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Exploring cavities in Type II Porous Liquids with Xenon

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Abstract:	<p>ABSTRACT. The porous topology of Type II Porous Liquids (PLs), prepared using Noria-OEt as an empty molecular host dissolved in 15-crown-5 solvent, is investigated with ^{129}Xe NMR Spectroscopy. Xenon NMR parameters, such as chemical shifts and T_1 relaxation times, measured in PLs solutions prepared at various Noria-OEt concentrations, are related to the intrinsic microporous structure of the material. The experimental data are interpreted on the basis of a multiple-site model for xenon atoms within the multiple PLs cavities. Diffusion NMR experiments show a similar mobility of xenon in PLs compared with the pure solvent.</p>
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Response to Reviewers:	

Dear editor,

We enclose for your consideration our manuscript entitled **“Exploring cavities in Type II Porous Liquids with Xenon”**, by Matteo Bovenzi, Michele Mauri, Francesca Alexander, Stuart L. James, Roberto Simonutti, Franca Castiglione, for publication in Journal of Molecular Liquids.

In this work, we studied the porous topology of Type II Porous Liquids (PLs) by ^{129}Xe NMR spectroscopy. We would like to emphasize that this is, as far as we know, the first attempt to use ^{129}Xe NMR spectroscopy to investigate an important class of porous liquids based on Noria-OEt, a derivative of the water-wheel like macrocycle, dissolved in the 15-crown-5 solvent. The strength of the work relies upon the basic idea that xenon NMR parameters, such as chemical shift, longitudinal relaxation time and diffusion coefficient provide information about the porous structure of these liquids holding molecular cages.

One of the current topics of research and scientific debate focuses on understanding the microporous structure in PLs, namely the organization/size, in the liquid state, of molecular cages dissolved in hindered solvents. In this work, we used xenon gas dissolved in type II PLs as NMR sensitive “spin probe” inside the void spaces of the solvent cage and the macromolecular cavities. The xenon chemical shift, detected through Xe-129 NMR, is sensitive to the compression effects brought about by the cavities dimension. The chemical shift variations observed, varying Noria-OEt concentration, and reported in our work are explained using a multiple-site model for xenon atoms exploring multiple-sized PLs cavities. Furthermore, relaxation parameters are also related to the free pore volume that are formed in PLs.

These results shed new light on the porous structure of type II PLs and, at the same time, highlight how Xe-129 NMR parameters normally related to static (chemical shift) and dynamic (diffusion and relaxation) properties are in fact strongly correlated and able to provide a coherent picture of the system, but also useful for a rational design of applications, suffice here to mention gas sorption in PLs.

Accordingly, we believe that the methodology, the results, the discussion and the fall-out of our findings can arouse the interest of a large readership of this journal.

Looking forward to hearing from you.

Yours sincerely,

Franca Castiglione

We thank the Reviewer for his/her careful reading of our manuscript and the significant improvements recommended. We have revised the paper according to his/her suggestions and below we report our point-by-point answers to the comments and criticisms. The changes to the original version of the manuscript have been highlighted in yellow. Reviewers' comments are in *italic* while our responses are in blue color normal font.

REVIEWER: This paper explores the confinement of Xe within a previously developed porous liquid (specifically Noria-OEt dissolved in 15-crown-5). The authors describe an unexpected chemical shift in Xe when the gas is dissolved in the porous liquid compared to the pure solvent or the solid cage via NMR spectroscopy. The work is novel, especially the realization of the need for more complex models to describe the chemical shift of Xe in the PL compared to the pure components. The methods are detailed and the results seem to be reproducible. The audience of this journal should enjoy reading this well written manuscript and find it impactful for similar endeavors. Minor edits and some additional data will clarify and enhance the manuscript.

AUTHORS' REPLY: We thank the Reviewer for his/her appreciation of our work.

REVIEWER: 1. Page 3- Classification system of porous liquids has been updated from 3 types to 4 types. One of the authors for this publication also contributed to the initial works where the 4 type classification system was introduced. Please address in introduction. Reference to the updated classification system is shown in the following works.

Rimsza, J. and Nenoff, T. "Porous Liquids: Computational Design for Targeted Gas Adsorption" ACS Appl. Mater. Interfaces 2022, 14, (16), 18005-18015.

Egleston, B.; Mroz, A.; Jelfs, K.; Greenaway, R. "Porous Liquids- The Future is Looking Emptier" Chem. Sci. 2022, 13, 5042-5054.

Bennet T.; Coudert, F.; James, S; Cooper, A. "The Changing State of Porous Materials" Nature Materials 2021, 20, 1179-1187.

AUTHORS' REPLY: We thank the Reviewer for pointing this out and we agree that Type IV porous liquids should be mentioned in our work, even though they are very rare. In this regard, we modified the introduction, adding some information about Type IV porous liquids, and inserted references to the works indicated by the Reviewer (references 14-16).

REVIEWER: 2. The authors reference several studies related to the utility of porous liquids for gas capture and separation in the introduction. A paper was recently published describing the first techno-economic analysis of porous liquids used for gas separations. This paper should also be referenced due to its relevance to this statement.

Borne, I.; Simon, N.; Jones, C. W.; Lively, R. P. "Design of Gas Separation Processes Using Type II Porous Liquids as Physical Solvents". Ind. Eng. Chem. Res. 2022, 61, (32), 11908-11921.

AUTHORS' REPLY: We thank the Reviewer for indicating this interesting and relevant paper. We inserted a reference to this work in the introduction (reference 25).

REVIEWER: 3. Page 4- Please state how the Noria-OEt/15-crown-5 porous liquid was confirmed to be porous (gas evolution test, isotherms, which probe gas was used, etc.)

AUTHORS' REPLY: The Noria-OEt/15-crown-5 system was confirmed to be porous via different techniques. First, the CH₄ uptake in both pure 15-crown-5 and Noria-OEt in 15-crown-5 (50 mg/mL) was measured at 303.15 K and at different pressures, demonstrating that the solubility of methane in the PL increased with respect to the pure solvent. Furthermore, a control experiment was performed with a solution of 3-ethoxyphenol in 15-crown-5 to ensure that the increased CH₄ solubility in the Noria-OEt PL was due to the presence of cavities and not to the solvating effect of the aromatic cage walls of Noria-OEt. Indeed, the CH₄ uptake of this sample was nearly identical to that of pure 15-crown-5, supporting the existence of cavities as being critical. As further confirmation, N₂ sorption on the Noria-OEt 50 mg/mL PL was performed at 77 K, giving a BET surface area of 105.118 m²/g. Lastly, MD simulations helped establish the existence of cavities in the PLs. Even though demonstrating the existence of pores in the PLs is of the utmost importance, in the manuscript we did not display these results because they are already reported in the referenced work in which the synthesis and the characterization of the Noria-OEt PLs are discussed (reference 37).

REVIEWER: 4. *Page 8- Do the authors know the maximum solubility of Noria-OEt in 15-crown-5? If so, please state that number and why the maximum concentration explored was 70 mg/mL. (If 70 mg/mL is the maximum solubility please state that).*

AUTHORS' REPLY: As reported in the pioneering work about these porous liquids, the Noria-OEt molecule was found to be soluble in 15-crown-5 up to 80 mg/mL (reference 37). Actually, we also investigated this concentration with ¹²⁹Xe NMR, but the high viscosity of the solution caused a significant decrease in the T₂* of dissolved xenon. This, in turn, greatly increased the linewidth of the ¹²⁹Xe peak, making it difficult to obtain good signal-to-noise ratios in the ¹²⁹Xe NMR spectra and making the data less reliable. For these reasons, we chose not to report the data for the 80 mg/mL PL which also do not contribute significantly to our understanding of the porous topology of these liquids.

REVIEWER: 5. *Page 8- Are there any other referenced works besides the Xe-cyclodextrin work that show an average or exchange signal accurately describes this system?*

AUTHORS' REPLY: There are a couple of works in which a multiple-site model has been employed to describe different systems. We inserted a reference to these works on page 9 of the manuscript (references 49 and 50).

