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Water as tuneable solvent : A perspective

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Water is the sustainable solvent of excellence, but its high polarity limits the solubility of non-polar compounds. Confinement of water in hydrophobic pores alters its hydrogen bonding structure and related properties such as dielectric constant and solvation power. Whether this special state of confined water can be rendered useful in chemical processes is hitherto underexplored. Confining water in hydrophobic nano-pores could be a way to modulate water solvent properties, enabling to use water as a tuneable solvent (WaTuSo). Applying pressure forces a heterogeneous mixture of poorly soluble molecules and water into hydrophobic nanopores of a host material where the lowered polarity of water enhances dissolution. Decompression after reaction causes expulsion of the solution from the pores and spontaneous demixing of reaction products because water returns to its normal polar state. Temporary dissolution enhancement during confinement is expected to be advantageous to chemical reaction and molecular storage. Nano-confined water offers a potential alternative to compression for storing CH₄ and H₂ gas, and opens new opportunities for green chemistry such as aqueous phase hydrogenation reactions which benefit from enhanced hydrogen solubility. Unprecedented control in time and space over H₂O solvation properties in a WaTuSo system will enable new technologies with major scientific and societal impact.

Introduction

Solvents are widely used in chemical industry. Solvent choices are critical as they impact not only the efficiency of dissolution, but also heat and mass transfer. Tuneable solvent systems, solvents with solvation properties that can be modulated *in situ* by changing temperature and pressure, are scarce but very attractive for designing chemical processes.^{1,2} In catalytic conversions, they enable to enhance the solubility of reagents during reaction and, by altering solvent conditions after reaction, facilitate product isolation. Currently available examples are partially miscible, fluoruous biphasic systems, supercritical fluids, and CO₂-expanded liquids.¹ The latter are operated in a pressure cycle. Pressurizing CO₂ to 6 MPa causes the desired reversible phase change.³ Compared to CO₂, the solvation properties of water are more difficult to tune. Dielectric behavior and solvation power of water depend on the molecular scale organization of the water molecules. Fourfold coordination of the water-oxygen atoms through hydrogen bonding, i.e. 'tetrahedrally bonded water' is enthalpically favored,⁴ and predominantly observed in ice. Entropy however drives the distortion of the hydrogen-bonding network, resulting in the denser structure of liquid water. Bulk liquid water forms a dynamical

network with local, small scale density fluctuations arising from the appearance of patches of tetrahedral water.^{4,5} On a macroscopic level however, the overall ensemble remains constant. The fraction of water molecules participating in different types of local water structures is temperature and pressure dependent.^{5,6} By increasing temperature and pressure near the critical point ($T_c = 374^\circ\text{C}$; $P_c = 22\text{ MPa}$), density and dielectric constant are lowered in such a way that dissolution of non-polar molecules is improved and water resembles organic solvents.^{7,8} Near- and supercritical water (NCW and SCW) are used commercially for performing demanding chemical reactions, such as oxidative destruction of chlorinated hydrocarbons.⁹ Unfortunately, widespread implementation of NCW and SCW technology is impeded by the extreme temperature and pressure conditions and the highly corrosive nature of SCW.¹⁰ Ideally, water solvent properties should be tuneable in a lower temperature and pressure regime. A water-based tuneable solvent (WaTuSo) system capable of dissolving polar as well as non-polar compounds depending on operational parameters would revolutionize the world of solvents.

1. State-of-the-art

1.1 Supramolecular organization of water

The supramolecular organization of water is very complicated and remains only partly understood. Its complexity is highlighted in scientific contributions by the Fuchs's group and by Parrinello's.^{11–14} In ambient conditions, water is a liquid instead of a gas because of the formation of a dynamic hydrogen bond network.¹⁵ Water, as a complex liquid, displays spatiotemporal fluctuations in its local dynamical behaviour. It is believed that this behaviour is linked to the

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appearance of local, transient order, that is, to the existence of patches or domains in which single-particle displacements are correlated.

