Exploring the use of CO$_2$-expanded ionic liquids as solvents in microextraction of 3,3′,4,4′-tetrachlorobiphenyl from aqueous solutions

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ABSTRACT

This paper explores the effect of adding supercritical carbon dioxide (scCO$_2$) to Ionic Liquids (ILs) for the microextraction of very diluted pollutants from aqueous matrices. The proposed system uses an IL, trihexyl-tetradecyl-phosphonium bis(trifluoromethylsulfonyl)imide ([P$_{6,6,6,14}$][Tf$_2$N]) and 1-hexyl-3-methyl-imidazolium tris(pentafluoroethyl)trifluorophosphate ([*hmim*][FAP]), as extractant, and scCO$_2$ as diluent that may change the solvent capacity by changing the solvent polarity. The study was first carried out for the extraction of 3,3′,4,4′-tetrachlorobiphenyl (PCB-77) from aqueous solutions using a designed microextraction cell. Different ILs, sample volumes and kinetics of extraction were investigated. Results show that within 15 min the maximum extraction percentage was achieved employing a scCO$_2$ partial pressure of 80 bar. To investigate the influence of the polarity change by the presence of carbon dioxide more broadly, other pollutants with different water solubilities were used. It was observed that scCO$_2$ (partial pressure) reduced the recoveries for benzophenone and PCB-77 but increased the extraction of triclosan. This is due to the change on solvent's polarity and viscosity of the mixture. This was corroborated through a ternary system simulation including IL-pollutant-scCO$_2$. All these results establish that the combination of CO$_2$ and IL can in some cases enhance the extraction, but the affinity between the pollutant and scCO$_2$ is a key parameter that discerns whether expanding the IL with scCO$_2$ is beneficial for the extraction.

Introduction

Polychlorinated biphenyls (PCBs) are classified as persistent organic compounds, are lipophilic, and are highly resistant to metabolism (Van den Berg et al., 2006). According to Borja et al. (Borja et al., 2005), due to these properties, the Chemical Treaty on Persistent Organic Pollutants (POPs) has listed these as priority chemicals for eventual elimination by 2025. This concern arises because they are carcinogens, and they alter the immune system function (Carpenter, 2006). Therefore, their control and quantification would be of great importance.

The main problem in quantifying PCBs is their low solubility in water. To make these compounds measurable by standard equipment such as gas chromatography (GC) or high-pressure liquid chromatography (HPLC); it is necessary to concentrate them multiple times in a solvent. Consequently, their quantification becomes challenging. The miniaturization of conventional techniques like Solid-Phase Microextraction (SPME) (Kumar et al., 2008) has appeared as a solution for this issue, however, SPME has the main disadvantage of prolonged extraction times due to slow kinetics. Another technique widely used is Hollow Fiber-Liquid Phase Microextraction (Rasmussen and Pedersen-Bjergaard, 2004) (HF-LPME), which faces similar problems as those of SPME, in addition to fiber breakage. Finally, Liquid-Liquid Phase Microextraction (LLME) (Shishov et al., 2022; Yang et al., 2019; Najafi and Hashemi, 2020) and Dispersive Liquid-Liquid Phase

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Microextraction (Rezaee et al., 2006; Tuzen et al., 2021; Rykowska et al., 2018) (DLLME) appears as a good alternative because it is less prone to mass transfer limitations than the two previous techniques, and it is inexpensive and simple to implement (Poole, 2020).

DLLME has the same basis as the traditional liquid-liquid extraction process (Schuur et al., 2019) but in its miniaturization, a few milliliters of a sample are brought in contact with a mixture of microliters of extractant (usually a conventional solvent) and a larger volume of dispersant with intermediate polarity between the sample and the extractant (Rezaee et al., 2006; Rezaee et al., 2010). The first solvent carries out the extraction of compounds of interest, while the second reduces the interfacial tension between the extractant and the sample to promote the creation of a dispersed solvent (emulsion), enhancing the mass transfer processes. In this context, different methodologies have been investigated for the quantification of POPs. For example, Rezaei et al. (Rezaei et al., 2008) used a combination of Chlorobenzene (extractant) and acetone (dispersant) for the extraction of 10 different PCBs (PCB-28, PCB-52, PCB-101, PCB-105, PCB-118, PCB-126, PCB-138, PCB-153, PCB-170 and PCB-180), obtaining extraction percentages (%E) from 92 to 105 %, and this variation depends on the PCB congener. Dai et al. (Dai et al., 2010) used a derivation of DLLME to quantify PCBs based on the melting point of extractant, a mixture of 1-undecanol and acetonitrile as the dispersant and extractant, respectively, obtaining %E between 80 and 108 %. Results over 100 % show the difficulty of this methodology in extracting pollutants from very diluted systems. Over 100 % is reached due to some error given by the analytical equipment being traduced in this kind of value.

Despite the high recovery rates reported in those studies, the problem related to using toxic and volatile solvents is present (Zhao et al., 2012). Additionally, high volumes of dispersant, around 3 - 10 times higher than extractant volumes (Sarafraz-Yazdi and Amiri, 2010; Rutkowska et al., 2019; Spietelun et al., 2014; Ezoddin et al., 2015), have been reported. The large volumes of dispersant can result in potential changes in the extractant's phase polarity, solubilization of the solvent in the aqueous phase decreasing or nullifying the extraction capability of highly non-polar compounds.

