Putting Together the Puzzle of Ion Transfer in Single-Digit Carbon Nanotubes: Ab Initio Meets Mean-Field

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Article

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Abstract

Nature employs channel proteins to selectively pass water across cell membranes, which inspires search for bio-mimetic analogues. Carbon nanotube porins (CNTPs) are intriguing mimics of water channels, yet ion transport in CNTPs still poses questions. As alternative to continuum models, here we present a molecular mean-field model, computing ab initio all required thermodynamic quantities for KCl salt and H\(^+\) and OH\(^-\) ions present in water. Starting from water transfer, the model considers transfer of free ions, along with ion-pair formation to address ion-ion interactions. High affinity to hydroxide, suggested by experiments and making it dominant charge carrier in CNTP, is revealed as an exceptionally favorable transfer of KOH pairs. Nevertheless, free ions, coexisting with less mobile ion-pairs, apparently control ion transport. The model explains well the observed effects of salt concentration and pH on conductivity,
transport numbers, anion permeation and its activation energies, and current rectifica-
tion. The proposed approach is extendable to other sub-nanochannels and help design
novel osmotic materials and devices.

The world faces a water stress, which is predicted to increase and spread to areas not
experiencing the shortage of fresh water today.¹ Production of fresh water via desalination
of sea, brackish, and waste water is a viable solution, yet currently used membrane desalina-
tion technology still leaves room for improvement and selectivity-tailoring. This motivates
research that looks into alternative materials for next-generation membranes with improved
water-salt and ion-ion selectivity.² Natural membrane proteins aquaporins efficiently separate
water from ions by forcing it through a short and narrow channel in a single-file arrangement
at rates exceeding $10^9$ water molecules per second with nearly ideal water-ion selectivity.³

Intriguingly, while the use of degradable aquaporins might be impractical, stable nanomate-
rials, such as atomically thin nanoporous nanosheets⁴–⁷ or narrow nanotubes,⁸–¹⁰ that can
mimic transport in aquaporins and offer an exciting next-generation alternative to currently
used polymeric membranes.¹¹,¹²

Single-digit carbon nanotube porins (CNTP) share many unique features of aquaporins
and demonstrated a water-salt selectivity of $10^5$, on par with benchmark polyamide reverse
osmosis membranes.¹³–¹⁵ Numerous theoretical¹⁶–²⁴ and experimental²⁵–²⁹ studies indicate
that, due to wall roughness smaller than the de Brogli length, water transport in CNTPs
narrower than about 1.5 nm and similarly narrow graphene slits, occurs in a scatter-less man-
er, at rates greatly exceeding hydrodynamic predictions⁹,³⁰,³¹ and even faster than water
permeation in aquaporins.²²,²⁵ However, while there is an overall consensus regarding water
transport in narrow CNTs, the physical mechanisms behind ion rejection still pose many
questions. For instance, it has been long believed that negative carboxylic charges at CNTP
rims control salt rejection,³²–³⁴ yet recent data on pH dependence of anion permeation down-
played this mechanism. Adsorption of OH⁻ ions was proposed as an alternative charging
mechanism in CNTs and a number of continuum-type models, solving Poisson-Boltzmann
and Navier-Stokes equation employed this and other ad hoc assumptions to describe trans-
port, charge formation and conduction in narrow and wide CNTPS and rationalize the
observed trends. In parallel, important insights to transport of ions at the molecular
level were obtained using molecular dynamics (MD) and ab initio computations.

The data on ion permeation in CNTPs have mainly come from two types of measure-
ments (a) ion permeation from stop-flow experiments with CNTP-loaded vesicles and (b)
conductance or current-voltage (I-V) measurements for CNTPs connecting two solutions
across a nanopore. These experiments yielded absolute values of permeabilities to different
ions and salts, conductivity and water-salt selectivity for various types of CNTPs and longer
tubes. They also determined trends that describe dependence of transport properties on salt
concentration and pH, as well as temperature dependence, from which appropriate activa-
tion energies could be derived. These trends are often highly characteristic and may serve
as fingerprints of physical mechanisms. The data, combined with simulations, e.g., using
classical MD and ab initio computations have significantly advanced understanding
of ion transport in CNTPs, yet a full and physically consistent picture unifying different
experimental findings is still missing.

Here, we develop a systematic molecular picture of ion transfer to CNTPs based on ab
initio computations integrated in an appropriate physical model that transparently describes
ion transfer to CNTPs, as an alternative to commonly considered continuum models. Since
KCl has been the salt most commonly used in experimental studies, we focus on K+ and
Cl− ions, adding to the picture the OH− and H+ ions inherently present in water. We focus
on (6,6) CNTP of diameter 0.8 nm, used in most experiments as benchmark sub-nanometer
(“single-digit”) channels but, in order to clarify the effect of CNTP diameter and water
arrangement, compare the results with narrower (5,5) channels, in which a single-file ar-
rangement is preserved. Importantly, we also consider the effect of the medium surrounding
CNTP that was shown to strongly affect ion transfer from a solution to CNTPs. We first
incorporate the computed thermodynamic values in a model considering only free ions, re-
taining their full translational freedom, which is shown to agree semi-quantitatively with most experimental results. Subsequently, we add to the picture formation of ion pairs, as a proxy of ion-ion-CNTP interactions, which removes most remaining inconsistencies. The resulting physical picture rationalizes most results on ion permeation, selectivity, conductance, and current rectification in CNTPs reported so far.

Internal arrangement of water and ion hydration: not necessarily a single file

The narrowest experimentally studied CNTPs, showing the largest water-ion selectivity, have been the (6,6) nanotubes. Classical MD simulations suggested that water in (6,6) tubes forms a single file, similar to (5,5) nanotubes, believed to be the narrowest ones that allow water and ion transport. Ions in (5,5) tubes are then solvated by only two adjacent water molecules, which is confirmed by computations. The low density of water in a single file and resulting high entropy were suggested to be an important factor in experimentally confirmed spontaneous filling of CNTPs with water. However, ab initio simulations recently indicated a possibility of a significantly distorted arrangement in (6,6) CNTPs, both in presence and absence of ions. For instance, while larger K$^+$ ions were still solvated by two water molecules, smaller Na$^+$ cations displayed a four-molecule solvation. Here, we find that significant distortions in (6,6) tubes may be even more common, even without ions.

