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

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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 rectification. 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 desalination 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 nanomaterials, 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 Broglie length, water transport in CNTPs narrower than about 1.5 nm and similarly narrow graphene slits, occurs in a scatter-less manner, at rates greatly exceeding hydrodynamic predictions^{9,30,31} 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 downplayed 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 transport, charge formation and conduction in narrow and wide CNTPS and rationalize the observed trends.^{27,35–41} In parallel, important insights to transport of ions at the molecular level were obtained using molecular dynamics (MD)^{42–45} and *ab initio* computations.^{13,46}

The data on ion permeation in CNTPs have mainly come from two types of measurements (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 activation 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^{42–45} and *ab initio* computations^{13,46} 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 arrangement 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.⁴⁷ 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.^{16,40,48,49} Ions in (5,5) tubes are then solvated by only two adjacent water molecules, which is confirmed by computations.⁴⁷ The low density of water in a single file and resulting high entropy were suggested⁵⁰ to be an important factor in experimentally confirmed spontaneous filling of CNTPs with water.⁵¹ 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.⁵² 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

94 system, the minimal-energy arrangement is not the equilibrium one, as it should minimize
 95 the free energy rather than energy. More elaborate computations of the thermodynamic
 96 functions and, in particular, excess entropy ΔS^{ex} and excess Gibbs energy ΔG^{ex} of water
 97 transfer into CNTP in Gaussian, help clarify this point. While ΔS^{ex} indicates whether
 98 water arrangement in CNTP is more constrained than in the bulk, ΔG^{ex} indicates how it
 99 compares with the equilibrium arrangement. For instance, focusing on $\epsilon = 2$ (see next),
 100 we observe that the negative $-T\Delta S^{ex} = -0.8$ kJ/mol of the zigzag arrangement indicates
 101 it is slightly less constrained (rarer) than bulk water, its negative $\Delta G^{ex} = -17.3$ kJ/mol
 102 indicates it is also rarer than the equilibrium one (open bars in Fig. 1b). On the other
 103 hand, the topologically different arrangement at the bottom of Fig. 1a, obtained as a local
 104 energy minimum upon energy optimization from a different initial arrangement with middle
 105 molecules bonded to three neighbors, has a positive $-T\Delta S^{ex} = 3.6$ kJ/mol, i.e., is denser
 106 than bulk water, yet its positive $\Delta G^{ex} = 19.7$ kJ/mol indicates it is also denser than the
 107 equilibrium state (cross-hatched bars in Fig. 1b). Apparently, the equilibrium arrangement
 108 in (6,6) tubes must be intermediate to the zigzag and triple-bonded ones, neither of which
 109 is a regular single file. Its thermodynamic properties may, in principle, be obtained by
 110 full quantum MD simulations, but the computational costs may be excessive. However, we
 111 may estimate the equilibrium properties by interpolating between the two arrangements.
 112 Since we essentially deal with two co-existing water phases, in the manner of Clapeyron
 113 equation, the equilibrium should correspond to $\Delta G^{ex} = 0$ (for water only, not for ions!).
 114 The interpolation yields $-T\Delta S^{ex} = -\Delta H \approx 2$ kJ/mol, which makes water within CNTP on
 115 average about twice denser, i.e., more constrained, than the bulk phase. We wish to stress
 116 that this ΔH should not be viewed as the activation energy of water transport. Rather,
 117 we presume that, when a water molecule needs to move or exchange with a neighbor, it is
 118 likely to temporarily assume the more constrained triple-bonded state, which would make its
 119 $\Delta H = 16$ kJ/mol representative of the relevant transition state. Indeed, Li et al. reported
 120 recently a reasonably close experimental activation energy 20 kJ/mol for water diffusion in

(6,6) CNTP.¹³ Notably, the above thermodynamic quantities for water are fairly weakly affected by the dielectric constant of the surrounding medium ϵ , unlike those of ions.

Similarly, a straight-file two-molecule hydration of OH^- and Cl^- anions, corresponding to the lowest energy in (5,5) CNTPs,⁴⁷ 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,⁵² two-molecule hydration was found here for K^+ and H^+ (essentially, H_3O^+) cations. Since the energy of internal hydration is a considerable part of the total ion transfer energy, e.g., about 50 % for K^+ and 25 % for Cl^- in (5,5) tubes,⁴⁷ 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 ΔG^{ex} and enthalpy ΔH , 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,⁴⁷ which adds a significant cost to ion transfer. It reaches a maximum in vacuum ($\epsilon = 1$) and vanishes when ϵ 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 membranes⁵³ 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.⁴⁷ 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 ΔG^{ex} and ΔH^{ex} of all ions relative to ion-specific base values.

