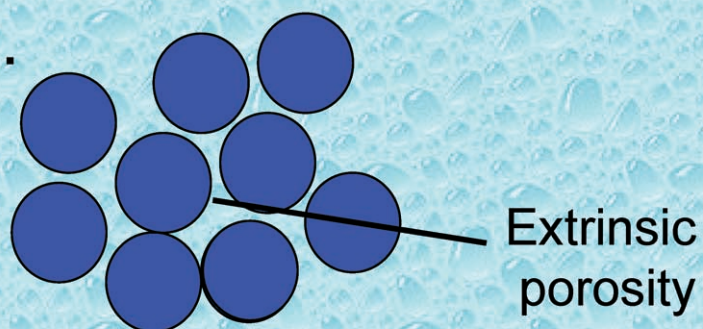
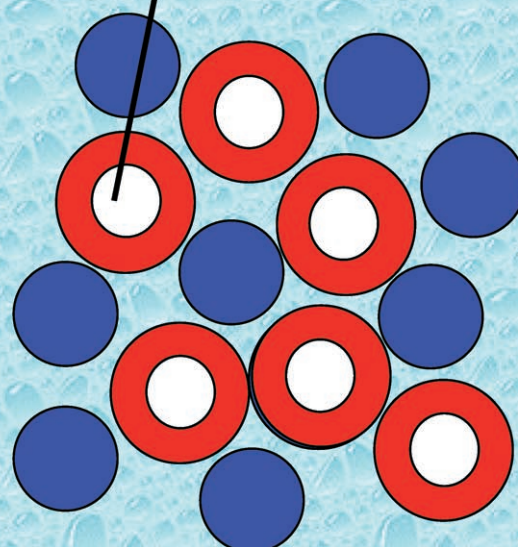
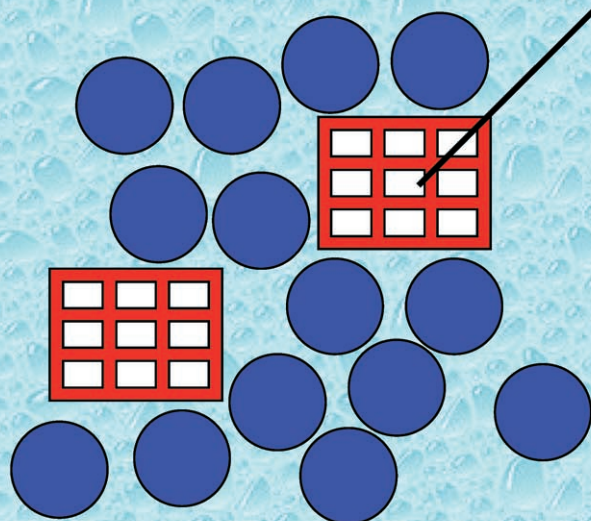
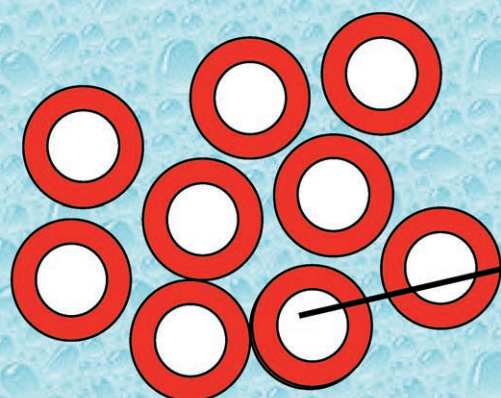


Conventional liquids...



