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Porous ionic liquids go green

Jocasta Avila,[†] Chiara Corsini,^{†,¶} Cintia M. Correa,^{†,¶} Martin Rosenthal,^{‡,§} Agilio Padua,[†] and Margarida Costa Gomes^{*,†}

[†]*Laboratoire de Chimie de l'ENS Lyon, CNRS and Université de Lyon, 46 allée d'Italie, 69364 Lyon, France*

[‡]*Department of Chemistry, KU Leuven, Celestijnenlaan 200F, Box 2404, 3001 Leuven, Belgium*

[¶]*Contributed equally to this work*

[§]*Dual-Belgian-Beamline (DUBBLE), European Synchrotron Radiation Facility (ESRF), 71 Avenue des Martyrs, CS40220, 38043 Grenoble, Cedex 9, France*

E-mail: margarida.costa-gomes@ens-lyon.fr

Abstract

This perspective points towards pathways to prepare porous ionic liquids using easily accessible materials, aiming for reduced environmental impact. We demonstrate that suspensions of porous solids are stable in eutectic mixtures, underscoring their potential for the preparation of porous ionic liquids. Porous ionic liquids retain the wide electrochemical window observed in their precursor pure ionic liquids, rendering them well-suited for green electrochemical reactions, particularly those involving gases, whose solubility is enhanced in the porous suspensions. Moreover, their capacity as gas-rich media point to sustainable biomedical and pharmaceutical applications, provided non-toxic, bio-compatible ionic liquids and porous solids are utilized.

Keywords

Ionic liquids, metal-organic frameworks, deep eutectic solvents, porous liquids

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Introduction

Ionic solvents appear as key to easily prepare porous liquids from *of-the-shelf* porous solid materials. Contrary to what is observed when dispersing porous solids in non-ionic solvents to prepare porous liquids, when ionic liquids are used the resulting porous suspensions are, more often than not, stable during periods of months or years without the need of surfactant addition or particle surface functionalization — solutions that are believed to improve solid-liquid interactions.¹ Porous ionic liquids, PoILs, have thus been prepared by dispersing metal organic frameworks, MOFs, with appropriate porosities in ionic liquids with voluminous ion pairs.^{2,3} PoILs were reported in 2018^{2,4} shortly after Zhang *et al.*⁵ and then Giri *et al.*⁶ proposed reliable ways of preparing and characterizing porous liquids. PoILs are stable and present permanent porosity, and have chemical and structural properties combining those of the porous solid and of the ionic liquid used.³ Porous liquids and especially PoILs have since shown great potential for applications in gas capture^{1,3,7,8} and separation.⁸ PoILs can be designed to improve selectivity in gas absorption⁹ or used as catalytic media for reactions involving gaseous reactants in milder, more sustainable conditions.¹⁰

A variety of porous solids, other than MOFs, could in principle be dispersed in ionic liquids but so far, only a limited number of zeolites, porous organic polymers, porous organic cages and hollow carbon nanospheres were reported to form porous suspensions.¹ The permanent porosity of the liquid was shown to depend on the appropriate combination of the porosity generator (the porous solid); on the nature of the sterically hindered ionic liquid; and, of course, on the concentration of the suspensions.² In the following pages, we highlight some of the directions that might lead to greener, more sustainable approaches to preparing and using porous ionic liquids. We include in this perspective original work and proof-of-concept results to support our claims.

Future design directions

Towards low cost, tailor-made porous deep eutectic solvents — porous-DES.

When designing a task-specific organic salt to prepare a PoIL it is possible to end up, after a difficult and costly synthesis, with a solid at the desired temperature. Predicting *a priori* the melting point of such a salt remains difficult. One easy way to circumvent this difficulty is to, instead of synthesising a pure salt, mixing two solids with the desired functionalities to form a liquid eutectic mixture. When the melting point is significantly lower than expected, these mixtures are commonly designated as deep eutectic solvents or DESs.¹¹ The liquid range, properties and cost of DESs can be adapted by appropriately choosing the constituents and the composition of the mixtures, which can often be prepared from accessible and renewable chemicals.¹²

The most common DESs are prepared combining salts and molecular compounds to form ion-rich mixtures with physical and chemical properties similar to those of ionic liquids. As such, they could be used to create stable suspensions of chosen porous solids.¹¹ To prove the concept of porous-DESs, we started by combining a voluminous phosphonium salt (methyltriphenylphosphonium bromide, $T_{\text{fus}} > 500$ K)

with a common organic compound, glycerol, to form a DES¹³ as described in Supplementary Information. This liquid phase is able to stabilize ZIF-8, a metal-organic framework, in a suspension and thus form porous liquid based on a DES.

