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Supported Ionic Liquid Membranes for Removal of Dioxins from High-Temperature Vapor Streams

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Ⓢ Supporting Information

ABSTRACT: Dioxins and dioxin-like chemicals are predominantly produced by thermal processes such as incineration and combustion at concentrations in the range of 10—100 ng of I-TEQ/kg (I-TEQ = international toxic equivalents). In this work, a new approach for the removal of dioxins from high-temperature vapor streams using facilitated supported ionic liquid membranes (SILMs) is proposed. The use of ceramic membranes containing specific ionic liquids, with extremely low volatility, for dioxin removal from incineration sources is proposed owing to their stability at very high temperatures. Supported liquid membranes were prepared by successfully immobilizing the ionic liquids tri-C_8–C_{10}-alkylmethylammonium dicyanamide ([Aliquat][DCA]) and 1-n-octyl-3-methylimidazolium dicyanamide ([Omim][DCA]) inside the porous structure of ceramic membranes. The porous inorganic membranes tested were made of titanium oxide (TiO_2), with a nominal pore size of 30 nm, and aluminum oxide (Al_2O_3), with a nominal pore size of 100 nm. The ionic liquids were characterized, and the membrane performance was assessed for the removal of dioxins. Different materials (membrane pore size, type of ionic liquid, and dioxin) and different operating conditions (temperature and flow rate) were tested to evaluate the efficiency of SILMs for dioxin removal. All membranes prepared were stable at temperatures up to 200 °C. Experiments with model incineration gas were also carried out, and the results obtained validate the potential of using ceramic membranes with immobilized ionic liquids for the removal of dioxins from high-temperature vapor sources.
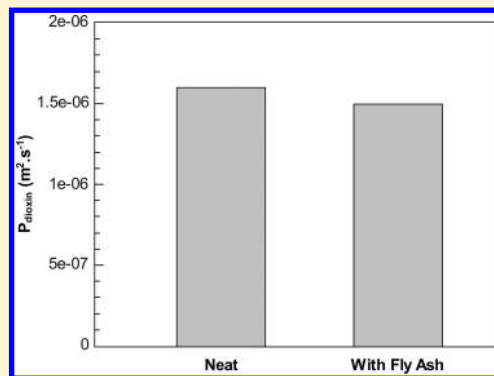
■ INTRODUCTION

Dioxins are a class of structurally and chemically related polyhalogenated aromatic hydrocarbons that mainly include polychlorinated dibenzo-p-dioxins (PCDDs or dioxins), dibenzofurans (PCDFs or furans), and the "dioxin-like" biphenyls (PCBs). They are formed during the combustion of chlorine-containing fuels in municipal solid waste incinerators, coal-fired power plants, and other thermal processes.[1] They are volatile, a property which permits these compounds to vaporize and eventually adsorb onto atmospheric particles. Dioxins and dioxin-like chemicals persist in the environment, bioaccumulate through the food web, and pose a risk of causing adverse effects to human health and the environment.[2] Hence, they are among the 12 POPs (persistent organic pollutants) included in the United Nations Environment Programme (UNEP) list.[3] Due to this, a discharge standard limit of 0.1 ng of international toxic equivalents (I-TEQ) of dioxin/m^3 was put forth by several agencies on the emission of gaseous effluents from thermal processes.[4−6]

Numerous technologies have been developed for dioxins' removal in response to legislation limiting their concentration in flue gases.[7] The most common technology adopted has been adsorption onto activated carbon, often combined with lime injection to remove acids and installed before bag filtration. This process yields solid residues containing carbon contaminated with dioxins, heavy metals, and other toxic compounds, which present a persistent disposal problem. Besides yielding contaminated waste, fixed carbon beds can also pose fire hazards.[8] More recently, the use of catalytic filters and selective catalytic reduction using titanium/vanadium catalysts was proposed for the removal and subsequent destruction of dioxins from the flue gas.[9,10] Using this approach, a high degree of dioxin removal was obtained at 100 °C by adsorption (82%). However, the process efficiency obtained was very dependent on the temperature tested since it influences the adsorption behavior and, in some cases, the dioxin may bond with the catalyst instead of being destroyed.[10]

An alternative strategy for the removal of dioxins from high-temperature vapor streams using supported ionic liquid membranes is proposed in this work. The approach followed in this work involved the development of ionic liquids stable at high
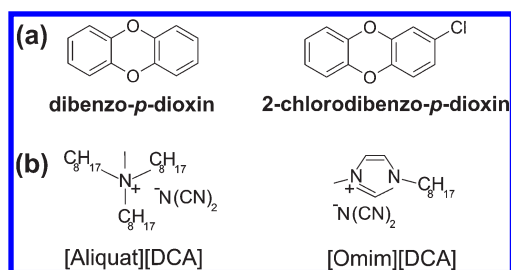
Figure 1. Chemical structures of the (a) dioxins and (b) ionic liquids used for the SILM preparation.