Development of new techniques and task-specific solvents arises to find alternative methods to quantify compounds in a safe way. As such, these new solvents may not only be applied for DLLME, but also for remediation and implementation in new greener techniques such as solvent-impregnated resins (Kabay et al., 2010; Kumar and Datta, 2022; Wieszczycka et al., 2020).

A specific example of new green solvents often reported in literature are the ionic liquids (ILs) (Chen et al., 2022; Wang et al., 2020; Liu and Xu, 2021; Salar-García et al., 2017; Sada Khan et al., 2021; Rabhi et al., 2022). ILs appear as an alternative to replace conventional solvents due to properties such as negligible vapor pressure, tunable properties, and high thermal resistance (Huddleston et al., 1998; Li et al., 2016; Zhang et al., 2013), among others. However, these compounds exhibit higher viscosity than conventional solvents resulting in long extraction times (Huddleston et al., 1998). For example, trihexyl-tetradecyl-phosphonium bis(trifluoromethyl-sulfonyl)imide IL (Fillion et al., 2017) has a viscosity of 318 [mPa·s] (at 298.15 K), which is significantly higher than the 0.892 [mPa·s] and 0.297 [mPa·s] values of the ordinary organic solvents cyclohexane and hexane (Aminabhavi et al., 1996), respectively. As with many other chemical engineering processes, thermodynamic equilibria and kinetic aspects often show a difference in optimum system performance. Despite the significant drawback of large mass transfer limitations, ILs have been applied in the microextraction of pollutants such as pesticides, insecticides, aromatic compounds, and chlorinated compounds (Meischl et al., 2019; He et al., 2009; Liu and Quan, 2020; Liu et al., 2009; Yao and Anderson, 2009; Han et al., 2012; Zhang et al., 2017), yielding high recovery rates. So, the thermodynamic solvent performance is beneficial while the kinetic behavior is challenging due to the high viscosity. Improvement of most of these quantifications employ conventional dispersants such as acetone, methanol, or ethanol. An alternative to using volatile organic compounds is the dissolution of carbon dioxide (CO_2) in ILs which has been studied and applied (Khanpour et al., 2014; Alvarez and Salda, 2012). This method, as demonstrated by Tomida et al. (Tomida et al., 2007; Tomida et al., 2011), Ahosseini et al. (Ahosseini et al., 2009), Morais et al. (Morais et al., 2019), and Li et al. (Li et al., 2021) can effectively reduce the viscosity of ILs when CO_2 is solubilized. For example, Tomida et al. (Tomida et al., 2011) reported a decrease of around 90 % in viscosity at 293 K and 20 MPa for 1-hexyl-3-methyl-imidazolium hexafluorophosphate; which could be translated into better kinetics and fast extraction of contaminants. The solubilization of CO_2 at supercritical conditions ($scCO_2$) in IL is commonly reported as a physisorption process (Farsi and Soroush, 2020; Schro et al., 2009) in which CO_2 uses the free space inside cations and anions. This reduces the polarity of the mixture produced by IL and $scCO_2$, which can be beneficial for the extraction of non-polar compounds. To our knowledge, this is the first time that the combination of two green solvents: $scCO_2$ dissolved in an IL, is used for the microextraction of toxic pollutants, specifically, polychlorinated biphenyls (PCBs) present in small concentrations in water. Thus, this new proposal for DLLME technique must be systematically evaluated in terms of operating parameters and how the $scCO_2$ influences microextraction.

Therefore, this work conducts a systematic analysis of the effect of adding supercritical Carbon Dioxide to Ionic Liquids for a new DLLME that combines the IL trihexyl-tetradecyl-phosphonium bis(trifluoromethylsulfonyl)imide [$P_{6,6,6,14}$][T_f2N] as extractant and $scCO_2$ as separation enhancer for the microextraction of 3,3′,4,4′-Tetrachlorobiphenyl (PCB) from aqueous solutions. Along with this, a polarity analysis is performed by extracting analytes with different water solubilities.

Experimental

Materials

3,3′,4,4′ Tetrachlorobiphenyl (PCB-77) with a purity of 98.7 % (by chromatographic analysis) was purchased from Sigma-Aldrich® (Merck KGaA, Darmstadt, Germany). Triclosan and Benzophenone were purchased from Merck© both with purities higher than 90 %. The ionic liquids trihexyl-tetradecyl-phosphonium bis(trifluoromethylsulfonyl) imide ([$P_{6,6,6,14}$][Tf_2N]) and 1-hexyl-3-methyl-imidazolium tris(pentafluoroethyl)trifluorophosphate ([$hmim$][FAP]) both with a purity higher than 98 % were obtained from IOLITEC (Heilbronn, Germany) and Merck® (Darmstadt, Germany), respectively. Carbon dioxide of 99.99 % (w/w) purity was purchased at GasLab® (Chile). For the chromatographic analysis, acetonitrile HPLC grade (99.9% w/w) was obtained from Merck® (Darmstadt, Germany). All the reagents were used without further purification.