As shown in Figure 1, the suspension of 5% ZIF-8 in the DES is stable for up to 5 months with the structure of the solid and the microscopic structure of the liquid being maintained in suspension as was previously observed with ionic liquids (Fig.S1). An increase in the absorption of N₂ and CO₂ is measured in the suspension (Fig.1 and Tables S5-S7) when compared to the DES alone, thus confirming the permanent porosity of the suspension.

The porous-DES suspension was modeled using molecular dynamics simulation (technical details included in Supplementary Information). Figure 2 shows that the DES ions and molecules are accommodated in the surface-accessible cavities of ZIF-8 but do not fill the pores of the solid. The snapshots and the number density profiles indicate that both components of the DES are found near the superficial pores of ZIF-8 with no preference detected for one component or the other. The anchoring of solvent molecules at the surface of the MOF was previously observed in the PoILs containing alkylphosphonium ILs and has been rationalized as one of the keys for preventing particle aggregation leading to stable suspensions over long periods of time.¹

Curiously enough, the simulations show that the composition of the mixture remains essentially constant near the solid pores. This indicates that even though glycerol, the molecular compound in the DES, possesses a small enough size to enter the pores of ZIF-8, it does not do so. Experimentally, there are indications that the salt in the DES can precipitate from the porous suspension at temperatures below 348 K (WAXS structures in Fig. S2-S3). As in any other utilisation of DES, this points towards the importance of a precise knowledge of the phase diagram of the mixture to guarantee that it remains liquid in the working temperatures and compositions.¹¹