REVIEWER: 6. *Page 10- Add references after this sentence "The result is shown in the inset of Fig. 1. The spectrum shows a single broad resonance centered at 177 ppm, a high chemical shift value which lies in the range usually associated to xenon confined in micropores."*

AUTHORS' REPLY: References to three different, representative works have been inserted at the end of the sentence (references 44-46).

REVIEWER: 7. *Page 11- The authors mention the side product R3-OEt that can form when synthesizing Noria-OEt. Does the presence of these larger oligomers impact other factors of the porous liquid (viscosity, solubility, etc.)? Can the authors mention or suggest methods to remove the larger oligomers after synthesizing Noria-OEt?*

AUTHORS' REPLY: The resorcinarene trimer, R3, is a structural isomer (same molecular weight) of Noria with different positions of the resorcinol and 1,5-pentanedial residues. However, both isomers have high

symmetry (D_{3h} and S₆ respectively) and similar structures with peripheral cavities and a single large hydrophobic cavity of about 5 Å at the centre. Due to similar structure and cavity size, both isomers form a porous liquid when dissolved in a size-excluded solvent. The synthesis and characterization of Noria-OEt/R3-OEt is extensively described in ref. 37. Although outside the scope of this work, our suggestion for the removal of higher molecular weight oligomers is the use of chromatographic methods.

REVIEWER: 8. Do the authors mention the overall gas uptake of Xe in Noria-OEt, the 15-crown-5, and the most concentrated porous liquid? If not, can the authors include that value as either single pressure uptakes or isotherms to confirm the porous liquid is porous to Xe via techniques other than NMR?

AUTHORS' REPLY: As we mentioned in the answer to the 3rd point, the porosity of the Noria-OEt PL was demonstrated mainly via CH₄ uptake measurements, and no direct Xe uptake was measured. However, since the xenon atom behaves very similarly to small alkanes, especially in solution, it can be viewed as the smallest, "ennobled" alkane. Moreover, the Noria molecule has been shown to have a cavity with a very high affinity for xenon, to the point that it has been called a Xe-selective molecule. We believe that these combined features point to the porous liquids analyzed in this work being porous to xenon.

REVIEWER: 9. Page 15- Can the authors comment on the diffusion coefficient of xenon in the more concentrated PL samples? Why are only the pure solvent and most dilute PL diffusion coefficient data presented? Please add in the diffusion coefficient of the more concentrated samples or explain why these values could not be obtained.

AUTHORS' REPLY: The diffusion coefficients of xenon in the most concentrated porous liquids would have been another significant parameter for the study of their porous topology. Actually, we tried to perform diffusion NMR experiments even for the more concentrated samples, but we could not obtain any reliable data. We believe that this is due to the low T_2^* of dissolved xenon in all but the most diluted porous liquid, which is indicated by the strong increase in the linewidth of the xenon peak with the increasing concentration. This prevented obtaining reliable data even when using short diffusion delays, which are needed when the diffusion coefficient is in the order of 10^{-10} m²/s. Thus, for the porous liquids with a Noria-OEt concentration higher than 11 mg/mL, the diffusion coefficient of xenon was not determined.

REVIEWER: 10. Also please comment on why the diffusion coefficient of xenon in the pure solvent and the PL are the same. Based on the previous results and the arguments presented throughout shouldn't the diffusivity of Xe be different in the pure solvent compared to the porous liquid?

AUTHORS' REPLY: The Reviewer evidences an interesting point which also puzzled us in the beginning. The diffusion coefficients of xenon in pure 15-crown-5 and in the most diluted porous liquid (11 mg/mL) are the same due to the low concentration of Noria-OEt in the PL. Indeed, even though the porosity of the PLs has been demonstrated thoroughly, the analyzed PL (Noria-OEt 11 mg/mL) is quite diluted. Thus, as we indicated in the last paragraph of the "Results and discussions" section, the Noria-OEt 11 mg/mL PL is diluted to the point that the diffusivity of xenon is mostly, if not completely, determined by the bulk solvent.

REVIEWER: 11. Reference 34 is missing

Page 12- End of final sentence, figure 2 should be Figure 2

AUTHORS' REPLY: We inserted the suggested corrections. Given that we added and moved some references when updating the manuscript, the former reference 34 is now reference 39. We thank the Reviewer for noticing these errors.

In addition to that, we improved the resolution of Figures 2, 3 and 4.

- Type II Porous Liquids microporous structure
- ^{129}Xe NMR Spectroscopy
- Multiple-site model for xenon atoms in PLs

Exploring cavities in Type II Porous Liquids with Xenon

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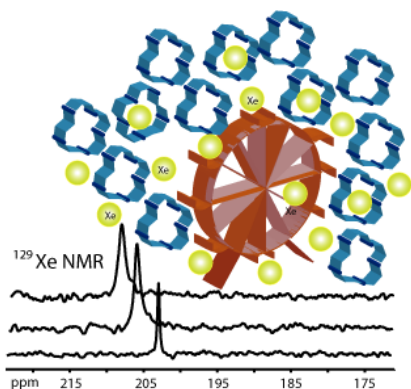
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ABSTRACT. The porous topology of Type II Porous Liquids (PLs), prepared using Noria-OEt as an empty molecular host dissolved in 15-crown-5 solvent, is investigated with ^{129}Xe NMR Spectroscopy. Xenon NMR parameters, such as chemical shifts and T_1 relaxation times, measured in PLs solutions prepared at various Noria-OEt concentrations, are related to the intrinsic microporous structure of the material. The experimental data are interpreted on the basis of a multiple-site model for xenon atoms within the multiple PLs cavities. Diffusion NMR experiments show a similar mobility of xenon in PLs compared with the pure solvent.

TOC GRAPHICS



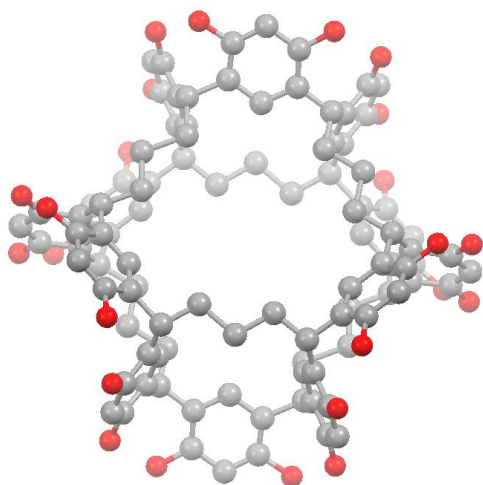
KEYWORDS Xenon NMR, Porous Liquids, Diffusion, Relaxation

Porous liquids (PLs) are a neoteric class of materials characterized by permanent cavities in the liquid state.¹⁻⁴ PLs, initially proposed by James et al.,¹ show peculiar physico-chemical properties which arise from merging a permanent rigid microporosity, derived from well defined porous solids, such as macrocyclic hosts or zeolites, dissolved or dispersed in a fluid liquid phase. Based on the nature of their porous structure, PLs can be divided into **four** different types. Type I PLs are pure liquids with permanent, rigid cavities whose shapes and dimensions prevent self-filling, guaranteeing the existence of a permanent porous structure.⁵⁻⁷ Type II PLs are rigid porous host molecules dissolved in size-excluded solvents which cannot enter the host cavities.⁸⁻¹⁰ Type III PLs are constituted by porous framework materials dispersed in size-excluded solvents.¹¹⁻¹³ **Finally, Type IV porous liquids are meltable, single component porous frameworks which retain their intrinsic porosity in the liquid state.**¹⁴⁻¹⁶ Among the three different categories, Type I **and Type IV** PLs are the least common due to the tough challenges posed by their design and synthesis. To date, there are only a few examples of Type I PLs, mostly based on the appropriate functionalization of porous molecular hosts.^{5,6,17,18} On the other hand, Type II and Type III PLs are generally easier to prepare, more versatile and more stable. Thanks to these combined features, various Type II and III porous liquids have been developed in the recent years, each with their own chemical and physical properties.

