO in [hmim][Cl] are also reported.

2. Equilibrium modeling

In order to describe the absorption process, an equilibrium model able to explain quantitatively the occurring reactions and phenomena is required. First we considered that all the copper (I) introduced in the reaction medium was active for the π-complexation reaction and that the strength of the π-bound formed between CO and the different copper based anionic species present at equilibrium (see table 2) was equal. Additionally, $CuCl_3^{2-}$ is the most abundant copper chloride species in the molar ratio of CuCl/[hmim][Cl] lower than 1 used in this work, according to [18-21]. The equilibrium reaction is shown in eq. 1 for the case of a 1:1 copper(I):carbon monoxide complex.

$$CO + CuCl_3^{2-} \rightleftharpoons Cu(CO)Cl_3^{2-} \quad (1)$$

The equilibrium constant is defined as follows,

$$K_{eq} = \frac{[Cu(CO)Cl_3^{2-}]}{[CO]\cdot[CuCl_3^{2-}]} \quad (2)$$

where $[Cu(CO)Cl_3^{2-}]$ is the equilibrium concentration of the complex, $[CO]$ is the equilibrium concentration of physically absorbed carbon monoxide and $[CuCl_3^{2-}]$ is the equilibrium concentration of copper (I) chloride anionic specie. The concentration of physically dissolved carbon monoxide is given by the Henry's law correlation,

$$[CO] = k_H\, p_{CO} \quad (3)$$

where k_H is the Henry's constant and p_{CO} is the partial pressure of carbon monoxide that is equal to the total pressure in the system when working with pure gases.

The following mass balance equations can be applied, where the equilibrium concentration of the total absorbed CO, $[CO]_T$, is obtained from the sum between the physically and chemically absorbed gas, eq. (4), and the concentration of copper (I) chloride anionic specie at equilibrium is given by the difference between the initial concentration, $[CuCl_3^{2-}]_0$, and the equilibrium concentration of the complex specie,

$$[CO]_T = k_H\, p_{CO} + [Cu(CO)Cl_3^{2-}] \quad (4)$$

$$[CuCl_3^{2-}] = [CuCl_3^{2-}]_0 - [Cu(CO)Cl_3^{2-}] \quad (5)$$

The equilibrium constant for the 1:1 reaction can be calculated by substitution of the mass balance (eqs. 4 and 5) into eq.(2), and subsequent rearrangement to a linear form, eq. (6),

$$[CO]_T = K_{eq} k_H\, p_{CO}(k_H\, p_{CO} + [CuCl_3^{2-}]_0 - [CO]_T) + k_H\, p_{CO} \quad (6)$$

The equilibrium constant of the complexation reaction is a function of temperature that can be described by means of the van`t Hoff equation (eq. 7):

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

where T is the temperature (K), ΔH_r is the enthalpy of reaction (kJ mol^{-1}) and R is the gas constant (kJ mol^{-1} K^{-1}).

3. Experimental

3.1. Preparation of the copper (I) based ionic liquid

The ionic liquid 1-hexyl-3-methyl-imidazolium chlorocuprate used in this study was prepared by mixing under vacuum for 1 h at 353.15 K specific amounts of 1-hexyl-3-methylimidazolium chloride ([hmim][Cl]) and CuCl in situ, prior to the absorption experiments. This procedure is similar to the one used by Huang et al. [20]. In that work they used heptane as a copartner of the mixture. Heptane had the purpose of acting as a "blanket" against hydrolysis [17] and thus avoiding working in a dry box. We assume that simply working under vacuum avoids hydrolysis. Our preparation procedure serves also to degas and remove trace amounts of volatile impurities and thus no further purification step is needed prior to the absorption experiments. Purified copper(I) chloride (>99%) was purchased from Sigma Aldrich and was immediately used without further purification. 1-hexyl-3-methyl-imidazolium chloride was purchased from Iolitec with a purity of 99%. The main impurities are water (0.795%) and 1-methylimizazole (<1%) as stated in the certificate of analysis.

3.2. Absorption set-up and measuring procedure

The experimental method is based on an isochoric saturation technique in which a known quantity of the gaseous solute is put in contact with a known quantity of degassed solvent at a constant temperature inside a known volume reactor. When thermodynamic equilibrium is attained, the pressure above the liquid solution remains constant and is directly related to the solubility of the gas in the liquid medium [22].

The apparatus and measurement procedure are basically identical to those described in a previous publication by our research group [23]. There are two minor differences: first the feed line was of pure carbon monoxide or nitrogen (Air Liquide, 99.97% purity) and it was connected

to the upper chamber of the set-up and second, we used a higher stirring speed, of 2500 rpm, due to the use of a significantly higher viscous ionic liquid (18.089 Pa.s for [hmim][Cl] compared with 0.1076 Pa.s for $BmimBF_4$ that was used in the previous study).

