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ARTICLE

Carbon neutral electrochemical conversion of carbon dioxide mediated by $[M^{+n}(cyclam)Cl_n]$ (M= Ni^{+2} y Co^{+3}) on mercury free electrodes and ionic liquids as reaction media.

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In this work, the electrochemical reduction of carbon dioxide using $[M^{+n}(cyclam)Cl_n]$ (M= Ni^{+2} y Co^{+3}) as electrocatalysts has been studied in 1-Butyl-3-methylimidazolium tetrafluoroborate and 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($BMImBF_4$ and $BMImNTf_2$ respectively) ionic liquids as reaction media. Complexes were characterized electrochemically in these salts and relevant parameters, such as an heterogeneous electron transfer rate were calculated. Results indicate a faster M(II)/M(I) redox process in $BMImBF_4$ despite its higher viscosity compared to $BMImNTF_2$. Cyclic voltammetry experiments demonstrated that $[Ni(cyclam)Cl_2]$ is the most active macrocycle, towards the reaction under survey. For this compound, potential controlled electrolysis was carried out at -1.4V vs Ag/AgCl in $BMImBF_4$ as solvent, yielding only CO as a reaction product, with a turn over frequency (TOF) of 0.73 h^{-1}. NMR spectra for the ionic liquids, after electrolysis, shows that applied potential does not affect the chemical structure of the salts. FT-IR thin layer spectroelectrochemical experiments in CO_2 saturated solution in $BMImBF_4$ at -1,4V vs Ag/AgCl, show the formation of $[Ni(cyclam)CO]^+$ as precursor species, and also the most stable $[Ni(CO)_4]$.

Introduction

Carbon dioxide concentration in the atmosphere has been growing during the last century by anthropogenic effects, giving rise to a climate change called global warming. In order to mitigate the effect of carbon dioxide over the global climate, many alternatives to reuse carbon dioxide have been investigated [1–3].

In order to produce an effective reduction in carbon dioxide levels, energy consumption plays a very important role. Since nowadays most of the energy produced comes from fossil fuels, carbon dioxide must be formed in order to obtain a certain amount of energy. Having this in mind, carbon balance is a key concept in carbon dioxide utilization. In a recent article, Kauffman and coworkers [4] estimated the amount of energy required for a 100% of faradaic efficiency conversion of 1 metric ton of carbon dioxide into different products considering an overpotential of 0 V; and compared that values with the amount of carbon dioxide required to produce that amount of energy from fossil-fuel-derived electricity. They concluded that carbon dioxide reduction energy requirements scale linearly with the number of electrons involved in the formation of a given product. Considering the amount of carbon dioxide generated to produce that quantity of energy, only carbon monoxide and formic acid formation produce less carbon dioxide than they consume; and hence, those are the only carbon neutral products from fossil fuel powered procedures, until now.

One of the most promising ways to reuse CO_2 is its fixation, a process involving the reincorporation of the CO_2 into different substrates in order to obtain useful products [5,6]. One classical example is the synthesis of cyclic carbonates, which has been achieved in molecular solvents [7–11], using either electrochemical or thermal activation.

Carbon dioxide stability is the main drawback for the application of electrosynthesis in industrial scale, since reduction of carbon dioxide involves a geometry change and consequently a very slow kinetics [12,13]. Electrosynthesis of useful products starting from CO_2, requires the application of large amount of energy, which is mainly required for the activation of the substrate, making the overall process extremely expensive, and then unviable [14].

In the context of green chemistry, the search for alternative solvents to replace conventional organic solvents is highly required, mainly because they are known for their harmful effects to the environment, safety and health. In order

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to avoid the use of molecular solvents, ionic liquids have emerged as alternative solvents since they are salts that are liquid at room temperature [15,16] and are considered "green" because of their negligible vapor pressure at room temperature, and also because of their reusability and recyclability.

Ionic liquids consist of bulky and asymmetric cations and a wide variety of anions, going from simple halides to fluorinated inorganic anions. Due to the asymmetry and chemical structure, attractive cation-anion forces are weaker than in the inorganic salts, this fact makes them liquid in a broad temperature range in many cases being close to room temperature. As a result of the large number of combinations between cations and anions, ionic liquids can be designed for specific tasks [17]. Ionic liquids have been widely used as a solvent in organic synthesis, electrochemistry and, thanks to its large thermal and chemical stability, as supporting electrolyte and solvent simultaneously [18–22]. Currently, ionic liquids have been used as solvents for electrosynthetizing organic molecules of interest such as cyclic carbonates and carbamates [15,23,24]