Chromatographic conditions

The quantification of the PCB-77 after microextraction was performed using High-Performance Liquid Chromatograph Jasco LC Net II system with a manual injector (IH-7725I), a quaternary gradient pump (PU-4180), and a diode array detector (MD-4010). The column was a C18 from Nova-pack® (4 μm particle size, 60 Å pore size, 150 mm x 3.9 mm), maintained at 40 °C in isocratic elution mode using acetonitrile: water (80:20) at a flow rate of 0.9 mL/min. The injection volume was 20 μL, and compound detection was carried out at 260 nm. For benzophenone quantification an isocratic elution was also employed, but the acetonitrile:water percentages were modified to 70:30. Finally, for triclosan quantification the mobile phase was established as acetonitrile: methanol:water at 35:35:30 percent, respectively. Both analytes were measured at 260 nm.

High-pressure microextraction setup

Fig. 1 shows the conceptual design of the microextraction process, which consists of three steps:

1 A vial charged with the sample and the IL is put into a microextraction cell that withstands high pressures. Then, the CO_2 is loaded at supercritical conditions.
2 The system is sonicated to ensure the CO_2 absorption by the IL, changing the polarity and reducing the viscosity, promoting the dispersion of the extractant phase to extract the analyte from the sample.
3 Finally, pressure is released, desorbing the CO_2 absorbed from IL, and depositing IL at the bottom of the vial. Then, the IL-phase, enriched with the analyte, is extracted and quantified in analytical equipment.

A flask or vial that can withstand supercritical conditions is required to use $scCO_2$ in the microextraction process. In the case of CO_2 (Kopcak and Mohamed, 2005), pressures above 7.4 MPa and temperatures above 304 K, reported as critical conditions should be overpassed. In addition, the vials containing samples and IL are designed to fit into a falcon tube. This tube is used in the next step, centrifugation, to split the phases and recover the IL charged with the analyte.

Fig. 2a shows the microextraction cell built with high-pressure-stainless-steel piping provided by Swagelok®. The design has a removable reduction in the middle to place the glass vial (Fig. 2c) with the sample and the extractant, previously loaded, inside. Two valves were considered (Fig. 2b) to control the inlet and outlet of CO_2. Additionally, a manometer and a needle valve from Swagelok® were installed before and after the system to ensure that CO_2 was not leaked and to avoid a violent depressurization.

Experimental procedure

A stock solution was prepared by mixing the PCB-77 with acetonitrile, with a concentration of 118.3 ppm. These solutions were used to prepare working and calibration standards. Then, the sample to analyze was prepared by mixing a small amount of this stock solution and milli-Q water (18.2 MΩ·cm). The final concentration was 1 ppm. The $scCO_2$ was supplied by an ISCO syringe pump Teledyne Model 500D.

5 mL of the aqueous sample were introduced inside the microextraction vial, along with 0.104 g of $[P_{6,6,6,14}][T_f2N]$ (around 100 μL). This IL was selected because of its high hydrophobicity of approximately 0.2% w/w (Freire et al., 2008), and high CO_2 absorption (Carvalho et al., 2010). The vial with the IL was placed inside the microextraction cell and connected to the $scCO_2$ line. The syringe pump was then loaded with $scCO_2$ at a desired temperature and pressure. After this step, the inlet valve was slowly opened to fill the microextraction cell with $scCO_2$. Then, this inlet valve was closed and the microextraction was performed for some minutes with the help of an ultrasonic bath (Elmasonic 30H). When finished, the inlet valve was closed, the outlet valve was opened, and the needle valve was slowly opened to control the release of $scCO_2$.

Finally, when the system was slowly depressurized, the vial was withdrawn from the cell, and the phases were centrifuged and separated. The ionic liquid phase was then recovered and analyzed in the HPLC-DAD.

Due to the high viscosity of the IL, containing the PCB extracted, a few microliters of acetonitrile were added to avoid pressure problems in the HPLC. This procedure was carried out either to construct the calibration curve or to quantify PCB-77 after the microextraction.

The results are expressed as recovery percentage through the formula depicted below:

$$\%R = \frac{[PCB]_{IL}}{[PCB]_{aq,0}} \cdot 100 \qquad (1)$$

Where $[PCB]_{IL}$ and $[PCB]_{aq,0}$ are the concentrations of the PCB-77 in the IL and the aqueous phase at the beginning, respectively. For the polarity analysis the same procedure was employed. But in this case to reduce the quantities, volume of the microextraction cell was reduced.

Results and discussion

Kinetics

Fig. 3 shows the recovery percentages obtained at different sonication times with a fixed partial pressure of $scCO_2$ of 80 bar. For the extraction kinetics, extraction time is considered once the $scCO_2$ is loaded into the system and sonication starts. In this way the conceptual design involved three process phases: 1) $scCO_2$-absorption by the IL, 2) the mass transfer of PCB-77 to the solvent phase and 3) release of $scCO_2$.