With the results described we have demon-

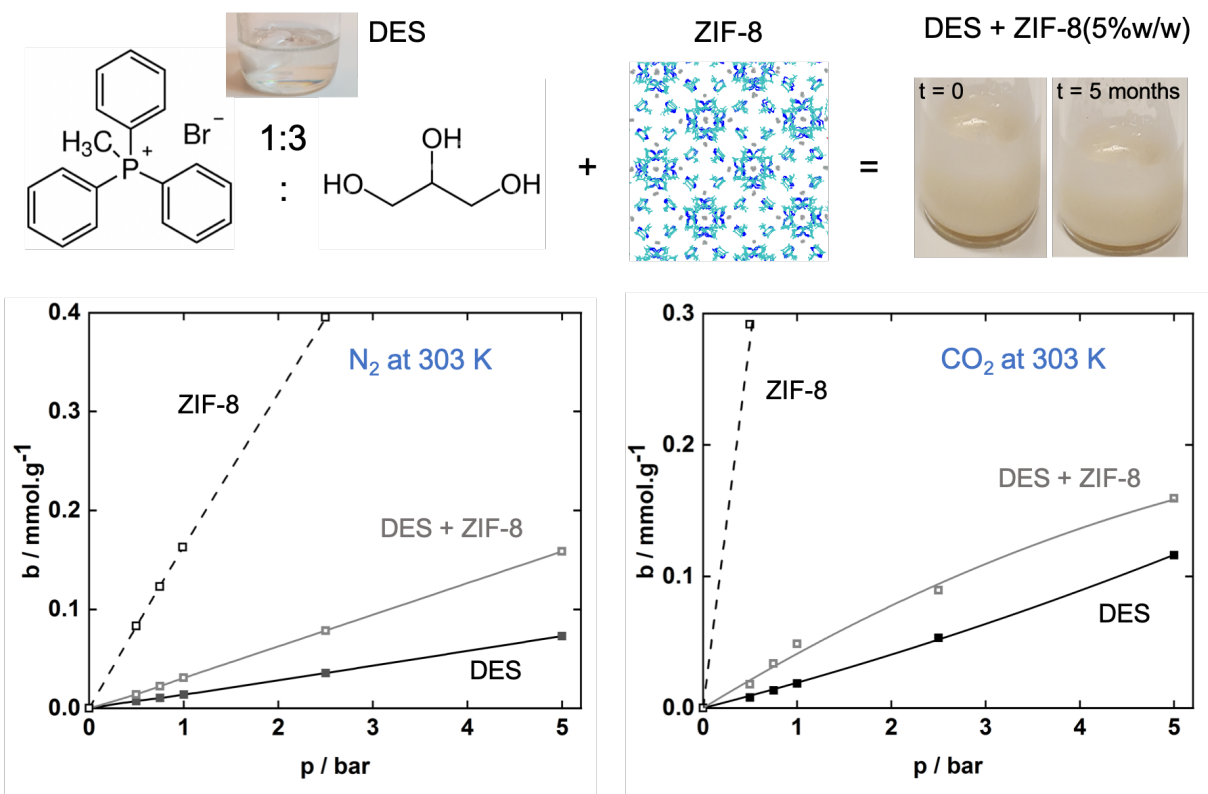


Figure 1: Chemical structure of the DES and isotherms of gas absorption in the pure DES,¹³ in pure ZIF-8 and in the porous DES. The physical aspect of the DES and of the porous-DES suspension is also shown.

strated that the liquid medium used to prepare a porous suspension can be based in low cost and biodegradable salts, even when they are not liquid at the temperatures of application. By choosing sustainable components and by tuning their composition in mixtures that form appropriate eutectics, they can easily be used to form greener porous ionic liquids.

Porosity coming from environmentally friendly or biocompatible porous materials. As shown above, the full tunability of ILs or DESs can be regarded as a valuable tool for creating more environmentally-friendly porous liquids by combining suitable cations, anions and molecular compounds. Likewise, versatility is a characteristic of commonly utilized porous materials. Taking MOFs as an illustrative example, these materials are self-assembled through the coordination of metal ions or clusters with organic ligands, providing a modular platform for designing multifunctional materials. As such, pore and aperture size and shapes, as well as chemical composition and affinity, can

be engineered to create permanent porosity.

The environmental impact of the porous materials are linked both to the methods and to the materials used in their preparation. Recent studies show that MOFs can be prepared following sustainable strategies, such as solvent-based synthesis using water, supercritical fluids, ionic liquids or bio-based solvents.¹⁴ Appropriate building blocks can also decrease the environmental impact of the MOF by using sustainable metal precursors and/or eco-friendly, bio-based linkers, either through a pre-design task-specific approach or by post-synthetic modification.¹⁵

Cyclodextrine-based MOFs, or CD-MOFs, are typical examples of porous solids easily prepared in aqueous solution using natural and biodegradable cyclic oligosaccharides with low toxicity.¹⁶ γ -CD is one of the most common cyclic oligosaccharides obtained from the enzymatic degradation of starch. It is composed of eight asymmetric α -1,4-linked D-glucopyranosyl residues that form a bucket-

