

Enhanced hydrogen solubility in nanosized ethanol and n-hexane confined in a silica aerogel matrix

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The physical properties of condensed matter are strongly dependent on size and confinement effects at the nanoscale. Finite-size effects are at the origin of phase transitions not found in the bulk phase (e.g. layering, wetting and commensurate-incommensurate transitions), as well as shifts in transitions (e.g. freezing, gas-liquid, liquid-liquid) that are familiar from bulk behaviour [1]. It is also well known that the density, viscosity, specific heat and dielectric constant of liquids in a mesoconfined environment can differ to a certain extent from bulk values. In most cases, these variations are attributed to the competition between fluid-wall and fluid-fluid forces, leading to liquid reconstruction and to possible changes in liquid dimensionality and order level.

In this line, we have recently provided evidence of a remarkable increase of gas solubility in mesoconfined liquids (or nanoliquids) overcoming the values predicted by Henry's Law [2]. This type of effect has been confirmed by Luzar & Bratko [3] using Molecular Dynamics (MD) for molecular nitrogen and oxygen in nanoconfined water. Hydrogen solubility in a series of solvents increases abruptly when the nanoliquid size is tuned to values lower than 15 nm. Above this value, hydrogen solubility tends asymptotically to the corresponding bulk values. Hydrogen solubility is enhanced up to 5-10 times over the corresponding bulk values for nanoliquid sizes lower than 5 nm. Moreover, for most of the mesoporous solids tested to date (coarse-grained γ -alumina and silica), gas solubility appears to be promoted as long as the gas/liquid interface is localized within the solid mesopores, namely for solvent loadings lower than the total pore volume of the target solid. In addition to wall effects, this observation suggests a crucial role of the surface excess concentration of the adsorbed gas at mesoconfined gas-liquid interfaces. At these conditions, a signal ascribed to dissolved hydrogen in CCl_4 in the presence of a mesoconfined gas-liquid interface could be unambiguously identified in $^1\text{H-NMR}$ spectra after peak deconvolution. We have also observed for a broad collection of gas/liquid/solid systems that although Henry's Law is not accomplished at the nanoscale, gas solubility still increases linearly with the applied pressure at higher slopes [4].

In light of all the comments stated above, it is the purpose of this study to elucidate the interplay between interfacial and wall effects on the observed gas oversolubility effects in nanoliquids. To this aim, hydrogen solubility has been measured in n-hexane and ethanol confined in the cavities of a series of alumina and silica materials showing different textures, pore structures and surface chemistry. Special insight has been given to mesoporous silica aerogels as model solids not only for their extremely low apparent densities and high porosities (up to 99%), making them interesting candidates as light reservoirs for gas storage, but also for their characteristic flexible and tenuous structures providing a unique physics of condensed matter under confinement.

Briefly, the mesoconfining solids used here were γ -alumina GFS-400 (Rhône-Poulenc), silica 432 (Grace-Davison), mesostructured MCM-41 ($\text{Si}/\text{Al} \rightarrow \infty$ and $\text{Si}/\text{Al}=1$) and SBA-15 silicas, and silica aerogel. **Table 1** summarizes the main textural properties of these solids. The mean pore size of coarse-grained γ -alumina and silica 432 filled by the liquid was measured from the pore size distribution of the solid by considering the liquid loading of the solid [2]. Following the guidelines of previous studies [2,4], the gas solubility experiments in coarse-grained γ -alumina and silica were performed for solvent loadings ensuring that most of the liquid is condensed in the solid pores rather than adhered as a film. Special care was taken in solvent desorption in the case of silica aerogel to avoid shrinkage during (and therefore formation of a xerogel collapsed structure) due to capillary pressure.

Figure 1 (left) summarizes the results obtained for hydrogen solubility in n-hexane and ethanol using the different confinement solids considered here. For coarse-grained γ -alumina and silica and mesostructured silicas (MCM and SBA), gas solubility is promoted by a factor in the range 7-16 over the bulk values. Among these samples, higher hydrogen solubility in mesoconfined n-hexane is observed in the order MCM-41 ($\text{Si}/\text{Al} \rightarrow \infty$) \gg SBA-15 $>$ Na- AlMCM-41 ($\text{Si}/\text{Al}=1$) $>$ silica 432 \approx γ -alumina, while the increasing order for ethanol is NaMCM-41 ($\text{Si}/\text{Al}=1$) $>$ MCM-41 ($\text{Si}/\text{Al} \rightarrow \infty$) \approx SBA-15 \gg γ -alumina. This trend suggests that, in addition to size effects ascribed to the surface excess concentration of adsorbed hydrogen at mesoconfined gas/liquid interfaces, wall effects in mesostructured silica pores cannot be ruled out. Hydrogen solubility is promoted for small pore mesoconfining solids with a surface polarity matching that of the solvent.