The absorption of CO in pure [hmim][Cl] and mixtures of [hmim][Cl] with CuCl was studied at temperatures from 273.15 K to 303.15 K, molar ratios CuCl/[hmim][Cl] from 0.13 to 0.75 and at pressures lower than 8 bar. After performing this first set of experiments the experimental set-up was adapted to stand higher pressures and some specific experiments were done at pressures up to 20 bar. This was done by changing the digital pressure gauge (Omega Engineering DPG1000B-30V100G with an accuracy of ±0.017 bar) with a new one (Keller 303010.0005, Leo 2/-1-30bar/81021, with an accuracy of 0.1% at full scale) capable to withstand higher pressures. All the other components of the set-up where left unchanged. When the reaction medium was to be reused in a new absorption experiment a desorption step was needed to get the regeneration of the mixture. The desorption was done by means of increasing the temperature up to 333.15 K and under high vacuum conditions. The complete regeneration of the reaction medium was checked by consecutive repetition of a similar absorption run. In order to assure the correct preparation of the ionic liquid we repeated absorption experiments with different solutions of the same concentration. The results were replicable and the weighted standard deviation is shown in the figures as error bars.

4. Results and discussion

4.1. Physical solubility

The physical solubility of CO in the reactive CuCl/[hmim][Cl] media cannot be measured directly. Therefore, it was estimated by analogy with the physical solubility of N_2 in the reactive CuCl/[hmim][Cl] medium. This estimation is based on a comparative study between the physical solubilities of N_2 and CO in the non-reactive [hmim][Cl] medium: N_2 has a molecular weight and size similar to CO. This approach has already been used in the literature by Hogendoorn et al. [24] to estimate the physical solubility of CO in reactive mixtures. A similar analogy is commonly used between N_2O and CO_2 [25-28]. The solubility of both CO and N_2 was measured in pure [hmim][Cl], and the solubility of N_2 was measured in CuCl/[hmim][Cl] reactive medium

(molar ratio of 0.5) at temperatures of 273.15, 283.15 and 293.15 K in the pressure range up to 20 bar. Due to the very low gas solubility we were unable to measure the physical solubility of CO and N_2 at temperatures from 303.15 K onwards. The resulting values of the Henry's constants (k_H) were obtained by fitting the experimental data to a straight line according to Eq. 3 (including 0,0 point) using a least squares regression method (see Table 3). The solubility of both gases increased linearly with the system pressure and decreased with the system temperature. In pure [hmim][Cl] the solubility parameters of CO and N_2 present similar values at the three temperatures under study, the slight differences are within the experimental error range. The resulting values of the k_H for CO physical absorption in [hmim][Cl] are between 15.3 and 2.7 x 10^{-3} mol kg^{-1} bar^{-1} and seem coherent with literature data listed in table 4 for other imidazolium based ionic liquids. Studies of the solubility of CO in [bmim][PF_6] by different research groups and different experimental techniques report data with a deviation higher that 100%. CO is a gas with a considerably lower solubility than CO_2 [29] and has been reported as undetectable by other authors when a gravimetric microbalance was used [30]. The resulting ideal separation factor obtained in the present work for carbon monoxide to nitrogen around 1 is within the range from 0.5 to 2.9 reported by J. Blath et al. in other ionic liquids [31].

When measuring the physical solubility of N_2 in the reactive medium formed by a mixture of CuCl/[hmim][Cl] of 0.5 molar ratio at 273.15 K, the data revealed that N_2 absorption is lower than in pure [hmim][Cl], $k_{H,N_2/(CuCl/[hmim][Cl])=0.5}$ = 8.9 x 10^{-3} mol kg^{-1} bar^{-1} in comparison with $k_{H,N_2/[hmim][Cl]}$=13.8 x 10^{-3} mol kg^{-1} bar^{-1}. Thus we can predict that the physical solubility of CO in the reactive medium is similar to the solubility of N_2.

The temperature dependence of the Henry's law constant was studied using a van't Hoff type equation.

$$k_H(T) = k_{H_0} e^{-\frac{\Delta H_{sol}}{RT}} \qquad (8)$$

Figure 1 shows the values of the Henry's constant for CO and N_2 absorption in pure [hmim][Cl] and for N_2 in the mixture CuCl/[hmim][Cl] = 0.5 molar ratio plotted against temperature. The k_H experimental values in pure [hmim][Cl] are overlapped for CO and N_2. As means of validation of our experimental data, apart from the experimental results, we also