Variability of hydrogen bonding is recognized as the cause of the often observed anomalous behaviour of water.^{4,5} Water is the one liquid that demonstrates the most anomalous properties relative to classical definitions of liquids. In liquid water, entropy driven distortion of the hydrogen bond network results in a structure more dense than ice I_h.^{4,5} Whereas hydrated ionic solutes easily blend into the dynamic hydrogen bonded network of bulk water, solvation of hydrophobic compounds, and especially of large molecules, requires an extensive rearrangement of the network structure.¹⁶ Anomalous behaviour such as the existence of super-cooled high-density liquid water at temperatures below 0 °C is explained by the persistence of irregular hydrogen bonding structures.^{12,13}

The fraction of water molecules participating in regular and irregular local structures is temperature and pressure dependent.^{5,6} As hydrogen bonding prevents individual water molecules from freely orienting their dipole in an applied electric field,¹⁷ the dielectric constant of water reflects the molecular level organization of its hydrogen bond network. Approaching the critical point, the hydrogen bonding network weakens and the high dielectric constant observed at room temperature is lowered.¹⁸ Simultaneously, the ¹H NMR chemical shift is modified and density decreases (Fig.1).^{7,19–22} The diminished hydrogen bonding shifts the bulk properties of water to those of non-hydrogen bonding polar organic solvents (Fig.1).²³ The solubility of permanent gases and non-polar organics is increased,^{24,25} while still allowing salt dissolution.⁸ Molecules with limited polarity such as benzene are readily dissolved in NCW and SCW.²⁶ The equilibrium constant of ionic dissociation of water into hydroxide and hydronium ions changes with increasing temperature, initially rising three orders of magnitude to reach a maximum value at 250 °C and then dropping by seven orders of magnitude with a further increase of temperature (Fig.1).^{20,27,28} This enhanced water autoprotolysis provides NCW with an enhanced acid-base reactivity.^{19,29} The favourable phase behavior, enhanced reactivity and enhanced mass transfer properties of NCW and SCW are used on commercial scale in oxidative destruction of chlorinated hydrocarbons.⁹ The solvation power of NCW also has caught the attention of researchers in the field of bio refinery, investigating

demanding reactions of hydrolysis and gasification of biopolymers.^{30–32} Despite its potential, modulation of bulk water properties is so energy intensive and technically demanding that it is infeasible for a large majority of practical applications.^{33,34} Ideally, water solvent properties should be made tuneable in a milder temperature and pressure regime.

1.2. Interaction of water with surfaces

Besides temperature and pressure, interaction with surfaces alters water properties.^{35,36} Water molecules near pore walls typically form fewer, shorter hydrogen bonds.³⁷ Water confined in reverse micelles, in cellulose nanocrystals, near surfaces or in the hydration sphere of the hydrophobic headgroups of tetramethylurea experiences a "stiffening" of its hydrogen bond network compared to bulk liquid water.^{38–45} Reduction of the number and length of hydrogen bonds in confined water, initially detected by neutron scattering and confirmed by theoretical predictions,^{42,44–47} causes the dielectric constant of water to decrease, as shown by dielectric imaging.³⁵ These alterations are manifested even at relatively large length scales.⁴⁸ *Van der Waals* interaction of water molecules with a surface, triggering a collective reorganization of the water hydrogen bonding structure, has been related to the supramolecular concept of hydrophobicity.^{49–52} Molecular dynamic simulations and vibrational sum frequency spectroscopy experiments indicate that water near hydrophobic surfaces exists with one of its hydrogen bonding groups pointing towards the hydrophobic surface, i.e. with the so called 'dangling bonds'.^{53–55} This specific surface re-arrangement of the hydrogen bonding network effectively renders the water structure less polar and, according to modeling, extends up to three or four water layers from the surface. A special manifestation of this hydrophobicity is the facilitation of clathrate formation. In methane clathrates, CH₄ forms very stable associations with water molecules by forcing the latter to organize their hydrogen bonding network into stable, highly ordered, ice-like configurations.^{56–58} Experiments with sand beds and methane at a pressure of 3.5 MPa and a temperature of 2 °C showed CH₄ clathrate hydrate to be more readily formed in the presence of sand particles made hydrophobic by silylation.⁵⁹ The induction times decreased steadily with increasing water contact angle (Fig.2), most likely as result of an increased propensity of water facing hydrophobic surface to form clathrates.⁵⁹ Hydrophobic micropores exert similar effects