Compared to its effect on water transfer, ΔS^{ex} seems to play a lesser role in ion transfer, therefore ΔG^{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 ΔG^{ex} and $-T\Delta S^{ex}$ for water transfer to CNTP for each arrangement at different ϵ . 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, ΔG^{ex} and ΔH , for transfer of H^+ , K^+ , OH^- , and 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.

147 CNTP, cations has a significantly lower transfer energy than anions. For instance, for $\epsilon =$
 148 2, K^+ transfer into CNTP is nearly athermal and, for (6,6) tubes, it is even more favorable
 149 than transfer of water, while transfer of anions is highly unfavorable. Enhanced interaction
 150 of potassium was already noted by Aydin et al. for slightly wider tubes and is reminiscent of
 151 the long-known complexation of cations with benzene, “cation- π interaction”.⁵⁴ Partly but
 152 less significantly, the differences between the ions are also related to different arrangement of
 153 water molecules and water-water interaction around the ion, different for cations and anions.
 154 We also note that proton transfers about as favorably as K^+ . Practically, that means that,
 155 in experiments that involve KCl solutions, K^+ will outcompete the more dilute protons and

156 must be the dominant cation species within CNTPs. However, uptake of K^+ is subject to
 157 limitations imposed by the requirements of overall electroneutrality. The latter will apply
 158 when either CNTP is much longer than the screening length⁵⁵ or bonding of ions to CNTP
 159 delocalizes their charge and sufficiently smears the potential variations.⁴⁷ Electroneutrality
 160 dictates that the uptake of a K^+ cation needs to be counter-balanced by uptake of an anion,
 161 either Cl^- and OH^- , both having a highly unfavorable ΔG^{ex} . As the simplest mean-field
 162 approximation, we may assume a uniform mean potential ϕ within the CNTP relative to
 163 bulk thus ion uptake is given by

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

164 where C 's are respective cation and anion concentrations in solution. The exponents are
 165 essentially ion partitioning coefficients, calculated by solving this equation for ϕ , given ΔG^{ex}
 166 for all ions. ΔG^{ex} should be understood as the appropriate statistical means, reflecting ion-
 167 ion interactions as well. Yet, in the simplest picture, when ions are assumed to collectively
 168 preserve electroneutrality but, otherwise, do not significantly interact with each other, we
 169 approximate ΔG^{ex} by the values computed for individual free ions. We consider available
 170 experimental data on ion transport in CNTPs along with present *ab initio* results to ju-
 171 diciously select the ions that need to be considered in eq. 1. Since the results of most
 172 measurements typically represent ion permeabilities rather than partitioning, the differences
 173 in ion mobilities need to be considered as well. We presume that in highly constrained ar-
 174 rangements within narrow CNTPs, the mobilities of water and ions may be fairly similar,
 175 except for proton and hydroxide that may employ the much faster Grotthuss mechanism. We
 176 then employ *ab initio* the results by Dellago et al.⁵⁶ who computed *ab initio* the mobility of
 177 proton, by the Grotthuss mechanism, and of water, associated with diffusion of orientation
 178 defects in the single file. We adopt the latter for the mobility of K^+ and Cl^- and the former,
 179 corrected by the ratio of hydroxide and proton diffusivities in bulk water ($\sim 50\%$), 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

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

The average $\Delta G_s^{ex} = \frac{1}{2}(\Delta G_K^{ex} + \Delta G_{Cl}^{ex})$ 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

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

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 $\Delta G_h^{ex} = \frac{1}{2}(\Delta G_K^{ex} + \Delta G_{OH}^{ex})$ replacing ΔG_s^{ex} . On the other hand, Cl^- will transfer as a trace species and its concentration in CNTP will be given by

$$\bar{C}_{Cl} \approx C_s^{3/2} C_{OH}^{-1/2} \exp\left(-\frac{2\Delta G_{Cl}^{ex} + \Delta G_K^{ex} - \Delta G_{OH}^{ex}}{2RT}\right) = C_s^{3/2} C_{OH}^{-1/2} \exp\left(-\frac{2\Delta G_s^{ex} - \Delta G_h^{ex}}{2RT}\right), \quad (4)$$