Analyzing Fig. 3, two regimes are observed. First, as extraction time increases, so do recovery percentages. This increase is sustained for up to
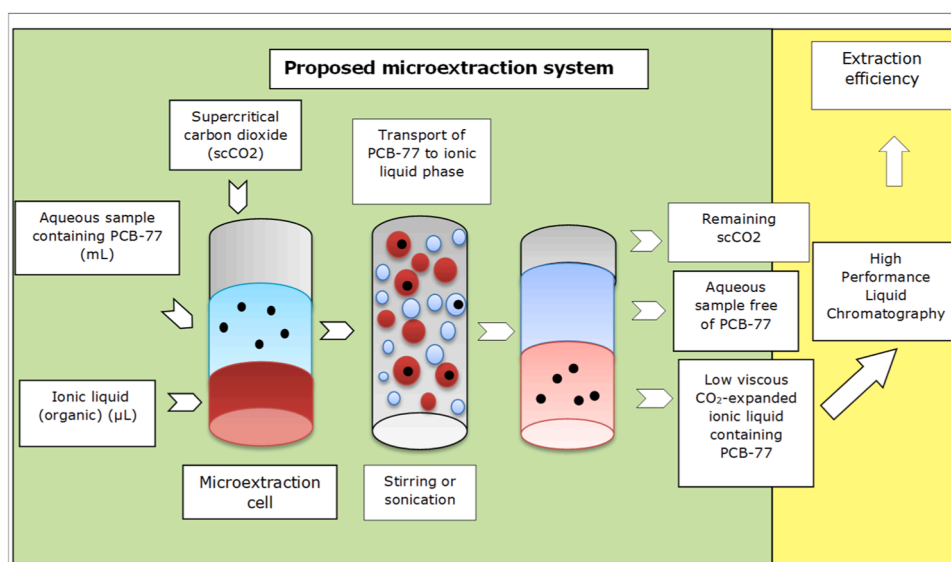

Fig. 1. Schematic representation of the conceptual design for the proposed microextraction process with ionic liquids using $scCO_2$ as a separation enhancer.
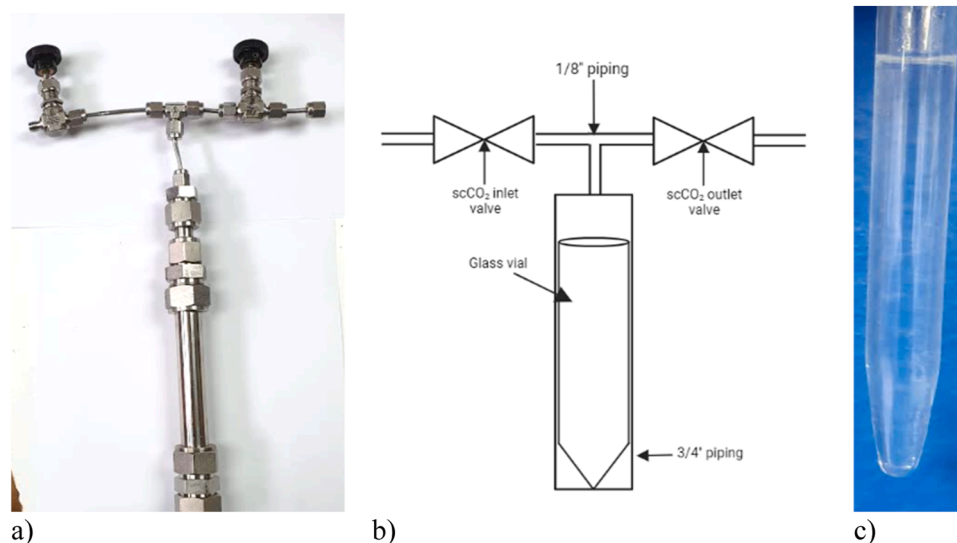
Fig. 2. a) Designed microextraction cell; b) Scheme of the microextraction cell; and c) Designed vial to carry out the microextraction.
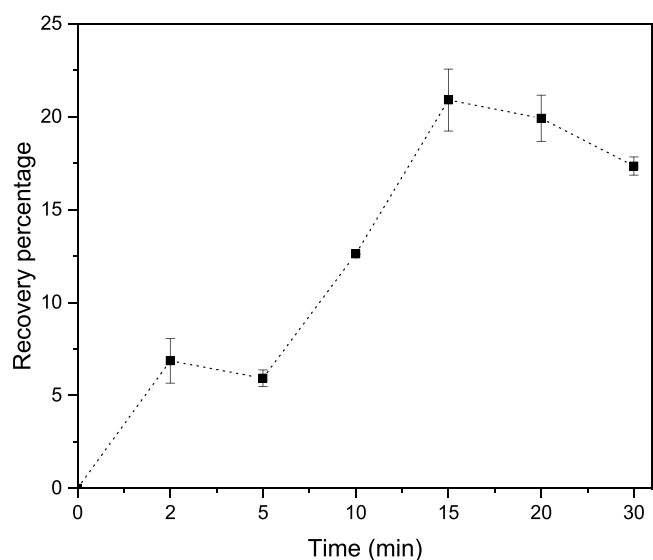

Fig. 3. Kinetics of extraction for PCB-77 at 80 bar of Carbon Dioxide Partial Pressure, initial concentration 1 ppm. Volume of IL and sample: 100 μL and 5 mL, respectively.