Some of the possible applications of porous liquids are the use in catalysis and membranes, chiral recognition and separation, and the use as electrolytes or heat transfer fluids. However, currently the most intensely investigated application of porous liquids is the use in the field of gas sorption. Several studies relate to their utility in gas capture¹⁹⁻²¹ and separation,²²⁻²⁵ **highlighting** that the sorption/separation capability strongly depends on the cavities shape and dimension,¹⁹ and on the mechanism of gas confinement. In view of these applications, a detailed understanding of the

porous structure and of the dynamic properties of gaseous species dissolved in PLs plays a central role, and it may help in the design of task-specific materials. Nuclear Magnetic Resonance (NMR) spectroscopy of noble gases,^{26,27} (especially xenon) loaded in nano/micro structured solid materials has been widely used to probe the structures and dynamic processes in porous media,²⁸ zeolites,²⁹ nano-channels³⁰ and polymers.^{31,32} Furthermore, the ¹²⁹Xe chemical shift and relaxation times have been used to investigate the interactions of xenon atoms with liquid solvents,³³ and the complex ionic liquids nano-structure consisting of entangled polar/apolar domains.³⁴⁻³⁶ In all these applications, the ¹²⁹Xe isotope (around 26% natural abundance) is used as inert NMR probe as it is extremely sensitive to the surrounding molecular environment, cage effect and confinement which through van der Waals interactions induce a remarkable deshielding effect and influence xenon relaxation times and diffusion motion.

In this paper, we study the porous topology of a series of PLs using ¹²⁹Xe NMR parameters, such as chemical shift, T_1 relaxation time, and xenon diffusion coefficient. The studied materials are porous liquids based on Noria-OEt, a derivative of the well-known paddlewheel-like molecular host Noria (Scheme 1), and 15-crown-5 ether as the bulky solvent. Indeed, as previously demonstrated, the functionalization of Noria with 12 scrambled ethyl substituents enhances its solubility in 15-crown-5, allowing the formation of chemically and thermally stable Type II porous liquids.³⁷ Moreover, it has been demonstrated that the cavity of solid Noria is both shape and size selective for a single xenon atom.³⁸ This important feature makes these porous liquids ideal for ¹²⁹Xe NMR characterization.



Scheme 1. Molecular structure of Noria, showing the carbon framework (grey), OH-functionalisation (red) and the central cavity.

Xenon shielding. The ^{129}Xe NMR spectra acquired at 298 K for all the samples are shown in **Figure 1**. The spectrum of xenon loaded in the pure component crown ether, 15-crown-5 (**Figure 1a**), shows a narrow resonance line at 202.97 ppm. Compared to the chemical shift of xenon in common organic solvents,³⁹ alkanes,³³ and oxygen- and nitrogen-substituted aliphatic compounds,⁴⁰ this relatively high chemical shift can be explained by a strong interaction of xenon with the crown ether molecules, possibly leading to the formation of a xenon-crown ether complexes similar to those of alkali metal cations with crown ethers. Indeed, a cage-deshielding effect on ^{129}Xe chemical shift has already been reported by Claessens et al.⁴¹ for xenon loaded in crown-ethers/chloroform solutions compared with their linear analogues. The authors classified 12-crown-4 and 15-crown-5 ethers, characterized by a specific inner cavity, as “host-molecules” capable of forming a xenon-ether complex through specific interactions. In addition, the formation

of a stable solid-state complex between a xenon compound and 15-crown-5 has also been recently reported, confirming that Xe is indeed able to form complexes with crown ethers.⁴²

The room temperature spectra of xenon loaded in Type II porous liquids prepared with different Noria-OEt concentrations are also shown in **Figure 1**. All the spectra show a single, intense line, arising from xenon dissolved in the porous liquid. The chemical shift values are reported in **Table 1**. The xenon chemical shift is responsive to the variation of the Noria-OEt concentration: an increase in the Noria-OEt concentration from 11 mg/mL (**Figure 1b**) to 70 mg/mL (**Figure 1g**) leads to a chemical shift increase of about 3 ppm. The signal of xenon in pure 15-crown-5 also follows this trend, having the resonance at the lowest chemical shift among all the liquids. A plot of the ¹²⁹Xe chemical shift as a function of the concentration of Noria-OEt is shown in **Figure 2**. To understand the nature of the Xe@PL signal, it should be remembered that ¹²⁹Xe NMR is a dynamic technique. If xenon atoms move rapidly and experience different environments on the NMR time scale, the resulting chemical shifts are averages of the chemical shifts of xenon nuclei in the different sites, weighted by the respective molar fractions. On the other hand, separated signals are only observed if the exchange of xenon nuclei between different sites is slow on the NMR time scale. Since it is well-known that Noria is a xenon-selective molecule,³⁸ we can assume that xenon interacts both with Noria and with 15-crown-5 on the NMR time scale, giving rise to an averaged or exchange signal. Similar behavior has already been reported for xenon dissolved in solutions of α -cyclodextrin.⁴³

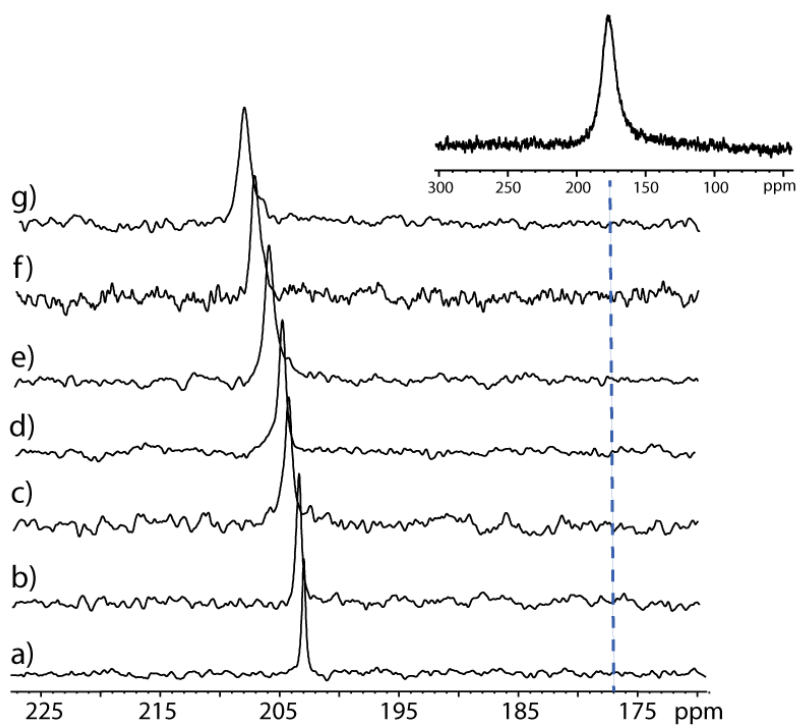


Figure 1. ^{129}Xe spectra of Type II porous liquids with increasing Noria-OEt concentration, a) pure 15-crown-5 b) 11, c) 28, d) 40, e) 50, f) 60, g) 70 mg/mL. The ^{129}Xe spectrum of xenon loaded in solid Noria-OEt is shown in the inset.

Table 1. Chemical shifts (δ) of ^{129}Xe dissolved in Type II porous liquids.

$C_{\text{Noria-OEt}}$ (mg/mL)	δ (ppm)
0*	202.97
11	203.26
28	204.24
40	204.56
50	205.73
60	206.16
70	206.56

*Pure 15-crown-5.