included the simulated value of the Henry's constant at 295.15 K for CO in [hmim][Cl]. This was based on the use of a simple correlation between the Henry's constant and the molar volume of an ionic liquid developed by Camper et al [32]. In the case of CO the simulation fits satisfactorily well to the experimental data. The standard solvation enthalpy for gas-to-liquid transfer (ΔH_{sol}) obtained from the fitting of the experimental data to eq. (8) is of -57.3 kJ mol^{-1} for CO and of -56.6 kJ mol^{-1} for N_2. In all the reported cases in the literature (see table 4) the solubility of CO in ionic liquids has a very low variation with temperature. It usually decreases as temperature increases and the resulting values of the solvation enthalpy are negative and close to zero. The solvation enthalpy is related to the molecular interactions in the solution and can give clues regarding to the molecular mechanism of solvation. Probably the higher magnitudes of solvation enthalpies found in our study can be related to a different molecular mechanism of solvation. It was reported that the solubility of CO is dependant on the nature of the ionic liquid [33]. The forces and interactions that govern the dissolution and solubility of different components in ionic liquids also control the melting points of ionic liquids. In general, increases in anion size give rise to reductions in the melting points of salts through reduction of the Coulombic attraction contribution to the lattice energy of the crystal and increasing covalency of the ions. In addition, large ions permit charge delocalization, reducing the overall charge density further on [17]. For example, with increasing radius of the anion, from Cl^- to $[PF_6]^-$ to $[Tf_2N]^-$, the melting points of the 1-ethyl-3-methylimidazolium-based ionic liquids decrease from 334.1 K to 307.1 K to 240.1 K [34]. In addition, [hmim][Cl] is significantly more viscous than second generation ionic liquids that incorporate large anionic groups. Thus, the solubility of solutes in [hmim][Cl] can be slightly different as well.

4.2. Total solubility

The influence of CuCl concentration and temperature over the total solubility (chemical and physical) of CO in the reactive medium formed by the mixture of CuCl and [hmim][Cl] was studied at pressures of up to 8 bar. Then, the saturation of reaction media was verified at pressures up to 20 bar.

Figure 2 shows the total (chemical and physical) solubility of CO in the reactive medium at molar ratios between CuCl/[hmim][Cl] from 0.13 to 0.75 and constant temperature of 303.15 K. It is observed that at higher concentrations of CuCl, the solubility of CO increases significantly. For operation pressures lower than 8 bar, the physical solubility is negligible in comparison with the total solubility and therefore the total solubility represents actually the chemical one. The maximum solubility obtained was of 533.8 x 10^{-3} mol kg^{-1} at a molar ratio CuCl/[hmim][Cl] of 0.75, 7.72 bar CO pressure and 303.15 K. The solid lines represent the simulated data provided by the equilibrium model together with the fitting parameters that where obtained as it will be described later on. The total solubility of CO in the chlorocuprate based ionic liquid media is expected to increase as the concentration of CuCl in [hmim][Cl] increases. At the same time, the viscosity of the mixture is function of the CuCl content. In literature it was demonstrated that the viscosity of CuCl/[emim][Cl] based ionic liquid mixtures presents a minimum at a molar ratio of 1 from which it begins to increase [18]. Therefore we did not further increased the concentration of CuCl and for molar ratios CuCl/[hmim][Cl] from 0.13 to 0.75, CuCl was soluble in [hmim][Cl]. After the absorption experiments no precipitates or cloudiness was observed, and the mixtures stored in sealed vials were stable in time long after the experiments were carried out.

In figure 3 the influence of temperature on the total solubility of CO is shown at a constant molar ratio between CuCl/[hmim][Cl] of 0.5. It is observed that the temperature presents a strong influence over the solubility of CO which is considerably higher at lower temperatures; therefore it is concluded that the complexation reaction is exothermic. Here also, the total solubility is practically equal to the chemical solubility. For instance at 293.15 K the total carbon monoxide solubility in the copper (I) based ionic liquid is 32 times the physical solubility when compared with the values obtained at a pressure of 7.4 bar. It can be also observed that even for the highest solubility of CO of 1032 x 10^{-3} mol kg^{-1}, the molar ratio between the total absorbed carbon monoxide (i.e. at the final experimental system pressure) and the initial concentration of copper (I) chloride (n_{CO}/n_{CuCl}) has the value of 0.52, as shown in table 5, far lower than unity. This indicates that if all the copper (I) added to the solution was active for complexation and a 1:1 stoichiometry is considered, the saturation of the reaction medium was not reached, and therefore there are still copper (I) species which have not reacted.