Microporous liquids



Porous Liquids

Niamh O'Reilly, Nicola Giri, and Stuart L. James*[a]

Abstract: The aim of this article is to put forward the novel concept of porous liquids, or, more precisely, liquids with permanent microporosity. In contrast to the small, transient cavities that exist between the molecules of any liquid (here called “extrinsic” porosity), we suggest that a truly microporous liquid could exist if it had empty pores *within* the molecules of the liquid (“intrinsic” porosity). By using rigid host molecules with restricted access windows, any unwanted occupation of the pores could be prevented (i.e., the pores could be kept empty and available so that the liquid would be genuinely microporous). The liquid could have permanent, well-defined, empty pores capable of molecular recognition when exposed to other species (e.g., gases etc.). We stress that these phases are not the same as simple solutions of host species, in which any pores would normally be occupied by solvent molecules. In microporous liquids, any solvent molecules, if present, would be deliberately sterically excluded from the host cavities, to leave them readily accessible. Microporous liquids would be of considerable fundamental interest. They could combine properties of microporous solids, such as size- and shape-selective sorption and so forth, with the rapid mass transfer, fluidity and fast kinetics of liquids. Some synthetic approaches to these materials are discussed in this article. Also, whilst the overall concept of microporous liquids is new, literature is described which suggests that some examples have arguably already been reported, even if they have not previously been recognised and characterised in such terms.

Keywords: liquids · porosity · solvent effects

Introduction

Porosity is a characteristic that is normally associated only with the solid state.^[1] Microporosity is usually taken to indicate empty pores of up to 2 nm, that is, sufficiently large to include other molecules. For example, zeolites are microporous, crystalline aluminosilicates that exhibit many useful properties arising from their ability to absorb and discriminate between guest molecules with different shapes, sizes and functional groups.^[2] Such microporous solids have robust, effectively infinite structures based on interconnected cages or channels. Recently, there has been an explosion of interest in porous solids based on organic molecular building blocks.^[3] For example, metal–organic frameworks have extended layer or framework structures based on metal ions bridged by organic ligands (Figure 1).

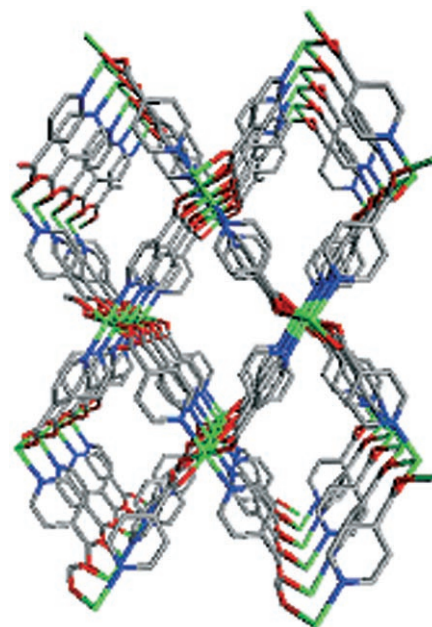


Figure 1. An example of extended three-dimensional connectivity in a crystalline solid exhibiting microporosity, specifically $[\text{Co}(\text{ina})_2]$ (ina = isonicotinic acid, $\text{NC}_5\text{H}_4\text{-4-CO}_2^-$).^[3g]

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There is evidently a great contrast between the relatively fixed, infinite structures of the above types of material, and the fluid structures of liquids, made up of discrete molecules (or ions^[4]) in constant motion. Although porosity also exists in the liquid state, it is limited to small, transient cavities between the molecules.^[5] It is initially counter-intuitive that well-defined micropores of at least molecular dimensions, as seen in solids, could exist in the liquid state. One aim of this article is to suggest how such porosity could be achieved in the liquid state. After a brief description of the limited porosity that exists between the molecules of conventional liquids (here termed “extrinsic” porosity), a number of approaches for the preparation of truly microporous liquids is put forward. In essence, these approaches rely on the generation of permanent, empty, well-defined cavities *within* molecules of the liquid, or in particles dispersed within it (here termed “intrinsic” porosity). These approaches are represented in cartoon form in Figure 2. Note that this not the