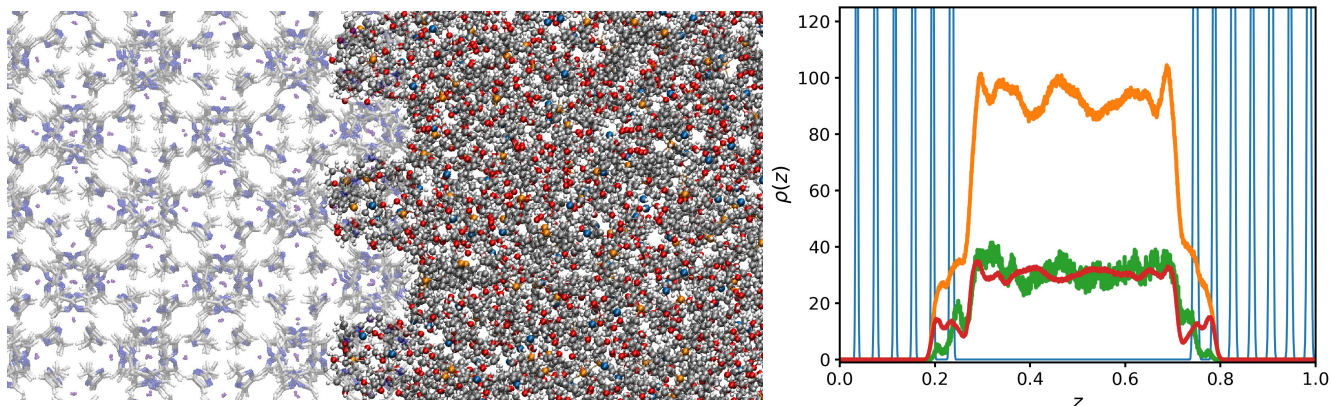


Figure 2: (Left) Snapshot of the DES ($P_1Ph_3Br:Glycerol (1:3)$)/ ZIF-8 interface after a 20 ns molecular dynamic simulation run. (Right) Number density profile in the slab geometry as functions of the fractional z coordinate of the simulation box. The density of the metal centers of the ZIFs, glycerol, cation and anion are represented in blue, orange, red and green, respectively.

shaped cavity of nanometric size. When combined with aqueous solutions of MOH salts ($M^+ = K^+, Rb^+ \text{ or } Cs^+$), environmentally benign, biocompatible and edible porous materials are obtained¹⁷ (CD-MOF-1, CDMOF-2 and CD-MOF-3, respectively).

The same arguments can be evoked when using other common porous solids to prepare porous suspensions, such as zeolites,¹⁸ covalent organic frameworks (COFs),¹⁹ or porous organic cages.²⁰ Zeolites appear as a well-established class of porous materials that occur naturally or can be synthesised following green synthetic routes,²¹ with more than 250 different structures identified and well described.²² COFs, on the other hand, are porous and crystalline polymers, composed of light-weight elements linked by strong covalent bonds, that can be prepared using mild routes.²³

Greening applications through porous ionic liquids

Gas separations. Porous liquids are currently proposed as media for gas absorption. Gases are, in general, only sparingly soluble in liquids at or near atmospheric pressure. Using fluids with a large free volume, as is the case of porous liquids, presents a real interest when trying to improve gas absorption in a liquid without having to increase pressure. This is particularly in-

teresting when the gas is a reactant, because the chemical reaction can proceed with increased yields at milder conditions.¹⁰

In PoILs the increase in gas absorption is spectacular but, unfortunately, not selective,³ since it is mainly determined by the free volume in the absorbent. Ionic liquids can be designed to react reversibly with certain gases that would then be selectively absorbed. This was done for carbon dioxide using carboxylate-based porous ionic liquids,⁹ with two advantages: the energy of desorption is relatively low and a significant part of the gas is only physically absorbed (as adsorbed in the pores), being therefore available for transformation if that is the aim. The design of porous ionic liquids is thus possible for selective separations that will be much less energy demanding. These absorbents can be used as alternatives in existing industrial equipment for gas separations which up to now have been based on the use of cryogenic distillation or use polluting solvents.²⁴

Because porous ionic liquids have a large capacity to absorb gases even at very low partial pressures, they appear as particularly suitable for applications, including the remediation of contaminated atmospheres by poisonous gases (such as hydrogen sulfide, sulfur dioxide²⁵ or carbon monoxide), the capture of carbon dioxide from the air or the desulfurisation of biogas.²⁶

Energy-related applications. An unex-

explored direction for the use of PoILs is linked to the qualities of the ILs, which are used in their preparation, as electrolytes. PoILs are thus expected to exhibit a dual nature, serving both as effective sorbents for various gases and as media for electrochemical reactions. As a result, PoILs have potential to become compelling candidates for electrochemical energy conversion, particularly in processes involving gases. Examples include oxygen electro-reduction for applications in fuel cells and metal-air batteries, electrochemical conversion of CO₂, electro-oxidation of CH₄, or in mild-pressure and temperature electro-reduction of nitrogen to ammonia.^{27,28}