15 min due to the contact between phases, which enables the transfer of PCB-77 from the aqueous to the IL phase. At prolonged contacting times, an apparent slight reduction in extraction yield was observed, slightly larger than the experimental errors. It is interpreted as an effect of the uptake of $scCO_2$ into the IL phase, and the free CO_2 which can extract PCB-77 from the system. According to Kawashima et al. (Kawashima et al., 2009; Kawashima et al., 2006), CO_2 can extract dioxins and dioxin-like compounds from fish oil, and one of the compounds reported with the highest removal efficiencies was PCB-77 (Kawashima et al., 2009). So, although there is some solubility of PCB-77 in $scCO_2$, the solubility of PCB-77 in the IL is higher. From the observed trends, it is concluded that initially due to the high level of dispersion due to the $scCO_2$ the extraction rate is enhanced towards the maximum solubility in the $scCO_2$-expanded IL phase. However, after a prolonged time, the IL phase becomes more and more saturated with $scCO_2$ and due to this, the polarity reduces, which in turn reduces the equilibrium solubility of PCB-77. Based on these results, 15 min were selected as extraction time.

Effect of the aqueous/organic ratio on the recovery percentage

Fig. 4 shows the effect of IL volume on the recovery percentage of PCB-77. It is observed that an increase in IL volume leads to a rise in the recovery percentage and maximum extraction is reached at 100 μL; this behavior is consistent with several works (Wang et al., 2010; Berijani et al., 2006). For volumes lower than 37 μL, the quantity of IL available to extract PCB is not enough to be dispersed in the whole volume of the cell, reducing the recovery percentages at fixed time (studied before). When increasing IL amounts, there is a point (100 μL) at which this volume is sufficient to be distributed in the whole sample and then extract the maximum quantity. Above 100 μL a significant decrease in the recovery percentage is found, which can be attributed to a combination between experimental procedures and IL-properties: the IL is put at the bottom of the cell to carry out the microextraction, and an excess of IL prevents a correct dispersion of this in the CO_2, which means low recoveries of the analyte, since the contact surface between the extractant and the analyte decreases. This situation makes IL dispersion difficult as it is denser than water even when $scCO_2$ is absorbed, yielding
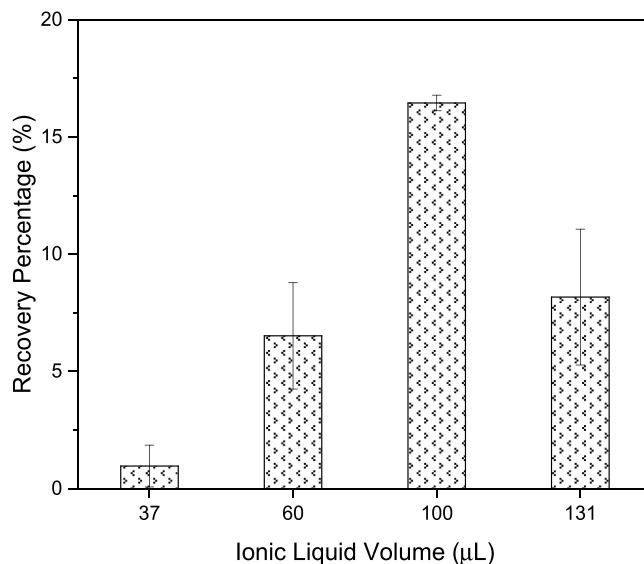

Fig. 4. Effect of IL volume on recovery percentages, initial concentration 1 ppm, extraction time 10 min, sample volume 5 mL.

the lower recovery values found. Besides this, this leads to a new problem that will be studied later, for higher amounts of IL, higher quantities of $scCO_2$ were absorbed, reducing the recoveries. Thus, 100 μL were selected as the extractant volume.

In turn, Fig. 5 shows the recovery percentages as a function of sample volume. According to these results, in general, an increase in PCB-77 recovery is achieved as the sample quantity increases, which has been reported in other works (Yao and Anderson, 2009; Xu et al., 2009). Despite this, a slight increase is observed in the recovery percentages from 2 to 4 mL. When a higher volume of sample is loaded, more PCB-77 is available to be extracted, so the extraction potential increases. It should be noted that a marked increase in recovery was obtained when using 5 mL of sample. The main reason for these results could be due to a combination between the sonication and the quantity added of water sample. When the volume is low, there is enough headspace for water droplets to "jump" until the beginning of the vial and then the effective mass of water which is in contact with the IL is reduced, resulting in lower extraction percentages. As water volume increases, the mass of water reduces this effect and its surface tension, not allowing the droplets to jump, thus enhancing the contact between the phases. A higher sample volume could not be tested since the glass vial allows a maximum of 5 mL. Despite both IL and sample volume optimizations, low recovery percentages are observed. This indicates that the dissolution of CO_2 in a hydrophobic IL at the conditions established is not enough to ensure high recovery percentages.

Additionally, to previous results, it is important to remark that not very high recovery percentages were reached. According to the main hypothesis, the carbon dioxide is solubilized into the IL phase, reducing the solvent's polarity. However, the results showed low values, which need to be explained. Furthermore, the amount of carbon dioxide loaded into the microextraction cell could act as a parallel extractant, which also can explain the low values obtained. In this context, an analysis of different pollutants will be carried out.