Carbon dioxide has a formal reduction potential of -2.21V vs SCE in dimethylformamide[12] for its first monoelectronic reduction, yielding a nonlinear anion radical, hence, many molecules, have been used as electrocatalysts to reduce the potential at which this reaction takes place. In this context, [M^{+n}(cyclam)Cl_n] (M= Ni^{+2} y Co^{+3}) has been used as electrocatalyst in aqueous solution and molecular solvents for the reduction of CO_2 [25–31], thus significantly decreasing the overpotential required to activate this molecule. Indeed, [Ni(cyclam)Cl_2] was first used in 1980 by Fisher and coworkers, to reduce carbon dioxide using mercury electrodes finding a very high selectivity towards the formation of carbon monoxide as well as a very high overpotential of H_2 formation, which is a common byproduct [26].

Later in 1988, Collin and Sauvage published an article reviewing all the investigation concerning homogeneous electrocatalytic reduction of carbon dioxide [32]. In that article authors state that from early experiences several points are noteworthy, being the most important the following:

- A reduced state of the complex is necessary to perform carbon dioxide reduction.
- The electrocatalytic nature of the processes was corroborated with a blank experiment. In absence of carbon dioxide, carbon monoxide was not produced.
- Protons are necessary to form carbon monoxide. In absence of a proton source, cobalt or nickel complexes are reduced to their monovalent state, but no further reaction with the CO_2 is produced.

The use of mercury electrodes for the reduction of carbon dioxide catalyzed by $[Ni(cyclam)]^{2+}$ involves the use of highly health hazardous material. One of the main risks to human health is Hg and its organic derivatives. Hg is a widely used electrodic material since it displays a very negative potential for proton reduction giving a large negative potential solvent window in aqueous media. Another interesting feature is that $[Ni(cyclam)]^{+}$ has shown a strong interaction with Hg surface, being absorbed and hence enhancing its catalytic activity toward CO_2 reduction [25,33,34].

In 2012, Fujita et al [25] used substituted cyclam complexes in aqueous media. In their work a reversible redox couple Ni(II)/Ni(I) at -1.24 V (vs. NHE) was observed using Hg electrodes at pH = 5.

Based on these literature supports, it can be said that this type of electrocatalytic tetraazamacrocycles are selective and effective for the conversion of CO_2 to CO on mercury electrodes in aqueous media. An analysis of the catalytic activity of these compounds concluded that Ni (I) is the active catalyst, since it is able to coordinate the CO_2 molecule axially by changing the geometry of the complex.

In order to avoid the use of hazardous materials, inert electrodic materials are highly desired. Kubiak and co-workers [26] have obtained CO on glassy carbon electrodes (GC) using N-substituted cyclam. In their work, it was found that $[Ni(cyclam)]^{+2}$ is a selective compound toward the reduction of CO_2 in a mixture composed of water:acetonitrile extending the electrochemical window of the solvent. By performing electrolysis at -1.4 V they estimated faradaic efficiency of 90% and TOF of $90s^{-1}$; they also conclude with theoretical calculations that the coordination of the carbon dioxide molecule to the metal center generate a change in the linearity of the substrate[26].

On the other hand, information about the electrochemical behavior of coordination compounds in ionic liquids is scarce, finding only a few examples of this kind of studies [35–37] where several properties such as electron transfer rates and coupled electrochemical reactions are driven by intrinsic properties of these salts [38].

In this work, two different ionic liquids were studied as solvents and supporting electrolytes toward the electrochemical reduction of carbon dioxide, using [M^{+n}(cyclam)Cl_n] (M= Ni^{+2} y Co^{+3}) as an homogeneous electrocatalyst. The complexes were electrochemically characterized in ionic liquids, finding that both compounds show diffusion coefficients (D_0) and heterogeneous electron-transfer constants, (k^0) highly dependent on the anion of the ionic liquid. Electrocatalytic activity of [M^{+n}(cyclam)Cl_n] (M= Ni^{+2} y Co^{+3}) has been also studied in both ionic liquids, finding that $BMImBF_4$ appears as the most efficient solvent to reduce carbon dioxide to carbon monoxide. IR spectroelectrochemical experiments show that in the case of [Ni(cyclam)Cl_2] a Ni(I) intermediary is present, forming a $[Ni(cyclam)CO]^{+}$ complex; also a stable [$Ni(CO)_4$] byproduct is formed, probably limiting the production of free CO.

