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Type 3 Porous Liquids for the Separation of Ethane and Ethene

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ABSTRACT: We assess the potential for formulating a porous liquid that could be used as a selective solvent for the separation of ethane and ethene. Ethane-ethene separation is performed on very large scales by cryogenic distillation, but this uses large amounts of energy. Solvents that are selective to ethane or ethene could potentially enable more efficient liquid-based separation processes to be developed, but such solvents have been elusive to date. Here, Type 3 porous liquids, which consist of microporous solids dispersed in size-excluded liquid phases, have been tailored toward the separation of ethane and ethene. High selectivity for ethene over ethane (25.6 at 0.8 bar) and high capacity was achieved for zeolite AgA dispersed in an Ag-containing ionic liquid. Unusually for liquid phases, selectivity for ethane over ethene (2.55 at 0.8 bar) could also be achieved using the MOF Cu(Qc)₂ (Qc = quinoline-5-carboxylate) dispersed in sesame oil, or ZIF-7 in sesame oil, the latter showing gated uptake. The efficiency of the Cu(Qc)₂ synthesis was increased by developing a mechanochemical method. Regeneration of Cu(Qc)₂ in sesame oil and ZIF-7 in sesame oil was also demonstrated suggesting that these or similar porous liquids could potentially be applied in cyclic separation processes.

1. Introduction

Porous liquids (PLs) are materials that combine permanent porosity with fluidity.¹ This blend of properties is unusual and potentially useful. In particular, the porosity of PLs can enable size-selective and/or shape-selective dissolution of solutes, whilst their fluidity enables them to be engineered into continuous cyclic separation processes. Three types of PLs have been proposed.¹ Type 1 are neat molecular hosts in liquid form, Type 2 consist of molecular-scale hosts dissolved in solvents that are size-excluded from the host's cavity, and Type 3 consist of particles of microporous solids dispersed in liquids that are size excluded from the pores (Figure 1).²⁻⁶ Type 3 PLs are currently the most economical to prepare. They are also compositionally diverse and some of their critical properties (such as gas uptake) are predictable, making them designable. Overall, they constitute a broad platform of selective liquid sorbents that may be tailored toward applications.⁷⁻¹⁴

The separation of ethane and ethene is one of the major industrial partitions.¹⁵ However, it is challenging due to the similar sizes and physical properties of these molecules. It is mostly achieved by cryogenic distillation, but this requires large amounts of energy,¹⁵ making the search for alternative methods important. Membrane technology is a potential alternative,^{16,17} but it can suffer from poisoning, low selectivity and mechanical failure. Liquid solvents that are selective for one gas over the other could enable continuous cyclic processes to be developed as alternatives to the above approaches. These would be analogous to existing liquid-based processes for natural gas sweetening (i.e. the separation of CO₂ and H₂S from

CH₄) currently performed with aqueous amines or oligoethylene glycol solvents. In this regard, ethene-selective solvents containing metal cations, often silver(I), dissolved in water or in ionic liquids have been investigated.¹⁸ Also, we have previously described preliminary work with a porous liquid based on zeolite AgA¹⁹ dispersed in paraffin oil, which is ethene selective.⁷ However, the potential of PLs for ethane-ethene separation has not been explored in any detail. Considering the benefits an appropriate PL could bring, it is important to assess their potential for this application more broadly.

Figure 1. Schematic of the formation of a Type 3 porous liquid.

Here we describe various approaches to this challenge. Five PLs have been formulated and evaluated. We include an Ag(I)-based porous liquid with very high ethene selectivity and capacity, and two PLs that, unusually for liquid solvents, exhibit significant ethane selectivity. These latter porous liquids can be readily regenerated making them amenable to continuous cyclic separations.

Table 1. Ethane/ethene solubility in porous solids and pure liquid components investigated for Type 3 porous liquids.

Materials	Ethane uptake at 0.8 bar (mmol/g)		Ethene uptake at 0.8 bar (mmol/g)		Ethene Selectivity at 0.8 bar
	Theo.	Exp.	Theo.	Exp.	
HKUST-1	4.79 ²⁰	4.19	-	6.1	1.45
Zeolite AgA	0.08 ¹⁹	0.125	2.12 ¹⁹	1.935	15.48
Cu(Qc) ₂	1.85 ²¹	1.662	0.78 ²¹	0.821	2.02*
Sesame oil	-	0.096	-	0.071	1.35*
AgIL	-	0.015	-	0.497	33.13

Table 2. Type 3 porous liquids investigated for their ability to selectively adsorb ethane and ethene.