Effect of polarity on extractive recovery yield

Next to PCB-77, also for other pollutants with different polarities a study on the extractive recovery has been performed, examining the recovery as a function of pressure. The pressure-dependent recovery was studied to find if this is a critical fact that establishes the role of carbon dioxide in the microextraction. The selected compounds for this analysis were PCB-77 (Walters et al., 2011; Huang and Hong, 2002)
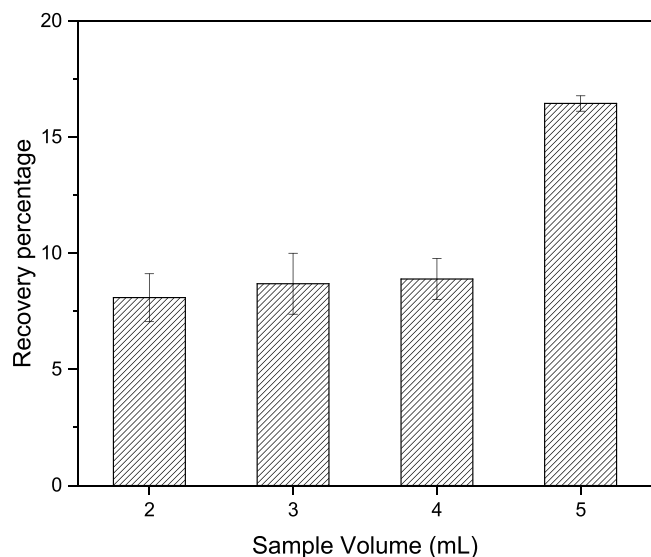
benzophenone (Ouyang et al., 2018) and triclosan (Silva and Nogueira, 2008; Yalkowsky et al., 2016).

For those experiments, the cell volume was reduced and built with a diameter of ½ inch to limit the free CO_2. Due to the reduction of the microextraction cell, the vial was also reduced to 1 mL because a further reduction in volume could make the mechanical drop separation from the aqueous phase difficult for the following chromatographic analysis.

Having discussed this, Fig. 6a and b show the recovery percentages obtained for all the pollutants when using $[P_{6,6,6,14}][Tf_2N]$ and $[hmim][FAP]$ as extractant respectively and the partial pressure of a value of zero corresponds to the system without CO_2, meaning pure IL was in contact with the aqueous solution. As these compounds have viscosities of 318 mPa•s and 45.38 mPa•s for $[P_{6,6,6,14}][Tf_2N]$ and $[hmim][FAP]$ respectively, firstly extraction time was established at 40 min as the necessary time to reach equilibrium when the IL was used as solvent without CO_2. Then this extraction time was used for the rest of $scCO_2$-DLLME experiments.

Due to the microextraction-cell volume reduction, the recovery percentage for PCB-77 improved. On the other hand, when pressure rises, there is a reduction in benzophenone and PCB-77 recovery. Although this behavior looks similar, it can be the effect of two different conditions. The decrease observed in PCB-77 extraction was due to a parallel extraction by CO_2 because of its high affinity with this pollutant. Indeed, this compound exhibits the lowest solubility in water, showing the lowest polarity among the other two pollutants analyzed here. On the other hand, benzophenone has the highest solubility in water (see Table 1) and therefore is more polar than the previous pollutant decreasing its affinity with the mixture CO_2-IL. This explains the decrease in extractive recovery. This assumption is based on the findings of several authors, who have indicated that the mechanism in which ILs absorb $scCO_2$ is related to physisorption (Farsi and Soroush, 2020; Huang and Rüther, 2009; Zanatta et al., 2020), in which the molecules of CO_2 occupy the free space of cation and anion. In this context, the CO_2 molecules produce a rearrangement of the IL structure, affecting their physico-chemical properties. Furthermore, this arrangement could create steric hindrance of the charge present either in the cation or anion of ILs, decreasing the polarity of these compounds and increasing the activity coefficients of polar compounds in CO_2-IL mixtures.

In turn, triclosan increases recovery as pressure rises. The enhancement could be due to the polarity reduction of the solvent mixture. The possibility of triclosan extraction by CO_2 is low, as reported by McAvoy et al. (2002), who addressed the extraction of this compound from 0.5 g of sludge, under operational conditions of 380 bar and 40 °C. They established a static extraction period of 15 min followed by 45 min of a dynamic period of 1 mL/min of CO_2 flow. Furthermore, it was necessary to improve the extraction to add formic acid as co-solvent. Consequently, in comparison with the conditions of the present proposal, it can be established that in terms of time and operational conditions, there are not enough conditions to significantly extract triclosan with CO_2.

While being able to distill some conclusions from the previous discussion, it has been a problem that there is a high deviation between measurements because the extraction takes place in two steps. Due to contact with water, the solubilization of CO_2 in the IL became non-homogeneous, causing an incomplete dispersion of the extractant mixture, which could be one of the reasons for the deviations observed. Additionally, the low amount of these pollutants in the IL generates low signals in the HPLC-DAD, where the noise of the system will contribute to these error bars.