Table 1. Ionic Liquids Tested in the Present Study and Their Most Relevant Properties at 30 °C

ionic liquid	$T_g{}^{a,21}$	$T_d{}^{b,21}$	density^{d,21}	water content ^{e,21}	viscosity^f
[Aliquat][DCA]	−89.94	>300	900	2900	0.198
[Omim][DCA]	−92.93	250	1020	11100	0.046

^{a} T_g = glass transition temperature (°C). ^{b} T_d = decomposition temperature (°C). ^{d} Density at 30 °C (kg·m^{-3}). ^{e} Water content (ppm, μg of H$_2$O·kg^{-1} of ionic liquid). ^{f} Measured viscosity at 30 °C (η, Pa·s).

temperature and their immobilization inside the porous structure of ceramic membranes. This procedure made possible the preparation of membranes with a high mechanical, structural, and chemical stability and also with a high affinity toward dioxin compounds.[11]

Ionic liquids are compounds consisting entirely of ions with a large organic cation and typically a smaller inorganic or organic anion. These compounds have unique properties such as their physical and chemical properties, which can be tuned by tailoring their structures. Therefore, it is possible to design a specific ionic liquid for a specific application. They are liquids at room temperature and have extremely low vapor pressure.

In recent studies,[12] it was proved that ionic liquids can be immobilized inside the porous structure of polymeric membranes, thus obtaining stable supported ionic liquid membranes (SILMs) at pressure differences up to 2 bar. These supported ionic liquid membranes offer high permeation and selectivity and exhibit high stability under harsh conditions. Regarding processing at high temperatures, it was proved that supported liquid membranes (SLMs) with immobilized ionic liquids are stable for gas—gas separations at pressure differences up to 1 bar.[13−15] Also, an absorption study of dioxins using different ionic liquids with different cation alkyl chain lengths and different anions has been reported, and a high affinity for dioxins was found with ionic liquids integrating the dicyanamide anion [DCA]$^-$.[16,17] There are also a number of works mentioning the use of different ionic liquids in ceramic membranes or ceramic fillers for different applications such as sulfur dioxide recovery, fuel cells, and green ester synthesis.[18−20]

Due to the observed ability of ionic liquids to absorb dioxin compounds from a vapor phase above room temperature, and due to their negligible vapor pressure, the concept of immobilizing ionic liquids in porous supports is expected to be an efficient process for the removal of toxic compounds from high-temperature sources by vapor permeation. Also, from an economical point of view, this process presents the advantage of using a small quantity of ionic liquid per membrane area, with a high affinity toward the target dioxin compounds, which are recovered in the downstream side of the vapor permeation system. Additionally, the ionic liquids used are permanently regenerated by stripping of the dioxin compounds to the downstream compartment.

In this work we evaluate the potential of supported ionic liquid membranes, which were prepared by immobilization of previously screened high-temperature stable ionic liquids inside porous ceramic membranes, to remove dioxins from simulated incineration sources at constant pressure conditions. The stability of the supported ionic liquid membranes at high temperatures (up to 200 °C) was determined, and the effect of using membranes with different pore sizes, types of ionic liquid cations

(keeping the [DCA]$^-$ anion), types of dioxins (nonchlorinated or chlorinated), and operating conditions (temperature and flow rate) was evaluated. Finally, a model vapor stream containing dioxins adsorbed in fly ashes was processed to validate the potential of these membranes for dioxin removal under experimental conditions similar to those of incineration and combustion processes.

■ EXPERIMENTAL SECTION

Materials. TiO$_2$ (nominal pore size of 30 nm) and Al$_2$O$_3$ (nominal pore size of 100 nm) inorganic porous membranes from Inocermic GmbH (Germany) were used as supports to prepare supported ionic liquid membranes. Both types of supporting membranes have the same average porosity value of 45%, a thickness of 2 mm, and an active membrane area of 7 cm^2. Scanning electron microscopy (SEM) was used to characterize the structure of these ceramic porous supports (results shown in the Supporting Information). Dibenzo-*p*-dioxin was purchased from TCI Europe, 2-chlorodibenzo-*p*-dioxin was purchased from AccuStandard Inc. (United States, and tri-C$_8$—C$_{10}$-alkylmethylammonium chloride (Aliquat 336) was purchased from Aldrich (Spain). The salt, 1-*n*-octyl-3-methylimidazolium chloride, and subsequent ionic liquids, tri-C$_8$—C$_{10}$-alkylmethylammonium dicyanoamide ([Aliquat][DCA]) and 1-*n*-octyl-3-methylimidazolium dicyanoamide ([Omim][DCA]), were prepared according to Kulkarni et al.[21] To obtain highly pure (optical grade) ionic liquids, the resultant product was collected by filtration and washed with dichloromethane (2 × 25 mL). The combined organic layers were collected, dried (MgSO$_4$), and filtered. The salt was then recovered after passage through a column containing silica and activated charcoal, and the solvent was removed under vacuum. The product was stirred under vacuum overnight. Before use (for analytical and experimental purposes), each ionic liquid was further purified by flash column chromatography (eluent dichloromethane) followed by removal of the volatile components under high vacuum (5 × 10^{-5} mbar) at room temperature for 4—5 h. The structures of the dioxin compounds and ionic liquids used in this work are depicted in parts a and b, respectively, of Figure 1.