Fig.1. Temperature and pressure (*P*) dependence of bulk water properties. Left: dielectric constant and ¹H NMR chemical shift (inset); middle: density; right: ionic product.^{19–22,28} Reprinted with permission from ref. 20. Copyright 2013 Elsevier.

promoting CH₄ clathrate hydrate formation at moderate pressure conditions (3 - 5 MPa) and with high yield.^{60,61}

Fig.2. Relationship between induction time of CH₄ clathrate formation and contact angle. The higher the contact angle, the more hydrophobic the sand particles are.⁵⁹ Reprinted with permission from ref. 59. Copyright 2015 American Chemical Society.

1.3. Water in nano-confinement

Confinement in a hydrophobic nano-volume clearly is a way to impose reorganization of the entire hydrogen bonding structure of the occluded water phase.^{39,49,62–68} The specific role of the interface and of the volume and shape of the nanospace on the behaviour of confined water cannot be overemphasized.⁶⁹ Confining water in a thin films has been reported to reduce the overall dielectric constant of the system, starting from the bulk water value $\epsilon_{\perp} = 80$ for 300 nm thick films, down to values of $\epsilon_{\perp} = 2.1$ for 1.5 - 2 nm films confined by graphite-hexagonal boron nitride (Fig 3) or even negative epsilon values for water confined between graphene sheets.^{35,70} As mentioned in several publications, the effect of confinement becomes spectacular at dimensions below 3 nm. There, the surface to volume ratio is large enough to produce considerable modulation of the physical properties of entire water bodies.^{37,71–74} Inside 2.6 nm wide hydrophobic pores, ice melts already at -65 °C.⁷¹ High-density ice structures are formed in carbon nanotubes and ordered mesoporous carbon.^{75–79} In hydrophobic zeolites with pore sizes of less than 1 nm, the thermicity of water intrusion was found dependent on the geometry of the pore system, being endothermic in MFI type zeolite with cylindrical pores, but exothermic in CHA type zeolite with interconnected cavities. Other salient observations in very small pores are the modified hydrogen gas formation kinetics during radiolysis of water in zeolite pores,⁸⁰ and the insertion of highly ordered water clusters in space-restricted cavities of aluminophosphate MIL-74.⁸¹

Nano-confinement also alters the interaction of water with dissolved molecules.⁸² Inside carbon nanotubes, reverse clathrate structures have been observed.⁷⁶ Small Angle X-ray Scattering studies revealed an enhancement of water solubility in toluene,

corresponding to a 40/60 molar ratio inside the pores of oxidized microporous carbon.⁸³ Methane solubility is enhanced in water contained in natural nanopores of coal and shale.^{84–86} Using microvolumetry, the solubility of CH₄ and H₂ gas was shown to increase up to an order of magnitude in water contained in nanopores of γ -alumina, ordered mesoporous silica or metal organic framework.^{87–89} Interestingly, the enhanced solubilization of these non-polar gases in confined water occurs at much milder temperature and pressure than needed to reach the critical point. Confinement in hydrophobic nanospaces has been shown to improve formation kinetics, stability and the overall adsorption capacity of CH₄ in clathrate hydrate.^{60,61,90–92} Casco *et al.* reported an exceptionally high storage capacity of CH₄ in pre-wetted activated carbon (63 wt.% at 3.5 MPa and 2 °C).⁶⁰ Such high capacity opens perspectives for CH₄ storage for automotive applications.⁹³