CO_2 – pollutant – IL system modeling

To better understand effects of CO_2 on the extraction of the solutes, the proposed ternary-two-phase-systems were modeled employing Privat et al. algorithm (Privat et al., 2013) with the Peng-Robinson Equation of State to predict fugacity coefficients in both phases. These
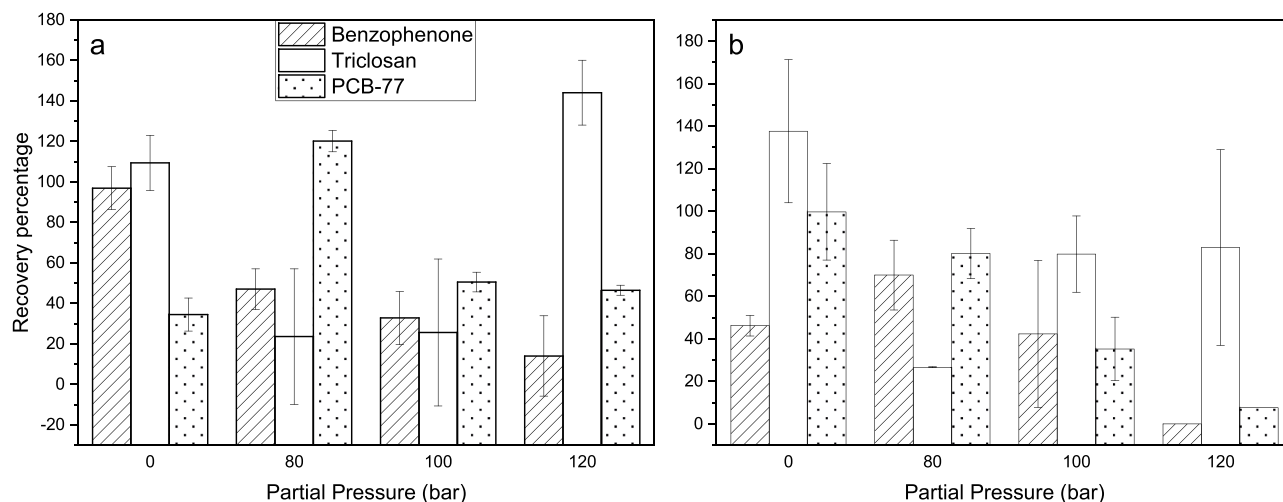
Fig. 5. Effect of sample volume on recovery percentages, initial concentration 1 [ppm], extraction time 10 [min], IL volume 100 [μL].

Fig. 6. Recovery percentages for different analytes studied using (a) $[P_{6,6,6,14}][Tf2N]$ and (b) [hmim][FAP], initial concentration of each pollutant 0.18 ppm, extraction time 40 min.

Table 1

Water solubility and Octanol-Water Partition coefficient of selected compounds.

Compound	Water solubility [ppm]	$\log(K_{OW})$
Benzophenone	114	3.18
Triclosan	10	5.42
PCB-77	$1.25 \cdot 10^{-3}$	6.36

corresponding equilibria are pollutant-IL, pollutant-CO_2 at supercritical conditions and CO_2-IL. For more descriptive information see reference (Ormazábal et al., 2020). Fig. 7a, b and c show the modeled distribution coefficient of PCB-77 between IL and scCO_2 as a function of the pressure. According to these results, as pressure rises, the distribution coefficient decreases, which implies that lower extraction of PCB-77 is achieved by each IL. This agrees with the hypothesis of a competitive parallel extraction given by CO_2. Additionally, PCB exhibits the lowest predicted distribution coefficient which means that this compound presents highest affinity toward carbon dioxide instead of the IL. On the other hand, triclosan shows the contrary behavior, showing its low affinity with scCO_2. For these predictions Van der Waals mixing rule was used since it does not require binary interaction parameters. Even though this will enhance the predictive capability of the model, deviations are expected due to the system being highly non-ideal. From this modeling, the trends can be predicted for the distribution coefficients, and the tendencies agree with the experimental results, establishing the main effect of carbon dioxide in the micro-extraction.