In the experimental range of variables used in this work, the ideal separation factor (α) between CO and N_2 obtained from the ratio of the pure gases solubilities in the reactive medium reached high values that were between 24 and 6. In the calculation of the values of the ideal separation factor $\alpha_{CO/N2}$ we used the solubility of N_2 obtained in the reactive medium at CuCl/[hmim][Cl] molar ratio of 0.5 (data listed in table 3) and the chemical solubility data for CO obtained from the mixtures CuCl/[hmim][Cl] with a molar ratio from 0.13 to 0.75, temperatures from 273.15 to 303.15 K and pressures below 8 bar. The values for CO/N_2 ideal separation factor present the same trend as the chemical solubility for CO: both parameters increase as the pressure decreases, the concentration of CuCl increases and the temperature decreases. The maximum value of 24 was obtained at 2.5 bar equilibrium pressure, 273.15 K and 0.5 molar ratio CuCl/[hmim][Cl].

In table 5 it is shown that for pressures below 8 bar and at constant temperature of 303.15 K, the ratio between the total number of moles of absorbed CO and the initial number of moles of CuCl, n_{CO}/n_{CuCl}, presents almost no variation with the concentrations of CuCl in [hmim][Cl] leading to an average value of 0.167. When temperature decreases the ratio n_{CO}/n_{CuCl} increases up to a value of 0.52 that is reached at 273.15 K. In comparison with a study of Huang et al [20] these values are significantly higher in all cases. These authors studied the absorption of thiophene in [bmim][Cl]/CuCl ionic liquids and based on their reported experimental conditions and results we have been able to calculate a value of 7.49×10^{-3} for $n_{thiophene}/n_{CuCl}$ molar ratio. In an attempt to verify the saturation of the reaction medium an additional experiment was performed at pressure up to 20 bar, at the lowest temperature studied of 273.15 K and for a molar ratio CuCl/[hmim][Cl] of 0.75. As shown in figure 4 at higher pressures the physical solubility begins to present values that cannot be ignored and therefore the chemical solubility was calculated as the difference between the total solubility and the physical one. The physical solubility of CO in the reaction medium was considered to be analogous to the solubility of N_2 in the chlorocuprate ionic liquid. It can be observed that the major part of the chemical complexation reaction took part at pressures below 10 bar. Beyond this point, the final slope of the equilibrium curve remains constant but still higher than the slope of the physical solubility, therefore the chemical complexation is still active. The final ratio between the absorbed number

of moles of carbon monoxide and the initial number of moles of copper (I) was of 0.9, a value close to 1 that corresponds to the maximum saturation described by a 1:1 stoichiometric ratio.

The viscosity of various samples of pure [hmim][Cl] and its mixtures with CuCl was measured at different temperatures. From figure 5 it is observed that the viscosity strongly decreases as the amount of added salt increases. At the highest molar ratio CuCl/[hmim][Cl] the viscosity decreased by two orders of magnitude. While the pure ionic liquid is transparent and highly viscous at room temperature the copper (I)-based ionic liquid has a brown yellow colour. The room temperature ionic liquids based on the mixtures of various metal chloride and alkyl-imidazolium chloride are eutectic mixtures [17] and have in general lower melting points, lower viscosity, higher density and higher specific conductivity than the pure alkyl-imidazolium chloride. These differences have been attributed in the literature to charge delocalization of [hmim] and $CuCl_x^{-x+1}$ (x = 2, 3) [19]. These differences in viscosity imply improved mass transfer coefficients for copper (I)-based ionic liquid medium in comparison with the ionic liquid alone which are important aspects involved in the design of absorption equipment.

The equilibrium constant defined in eq. (2) was calculated from the slope of the linear regression line obtained from the fitting of the experimental data to eq. (6). In all cases, the physical solubility of CO was considered to be analogous to the solubility of N_2 in the reactive medium. As shown in table 5 the equilibrium constant of the complexation reaction is dependant on temperature, increases as the temperature decreases, and has values comprised between 16.0 kg mol^{-1} and 8.49 kg mol^{-1} in the temperature range from 273.15 K to 303.15 K. Applying the van't Hoff relation expressed in eq. (7) with 298.15 K as reference temperature the resulting enthalpy of complexation has a negative value of ΔH_r = -13.4 kJ mol^{-1}. This indicates that the complex formation between CO and copper (I) chloride anionic species present in the ionic liquid 1-hexyl-3-methylimidazolium-chlorocuprate in a basic environment is an exothermic process.

The goodness of the data fitting is presented in the parity graph shown in figure 6. Predicted concentration values, $[CO]_{sim}$, are plotted versus experimental data, $[CO]_{exp}$, for results obtained at pressures lower than 8 bar and from 273.15 K to 303.15 K. All the results of $[CO]_{sim}$

fall within the interval Cexp ±10% Cexp, proving that the proposed model offers a satisfactory description of the reactive absorption equilibrium.

In this study we report the thermodynamic equilibrium for the solubility of CO in the reactive system which is enhanced at lower temperatures, as the absorption process is exothermic. In a further step the kinetics of the system will be studied, thus allowing us to determine the optimal conditions to develop the process, which should be a trade-off between this two effects.