2. Advanced methodologies for confined water characterization

¹H Nuclear Magnetic Resonance (NMR) spectroscopy, dielectric relaxation spectroscopy (DRS), Fourier-transform infrared (FTIR) spectroscopy, high resolution neutron scattering and their combinations have revealed unusual hydrogen bonding networks in nanopore water confined in organic and inorganic nanoporous materials (carbon nanotubes, silica, metal organic framework, single

Fig.3. Out-of-plane dielectric constant of water under strong confinement measured using scanning dielectric microscopy. **Inset A:** three layer assembly (hBN (hexagonal boron nitride) - hBN - graphite) with 200 nm wide slit like pores whose height (h) can be varied, thus controlling the degree of confinement. **Inset B:** The model used to fit the experimental data assumes the presence of an interfacial water layer with $\epsilon_i = 2.1$ and variable thickness h_i ; the remainder of the channel ($= h - 2 \times h_i$) is filled with bulk like water. **Main display:** The dotted, dashed and dashed-dotted red curves represent theoretical $\epsilon_{\perp}(h)$ curves for the capacitance model shown in inset B obtained with $h_i = 3 \text{ \AA}$, $6 \text{ \AA}$ and $9 \text{ \AA}$, respectively. The solid red curve shows the best experimental fit, yielding $h_i = 7.4 \text{ \AA}$. Horizontal black lines: dielectric constant of bulk water (solid) and hBN (dashed). $\epsilon_{\perp}$ of water at optical frequencies is shown by the black dotted line.³⁵ Reprinted with permission from ref. 35. Copyright 2018 AAAS.

wall carbon nanotubes (SWNTs), PMO, clay, etc.).^{44,46,101,102,54,94–100} Neutron scattering experiments evidenced a reduction of the number and the length of hydrogen bonds in nanopore water of Vycor glass.^{45,63} High-density ice structures, characterized with X-ray and neutron scattering techniques, formed in multi-walled carbon nanotubes and in the pores of ordered mesoporous carbon demonstrate a quasi-high-pressure effect of confinement in these materials.^{75–77,100,101} Spontaneous uptake of water into hydrophobic materials such as SWNTs upon exposure to water vapour appears paradoxical, but is another manifestation of the formation of unique supramolecular water structures.^{100,103}

Changes in hydrogen bond length are sensitively probed by the chemical shift in ^1H Nuclear Magnetic Resonance spectroscopy (NMR), which spans a 20 ppm range depending on hydrogen bond length.^{14,104–109} Mono- and multidimensional NMR can be used to identify and quantify the chemical environments of water and solutes,^{110–112} revealing dynamics (exploiting relaxation behaviour and chemical exchange), yield diffusion coefficients, speciation, kinetics of chemical reactions, and deliver molecular and material structures. The evolution of the ^1H (or ^2H) and ^{17}O chemical shift and associated relaxation parameters are key measurements, revealing the evolution of the water hydrogen bonding network and the formation of water pools with different properties or in different environments.^{105,106,120,112–119} Interface structures can be determined by disentangling restricted motion spectral components, modifying relaxation and residual dipolar interactions. This allows selective probing of atom proximities in different water clusters. Water adsorption isotherm determination traditionally relies on relaxation time measurements.¹²¹ Combining ^1H MAS NMR with standard addition absolute quantification of water in nanoporous hosts has become experimentally easy.¹¹⁰ The ^1H chemical shift can be used to probe the co-existence of different types of water: (i) weakly bound high-density water present as individual molecules, small clusters or interstitial water with strongly distorted hydrogen bonds, and (ii) strongly bound interfacial water associated with larger clusters, nano- and micro domains, and continuous interfacial layers with both high- and low-density water (Fig.4).^{105,122} This approach can be extended from water vapor adsorption to liquid water intrusion and is similar to NMR cryoporosimetry.¹²³ Solid-state NMR spectroscopy also allows to detect and quantify *in situ* hydrolysis of siloxane bridges in the walls of adsorbents (if any) and its kinetics during water intrusion, assessing the robustness of the host material.