Experimental Part

Materials

Reagents and solvents were of analytical grade or higher, purchased from Sigma Aldrich and used without further purification. [M^{+n}(cyclam)Cl_n] (M= Ni^{+2} y Co^{+3}) were synthesized following previously reported synthetic routes [39,40]. Both complexes present elemental percentages in well

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agreement with predicted values being %CHN_{found}: 36.84%, 7.25% and 17.1% (%$CHN_{predicted}$: 36.4%, 7.28% and 17.0%) in case of [$Ni(cyclam)Cl_2$] and %CHN_{found}: 34.12%, 6.91% and 15.1% (%$CHN_{predicted}$: 32.84%, 6.63% and 15.33%) for [$Co(cyclam)Cl_3$]. Tetrabutyl ammounium perchlorate (TBAP), $BMImBF_4$ (1-butyl-3-methylimidazolium tetrafluoroborate) and $BMImNTf_2$ (1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) (>98.5%) were purchased from Sigma Aldrich. Both ionic liquids were dried prior to use under vacuum at 80°C during 24 hours. Water content was analized with a Karl Fisher titrator, being in all cases less than 1% w/w. Solvent was handled using syringes and cannulas in air free conditions [41].

Instruments

UV-Vis spectra were recorded in a Shimadzu Multispec 1501 spectrometer; Elemental analysis was carried out in EAGER 2000 instrument. FT-IR measurements were carried out using a Thermo Nicolet iS10. Water titrations were recorded using a CRISON Titromatic KF 2S-2B. NMR measurements were made using a BRUKER AVANCE III HD-400MHz. Electrochemical measurements were carried out using a CH instrument 760C and a BASi PWR-3 potentiostat. Gas chromatography analysis was made with a DANI MASTERS GC, with a fused silica capillary column (Supelco Mol Sieve 5A plot, 30m x 0.53mm) coupled with a micro thermal conductivity detector (μTCD).

Electrochemical measurements

Cyclic voltammetry (CV) was carried out using a glassy carbon electrode (GC) (CH Instruments Austin, TX; diameter: 3mm) and for potential controlled bulk electrolysis (PCBE) a glassy carbon plate (SPI West Chester, PA, USA; Geometric area: 3.25 cm^2) was used. In all cases, a Pt wire was used as counter electrodes. Before carrying out electrochemical measurements, the surface of the working electrode was polished with 0.5 um alumina powder and then washed with bidistilled water.

All the potential values are informed using a saturated Ag/AgCl reference electrode which has been sealed and separated from the solution using a Pt bridge, working as a Luggin capillary, avoiding moisture contamination to the working solution in the experiment timescale [42]. Potential of the reference electrode was calculated using a ferrocene/ferrocenium couple, being 0.191 V vs. NHE for the electrode immersed in $BMImBF_4$.

Potential dependent IR spectroscopy experiments were carried out using transmission mode with a Specac Omni-Cell demountable system with a CaF_2 window, a 1mm Teflon spacer in which a 3 electrodes array was placed. Working electrode was a Pt grid, a Pt wire as counter electrode and an Ag wire as quasi-reference electrode.

A typical experiment consisted in recording a single spectrum at open circuit potential, after that, -1.4V vs Ag/AgCl were applied to the cell, during the electrolysis. Each 30 seconds a new spectrum was recorded until 10 minutes of electrolysis passed. Samples were prepared by dissolving $[Ni(cyclam)]^{2+}$ (80mM) in ionic liquid. Solutions were saturated with N_2 or CO_2 respectively previous to the IR measurements. Spectra were recorded using 16 scans and were completed in 20s approximately.

Electrocatalytic studies

Carbon dioxide reduction in $BMImBF_4$ and $BMImNTf_2$ with the complexes in solution was evaluated in a CO_2 saturated medium (93 mM for $BMImBF_4$ and 104.8 mM for $BMImNTf_2$)[43], where the ionic liquid acts as supporting electrolyte and solvent. The study of the electrocatalytic activity was carried out using CV and PCBE into an undivided glass cell, using the three electrodes arrangement previously described.

Gas chromatography measurements of reaction products were carried out using an isothermal program at 40°C, relating the chromatographic area of carbon monoxide with a previously constructed calibration curve.

Results and Discussion

Electrochemical characterization.

The electrochemical behavior of [$M^{+n}(cyclam)Cl_n$] (M= Ni^{+2} y Co^{+3}) complexes used in this work is unknown in ionic liquid media, thus its interfacial electrochemistry was measured in order to characterize relevant parameters for the electrocatalytic performance such as the diffusion coefficient (D_0) and the heterogeneous electron-transfer rate constant (k^0). For that purpose, solutions of the complexes were prepared in $BMImBF_4$ and $BMImNTf_2$, using the ionic liquids as solvent and supporting electrolyte. Results of the cyclic voltammetry using glassy carbon electrodes are shown Figure 1.

