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Separation Science and Engineering

Recovery of carbon monoxide from flue gases by reactive absorption in ionic liquid imidazolium chlorocuprate(I): Mass transfer coefficients*

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Abstract Recovery of carbon monoxide from flue gases by selective absorption of carbon monoxide in an imidazolium chlorocuprate(I) ionic liquid is considered in this work as alternative to the use of molecular volatile solvents such as aromatic hydrocarbons. The present work evaluates the CO mass transfer rates from the gas phase to the ionic liquid solutions in the absence of chemical reaction. To that end, carbon dioxide was employed as inert model gas and absorption experiments were performed to assess the influence of different process variables in a batch reactor with flat gas-liquid interface. The experimental mass transfer coefficients showed significant variation with temperature,(3.4-10.9)× 10^{-7} m·s^{-1} between 293 and 313 K; stirring speed, (10.2-33.1)×10^{-7} m·s^{-1} between 100 and 300 r·min^{-1}; and concentration of copper(I), （6.6-10.2）×10^{-7} m·s^{-1} between 0.25 and 2 mol·L^{-1}. In addition, the mass transfer coefficients were eventually found to follow a potential proportionality of the type $k_L \propto \mu^{-0.5}$ and the dimensionless correlation that makes the estimation of the mass transfer coefficients possible in the studied range of process variables was obtained: $Sh = 10^{-2.64} \cdot Re^{1.07} \cdot Sc^{0.75}$. These results constitute the first step in the kinetic analysis of the reaction between CO and imidazolium chlorocuprate(I) ionic liquid that determines the design of the separation units.

Keywords: Carbon monoxide; ionic liquid; copper(I); reactive absorption; mass transfer kinetics; mass transfer coefficient; carbon dioxide.

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1. INTRODUCTION

Research focused on the use of ionic liquids is becoming increasingly important in applications that involve the presence of a gas phase due to the combination of a wide variety of desirable properties, including no effective vapor pressure, chemical and physical stability and great solvent capacity among others [1], which can lead to process improvements compared to using molecular volatile solvents for the same purpose. For instance, they are seen as alternative clean solvents for a large number of catalytic reactions [2] as well as several gas separation processes, where great expectations have been placed on carbon dioxide capture and natural gas purification [3, 4]. In the field of gas separation, the use of ionic liquids for carbon monoxide separation and recovery has also been proposed [5, 6], since it can be employed as an alternative raw material for the synthesis of a number of chemicals and fuels, particularly if the CO could be efficiently removed from relatively inexpensive sources such as flue gases as the price of crude oil rises [7, 8]. In this respect, our previous works dealt with the selective recovery of CO by means of its reversible complexation reaction with copper(I) in ionic liquid phase, given the well-known ability of CO to form π-complexation bonds with transition metals [9]. First, it was observed that the solubility of CO was greatly enhanced over that of nitrogen in an imidazolium chlorocuprate(I) ionic liquid and the thermodynamic equilibriums of this system were assessed [6]. Similarly, Chen *et al.* [10] described the use of copper(I)-based ionic liquids as absorbents for propylene/propane separation. Afterwards, supported ionic liquid membranes were prepared with that ionic liquid and the performance for CO/N_2 separation was determined [11, 12]. In this way, the current energy intensive processes for CO separation could be replaced by a compact

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technology employing a benign and no volatile solvent instead of the aromatic hydrocarbons used in the COSORB process [13, 14].

Another essential aspect that has to be considered in the design of reactive absorption processes, apart from the solubility and equilibrium data, is the reaction kinetics, as it is fundamental to understand how the chemical reaction affects mass transfer and how the reaction rate is affected by process variables [15]. In recent years, several works have been published describing the mass transfer of gases into ionic liquids and, if applicable, the effect of chemical reaction. Different approaches have been applied for CO_2 capture: Galán and co-workers [16] functionalized the ionic liquid [bmim][BF_4] with a primary amine, whereas Ahmady *et al.* [17] employed mixtures of alkanolamines with [bmim][BF_4] and Albo *et al.* [18] studied the intensified physical absorption of CO_2 in [emim][$etSO_4$] using a membrane contactor. With respect to other gas separation processes, the ionic liquid [emim][$etSO_4$] was also employed by Luis *et al.* [19] in order to substitute the *N,N*-dimethylaniline solvent for the separation and concentration of sulfur dioxide in a membrane contactor. Furthermore, the intensification of the olefin/paraffin separation and purification process has also been evaluated employing ionic liquid solvents and silver cations as complexing agents [20-22].