NMR can be exploited to acquire adsorption isotherms for solutes with detectable nuclear spins such as H_2 , CH_4 or Xe. Xe has been used as one of the first gases to probe nanoporous materials as the ^{129}Xe chemical shift is strongly dependent on its interaction with pore walls. It even probes the shape of pores and the dynamics of exchange between different adsorption sites.^{124,125} Both gaseous and dissolved Xe have already been investigated.^{126–129} With similar approaches as demonstrated for water quantification in microporous hosts,¹¹⁰ it is possible to quantify the solubility of Xe gas and monitor its dissolution rate using NMR. Gases like nitrogen or hydrogen are also amenable to similar measurements. NMR provides information on water-solute and solute-pore wall interactions and

allows to establish the relation between confined water structure and solute content, as well as hydrophilic/hydrophobic character. Solubility constants, dynamics of exchange and local structure of gas hydrates can be accessed.

Fig.4. Room-temperature ^1H solid-state NMR spectra of water in pores of ordered mesoporous materials varying water content. a) MCM-41 ($D=4.0$ nm); b) SBA-15 ($D=8.9$ nm). $n\text{H}_2\text{O}$ = number of water molecules per nm^2 of the pore walls.¹⁰⁵ Reprinted with permission from ref. 105. Copyright 2004 John Wiley and Sons.

Broadband (0.2 Hz – 2 THz) absorption and dispersion spectra of water in inverse micelles have demonstrated that confinement mainly disrupts slower dielectric relaxation processes, as if the confined fluid experiences a "stiffening" of its hydrogen bond network thereby inhibiting large amplitude long-range collective motions inducing relaxation in bulk water.¹³⁰ Gigahertz dielectric relaxation spectroscopy of water contained in nanometric reverse micelles demonstrated a fivefold decrease of the dielectric response of nano-confined water as compared to its bulk response.³⁹ Also upon freezing the features in the dielectric permittivity curves of liquid water at 0°C shift from the 100 GHz to kHz frequency domain (Fig.5).¹³¹ A similar observation has been made for water molecules in the hydration shell of the hydrophobic groups of tetramethylurea.¹³² Combining dielectric relaxation spectroscopy (10 Hz to 1 MHz) and ^1H NMR (700 MHz) has been successfully used to reveal changes in the hydrogen bonding network of water confined in clay and mesoporous silica (MCM-41).^{102,105,133}

X-ray and neutron scattering provide direct access to any evolution of the water density (SAXS, SANS),^{134–136} revealing formation of structured water clusters or ice-like periodicity, if any, via the radial distribution functions^{63,137} analyzed with full pattern

Fig.5. Conceptual representation of the real (ϵ') and imaginary (ϵ'') part of the dielectric permittivity of water and ice as function of the measurement frequency (Debye model).¹³¹ Reprinted with permission from ref. 131. Copyright 2014 Taylor and Francis.

fitting using Pair Distance Distribution Analysis (PDF, total scattering) and Rietveld refinement (XRD, Bragg diffraction). SAXS provides direct information on density evolutions in fluids and has e.g. been used to detect inhomogeneity near the critical point of water.^{134–136,138} These conventional scattering methods however only yield ensemble-averaged information. Therefore the use of higher order correlation functions obtained by X-Ray Photon Correlation Spectroscopy (XPCS) and X-ray Cross Correlation Analysis (XCCA) has been pioneered.^{139–141} This has allowed to gain information on local order and dynamics in disordered systems such as water.

