

Enhanced Oxygen Solubility in Metastable Water under Tension

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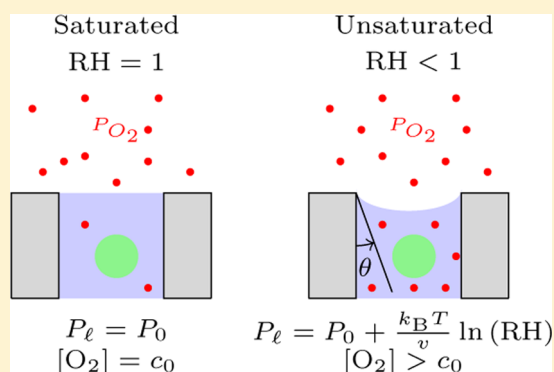
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Supporting Information

ABSTRACT: Despite its relevance in numerous natural and industrial processes, the solubility of molecular oxygen has never been directly measured in capillary-condensed liquid water. In this article, we measure oxygen solubility in liquid water trapped within nanoporous samples, in metastable equilibrium with a subsaturated vapor. We show that solubility increases two fold at moderate subsaturations (relative humidity ~ 0.55). This evolution with relative humidity is in good agreement with a simple thermodynamic prediction using properties of bulk water, previously verified experimentally at positive pressure. Our measurement thus verifies the validity of this macroscopic thermodynamic theory to strong confinement and large negative pressures, where significant nonidealities are expected. This effect has strong implications for important oxygen-dependent chemistries in natural and technological contexts.



INTRODUCTION

Many essential chemical processes in the environment and in technological applications involve reaction of solvated gases, typically in aqueous conditions: before reaching reactive sites, gas species are captured from the atmosphere by dissolution in a solvent. Examples include gases like molecular oxygen or dioxygen for biochemistry and respiration,¹ geochemistry,² corrosion,^{3,4} soil remediation,⁵ metallurgy,^{6,7} and cathodic reductions;^{8,9} molecular nitrogen for nitrogen fixation in soils;¹⁰ and carbon dioxide for photosynthesis,¹¹ carbon dioxide sequestration, and the formation of carbonates.^{12,13} In these scenarios, solubility defines the concentration of dissolved solute; in turn, concentration controls rates of mass transfer and reaction.¹⁴ In general, the solvent is present as an absorbate, in confinement within pores, or both.

Significant research has been conducted to describe the dynamics and the equilibrium state for the adsorption of species.^{15–18} The topic of gas solubility in nanoconfined solvents has more specifically received significant attention over the past two decades.^{19–31} Model predictions, numerical simulations as well as experiment indicate that the solubility of gases tends to be larger in nanoconfined solvents than in the bulk. Two perspectives on this oversolubility have emerged in the literature.

Starting with simulations by Luzar and Bratko^{21,32} and experiments by Miachon et al.,²² a literature on oversolubility in nanoconfined solvents emerged in the context of catalysis. These studies focused on gas solubilities in synthetic mesoporous matrices wetted with organic solvents or water. These studies document dramatically increased solubilities (over 10-fold) of H_2 , CO_2 , and noncondensing organics as the confinement of the solvent increases and the solvent loading of the pore space decreases.^{21,22,25,28,29} These investigators explain the observed oversolubility by a combination of adsorption at the pores wall and at the liquid–gas meniscus and enhanced solvation due to confinement-induced layering of the solvent molecules, depending on the chemical characters of the host matrix, the solvent, and the solute.

Simultaneously, research led by Mercury and collaborators have emphasized the importance of capillary stress in solvents on the equilibrium constants of dissolution from both solid phases and gases in the context of geochemistry.^{20,33–35} In the context of a solvent condensed in small pores, the capillary stress is a reduction of pressure (possibly down to negative values) controlled by Kelvin equilibrium with an unsaturated atmos-

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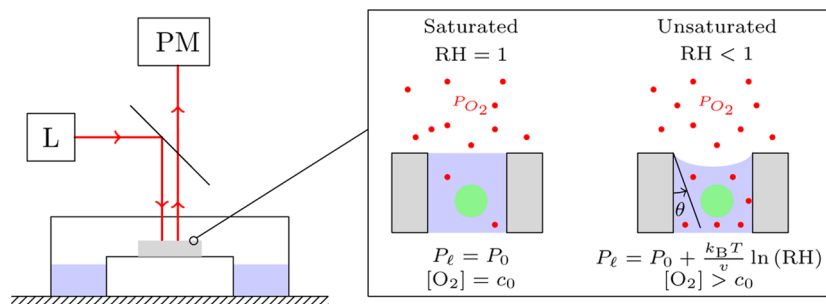


Figure 1. Measuring relative concentrations of oxygen in pore liquid under tension with phosphorescence lifetime. A porous sample wetted with an aqueous solution of phosphorescent dye (green circles in the expanded view) was placed in a box of controlled atmosphere of water vapor, oxygen (red circles in the expanded view), and other inert gases, in equilibrium with osmotic solutions imposing relative humidity RH. Phosphorescence lifetime was accessed by illuminating the sample with pulsed laser (L) and measuring the decay of phosphorescence signal with a photomultiplier (PM).

phere of the solvent's vapor; concavely curved menisci pinned at the mouth of the wettable pores maintain the difference in pressure between the gas phase (positive pressure, P_g) and that of the solvent (reduced or even negative pressure, P_l). The reduction of pressure in the pore solvent modifies solubilities according to the rules of classical thermodynamics of bulk substances. In particular, as discussed in detail below, for solutes with positive partial molar volumes of mixing, one expects solubility to increase with decreasing solvent pressure. With a focus on water as a solvent in geological contexts (i.e., porous minerals as hosts), these investigators have used state-of-the-art descriptions³⁶ of aqueous solutions as a function of pressure, temperature, and composition to predict the dependence of solubilities on the saturation of the water vapor (relative humidity (RH) = $P_g/P_{\text{sat}}(T)$ where P_{sat} is the saturation pressure) with which the pore liquid is in equilibrium.¹⁹ With elegant analysis and experimentation, they have shown that this Kelvin mechanism can explain measured equilibria within hydrated reactive minerals as a function of the RH of water vapor.^{20,31} Of note for our study, these works provide convincing yet indirect evidence that the solubilities of CO_2 and O_2 increase with decreasing RH due to the reduced pressure within pore solvent.

Experiments to measure solubility in nanoconfined solvents have used both macroscopic and microscopic techniques. Some studies^{20,23,25,26,28,29,31,37} used macroscopic measurements of phase equilibrium, for example, by measuring the equilibrium partial pressure of CO_2 in contact with hydrated carbonate mineral³¹ or of H_2 in contact with a mesoporous matrix wetted by organic solvents.^{23,26} Miachon et al., on the other hand, used integrate peak size in NMR spectra of confined solutions to extract solute concentrations.²²

In this work, we show that the solubility of molecular oxygen (O_2) in capillary-condensed water in the pores of a wettable solid increases when the RH of the gas atmosphere decreases (see Figure 1). To do so, we introduce a new microscopic technique based on phosphorescence lifetime to evaluate relative changes in oxygen concentration in liquid water in the pores of two porous media with pore radii of a few nanometers. This study represents the first direct measurement of O_2 solubility in nanoconfinement as a function of the degree of vapor saturation. To explain our results, we adopt the Kelvin mechanism of Mercury et al., although with simpler assumptions about the properties of the solvent. This model successfully captures the observed evolutions and is consistent with previous studies on oxygen solubility in water under high positive pressure.^{38,39}

We organize the remainder of our presentation as follows. First, we explain in more detail the Kelvin mechanism leading to equilibrium between pore liquid and an unsaturated vapor and its consequences on the solubility of gases. Second, we describe the experimental setup and present the phosphorescent dye and the porous media used in the study. Then, we show the results obtained from the experiments and compare them with theoretical predictions. Finally, we discuss these results relative to the aforementioned literature.

THEORETICAL BACKGROUND

Figure 1 presents our experimental system. In the expanded view, we show an individual pore containing liquid water in equilibrium with a gas phase containing oxygen and either saturated water vapor (left) or unsaturated vapor (right). This simple representation of the pore architecture does not capture the full complexity of pores within the porous media studied here (Vycor and porous silicon) with respect to interconnectedness, distribution of pore size, or surface roughness (see Section 1 in Supporting Information for more details on porous media). Nonetheless, the consideration of a simplified pore geometry (cylindrical with smooth walls and uniform diameter) allows us to capture the relevant physics for this study.

In the following theoretical development, we assume that the macroscopic thermodynamic properties and relations remain relevant in the pore solvent despite significant confinement (pore diameters below 10 nm). By confronting the predictions of this approach with our experimental observations (see Results section), we show that within the context of this study, these macroscopic arguments are indeed relevant. We do not exclude the possibility that nanoscale confinement has some influence on the properties of the pore liquid, we simply conclude that any such effects are not resolvable by our measurements of the variation of solubility with imposed relative humidity in pores of radius greater than ~ 1.5 nm.

Classical arguments from thermodynamics predict that a capillary-condensed pore liquid in equilibrium with a subsaturated vapor exists in a superheated state at reduced pressure P_l (MPa) defined by the Kelvin–Laplace relation^{43,44}

$$P_l = P_g + \rho_l RT \ln(\text{RH}) = P_g - \frac{2\gamma \cos \theta}{r_p} \quad (1)$$

where P_g (MPa) is the total gas pressure, ρ_l ($\text{mol}\cdot\text{m}^{-3}$) is the molar density of the liquid phase, $\text{RH} = P_{\text{H}_2\text{O}}/P_{\text{sat}}(T)$ is the relative humidity of the gas phase ($P_{\text{sat}}(T)$ (MPa) being vapor saturation pressure), γ ($\text{J}\cdot\text{m}^{-2}$) is the surface tension (for pure

bulk water, $\gamma = 72 \text{ mJ}\cdot\text{m}^{-2}$, but this value could depend on the curvature of the meniscus and of the concentration of dissolved gases) of the liquid, and θ (rad) is the contact angle with the solid at the pore mouth. Equation 1 predicts that the pressure P_1 in the pore liquid decreases (and eventually becomes negative) as RH drops; this state persists until cavitation occurs or until the contact angle of the meniscus reaches its receding value. Modest changes in RH should induce large changes in the pressure experienced in the adsorbate, for instance, although pressure in saturated conditions (RH = 1) is about, $P_1 = 0.1 \text{ MPa}$ it decreases to $P_1 = -80 \text{ MPa}$ for a moderate unsaturation RH = 0.5.

We^{45–47} and other groups^{48,49} have recently shown that predictions of eq 1 hold to extremes of confinement (pore radius down to 1.4 nm) and pressure ($P_1 = -70 \text{ MPa}$). In the following, we use eq 1 to interpret responses to changes in RH in terms of changes in solvent pressure. This approach provides a simple route to pursue an unprecedented study of solubility at reduced pressures, extending previous studies conducted under elevated pressures.³⁹

The effect of solvent pressure on the solubility can be modeled by using simple arguments based on macroscopic thermodynamics. If we assume that the partial molar volume of oxygen in water v_2 ($\text{m}^3\cdot\text{mol}^{-1}$) is independent of pressure, Gibbs–Duhem equation can be easily integrated to give the change of chemical potential with pressure. If we further assume that the gas phase is ideal, we get the Krichevsky and Kasarnovsky equation³⁸

$$\frac{c(P_1)}{c_{\text{sat}}} = \frac{\rho_1(P_1)}{\rho_{1,\text{sat}}} e^{-v_2(P_1 - P_{\text{sat}})/RT} \quad (2)$$

We provide a derivation of this relation in Section 4 of SI. These arguments assume that the pore liquid can be treated as having a well-defined pressure and bulk behavior despite the significant confinement imposed by the walls of the nanoscale pores. For the pore dimensions used in this study ($r_p = 1.4$ and 3.8 nm), our previous work⁴⁶ and that of others⁵⁰ suggest that this assumption of macroscopic thermodynamic behavior should hold. The success of this treatment in describing our data (see Results section) serves as a test of its consistency. In Section 4 of SI, we also provide a more general relation directly between the imposed RH and the solubility. Variations of molar volume (v_2) with pressure can be accounted for by using van der Waals-like equations of state.^{51,52}

MATERIALS AND METHODS

The experimental setup is described in Figure 1. Initially, we filled a dry porous sample with a solution of oxygen-sensitive phosphorescent dye with concentration $\sim 100 \mu\text{mol}\cdot\text{L}^{-1}$: we placed a drop of solution on the sample and left it at rest for about 15 min to allow filling by capillary imbibition. After carefully drying the surface of the sample, we placed it in a closed chamber with controlled humidity RH and oxygen pressure P_{O_2} and allowed equilibration of pore liquid with the atmosphere for ~ 5 min before measurements. We used two different porous solids—porous glass (pore radius $r_p = 3.8 \pm 0.3 \text{ nm}$) and porous silicon ($r_p = 1.4 \pm 0.1 \text{ nm}$)—to host the condensed water. Some details on the porous samples are given in Section 1 in SI.

The composition of the atmosphere for each experiment was either air or a mixture of oxygen and nitrogen at atmospheric pressure $P_g = 1$ bar and with the ratio controlled by a gas mixer (Oxydial); the mixer was calibrated with respect to the Clark electrode. The humidity of the atmosphere was imposed by the saturation vapor pressure of salt solutions placed in the box; no direct contact occurred between this solution and the porous sample. In this experiment, solutions of sodium or lithium chloride at various concentrations were used to impose liquid pressures ranging from $P_1 = P_{\text{sat}}$ (pure water, saturated atmosphere) to

-70 MPa . For each solution and before every experiment, water potential was measured using a chilled mirror hygrometer (WP4C, Meter Group⁵³). The experiment was performed at a temperature of $T = 20 \text{ }^\circ\text{C}$: in the following, all numerical results and theoretical predictions will be given at his temperature.

To measure the concentration, c ($\text{mol}\cdot\text{m}^{-3}$), of dissolved oxygen in pore liquid water, we exploited the oxygen quenching of the phosphorescence of specific dyes:^{54,55} we used a rhenium-based phosphor⁵⁶ synthesized by our team (details in Section 3 of SI). This dye presents the advantage over commercial ones by yielding significant luminescence signal and being water soluble and small enough to fit within the nanoscale pores. By fitting the luminescence signal following pulsed laser excitation of the phosphor, we measured the phosphorescence lifetime, τ (s) of the dye (see Figure 2a and Section 2 in SI for more details on the optical setup).

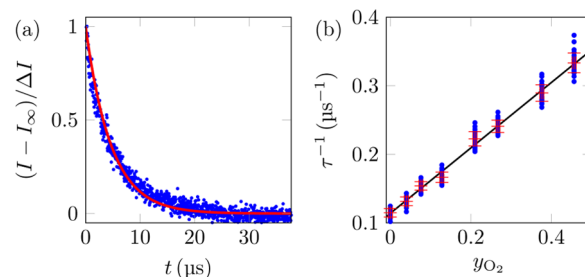


Figure 2. Phosphorescence lifetime of dye in pore liquid. (a) Example of phosphorescence signal and exponential fit, with lifetime $\tau = 4.7 \mu\text{s}$, amplitude $\Delta I = 479$, and noise level $I_\infty = 135$. (b) Evolution of lifetime in Vycor with mole fraction of oxygen, y_{O_2} , in saturated atmosphere.

The blue dots are the measured lifetimes at different positions on the porous glass ($N = 25$), the red crosses represent the average lifetime and error bars correspond to standard deviations over the sample. The black line corresponds to a linear fit (eq 4) with $\tau_0 = 8.7 \pm 0.3 \mu\text{s}$ and $k_{\text{sat}} = 0.48 \pm 0.02 \mu\text{s}^{-1}$.

For both substrates, we observed variations of lifetime when we performed measurements at different locations across the samples. However, the size of the laser spot (diameter $\sim 200 \mu\text{m}$) was larger than the typical pore size and we thus expected to observe a homogeneous value. It is known that lifetime of fluorescent dyes can display fluctuations due to molecular conformation,^{54,57} but this effect should not affect significantly our measurement as the spot size is larger than the typical pore size. However, it has been observed that Stern–Volmer parameters can display significant variations on micrometric scales on a priori homogeneous surfaces.^{58,59} Furthermore, as was seen with other dyes,^{60,61} we observed a significant variation of lifetime between the different porous media and with respect to bulk solution (see Section 3 in SI for more details): this observation hints at a strong interaction between the dye and the solid glass matrix, which could explain the observed spatial variations, as small variations of the glass properties on large scale could significantly impact measured lifetimes. To moderate the impact of these fluctuations, we repeated measurements for each value of RH at different places of the samples ($N = 25$) and computed average lifetimes. Uncertainties are represented by the standard deviation of the measured series.

We expect the relationship between the lifetime, τ , and the concentration, c , of oxygen in the pore liquid to be given by the Stern–Volmer relation

$$\frac{1}{\tau} = \frac{1}{\tau_0} + Kc \quad (3)$$

where τ_0 (s) and K ($\text{m}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$) are parameters to be determined by calibration, which depend on the nature of the substrate. The concentration is related to the oxygen pressure through Henry's law $c = \mathcal{H}P_{\text{O}_2}$, so we predict

$$\frac{1}{\tau} = \frac{1}{\tau_0} + k y_{\text{O}_2} \quad (4)$$

where $k = \mathcal{H}KP_g$ and $y_{\text{O}_2} = P_{\text{O}_2}/P_g$ is the mole fraction of O_2 in the atmosphere.

To calibrate the sensor, we filled the experimental cell with a mixture of oxygen and nitrogen with a controlled ratio and at atmospheric total pressure $P_g = P_{\text{atm}}$, saturated with water vapor ($\text{RH} = 1$). The lifetimes we obtained for different mole fractions of oxygen in the gas phase are presented in Figure 2b. For both substrates, the eq 4 describes satisfactorily our measurements, and this calibration allows us to determine the values of τ_0 and $k_{\text{sat}} = \mathcal{H}_{\text{sat}}K$, where subscript sat indicates that this value is valid at saturation. Values of the parameters for the two substrates are given in Section 3 in SI.

For any value of RH, we have

$$\frac{1}{\tau} = \frac{1}{\tau_0} + k_{\text{sat}} y_{\text{O}_2} \frac{c}{c_{\text{sat}}} \quad (5)$$

As we control y_{O_2} and by assuming that the determined values of τ_0 and k_{sat} do not depend on the pressure in the liquid, our measurements of lifetime give us access to c/c_{sat} . In other words, we can track relative changes in the concentration of O_2 in the pore liquid with this technique; we cannot determine absolute concentrations.

RESULTS

Figure 3 represents the observed evolution of the relative concentration of dissolved oxygen in the pore liquid (aqueous

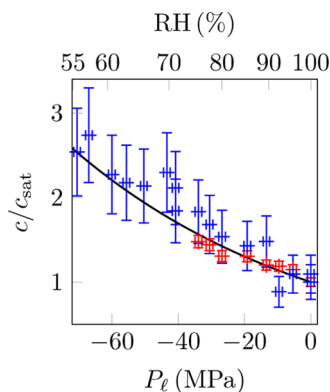


Figure 3. Evolution of oxygen concentration c with liquid pressure P_l in metastable water, with respect to its value c_{sat} at saturation. The red symbols correspond to measurements in Vycor glass and the blue symbols to measurements in porous silicon. The black line is the prediction of the simple model (eq 2).

solution of phosphor) for fixed mole fraction in the gas phase ($y_{\text{O}_2} = 0.21$) and various values of RH. We used calibration curves as in Figure 2 to evaluate the relative concentration from phosphorescence lifetimes, with the value at saturation ($\text{RH} = 1$), c_{sat} as a reference. We report the imposed RH on the top axis and the corresponding pressure in the pore liquid (calculated with eq 1) on the bottom axis.

The range of RH (or pore pressure) over which we report concentrations for each sample type ($\sim 0.75 \leq \text{RH} \leq 1$ for Vycor and $\sim 0.55 \leq \text{RH} \leq 1$ for porous silicon) was limited from below by the disappearance of detectable phosphorescence for drier conditions. We interpret this loss of signal as occurring at the point at which the pore liquid receded into the pores when the stress implied by the Kelvin equation ($\rho_l RT \ln \text{RH}$ in eq 1) exceeded the maximum capillary stress sustainable in the pores⁶² ($2\gamma \cos \theta_r/r_p$ in eq 1 where θ_r is the receding contact angle of

water on the pore wall). For Vycor, with $r_p = 3.8$ nm, we expect this drying transition to occur at $\text{RH} = 0.8$; for porous silicon, with $r_p = 1.4$ nm, we expect it at $\text{RH} = 0.54$. In both cases, we use a reasonable value $\theta_r = 40^\circ$ and find reasonable agreement with the observed transitions.

We now remark the good agreement in the measured values of relative concentration as a function of RH for the two substrates over the shared portion of their ranges ($\sim 0.75 \leq \text{RH} \leq 1$). We further note the large (over 2-fold) increase in relative concentration of dissolved O_2 as the vapor goes from saturation to $\text{RH} = 0.55$. We conclude that a modest degree of subsaturation in the vapor phase, commonly encountered in our environment, has a dramatic effect on the solubility of RH of O_2 in the pore liquid.

The black line in Figure 3 represents the prediction of Krichevsky and Kasarnovsky (eq 2) for a literature value for the molar volume^{39,63} of O_2 in water: $v_2 = 3.21 \times 10^{-5} \text{ m}^3 \cdot \text{mol}^{-1}$. Predictions of the more sophisticated model detailed in Section 5 of SI match those of the simple model within a few percent, well within the experimental uncertainty. Thus, our theory agrees quantitatively with experimental results. Importantly, we employed no fitting parameter in performing this comparison. Interestingly, the same Krichevsky and Kasarnovsky equation had previously been used to describe the evolution of oxygen solubility at positive pressures;³⁹ our experiment thus extends its range of validity by a factor 2 and for the first time into the regime of negative pressure.

DISCUSSION

Comparison with Literature. Given the structural and chemical distinctions between the two substrates, the agreement between data acquired for both of them and our model for a wide range of vapor saturations demonstrates:

1. the appropriateness of interpreting the impact of subsaturation as the impact of the thermodynamic state of the pure fluid imposed by metastable equilibrium with its vapor (eq 1) and not of the detailed characteristics of the host matrix and
2. the relevance of bulk thermodynamics relations for multiphase, multicomponent equilibrium for nanoconfined pore liquids.

This success supports the perspective put forward by Mercury, Lassin et al.^{19,20,31,64,65} that the Kelvin stress within the pore fluid plays an essential role in defining the solubility of gases in unsaturated porous media. Our model relies on a far simpler description of the thermodynamic properties of the solute and solvent than that employed by these authors.^{31,36} However, the matrices used in our study should be completely unreactive (except for the possible deprotonation of silanol groups) such that pore liquid remains essentially pure water and ion effects should be minimal. In contrast, within the geological samples of interest to them, account for these effects was necessary. The good agreement between Krichevsky and Kasarnovsky equation and a more complete model with an equation of state for the mixture of oxygen and liquid water (see Section 5 in SI) can be explained by the small variation of the partial molar volume v_2 of oxygen with pressure.¹⁹

We further consider the interplay between Kelvin mechanism and the studies following experiments by Miachon²² and Ho,²⁵ in which the effects of the saturation of the solvent vapor were not explored. Our experiments are restricted to a situation, in which the porous solid remains completely filled with the liquid

and the liquid achieves equilibrium with a nanoscopic deformation of the menisci pinned at the pore mouths (see expanded view in Figure 1). In this filled state, the extent of liquid–solid and liquid–vapor interfaces within the host stays constant as we vary RH, such that we expect the interfacial effects involved by Miachon and Ho should not impact the variation of relative solubility, c/c_{sat} that we report here. On the other hand, we expect that this mechanism should impact the absolute concentrations in our host media (e.g., the concentration at vapor saturation, c_{sat} may be larger than in bulk water). However, due to our calibration procedure, we only measure directly the ratio c/c_{sat} of concentration at a given humidity over its reference saturated value. We do observe a significant discrepancy between the average lifetime of the dye in bulk solution and in pores under saturated conditions, however, we cannot interpret this observation as an effect of confinement on solubility as the behavior of the dye itself is likely affected by the confinement as we noted previously (see Section 3 in SI for a comparison of lifetimes in solid substrates and in bulk solutions).

We cannot exclude that the confinement-induced oversolubility mechanism would play a role in our system at low saturations for which gas and liquid would be interspersed through the whole pore space. Our method of observation was not sensitive enough to obtain phosphorescence signal in this regime. Although the mechanism proposed by Miachon and Ho is likely to be dominant in the very dry regime, where the liquid only remains as an adsorbate on the pores walls, it should be corrected by the Kelvin mechanism in the more humid regime when capillary condensation starts to occur.

Absence of Anomalous Hydrophobic Effect. Under the relative humidities involved in our study, we predict that liquid pressure reaches ~ -70 MPa, for which density should decrease by about $\sim 4\%$ with respect to saturation. It is surprising that our simple model, based on thermodynamic assumptions of ideality and bulk properties of water, holds in this notably stretched state and at such confinement, in pores of diameter of the order of a few molecular diameters.

In particular, the solubility of species in water under tension has been investigated numerically in the context of hydrophobic interactions, involved for instance in protein folding.⁶⁶ In this regime, there are strong numerical clues that the properties of solvent should be significantly altered and that an anomalous solvation effect occurs for hydrophobic molecules.⁶⁷

Oxygen has not been specifically studied with respect to the hydrophobic effect, but its apolar nature and the non-monotonous behavior of its solubility with temperature^{68,69} hint at a hydrophobic character. The agreement with our theory is thus particularly striking. Further studies involving more hydrophobic and larger molecules would be of strong interest.

Impact on Physicochemical Processes. Such a dependency of the solubility of oxygen on RH for capillary-condensed water is expected to impact various physicochemical processes. In natural conditions, capillary-condensed water is mostly found in soils: there, dissolved oxygen can be beneficial, for instance in agriculture as it enhances root growth^{70,71} and microbial activity,⁷² or detrimental, for instance as it triggers the formation of polluting sulphidic compounds in mine tailings.⁷³ Significant work has been done on the modeling of oxygen transport within unsaturated soils,⁷⁴ and incorporation of our result could help to reach more quantitative predictions.

Electrochemical transformations represent important class of processes susceptible to be impacted by this phenomenon. Dry

corrosion of metals, which happens in contact with an unsaturated medium, is one of the most widely studied physicochemical phenomenon due to the enormous industrial cost it represents for the maintenance of pipes and structural materials.⁷⁵ Many studies have reported effects of the relative humidity in the gas phase on corrosion rates in several contexts like atmospheric corrosion,^{76–80} corrosion by hot steam,⁸¹ or soil corrosion.^{82,83} In all these cases, the metals are covered by a thin liquid film, and any asperity of the surface may host a pocket of water under tension. Our findings are thus highly relevant in this context and may be a key phenomenon for the understanding of these observations.

In the context of research for sustainable power sources, a significant effort is devoted to fuel cells where oxygen is delivered in a gaseous phase to serve as an oxidant. Among these various technologies, air breathing fuel cells operate with reactants supplied to the electrodes by gas flows with controlled RH to maintain hydration of the electrodes.^{84,85} At high current density, the efficiency is limited by oxygen transport,^{86–89} and it has been shown that the relative humidity of the gas has an impact on this efficiency.^{87,90,91} Our results offer a possible basis for rationalizing this observation. Moreover, it opens the way for new design of porous cathodes that could exploit this enhanced oxygen solubility in unsaturated conditions to improve significantly the performance of this technology.

CONCLUSIONS

We have shown in the present work that the solvation of oxygen in adsorbed water is strongly influenced by the relative humidity of the surrounding atmosphere and that this effect can be described quantitatively by thermodynamic models using bulk properties of water. This success extends the conclusions made by our team^{45–47} and others^{48,49} that the bulk thermodynamic behaviors of liquid water persist to strong confinement and large tension. The Krichevsky and Kasarnosky theory is not restricted to dioxygen and predicts a similar exponential variation of the solubility of any gas with pressure. Consistent to Le Chatelier's principle, the solubility of solutes with positive partial molar volumes of mixing should increase with increasing tension, whereas the solubility of solutes with negative partial molar volumes of mixing should decrease. Beyond this dependence on the partial molar volume, this prediction does not depend on the identity or microscopic details of the solvent and solute. Further work should confront this prediction by considering other molecules that display a strong hydrophobic character and for which we may expect qualitative changes of the solvent properties of pore-confined liquid water under tension.

This modification of gas solubility in adsorbed water is likely to affect important chemical processes like corrosion and it may be a missing ingredient for modeling in many situations, in which dependence on RH has been observed. More interestingly, this study calls for the development of chemical processes exploiting capillary-condensed water as a tunable solvent in the context of green chemistry: although most of studies on the effect of pressure have focused on the supercritical regime, our study shows that pressure quantitatively affects the solubility in water in a regime easier to access in practice and opens the path to the study of chemistry in metastable water, interesting for both fundamental and applied perspectives.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.8b02408.

Samples, experiments and theories (PDF)

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Notes

The authors declare no competing financial interest.

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