The present work aims to evaluate the mass transport of CO from a gas phase into the ionic liquid 1-hexyl-3-methylimidazolium chlorocuprate(I) in a stirred batch reactor; the experimental analysis of the influence of process variables concludes with the establishment of a dimensionless correlation which allows estimating the mass transfer coefficients. Therefore, this work reports for the first time the first step of the kinetic assessment on the reactive absorption of carbon monoxide in an ionic liquid medium containing copper(I).

2 THEORETICAL BACKGROUND

2.1 Physical absorption

The interfacial absorption of one gas into a liquid in the absence of chemical reaction is generally described in terms of a mass transfer coefficient that depends on the hydrodynamics of the system, namely geometry and stirring speed, and the physical properties of the liquid [23]. For the case of pure CO absorption into an ionic liquid,

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assuming that there is no gas-phase limitation, the absorption flux is proportional to the concentration difference at the liquid interface:

$$J_{\mathrm{CO}}^{\mathrm{IL}} \cdot a = k_{\mathrm{L}} a \cdot \left(C_{\mathrm{CO}}^{i} - C_{\mathrm{CO}}^{\mathrm{IL}} \right) \quad (1)$$

In addition, it is generally assumed that the gas and liquid phases are in equilibrium at the interface [24]. Therefore, the solute concentration at the liquid interface is connected with the concentration in the adjacent gas phase according to an equilibrium expression such as the Henry's law for gas-liquid absorption:

$$C_{\mathrm{CO}}^{i} = H_{\mathrm{CO}} \cdot P_{\mathrm{CO}} \quad (2)$$

Hence for maximum driving force, i.e. negligible solute concentration in the bulk liquid phase, the CO flux from the gas phase to the ionic liquid is:

$$J_{\mathrm{CO}}^{\mathrm{IL}} \cdot a = k_{\mathrm{L}} a \cdot C_{\mathrm{CO}}^{i} = k_{\mathrm{L}} a \cdot P_{\mathrm{CO}} \cdot H_{\mathrm{CO}} \quad (3)$$

The mass transfer coefficient can be experimentally obtained from the decrease in pressure of the pure gas which occurs during gas absorption experiments performed in a batch stirred reactor [25]. Considering the conservation law and the ideal gas law, the mass balances to the CO solute in the gas and ionic liquid phases in that system are described by Eq. (4) and Eq. (5), respectively:

$$\frac{\mathrm{d}n_{\mathrm{CO,G}}}{\mathrm{d}t} = \frac{V_{\mathrm{G}}}{R \cdot T} \cdot \frac{\mathrm{d}P_{\mathrm{CO}}}{\mathrm{d}t} = -\frac{\mathrm{d}n_{\mathrm{CO,IL}}}{\mathrm{d}t}; \; t = 0 \rightarrow P_{\mathrm{CO}} = P_{\mathrm{CO}}^{0} \quad (4)$$

$$\frac{1}{V_{\mathrm{IL}}} \frac{\mathrm{d}n_{\mathrm{CO,IL}}}{\mathrm{d}t} = k_{\mathrm{L}} a \cdot \left(C_{\mathrm{CO}}^{i} - C_{\mathrm{CO}}^{\mathrm{IL}} \right); \; t = 0 \rightarrow n_{\mathrm{CO,IL}} = 0 \quad (5)$$

After simultaneous solution of Eqs. (2), (4) and (5) and subsequent linearization, the following expression that determines the volumetric mass transfer coefficient from an absorption experiment is obtained [16, 22]:

$$k_{\mathrm{L}} a \cdot t = \frac{\beta}{1+\beta} \cdot \ln\left(\frac{P_{\mathrm{CO}}^{m}}{(1+\beta) \cdot P_{\mathrm{CO}}(t) - \beta \cdot P_{\mathrm{CO}}^{m}} \right)$$

with $\beta = \dfrac{V_{\mathrm{G}}}{V_{\mathrm{IL}} \cdot R \cdot T \cdot H_{\mathrm{CO}}}$ (6)

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The β coefficient is also related to the initial pressure in the reactor before start-up, the maximum pressure loaded and the equilibrium pressure reached after the absorption experiment [26] as shown in Eq. (7). Therefore, the mass transfer coefficient and the gas solubility coefficient, if unknown beforehand, can be determined by combination of Eqs. (6) and (7) with data from a single absorption experiment:

$$\beta = \frac{P_{\mathrm{CO}}^{\mathrm{e}} - P_{\mathrm{CO}}^{\mathrm{o}}}{P_{\mathrm{CO}}^{\mathrm{m}} - P_{\mathrm{CO}}^{\mathrm{e}}} \quad (7)$$