The properties of the ionic liquids used in this work are given in Table 1. Some properties of the dioxins tested are shown in Table S1 in the Supporting Information. Both ionic liquids are stable at temperatures higher than 200 °C. All other chemicals were obtained from Fluka (Germany) and were used as received. The gas used in the permeation experiments was nitrogen (industrial grade (99.99%)) from Praxair (United States).

Measurement of Ionic Liquid Viscosity. The viscosity of the ionic liquids selected ([Aliquat][DCA] and [Omim][DCA]) was measured with an RS 75 Rheostress rheometer. The measurements were performed at different temperatures, from 30 to 200 °C.
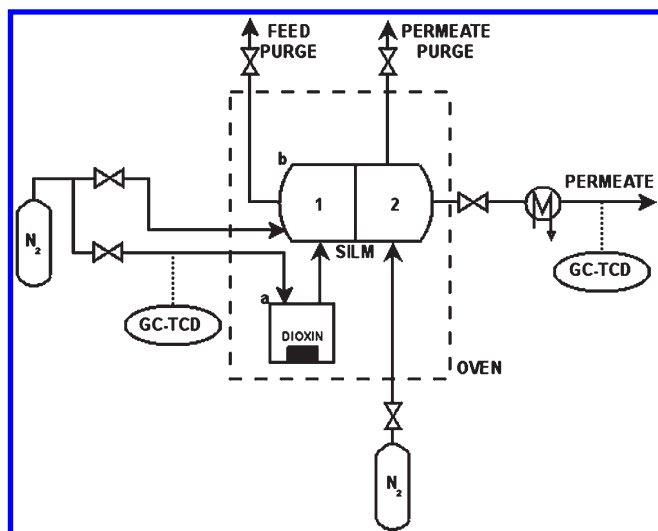
Figure 2. Schematic drawing of dioxin removal from a model incineration source.

Preparation of Supported Ionic Liquid Membranes. To immobilize the selected ionic liquids inside the porous structure of the ceramic membranes, the supporting membrane and ionic liquids were placed inside a vacuum-tight glass chamber, separately. A high vacuum of 8×10^{-6} mbar was applied for 3 h to remove air from the pores, allowing the ionic liquid to be introduced into the pores of the membrane easily. Later, the vacuum was turned off, and the membrane was immersed in the ionic liquid and left overnight for complete immobilization. After immobilization, the membrane surface was cleaned with tissue paper. The amount of ionic liquid immobilized inside the membrane was determined gravimetrically by weighing the membrane before and after the immobilization process.

Dioxin Permeation Experiments. A schematic drawing of the dioxin removal apparatus is shown in Figure 2. It is mainly composed of an oven inside which a stainless steel dioxin vapor generation cell (a) and a vapor permeation cell (b) were placed. To evaluate the potential of SILMs for the removal of dioxins, experiments were conducted at different temperatures (between 150 and 200 °C). First, a small amount of dioxin in the solid state was placed in the dioxin vapor generation cell, and the temperature was increased over 1 h (between 150 and 200 °C) to melt the solid dioxin to its liquid form. Afterward, a N_2/dioxin mixture was generated by sparging N_2 into this reservoir at a controlled mass flow rate. It should be noted that both compartments in the vapor permeation cell are always purged with N_2 before each experiment. This stream, enriched with dioxin vapor, was fed continuously through compartment 1 in the vapor permeation cell, which comprises two identical compartments separated by the SILM. The N_2 partial pressure in the feed compartment (compartment 1) and in the permeate compartment (compartment 2) was kept constant. The volume of both compartments is 15×10^{-6} m^3. A gas flow meter was used to measure the gas flow in both compartments. Dioxin permeation experiments were performed for 5 h. All experiments were performed in duplicate to confirm the reproducibility of the data obtained. Permeates were collected by using cold traps with dry ice and liquid N_2. The collecting traps were washed with dichloromethane, and the dioxin transported through the SILM was determined using gas chromatography with thermal conductivity detection (GC-TCD).[16]

The specifications of the GC-TCD analysis are provided in the Supporting Information. The membrane weight was measured, before and after the permeation experiments, to evaluate its stability at high operating temperatures.