Figure 1a displays two arrangements of water molecules within (6,6) CNTP, composed of a central water molecule surrounded by three other molecules on each side, while corresponding computed thermodynamic quantities are shown in Fig. 1b. Upon energy optimization, the straight file transforms to a zig-zag arrangement shown on top of Fig. 1a. The latter has a lower energy yet is still preserves the topology of the single file, as each water molecule still interacts only with two closest neighbors. Its thermodynamic properties are fairly similar to those computed for (5,5) tubes (see Supplementary). However, since CNTP is an open
system, the minimal-energy arrangement is not the equilibrium one, as it should minimize the free energy rather than energy. More elaborate computations of the thermodynamic functions and, in particular, excess entropy $\Delta S^\text{ex}$ and excess Gibbs energy $\Delta G^\text{ex}$ of water transfer into CNTP in Gaussian, help clarify this point. While $\Delta S^\text{ex}$ indicates whether water arrangement in CNTP is more constrained than in the bulk, $\Delta G^\text{ex}$ indicates how it compares with the equilibrium arrangement. For instance, focusing on $\epsilon = 2$ (see next), we observe that the negative $-T\Delta S^\text{ex} = -0.8 \text{ kJ/mol}$ of the zigzag arrangement indicates it is slightly less constrained (rarer) than bulk water, its negative $\Delta G^\text{ex} = -17.3 \text{ kJ/mol}$ indicates it is also rarer than the equilibrium one (open bars in Fig. 1b). On the other hand, the topologically different arrangement at the bottom of Fig. 1a, obtained as a local energy minimum upon energy optimization from a different initial arrangement with middle molecules bonded to three neighbors, has a positive $-T\Delta S^\text{ex} = 3.6 \text{ kJ/mol}$, i.e., is denser than bulk water, yet its positive $\Delta G^\text{ex} = 19.7 \text{ kJ/mol}$ indicates it is also denser than the equilibrium state (cross-hatched bars in Fig. 1b). Apparently, the equilibrium arrangement in (6,6) tubes must be intermediate to the zigzag and triple-bonded ones, neither of which is a regular single file. Its thermodynamic properties may, in principle, be obtained by full quantum MD simulations, but the computational costs may be excessive. However, we may estimate the equilibrium properties by interpolating between the two arrangements. Since we essentially deal with two co-existing water phases, in the manner of Clapeyron equation, the equilibrium should correspond to $\Delta G^\text{ex} = 0$ (for water only, not for ions!). The interpolation yields $-T\Delta S^\text{ex} = -\Delta H \approx 2 \text{ kJ/mol}$, which makes water within CNTP on average about twice denser, i.e., more constrained, than the bulk phase. We wish to stress that this $\Delta H$ should not be viewed as the activation energy of water transport. Rather, we presume that, when a water molecule needs to move or exchange with a neighbor, it is likely to temporarily assume the more constrained triple-bonded state, which would make its $\Delta H = 16 \text{ kJ/mol}$ representative of the relevant transition state. Indeed, Li et al. reported recently a reasonably close experimental activation energy $20 \text{ kJ/mol}$ for water diffusion in
Notably, the above thermodynamic quantities for water are fairly weakly affected by the dielectric constant of the surrounding medium $\epsilon$, unlike those of ions.

Similarly, a straight-file two-molecule hydration of $\text{OH}^-$ and $\text{Cl}^-$ anions, corresponding to the lowest energy in (5,5) CNTPs, transforms upon optimization to a four-molecule hydration within (6,6) CNTP with a lower energy, as shown in Figs. 1c and d. Nevertheless, that was not the case for all ions and, in agreement with other reports, two-molecule hydration was found here for $\text{K}^+$ and $\text{H}^+$ (essentially, $\text{H}_3\text{O}^+$) cations. Since the energy of internal hydration is a considerable part of the total ion transfer energy, e.g., about 50% for $\text{K}^+$ and 25% for $\text{Cl}^-$ in (5,5) tubes, this difference may affect the energy of ion transfer from water to CNTP.

**How much does it costs to transfer ions?**

Figures 1e and f illustrate the ion transfer process and display the key transfer quantities, excess Gibbs energy $\Delta G_{ex}$ and enthalpy $\Delta H$, for moving ions into a water-filled (6,6) CNTP. (Complete data and comparison with (5,5) tubes are presented in Supplementary Figs. S2 and S3.) These quantities are plotted versus $1/\epsilon$ and the slope highlights the contribution by the dielectric energy, i.e., polarization of the medium surrounding CNTP, which adds a significant cost to ion transfer. It reaches a maximum in vacuum ($\epsilon = 1$) and vanishes when $\epsilon$ goes to infinity, i.e., at $1/\epsilon = 0$. Neither of these extremes reflect typical experimental conditions, yet $\epsilon = 2$ ($1/\epsilon = 0.5$) may reasonably represent lipid membranes embedding CNTPs in most experiments. The slopes for the anions are somewhat smaller than for cations. This may be a result of stronger bonding of cations to CNTP and charge delocalization, decreasing the dielectric energy. Yet, the slopes of all ions are reasonably close and similar to results for (5,5) CNTPs (Supplementary Fig. S3). This contribution is then about rigidly shifts $\Delta G_{ex}$ and $\Delta H_{ex}$ of all ions relative to ion-specific base values.

Compared to its effect on water transfer, $\Delta S_{ex}$ seems to play a lesser role in ion transfer, therefore $\Delta G_{ex}$ is mainly controlled by enthalpy. Due to more favorable interaction with
Figure 1: Molecular arrangement and transfer quantities for water and ions in (6,6) CNTP. (a) Zigzag (top) and triple-bonded (bottom) arrangement of water in CNTP and (b) computed $\Delta G^{ex}$ and $-T\Delta S^{ex}$ for water transfer to CNTP for each arrangement at different $\epsilon$. Water arrangement around chloride (c) and hydroxide (d) ions in water-filled CNTP. (e) Schematic illustration of single ion transfer process from bulk water to water-filled CNTP and (f) computed transfer quantities, $\Delta G^{ex}$ and $\Delta H$, for transfer of $\text{H}^+$, $\text{K}^+$, $\text{OH}^-$, and $\text{Cl}^-$ as single ions plotted versus $1/\epsilon$. The sloped line and the value of the slope highlight the effect of dielectric energy. Oxygen, carbon, and hydrogen atoms and chloride ions are depicted in red, grey, white and green, respectively.

CNTP, cations has a significantly lower transfer energy than anions. For instance, for $\epsilon = 2$, $\text{K}^+$ transfer into CNTP is nearly athermal and, for (6,6) tubes, it is even more favorable than transfer of water, while transfer of anions is highly unfavorable. Enhanced interaction of potassium was already noted by Aydin et al. for slightly wider tubes and is reminiscent of the long-known complexation of cations with benzene, “cation-π interaction”. Partly but less significantly, the differences between the ions are also related to different arrangement of water molecules and water-water interaction around the ion, different for cations and anions. We also note that proton transfers about as favorably as $\text{K}^+$. Practically, that means that, in experiments that involve KCl solutions, $\text{K}^+$ will outcompete the more dilute protons and...
must be the dominant cation species within CNTPs. However, uptake of $K^+$ is subject to
limitations imposed by the requirements of overall electroneutrality. The latter will apply
when either CNTP is much longer that the screening length\textsuperscript{55} or bonding of ions to CNTP
delocalizes their charge and sufficiently smears the potential variations.\textsuperscript{47} Electroneutrality
dictates that the uptake of a $K^+$ cation needs to be counter-balanced by uptake of an anion,
either $Cl^-$ and $OH^-$, both having a highly unfavorable $\Delta G^{ex}$. As the simplest mean-field
approximation, we may assume a uniform mean potential $\phi$ within the CNTP relative to
bulk thus ion uptake is given by

$$\sum_{i (\text{cations})} C_i \exp \left( -\frac{\Delta G_i^{ex} + F \phi}{RT} \right) = \sum_{j (\text{anions})} C_j \exp \left( -\frac{\Delta G_j^{ex} - F \phi}{RT} \right),$$  \hspace{1cm} (1)$$

where $C$’s are respective cation and anion concentrations in solution. The exponents are
essentially ion partitioning coefficients, calculated by solving this equation for $\phi$, given $\Delta G^{ex}$
for all ions. $\Delta G^{ex}$ should be understood as the appropriate statistical means, reflecting ion-
ion interactions as well. Yet, in the simplest picture, when ions are assumed to collectively
preserve electroneutrality but, otherwise, do not significantly interact with each other, we
approximate $\Delta G^{ex}$ by the values computed for individual free ions. We consider available
experimental data on ion transport in CNTPs along with present \textit{ab initio} results to ju-
diciously select the ions that need to be considered in eq. 1. Since the results of most
measurements typically represent ion permeabilities rather than partitioning, the differences
in ion mobilities need to be considered as well. We presume that in highly constrained ar-
rangements within narrow CNTPs, the mobilities of water and ions may be fairly similar,
except for proton and hydroxide that may employ the much faster Grotthuss mechanism. We
then employ \textit{ab initio} the results by Dellago et al.\textsuperscript{56} who computed \textit{ab initio} the mobility of
proton, by the Grotthuss mechanism, and of water, associated with diffusion of orientation
defects in the single file. We adopt the latter for the mobility of $K^+$ and $Cl^-$ and the former,
corrected by the ratio of hydroxide and proton diffusivities in bulk water ($\sim50\%$), for the
mobility of OH$^-$.

When KCl transfers as free ions and the effect of pH is negligible, i.e., H$^+$ and OH$^-$ do not affect salt uptake, K$^+$ and Cl$^-$ hence salt concentrations within CNTP, denoted with a bar, will all be about identical and linearly depend on the salt concentration in solution $C_s$, as follows

$$\bar{C}_s = \bar{C}_K = \bar{C}_{Cl} = C_s \exp \left(-\frac{\Delta G_{ex}^{K} + \Delta G_{ex}^{Cl}}{2RT}\right),$$

(2)

The average $\Delta G_{ex}^s = \frac{1}{2}(\Delta G_{ex}^{K} + \Delta G_{ex}^{Cl})$ essentially plays here the role of excess Gibbs energy for pH-independent salt transfer. However, the non-linear scaling of conductivity observed at pH 7.5 in Fig. 2a indicates that such a pH-independent scenario operates only at low pH. Apparently, pH comes into play in neutral conditions as preferential uptake of OH$^-$ ions, as reported for wider tubes and observed in $ab$ initio simulations of graphene surfaces in water.$^{27,57}$ When OH$^-$ is strongly favored over Cl$^-$, eq. 1 has to be replaced with

$$\bar{C}_K \approx \bar{C}_{OH} \approx (C_s C_{OH})^{1/2} \exp \left(-\frac{\Delta G_{ex}^{K} + \Delta G_{ex}^{OH}}{2RT}\right),$$

(3)

where $C_{OH} = 10^{pH-14}$ in M units. The unusual 1/2 scaling of conductivity with $C_s$ predicted by eq. 2 and observed by Tunuguntla et al at pH 7.5 is a signature of such a pH-dependent ion partitioning.$^{35}$ In this scenario, the potassium mainly transfers in combination with hydroxide, i.e., KOH, with a transfer energy $\Delta G_{ex}^{h} = \frac{1}{2}(\Delta G_{ex}^{K} + \Delta G_{ex}^{OH})$ replacing $\Delta G_{ex}^s$. On the other hand, Cl$^-$ will transfer as a trace species and its concentration in CNTP will be given by

$$\bar{C}_{Cl} \approx C_s^{3/2} C_{OH}^{-1/2} \exp \left(-\frac{2\Delta G_{ex}^{Cl} + \Delta G_{ex}^{K} - \Delta G_{ex}^{OH}}{2RT}\right) = C_s^{3/2} C_{OH}^{-1/2} \exp \left(-\frac{2\Delta G_{ex}^{Cl} - \Delta G_{ex}^{h}}{2RT}\right),$$

(4)

Since, as the minority species, Cl$^-$ controls KCl permeability in this regime, the salt and Cl$^-$ permeation rates should scale with salt concentration as $C_s^{3/2}$ and the quantity $\Delta \bar{G}_{ex}^s = \Delta G_{ex}^s - \frac{1}{2}\Delta G_{ex}^{h}$ should replace $\Delta G_{ex}^s$ for chloride transfer in this scenario. Along with 1/2
scaling of conductivity, these features are another signature of the pH-controlled ion transfer. Obviously, when OH\(^-\) concentration drops, e.g., by 4.5 orders of magnitude at pH 3, this regime should transition to “regular” linear KCl transfer.

Li et al.\(^{46}\) measured chloride permeation rates using stop-flow experiment in vesicles and derive chloride permeability in CNTPs \(P_{Cl}\) by fitting the anion permeation rate to a linear dependence on \(C_s\). However, the observed trend was clearly non-linear and a much better fit is obtained for \(C_s^{3/2}\) scaling, in agreement with eq. 4, as shown in Fig. 2b (see also Supplementary Fig. S3). We also note that \(P_{Cl}\) of chloride derived from above stop-flow anion permeation experiments in vesicles for similar solution compositions at pH 7.5 is of the order \(10^{-18} - 10^{-17}\) cm\(^3\)/s, equivalent to conductance \(\frac{F^2}{RT}C_{Cl}P_{Cl}\) of a few fS per channel. On the other hand, electrical measurement by Tunuguntla et al. in Fig. 2a show a much larger electrical conductance of the order 2-30 pS per channel at this pH. In addition, these authors also estimated ion transport numbers using reverse potential measurements.\(^{25}\) Potassium transport number \(t_K\) was found to be under 0.1 at pH 7.5, as reasonable when the rest of the current is carried by highly mobile hydroxide. The small chloride permeability measured in stop-flow experiments at pH 7.5 is then another manifestation of chloride being a minority anionic species within CNTP at this pH. Yet, \(t_K\) increased to about 0.65-0.85 at pH 3, as expected when chloride takes over as the dominant anion.

In another report, Tunuguntla et al. employed permeation in vesicles loaded with a pH sensitive dye at pH 7.5 to measure proton transfer rates in CNTPs under a pH gradient.\(^{26}\) The observed rates were interpreted as a fast proton transfer, presumably involving the Grotthuss mechanism. We note, however, that proton flux \(J_H\) is indistinguishable from oppositely directed transfer of hydroxide \(J_{OH}\) or simultaneous transfer of both ions in the form of alkalinity flux \(J_{OH} - J_H\). The present analysis strongly suggests the actual permeating species was OH\(^-\). The higher affinity of narrow CNTPs to hydroxide also readily explains their larger conductivity, compared with wider 1.5 nm CNTPs. It is also notable that the measured rate of alkalinity transfer is equivalent to a conductance of the order 1 fS, again,
Figure 2: **Key experimental results on ion transport in 0.8 nm CNTPs.** (a) CNTP conductivity in KCl solutions at pH 3 and 7.5 reported by Tunuguntla et al.\(^{25}\) Solid and dashed lines were computed using, respectively, eqs. 2 and 3 with mobilities estimated based on Dellago et al.\(^{56}\) and \(\Delta G_{s}^{\text{ex}}\) and \(\Delta G_{h}^{\text{ex}}\) viewed as adjustable parameter with best-fit value indicated. (b) Rate of chloride permeation per CNTP measured in vesicles at pH 7.5 vs. \(C_{s}\) as reported by Li et al.\(^{13}\) Solid line is a linear fit to eq. 4 with mobilities estimated based on Dellago et al.\(^{56}\) and \(\Delta G_{s}^{\text{ex}}\) viewed as fitting parameters with best-fit value indicated. The insets highlight non-linear dependence obtained by plotting the same data vs. \(C_{s}\) and \(C_{2s}\). (c) Current-voltage dependence of CNTP connecting two 0.1 M KCl solutions of pH 3 and 7.5 (green squares) and of the same pH 7.5 (red circles), reported by Tunuguntla et al.\(^{25}\) All data were digitized from original reports.

Commensurate with anion transfer data, yet four orders of magnitude smaller than results of conductivity measurements. This discrepancy manifests coupling of alkalinity transfer, i.e., OH\(^{-}\) permeation, to much slower transfer of K\(^{+}\). In absence of electric current, its rate is limited by K\(^{+}\) diffusivity and may no more benefit from the fast Grotthuss mechanism. The reported blocking effect of Ca\(^{2+}\) is also consistent with this picture, as it should bind to CNTP more strongly and have a lower mobility than K\(^{+}\) due to double charge and thus further slow down hydroxide permeation.

Finally, activation energies \(E_{a}\) of permeation offer yet another way of comparing computations with experiments. They should be dominated by the enthalpies of ion transfer, i.e., \(\Delta H\), displayed in Fig. 1f as well. For instance, Li et al.\(^{13}\) reported activation energies for permeation of halide anions, however, the present model indicates they may not be compared directly with \(\Delta H\) for respective anions due to coupling to other ions. Thus, depending on whether eqs. 2 or 4 describes chloride transfer, the apparent activation energy
for Cl⁻ permeation should be - using notation analogous to $\Delta G^{\text{ex}}$ - either $\Delta H_s$ or $\Delta \tilde{H}_s$, respectively. Li et al.’s reported $E_a = 52$ kJ/mol for chloride permeation in vesicles, which they compared with computed chloride transfer energy 63 kJ/mol. It is unclear why the latter value, computed for CNTP in vacuum ($\epsilon = 1$), is so different from the present $\Delta H_{\text{Cl}} \approx 166$ kJ/mol for $\epsilon = 1$ and is much closer to the present result for $\epsilon = 100$. We presume this might be affected by the fact that, in computations by Li et al., CNTP was connected to highly polarizable graphene sheets, which could strongly reduce the dielectric contribution by essentially "grounding" the CNTP. Nevertheless, the activation energy of chloride transfer may not be identified with $\Delta H_{\text{Cl}}$ in either case and the agreement could be fortuitous.

The present analysis suggests that observed $E_a = 52$ kJ/mol of chloride permeation should be compared with either $\Delta H_s \approx \frac{1}{2}(-37.1 + 121.7) = 42.3$ kJ/mol for the pH-independent scenario, eq. 2, or with $\Delta \tilde{H}_s = \Delta H_{\text{Cl}} + \frac{1}{2}(\Delta H_K - \Delta H_{\text{OH}}) \approx 121.7 + 0.5 \times (-37.1 - 122.4) = 42.0$ kJ/mol for pH-controlled one, eq. 4. These values are close, due similar transfer energies for chloride and hydroxide and may not differentiate between the two theoretical expressions, however, the scaling of conductivity and permeation rate with $C_s$ in Fig. 3 strongly favors $\Delta \tilde{H}_s$ as the appropriate one. The above $\Delta H$ values are for $\epsilon = 2$ (Fig. 2f), however, sensitivity to $\epsilon$ (see Fig. 2) presents a substantial uncertainty. For instance, when $\epsilon = 2$ is replaced with $\epsilon = 2.4$, better representing lipids, above estimates drop by about 20 kJ/mol. Nevertheless, the above $\Delta \tilde{H}_s$ is also fairly close the $\Delta \tilde{G}^{\text{ex}}_h = 50$ kJ/mol that fits the experimental chloride permeation rates in Fig. 2b to eq. 4 with mobilities estimated as explained above.

Based on the same argument, eq. 4 predicts that the activation energy for alkalinity permeation should be $\Delta H_h = \frac{1}{2}(\Delta H_K + \Delta H_{\text{OH}}) \approx 0.5 \times (-37.1 + 122.4) = 42.6$ kJ/mol for $\epsilon = 2$. This is again fairly close to the experimental value 55 kJ/mol reported by Tunuguntla et al. 25 The fact that theoretical $\Delta H$ values underestimate the experimental activation energies could be related to the unaccounted for activation energy of diffusion, which may be fairly close to that of water discussed above, 15-20 kJ/mol. The remaining
discrepancy could also be related to the sensitivity of transfer energies to $\epsilon$, as well as deviations from the simple mean-field picture, i.e., ion-ion interactions that should reduce the transfer energies (see next).

The puzzle of hydroxide: why it is favored and how it conducts

Above comparison with experiments demonstrate that computed values of $\Delta G^{ex}$ for free ions combined with simple mean-field relations may rationalize most experimental observations and trends. However, two points raise questions. First, despite the fact that the $C_s$ scaling of experimental data in Fig. 2 strongly suggests that CNTP has a strong preference to hydroxide, transfer energies of single chloride and hydroxide anions in Fig. 1f do not display as much difference. More explicitly, viewing $\Delta G^{ex}_s$ and $\Delta G^{ex}_h$ as adjustable parameters and fitting them to the conductivity data at pH 3 and 7.5 to eqs. 2 and 4, respectively, yields significantly different $\Delta G^{ex}_s \approx 14$ kJ/mol and $\Delta G^{ex}_h \approx -6$ kJ/mol (see Fig. 2a and Supplementary for detail). We may only speculate below as to why these fits deviate so much from theoretical values that, otherwise, reasonably agree with stop-flow permeation data. However, the much different fitted $\Delta G^{ex}_s$ and $\Delta G^{ex}_h$ once again manifest a high affinity of CNTP to hydroxide and it is necessary to consider more involved scenarios that would favor this ion.

Second, concurrent permeation of free cations and anions, like in stop-flow experiments in vesicles, may proceed with minimal mutual interference, however, in electrical measurements, ions migrate in opposite directions and, at some point, meet and need to pass each other. It is not obvious whether ions squeezing past each other in a narrow channel does not present a prohibitive kinetic barrier. Admittedly, this barrier would be eliminated in a scenario recently analyzed by Levy et al. who argued that electroneutrality could break down in a narrow and short channel thereby ions could pass the entire channel one at a time.55 This mechanism was justified on the ground that screening length in a CNTP becomes exponentially large due to 1D dimensionality of the ”solution” in a narrow channel. However, in such a scenario, K$^+$
transfer as a lone charge carrier would be decoupled from OH\(^{-}\) and, instead, coupled to Cl\(^{-}\). Indeed, we do not anticipate any ion-specific effect in solution outside CNTP therefore far more dilute hydroxide would be unable to outcompete chloride and would have a negligible effect on potassium transfer. Conversely, hydroxide transfer as a lone species within CNTP must be strongly suppressed by its prohibitive transfer energies (Fig. 1f), which disagrees with its high transfer number. It seems that experimental data and present \textit{ab initio} results rule out the electroneutrality breakdown mechanism.

A more plausible alternative is that the system may substantially deviate from the simple mean-field picture due to ion-ion interactions. Specifically, when ions approach each other, the electrostatic part of the highly unfavorable interaction of anions with CNTP may be attenuated or, when ions associate, eliminated thus ion-specific effects may come into play. As a proxy of such situation, we consider ion pairing, thereby ions within CNTP may be present as coexisting pairs and free ions. Essentially, this model is a one-dimensional analogue of the Bjerrum model of electrolytes solutions, in which ions pairs coexist with a free-ion solution treated in the mean-field manner.\(^{58}\) Although the need to squeeze cation and anion past each other to allow conduction may not be avoided, OH\(^{-}\) uptake within a pair could become more favorable and reduce the corresponding barrier as well. Analyzing this scenario requires transfer energies for pairs formed within CNTP, which we compute here \textit{ab initio}.

Figure 3a shows transfer energies of the possible ion pairs in (6,6) CNTP in vacuum and \(\epsilon = 2\). To reduce computational costs, we simply consider here the electronic transfer energy \(\Delta E\), given \(\Delta E\) and \(\Delta G^{\text{ex}}\) show identical trends and reasonably small differences for free ions (see Supplementary). It is immediately notable that the KOH pair has an exceptionally low transfer energy compared to the other pairs, which may now rationalize the strong preference of narrow CNTPs for OH\(^{-}\) over Cl\(^{-}\). Similar to water, which is formally the H\(^{+}\)OH\(^{-}\) pair, the transfer energies of all ion pairs \(\Delta E_{\text{pair}}\) are weakly affected by \(\epsilon\). Compared to transfer energy of the pair as free ions, i.e., \(\frac{1}{2}(\Delta E_{+} + \Delta E_{-})\), there is a gain of several tens kJ/mol for all salts. However, \(\Delta E\) or \(\Delta G^{\text{ex}}\) for pairs and free ions may not be directly compared, since
pairing also involves a significant entropy loss. Considering dilute solutions and neglecting the solution non-ideality and different sizes of ions and pair, the concentration of KOH pairs in CNTP is given by

\[ \bar{C}_{\text{KOH}} = \frac{C_K C_{\text{OH}}}{C_w} \exp \left( -\frac{\Delta G_{\text{KOH}}^{\text{ex}}}{RT} \right), \]

(5)

where \( C_w = 55.6 \text{ M} \) in the denominator comes from the fact that the ideal solution entropy needs to be computed using concentrations expressed in molar fractions. We compare eqs. 2 and 5 and, specifically, consider the exponential factor that multiplies in eq. 2 the product \((C_K C_{\text{OH}})^{1/2}\) that gauges the activity of the KOH ”salt” in solution. This shows that the free-ion transfer energy \( \Delta G_h^{\text{ex}} \approx 62.6 \text{ kJ/mol} \) (for \( \epsilon = 2 \)) in eq. 2 is to be compared with \( \Delta C_{h, \text{pair}}^{\text{ex}} = \Delta C_{\text{KOH}}^{\text{ex}} + RT \ln[C_w/(C_K C_{\text{OH}})^{1/2}] \) for KOH uptake as ion pairs. The second term in the last expression accounts for the loss of translational entropy upon pairing and, for \( C_s \) in the range \( 10^{-3} \) to 1 M and \( 3 \leq pH \leq 7 \), it amounts to about 30 to 50 kJ/mol. To complete this analysis, we obtained in Gaussian \( \Delta G_{\text{KOH}}^{\text{ex}} = -61.6 \text{ kJ/mol} \) for \( \epsilon = 2 \), which turns out to be only slightly above \( \Delta E_{\text{KOH}} \) (see Fig. 3). Ultimately, the terms sum up to \( \Delta C_{h, \text{pair}}^{\text{ex}} \approx -31 \) to -11 kJ/mol for the above composition range. It is obviously far below the free-ion counterpart and indicates that majority of K\(^+\) and OH\(^-\) ions partition to CNTP as KOH pairs.

Similar analysis for the other pairs shows that, even if their formation is not as favorable as KOH, they are likely to contribute at least as much as corresponding combination of free ions. While pairs represent only the simplest form of ion-ion interactions deviating from mean-field treatment, present analysis highlights the crucial role of such interactions in controlling ion partitioning and transport in CNTPs and, in particular, high affinity towards OH\(^-\). We note, however, that presence of pairs in CNTP does not necessarily directly translate to transport, since pair mobility may be small. Indeed, we note that, in the case of chloride permeation, if this ion was mainly transferred as KCl pairs, its permeation rate would be proportional to \( C_s \) squared. The inset in Fig. 2b (see also Fig. S3 in Supplementary) indicate this scaling disagrees with experiment and questions any significant contribution of ion pairs.
to ion permeation by diffusion.

Figure 3: **Ion pair formation and conduction mechanism in (6,6) CNTP.** (a) $\Delta G_{ex}$ of ion-pair formation in CNTP for different ion pairs for $\epsilon = 1$ and $\epsilon = 2$. (b) Schematic energy profile encountered by the potassium and hydroxide ions along the conduction pathway, including free-ion uptake, downfield migration, transient pair formation, flip, and dissociation. (c) Possible mechanism of electro-osmosis: water flow coupled to potassium migrations and decoupled from hydroxide migrating by the Grotthuss mechanism.

**CNTP conductance: what is the rate-controlling step**

Even if abundant within CNTP, pairs may not contribute to conductance not only due to low mobility, but also since they are neutral and cannot carry an electric current. A cation and an anion migrating in an electric field in the opposite directions may then temporarily form a pair, however, it will have to flip and split up thereafter to let the ions keep migrating. In the spirit of the Eyring-Polanyi transition-state theory, we may consider the flip and its Gibbs energy $\Delta G_{KOH}$ relative to the ”ground state” of the pair aligned parallel to the main CNTP axis. Presumably, the height of the kinetic barrier correspond to the pair aligned perpendicular to the CNTP main axis. We estimated this height to be $\Delta G_{KOH} \approx 23$ kJ/mol above the ”ground state” $\Delta G_{h,pair}^{ex}$, which places the barrier height at -8 to 12 kJ/mol relative to the solution. It is well below the free-ion energy $\Delta G_{h}^{ex} \approx 62.6$ kJ/mol ($\epsilon = 2$). We
then conclude that CNTP conductance should indeed be controlled by the partitioning and
transport of free ions, in agreement with most experimental data. Figure 3b schematically
depicts the suggested pathway and energy profile encountered jointly by the potassium and
hydroxide ions upon conduction. It starts from their uptake as free ions from solution at
opposite ends of CNTP, followed by free-ion migration, pair formation, flip, dissociation back
to free ions, and, ultimately, exit to the solution at the opposite end. The entire profile is
slightly inclined due to applied electric potential difference $\Delta \phi$ and the shown sequence may
repeat, if CNTP contains more than one pair. The larger number of KOH pairs relative to
other possible pairs, due to exceptionally low $\Delta G_{\text{KOH}}^{\text{ex}}$, is apparently the reason behind the
hydroxide dominating ion conductance at neutral conditions.

One may ask what happens to water molecules within CNTP when $K^+$ and $OH^-$ (or $Cl^-$)
migrate in electric field and induce an electro-osmotic flow of water, as demonstrated for
wider 1.5 nm CNTPs. The partitioning-controlled scaling of conductivity with $C_s$ suggests
electro-osmosis in single-digit CNTPs is apparently not as strong as in wider tubes. Yet,
if both ions experience strong friction with water, ions will hinder each other’s migration.
Indeed, when the ion with the larger friction dictates the ultimate direction of electro-osmosis,
the other will be forced to squeeze past all water molecules, in a manner similar to the ion
pair flip. However, the Grotthuss mechanism may help circumvent this obstacle, permitting
a nearly friction-less $OH^-$ transfer as a fast shuttling of electron and hydrogen between $OH^-$
and a neighboring water molecule followed by minor local atom rearrangement. This may
readily occur against water flow and will not interfere with the electro-osmosis induced by
$K^+$ migration, minimizing this ion’s friction with water as well. This mechanism, whereby
$OH^-$ ions may rapidly migrate downfield regardless of electro-osmosis induced by potassium,
is schematically illustrated in Fig. 3c and may explain insignificant electro-osmosis in (6,6)
tubes and the large transport number of $OH^-$ at pH 7.5. Note that, within this picture,
the ion pair flip is still required, otherwise $K^+$ will separate between the $OH^-$ ion and next
water molecule and prevent shuttling of electron and hydrogen.
At this point, we note that, in reality, there is obviously no sharp distinction between free ions and pairs assumed in our highly simplified picture. The long-range nature of the electrostatic attraction between cation and anion must smear the heights and valleys of the profile in Figure 3b. Perhaps more importantly, the ion-ion interaction should both eliminate a part of the dielectric energy and allow anions interact more favorably with CNTP walls. This should reduce the free-ion transfer energy well below simple combination of single-ion transfer energies. This might partly explain why very low $\Delta G_s^{ex}$ and $\Delta G_h^{ex}$ fitted to conductance data and shown in Fig. 2a are closer to $\Delta G^{ex}$ for corresponding pairs with pairing entropy correction than to their free-ion counterparts. On the other hand, the rates and activation energies of chloride and alkalinity permeation measured in stop-flow experiments agree better with the simple free-ion estimates. Not unlikely, part of the answer may have to deal with the fact that the conductivity is controlled by the faster ion of the pair, i.e., OH$^-$ in the case of KOH, while the permeability measured in stop-flow experiments is determined by the slower one, i.e., K$^+$. We also speculate that effects absent or ignored in the present analysis, e.g., alternative conduction paths, or different settings and CNTP environment in electrical and stop-flow measurements, changing the effective value of $\epsilon$, may affect the results. We presume these questions will be clarified, as more data on ion transport in CNTPs become available.

**Current rectification explained**

Finally, we will show that the strong dependence of conductance on OH$^-$ readily explains current rectification between solutions of different pH and, specifically, blockage of current in the direction from low to high pH. The mean-field relation, eq. 3, may be incorporated in Nernst-Planck-type relations, which yields the following relation between the current ($I$) and applied voltage ($\Delta \varphi$) and solution composition differences (see Supplementary for derivation)

$$I = G \left( -\Delta \varphi + t_{OH} \frac{RT}{F} \Delta \ln C_{OH} - t_K \frac{RT}{F} \Delta \ln C_K \right),$$  \hspace{1cm} (6)
where $\Delta$ designates differences between the two solutions and $t_{OH}$ and $t_K$ are respective ion transport numbers within CNTP. $G$ is the effective CNTP conductivity, having the following dependence on the solution concentrations

$$G \propto \frac{\Delta (C_K C_{OH})^{1/2}}{\Delta \ln(C_K C_{OH})^{1/2}} = \langle (C_K C_{OH})^{1/2} \rangle_{l.m.},$$

(7)

where the omitted proportionality constant accounts for the partitioning (related to the transfer energies), ion mobilities and CNTP geometry. Eq. 6 shows that $G$ is proportional to the logarithmic mean of the products $(C_K C_{OH})^{1/2}$ of the two solutions, thereby it is mainly determined by the solution with the larger $(C_K C_{OH})^{1/2}$. For instance, in experiments by Tunuguntla et al., displayed in Fig. 2c, current rectification was observed between solutions with pH 7.5 and 3 containing 0.1 M KCl on both sides (green squares). The driving force, i.e., expression in brackets in eq. 6, depends on both pH values and becomes zero when the applied potential equals the threshold voltage indicated in Fig. 2c. Above this potential, the conductance $G$, i.e., the I-V slope, determined by pH 7.5, is indeed similar to the case when both solutions have the same pH 7.5 (red circles in Fig. 2C). However, the conductance sharply drops and current is blocked below this potential due to local pH changes induced by polarization.

Equations 6 and 7 may not predict rectification, since it comes from polarization, i.e., ion depletion or enrichment in solution next to CNTP mouth, when a DC current enters or exits CNTP. The large excess of salt in above experiments facilitates the analysis of polarization, since it eliminates the potential gradients in the solution, therefore depletion or enrichment of $OH^-$ next to a CNTP mouth is controlled primarily by its diffusion away from or towards CNTP and the magnitude and direction of the current carried by $OH^-$, $It_{OH}$. Different situations encountered in conduction and rectification experiments are schematically illustrated in Fig. 4. Considering semi-spherical boundary layer of solution centered at CNTP mouth, the $OH^-$ concentration at the mouth will depend on $It_{OH}$ and the bulk concentration as
Figure 4: The mechanism of current rectification in CNTP between two solutions. (a) Solutions of the same pH: applied voltage and passing of current weakly affects CNTP conductance, showing no rectification. (b) Voltage applied in forward direction from high to low pH: local pH raised at high pH end results in a minor increase in CNTP conductance, no current blockage. (c) Voltage applied in backward direction from low to high pH: local pH drops at high pH end results in a major drop in CNTP conductance, blocking the current. Large red arrows indicate current direction. Thin arrows next to CNTP mouths indicate ion diffusion, resulting in concentration polarization and a change in local pH. The star indicates local pH controlling CNTP conductivity.

\[ C_{OH, mouth} = C_{OH, bulk} \pm \frac{I t_{OH}}{2 \pi F D_{OH} r_c}, \]  

where \( D_{OH} \) is the OH\(^-\) diffusivity in solution, \( r_c \) is the channel radius, and the sign is positive or negative when OH\(^-\) ions move away from or towards the CNTP. The conductivity will be controlled by the higher pH faced by CNTP, marked with the star Fig. 4. Thus the higher pH will always rise and the current will flow unobstructed, when CNTP faces two identical solutions (Fig. 4a). Similarly, no blockage will be observed when the current - by definition,
opposite to OH$^-$ flow - is towards the low-pH solution, since it increases $C_{OH,mouth}$ at high-pH end and hence $G$, as shown in Fig. 4b. However, as depicted in Fig. 4C, when the current reverses, $C_{OH,mouth}$ at high-pH end drops, sharply reducing $G$ and blocking the current. Since chloride does not allow as much conductivity as hydroxide (cf. Fig 2a), we ignore the takeover by chloride at low pH and take the maximal (limiting) current $I_{lim}$ as approximately corresponding to $C_{OH,mouth} = 0$. Using $D_{OH} = 6.8 \times 10^{-9}$ m$^2$/s, $r_c = 0.4$ nm, $t_{OH} = 0.9$, and $C_{OH,bulk} = 10^{-6.5}$ M (pH 7.5), we estimate $I_{lim} = (2\pi F D_{OH} r_c C_{OH,bulk})/t_{OH} \sim 1$ fA, which is far smaller than pA currents measured in forward direction, thereby backward current will be effectively blocked, i.e., rectification will be observed. More accurate relations, accounting for the pH changes at both ends and yielding the entire I-V curve may be easily developed, by combining eqs. 6 and 7 with mass transfer in solutions,$^{14}$ but they do not change the above conclusion. Note, the full model must also address the fact that $I_{tOH}$ flows in solution as an alkalinity flow, carried by both OH$^-$ and H$^+$. The effective diffusivity of OH$^-$, yielding the total alkalinity flux, then becomes pH-dependent, $D_{OH} + D_H 10^{14-2pH}$. Obviously, the actual species carrying most alkalinity flow in pH 3 solution (and, in general, at any pH $\leq 7$) is H$^+$ rather than OH$^-$, as indicated in Fig. 4b and c.

**Conclusions**

We have demonstrated that most experimental data on ion transport in narrow (6,6) CNTPs, including both diffusion or electrical measurements, may be rationalized using presented molecular model, as alternative to commonly considered continuum-like models. The model treats ion partitioning in the mean-field manner considering uptake of free ions, subject to electroneutrality, to which ion pairing is added to better account for ion-specific effects, with all relevant thermodynamic quantities computed *ab initio*. We note that, despite the fact that experimental data and their pH and salt concentration dependence strongly suggest a high affinity of (6,6) CNTPs towards hydroxide, the computed transfer energies for single
ions do not indicate any such preference. However, computations for ion pairs do reveal a strong affinity to hydroxide, as the exceptionally favorable transfer energy for the KOH pair. In experiments with KCl solutions, this makes K\(^+\) and OH\(^-\) ions dominant species within CNTP at neutral conditions, which change to K\(^+\) and Cl\(^-\) in acidic conditions. We conclude that the ion transport is apparently controlled by free ions, coexisting with more abundant, but less mobile ions pairs. This also makes hydroxide ions the main charge carrier species in conductance experiments, contrary to the views in the literature considering potassium as the main charge carrier. The model successfully explains most observed effects of salt concentration and pH on conductivity and anion and alkalinity permeation in stop-flow experiments, current rectification, and measured activation energies, as well as molecular mechanisms behind ion transfer and conductance in narrow CNTPs. The only significant discrepancy is found for ion transfer energies fitted to conductivity data, which yields values lower and, as a result, ion permeability higher than model predictions. Presumably, this may be related to the ion-ion interactions that may reduce transfer energy for anions and may be clarified, as more data become available. The proposed modeling approach may be extended to other sub-nanometer nanochannels and help design next-generation desalination and osmotic energy harvesting materials and devices.

Methods

Computational Details

The transfer of H\(_2\)O and ions (H\(^+\), OH\(^-\), K\(^+\), and Cl\(^-\)) was computed for the metallic (5,5) and (6,6) nanotubes of diameters 0.68 and 0.80 nm, respectively. For both types, the CNTP fragments used in computations were 1.72 nm long. The dangling bonds at the rims were terminated with hydrogen atoms. The species of interest (an ion or a water molecule) was placed in the center of CNTP and surrounded by four water molecules, two on each side, for (5,5) tube and by six water molecules, three on each side, for (6,6) tube. The
CNTP with its content was embedded in a dielectric continuum of a dielectric constant $\epsilon$, viewed as a parameter. For evaluating the thermodynamics of hydration in bulk water, the species of interest was surrounded by 6 water molecules, forming a finite cluster embedded in a polarizable continuum IEFPCM$^{59}$ with dielectric constant 78.36. Our earlier estimates showed that the use of larger clusters leads to only a marginal improvement, for instance, the difference in ion hydration between 6- and 7-molecule clusters was less than 2 kJ/mol.$^{47}$ Published data were used to set up the initial cluster geometries for hydrated $\text{H}_2\text{O}, \text{H}^+$, $\text{OH}^-$, $\text{K}^+$, and $\text{Cl}^-$.$^{60-64}$ To benchmark the computations for interactions of water and ion with aromatic CNT walls, the energies of $\text{H}_2\text{O}$ and $\text{K}^+$ binding to benzene were computed and compared with experimental values.

The geometries of all structures and thermodynamic properties were calculated \textit{ab initio} in Gaussian 09 Rev. B.01.$^{68}$ The computations employed the combination of wB97X-D functional$^{69}$ including Grimme’s D2 dispersion correction$^{70}$ and 6-31G(d,p) basis set, which was found to yield the best agreement with experimental data on hydration in water. The optimization of structures within CNTP was performed starting from several initial geometries; thereafter, the optimized structure with minimal total electronic energy ($E$) was selected for further analysis. The IEFPCM polarizable continuum model was used to simulate the dielectric environment around the CNTP. Zero-point correction energy was computed to convert electronic energies $E$ to enthalpies ($H$). This correction did not include the vibrational frequency scaling factor, as associated error should not exceed 1 kJ/mol at the chosen level of theory.$^{71}$ Basis set superposition error (BSSE) was estimated using the Boys and Bernardi method$^{72}$ in water/ion clusters and in CNTPs. Apart from electronic energy, the required thermodynamic quantities, i.e., $H$, excess Gibbs energies ($G^{ex}$), and excess entropies ($S^{ex}$), included only the vibrational contributions computed by Gaussian, while rotational and translation contributions were discarded, as they consider corresponding motions of the cluster as a whole and are irrelevant for deriving thermodynamics variables for individual molecules or ions. Ultimately, the thermodynamic quantities for the transfer of a species from
bulk water to water-filled CNTP, $\Delta X[\text{Ion}]$, were computed using the following relation\textsuperscript{47}

$$
\Delta X[\text{Ion}] = X[\text{CNTP}(\text{H}_2\text{O})_m\text{Ion}] + X[(\text{H}_2\text{O})_n] - X[\text{CNTP}(\text{H}_2\text{O})_m] - X[\text{Ion}(\text{H}_2\text{O})_n].
$$

(9)

The analogous expression for transfer of a cation $C^+$ and an anion $A^-$ from bulk solution and formation of an ion pair $C^+A^-$ within CNTP was as follows

$$
\Delta X[C^+A^-] = X[\text{CNTP}(\text{H}_2\text{O})_mC^+] + 2X[(\text{H}_2\text{O})_6] - X[\text{CNTP}(\text{H}_2\text{O})_m] - X[(\text{H}_2\text{O})_6C^+] - X[(\text{H}_2\text{O})_6A^-].
$$

(10)

We emphasize that, since thermodynamic parameters of water in CNTP depended on the water arrangement, yielding distinct local energy minima upon energy optimization (Fig. 1a and b), the terms $X[\text{CNTP}(\text{H}_2\text{O})_m]$ used in the above expressions for specific ions and pairs corresponded to the water arrangement closest to the one observed for hydrated ions and pairs within CNTP to minimize the error associated with different water-water interactions and terminal energies of the finite files. Figure S1 in Supplementary schematically illustrates transfers processes defined by eqs. 9 and 10.

**Benchmarking ab initio computations**

The transfer quantities critically depend on the reference values for hydration in water. We then first benchmarked computational procedures versus experimental bulk hydration quantities. Fig. S2 in Supplementary demonstrate a good agreement between computed and experimental values. The deviations for hydration enthalpies $H$ are 3 to 7% of the absolute values. Similar errors were obtained for excess Gibbs energies $\Delta G^{ex}$, but for much smaller entropic terms $T\Delta S^{ex} = \Delta H - \Delta G^{ex}$, the deviations were larger, 1% for water molecule and $K^+$, 10% for $\text{Cl}^-$, and ca. 30% for $\text{H}^+$ and $\text{OH}^-$. These errors were considered acceptable, as they may partly cancel out in transfer energies. Besides, the magnitude and sign of deviations, positive for cations and negative for anions, are highly unlikely to affect the
physical picture developed below. The present values also agree within a few kJ/mol with computations using a higher level of theory\textsuperscript{60,63,65} and COSMO-based computations.\textsuperscript{73,74}

As another benchmarking, most pertinent to interactions with the inner walls of CNT, we computed the enthalpies of interactions of H$_2$O and K$^+$ with benzene, for which both experimental data\textsuperscript{75–77} and computations\textsuperscript{77–81} were reported. Comparison with most accurate data,\textsuperscript{76,77} presented in Fig. S2 in Supplementary, shows deviations under 4 kJ/mol or 6 % of the computed enthalpy for H$_2$O and 1 kJ/mol or 30 % for K$^+$. Our calculations also indicate a negligible interaction of benzene with Cl$^-$, in agreement with other reports.\textsuperscript{82,83}

The agreement was significantly poorer when no dispersion correction was used. This and above results indicate that the selected level of theory (wB97X-D/6-31G(d,p)) with dispersion correction was adequate for the present study, given the problem of accurately predicting hydration and solvation energies \textit{ab initio} still have many issues.\textsuperscript{84}

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**Author Contributions**

V.F. conceived the idea and supervised the work. V.N. performed the quantum chemical computations. Both authors analyzed the data and wrote the manuscript.

**Competing Interests statement**

The authors declare no competing financial interests.
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