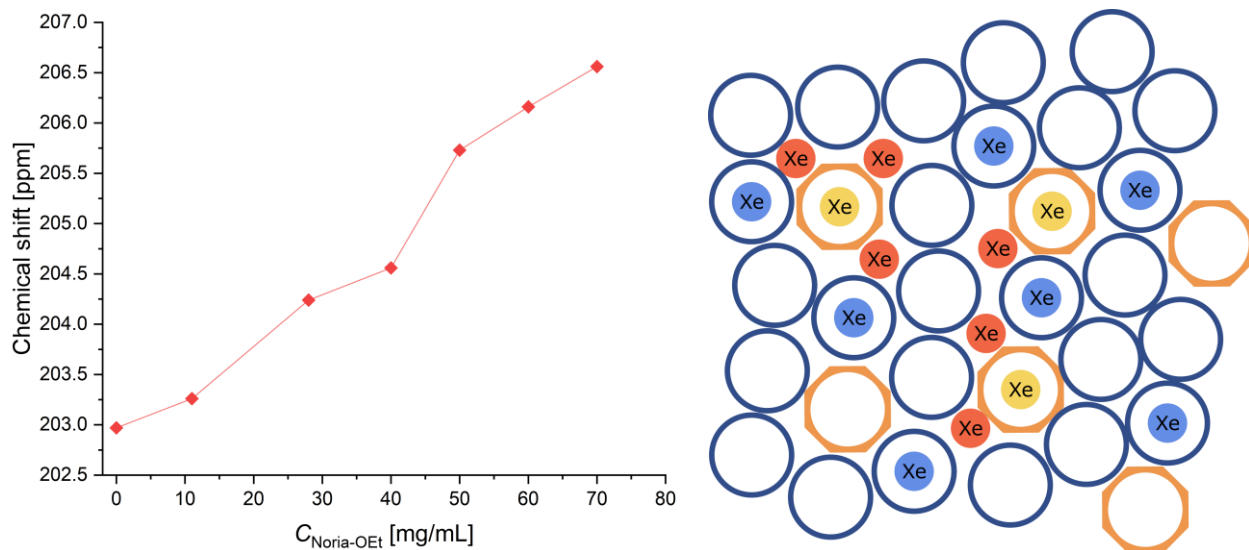


Figure 2. (left) Room temperature ^{129}Xe chemical shift in Type II porous liquids as a function of the Noria-OEt concentration. The sample with concentration 0 is pure 15-crown-5. The lines are visual aids only. (right) Sketch of the multiple-site model for Xe@PLs (orange polygons represent Noria-OEt, blue circles represent 15-crown-5 species).

To further understand the underlying origin of the Xe@PL resonance, we decided to acquire a spectrum of xenon in solid Noria-OEt. The result is shown in the inset of **Figure 1**. The spectrum shows a single broad resonance centered at 177 ppm, a high chemical shift value which lies in the range usually associated to xenon confined in micropores.⁴⁴⁻⁴⁶ According to the model developed by Demarquay and Fraissard for microporous zeolites,⁴⁷ in the absence of strong adsorption sites, such as highly charged cations, and paramagnetic species, provided that Xe-Xe interactions are absent or negligible, the chemical shift of confined xenon is related to its mean free path, λ , expressed in Å, by the following relationship.

$$\delta_{Xe} = 243 \left(\frac{2.054}{2.054 + \lambda} \right) \quad (1)$$

The mean free path can be used to calculate the pore diameter in the two limiting cases of spherical and cylindrical pores: in the former case, $D_s = 2\lambda + D_{Xe}$, while, in the latter, $D_c = \lambda + D_{Xe}$, where $D_{Xe} = 4.4 \text{ \AA}$ is the xenon van der Waals diameter. By inserting the chemical shift of xenon in solid Noria-OEt in Equation 1, we obtain a mean free path of 0.77 \AA which leads to a spherical pore diameter $D_s = 5.9 \text{ \AA}$ and to a cylindrical pore diameter $D_c = 5.2 \text{ \AA}$. These results are in good agreement with crystal structure data which indicate that the central cavity of Noria has a diameter in the $5\text{-}7 \text{ \AA}$ range.^{38,48} Indeed, in the ethylated derivative under study, Noria-OEt, the 12 ethyl groups are randomly distributed on the 24 outer oxygen sites, and do not have a significant effect on the size of the inner cavity.

The broadness of the xenon signal could be attributed to xenon diffusing in solid particles having different orientations with respect to the external magnetic field and to the presence of various species with very similar cavity sizes. As reported previously, the typical synthesis of Noria yields a mixture of many different oligomers, mainly Noria itself and a structural isomer, the resorcinarene trimer called R3, which have very similar central cavity sizes. Thus, it is most likely that the synthesis of Noria-OEt also yields the ethylated resorcinarene trimer, R3-OEt, and other oligomers, in the same manner as the typical synthesis of Noria.³⁷ In addition, only considering the Noria-OEt molecule itself, there are 64 possible geometrical isomers due to the possible distributions of the 12 ethyl substituents on the outer oxygen atoms. All these different species are expected to have cavities of effectively the same size. The broad ^{129}Xe signal of bulk Noria-OEt extends from roughly 160 ppm to 190 ppm, indicating that xenon does not explore a single microporous species but rather a wide distribution of micropores ranging from 5 to 7 \AA (as calculated from Equation 1).

The comparison of the xenon chemical shift values of solid Noria-OEt, pure 15-crown-5, and Type II porous liquids reveals interesting details about their structural features. In a simple two-site model for the PLs, where xenon interacts with the cavities of both Noria-OEt and 15-crown-5 in the NMR time scale, the ^{129}Xe chemical shift would be an average of the chemical shifts of xenon in the two pure species, 177 ppm for solid Noria-OEt and 202.97 ppm for pure 15-crown-5, weighted by the respective molar fractions. In this case, one would expect the Xe@PL chemical shift to be in-between those two limiting values, and to be inversely proportional to the host concentration due to the Xe@Noria-OEt molar fraction increasing with the concentration of Noria-OEt. On the contrary, the measured Xe@PL chemical shifts are always higher than the Xe@15-crown-5 chemical shift, and they increase with the host concentration, following an opposite trend with respect to the predictions. Thus, a two-site model is too naive for the system under study and does not represent it adequately. A better representation of the structure of these porous liquids can be provided by a multiple site model.^{43,49,50} In addition to being in the cavities of the host and of the solvent, xenon can also be found in the immediate vicinity of the Noria-OEt molecules, where it interacts with their structural indentations, and this influences the chemical shift value. This interpretation is in accordance with molecular dynamics (MD) simulations performed on this system.³⁷ The radial distribution function between the Noria-OEt centers and the solvent molecules showed two distinct maxima, one corresponding to the outer solvation shell and the other to the six indentations outside the Noria-OEt cavity. Overall, these experimental results indicate that dissolving a porous host molecule in a solvent having a defined internal cavity leads to the formation of smaller cavities that may host xenon atoms. A sketch of the multiple site model is shown in **Figure 2**.

To investigate the effect of temperature on our systems, we performed variable temperature ^{129}Xe NMR experiments on 15-crown-5 and on Type II PLs with Noria-OEt concentrations equal to 11 mg/mL and 60 mg/mL. The results are shown in **Figure 3**.

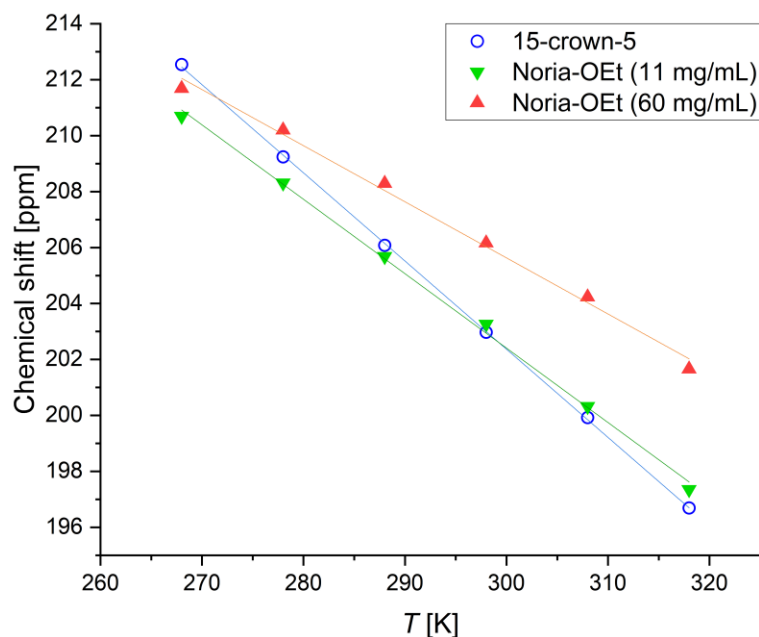


Figure 3. Variable temperature ^{129}Xe chemical shift of 15-crown-5 and selected Type II porous liquids. The lines are linear fits to the data.