■ RESULTS AND DISCUSSION

A synthetic dioxin vapor stream with concentrations in the range of $1-10$ mg·m^{-3} was prepared by using either dibenzo-*p*-dioxin or 2-chlorodibenzo-*p*-dioxin. Ionic liquids [Aliquat][DCA] and [Omim][DCA] were used due to the fact that they are stable at high temperatures. In a previous study these ionic liquids exhibited the highest dioxin absorption ability at 100 °C when compared with other ionic liquids. The absorption loadings obtained at 100 °C for [Omim][DCA] and [Aliquat][DCA] were 18% and 15.6% ($g_{dioxin}/g_{ionic\ liquid}$), respectively, while for the other ionic liquids tested the absorption loadings were always lower than 5% ($g_{dioxin}/g_{ionic\ liquid}$).[16] Permeation studies were performed at constant pressure conditions and different temperatures, between 150 and 200 °C. A control experiment in the absence of a selective permeating membrane was performed to measure the concentration of dioxin in the feed phase at a given temperature and flow rate.

The dioxin permeability can be obtained from the flux and concentration data from compartments 1 and 2 (shown in Figure 2) according to the following equation:

$$J = K(C_f - C_p) = \frac{P}{l}(C_f - C_p) \tag{1}$$

where J is the dioxin flux (mg·s^{-1}·m^{-2}), K is the mass transfer coefficient (m·s^{-1}), C_f is the dioxin concentration in the feed, compartment 1 (mg·m^{-3}), C_p is the dioxin concentration in the permeate, compartment 2 (mg·m^{-3}), P is the permeability (m^2·s^{-1}), and l is the membrane thickness (m). It is also important to mention that all data presented are average values with a standard deviation lower that 3%.

Effect of the Nominal Pore Size of the Ceramic Supporting Membrane. To study the effect of the nominal pore size of the membranes used to prepare the supported ionic liquid membranes, the ionic liquid [Aliquat][DCA] was immobilized in the 100 nm Al$_2$O$_3$ and in the 30 nm TiO$_2$ ceramic supports. It was observed that the main difference between these supports is that the 30 nm TiO$_2$ support has a thin top layer with a pore size lower than that of the membrane support, while for the 100 nm Al$_2$O$_3$ ceramic support, this pore size difference between the top layer and the support was not detected. It is important to mention that, even though these membranes present a different pore size, they have the same volumetric porosity (approximately 45%). After immobilization of the ionic liquid in the support, the membrane weight was measured and compared with the initial membrane weight (without ionic liquid), and as was expected since both supports have the same size, thickness, and porosity, the amount of ionic liquid immobilized was similar in both ceramic supports (17%, weight of ionic liquid/weight of dry membrane).

Dibenzo-*p*-dioxin gas permeation experiments were carried out at 150 °C with a flow rate of 100 cm^3·min^{-1}. No loss or degradation of the ionic liquid [Aliquat][DCA] was observed at this temperature. This was concluded by weighing the membrane after the experiment and comparing its weight with the initial membrane weight (weight loss lower than 0.05%). These results demonstrate the stability of ceramic membranes with immobilized ionic liquids at high temperatures in both ceramic supports.
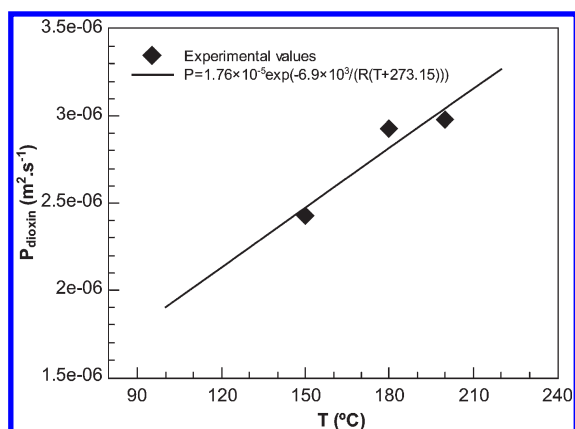
Figure 3. Dibenzo-*p*-dioxin permeability through a 100 nm Al$_2$O$_3$ ceramic membrane with immobilized [Aliquat][DCA] as a function of temperature. Flow rate of 100 cm$^3 \cdot$ min^{-1}.

Figure 4. Logarithm representation of [Aliquat][DCA] and [Omim][DCA] viscosity with the inverse of temperature.