Electrochemical reactions are often considered as greener than other pathways, since they generally involve less polluting compounds and make use of electric current instead of harsh oxidizing and reducing agents.²⁹ As the applied potential modulates the energy of the electrons, the target reaction can be started at or near room conditions, decreasing environmental impact and energy consumption. Furthermore, many chemical reactions are assisted by volatile organic solvents, whereas electrochemistry increasingly replaces molecular solvents with more environmentally friendly and stable media,²⁹ such as ILs³⁰ and DESs.³¹

In order for PoILs to function effectively as gas-storage media and as electrolytes, it is crucial that they exhibit good electrochemical stability, allowing a large number of reactions to take place. Good stability is often observed in pure ILs, which possess wide electrochemical windows of up to 5–6 V.³⁰ We carried out electrochemical experiments using PoILs based on [P_{6,6,6,14}][NTf₂] with two different MOFs: ZIF-8 and HKUST-1. The addition of these MOFs to the IL does not impact the electrochemical window of the system, as depicted in Figure 3, on the left for the pure IL or PoIL and on the right in presence of dissolved ferrocene.

In view of these results, we anticipate the use of PoILs in energy-related applications involving gases or small molecules that can be stored in the pores of the PoIL thus increasing their availability at mild conditions in the liquid.

Biomedical applications. Given the wide

range of materials available, including biocompatible liquids and porous solids, which can be utilized to create PoILs, there is a potential for biomedical applications. Recently, an approach involving aqueous porous liquid phases based on zeolites and MOFs with hydrophobically functionalized internal cavities has been proposed as a solution for solubilizing significant quantities of gases, such as CO₂ and O₂.^{32,33} This development allows for *in vivo* gas delivery, with potential therapeutic applications ranging from antithrombosis to vasodilation.³⁴ Non-aqueous, ionic-based porous liquids offer distinct advantages, leveraging the vast array of available ions, including numerous stable and biocompatible ILs,³⁵ which can have beneficial active roles.

Shamshina *et al.*³⁶ have highlighted that approximately half of all currently used drugs are ionic compounds, and that several promising ones exhibit low solubility in bodily tissues when in the form of salts, thereby diminishing their efficiency and often requiring the administration of larger quantities, resulting in waste and negative environmental impact. The use of liquid salts, as well as their mixtures, at room or body temperature can substantially enhance solubility and absorption rates.^{3,37,38} Moreover, the combination of two or more ions can boost the simultaneous delivery of multiple active ingredients. Biocompatible ILs are already being employed in tissue engineering and in the food industry, with certain salts being mixed with naturally occurring compounds to form DESs,³⁹ which are likely to exhibit biocompatibility as well.³⁵

As far as the porous materials are concerned, several MOFs that form PoILs have already been proposed in drug-delivery applications.⁴⁰ Notably, ZIF-8 has demonstrated therapeutic properties linked to its customizable functionality, high loading capacity, excellent thermochemical stability, and non-toxic nature, which enable effective drug adsorption and controlled release.¹⁴ Cyclodextrin-based CD-MOFs combine supramolecular and porous solid properties and are already used in cosmetic applications.⁴¹ Additionally, various other MOFs,⁴² as well as natural and synthetic zeolites,⁴³ have