2.2 Carbon monoxide-carbon dioxide analogy

The intrinsic CO mass transfer coefficient cannot, however, be measured directly in this liquid phase owing to the chemical complexation reaction between CO and the chlorocuprate(I) ionic liquid. Consequently, an inert model gas which resembles carbon monoxide should be employed instead. The film theory, which is the simplest theory for interfacial mass transfer, states that the mass transfer coefficient is proportional to the diffusion coefficient of the solute [23]:

$$k_{\mathrm{L}} = \frac{D}{l} \quad (8)$$

Therefore, the CO mass transfer coefficient can be calculated by determining that of the model gas and thereafter making a correction that takes into account the ratio of diffusivities between CO and the inert model gas [13]. The diffusivity of gases in imidazolium ionic liquids can be estimated with theoretical models such as the Morgan's predictive model, providing that the solute liquid molar volume at atmospheric boiling point is known [27]:

$$D = 2.66 \times 10^{-7} \frac{1}{\mu_{\mathrm{IL}}^{0.66} \cdot \overline{V}^{1.04}} \quad (9)$$

For that reason, we have employed carbon dioxide as model gas since CO and CO_2 have almost identical liquid molar volumes, 33.0 and 33.3 cm^3 mol^{-1}, respectively, as determined with the Tin and Calus method [28]. Hence, according to this model the CO and CO_2 diffusivities in the chlorocuprate(I) ionic liquid are identical and can be calculated as a function of the ionic liquid viscosity. Consequently, the ratio of CO to CO_2 diffusivities is 1 and the CO mass transfer coefficient is assumed to be the

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experimentally obtained as described in the previous section but substituting the reactive gas CO for the inert gas CO_2 in Eqs. (1) to (7). Similar approaches have already been employed, for instance, Hogendoorn and co-workers [13] estimated the solubility and mass transfer coefficient of CO in COSORB solutions employing N_2 as model gas. Likewise, nitrous oxide is frequently used as model gas to estimate the CO_2 solubility and diffusivity in aqueous amine solutions [29].

3 EXPERIMENTAL

3.1 Materials

The Lewis acid-based ionic liquid 1-hexyl-3-methylimidazolium chlorocuprate(I) was obtained by the direct mixture of a metal halide salt, copper(I) chloride (Sigma Aldrich, minimum purity of 99%), with the ionic liquid 1-hexyl-3-methylimidazolium chloride (Iolitec, purity of 99.5%), [hmim][Cl], at the desired ratio in a stirred vessel. Vacuum conditions and 333 K were applied for 2–3 h so as to avoid the oxidation of copper(I) as well as to remove the possible trace amounts of water and other volatile compounds that may be present in the ionic liquid. The employed carbon dioxide was supplied by Air Liquid.

3.2 Equipment

The absorption experiments were performed in a jacketed glass stirred cell reactor (model Picoclave type 1/100 ml, Buchi) which allows controlling that the absorption process proceeds with a flat liquid interface, a requirement in order to keep the hypothesis of constant gas-liquid interfacial area. The main features of the reactor are gathered in Table 1. Two impellers were installed in the solid stirrer shaft at different levels so the gas and liquid phases were perfectly mixed. In addition, the reactor is equipped with a pressure transducer (Aplisens, model PCE-28, 0.2% accuracy) connected to a data acquisition device (Memograph M, Endress+Hausser), which monitors the pressure inside the reactor, and a Pt-100 temperature sensor connected to a cryothermostatic bath (Julabo, model F25-ME), which regulates the temperature inside the reactor ($\pm$0.01 K). A vacuum pump (Edwards) was employed both for preparation of the ionic liquid and regeneration after the absorption experiment.

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The dynamic viscosity of the ionic liquid was measured as a function of temperature and CuCl concentration employing a rotational viscometer (Fungilab, Alpha series) equipped with a special spindle for low volume samples.

Table 1
Characteristics of the glass stirred cell reactor.

Element	Description
Total volume/ L	0.16
Liquid volume/L	0.04
Interfacial area /m^2	2.12×10^{-3}
Stirrers:	
Number	2
Type	6-Blade Rushton turbine
Diameter /m	0.035
Maximum pressure/MPa	1

3.3 Measurement procedure

Before each absorption experiment, the ionic liquid was degassed at 333 K applying vacuum for 2-3 h. Afterwards, the desired temperature and stirrer speed for the experiment were set and once the equilibrium had been reached, the reactor was loaded with CO_2. Since absorption starts immediately after opening the inlet valve, the gas injection should be done in a very short time, preferentially less than 1 s [30]. The pressure inside the reactor was digitally recorded every second until a constant equilibrium pressure was reached. Each experiment was replicated and data showed good reproducibility with relative standard deviations lower than 2%.