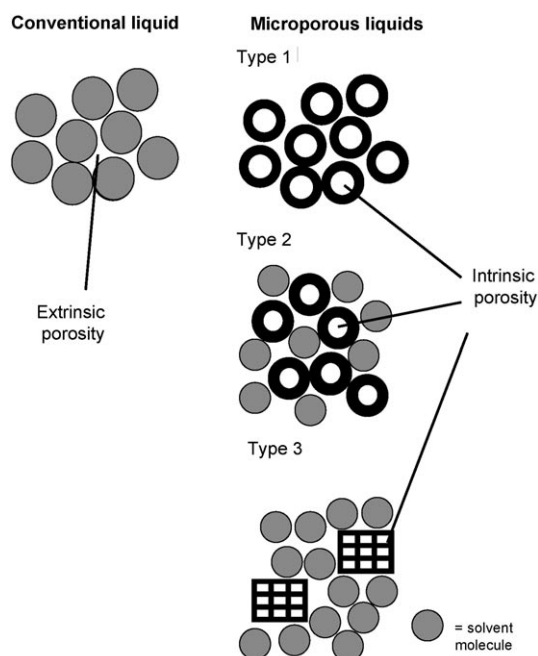


Figure 2. Cartoon diagram to represent molecules in a conventional liquid, which has only “extrinsic” porosity between the molecules (small, irregular, transient cavities), and microporous liquids that have “intrinsic” porosity within the molecules (molecule-sized, regular, permanent empty cavities). Type 1: neat liquid hosts that cannot collapse or interpenetrate. Type 2: Rigid hosts dissolved in solvents that are too sterically hindered to occupy the cavities. Type 3: Particles of microporous frameworks dispersed in sterically hindered solvents.

same as simply dissolving up host species, since in those cases the cavities of the host would normally be occupied by solvent molecules. To satisfy the definition “microporous” the liquid would have to be able to support persistent, *empty* cavities. Such cavities would therefore be readily accessible to potential guests (e.g., gases) when exposed to them and fast shape- and size-selective inclusion would be expected. Although the concept of microporous liquids appears to be new, some literature is also discussed which sug-

gests not only that their preparation is feasible, but that some are arguably already known, even if they have not previously been recognised in such terms.

Conventional, “Extrinsic” Porosity in Liquids

The existence of small, transient pores between the molecules of liquid phases is well recognised, and has been the subject of theoretical studies.^[5] The relative concentrations and sizes of such pores are recognised as important factors in determining solubility in the liquid. Figure 3 is repro-

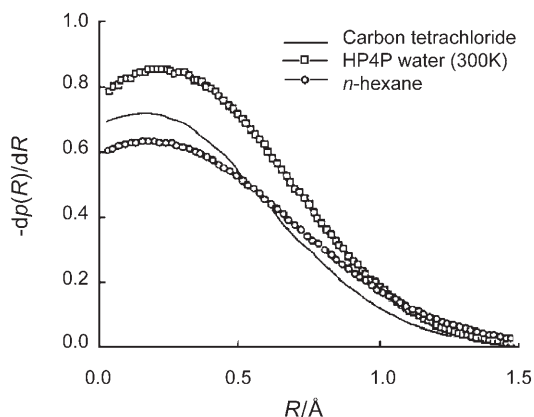


Figure 3. The probability density, $-dp(R)/dR$, that the maximum size sphere (cavity) that could be implanted in a given liquid would have radius R , plotted over the range $R=0.0-1.5$ Å. Modified with permission from reference [5a].

duced from reference [5a] and shows the calculated probability densities for pores of radius R in carbon tetrachloride, water and *n*-hexane. For each liquid, the most probable cavity size lies between $R=0.1$ and 0.4 Å, and cavities above a radius of approximately 1.5 Å are expected to be very rare; that is, the pore sizes are smaller than typical molecular sizes.