From the cyclic voltammetry experiments shown in Figure 1 it is clear that none of the ionic liquids present any redox response in the potential window studied. For BMImBF4 the electrochemical window is approximately 3.1V and for $BMImNTf_{2\ it}$ is approximately 3.7V (not shown). In both cases potential limits correspond to the decomposition of the ionic liquid, *i.e.* reduction of the cation or oxidation of the anion, being concordant with previously reported data [44–46].

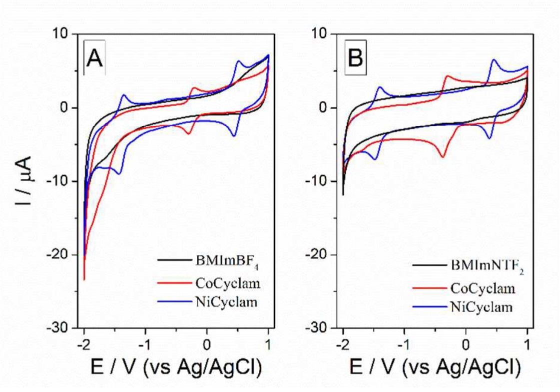

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Figure 1: Electrochemical behavior of the complexes in BMImBF$_4$ (A), and BMImNTf$_2$ (B). Black lines correspond to the electrode in the solvent without the complex and red and blue lines are the response of Co and Ni complexes (2 mM and 9.7 mM) respectively in ionic liquid solvents. In all cases, the solutions were saturated with N$_2$ at 100 mV/s.

The electrochemical behavior of the [Ni(cyclam)Cl$_2$] dissolved in BMImBF$_4$ shows two well defined redox processes, one centered at E$_{1/2}$: 0.42V attributed to the Ni(III)/Ni(II) process, and the other related to Ni(II)/Ni(I) redox couple centered at E$_{1/2}$: -1.40 V. In the case of BMImNTf$_2$ the response is similar showing two well defined processes at E$_{1/2}$: 0.40V for Ni(III)/Ni(II) and other at E$_{1/2}$: -1.45V for Ni(II)/Ni(I).

For Co complex a single process is observed at E$_{1/2}$: -0.32 V and E$_{1/2}$: -0.38 V for BMImBF$_4$ and BMImNTF$_2$ respectively, assigned to the Co(II)/Co(I) redox couple. Also an irreversible process is present at E$_{1/2}$: 1.2 V in both solvents (supporting information S2) assigned to the Co(III)/Co(II) redox process. The irreversible process at *c.a.* -1.8 V is assigned to Co(I)/Co(0) redox couple [47,48].

Table I summarizes the Ep values for the complexes in IL´s and also the corresponding values for molecular solvents available in literature [26].

The main difference in the redox behavior corresponding to the couple M(II)/M(I) of the complexes dissolved in different media is the observed electrochemical reversibility. In fact, in H$_2$O:ACN[26], redox couple appears at -1.45V, with a peak to peak separation of 50 mV, representing a totally reversible redox process. In the case of BMImNTf$_2$, the oxidation peak appears at -1.39V, with a ΔE$_p$ of 100mV, a quasi-reversible process. The same redox couple in BMImBF$_4$ present a ΔE$_p$ of 64mV, corresponding to a quasi-reversible process. For the cobalt complex, M(II)/M(I) the redox couple is quasi-reversible for both solvents. Consequently, considering that BMImBF$_4$ is three times more viscous than BMImNTf$_2$ (154 and 52 mPaS respectively) [21], mass transport is not a determinant factor in the redox reaction . Thus, it is necessary to carry out a more detailed study of the M(II)/M(I) electrochemical system in both ionic liquids.

Figure 2 displays the behavior of the complexes at different scan rate. In order to evaluate the diffusional behavior of the Ni(II)/Ni(I) and the Co(II)/Co(I) redox couple, Ip vs v$^{1/2}$ was plotted (inset of Figure 2A and 2B). Results show that the redox processes are diffusion controlled in all the range of scan rate evaluated, for both ionic liquids.

Table I: Potentials of the M(II)/M(I) redox couple in different media versus Ag/AgCl. Scan rate 5 mv/s.