5. Conclusions

In this work, the absorption of carbon monoxide via copper (I) complexation has been successfully carried out in the ionic liquid 1-hexyl-3-methyl-imidazolium chlorocuprate prepared by the direct mixture of copper(I) chloride (CuCl) with 1-hexyl-3-methylimidazolium chloride ([hmim][Cl]).

First, it was observed that the solubilities of both carbon monoxide and nitrogen in the pure [hmim][Cl] were very similar, with values of Henry's constants in the range 15.3 x 10^{-3} mol kg^{-1} bar^{-1} to 2.7 x 10^{-3} mol kg^{-1} bar^{-1} as the temperature increased from 273.15 to 293.15 K. After addition of CuCl to [hmim][Cl], the carbon monoxide absorption capacity of the ionic liquid was improved by a large factor, while nitrogen solubility was maintained in the low values previously observed for the pure [hmim][Cl]. Thus it was concluded that the CuCl/[hmim][Cl] mixture enhances the carbon monoxide absorption via the chemical πcomplexation of CO with copper (I) species formed in the reactive ionic liquid. This conclusion is also supported by the increasing capacity for CO absorption at higher contents of CuCl in the reactive ionic liquid media. The equilibrium solubility study showed that the reaction takes place in the whole pressure range studied; the major part of the complexation reaction took place at pressures up to 10 bar and was almost complete at pressures of 20 bar showing the importance of this operation variable. The solubility of carbon monoxide in the absorbing liquid decreased at higher temperatures due to the fact that the π-complexation reaction is exothermic. The calculated enthalpy of complexation presents a negative value of -13.4 kJ mol^{-1}. The highest value of the ideal separation factor for carbon monoxide to nitrogen was 24, in the experimental range studied.

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Figure 1. CO and N_2 Henry's constant as function of temperature in [hmim][Cl] ionic liquid and in chlorocuprate based ionic liquid at a molar ratio CuCl/[hmimCl][Cl] of 0.5.

Figure 2. Carbon monoxide solubility in copper(I)-based ionic liquid at various molar ratios CuCl/[hmim][Cl] and constant temperature of 303.15 K. Experimental data and simulated results (lines).

Figure 3. Carbon monoxide solubility in copper(I) based ionic liquid at constant molar ratio CuCl/[hmim][Cl] = 0.5 and various temperatures. Experimental data and simulated results (lines).

Figure 4. Saturation of the copper (I) based reaction media at pressure up to 20 bar and 273.15 K.

Figure 5. Viscosity of pure [hmim][Cl] and its mixtures with CuCl at various molar ratios.

Figure 6. Parity graph between experimental and simulated results of CO adsorption. Data obtained at various temperatures and CuCl/[hmim][Cl] molar ratios are included.