As recently demonstrated,^{142,143} the density of water adsorbed in micropores can be extracted from SAXS profiles. Diffraction and total scattering techniques offer radial distribution functions very naturally,^{63,137} but rely on reverse Monte Carlo techniques using force-field models to obtain further structural information. X-ray diffraction is sensitive to electron density, which for water of course is highest around the oxygen atoms, and so this technique is particularly useful in obtaining the O–O radial distribution functions (Fig. 6).^{137,144–147} To characterize the interaction of water and solutes with porous hosts, synchrotron and neutron facilities have demonstrated their merits.¹⁴⁸ Bragg scattering materials can also be thoroughly analyzed to derive the location of systematically adsorbed guest species.⁹⁹

For water localization, also neutron diffraction on deuterated samples can assist.^{149,150} Combination of *in situ* sum frequency generation (SFG) vibrational spectroscopy and Fourier Transform Infrared (FTIR) spectroscopy offers additional insight into local water structures (interfacial vs. bulk like confined water), water-induced structural changes of the matrix material and the interfaces.^{53,151,152}

To optimally study systems enabling water as a tuneable solvent, new experimental setups to perform pressure-swing cycles with *in situ* diagnostics (NMR, EIS, DRS, X-ray scattering, microvolumetry), probing solute, solvent, host material and their interactions would be helpful. NMR, DRS and X-ray scattering allow to probe the hydrogen bonding network, dielectric properties and density of water confined in porous materials.^{44,46,155–158,83,96,102,105,142,146,153,154} Microvolumetry enables to determine the solubility of permanent gases in nanopore water.^{87–89} Combined with NMR detection, this is

a powerful tool to unravel the chemical and physical processes impacting solubility.

Dielectric properties and hydrogen bonding network of nano-confined water can be characterized using electrochemical impedance spectroscopy (EIS), dielectric relaxation spectroscopy (DRS) and ¹H NMR during water vapour adsorption and liquid water intrusion-extrusion cycling. Measurement of the impedance (EIS) enables a simple broadband detection of any relevant changes to the (dielectric) properties of a confined water system.¹⁵⁹ DRS complements this information with the evolution of the complex dielectric properties of water and its dielectric relaxation constants.¹¹³ The evolution of the permittivity and ¹H NMR spectra with water content, temperature and pressure enables deconvolution of the dielectric properties of water and the confining matrix.^{160–163} Evolution of the X-ray scattering will reveal changes in the local water structure and density and is part of a global NMR crystallography approach.^{163–165} Combination of *in situ* sum frequency generation (SFG) vibrational spectroscopy and FTIR spectroscopy will offer additional insight in water structures and dynamics,^{95,166} water-induced structural changes of the matrix material and the solid-liquid interfaces inside the pores.¹⁵¹

Solvation properties can be probed using gas adsorption. Although gas adsorption isotherms are a good starting point to investigate and characterize these processes, classical adsorption isotherm measurements generally only determine the volume or weight of the gas dosed.¹⁶⁷ Striking increase of gas solubility in nano-confined liquids with respect to values predicted by Henry's law is referred to as oversolubility. This phenomenon is linked to the properties of the triphasic gas/liquid/solid system. The effect can be related either to adsorption or to solubility, depending on the strength of the gas/solid (F_{GS}) and liquid/solid (F_{LS}) interactions. These interactions correlate directly to experimental adsorption enthalpies of the gas ($\Delta H_{ads[G]}$) and liquid phase ($\Delta H_{ads[L]}$), respectively. When $F_{GS} > F_{LS}$ the effect is governed mainly by adsorption, while solubilization drives the process if $F_{GS} < F_{LS}$. Simulation studies on mesoporous silica surfaces indicated H_2 follows the solubilization mechanism ($F_{GS} < F_{LS}$), while CO_2 , due to its quadrupole interaction with the -OH dipoles, undergoes strong

Fig. 6. a) Radial distribution function (RDF) of bulk liquid water and water adsorbed in 1.13 nm slit pores; b) Evolution of the RDF of the water adsorbed in 1.13 nm slit pores with temperature.¹⁴⁶ Reprinted with permission from ref. 146. Copyright 1997 Elsevier.