Porous liquid	Porous solid component (wt.%)	Liquid component	Ethane uptake at 0.8 bar (mmol/g)			Ethene uptake at 0.8 bar (mmol/g)			Ethene Selectivity at 0.8 bar
			Cal.	Exp.	σ	Cal.	Exp.	σ	
1	HKUST-1 (12.5)	Sesame oil	0.61	0.67	0.01	0.83	0.84	0.01	1.25
2	Zeolite AgA (12.5)	AgIL	0.02	0.02	0.00	0.67	0.61	0.01	25.6
3	Zeolite AgA (25.0)	AgIL	0.04	†0.04	-	0.86	†0.84	-	21.0
4	Cu(Qc) ₂ (12.5)	Sesame oil	0.29	0.28	0.00	0.16	‡0.11	0.00	2.55*
5	ZIF-7 (12.5)	Sesame oil	-	0.016**	-	-	0.12**	-	7.5**

Key: Theo. is the literature gas uptakes, Cal. is the calculated or predicted uptake, i.e. the weighted averages of the uptakes of the individual liquid and solid components, Exp. is the experimental uptake and σ is the standard deviation. AgIL = 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide saturated with silver trifluoromethanesulfonate. * indicates ethane selectivity, † indicates measurements completed once and ‡ indicates values outside 10% of the predicted value. ** indicates the ethane/ethene uptakes and ethane selectivity of **PL-5** were measured and calculated barometrically at 0.1 bar.

2. Results and discussion

In a previous general study, the gas uptakes of Type 3 porous liquids with typical solid loading of 12.5 wt.% were found to be dominated by the solid component.⁷ Therefore, we began by selecting solid components that, from literature, have high uptakes or selectivities for ethane or ethene. The solid and liquid components of the five compositions investigated, **PL-1-5**, are summarised in Table 1, and the composition themselves are summarized in Table 2. Each consisted of 12.5 wt.% of solid dispersed in the liquid phase, unless otherwise stated, and were prepared by vigorously stirring (600 rpm) the solid in the liquid phase for 2 hours to give homogeneous dispersions that were found to be stable to sedimentation for at least 2 days.

Regarding the solids investigated, open metal sites can be effective for preferentially binding ethene through π -coordination, as in HKUST-1 (a MOF with open Cu(II) sites)²² or zeolite AgA (zeolite A containing Ag(I) cations). Conversely, selectivity for ethane over ethene in microporous solids is rare and there are no simple design strategies to achieve this. However, significantly, certain

MOFs such as Cu(Qc)₂ (Qc = quinoline-5-carboxylate) and ZIF-7 have recently been shown to exhibit ethane selectivity, which has been ascribed to the greater polarizability of ethane over ethene²¹ or the pore window shape²³.

Regarding the liquid components investigated, sesame oil (a triglyceride) and the Ag-containing ionic liquid (IL) 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide saturated with silver trifluoromethanesulfonate (0.18 g/mL), here denoted AgIL, were chosen.^{18,24} Critically, both these liquids should be sterically excluded from the pores of the solids due their branched structures, so that the pores remain empty and available to gases. Sesame oil has the advantage of being inexpensive and innocuous. Normal solvents are typically unselective for either ethane or ethene, with organic solvents commonly having modest selectivity for ethane over ethene. For example, sesame oil shows ethane selectivity of 1.35 (0.8 bar) (SI 7, Table S5/S7). In contrast, Ag-based ionic liquids show considerable selectivity for ethene (e.g., 33.13 for AgIL at 0.8 bar). The gas uptakes were screened initially using an isochoric method (at 0.8 bar) to confirm that the pores of the solids were indeed available to gases, before investigating higher

pressures (1–5 bar) using a barometric method.⁷ All measurements equilibrated within two hours and were reproducible. Pure gases were used and selectivities were calculated using the ratio of the molar uptakes. Thus this data provide indicative values for selectivity despite the potential for differences between pure gases and binary mixtures as well as non-ideality. As hoped, and in line with previous work on porous liquids with N₂, CH₄ and CO₂,⁷ the experimental ethane and ethene uptakes of the porous liquids were within 10% of the weighted averages of the uptakes of their individual solid and liquid components unless otherwise stated. Uptake of gases in the porous solids were also similar to previously reported values (Table 1).