For all the three samples, the chemical shift shows a linear dependence on the temperature in the range 268-318 K. For 15-crown-5, a linear fit gives a slope of -0.32 ppm/K, analogous to the values reported by Morgado et al. for xenon dissolved in a wide variety of *n*-alkanes, branched alkanes and cycloalkanes.³³ In the case of porous liquids, the temperature dependence of the chemical shift is a function of the of the Noria-OEt concentration: -0.25 ppm/K for 11 mg/mL and -0.18 ppm/K for 60 mg/mL.. Increasing the Noria-OEt, concentration makes the Xe chemical shift less sensitive to temperature. This behavior can be explained based on the molecular dynamics calculations reported by Jameson and coworkers,⁵¹ which demonstrates that the main determinant of the

average chemical shift variation as function of temperature is the modification of the cage (site) free volume, available to the Xe atom. Large free volume variations lead to large changes in chemical shift, as in the case of crown ether, an extremely flexible molecule (with a slope of -0.32 ppm/K). Conversely, in the case of the porous liquids, in addition to this cage there are other two sites (inside Noria and close to the Noria surface) that do not change dimensions significantly as the temperature varies.

Xenon T_1 relaxation. Due to the high sensitivity of the spin-lattice relaxation process of dissolved xenon on the surrounding environment, the associated relaxation times (T_1) have previously been used to characterize a variety of isotropic and anisotropic liquids,⁵²⁻⁵⁴ and, more recently, ionic liquids.^{36,55} The most important contribution to the spin-lattice relaxation of dissolved xenon is the ^{129}Xe - ^1H dipolar coupling, with other spin-active nuclei resulting in additional contributions. The spin-lattice relaxation times of xenon dissolved in the PLs samples with various Noria-OEt concentrations, measured at 300 K, are shown in **Figure 4**. These values were obtained by fitting the data of the Inversion Recovery pulse sequence with a single exponential, further confirming that xenon experiences a single average environment in the scale of the NMR experiment. The T_1 values are responsive to the host concentration as they vary from 32 s for the pure 15-crown-5, to 22.1 s for the Noria-OEt 60 mg/mL PL, but, contrary to the chemical shift, they decrease with the host concentration. This suggests that the dipolar coupling interaction between xenon and other spin active nuclei becomes progressively stronger with increasing the Noria-OEt concentration. This is consistent with greater interaction occurring with the H atoms of the Noria-OEt host than with the 15-crown-5 binding. This is reasonable based on the close proximity of many H atoms to the central cavity in the Noria-OEt structure.

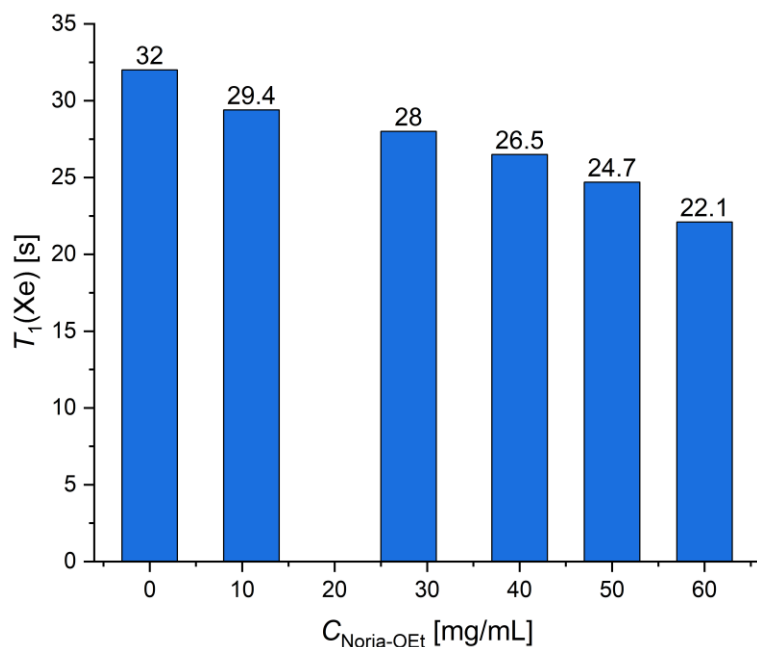


Figure 4. Xenon spin-lattice relaxation times, measured at 300 K, represented as a function of the Noria-OEt concentration.

Xenon diffusion. The diffusion coefficient of xenon, $D(\text{Xe})$, loaded in the pure 15-crown-5 and in the PL with 11 mg/ml Noria-OEt are both $(2.15 \pm 0.07) \cdot 10^{-10} \text{ m}^2/\text{s}$. Xenon diffusion is apparently unchanged by the presence of Noria-OEt as **its value is mostly, if not completely determined by the bulk solvent**. For context, the observed $D(\text{Xe})$ is many orders of magnitude smaller than that of free xenon gas ($5.3 \cdot 10^{-6} \text{ m}^2/\text{s}$),⁵⁶ and about one order of magnitude smaller than xenon dissolved in water ($2.2 \cdot 10^{-9} \text{ m}^2/\text{s}$)⁵⁷ or in alkanes.⁵⁵

In summary, ^{129}Xe NMR techniques have been used for the first time to characterize the porous structure of Type II porous liquids based on Noria-OEt paddlewheel-like macrocycle dissolved in the size excluded solvent 15-crown-5. ^{129}Xe chemical shift changes, observed varying Noria-OEt concentration, reveal the presence of multiple sites, explored by xenon atoms, which are formed by the arrangement of the host cavities within the porous solvent. Relaxation

parameters decrease with increasing Noria-OEt concentration which is consistent with the pores being relatively rigid.

ASSOCIATED CONTENT

Supporting Information. Experimental details for Synthesis of Noria-OEt, preparation of Type II PLs, xenon loading, NMR sample preparation, acquisition and processing of the ^{129}Xe NMR data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interests.

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Exploring cavities in Type II Porous Liquids with Xenon

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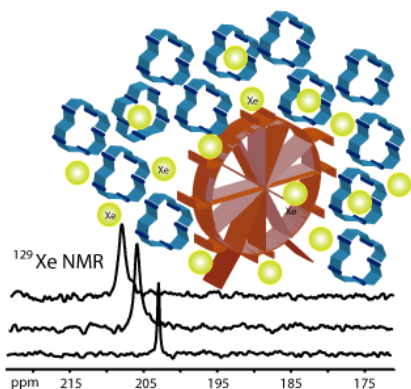
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ABSTRACT. The porous topology of Type II Porous Liquids (PLs), prepared using Noria-OEt as an empty molecular host dissolved in 15-crown-5 solvent, is investigated with ^{129}Xe NMR Spectroscopy. Xenon NMR parameters, such as chemical shifts and T_1 relaxation times, measured in PLs solutions prepared at various Noria-OEt concentrations, are related to the intrinsic microporous structure of the material. The experimental data are interpreted on the basis of a multiple-site model for xenon atoms within the multiple PLs cavities. Diffusion NMR experiments show a similar mobility of xenon in PLs compared with the pure solvent.