Solvent- [M^{+n}(cyclam)Cl$_n$] (M= Ni^{+2} y Co^{+3})	**E$_{pa}$ (V)**	**E$_{pc}$ (V)**	**ΔE$_p$ (mV)**	**Reversibility**
H$_2$O:ACN [26]-Ni^{+2}	-1.43	-1.48	50	Reversible
BMImBF$_4$-Ni^{+2}	-1.36	-1.42	64	Quasi-reversible
BMImNTf$_2$-Ni^{+2}	-1.39	-1.49	100	Quasi-reversible
ACN-Co^{+3}	-0.20	-0.29	90	Quasi-reversible
BMImBF$_4$-Co^{+3}	-0.16	-0.27	104	Quasi-reversible
BMImNTf$_2$-Co^{+3}	-0.26	-0.35	98	Quasi-reversible

Despite of the quasi-reversibility of the electrochemical systems studied, diffusion coefficient (D$_0$) was determined for [M^{+n}(cyclam)Cl$_n$] (M= Ni^{+2} y Co^{+3}) in both BMImNTf$_2$ and BMImBF$_4$ from the voltammograms using Randles-Sevcik equation (1) [49,50]:

$$I_p = 0{,}4463\,(n\,F)^{3/2}\,A\,C_0\,D_0^{\,1/2}\,v^{1/2}\,(RT)^{-1/2} \qquad (1)$$

Where n is the number of electrons, F the Faraday's constant, A the electrode area in cm^2, C$_0$ the complex concentration in mol cm^{-3}, D$_0$ the diffusion coefficient of the electroactive species, v the scan rate in V s^{-1}, R the gas constant in J mol^{-1}K^{-1} And T the absolute temperature in K. In order to stablish a point of comparison between both systems in terms of the charge transfer rate for the M(II)/M(I) redox couple, standard rate constant k$_0$ was calculated using Nicholson's method previously reported in literature [51]. Where the faster M(II)/M(I) electrochemical system is for Ni complex in BMImBF$_4$.

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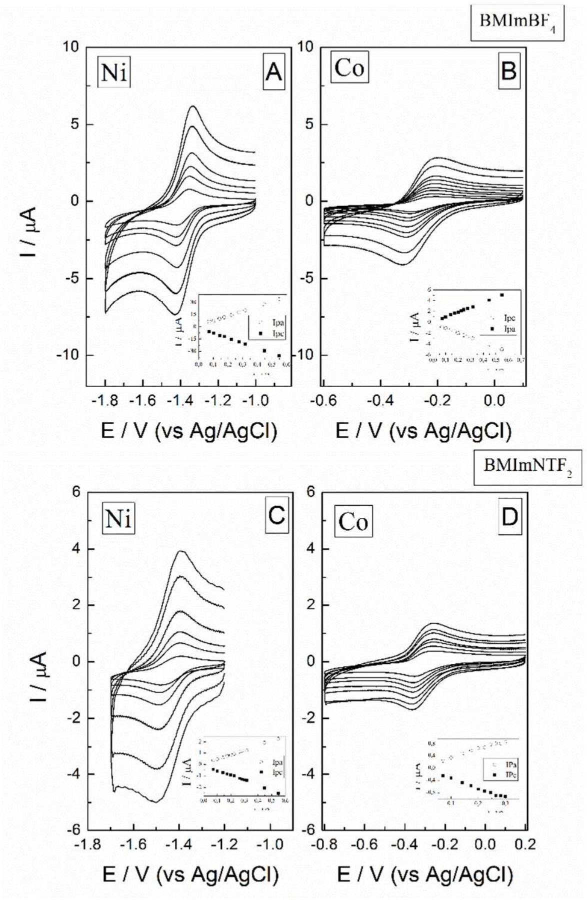

Figure 2: Electrochemical behavior of the redox couple [M^{+n}(cyclam)Cl_n] (M= Ni^{+2} y Co^{+3}) dissolved in $BMImBF_4$ (A and B), and $BMImNTf_2$ (C and D); when the scan rate varies from 5 to 300 mVs^{-1}. 5,10, 20, 30, 50, 75, 100, 200 300. The inset of each figure corresponds to the plot of Ip versus $v^{1/2}$.

From the results shown in table II, it is possible to observe that D_0 for the complexes in $BMImNTf_2$ is one order of magnitude smaller than the calculated in $BMImBF_4$, considering that the redox reaction under survey is a mass controlled process, D_0 has a direct impact in the ΔEp value of the redox couple and also, due to the calculation method used, on the K_0 value. It seems contradictory considering that according to the Stokes-Einstein relationship [38], diffusion of a species depends inversely on the viscosity of the medium and also on the size of the species at a given temperature , hence the complex in $BMImNTf_2$ should have a bigger D_0 value.

A possible explanation to these results can be given in terms of the diffusion phenomena of charged species in ionic liquid media. According to Katayama [38], diffusion of charged species in ionic liquids strongly depends on coulombic interactions between diffusing species and the ionic liquid ions. Thus, considering the size and the structure of the NTf_2^- anion with a localized charge between nitrogen and sulfur atoms and also a strong tendency to form hydrogen bonds with the most acidic proton of the imidazolium cation; diffusion coefficients of $[M(cyclam)]^{+2/+1}$ might present a higher resistance to the transport of species trough the structure of the solvent, leading to a lower diffusion coefficient than $BMImBF_4$ ionic liquid. This trend is in well agreement with the experimental data obtained (See Table II).