Engineering Permanent Microporosity in the Liquid State

Type 1 porous liquids—neat liquids: A neat liquid could be expected to be microporous if its constituent molecules 1) have an internal cavity, 2) are rigid, that is, they cannot collapse, and 3) have shapes incapable of intermolecular self-filling. Even leaving aside temporarily the key issue of the melting point, we could initially consider some known types of organic hosts, such as crown ethers or calixarenes and so forth, but discount them due to their inappropriate shapes and/or high flexibilities. Crown ethers have shallow cavities that could be easily filled in an intermolecular fashion, and they are also highly flexible species with cavities liable to collapse in the absence of guests. Clues as to the possible liquid-state behaviour of pure hosts with more complicated

shapes can be obtained from their crystal structures in pure, guest-free states. These reveal, for example, that the irregular shapes of *tert*-butylcalix[4]arenes are such that they too can readily form significantly self-filled structures in either the guest-free state^[6a,b] or when combined with guests that only bind outside the central cavity.^[6c] The more regular tubelike shapes of cyclodextrins^[7] (CDs) could be expected to prevent their intermolecular self-filling and so to preserve their cavities in the guest-free state. Another attractive aspect of CDs in the context of porous liquids is that, although unfunctionalised CDs are high-melting point solids^[7] consistent with the formation of stable hydrogen-bonded networks, alkylation dramatically lowers their melting points.^[8] For example, permethyl- β -CD melts at 148 °C^[8a] and perpentyl β -CD is liquid at room temperature.^[8b] However, any long chain substituents are likely to become included within the cavities (inter- or intramolecularly) and remove the porosity. In fact, even the short chain substituents of permethyl- β -CD allow significant intermolecular self-filling when this compound is crystallised in the guest-free state (Figure 4). Additionally, the flexibility of the host

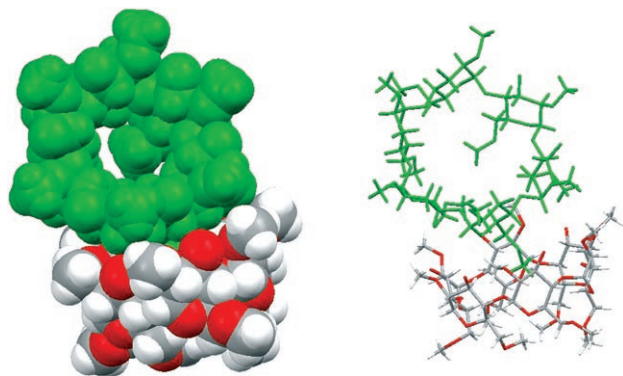


Figure 4. Structure of permethyl β -cyclodextrin. In the crystalline state in the absence of included guests the cavities of permethyl- β -CD^[8a] are largely filled in both an inter- and intramolecular fashion, with an $-\text{OCH}_3$ substituent of one CD (green) occupying the cavity of another, and a twisted conformation of one sugar residue. It suggests that cavities may effectively be filled in the pure liquid state.

is revealed as one methyl glucose residue adopts a conformation in which one of its methyl groups also occupies part of the cavity space (i.e., there is a degree of intramolecular self-filling).^[8a] Despite the likelihood of self-filling in the liquid state, alkylated cyclodextrins are effective stationary phases for enantioselective gas chromatography.^[8c,d]

The discussion above highlights some of the issues to consider in choosing appropriate hosts for the formation of Type 1 porous liquids (i.e., pure liquid hosts with empty cavities), and suggests that solving all the issues may be nontrivial. However, there are many further known host systems that could be considered and adapted, and new host types could of course be designed specifically for the purpose of forming porous liquid phases. Alternatively, a way to get around some of the issues in designing porous liquids based

on pure host molecules is to use solvents, or to form eutectics, so that liquid phases can be more readily obtained at room temperature. We describe these as Type 2 porous liquids.

Type 2 porous liquids—empty hosts dissolved in sterically hindered solvents: In this type of porous liquid the host is dissolved in a solvent. It would be essential not only that the host be rigid and so unable to collapse in the absence of a guest, but also that no part of any solvent molecules could occupy the host's cavities. In this regard, solutions of calixarenes, for example, are again not promising, since they have wide open and easily accessible cavities.