Since a similar quantity of the same ionic liquid [Aliquat][DCA] is immobilized inside the two ceramic supports (with a similar volumetric porosity and similar transport length), the permeability of dioxin was expected to be very similar. However, the experimental results showed that the dioxin (dibenzo-*p*-dioxin) permeability at 150 °C using a flow rate of 100 cm$^3 \cdot$ min^{-1} for the 30 nm TiO$_2$ membrane is lower ($P_{\text{dioxin}} = 1.25 \times 10^{-6}$ m$^2 \cdot$s^{-1}) than that obtained when using the 100 nm Al$_2$O$_3$ ceramic support ($P_{\text{dioxin}} = 2.43 \times 10^{-6}$ m$^2 \cdot$s^{-1}).

The fact that the dioxin permeability is lower for the ceramic support with the smaller pore size may be related to an increase in viscosity of the ionic liquid in more confined pores. Therefore, in the presence of a more viscous, confined, and structured environment, the diffusion of the dioxin through the supported ionic liquid membrane would be more difficult, leading to a lower permeability.

Considering that the porous structure may be represented by an array of cylindrical pores and that their walls are covered by a single monolayer of ionic liquid (diameter 1.8 nm, estimated by using the Avogadro software) with an increased viscosity of $\mu_{\text{layer}} = 10\mu_0$,[22] and considering also that the central part of the pore has the viscosity of bulk ionic liquid, the average viscosity may be given by the following expression:

$$\frac{\mu}{\mu_0} = 1 + 18\left(\frac{d}{r_{\text{p}}}\right) - 9\left(\frac{d}{r_{\text{p}}}\right)^2 \qquad (2)$$

where μ is the area-averaged solvent viscosity within pores (N·s·m^{-2}), μ_0 is the bulk solvent viscosity (N·s·m^{-2}), d is the thickness of the oriented solvent layer near the pore wall (m), and r_{p} is the effective pore radius (m). Substituting all parameters in eq 2, for a pore radius of 100 nm, indicates that the viscosity of [Aliquat][DCA] would increase approximately 1.3-fold in comparison with its viscosity in the bulk, while for a pore radius of 30 nm this increase would be 2.1-fold. These values should be taken as a qualitative indication of increasing viscosity in confined pores, as they were derived on the assumption of having a pore wall viscosity 10 times higher than that of the bulk.[22] Therefore, it is reasonable to expect the viscosity of the ionic liquid in the 30 nm ceramic support to be higher than that in the 100 nm ceramic support, which contributes to the dioxin permeability difference observed. It is important to mention that this analysis
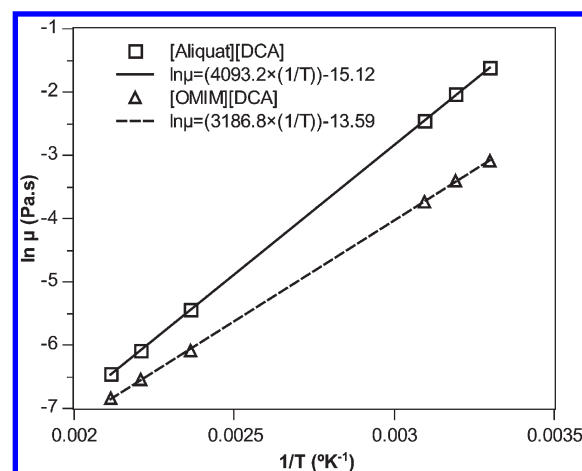
was made considering that both membranes have only pores of 30 and 100 nm size. As observed by SEM images, this is not exactly true. Therefore, differences in morphology, tortuosity, and pore size distribution of both ceramic supports also have to be considered in the analysis of the dioxin permeability differences observed. Even though the porosity is the same, the pore size distribution in both membranes may be different. By SEM image analysis, the 30 nm TiO$_2$ ceramic membrane seems to have a number of rather small pores. Therefore, the effect of increasing viscosity in smaller pore sizes may have a higher impact in the 30 nm TiO$_2$, which results in a lower dioxin permeability.

Effect of Temperature on the Dioxin Permeability. In real conditions, the release of dioxins from thermal sources occurs at temperatures higher than 100 °C. Therefore, permeation studies were carried out at different temperatures to verify their impact on dioxin (dibenzo-*p*-dioxin) permeability. Experiments were conducted at 150, 180, and 200 °C. For this purpose the [Aliquat][DCA] ionic liquid was immobilized in a 100 nm Al$_2$O$_3$ ceramic membrane, and a flow rate of 100 cm^3 N$_2 \cdot$ min^{-1} was kept in both the compartments.