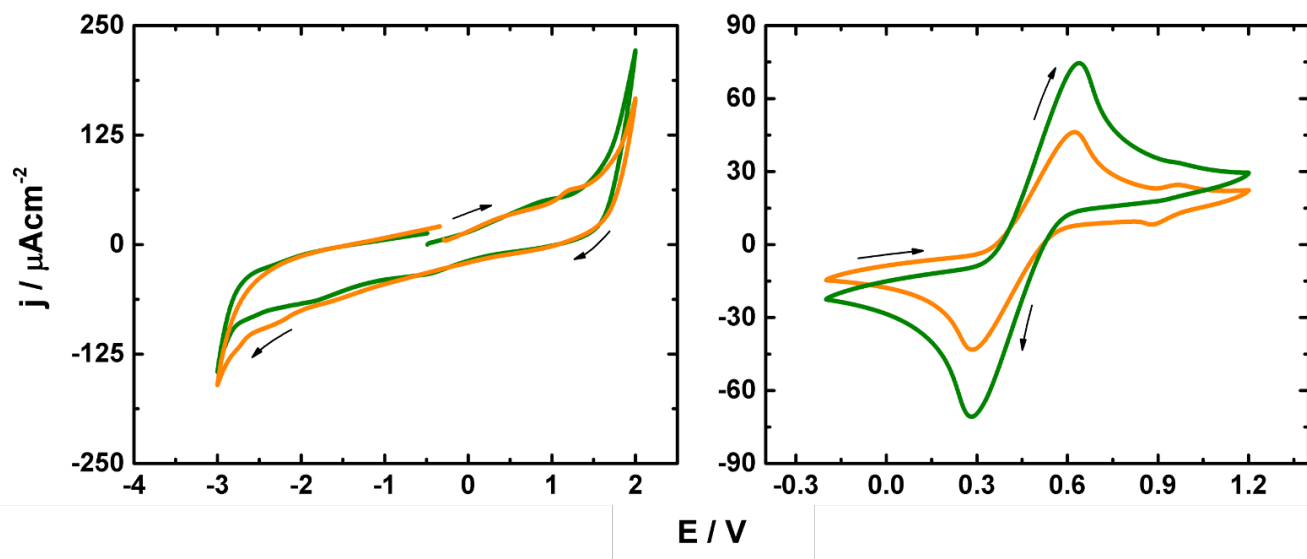


Figure 3: (Left) j/E potentiodynamic profiles of $[P_{6,6,6,14}][NTf_2]$ (green), $[P_{6,6,6,14}][NTf_2]$ ZIF-8 5% (orange). (Right) Same samples containing 12 mmol of ferrocene. Working electrode: glassy carbon (geometric area: 0.07 cm^2); pseudo-reference electrode: Ag wire; counter electrode: platinum; scan rate: (left) 100 mV s^{-1} , (right) 10 mV s^{-1} .

found biomedical applications in fields such as bioimaging, antibacterial agents, biosensors (targeting glucose, gases, biomacromolecules, or pathogenic bacteria), as well as serving as biocatalysts.

With the difficulties related to individual testing of materials for biomedical applications in mind, the preparation of PoILs, which use already-tested components, emerges as an alternative direction for various therapeutic purposes. These porous fluids hold potential as *in vivo* gas carriers, drug delivery systems, and other therapeutic applications in advanced biomedical research and development.

Conclusions

While recent publications point towards the use of surface deposition strategies to prepare stable porous suspensions,⁴⁴ the findings presented in this perspective present pathways for the synthesis of porous ionic liquids using readily available materials. A recent publication suggests the utilization of porous deep eutectic solvents (DES),⁴⁵ but a definitive proof of porosity in the reported systems is still lack-

ing. Our study provides experimental evidence that eutectic mixtures can be readily employed to make stable porous suspensions, highlighting the potential of such materials for the preparation of porous ionic liquid phases with reduced environmental impact, when compared to previous porous ionic liquids. Our initial results raise important questions regarding the nature of eutectic mixtures and emphasize the significance of having an accurate knowledge of the phase diagrams to prevent the formation of undesired solid phases from the individual components of the DES. The effective development of advanced porous liquids based on ionic and eutectic mixtures are expected.

Porous ionic liquids hold potential for a myriad of applications and can offer efficiency and reduced environmental impact. We demonstrate that the wide electrochemical window exhibited by ILs is preserved when forming PoILs indicating their suitability as media for electrochemical reactions, particularly involving gases, enabling greener electrochemical processes. Moreover, the capacity of PoILs to act as gas-rich liquid media or carriers of different active ingredients presents possibilities for biomedical and pharmaceutical applications,

fostering sustainable and innovative solutions.

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Supporting Information Available

Experimental detail and numerical data in density, viscosity, gas absorption measurements. WAXS experimental procedure. Molecular simulation details.

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