Figure 1

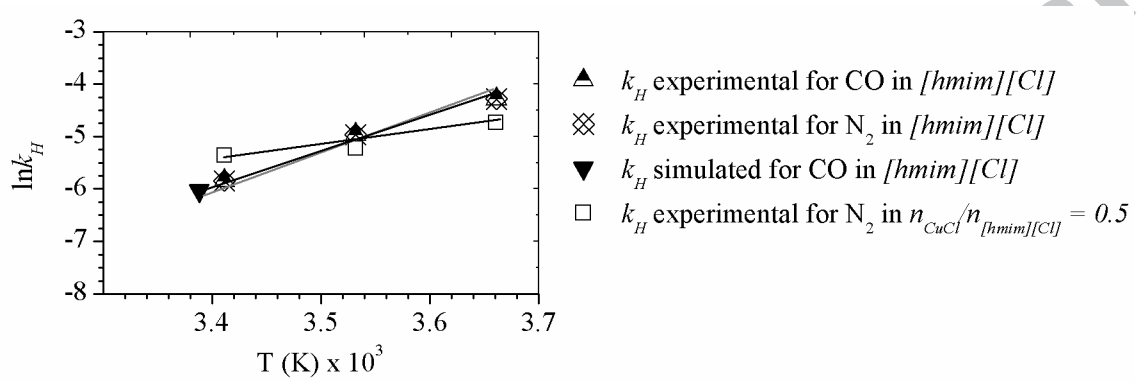

Figure 2

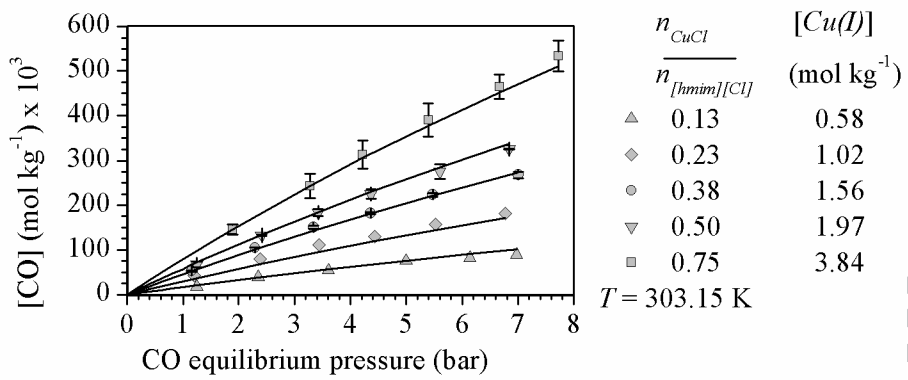

Figure 3

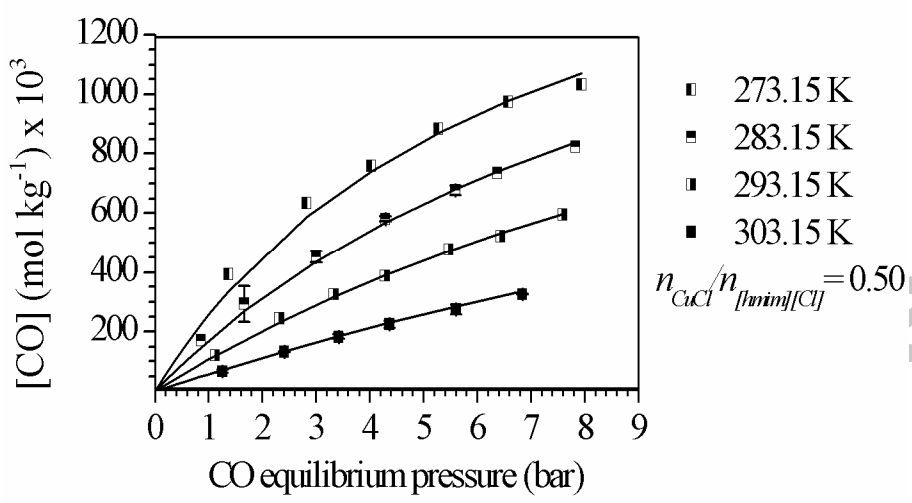

Figure 4

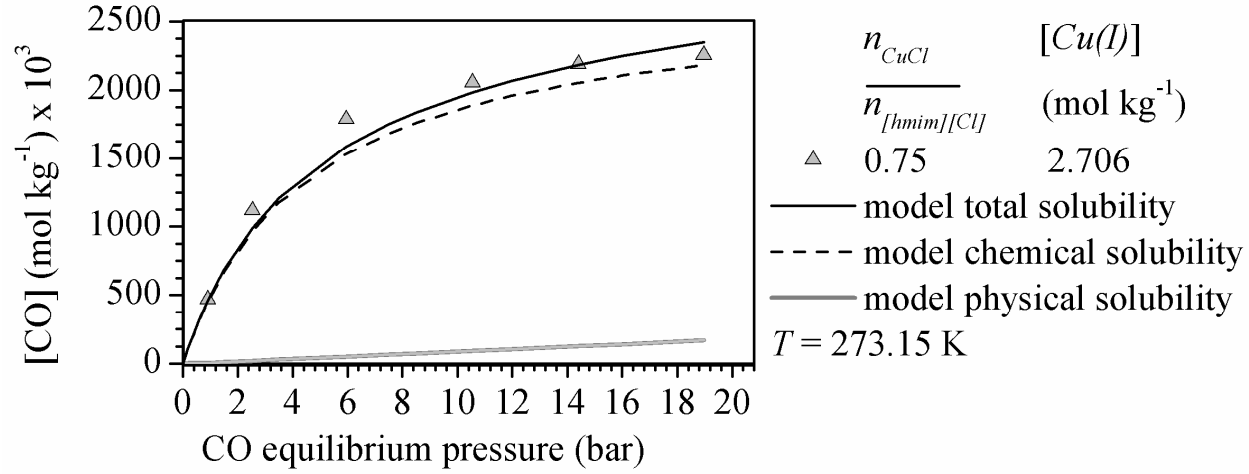

Figure 5

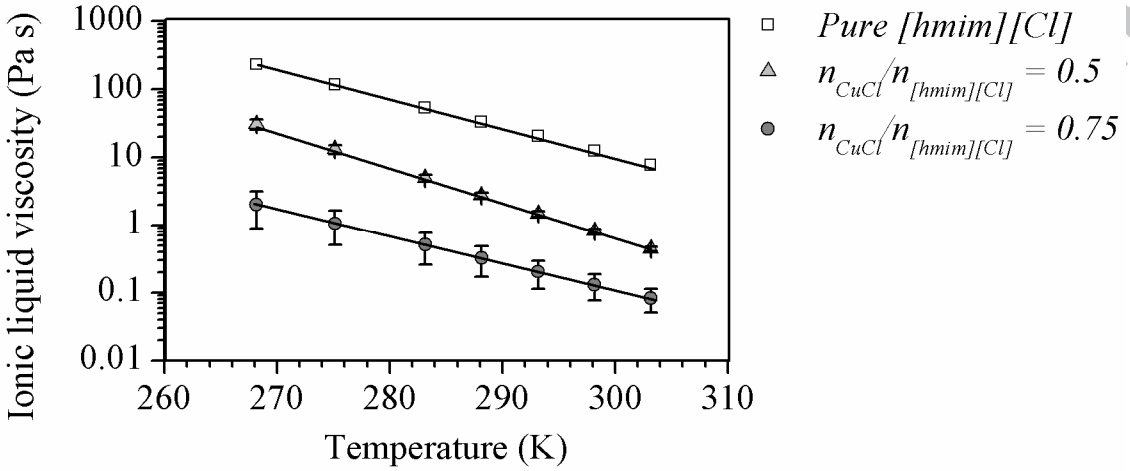

Figure 6

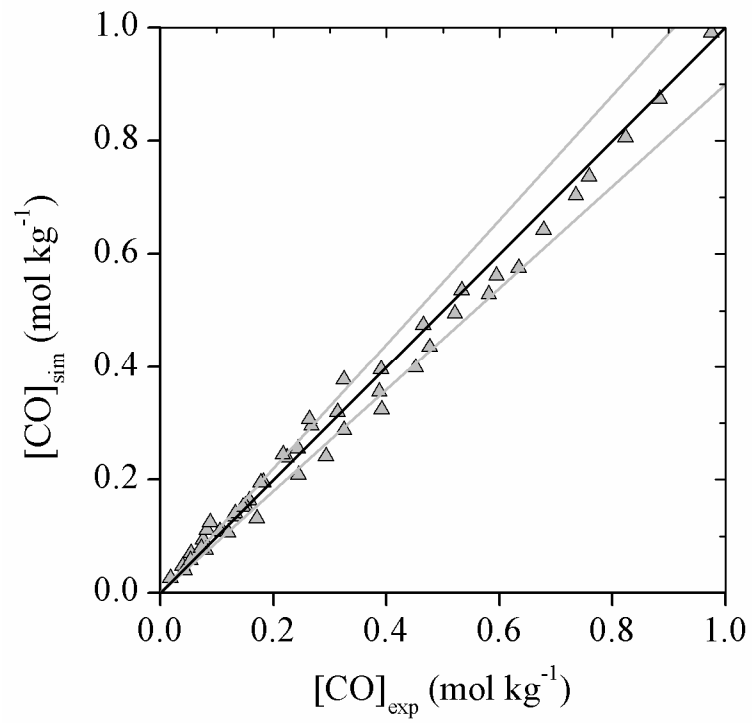

Table 1. Equilibrium constants (K_{eq}) for CO complexation with transition metal derivatives

Element	Coordination complex	Experimental conditions	K_{eq} (kg mol^{-1})	Ref
Cu^{+}	$CuCl_3^{2-}$	0.2 M CuCl, 1.0 M KCl, 0.1 M HCl in water	1000	[2, 35]
		0.1 M CuCl, 1.0 M KCl, 0.2 M HCl in water		[36]
	$CuAlCl_4tol_2$	p_{CO} max = 1 bar, 0.15 - 1.7 M in toluene	447[e]	[24]
	$CuI/NMIm$[a]	2 x10^{-5}M in Dimethyl sulfoxide	1700	[37]
	$CuSCN/NMIm$		570	
	$L^bCuB(C_6F_5)_4$	Tetrahydrofuran solvent	660-56000	[38]