Several absorption experiments were performed to assess the accuracy of this procedure. The solubility of CO_2 was determined in a common ionic liquid such as 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF_6]. The experimental Henry's coefficients obtained at different temperatures are plotted in Fig. 1 and show good agreement with several data found in literature.

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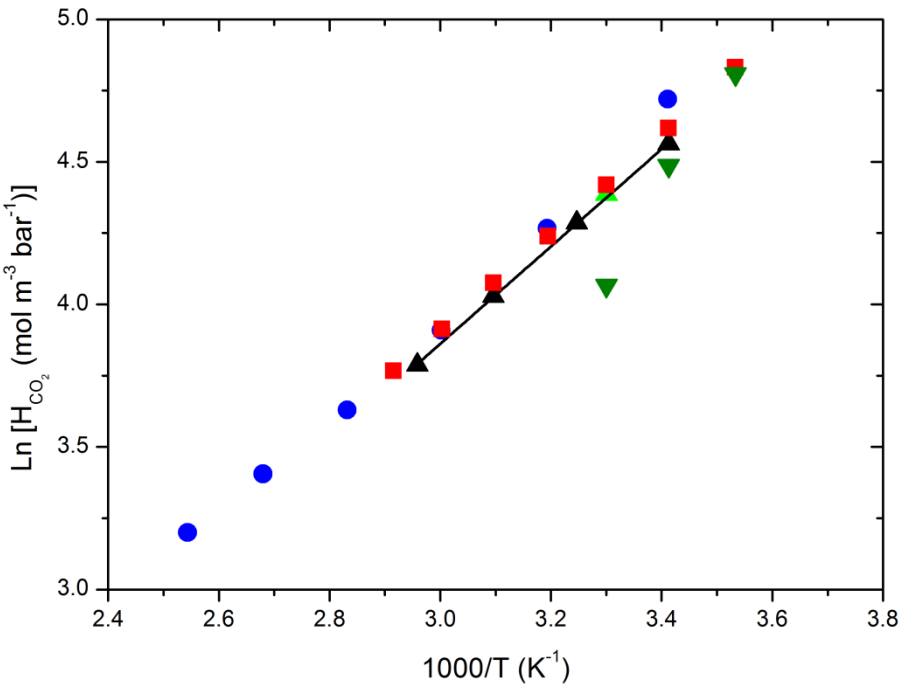

Fig. 1 Solubility of CO_2 in [bmim][PF_6] as a function of temperature: this work (▲) and literature data: [31] (●), [32] (▲), [33] (■), [34] (▼). The solid line is the linear fitting of the data (R^2 = 0.9999).

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4 RESULTS AND DISCUSSION

4.1 Viscosity

The viscosity of the chlorocuprate(I) ionic liquid was measured at several copper(I) salt concentrations as a function of temperature in the range 293-323 K. The results are plotted in Fig. 2 together with the viscosity of the precursor [hmim][Cl] ionic liquid. The viscosity of [hmim][Cl] and that of the ionic liquids with CuCl concentration lower than 0.5 mol·L^{-1} are very similar, but at higher concentrations of CuCl the viscosity decreases considerably. For this reason, the mass transfer coefficients will be enhanced at high CuCl concentrations and therefore, a variable mass transfer coefficient should be considered in the assessment of the reaction kinetics, which is not a commonly reported situation. In addition, the mass transfer is also improved at higher temperatures since the viscosity decreases as temperature increases, being this influence very similar in all cases as can be appreciated from the almost parallel lines.