Due to the large pore volume (0.71 cm³/g) of HKUST-1, **PL-1** was able to adsorb large amounts of both ethene and ethane (0.84 and 0.67 mmol/g respectively) (Table 2). As expected, due to the presence of free Cu(II) sites,²² it was selective to ethene. However, the selectivity of the porous liquid (1.25) was modest overall since the liquid component, sesame oil, is slightly selective to ethane (1.35 for sesame oil) (SI 7, Table S5). Greater selectivity might be expected if mixed gases were used, as observed for the solid HKUST-1.²⁵

To improve selectivity for ethene, we combined AgA as the most ethene-selective solid¹⁹ with AgIL as the most ethene selective liquid (to give **PL-2** and **PL-3**). Ionic liquids have been reported as size-excluded liquid components for Type 3 porous liquids^{7–14} and can also dissolve Ag(I) salts to make them ethene-selective.¹⁸

Zeolite AgA was dispersed in the bulky ionic liquid 1-butyl-3-methylimidazoliumbis(trifluoromethylsulfonyl)imide saturated with silver trifluoromethanesulfonate (0.18 g/mL) to give a highly ethene selective porous liquid (**PL-2**, Table 2). Notably, although its ethene/ethane selectivity (25.6 for 12.5 wt.%, 0.8 bar and 21.0 for 25.0 wt.%; 0.8 bar) was lower than that of the pure AgIL (33.13, 0.8 bar) due to the relatively lower ethene selectivity of zeolite AgA (15.48, 0.8 bar). However, its capacity was substantially greater (0.61 mmol/g vs. 0.50 mmol/g) due to zeolite additive, which could be advantageous in separation processes (SI 7, Table S6). **PL-2** therefore illustrates that addition of an appropriate porous solid can increase the gas capacity of an ionic liquid even when it is saturated with a metal salt. **PL-2** and **PL-3** were stable for at least 2 days before sedimentation was observed visually and by PXRD⁷ (SI 8, Figure S23). The stability could potentially be improved further if required by reducing the AgA particle size or by surface modification for example.

The selectivity of **PL-2** remains high at greater pressures (9.5 at 5 bar) suggesting gas separation potential by pressure swing. However, despite its promising selectivity and capacity **PL-2** was unexpectedly difficult to regenerate, requiring ca. 2 hours at 150°C (SI 7, Figure S21). Also, unexpectedly, Ag(I) was observed to deposit from the IL onto the solid AgA over time which reduces the gas uptakes (Figure 2) of the porous liquid (SI 6, Table S4). These aspects clearly limit the applicability of this porous liquid. Since conventional liquid solvents have not yet been reported to show high selectivity for ethane, we turned to the interesting possibility of making an ethane-selective porous

liquid. Cu(Qc)₂ (Qc = quinoline-5-carboxylate) is a recently-reported microporous MOF material that shows selective uptake of ethane over ethene (3.70 at 1 bar).²⁶ It has a number of other attractive features including the low cost of its components and its stability to water vapour under ambient conditions.

Figure 2. Barometric gas measurements of **PL-2** (zeolite AgA in AgIL) and **PL-4** (Cu(Qc)₂ in sesame oil); black squares indicate ethane uptake and red circles indicate ethene uptake. Error bars for ethane are indistinguishable from the data points.

However, its reported solvothermal synthesis is low yielding (6.9%).²¹ We initially sought, therefore, to synthesise Cu(Qc)₂ mechanochemically since this method can give quantitative yields for closely related MOFs such as Cu(ina)₂ (ina = isonicotinic acid).²⁷ After some optimisation, ball milling Cu(OH)₂ with HQc in a steel jar at 25 Hz for 15 minutes in the presence of small amounts (0.25 mL) of DMF and EtOH, gave quantitative conversion to Cu(Qc)₂ (isolated yield 73.5%) with no starting materials or by-products observed by PXRD (SI 5, Figure S2). N₂-Brunauer–Emmett–Teller (N₂-BET) surface areas of the mechanochemically prepared and conventionally prepared Cu(Qc)₂ were similar at 340 m²/g and 437 m²/g respectively. Both compare favourably to the literature value (222 m²/g).²¹ Since vibrational milling gives ready access to gram amounts of Cu(Qc)₂ it is likely that larger scale twin screw extrusion techniques²⁸ could provide give kg amounts if required. Furthermore, the particle size of the mechanochemically prepared Cu(Qc)₂ (150 nm) is smaller than the conventionally prepared Cu(Qc)₂ (4 μm). Porous solids with smaller particle size should lead to better dispersion stability when formulating the porous liquid.