Figure 3 shows that with an increase in temperature the permeability of dioxin (dibenzo-*p*-dioxin) increases. Furthermore, there was no loss of the ionic liquid [Aliquat][DCA] at all temperatures tested, which was verified by weighing the membrane before and after the experiment. These results demonstrate the operating stability of ceramic membranes with immobilized ionic liquids at high temperatures.

In a liquid membrane, the transport of the species occurs generally according with a solution-diffusion mechanism, defined by the relation

$$P = DS \qquad (3)$$

where P is the dioxin permeability and S and D are, respectively, the solubility and diffusivity of the dioxin in the ionic liquid.

Since the diffusion coefficient of a permeating species is directly affected by the viscosity of the ionic liquid, the rheological behavior of the ionic liquids [Aliquat][DCA] and [Omim][DCA] at different temperatures was determined. Figure 4 summarizes the experimental results obtained. The viscosity of both ionic liquids was found to be independent of the shear rate applied, which means that the fluids studied exhibit a Newtonian behavior. The viscosity profile is similar for both ionic liquids, and a decrease in viscosity

was observed when the temperature was increased. This decrease obeys an Arrhenius relationship in the temperature range tested (see Figure 4).

In the literature,[23−25] a number of different correlations are reported for estimation of diffusion coefficients of liquids and gases in ionic liquids. In all these correlations, the diffusion coefficient (D) is proportional to $(1/\mu)^\beta$, μ being the ionic liquid viscosity and β the exponent of correlation. Therefore, it is expected that the effect of temperature on viscosity will have a direct impact in the diffusion coefficient. The diffusion coefficient increases with a temperature increase, and in this case, the transport of dioxin (dibenzo-p-dioxin) through the membrane becomes facilitated at higher temperatures. Therefore, the increase in permeability observed in Figure 3 is explained by the decrease in viscosity of the ionic liquid with the increase of the operating temperature.

Assuming that in the temperature range tested (between 150 and 200 °C), for this specific ionic liquid, the permeability is directly affected by the diffusion coefficient, the experimental permeability results obtained for a 100 nm Al_2O_3 ceramic membrane with immobilized [Aliquat][DCA] were represented as a function of the [Aliquat][DCA] viscosity, as shown in Figure 5. Combining both Arrhenius equations for the permeability and ionic liquid viscosity presented in Figures 3 and 4, respectively, leads to the expression

$$P = (1.76 \times 10^{-5}) \exp\left[-0.203 \ln\left(\frac{\mu}{3.02 \times 10^{-7}} \right) \right] \quad (4)$$

This equation is represented with a dashed line in Figure 5, and it can be observed that for the temperature range tested it is reasonable to assume that the increase in permeability is directly related to a decrease in the ionic liquid viscosity and corresponding increase of the diffusion coefficient of the permeating species. For a given ionic liquid, even if the solubility varies with temperature, its effect on permeability seems to be negligible when compared with the diffusivity effect.

Effect of the Type of Ionic Liquid. The effect of the type of ionic liquid cation (keeping the same ionic liquid anion) was studied by using the 30 nm TiO_2 membrane with two different ionic liquids, [Aliquat][DCA] and [Omim][DCA]. At 150 °C, a higher permeability was observed in the case of the membrane containing the ionic liquid [Omim][DCA] ($P_{dioxin} = 1.60 \times 10^{-6}$ m$^2 \cdot$s^{-1}) when compared with the membrane containing the ionic liquid [Aliquat][DCA] ($P_{dioxin} = 1.25 \times 10^{-6}$ m$^2 \cdot$s^{-1}).

As previously mentioned, the transport of the species occurs generally according to a solution-diffusion mechanism. The diffusion coefficient is directly related to the viscosity of the ionic liquid, and as shown in Figure 4, at 150 °C the ionic liquid [Aliquat][DCA] is 1.9 times more viscous than the ionic liquid [Omim][DCA], leading to a higher resistance to the transport of dioxins. Regarding the solubility coefficient, the dibenzo-p-dioxin absorption equilibrium with different ionic liquids was determined in a previous study.[16] The absorption of this dioxin at 150 °C was not determined, but for a temperature of 100 °C, the absorption by the ionic liquid [Omim][DCA] was 18% (w/w) and that for the [Aliquat][DCA] ionic liquid was 15.6% (w/w). Therefore, since the [Omim][DCA] ionic liquid presents a higher affinity toward this dioxin and it is less viscous, a higher permeability could be anticipated.