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 $\Delta \tilde{G}_s^{ex} = \Delta G_s^{ex} - \frac{1}{2}\Delta G_h^{ex}$ should replace ΔG_s^{ex} 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 Thunuguntla 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 ΔG_s^{ex} and ΔG_h^{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. $C_s^{3/2}$, 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 $\Delta \tilde{G}_s^{ex}$ 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_s^2 . (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 Ca²⁺ 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., ΔH , 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 ΔH 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 ΔG^{ex} - either ΔH_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 $\Delta H_{Cl} \approx 166$ 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 ΔH_{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 $\Delta \tilde{H}_s = \Delta H_{Cl} + \frac{1}{2}(\Delta H_K - \Delta H_{OH}) \approx 121.7 + 0.5 \times (-37.1 - 122.4) = 42.0$ 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 ΔH values are for $\epsilon = 2$ (Fig. 2f), however, sensitivity to ϵ (see Fig. 2) presents a substantial uncertainty. For instance, when $\epsilon = 2$ is replaced with $\epsilon = 2.4$, better representing lipids,⁵³ above estimates drop by about 20 kJ/mol. Nevertheless, the above $\Delta \tilde{H}_s$ is also fairly close the $\Delta \tilde{G}_h^{ex} = 50$ 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 $\Delta H_h = \frac{1}{2}(\Delta H_K + \Delta H_{OH}) \approx 0.5 \times (-37.1 + 122.4) = 42.6$ 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 ΔH 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 ϵ , 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 ΔG^{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 ΔG_s^{ex} and ΔG_h^{ex} 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 $\Delta G_s^{ex} \approx 14$ kJ/mol and $\Delta G_h^{ex} \approx -6$ 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 ΔG_s^{ex} and ΔG_h^{ex} 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 *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 *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 ΔE , given ΔE and ΔG^{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 ΔE_{pair} are weakly affected by ϵ . 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, ΔE or ΔG^{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

$$\bar{C}_{KOH} = \frac{C_K C_{OH}}{C_w} \exp\left(-\frac{\Delta G_{KOH}^{ex}}{RT}\right), \quad (5)$$

where $C_w = 55.6$ 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 $(C_K C_{OH})^{1/2}$ that gauges the activity of the KOH "salt" in solution. This shows that the free-ion transfer energy $\Delta G_h^{ex} \approx 62.6$ kJ/mol (for $\epsilon = 2$) in eq. 2 is to be compared with $\Delta G_{h,pair}^{ex} = \Delta G_{KOH}^{ex} + RT \ln[C_w / (C_K C_{OH})^{1/2}]$ 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 $\Delta G_{KOH}^{ex} = -61.6$ kJ/mol for $\epsilon = 2$, which turns out to be only slightly above ΔE_{KOH} (see Fig. 3). Ultimately, the terms sum up to $\Delta G_{h,pair}^{ex} \approx -31$ 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

346 to ion permeation by diffusion.

Figure 3: **Ion pair formation and conduction mechanism in (6,6) CNTP.** (a) ΔG^{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.

347 CNTP conductance: what is the rate-controlling step

348 Even if abundant within CNTP, pairs may not contribute to conductance not only due to low
 349 mobility, but also since they are neutral and cannot carry an electric current. A cation and
 350 an anion migrating in an electric field in the opposite directions may then temporarily form
 351 a pair, however, it will have to flip and split up thereafter to let the ions keep migrating.
 352 In the spirit of the Eyring-Polanyi transition-state theory, we may consider the flip and
 353 its Gibbs energy $\Delta G_{KOH}^\ddagger$ relative to the "ground state" of the pair aligned parallel to the
 354 main CNTP axis. Presumably, the height of the kinetic barrier correspond to the pair
 355 aligned perpendicular to the CNTP main axis. We estimated this height to be $\Delta G_{KOH}^\ddagger \approx 23$
 356 kJ/mol above the "ground state" $\Delta G_{h,pair}^{ex}$, which places the barrier height at -8 to 12 kJ/mol
 357 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 ΔG_{KOH}^{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.⁴⁰ 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 ΔG_s^{ex} and ΔG_h^{ex} fitted to conductance data and shown in Fig. 2a are closer to ΔG^{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 ϵ , 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)

$$I = G \left(-\Delta\varphi + t_{\text{OH}} \frac{RT}{F} \Delta \ln C_{\text{OH}} - t_{\text{K}} \frac{RT}{F} \Delta \ln C_{\text{K}} \right), \quad (6)$$

where Δ 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

$$G \propto \frac{\Delta(C_K C_{OH})^{1/2}}{\Delta \ln(C_K C_{OH})^{1/2}} = \langle (C_K C_{OH})^{1/2} \rangle_{l.m.}, \quad (7)$$

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.,²⁵ 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 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 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 indicates 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.