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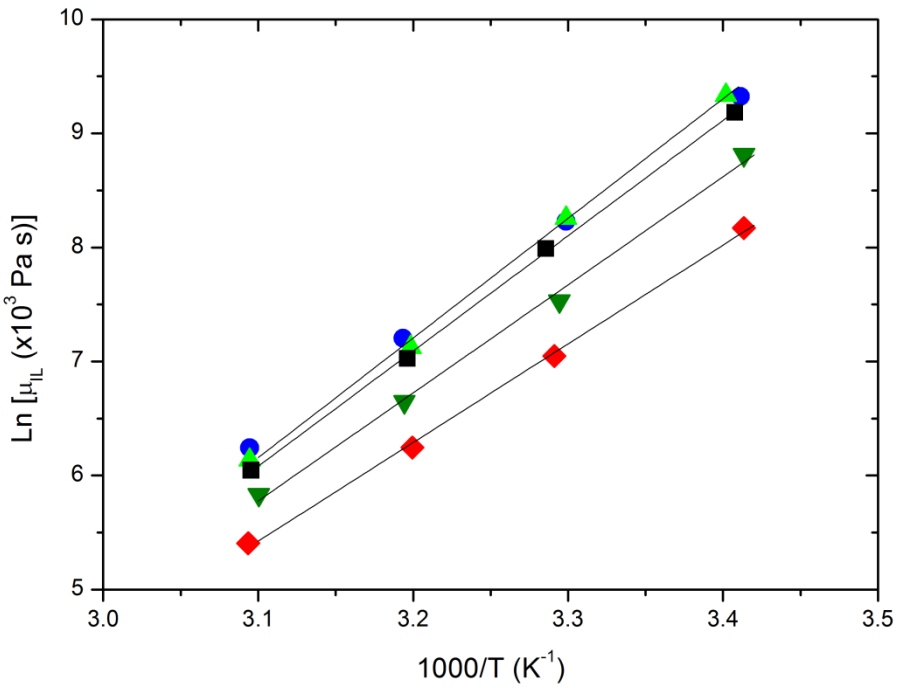

Figure 2. Ionic liquid viscosity as a function of temperature and copper(I) concentration: 0 (●), 0.25 (▲), 0.5 (■), 1 (▼) and 2 (♦) mol copper(I) L^{-1}. The solid lines are the linear fitting of the data.

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4.2 Mass transfer coefficient

In this section, the gas-liquid mass transfer coefficients of CO_2 in the chlorocuprate(I) ionic liquid are reported at different operational conditions, namely temperature, stirring speed and CuCl concentration. The volumetric mass transfer coefficient is directly obtained from experimental data of absorption at certain conditions by plotting the right hand side of Eq. (6) versus time. A typical result is depicted in Fig. 3 where the value of the volumetric mass transfer coefficient is the slope of the straight line that fits the experimental data that correspond to approximately 20% to 70% of the total pressure variation [25].

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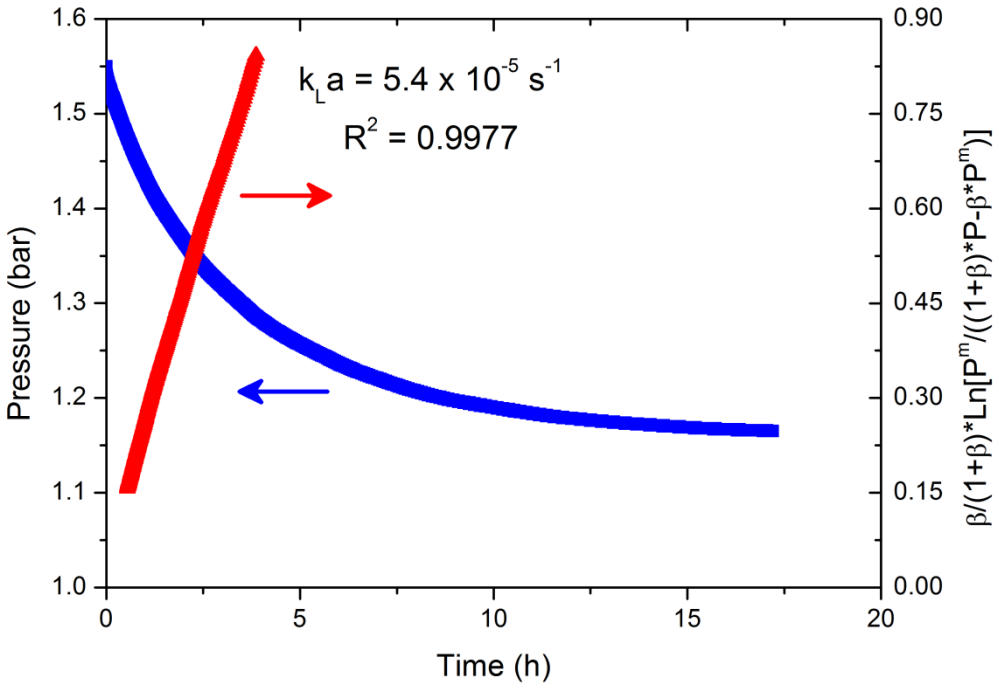

Figure 3. Determination of the gas-liquid volumetric mass transfer coefficient from an individual absorption experiment (303 K, 100 r·min^{-1}, 2 mol copper(I) ·L^{-1}): pressure (■) and representation of Eq. (6) (▲).

