



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 ($[\text{hmim}][\text{Cl}]$).

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 $[\text{hmim}][\text{Cl}]$, and in mixtures $\text{CuCl}/[\text{hmim}][\text{Cl}]$ is presented. The gas equilibrium solubility experimental work was carried out in the $\text{CuCl}/[\text{hmim}][\text{Cl}]$ molar ratio range from 0 to 0.75, temperature from 273.15 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 $[\text{hmim}][\text{Cl}]$ changed from 15.3×10^{-3} to $2.7 \times 10^{-3} \text{ mol kg}^{-1} \text{ bar}^{-1}$ 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 $\text{CuCl}/[\text{hmim}][\text{Cl}]$ molar ratio of 0.75 and 273.15 K.

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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

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separation efficiency. Furthermore the use of an ionic liquid as the immobilized 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 $2 \times 10^2 \text{ M}^{-1}$ and $2 \times 10^4 \text{ M}^{-1}$ for facilitated transport of gases in liquid membranes at solubilities around $5 \times 10^{-3} \text{ M}$ and partial pressures from $1.01 \times 10^4 \text{ Pa}$ to $1.01 \times 10^5 \text{ Pa}$. 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, $[\text{Rmim}][\text{Cl}]$, as solvent because it is able to solubilize high amounts of CuCl and at the same time the $\text{CuCl}/[\text{Rmim}][\text{Cl}]$ mixture is stable to oxidation and disproportionation. The mixture

of CuCl with $[\text{Rmim}][\text{Cl}]$ 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 $[\text{Rmim}][\text{Cl}]$ 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 $[\text{hmim}][\text{Cl}]$ 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 $[\text{hmim}][\text{Cl}]$ 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 $\text{CuCl}/[\text{hmim}][\text{Cl}]$ 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.



The equilibrium constant is defined as follows,

$$K_{eq} = \frac{[\text{Cu}(\text{CO})\text{Cl}_3^{2-}]}{[\text{CO}] \cdot [\text{CuCl}_3^{2-}]} \quad (2)$$

where $[\text{Cu}(\text{CO})\text{Cl}_3^{2-}]$ is the equilibrium concentration of the complex, $[\text{CO}]$ is the equilibrium concentration of physically absorbed carbon monoxide and $[\text{CuCl}_3^{2-}]$ 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,

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]
	$\text{CuAlCl}_4\text{tol}_2$	0.1 M CuCl , 1.0 M KCl , 0.2 M HCl in water		[36]
	$\text{CuI}/\text{NMI}^{\text{a}}$	p_{CO} max = 1 bar, 0.15–1.7 M in toluene	447 ^e	[24]
	$\text{CuSCN}/\text{NMI}^{\text{a}}$	$2 \times 10^{-5} \text{ M}$ in Dimethyl sulfoxide	1700	[37]
	$\text{L}^{\text{b}}\text{CuB}(\text{C}_6\text{F}_5)_4$	Tetrahydrofuran solvent	570	
Fe^{2+}	$\text{Fe}(\text{TIM}^{\text{c}})(\text{C}_6\text{H}_5\text{CN})_2\text{Cl}_2$	0.015 M in Benzonitrile	420 ^e	[1]
	$\text{Fe}(\text{Me}_4\text{TIM})(\text{C}_6\text{H}_5\text{CN})_2\text{Cl}_2$	0.046 M in Benzonitrile	180 ^e	
	$\text{Fe}(\text{Me}_2\text{Ph}_2\text{TIM})(\text{C}_6\text{H}_5\text{CN})_2\text{Cl}_2$	0.050 M in Benzonitrile	130 ^e	
	$\text{Fe}(\text{Ph}_4\text{TIM})(\text{C}_6\text{H}_5\text{CN})_2\text{Cl}_2$	0–0.064 M in Nitrobenzene	190.1 ^e	[39]
Pd^0	$\text{Pd}_2(\text{dpm}^{\text{d}})_2\text{NCO}_2$	Dimethylacetamide	370,000	[40]
	$\text{Pd}_2(\text{dpm})_2\text{Cl}_2$		240,000	
	$\text{Pd}_2(\text{dpm})_2\text{Br}_2$		35,000	
	$\text{Pd}_2(\text{dpm})_2\text{I}_2$		1300	

^a *N*-methylimidazole ligand.

^b Ligand– Cu(I) complexes based on pyridylalkylamine compounds.

^c Tetraimine macrocyclic ligand (2,3,9,10-tetramethyl-1,3,8,11-tetraazacyclotetradeca-1,3,8,10 tetraene).

^d $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ 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 toluene, benzonitrile and nitrobenzene, respectively.

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