Fig. 7. WaTuSo (**W**ater **T**uneable **S**olvent) concept implemented in a pressure swing cycle: a heterogeneous mixture of non-polar compounds and water intrudes the nanoporous host material where the mixture becomes a single phase suitable for storage or catalysis. Depressurization causes extrusion; water regains its bulk properties and non-polar compounds segregate again.

surface adsorption ($F_{GS} > F_{LS}$) in the case of a non-polar solvent like octamethylcyclotetrasiloxane (OMCTS).⁸⁹ When water was used as solvent, confinement induced oversolubility predominated because of the strong interaction of water with the host porous material ($F_{GS} < F_{LS}$).¹⁶⁸ In the case of partially filled hydrophobic pores, adsorption at gas/liquid interface has been shown to significantly contribute to the so-called oversolubility effect.^{53,169} Since (a combination of) all these mechanisms will be involved, highly detailed characterization of the triphasic gas/liquid/solid system is essential. Water adsorption and intrusion isotherms initially recorded on stand-alone instruments will therefore also be investigated in more detail using the adsorption/intrusion microvolumetric setups with in situ NMR, EIS, DRS and X-ray scattering detection. High pressure X-ray and NMR cells have already been developed.^{170,171} NMR will provide quantification of solutes with observable nuclear spins (e.g. H_2 , CH_4 , CO_2 and Xe), and can be correlated with micro-volumetric data. The evolution of the 1H (and 2H) chemical shift and associated relaxation constants will reveal the evolution of water hydrogen bonding network and the formation of water pools with different properties or in different environments.^{105,106,111,113} For solutes with NMR observable nuclei (1H , ^{13}C , ^{129}Xe , etc.), also changes in their local chemical environment will be revealed.^{57,172,173} Via the speciation of dissolved CO_2 , ^{13}C NMR of samples intruded with CO_2 -containing water will provide information on the *in situ* pH conditions of confined aqueous solvent.¹⁷⁴

3. Turning water into a tuneable solvent – the outlook

An envisioned process exploiting water as tuneable solvent (Fig. 7), would involve intrusion of a heterogeneous mixture of water and poorly soluble compounds (organic molecules, gases like H_2 and CH_4) in the pores of a hydrophobic host material. Upon confinement, water solvent properties change and the mixture becomes a single phase. Water intrusion in hydrophobic pores with diameters of 1–10 nm requires pressures from 0.5 up to 20 MPa.^{175–181} Upon decompression, the solution automatically vacates the pores and spontaneously separates out as non-polar compounds become insoluble again. For instance, in a liquid phase hydrogenation reaction, the solubility of organic reactants and H_2 gas in water would be temporarily enhanced inside the pores, accelerating the reaction. Hydrogenation reactions could be performed either in a pressure

swing cycle or in alternative schemes such as high-pressure continuous-flow mode.

An example of reversible water intrusion-extrusion cycling in Posisil foam (co-polymer of double four-ring silicate and dimethylsilicone, $D4R-(DMS)_8)_n$) is shown in Fig. 8.¹⁸² After global compression of the material by 40% (Intrusion1 trace), reversible water intrusion-extrusion was obtained, with hysteresis characteristic of a shock absorber. Closure of the hysteresis loop and almost perfect overlap of intrusion and extrusion curves was observed in consecutive cycles. In this particular sample, mesopore filling (1 mL/g) occurred at pressures up to 5 MPa. Reversible filling of micropores (0.2 mL/g) accounted for the uptake from 5 to 200 MPa. Quantitative extrusion occurred spontaneously upon decompression, demonstrating the selected nanoporous organosilicate materials survive water intrusion-extrusion cycles up to 200 MPa. This reversibility of intrusion and extrusion after initial compression and the robustness of this material are unique. Many zeolites e.g. do not survive such treatment because of limited framework flexibility.^{175,178,180,181,183}

Fig. 8. Water intrusion-extrusion cycles on $(D4R-(DMS)_8)_n$ silicone copolymer foam.¹⁸² Reprinted with permission from ref. 105. Copyright 2019 John Wiley and Sons.