The resultant mass transfer coefficients can be calculated providing that the specific area of the system is known: in our reactor a = 53.1 m^2·m^{-3}. The results are collected in Table 2, along with the CO_2 Henry's coefficients derived from the combination of Eqs. (6) and (7), which are reported for the first time in this ionic liquid. It is worth mentioning at this point that although the mass transfer coefficient of CO_2 and CO are alleged to be the same due to their almost identical diffusivities in ionic liquid media, the solubility of both gases significantly differs by one order of magnitude, according to the results of CO solubility reported in a previous work [5]. In connection with the gas-liquid mass transfer rates, all the operational conditions studied have, as expected, a positive effect on the mass transfer coefficient. Regarding the hydrodynamics, in terms of the film theory, increasing the stirring speed induces a decrease in the film thickness due to increasing the turbulence in the system and therefore, enhanced mass transfer coefficients are achievable. In this work, the effect of the stirring speed was assessed between 100 and 300 r·min^{-1} at 303 K with 2 mol copper(I)·L^{-1} solutions and mass transfer coefficients that ranged from 10.2 to 33.1 m·s^{-1} were found. The initial

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condition of a flat gas-liquid interface can be verified by the linearity of the data of the mass transfer coefficient represented against the stirring rate in a logarithmic plot [22]. On the other hand, the dependence of the mass transport coefficient on temperature and CuCl concentration is related to the influence of those variables on the gas diffusivity and eventually, on the ionic liquid viscosity. Since according to the Morgan's model $D \propto \mu^{-0.66}$, it is expected that the mass transfer coefficient varies with the viscosity in a similar fashion, given that the interfacial mass transfer theories express the relationship between the mass transfer coefficients and the diffusivity as $k_L \propto D^n$, with *n* between 0.5 (surface-renewal models) and 1 (film model) [35, 36]. In this work, the relationship between the mass transfer coefficient and the viscosity is shown in Fig. 4, and for the experiments performed at the same stirring speed it can be expressed as $k_L \propto \mu^{-0.5}$. Hogendoorn *et al.* [13] obtained CO mass transfer coefficients in a 2.3 mol·L^{-1} COSORB solution that were two orders of magnitude larger than those obtained in this work, a difference that can be attributed to the higher viscosity of the chlorocuprate(I) ionic liquid.

Table 2
Gas-liquid mass transfer coefficients and CO_2 solubility in a chlorocuprate(I)-based ionic liquid.

T /K	P_{CO2} /MPa	Stirring speed /r·min^{-1}	[CuCl]/mol·L^{-1}	$k_L \cdot a \times 10^5$ /s^{-1}	$k_L \times 10^7$ /m·s^{-1}
293	11.8	100	0.25	1.8	3.4
			0.5	2.0	3.8
303	13	100	0.25	3.5	6.6
			0.5	3.6	6.8
			1	3.7	6.9
			2	5.4	10.2
		200	2	11.0	20.7
		300	2	17.6	33.1
313	14.1	100	0.25	5.8	10.9
			0.5	6.4	12.0

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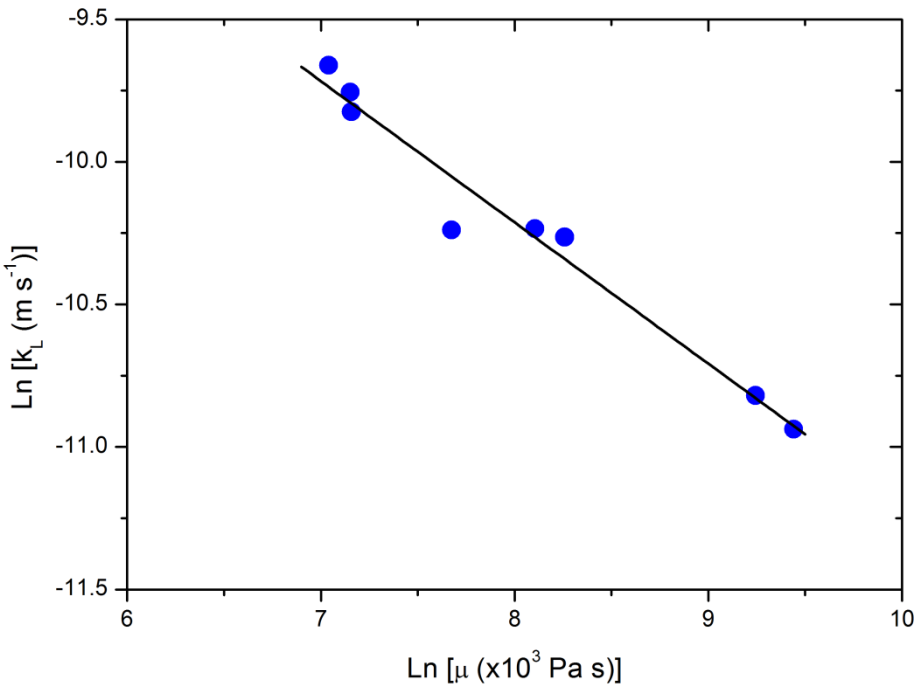