Effect of the Type of Dioxin. Dioxins are polychlorinated aromatic compounds whose toxicity depends on the number and positions of chlorine atoms attached to the aromatic ring. It was,
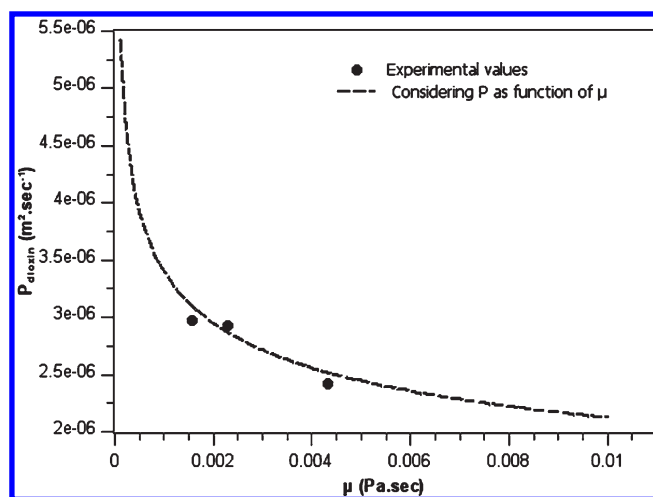

Figure 5. Dibenzo-p-dioxin permeability through a 100 nm Al_2O_3 ceramic membrane with immobilized [Aliquat][DCA] as a function of [Aliquat][DCA] viscosity.

therefore, thought desirable to study the effect of the dioxin type on the permeation process. A chlorinated dioxin compound, namely, 2-chlorodibenzo-p-dioxin was selected for these studies. Experiments were performed under similar conditions of temperature (150 °C), flow rate (100 cm$^3 \cdot$min^{-1}), and time (5 h) through a 100 nm Al_2O_3 support with immobilized [Aliquat][DCA]. The results obtained for this chlorinated dioxin were compared with the results obtained for the dibenzo-p-dioxin at the same temperature. The chemical structures of both dioxins are shown in Figure 1. An increase in the permeability for 2-chlorodibenzo-p-dioxin ($P_{dioxin} = 3.37 \times 10^{-6}$ m$^2 \cdot$s^{-1}) was obtained when compared with the permeability obtained for dibenzo-p-dioxin ($P_{dioxin} = 2.43 \times 10^{-6}$ m$^2 \cdot$s^{-1}).

It should be expected that the diffusion of the largest dioxin compound (2-chlorodibenzo-p-dioxin) through the [Aliquat][DCA] ionic liquid would be lower when compared with that of the smaller dioxin (dibenzo-p-dioxin). However, the presence of a chloride atom in the structure of 2-chloro-p-dibenzodioxin affects its solubility coefficient in the ionic liquid. The presence of this chloride atom in the chemical structure of the dioxin makes it more hydrophobic. This fact is supported by the water solubility values for both dioxins, presented in Table S1 (shown in the Supporting Information). Since [Aliquat][DCA] is a rather hydrophobic ionic liquid, the more hydrophobic dioxin (2-chloro-p-dibenzodioxin) presents a higher affinity toward this ionic liquid, which results in a higher solubility value. Therefore, these results indicate that even though the diffusion coefficient of 2-chlorodibenzo-p-dioxin is lower, its higher solubility determines the higher permeability values observed.

Effect of the Feed and Stripping Flow Rates. The effect of the feed and stripping flow rates on the permeability of dioxin (dibenzo-p-dioxin) was studied by increasing the flow rate of N_2 in both compartments from 100 to 300 cm$^3 \cdot$min^{-1}. The main objective of the experiments carried out using different N_2 flow rates was to study the effect of fluid dynamics, and three different flow rates were selected. Since these experiments were carried out by continuously feeding a compartment with a gas enriched with dioxin (it is not in a circulated mode of operation), by increasing the flow rate, the residence time decreases and the removal
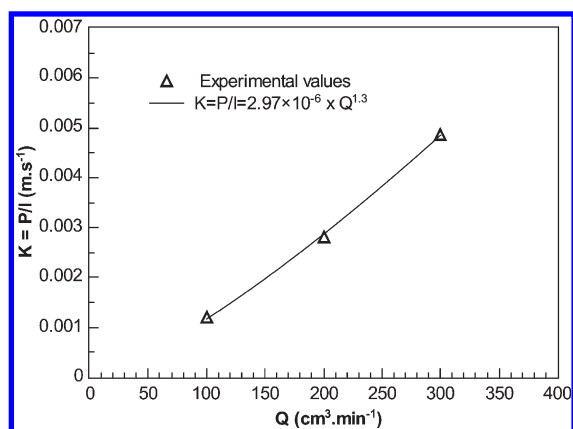
Figure 6. Dibenzo-*p*-dioxin mass transfer coefficient (K) through a 100 nm Al_2O_3 membrane with immobilized [Aliquat][DCA] as a function of the flow rate at a temperature of 150 °C.
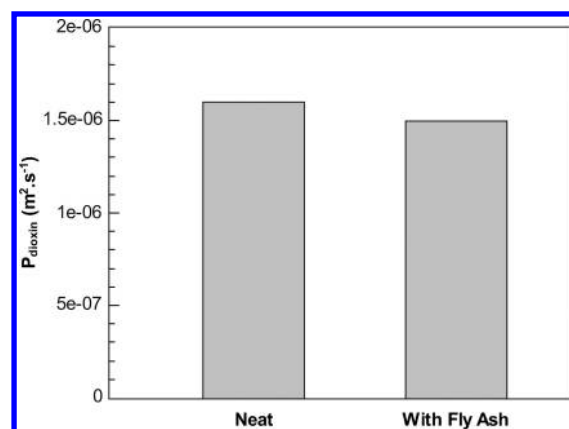