The mechanochemical product dispersed readily into sesame oil by simple magnetic stirring (600 rpm) for 2 hours to give a purple suspension, PL-4 (Table 2) with high gas uptake compared to sesame oil alone (Figure 2) and increased selectivity for ethane over ethene at both 1 and 5 bar (2.17 and 1.33 respectively). Remarkably, despite the simple preparative method, it was stable to sedimentation for at least 14 days as determined by PXRD analysis and

visual inspection (SI 8, Figure S22). Significantly, consistent with the physical rather than chemical binding of the ethane, it was also easily regenerated under mild conditions (40°C, 1 hour) to regain, within error, similar gas uptake capacity (Figure 3), suggesting potential for cyclic separations.

Figure 3. Ethane uptake of **PL-4**, $\text{Cu}(\text{Qc})_2$ in sesame oil. Regeneration conditions were 40°C for 1 hour.

Figure 4. Barometric gas measurements of ZIF-7 in sesame oil. black squares indicate ethane uptake and red circles indicate ethene uptake. Error bars for ethane are indistinguishable from the data points.

A further porous liquid investigated was based on ZIF-7, $\text{Zn}(\text{benzimidazole})_2$, a solid which shows gating behaviour with regard to ethane and ethene uptake. Specifically, due to flexibility in the framework increasing gas pressure causes a structural change that allows gas to enter above a threshold pressure (< 0.1 bar for ethane; 0.2-0.3 bar for ethene).²³ There is thus a pressure window between 0.1-0.2 bar where it shows high selectivity to ethane. Gated effects can be advantageous in gas uptake and release because large amounts of gas adsorb and desorb by small pressure change.^{23,29}

ZIF-7 was dispersed in sesame oil to form **PL-5**. Ethane and ethene uptakes were measured from 0-3 bar. As hoped, the gating behaviour of the MOF was preserved upon dispersion in the oil, and **PL-5** showed high ethane selectivity of 7.5 at 0.1 bar (Figure 4). The ethane selectivity decreases markedly above ca. 0.25 bar suggesting that 0.1-0.2 bar is the optimum pressure range to separate ethane/ethene at 298 K. Furthermore, **PL-5** was easily regenerated with mild heating (50°C) (SI 7, Figure S20) suggesting applicability in temperature swing absorption.

PL-5 demonstrates how relatively complex gas uptake behaviour (i.e., gating) that is well documented in framework solids can be readily imparted to the liquid state through dispersion in a size-excluded liquid. As such the uptake isotherms of **PL-5** are very unusual, and possibly unique, for liquid phases.

3. Conclusions

In summary, in this study five PLs were formulated and evaluated for their potential in ethane/ethene separation. Some key observations are *i.* ethene capacity can be increased by adding a porous solid even when the liquid component is saturated with metal ions (**PL-2**), *ii.* PLs provide a way to make liquid phases with higher ethane selectivity than is possible for conventional solvents (**PL-4** and **PL-5**), *iii.* regeneration is readily achieved for ethane-selective PLs that bind gases through physical rather than chemical interactions (**PL-4** and **PL-5**), and *iv.* gated gas uptake behaviour of MOFs can be transferred to porous liquids (**PL-5**).

Regarding the relative merits of each porous liquid, **PL-1** (HKUST-1 in sesame oil) has high uptake but low selectivity, limiting its applicability. **PL-2** (zeolite AgA in AgIL) has high ethene selectivity, but is hard to regenerate and has low chemical stability. Conversely, ethane-selective **PL-4** ($\text{Cu}(\text{Qc})_2$ in sesame oil) and **PL-5** (ZIF-7 in sesame oil) are easily regenerated and have high chemical stabilities. While **PL-5** exhibits interesting gated behaviour, we note that the broader pressure range of ethane selectivity exhibited by **PL-4**, together with its ease of synthesis and high stability to sedimentation make this porous liquid of particular interest for ethane/ethene separation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Synthesis details, characterization, ethane/ethene uptakes results (PDF)

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Notes

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ABBREVIATIONS

PLs, porous liquids; T3PLs, Type 3 porous liquids; AgIL, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide saturated with silver trifluoromethanesulfonate.

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