433 follows¹⁴

$$C_{OH,mouth} = C_{OH,bulk} \pm \frac{It_{OH}}{2\pi F D_{OH} r_c}, \quad (8)$$

434 where D_{OH} is the OH^- diffusivity in solution, r_c is the channel radius, and the sign is positive
 435 or negative when OH^- ions move away from or towards the CNTP. The conductivity will be
 436 controlled by the higher pH faced by CNTP, marked with the star Fig. 4. Thus the higher
 437 pH will always rise and the current will flow unobstructed, when CNTP faces two identical
 438 solutions (Fig. 4a). Similarly, no blockage will be observed when the current - by definition,

439 opposite to OH^- flow - is towards the low-pH solution, since it increases $C_{\text{OH},\text{mouth}}$ at high-pH
 440 end and hence G , as shown in Fig. 4b. However, as depicted in Fig. 4C, when the current
 441 reverses, $C_{\text{OH},\text{mouth}}$ at high-pH end drops, sharply reducing G and blocking the current.
 442 Since chloride does not allow as much conductivity as hydroxide (cf. Fig 2a), we ignore the
 443 takeover by chloride at low pH and take the maximal (limiting) current I_{lim} as approximately
 444 corresponding to $C_{\text{OH},\text{mouth}} = 0$. Using $D_{\text{OH}} = 6.8 \times 10^{-9} \text{ m}^2/\text{s}$, $r_c = 0.4 \text{ nm}$, $t_{\text{OH}} = 0.9$, and
 445 $C_{\text{OH},\text{bulk}} = 10^{-6.5} \text{ M}$ (pH 7.5), we estimate $I_{\text{lim}} = (2\pi F D_{\text{OH}} r_c C_{\text{OH},\text{bulk}})/t_{\text{OH}} \sim 1 \text{ fA}$, which is
 446 is far smaller than pA currents measured in forward direction, thereby backward current will
 447 be effectively blocked, i.e., rectification will be observed. More accurate relations, accounting
 448 for the pH changes at both ends and yielding the entire I-V curve may be easily developed,
 449 by combining eqs. 6 and 7 with mass transfer in solutions,¹⁴ but they do not change the
 450 above conclusion. Note, the full model must also address the fact that It_{OH} flows in solution
 451 as an alkalinity flow, carried by both OH^- and H^+ . The effective diffusivity of OH^- , yielding
 452 the total alkalinity flux, then becomes pH-dependent, $D_{\text{OH}} + D_{\text{H}}10^{14-2\text{pH}}$. Obviously, the
 453 actual species carrying most alkalinity flow in pH 3 solution (and, in general, at any $\text{pH} \leq$
 454 7) is H^+ rather than OH^- , as indicated in Fig. 4b and c.

455 Conclusions

456 We have demonstrated that most experimental data on ion transport in narrow (6,6) CNTs,
 457 including both diffusion or electrical measurements, may be rationalized using presented
 458 molecular model, as alternative to commonly considered continuum-like models. The model
 459 treats ion partitioning in the mean-field manner considering uptake of free ions, subject to
 460 electroneutrality, to which ion pairing is added to better account for ion-specific effects, with
 461 all relevant thermodynamic quantities computed *ab initio*. We note that, despite the fact
 462 that experimental data and their pH and salt concentration dependence strongly suggest a
 463 high affinity of (6,6) CNTs 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_2O 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 ϵ ,
 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 IEFPCM⁵⁹ 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 H₂O,⁶⁰⁻⁶² H⁺,⁶³
 OH⁻,^{63,64} K⁺⁶⁵ and Cl⁻.^{66,67} To benchmark the computations for interactions of water and
 ion with aromatic CNT walls, the energies of H₂O and K⁺ binding to benzene were computed
 and compared with experimental values.

The geometries of all structures and thermodynamic properties were calculated *ab initio*
 in Gaussian 09 Rev. B.01.⁶⁸ The computations employed the combination of wB97X-D func-
 tional⁶⁹ including Grimme’s D2 dispersion correction⁷⁰ and 6-31G(d,p) basis set, which was
 found to yield the best agreement with experimental data on hydration in water. The opti-
 mization 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 vibra-
 tional 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 method⁷² 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

516 bulk water to water-filled CNTP, $\Delta X[\text{Ion}]$, were computed using the following relation⁴⁷

$$\Delta X[\text{Ion}] = X[\text{CNTP}(\text{H}_2\text{O})_m \text{Ion}] + X[(\text{H}_2\text{O})_n] - X[\text{CNTP}(\text{H}_2\text{O})_m] - X[\text{Ion}(\text{H}_2\text{O})_n]. \quad (9)$$