Figure 7. Dibenzo-*p*-dioxin permeability through a membrane consisting of ionic liquid [Omim][DCA] supported on a 30 nm TiO_2 ceramic membrane at a temperature of 150 °C and a flow rate of 100 cm^3·min^{-1}.

of dioxins decreases. The flow rates used represent a compromise between fluid dynamic conditions and the removal rate. These experiments were conducted at the same temperature, 150 °C. The overall mass transfer coefficient $K = P/l$ (where l is the membrane thickness) of the dibenzo-*p*-dioxin as a function of the N_2 flow rate is presented in Figure 6. With an increase in flow rate, an increase in the dioxin permeability is observed. The mass transfer coefficient dependence on the flow rate was determined to be 1.3. Due to the low values of the Reynolds number used in these experiments ($Re < 20$), this result was expected. A dependence of the mass or heat transfer coefficients on the Reynolds number exponent close to 1 was also observed for values of $Re < 100$.[26] As can be observed in Figure 6, the process is still limited by external mass transfer, meaning that dioxin mass transfer (and permeability) can still be improved by operation at higher flow rates.

It should be stressed that the high values of the mass transfer coefficient obtained, as a result of the excellent affinity of the ionic liquids selected toward the target dioxin solutes, lead to a very low value of the height of a transfer unit (HTU), which is a measure of the separation efficiency of the equipment for a particular separation process. The more efficient the mass transfer (i.e., larger mass transfer coefficient), the smaller the value of HTU, which is defined as

$$HTU = \frac{v}{Ka} \qquad (5)$$

where v is the gas velocity, K is the mass transfer coefficient, and a is the contact area per unit volume of the equipment. In fact, the experimental value of HTU obtained for this process (HTU = 0.73 cm) is much lower than the usual values for packed towers, which are between 0.3 and 1 m.[23] This result means that an industrial process operating according to this technology would be extremely efficient, requiring small areas for mass transfer.

This process can be implemented using a multi tubular membrane contactor, which can provide a contact area per unit volume 20−100 times higher than that of conventional equipment, and it can operate at a wide range of flow rates with no loading or flooding constraints. The modular character of this equipment will allow an easy, straightforward scale-up procedure to be applied in real conditions at the outlet of gas conducts of units where dioxins are produced.

Experiments with Model Incineration Gas. Under real operating conditions the dioxins formed in technical incineration processes may adsorb onto fly ashes.[27] To test the applicability of the present method to real conditions, a wood-burned fly ash was used and 10% (w/w) dibenzo-*p*-dioxin was physically adsorbed. The adsorption process was accomplished by dissolving both components in dichloromethane solvent and then evaporating the solvent to dryness. The 30 nm TiO_2 ceramic membrane with the ionic liquid [OMIM][DCA] immobilized was used for the SILM study at 150 °C over 5 h. It was found that the dioxin permeability was slightly decreased in comparison with that observed under neat conditions (fly ash, 1.497×10^{-6} m^2·s^{-1}; neat, 1.599×10^{-6} m^2·s^{-1}) (Figure 7). However, the difference obtained for dioxin removal comparing the process under neat conditions with that using fly ash is less than 1% (w/w). This experiment mimics the actual conditions of dioxin formation in incineration and combustion processes and validates the potential of using ceramic membranes with immobilized ionic liquids for the removal of dioxins from high-temperature sources. After removal from the high-temperature vapor stream, dioxins can be safely destroyed using the most appropriate available technologies, for example, dechlorination by using metallic calcium in ethanol.[28] This process proved to be efficient for dioxin removal from incineration and combustion processes using compact equipment with excellent mass transfer rates and significantly less demand of energy than current remediation technologies of dioxins.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** SEM images of the porous ceramic supports and the supported ionic liquid membranes prepared and specifications of the GC-TCD system for the dioxin analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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