TOC GRAPHICS



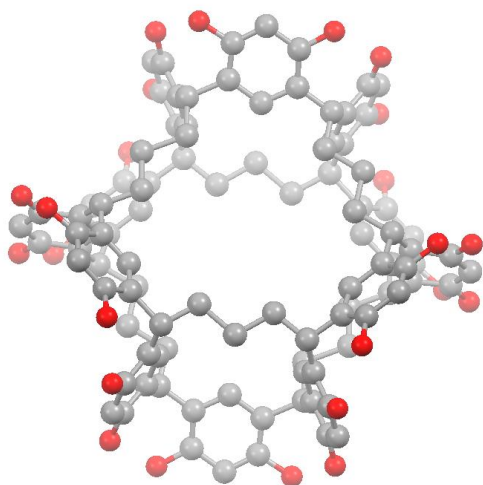
KEYWORDS Xenon NMR, Porous Liquids, Diffusion, Relaxation

Porous liquids (PLs) are a neoteric class of materials characterized by permanent cavities in the liquid state.¹⁻⁴ PLs, initially proposed by James et al.,¹ show peculiar physico-chemical properties which arise from merging a permanent rigid microporosity, derived from well defined porous solids, such as macrocyclic hosts or zeolites, dissolved or dispersed in a fluid liquid phase. Based on the nature of their porous structure, PLs can be divided into four different types. Type I PLs are pure liquids with permanent, rigid cavities whose shapes and dimensions prevent self-filling, guaranteeing the existence of a permanent porous structure.⁵⁻⁷ Type II PLs are rigid porous host molecules dissolved in size-excluded solvents which cannot enter the host cavities.⁸⁻¹⁰ Type III PLs are constituted by porous framework materials dispersed in size-excluded solvents.¹¹⁻¹³ Finally, Type IV porous liquids are meltable, single component porous frameworks which retain their intrinsic porosity in the liquid state.¹⁴⁻¹⁶ Among the three different categories, Type I and Type IV PLs are the least common due to the tough challenges posed by their design and synthesis. To date, there are only a few examples of Type I PLs, mostly based on the appropriate functionalization of porous molecular hosts.^{5,6,17,18} On the other hand, Type II and Type III PLs are generally easier to prepare, more versatile and more stable. Thanks to these combined features, various Type II and III porous liquids have been developed in the recent years, each with their own chemical and physical properties.

Some of the possible applications of porous liquids are the use in catalysis and membranes, chiral recognition and separation, and the use as electrolytes or heat transfer fluids. However, currently the most intensely investigated application of porous liquids is the use in the field of gas sorption. Several studies relate to their utility in gas capture¹⁹⁻²¹ and separation,²²⁻²⁵ highlighting that the sorption/separation capability strongly depends on the cavities shape and dimension,¹⁹ and on the mechanism of gas confinement. In view of these applications, a detailed understanding of the

porous structure and of the dynamic properties of gaseous species dissolved in PLs plays a central role, and it may help in the design of task-specific materials. Nuclear Magnetic Resonance (NMR) spectroscopy of noble gases,^{26,27} (especially xenon) loaded in nano/micro structured solid materials has been widely used to probe the structures and dynamic processes in porous media,²⁸ zeolites,²⁹ nano-channels³⁰ and polymers.^{31,32} Furthermore, the ¹²⁹Xe chemical shift and relaxation times have been used to investigate the interactions of xenon atoms with liquid solvents,³³ and the complex ionic liquids nano-structure consisting of entangled polar/apolar domains.³⁴⁻³⁶ In all these applications, the ¹²⁹Xe isotope (around 26% natural abundance) is used as inert NMR probe as it is extremely sensitive to the surrounding molecular environment, cage effect and confinement which through van der Waals interactions induce a remarkable deshielding effect and influence xenon relaxation times and diffusion motion.

In this paper, we study the porous topology of a series of PLs using ¹²⁹Xe NMR parameters, such as chemical shift, T_1 relaxation time, and xenon diffusion coefficient. The studied materials are porous liquids based on Noria-OEt, a derivative of the well-known paddlewheel-like molecular host Noria (Scheme 1), and 15-crown-5 ether as the bulky solvent. Indeed, as previously demonstrated, the functionalization of Noria with 12 scrambled ethyl substituents enhances its solubility in 15-crown-5, allowing the formation of chemically and thermally stable Type II porous liquids.³⁷ Moreover, it has been demonstrated that the cavity of solid Noria is both shape and size selective for a single xenon atom.³⁸ This important feature makes these porous liquids ideal for ¹²⁹Xe NMR characterization.



Scheme 1. Molecular structure of Noria, showing the carbon framework (grey), OH-functionalisation (red) and the central cavity.

Xenon shielding. The ^{129}Xe NMR spectra acquired at 298 K for all the samples are shown in **Figure 1**. The spectrum of xenon loaded in the pure component crown ether, 15-crown-5 (**Figure 1a**), shows a narrow resonance line at 202.97 ppm. Compared to the chemical shift of xenon in common organic solvents,³⁹ alkanes,³³ and oxygen- and nitrogen-substituted aliphatic compounds,⁴⁰ this relatively high chemical shift can be explained by a strong interaction of xenon with the crown ether molecules, possibly leading to the formation of a xenon-crown ether complexes similar to those of alkali metal cations with crown ethers. Indeed, a cage-deshielding effect on ^{129}Xe chemical shift has already been reported by Claessens et al.⁴¹ for xenon loaded in crown-ethers/chloroform solutions compared with their linear analogues. The authors classified 12-crown-4 and 15-crown-5 ethers, characterized by a specific inner cavity, as “host-molecules” capable of forming a xenon-ether complex through specific interactions. In addition, the formation

of a stable solid-state complex between a xenon compound and 15-crown-5 has also been recently reported, confirming that Xe is indeed able to form complexes with crown ethers.⁴²

The room temperature spectra of xenon loaded in Type II porous liquids prepared with different Noria-OEt concentrations are also shown in **Figure 1**. All the spectra show a single, intense line, arising from xenon dissolved in the porous liquid. The chemical shift values are reported in **Table 1**. The xenon chemical shift is responsive to the variation of the Noria-OEt concentration: an increase in the Noria-OEt concentration from 11 mg/mL (**Figure 1b**) to 70 mg/mL (**Figure 1g**) leads to a chemical shift increase of about 3 ppm. The signal of xenon in pure 15-crown-5 also follows this trend, having the resonance at the lowest chemical shift among all the liquids. A plot of the ¹²⁹Xe chemical shift as a function of the concentration of Noria-OEt is shown in **Figure 2**. To understand the nature of the Xe@PL signal, it should be remembered that ¹²⁹Xe NMR is a dynamic technique. If xenon atoms move rapidly and experience different environments on the NMR time scale, the resulting chemical shifts are averages of the chemical shifts of xenon nuclei in the different sites, weighted by the respective molar fractions. On the other hand, separated signals are only observed if the exchange of xenon nuclei between different sites is slow on the NMR time scale. Since it is well-known that Noria is a xenon-selective molecule,³⁸ we can assume that xenon interacts both with Noria and with 15-crown-5 on the NMR time scale, giving rise to an averaged or exchange signal. Similar behavior has already been reported for xenon dissolved in solutions of α -cyclodextrin.⁴³

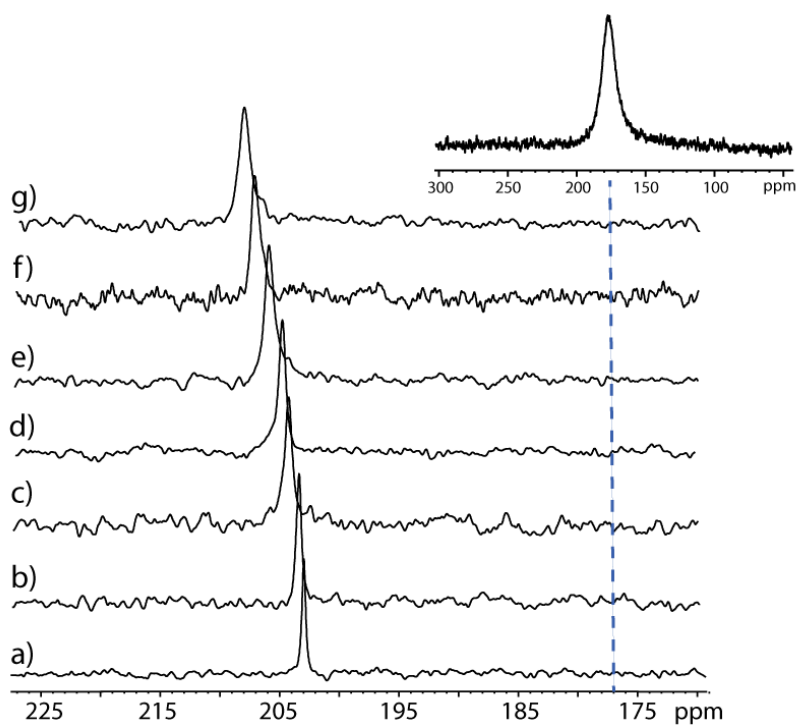


Figure 1. ^{129}Xe spectra of Type II porous liquids with increasing Noria-OEt concentration, a) pure 15-crown-5 b) 11, c) 28, d) 40, e) 50, f) 60, g) 70 mg/mL. The ^{129}Xe spectrum of xenon loaded in solid Noria-OEt is shown in the inset.