On the other hand, k^0 values follow the same trend observed for D_0, giving important insights about the electrochemical reaction at the electrodic surface. According to Marcus theory, [38] k^0 values depends on a series of parameters, among them the viscosity of the solvent and the reorganization energy. For $BMImBF_4$, k^0 value is ten times larger than for $BMImNTf_2$ and its viscosity is lower than $BMImBF_4$. Then it is possible to infer that metal center reduction (Ni(II)/Ni(I)) in $BMImBF_4$ requires a lower reorganization energy, hence, solvent molecules favor geometrical changes in the reduced complex.

On the other hand, a possible explanation for $BMImNTf_2$ behavior can be based in its ability to produce stronger cation-anion interactions, stabilizing one of the oxidation states of the complex, explaining the higher ΔE_P observed, hence its reorganization energy is high enough to ignore the fact that viscosity is considerably lower in case of $BMImNTf_2$.

Table II: Electrochemical parameters calculated.

Ionic Liquid -[M^{+n}(cyclam)Cl_n] (M= Ni^{+2} y Co^{+3})	D_0 (cm^2/s)	ko (cm/s)
$BMImBF_4$-Ni^{+2}	1.92 * 10^{-9}	(1.86± 0.07)* 10^{-4}
$BMImBF_4$–Co^{+3}	2.80* 10^{-9}	(4.86±0.16)*$10-^5$
$BMImNTf_2$-Ni^{+2}	4.09* 10^{-10}	(2.06±0.09)* 10^{-5}
$BMImNTf_2$-Co^{+3}	2.98* 10^{-9}	(1.31±0.1)*10^{-5}

Electrocatalytic activity experiments.

The electrochemical activity of the complexes dissolved in ionic liquids toward the reduction of CO_2 is shown in Figure 3. In the case of $[Ni(cyclam)]^{+2,}$ an increase in the current at -1.4 V is observed at the potential where the redox couple Ni(II)/Ni(I) takes place [26] in both ionic liquids. According to previously reported works [26,52,53], a possible mechanism for this complex toward the reduction of carbon dioxide in ionic liquids can be stated considering the information available in molecular solvents, being the reduced catalyst ($[Ni(I)(cyclam)]^+$) the responsible of the reduction of CO_2, coordinating the carbon atom to the metallic center. Carbon dioxide is then monoreduced to form CO and oxalate, then it could be reduced again to form multiple products. Regarding the Co(cyclam) complex there is not an observable change in current associated to the Co(II)/Co(I) redox couple, thus

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electrocatalytic activity of [Co(cyclam)Cl_3] evaluated by this method can be considered as sluggish. Those facts must be confirmed by potential controlled electrolysis. To identify the reaction products from the reduction of CO_2 in BMImBF$_4$ and BMImNTf$_2$, controlled-potential electrolysis (CPE) at -1.4 V was performed.

As a control experiment, electrolysis without the presence of carbon dioxide were carried out, after the electrolysis carbon monoxide was not detected in the gas phase, evidencing that CO production is directly related to CO_2 presence. occurring at similar potentials in molecular solvents, fact corroborated by the high value of faradaic efficiency calculated and shown in table III.

In the case of [Ni(cyclam)Cl_2], after four hours of electrolysis, carbon monoxide was detected in a gas phase, yielding 47.3 mmol in BMImBF$_4$. CO was the only reaction product detected in the head space [32], confirming the selectivity of the catalyst toward the CO production over other electrode processes

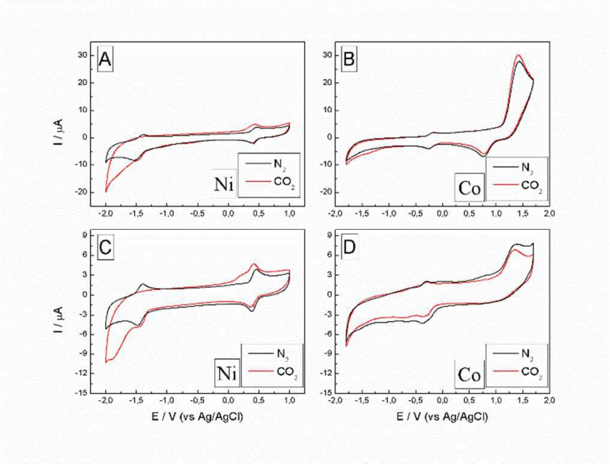

Figure 3: Electrochemical behavior of the system in BMImBF$_4$ (A and B) and BMImNTf$_2$ (C and D), [Ni(cyclam)Cl_2] and [Co(cyclam)Cl_2]Cl at 9,7 mM and 2 mM respectively, both saturated with N_2 (black line) and CO_2 (red line), at 100 mV/s .