Figure 4. Dependence of the mass transfer coefficient on the ionic liquid viscosity for the experiments performed at 100 rpm. The solid line is the linear regression of the data (R^2 = 0.9679).

It is usually convenient to employ dimensionless correlations as a compact way of expressing experimental results that afterwards can be employed to make reasonably quick and accurate estimations under different operating conditions. For gas-liquid mass transfer in stirred reactors, the following type of correlation usually applies [23, 26, 30, 37]:

$$Sh = 10^a \cdot Re^b \cdot Sc^c \quad (10)$$

From the experiments performed at different temperatures, CuCl concentrations and stirring speeds, the estimated values of the coefficients in Eq. (10) are $a = -2.64$, $b = 1.07$ and $c = 0.75$. The accuracy of the predictions in this work was assessed by the relative root-mean square deviation (RMSD), which is lower than 8%. The parity graph of predicted versus experimental volumetric mass transfer coefficients is presented in Fig. 5. There are several studies that report similar values of the mass transfer coefficients, for instance, Sharma et al. and Meille et al. [25, 35] obtained that the Sh number relies on the Re number to a power slightly higher than 1. Moreover, although

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the exponent of the *Sc* number is usually 0.5 according to the penetration theory, Sharma *et al.* [25] determined some correlations without that restriction and obtained higher values. For a value of the exponent *c* of 0.5 in this work, the resulting correlation gives a larger value of RMSD, around 13%.

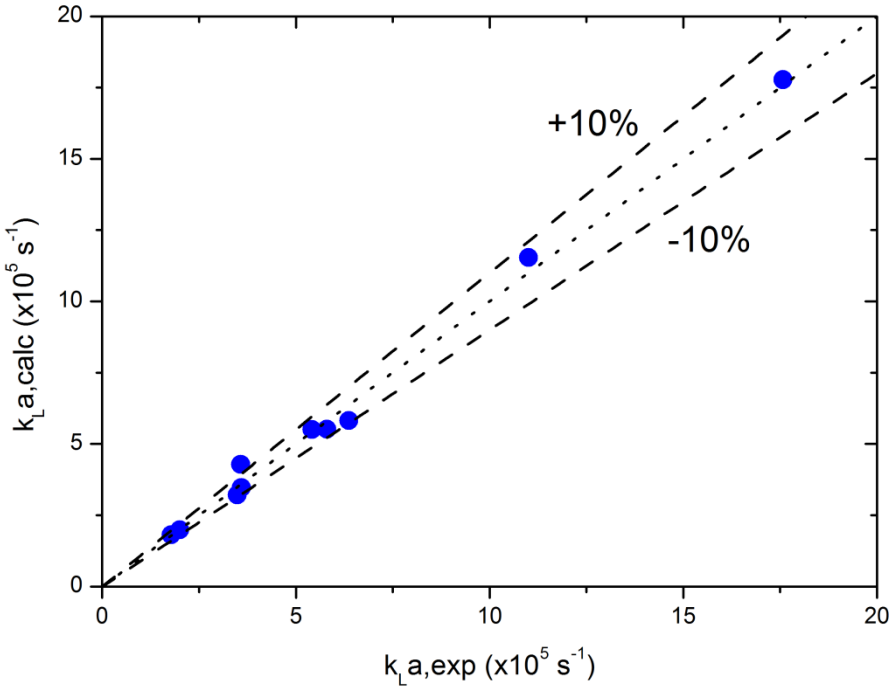

Figure 5. Comparison between experimental and calculated volumetric mass transfer coefficients.