Cucurbiturils (CBs),^[9–11] however, are more promising in this regard. These are cyclic structures based on five or more glycouril groups (Figure 5). They are apparently rigid

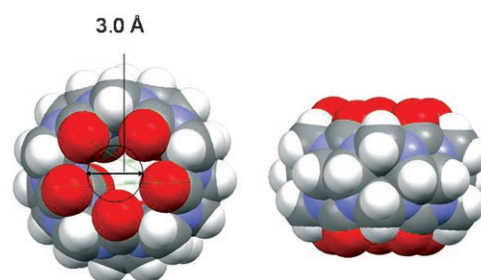


Figure 5. Structures of the cucurbituril CB[5] adapted from the single-crystal structure of the trihydrate^[12] with water molecules removed to give an impression of the empty host, and dimensions of the portal indicated.

structures with molecular-sized cavities, but, crucially, they have very restricted access windows (Figure 5). For example, the cyclic pentamer CB[5] has been found able only to include small species such as H_2O , N_2 , O_2 , CH_3OH or CH_3CN .^[10] The notoriously low solubilities of CBs in organic solvents can be increased by adding organic substituents to their peripheries.^[9,11] Resulting solutions, even in modestly bulky solvents such as cyclohexane, are therefore potential examples of Type 2 porous liquids. There are no X-ray crystal structures of the empty CB[5] host, and therefore the hydrate^[12] is shown in Figure 5 with the H_2O guest artificially removed to give an impression of the empty molecular structure.

It is interesting to note that Cram actually demonstrated the concept of empty hosts dissolved in sterically hindered solvents.^[13] Hemicarcerands, such as **1** shown in Figure 6, have cavities large enough to include small molecules such as CH_2Cl_2 or $(\text{CH}_3)_2\text{NCOCH}_3$, but too small to include molecules such as diphenyl ether. When the inclusion complex **1**· $(\text{CH}_3)_2\text{NCOCH}_3$ was dissolved in diphenyl ether and heated to 195 °C for 5 days, ^1H NMR spectroscopy showed that the small formamide guest was indeed removed to leave the empty host dissolved in the sterically hindered solvent. Consideration of CPK models suggested also that the framework should not collapse when empty, and therefore

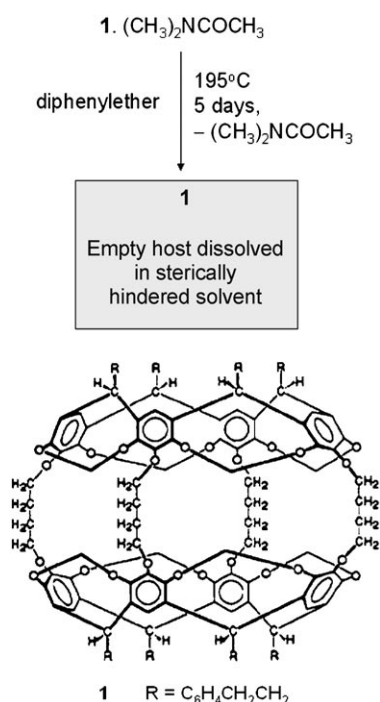


Figure 6. Hemicarcerands, **1**, described by Cram, from which guests were removed in solution of a sterically hindered solvent. Adapted with permission from reference [13].

the guest-free host dissolved in diphenyl ether seems to be a strong candidate for a truly microporous liquid. However, despite the great significance of this work, no *direct* evidence was obtained for the existence of an empty cavity.

Inorganic examples of possible Type 2 porous liquids could be based on cyano-bridged cage structures, such as the neutral, discrete metallocube $[\{\text{CpCo}(\text{CN})_3\}_4(\text{Cp}^*\text{Ru})_4]$, “ Co_4Ru_4 ” (Figure 7) described by Rauchfuss et al.^[14] The framework is apparently rigid, that is, unable to collapse even when the cavity is empty, due to the use of short, linear, rigid connectors. The central cavity, although small, is capable of including guests such as CH_3NH_3^+ , K^+ or Cs^+ . Importantly, the compound can also be prepared in the empty guest-free state, and it dissolves in a range of solvents. Due to its very small access windows (ca. $1.85 \times 1.85 \text{ \AA}$), even solutions in non-sterically hindered solvents such as acetonitrile, which have already been reported,^[14] are possible Type 2 porous liquids. In fact Co_4Ru_4 co-crystallises with acetonitrile, but the solvent in the crystal is outside the host, and the cavity remains apparently empty.^[14]