Fe^{2+}	$Fe(TIM^c)(C_6H_5CN)_2Cl_2$	0.015 M in Benzonitrile	420[e]	[1]
	$Fe(Me_4TIM)(C_6H_5CN)_2Cl_2$	0.046 M in Benzonitrile	180[e]	
	$Fe(Me_2Ph_2TIM)(C_6H_5CN)_2Cl_2$	0.050 M in Benzonitrile	130[e]	
	$Fe(Ph_4TIM)(C_6H_5CN)_2Cl_2$	0-0.064 M in Nitrobenzene	190.1[e]	[39]
Pd^0	$Pd_2(dpm^d)_2NCO_2$	Dimethylacetamide	370000	[40]
	$Pd_2(dpm)_2Cl_2$		240000	
	$Pd_2(dpm)_2Br_2$		35000	
	$Pd_2(dpm)_2I_2$		1300	

[a] N-methylimidazole ligand, [b] Ligand-Cu(I) complexes based on pyridylalkylamine compounds, [c] Tetraimine macrocyclic ligand (2,3,9,10-tetrametbyl-l,3,8,11-tetraazacyclotetradeca-1,3,8,10 tetraene), [d] $Ph_2PCH_2PPh_2$ ligand, [e]: the presented values belong to the reduced equilibrium constant (M^{-1}) defined as the ratio between the equilibrium constant (-) and the constant concentration (M) of touene, benzonitrile and nitrobenzene respectively.