On the other hand, electrolysis carried out with [Co(cyclam)Cl_3] in solution at -1,4V shows a very small production of CO, being 10 times smaller than what is produced by [Ni(cyclam)].

In case of BMImNTf$_2$, it is observed that production of CO is similar and considerably lower in both complexes, due to the effect of the NTF$_2$ anions on the electrochemistry of carbon dioxide. This effect can be intimately related with the capacity of the solvent to dissolve carbon dioxide, property which is mainly given by the fluorinating degree of the anion [54].

Considering the last, BMImNTf$_2$ could absorb a greater quantity of carbon dioxide, the anion-CO_2 interaction would impede the availability of free carbon dioxide for its further reduction, lowering the overall efficiency of the process [54].

Since fluorinated anions overcome decomposition in presence of water [19,55], leading to formation of H^+, F^- and BFO$_x$ species, hydrolysis of the anions of the ionic liquids was studied in a blank electrolysis carried out in presence of the catalyst and with the dried ionic liquid saturated with N_2.

The catholyte was analyzed with F^{19}NMR and H^1NMR, spectra are shown in Figure 4.

Figure 4A shows the H^1NMR spectrum of the catholyte analyzed after bulk electrolysis, it is clear that all the protons are present and the chemical structure of the anion keeps its original integrity. After analysis of chemical shift and integration (see supporting information), stability of the cation can be checked by confirming the presence of the singlet at 8.54 ppm, which is associated to the most acidic proton of the imidazolium cation, its presence ensures the integrity of the ionic liquid after the electrolysis. Figure 4B shows the F^{19}NMR spectra. In the range studied it is possible to observe only one signal, meaning that only one species of fluorine (BF_4^-) is present in the ionic liquid, and hence, no HF is produced as a result of hydrolysis of the anion, meaning that the reactions that take place during the electrolysis and the production of CO do not depend on possible decomposition products coming from hydrolysis of the ionic liquid (BMImBF$_4$).

TON and faradaic efficiency values are well related with the electrochemical data previously shown, indicating that [Ni(cyclam)Cl_2] shows a higher activity towards the electrocatalytic reduction of carbon dioxide, this result can be explained by the existence of the Ni(I) species, which can be considered as the active site of the complex. Faradaic efficiency calculated for both complexes in BMImBF$_4$ are considerably

Table III : Product distribution for carbon dioxide reduction in the ionic liquids and complexes studied.

Property	***BMImBF$_4$ – Ni(cyclam)***	***BMImBF$_4$ – Co(cyclam)***	***BMImNTf$_2$- Ni(cyclam)***	***BMImNTf$_2$- Co(cyclam)***
CO formed (μmol)	47.30	4.49	3.50	2.26
TON	2.19	0.22	0.17	0.11
TOF (h^{-1})	0.73	0.08	0.06	0.04
Faradaic Efficiency %	95.2	84.9	75.1	62

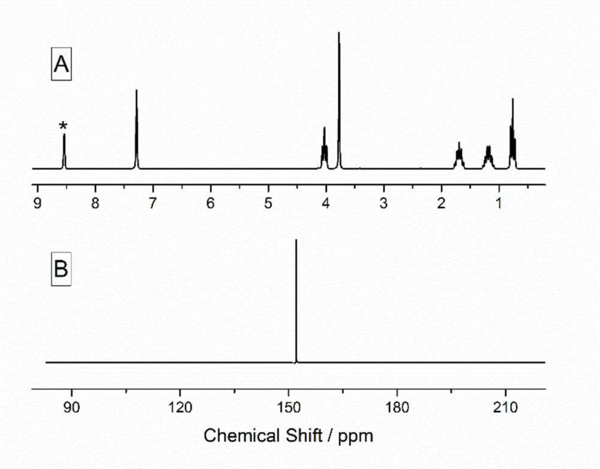

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Figure 4: A) H^1NMR and B) F^{19}NMR spectra of $BMImBF_4$ after 4 hours of potential controlled electrolysis at -1,4V vs Ag/AgCl.

high (95.2% and 85.9% respectively), meaning that under these conditions, CO is the main product, however the particularly low TON values calculated for [Ni(cyclam)Cl_2] indicate that the complex may deactivate during the electrolysis.