Type 3 porous liquids—framework materials dispersed in hindered solvents:

In addition to molecular porous liquids, particles of solid microporous framework materials could be dispersed in liquids to give fluid porous phases. In this regard the dispersion of cyano-bridged coordination frameworks has been described.^[16a] In addition, zeolite nanocrystals have been surface-modified with organic groups that enable them to form transparent dispersions in organic solvents, such toluene.^[16b] As with Type 2 porous liquids, it

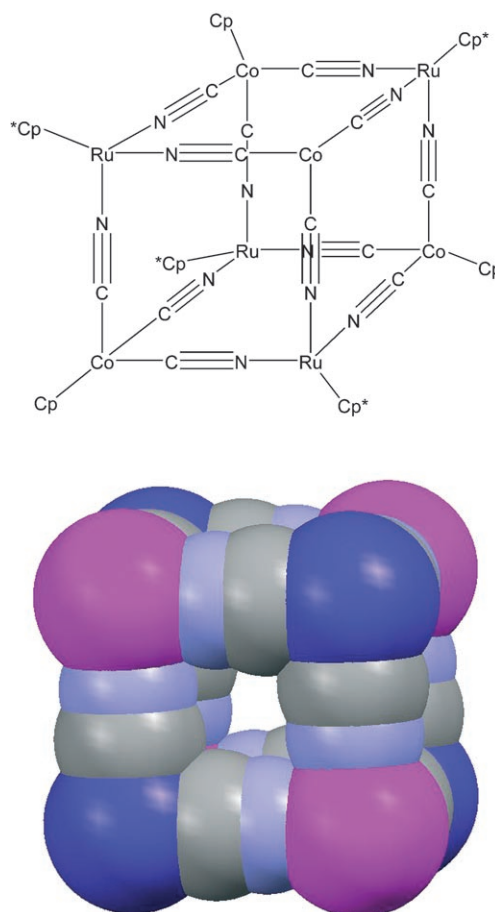


Figure 7. Empty cyano-bridged metallocubes^[14] that are rigid, have small access windows of about $1.85 \times 1.85 \text{ \AA}$, have internal cavities which are capable of including guests or being empty, and which are soluble in a range of solvents. (Windows size estimation is based on a typical C...N distance of 5.1 \AA , taking into account the van der Waals radii of C, 1.70 , and N, 1.55 \AA ^[15]). The space-filling diagram shows the core of the cage from the X-ray crystal structure with the peripheral Cp and Cp* ligands omitted for clarity.

would be important that the liquid molecules be too sterically hindered to enter the cavities of the framework.

With Type 2 and 3 porous liquids, in order to produce “permanent”, non-evaporating phases, ionic liquids^[4] would also be of interest as solvents. The ordering and ion-ion attraction within ionic liquids would be additional points of interest, since they could disfavour the inclusion of the solvent ions in the host cavity.

Conclusion and Outlook

Engineering permanent microporosity into the liquid state is a novel concept that is of interest both fundamentally and, given the usefulness of microporous solids, potentially even in the long term for applications. Synthetic approaches to porous liquids can be envisaged based on engineering empty pores *within* molecules (or particles) in the liquid phase, that is, porosity “intrinsic” to the mobile species, but which

are inaccessible to other constituents of the liquid. Despite the novelty of the concept, such materials are not purely speculative. They are practically achievable, and some literature exists to suggest that some may already be known, although not previously recognised and characterised in such terms.

Acknowledgements

The concept of porous liquids arose from a discussion with Dr. David Rooney, who suggested dispersing porous coordination frameworks in liquids to produce fluid absorbents. We are also indebted to Cristina Lagunas, Gerhard Wenz, Chris Hardacre, A. P. de Silva and Mario Del Pòpolo for important discussions. We are grateful to EPSRC (grant no. EP/C00776X/1) for funding our work in this area.

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Published online: March 12, 2007