Additionally, as mentioned before, the solubilization of scCO_2 would lead to a viscosity decrease in this mixture with IL, as reported by Li et al. (Li et al., 2021) for tris(perfluoroethyl)trifluorophosphate-based (FAP) ILs, and by Tomida et al. (Tomida et al., 2007; Tomida et al., 2011) for imidazolium-based ILs. Therefore, due to the impossibility of measuring
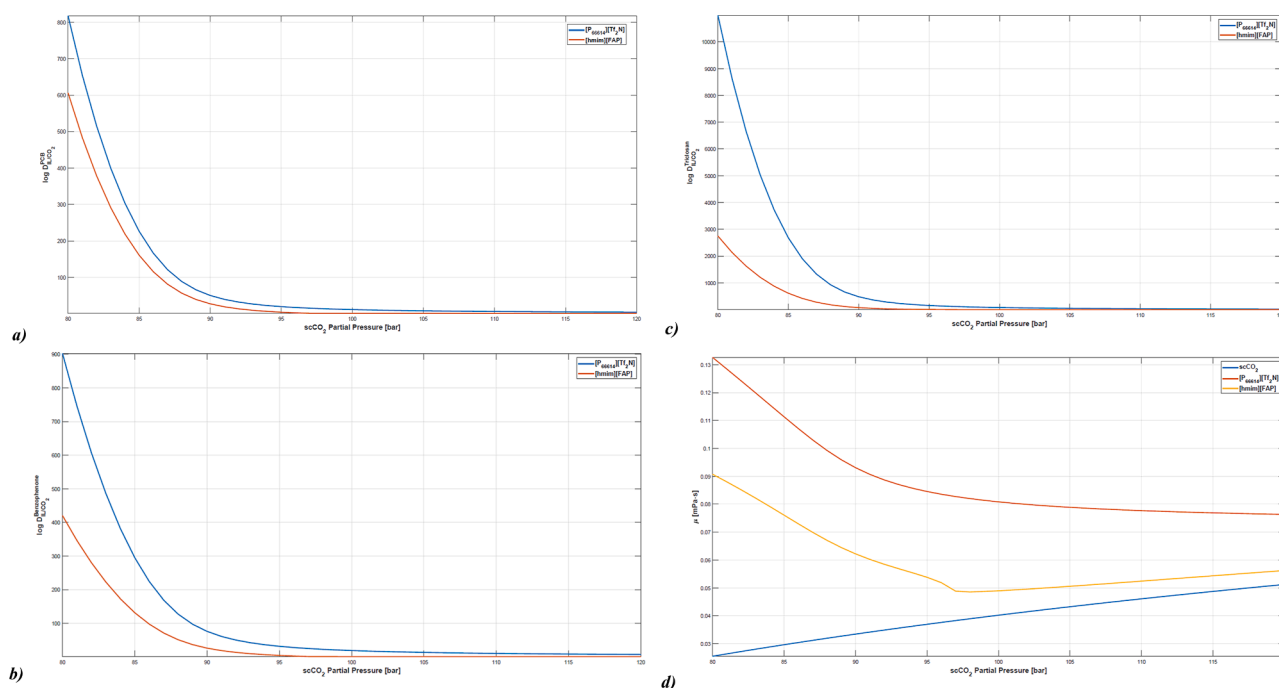

Fig. 7. Predicted distribution coefficient (mass based) of PCB (a), Benzophenone (b), Triclosan (c) between IL and scCO_2 and d) predicted viscosity for CO_2 and its mixture with IL all at 40 °C.

the viscosity of the mixture and establishing the effect of scCO$_2$ on the viscosity of the extracting phase, a predicting simulation was conducted. To this end, Eyring's viscosity model with Peng-Robinson Equation of State was employed (Macías-Salinas et al., 2009). The viscosity of pure ILs is around 318 *mPa·s* and 45.38 *mPa·s* for [P$_{6,6,6,14}$][Tf$_2$N] and [hmim][FAP], respectively. Fig. 7d shows the predicted viscosity values for the mixture at different pressures. According to the modeled results, a significant decrease in viscosity can be observed, reaching values lower than 0.13 mPa●s. This reduction would explain the kinetics previously depicted, Section 3.1, and clearly indicates the existence of viscosity reduction in the IL by scCO$_2$ solubilization. However, when compared with other reports, based on DLLME, the kinetics of this proposed system requires longer times than other IL-based methodologies (He et al., 2009; Fan et al., 2008), which can be explained because the extraction in this system probably will be a two-step process. At first, the IL must absorb CO$_2$; then, the dispersion of the mixture is easily achieved, allowing for the extraction of the pollutant. However, there is a problem with the carbon dioxide which acts as parallel extractant, reducing the IL's extraction capability.

Conclusions

A new methodology for DLLME system has been proposed for PCB-77 extraction, replacing conventional organic solvents with ionic liquids as the extractant and supercritical CO$_2$ as the dispersant phase. To achieve this goal, a microextraction cell was designed to work under supercritical conditions. Variable optimization indicates that 100 μL of [P$_{6,6,6,14}$][Tf$_2$N] and 5 mL of the sample are necessary to obtain the highest recovery percentages. Kinetics in initial experiments showed that around 15 min are enough to reach >25 % of recovery employing a scCO$_2$ partial pressure of 80 bar. These recovery percentages were lower than other microextraction techniques such as DLLME, but by reduction of the cell-volume of the microextraction cell the yields could be much improved. This study showed that it is possible to manipulate the extraction yield by use of scCO$_2$ in combination with ILs in microextraction. A polarity analysis employing Benzophenone, PCB-77 and Triclosan indicated that carbon dioxide plays an important role in the extraction. For PCB-77, scCO$_2$ acts as a parallel extractant, and in the case of Triclosan and Benzophenone, it modifies the polarity of the IL resulting in an increase of the recoveries for Triclosan and a reduction for Benzophenone given by the medium and high polarity of these last two pollutants, respectively. Thus, results reported in this work indicated that scCO$_2$ could help the microextraction, but it mainly depends on the pollutant's polarity. Nevertheless, the optimization of other parameters such as depressurization of the system and mixing to reduce the errors is still necessary.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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