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Table 2. Anionic species presented in equilibrium at various molar rations of CuCl and [Rmim][Cl] [18-21]

Molar ratio CuCl/[Rmim][Cl]	Environment	Reactions	Predominant anionic specie
[0/1→1/1]	Basic (chlorine rich)	$CuCl^- + Cl^- \rightleftarrows CuCl_2^-$	$CuCl_3^{2-}$
		$CuCl_2^- + nCl^- \rightleftarrows CuCl_{2+n}^{(1+n)-}$	
		(n = 1, 2)	
1/1	Neutral	$CuCl^- + Cl^- \rightleftarrows CuCl_2^-$	$CuCl_2^-$
		$2\,CuCl_2^- \rightleftarrows Cu_2Cl_3^- + Cl^-$	
[1/1→2/1]	Acidic (chlorine poor)	$CuCl_2^- + y\,CuCl^- \rightleftarrows Cu_{1+y}Cl_{2+y}^-$	$Cu_2Cl_3^-$
		(y = 1, etc.)	$Cu_3Cl_4^-$

Table 3. CO and N_2 solubility results in ionic liquid media

Gas	Ionic liquid media	T (K)	k_H x 10^3 (mol kg^{-1} bar^{-1})	ΔH_{sol} (kJ mol^{-1})	R^2
CO	*[hmim][Cl]*	273.15	15.3	-57.3	0.992
		283.15	6.8		0.996
		293.15	2.7		0.996
N_2	*[hmim][Cl]*	273.15	13.8	-56.6	0.990
		283.15	7.0		0.963
		293.15	2.9		0.849
N_2	$n_{CuCl}/n_{[hmim][Cl]} = 0.5$	273.15	8.9	- 21.4	0.979
		283.15	5.4		0.986
		293.15	4.7		0.946

Table 4. Literature data for the solubility of CO in ionic liquids

RTIL (abbreviation)										Experimental technique	Ref.
[bmim][PF_6]	T	293.2	313.8	334.5	354.35	374.15				Bubble point	[4]
	$k_H x10^3$	1.81	1.79	1.82	1.79	1.79					
	T	283.16	293.2	303.38	303.41	313.33	323.25	333.57		Isochoric saturation	[41]
	$k_H x10^3$	0.40	0.39	0.39	0.39	0.38	0.37	0.36			
	T	295								NMR spectroscopy	[33]
	$k_H x10^3$	1.1									
[bmim][CH_3SO_4]	T	293.15		333.15		373.15	413.15			Bubble point	[42]
	$k_H x10^3$	1.07		1.13		1.19	1.27				
[bmim][Tf_2N]	T	303.2	313.11		323	333				Isochoric saturation	[43]
	$k_H x10^3$	5.27	5.23		4.71	4.22					
[bmim][BF_4]	T	283.18	293.16	303.39	313.27	313.28	323.2	333.09	343.04	Isochoric saturation	[22]
	$k_H x10^3$	3.11	3.10	3.07	3.07	3.10	3.03	3.04	3.01		
[hmim][Tf_2N]	T			333						Isochoric saturation	[31]
	$k_H x10^3$			4.44							
	T	293.3		333.2		373.25	413.15			Bubble point	[44]
	$k_H x10^3$	3.13		2.98		2.88	2.91				
[hmim][Cl]	T	273.15	283.15	293.15						Isochoric saturation	This work
	$k_H x10^3$	15.3	6.8	2.7							

Note: T expressed in Kelvin, k_H expressed in mol kg^{-1} bar^{-1}

Table 5. The CO saturation study of the complexating agent

Temperature (K)	$n_{CuCl}/n_{[hmim][Cl]}$	*Final pressure (bar)*	n_{CO}/n_{CuCl}	K_{eq} *(mol* Kg^{-1}*)*
273.15	0.50	7.94	0.523	16.00
281.15	0.50	7.83	0.417	13.43
293.15	0.50	7.59	0.303	12.05
	0.75	7.72	0.145	
	0.50	6.85	0.167	
303.15	0.38	7.01	0.169	8.49
	0.23	6.77	0.175	
	0.13	6.98	0.151	

Highlights

>Carbon monoxide recovery from the tail gas stream obtained in the production of carbon black. > Carbon monoxide absorbtion via copper (I) complexation in 1-hexyl-3-methyl-imidazolium chlorocuprate. > Enhanced the carbon monoxide absorption > High CO/N_2 ideal separation factor.