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

$$\begin{aligned} \Delta X[\text{C}^+\text{A}^-] = & X[\text{CNTP}(\text{H}_2\text{O})_m \text{C}^+] + 2X[(\text{H}_2\text{O})_6] - X[\text{CNTP}(\text{H}_2\text{O})_m] - \\ & - X[(\text{H}_2\text{O})_6 \text{C}^+] - X[(\text{H}_2\text{O})_6 \text{A}^-]. \end{aligned} \quad (10)$$

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

526 **Benchmarking *ab initio* computations**

527 The transfer quantities critically depend on the reference values for hydration in water.
528 We then first benchmarked computational procedures versus experimental bulk hydration
529 quantities. Fig. S2 in Supplementary demonstrate a good agreement between computed and
530 experimental values. The deviations for hydration enthalpies H are 3 to 7 % of the absolute
531 values. Similar errors were obtained for excess Gibbs energies ΔG^{ex} , but for much smaller
532 entropic terms $T\Delta S^{ex} = \Delta H - \Delta G^{ex}$, the deviations were larger, 1 % for water molecule and
533 K^+ , 10 % for Cl^- , and ca. 30 % for H^+ and OH^- . These errors were considered acceptable,
534 as they may partly cancel out in transfer energies. Besides, the magnitude and sign of
535 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^{60,63,65} and COSMO-based computations.^{73,74}

As another benchmarking, most pertinent to interactions with the inner walls of CNT, we computed the enthalpies of interactions of H₂O and K⁺ with benzene, for which both experimental data^{75–77} and computations^{77–81} were reported. Comparison with most accurate data,^{76,77} presented in Fig. S2 in Supplementary, shows deviations under 4 kJ/mol or 6 % of the computed enthalpy for H₂O and 1 kJ/mol or 30 % for K⁺. Our calculations also indicate a negligible interaction of benzene with Cl[−], in agreement with other reports.^{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 *ab initio* still have many issues.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.

References

- (1) Mark, A. Science and technology for water purification in the coming decades. *Nature* **2008**, *452*, 20.
- (2) Werber, J. R.; Deshmukh, A.; Elimelech, M. The critical need for increased selectivity, not increased water permeability, for desalination membranes. *Environ. Sci. Technol. Lett.* **2016**, *3*, 112–120.
- (3) Agre, P.; King, L. S.; Yasui, M.; Guggino, W. B.; Ottersen, O. P.; Fujiyoshi, Y.; Engel, A.; Nielsen, S. Aquaporin water channels—from atomic structure to clinical medicine. *J. Physiol.* **2002**, *542*, 3–16.
- (4) Kidambi, P. R.; Jang, D.; Idrobo, J.-C.; Boutilier, M. S.; Wang, L.; Kong, J.; Karnik, R. Nanoporous atomically thin graphene membranes for desalting and dialysis applications. *J. Adv. Mater.* **2017**, *29*, 1700277.
- (5) Jang, D.; Idrobo, J.-C.; Laoui, T.; Karnik, R. Water and solute transport governed by tunable pore size distributions in nanoporous graphene membranes. *ACS Nano* **2017**, *11*, 10042–10052.
- (6) Wang, L.; Williams, C. M.; Boutilier, S. H., Michael; Kidambi, P. R.; Karnik, R. Single-layer graphene membranes withstand ultrahigh applied pressure. *Nano Lett.* **2017**, *17*, 3081–3088.
- (7) Kidambi, P. R.; Terry, R. A.; Wang, L.; Boutilier, M. S.; Jang, D.; Kong, J.; Karnik, R. Assessment and control of the impermeability of graphene for atomically thin membranes and barriers. *Nanoscale* **2017**, *9*, 8496–8507.
- (8) Hinds, B. J.; Chopra, N.; Rantell, T.; Andrews, R.; Gavalas, V.; Bachas, L. G. Aligned multiwalled carbon nanotube membranes. *Science* **2004**, *303*, 62–65.

- (9) Holt, J. K.; Park, H. G.; Wang, Y.; Stadermann, M.; Artyukhin, A. B.; Grigoropoulos, C. P.; Noy, A.; Bakajin, O. Fast mass transport through sub-2-nanometer carbon nanotubes. *Science* **2006**, *312*, 1034–1037.
- (10) Holt, J. K.; Noy, A.; Huser, T.; Eaglesham, D.; Bakajin, O. Fabrication of a carbon nanotube-embedded silicon nitride membrane for studies of nanometer-scale mass transport. *Nano Lett.* **2004**, *4*, 2245–2250.
- (11) Werber, J. R.; Osuji, C. O.; Elimelech, M. Materials for next-generation desalination and water purification membranes. *Nat. Rev. Mater.* **2016**, *1*, 1–15.
- (12) Lu, X.; