



# Kinetics of the carbon monoxide reactive uptake by an imidazolium chlorocuprate(I) ionic liquid



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## HIGHLIGHTS

- The kinetics of CO reaction with a chlorocuprate(I)-based ionic liquid are reported.
- Enhancement factors varied with temperature and Cu(I) concentration between 2 and 7.
- Kinetic reaction is first order in CO and first order in Cu(I).
- Second order kinetic constant of reaction and the activation energy are determined.

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## ABSTRACT

In this work, the kinetics of a new process for the selective recovery of CO from industrial flue gases based on the reactive absorption of carbon monoxide in a chlorocuprate(I) ionic liquid have been assessed; the experimental analysis has been performed in a stirred tank reactor at temperatures ranging from 293 to 313 K and copper(I) concentrations from 0 to 2 kmol m<sup>-3</sup>. To the best of our knowledge, this is the first study on the kinetics of CO reactive uptake in ionic liquid media, since only kinetic data of CO reactive absorption in COSORB solutions have been previously reported. The enhancement factors obtained from the experimental CO absorption fluxes varied from 2.1 to 6.8; however, the infinite enhancement factors were not achieved at any operating condition so the instantaneous kinetic regime was not met. Therefore, the kinetic results, apparently obtained in the fast reaction regime, were interpreted both from a point of view of pseudo-first order reaction and using the DeCoursey approximation based on the Danckwerts surface-renewal model with an enhancement factor corrected for reversible reactions of finite rate. The overall pseudo-first order kinetic constants obtained with both approaches are very similar, indicating that the reaction very likely took place in the pseudo-first order reaction regime. Besides, the reaction rate could be interpreted in terms of first order in both reactants, thus the second-order forward rate constant at 303 K and the activation energy found for this reaction are  $2.5 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and 23.7 kJ mol<sup>-1</sup>, respectively.

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## 1. Introduction

The development of an efficient and economically viable technology for the separation and purification of carbon monoxide is a matter of utmost interest for the C<sub>1</sub> chemistry processes employing CO as starting material [1]. Besides, it could also attract attention of some industrial processes that release huge amounts of CO in their flue gases, such may be the cases of the ceramic industry, where CO has to be removed from argon [2,3] and carbon black manufacturing, where the alluring separation is the removal of CO and hydrogen from nitrogen [4]. The recovery and later use of

the CO present in these exhausted streams would also be in line with one of the greatest challenges for the 21st century, i.e. the mitigation of greenhouse gas emission, given that this CO is generally converted to carbon dioxide prior to emission.

For the purpose of CO recovery, the initial composition of the gas stream plays an important role in the efficiency of the separation. Thus, if the N<sub>2</sub> content is high, cryogenic distillation becomes inefficient due to the similar boiling point of both compounds. Moreover, if CO<sub>2</sub> is present in the feed stream, it has to be completely removed in order to avoid solid freeze up in the extremely cold environment. In these conditions, the use of reactive gas absorption systems is preferred. The CO absorption process currently available at commercial scale is based on the complexation/decomplexation reaction between carbon monoxide and

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**Nomenclature**

$a$	specific surface area ( $\text{m}^2 \text{m}^{-3}$ )	$Re = \rho \cdot N \cdot d^2 / \mu$ , Reynolds number (–)
$C$	concentration ( $\text{mol m}^{-3}$ )	$Sc = \mu / (\rho \cdot D)$ , Schmidt number (–)
$d$	stirrer diameter (m)	$Sh = k_L a \cdot d^2 / D$ , Sherwood number (–)
$D$	diffusion coefficient ( $\text{m}^2 \text{s}^{-1}$ )	$t$
$E$	enhancement factor (–)	$T$
$E_\infty$	infinite (asymptotic) enhancement factor (–)	$V$
$H$	Henry coefficient ( $\text{mol m}^{-3} \text{bar}^{-1}$ )	
$Ha$	Hatta number (–)	
$J$	molar flux ( $\text{mol m}^{-2} \text{s}^{-1}$ )	<i>Greek letter</i>
$K$	equilibrium constant ( $\text{m}^3 \text{mol}^{-1}$ )	$\mu$
$k_2$	second order forward rate constant ( $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$ )	$\rho$
$k_{-1}$	backward rate constant ( $\text{s}^{-1}$ )	
$k_{ov}$	pseudo-first order kinetic constant ( $\text{s}^{-1}$ )	<i>Superscript/subscript</i>
$k_L$	liquid phase mass transfer coefficient ( $\text{m s}^{-1}$ )	CO
$k_L a$	volumetric mass transfer coefficient ( $\text{s}^{-1}$ )	Cu
$N$	stirring rate ( $\text{s}^{-1}$ )	G
$P$	pressure (bar)	i
$r$	reaction rate ( $\text{mol m}^{-3} \text{s}^{-1}$ )	IL
$R$	universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ )	m

copper(I) aluminum chloride salt,  $\text{CuAlCl}_4$ , dissolved in an aromatic hydrocarbon, usually toluene [5].

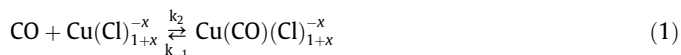
However, in the field of gas absorption, research in progress is focused on the development of more efficient fluids that prevent solvent degradation and possible losses due to solvent evaporation. In this respect, the use of ionic liquids is considered a suitable alternative for traditional absorbents in several processes owing to their extraordinary physicochemical properties, namely, the negligible vapor pressure of ionic liquids could improve the energy efficiency of the absorption process as they do not evaporate at the temperatures usually employed during the regeneration step [6]. In this sense, carbon dioxide capture is the foremost application under research [7], although there are other processes where the use of ionic liquids is regarded with interest, for instance, natural gas purification [8], sulfur dioxide removal [9] and olefin/paraffin separation [10]. In addition, we proposed in a previous work the use of a chlorocuprate(I)-based reactive ionic liquid for the selective recovery of CO, therefore avoiding the use of hydrocarbon molecular solvents while providing high  $\text{CO}/\text{N}_2$  selectivities and CO capacity [4]. Besides, the performance of facilitated-transport supported ionic liquid membranes prepared with that ionic liquid was assessed [11,12].

The reactive gas absorption in ionic liquids has been explored as a way to further increase the absorption capacity of ionic liquids at low partial pressures of the target compound, principally in post-combustion  $\text{CO}_2$  capture, whereas physical absorption in pure ionic liquids seems to be limited to high pressure applications [13]. Therefore, apart from the equilibrium data, knowledge of the reaction kinetics is required for a proper design of reactive absorption units [14]. While there is a huge number of kinetic studies regarding the reactive absorption of  $\text{CO}_2$  in alkanolamines and piperazine aqueous solutions [15–18], amino-functionalized ionic liquids [19], ionic liquids containing amino acids anions [20–22] and mixtures of amines with ionic liquids [23,24], the number of kinetic studies concerning the reactive absorption of CO with copper(I) is very scarce in literature and they are limited to COSORB solutions [25–27]. In ionic liquid media, only the equilibrium data of absorption have been reported in few works: Sharma et al. [28] determined the solubility and mass transfer of CO and  $\text{H}_2$  in  $[\text{bmim}][\text{PF}_6]$  in the study of the use of ionic liquids as new reaction media to perform hydroformylation of olefins [29]; in addition, pursuing the purpose of flue gas purification,

we studied the reactive absorption of CO in a copper(I)-based ionic liquid at pressures up to 2 MPa and Raeissi et al. [30] obtained the solubility of CO and other gas impurities at high pressures, up to 10 MPa, in the ionic liquid  $[\text{bmim}][\text{Tf}_2\text{N}]$ . Therefore, the present work represents the first study on the reactive absorption kinetics between CO and an ionic liquid; particularly, the complexation reaction between CO and the Lewis acid-based 1-hexyl-3-methylimidazolium chlorocuprate ionic liquid is assessed.

## 2. Mass transfer rates

In the chlorocuprate(I)-based ionic liquid, copper(I) is present in a complex form, giving, in basic conditions (i.e. chloride-rich),  $\text{Cu}(\text{Cl})_{1+x}^{-x}$  anionic species that exist in equilibrium as a function of the chloride concentration [31]. These anionic species reversibly react with CO according to the following reaction [32]:



with the relation between kinetic constants being:

$$K = \frac{k_2}{k_{-1}} = \frac{[\text{Cu}(\text{CO})(\text{Cl})_{1+x}^{-x}]}{[\text{CO}][\text{Cu}(\text{Cl})_{1+x}^{-x}]} \quad (2)$$

An overall second order reaction, first order with respect to free copper(I) concentration and first order with respect to CO partial pressure, is proposed. This hypothesis seems reasonable according to expressions reported in similar studies on the kinetics of the reactive absorption of copper(I) with olefins [33], which is based on the same reaction mechanism, as well as the reactions of CO and  $\text{CO}_2$  with amines [15,23,34]; nevertheless, the validity of this assumption will be assessed throughout this kinetic study.

### 2.1. Physical absorption

In the absence of chemical reaction, the interfacial absorption of CO into the ionic liquid assuming no gas-phase mass transfer resistance, equilibrium at the gas-liquid interface and employing fresh solutions is given by:

$$J_{\text{CO}}^{\text{IL}} \cdot a = k_L a \cdot C_{\text{CO}}^i = k_L a \cdot H_{\text{CO}} \cdot P_{\text{CO}} \quad (3)$$

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