5 CONCLUSIONS

In this work, the mass transfer rate of CO absorption from a gas phase into 1-hexyl-3-methylimidazolium chlorocuprate(I) ionic liquid is assessed, hence providing the needed basis for the kinetic analysis and modeling of the reversible reaction between CO and the chlorocuprate(I) complex in a further step [38]. The present study could not be experimentally performed with CO in the non-reactive precursor [hmim][Cl] ionic liquid, since the addition of CuCl to this ionic liquid significantly modifies physical properties of the medium that affect mass transfer, such as the ionic liquid viscosity;

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therefore, variable mass transfer coefficients should be considered. To that end, CO_2 was employed as an inert model gas with similar diffusion properties to CO and several absorption experiments were performed by a pressure decrease method in a stirred reactor varying the operational conditions, namely temperature, stirring speed and CuCl concentration. The liquid side mass transfer coefficient was found to be strongly affected by temperature and agitation: k_L increased from 3.4× 10^{-7} to 10.9 × 10^{-7} m·s^{-1} in the temperature range 293-313 K; and from 10.2 × 10^{-7} to 33.1 × 10^{-7} m·s^{-1} when the stirring speed was shifted from 100 to 300 r·min^{-1}. Moreover, although the addition of low concentrations of copper(I) had a weak effect on k_L, this effect is significant at the highest CuCl concentrations and thus, this variable has to be taken into account accordingly. The global effect of temperature and copper(I) concentration can be related to the changes in the ionic liquid viscosity according to a potential relationship of the type $k_L \propto \mu^{-0.5}$. Finally, a correlation based on dimensionless numbers is proposed: $Sh = 10^{-2.64} \cdot Re^{1.07} \cdot Sc^{0.75}$. This correlation allows estimating the mass transfer coefficient within the studied range of temperatures, CuCl concentrations, and stirring speeds.

NOMENCLATURE

a specific surface area, m^2 ·m^{-3}

C concentration, mol · m^{-3}

D diffusion coefficient, m^2 ·s^{-1}

d stirrer diameter, m

E_A enhancement factor

H Henry coefficient, mol · m^{-3} ·MPa^{-1}

J molar flux, mol· m^{-2} · s^{-1}

k_L liquid phase mass transfer coefficient, m· s^{-1}

$k_L a$ volumetric mass transfer coefficient, s^{-1}

l film thickness, m

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N stirring rate, $r \cdot min^{-1}$

n molar hold-up, mol

P pressure, MPa

R universal gas constant, $MPa \cdot m^3 \cdot mol^{-1} \cdot K^{-1}$

Re Reynolds number($= \rho \cdot N \cdot d^2 / \mu$)

Sc Schmidt number[$= \mu / (\rho \cdot D)$]

Sh Sherwood number ($= k_L a \cdot d^2 / D$)

t time ,s

T temperature,K

V volume , m^3

$\overline{V}$ liquid molar volume at atmospheric boiling point, $cm^3 \cdot mol$

β group of parameters in Eq. (6)

μ viscosity,$Pa \cdot s$

ρ density ,$kg \cdot m^{-3}$

Superscripts and Subscripts

CO carbon monoxide

Cu copper

e equilibrium

G gas phase

i interface

IL ionic liquid phase

m maximum

o initial

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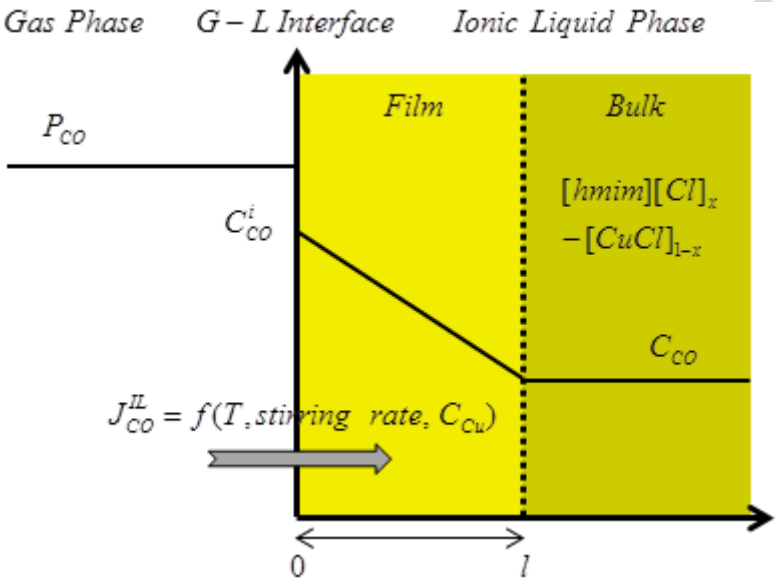

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