Preliminary experiments on water intrusion in pores of Posisil foam provide proof of concept for the modulation of water properties through confinement. Dielectric shift and direct excitation 1H NMR spectra were recorded on water added to a MAS NMR rotor packed with Posisil powder and spun at different MAS speeds to vary

the pressure (Fig.9). With increasing spinning speed, centrifugal forces increase and generate a pressure up to 4.5 MPa at 15 kHz. This pressure forces water to gradually penetrate the hydrophobic pores of Posisil. Occurrence of intrusion was confirmed by synchrotron SAXS measurements (performed up to 3 MPa). Forced water penetration in the hydrophobic pores of Posisil also resulted in modified dielectric properties (Fig.9, lower inset), as well as an upfield shifted ^1H NMR spectrum of the water phase (Fig.9, main display). In addition, the chemical shift anisotropy revealed on the spinning sidebands allowed to resolve multiple spectral changes with increasing intrusion pressure (Fig.9, upper inset). These results indisputably demonstrate a change in the water properties upon intrusion in Posisil and are in line with the literature presented in the state-of-the-art. This implies that water forced into hydrophobic nanopores adapts its hydrogen bond network to accommodate to this new environment. As indicated by the modified dielectric shift, this change immediately impacts its static dielectric constant and, consequently, also its solvation properties.

Fig.9. Isothermal (22 C) evolution of the ^1H NMR spectrum of water in Posisil foam with MAS frequency (15 kHz = $\pm$ 4.5 MPa intrusion pressure). Inset (top): Left spinning sideband, frequency offset corrected. Inset (bottom): Evolution of the dielectric shift (compared to a static sample).

4. Applications and Impact

Catalysis and gas storage are among the most straightforward showcase applications gaining from improved solvent properties of confined water. Partial intrusion conditions, leaving the smallest pores unfilled, are expected to be beneficial for maximizing the gas-liquid interphase. Hence clever design of pore architecture and surface chemistry will enable to maximize contact between intruded water and gas molecules adsorbed in a hierarchical network of pores.¹⁸⁴ Among all possible gaseous molecules to be investigated, some emerge of utmost importance: H_2 , CO_2 and CH_4 . Enhanced H_2 and CO_2 dissolution in water is of direct interest to electro- and chemo catalysis and (photo)electrochemical solar fuel devices.^{185–187} Hydrogenation catalysis in water can gain tremendously from

enhanced hydrogen dissolution, with production of renewables by aqueous catalytic hydrogenation of biomass carbohydrate derivatives as prominent envisaged application.^{188–190} Enhanced solubility of CH_4 in water confined in channels of mesoporous silica nanoparticles (440 – 500 fold solubility increase) and alkyl functionalized MCM-41 (200–300 fold increase) was recently demonstrated, both theoretically and experimentally.^{89,191} When a heterogeneous catalyst was prepared by immobilizing a tricopper complex in this mesoporous silica material, the enhanced CH_4 solubility induced a 25 fold higher TON for the conversion of CH_4 to CH_3OH compared to the same tricopper complex in a homogeneous system.¹⁹¹

Hydrogen is seen as a key energy vector for low carbon energy supply schemes and it has the potential to dramatically reduce the world's dependence on fossil carbon sources. Hydrogenation catalysis would significantly benefit from enhanced hydrogen dissolution. WaTuSo technology could be implemented in carbon capture and utilization schemes. It could assist dissolution of hydrogen in fuel cell devices and in solar fuel production systems by assisting the management of CO_2 , H_2 and synthetic CH_4 .^{185–187} Confined CH_4 clathrates for storage is another very relevant target. In a totally different field, NMR sensitivity enhancement using magnetization transfer from p- H_2 enabled by the WaTuSo concept would boost scientific progress in many disciplines relying on NMR analytical tools, and especially biomedical, biological, pharmaceutical, food science & materials science research.

Conclusions

Unprecedented control in time and space over dissolution in a WaTuSo system will enable new technologies with major scientific and societal impact. WaTuSo technology will revolutionize chemical manufacturing and gas storage and the concept could spill over to many more solvent-based processes. Successfully modulating water properties, the WaTuSo concept will contribute to a greener, more sustainable chemical industry, while at the same time extending the fundamental understanding of water.

Conflicts of interest

There are no conflicts to declare.

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