Table 1. Chemical shifts (δ) of ^{129}Xe dissolved in Type II porous liquids.

$C_{\text{Noria-OEt}}$ (mg/mL)	δ (ppm)
0*	202.97
11	203.26
28	204.24
40	204.56
50	205.73
60	206.16
70	206.56

*Pure 15-crown-5.

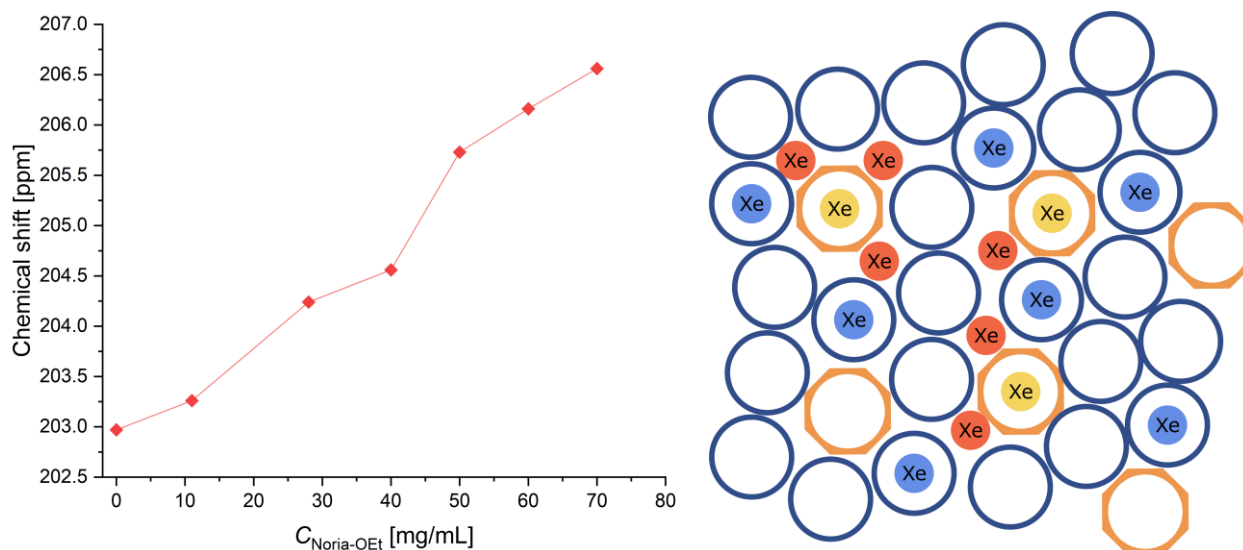


Figure 2. (left) Room temperature ^{129}Xe chemical shift in Type II porous liquids as a function of the Noria-OEt concentration. The sample with concentration 0 is pure 15-crown-5. The lines are visual aids only. (right) Sketch of the multiple-site model for Xe@PLs (orange polygons represent Noria-OEt, blue circles represent 15-crown-5 species).

To further understand the underlying origin of the Xe@PL resonance, we decided to acquire a spectrum of xenon in solid Noria-OEt. The result is shown in the inset of **Figure 1**. The spectrum shows a single broad resonance centered at 177 ppm, a high chemical shift value which lies in the range usually associated to xenon confined in micropores.⁴⁴⁻⁴⁶ According to the model developed by Demarquay and Fraissard for microporous zeolites,⁴⁷ in the absence of strong adsorption sites, such as highly charged cations, and paramagnetic species, provided that Xe-Xe interactions are absent or negligible, the chemical shift of confined xenon is related to its mean free path, λ , expressed in Å, by the following relationship.

$$\delta_{Xe} = 243 \left(\frac{2.054}{2.054 + \lambda} \right) \quad (1)$$

The mean free path can be used to calculate the pore diameter in the two limiting cases of spherical and cylindrical pores: in the former case, $D_s = 2\lambda + D_{Xe}$, while, in the latter, $D_c = \lambda + D_{Xe}$, where $D_{Xe} = 4.4 \text{ \AA}$ is the xenon van der Waals diameter. By inserting the chemical shift of xenon in solid Noria-OEt in Equation 1, we obtain a mean free path of 0.77 \AA which leads to a spherical pore diameter $D_s = 5.9 \text{ \AA}$ and to a cylindrical pore diameter $D_c = 5.2 \text{ \AA}$. These results are in good agreement with crystal structure data which indicate that the central cavity of Noria has a diameter in the $5\text{-}7 \text{ \AA}$ range.^{38,48} Indeed, in the ethylated derivative under study, Noria-OEt, the 12 ethyl groups are randomly distributed on the 24 outer oxygen sites, and do not have a significant effect on the size of the inner cavity.

The broadness of the xenon signal could be attributed to xenon diffusing in solid particles having different orientations with respect to the external magnetic field and to the presence of various species with very similar cavity sizes. As reported previously, the typical synthesis of Noria yields a mixture of many different oligomers, mainly Noria itself and a structural isomer, the resorcinarene trimer called R3, which have very similar central cavity sizes. Thus, it is most likely that the synthesis of Noria-OEt also yields the ethylated resorcinarene trimer, R3-OEt, and other oligomers, in the same manner as the typical synthesis of Noria.³⁷ In addition, only considering the Noria-OEt molecule itself, there are 64 possible geometrical isomers due to the possible distributions of the 12 ethyl substituents on the outer oxygen atoms. All these different species are expected to have cavities of effectively the same size. The broad ^{129}Xe signal of bulk Noria-OEt extends from roughly 160 ppm to 190 ppm, indicating that xenon does not explore a single microporous species but rather a wide distribution of micropores ranging from 5 to 7 \AA (as calculated from Equation 1).

The comparison of the xenon chemical shift values of solid Noria-OEt, pure 15-crown-5, and Type II porous liquids reveals interesting details about their structural features. In a simple two-site model for the PLs, where xenon interacts with the cavities of both Noria-OEt and 15-crown-5 in the NMR time scale, the ^{129}Xe chemical shift would be an average of the chemical shifts of xenon in the two pure species, 177 ppm for solid Noria-OEt and 202.97 ppm for pure 15-crown-5, weighted by the respective molar fractions. In this case, one would expect the Xe@PL chemical shift to be in-between those two limiting values, and to be inversely proportional to the host concentration due to the Xe@Noria-OEt molar fraction increasing with the concentration of Noria-OEt. On the contrary, the measured Xe@PL chemical shifts are always higher than the Xe@15-crown-5 chemical shift, and they increase with the host concentration, following an opposite trend with respect to the predictions. Thus, a two-site model is too naive for the system under study and does not represent it adequately. A better representation of the structure of these porous liquids can be provided by a multiple site model.^{43,49,50} In addition to being in the cavities of the host and of the solvent, xenon can also be found in the immediate vicinity of the Noria-OEt molecules, where it interacts with their structural indentations, and this influences the chemical shift value. This interpretation is in accordance with molecular dynamics (MD) simulations performed on this system.³⁷ The radial distribution function between the Noria-OEt centers and the solvent molecules showed two distinct maxima, one corresponding to the outer solvation shell and the other to the six indentations outside the Noria-OEt cavity. Overall, these experimental results indicate that dissolving a porous host molecule in a solvent having a defined internal cavity leads to the formation of smaller cavities that may host xenon atoms. A sketch of the multiple site model is shown in **Figure 2**.

To investigate the effect of temperature on our systems, we performed variable temperature ^{129}Xe NMR experiments on 15-crown-5 and on Type II PLs with Noria-OEt concentrations equal to 11 mg/mL and 60 mg/mL. The results are shown in **Figure 3**.