Figure 1 (left) shows that, among the solids here considered, the use of mesoporous silica aerogel as confinement solid provides the highest hydrogen solubility in *n*-hexane and ethanol. Under confinement (i.e. for solvent loadings lower than 100%), the hydrogen solubility is promoted by a factor of 17 in ethanol compared to the bulk value. Unlike the other solids tested, an increase of hydrogen solubility is also observed for bulk ethanol in the presence of the silica aerogel for a solvent loading about 150%. **Figure 1** (right) shows the evolution of the dissolved hydrogen concentration in ethanol at room temperature as a function of the equilibrium pressure using silica aerogel as confining solid. The concentration of dissolved hydrogen increases linearly with the equilibrium pressure in the range 1-60 bar. This trend is in good keeping with the results reported in a previous study [4]. Two hypotheses can be proposed to explain the strong enhancement of hydrogen solubility in ethanol and *n*-hexane when confined in silica aerogel. The first hypothesis involves the generation of confined and highly localized gas/liquid interfaces or fluid clusters in silica aerogel during gas desorption that might act as active centres for hydrogen adsorption as has been recently proposed by Detcheverry et al. [5]. The second hypothesis relies on the strong interaction between confined *n*-hexane and ethanol and silica aerogel, approaching in principle to that between a liquid and a solute, that might be at the origin of a restructuring of solvent molecules in the aerogel porosity, providing a stronger (adsorption or solvation) interaction between hydrogen and the solvent than when confined in coarse-grained silica and mesostructured silica pores.

On the basis of the results presented in this study, the confinement of solvents in mesoporous silica aerogel appears to be a promising strategy to achieve fast and reversible hydrogen storage at near-room temperature and reduced pressures.

References

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Tables & Figures

Table 1. Textural characterization of the solids used in this study from He picnometry and N₂ adsorption at 77 K.

Property	γ -alumina (GFS)	Silica (432)	MCM-41 (Si/Al $\rightarrow\infty$)	NaMCM-41 (Si/Al= 1)	SBA-15	Silica aerogel [‡]
Skeletal density (g cm ⁻³)	3.5	2.1	2.3	2.2	0.93	0.10
BET specific surface (m ² g ⁻¹)	235	309	1065	506	793	481
Mesopore volume (cm ³ g ⁻¹)	0.619 [*]	1.12 [*]	1.086 [†]	0.230 [†]	1.282 [†]	0.632 [†]
Mean pore size (nm)	10.9 [*]	13.0 [*]	3.4 [†]	3.1 [†]	6.8 [†]	8.6 [†]

^{*} BDB: Brockhoff-de-Boer (slit-like pores), [†] BJH: Barrer-Joyner-Halenda (cylindrical pores), [‡] Crushed before characterization

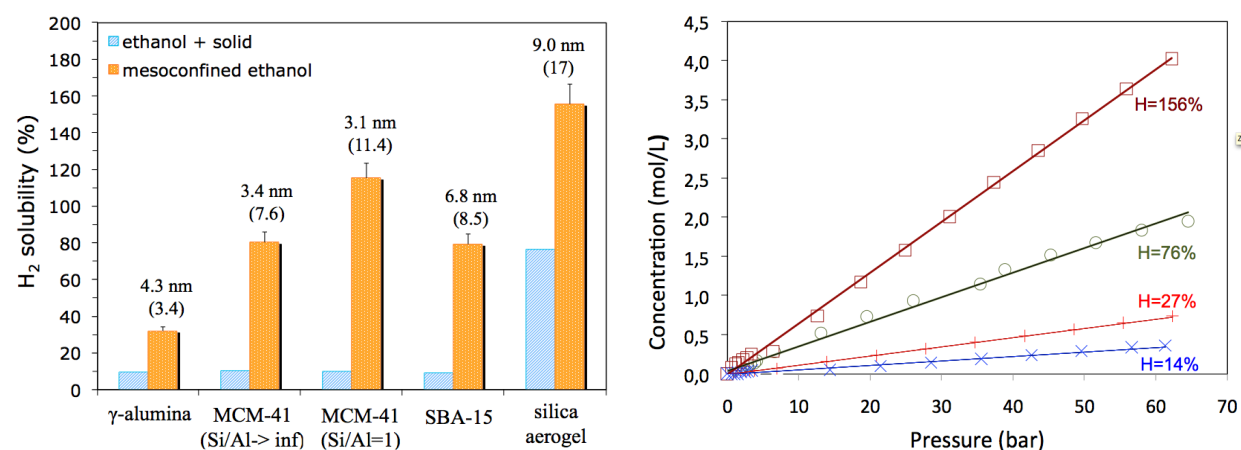


Figure 1. Left, comparison of bulk and nanoliquid H₂ solubility in ethanol for different confining solids, showing the nanoliquid size and oversolubility factor on top of the mesoconfined solvent histogram bar; right, variation of the concentration of dissolved H₂ in ethanol with pressure for different nanoliquid sizes confined in silica aerogel.