FT- IR Spectroelectrochemical Study

In order to establish a possible mechanism for the reduction of carbon dioxide with [Ni(cyclam)Cl_2] in $BMImBF_4$, FT-IR spectroelectrochemical measurements were carried out.

Figure 5 shows IR spectra carried out before and after 10 minutes of electrolysis at -1.4V. Inset of Figure 5 shows the spectroelectrochemical behavior of the complex under inert atmosphere in which it is possible to observe a signal at 2330cm^{-1}, assigned to an anti-symmetric tension of the CO bond in the CO_2 molecule; absorbance of this band remains constant during the application of the potential, indicating that carbon dioxide detected in the spectra correspond to traces present in air of the sampling chamber.

After saturation of the complex solution with carbon dioxide, a great increase in the band at 2330cm^{-1} is observed at open circuit potential (solid line), also, no other bands with considerable intensity are observed.

After application of -1.4 V vs Ag/AgCl (dashed line), a decrease in the vibration at 2330 cm^{-1} is observed, as well as the progressive apparition of two new vibrations at 2042 cm^{-1} and 1950 cm^{-1}. These results indicate that carbon dioxide is consumed and that new species are generated during the application of electrochemical potential. Further search for other probable products such as oxalate was carried out with no observable results within the sensitivity capabilities of the instrument.

According to Kubiak and co-workers in a previously reported work [53], the band at 2042 cm^{-1} can be associated to the apparition of the intermediary specie [Ni(cyclam)(CO)]$^+$. On the other hand, band at 1950cm^{-1}, can be attributed to the generation of $Ni(CO)_4$ [53] *(**Warning**: Small amounts of highly toxic $Ni(CO)_4$ can be generated during the reduction of Ni complexes in the presence of CO.).*

Taking the last result in account and also the work made by Kubiak and co-workers in molecular solvents [53], it is possible to affirm that the active species toward the reduction of carbon dioxide is the reduced complex i.e. [Ni(cyclam)]$^+$, which can coordinate carbon dioxide to reduce it afterwards, forming CO as the main product. Once CO is formed, the reduced complex reacts with it, forming [Ni(cyclam)]$^+$ and due to the higher complex formation constant [25,53,56], $Ni(CO)_4$ is formed. This last phenomenon could deactivate the complex and probably explain the unexpected low TON values shown.

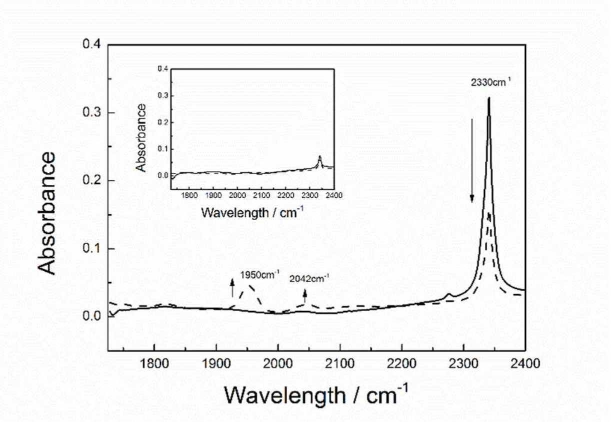

Figure 5: IR-in situ spectroelectrochemical behavior of the [Ni(cyclam)Cl_2] complex in $BMImBF_4$ saturated with N_2 (Insert) and CO_2 at open circuit potential (solid line) and after 10 minutes of electrolysis at -1.4V (dashed line).

Conclusions

The electrochemical reduction of carbon dioxide using [M^{+n}(cyclam)Cl_n] (M= Ni^{+2} y Co^{+3}) complexes in ionic liquids was studied for the first time, finding that [Ni(cyclam)Cl_2] shows a better performance than [Co(cyclam)Cl_3]. The effect of the solvent was studied using two different ionic liquids, finding that an hydrophilic ionic liquid like $BMImBF_4$ increases the catalytic activity of the system, while $BMImNTf_2$ shows very low values of TON, indicating that the solvent has a major impact on the performance of the system.

The products were analyzed from the gas phase in all the systems studied, finding only CO, a carbon neutral product, as the only reaction product, meaning that the system is selective towards the formation of carbon monoxide over the proton reduction, process that could be an interferent, especially in hydrophilic media in which the presence of water could lead to H_2 production or either more reduced products.

In $BMImBF_4$, [Ni(cyclam)Cl_2] presents an spectroelectrochemical behavior similar to molecular solvents. Potential controlled electrolysis followed by in-situ FT-IR carried out at -1.4V vs Ag/AgCl shows the formation of [Ni(cyclam)CO]$^+$ which appears as a reaction intermediary.

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