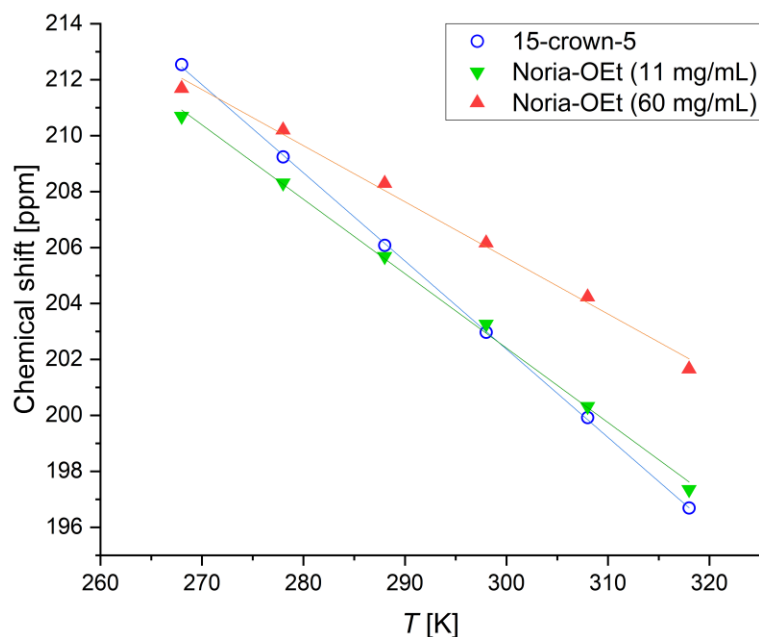


Figure 3. Variable temperature ^{129}Xe chemical shift of 15-crown-5 and selected Type II porous liquids. The lines are linear fits to the data.

For all the three samples, the chemical shift shows a linear dependence on the temperature in the range 268-318 K. For 15-crown-5, a linear fit gives a slope of -0.32 ppm/K, analogous to the values reported by Morgado et al. for xenon dissolved in a wide variety of *n*-alkanes, branched alkanes and cycloalkanes.³³ In the case of porous liquids, the temperature dependence of the chemical shift is a function of the of the Noria-OEt concentration: -0.25 ppm/K for 11 mg/mL and -0.18 ppm/K for 60 mg/mL.. Increasing the Noria-OEt, concentration makes the Xe chemical shift less sensitive to temperature. This behavior can be explained based on the molecular dynamics calculations reported by Jameson and coworkers,⁵¹ which demonstrates that the main determinant of the

average chemical shift variation as function of temperature is the modification of the cage (site) free volume, available to the Xe atom. Large free volume variations lead to large changes in chemical shift, as in the case of crown ether, an extremely flexible molecule (with a slope of -0.32 ppm/K). Conversely, in the case of the porous liquids, in addition to this cage there are other two sites (inside Noria and close to the Noria surface) that do not change dimensions significantly as the temperature varies.

Xenon T_1 relaxation. Due to the high sensitivity of the spin-lattice relaxation process of dissolved xenon on the surrounding environment, the associated relaxation times (T_1) have previously been used to characterize a variety of isotropic and anisotropic liquids,⁵²⁻⁵⁴ and, more recently, ionic liquids.^{36,55} The most important contribution to the spin-lattice relaxation of dissolved xenon is the ^{129}Xe - ^1H dipolar coupling, with other spin-active nuclei resulting in additional contributions. The spin-lattice relaxation times of xenon dissolved in the PLs samples with various Noria-OEt concentrations, measured at 300 K, are shown in **Figure 4**. These values were obtained by fitting the data of the Inversion Recovery pulse sequence with a single exponential, further confirming that xenon experiences a single average environment in the scale of the NMR experiment. The T_1 values are responsive to the host concentration as they vary from 32 s for the pure 15-crown-5, to 22.1 s for the Noria-OEt 60 mg/mL PL, but, contrary to the chemical shift, they decrease with the host concentration. This suggests that the dipolar coupling interaction between xenon and other spin active nuclei becomes progressively stronger with increasing the Noria-OEt concentration. This is consistent with greater interaction occurring with the H atoms of the Noria-OEt host than with the 15-crown-5 binding. This is reasonable based on the close proximity of many H atoms to the central cavity in the Noria-OEt structure.

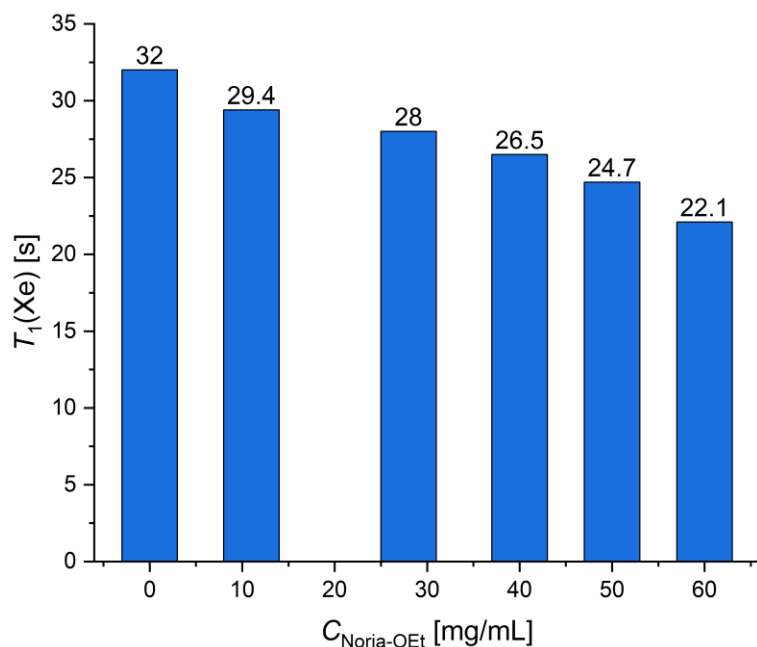


Figure 4. Xenon spin-lattice relaxation times, measured at 300 K, represented as a function of the Noria-OEt concentration.

Xenon diffusion. The diffusion coefficient of xenon, $D(\text{Xe})$, loaded in the pure 15-crown-5 and in the PL with 11 mg/ml Noria-OEt are both $(2.15 \pm 0.07) \cdot 10^{-10} \text{ m}^2/\text{s}$. Xenon diffusion is apparently unchanged by the presence of Noria-OEt as its value is mostly, if not completely determined by the bulk solvent. For context, the observed $D(\text{Xe})$ is many orders of magnitude smaller than that of free xenon gas ($5.3 \cdot 10^{-6} \text{ m}^2/\text{s}$),⁵⁶ and about one order of magnitude smaller than xenon dissolved in water ($2.2 \cdot 10^{-9} \text{ m}^2/\text{s}$)⁵⁷ or in alkanes.⁵⁵

In summary, ^{129}Xe NMR techniques have been used for the first time to characterize the porous structure of Type II porous liquids based on Noria-OEt paddlewheel-like macrocycle dissolved in the size excluded solvent 15-crown-5. ^{129}Xe chemical shift changes, observed varying Noria-OEt concentration, reveal the presence of multiple sites, explored by xenon atoms, which are formed by the arrangement of the host cavities within the porous solvent. Relaxation

parameters decrease with increasing Noria-OEt concentration which is consistent with the pores being relatively rigid.

ASSOCIATED CONTENT

Supporting Information. Experimental details for Synthesis of Noria-OEt, preparation of Type II PLs, xenon loading, NMR sample preparation, acquisition and processing of the ^{129}Xe NMR data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interests.

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Declaration of interests

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

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

CRedit authorship contribution statement

Matteo Boveni: Methodology, Investigation, Writing - original draft. **Michele Mauri:** Methodology, Investigation, Writing - review & editing. **Francesca Alexander:** Synthesis, Methodology, Writing - review & editing. **Stuart L. James:** Investigation, Writing - review & editing. **Roberto Simonutti:** Conceptualization, Supervision, Writing - review & editing. **Franca Castiglione:** Conceptualization, Supervision, Project administration, Writing - review & editing.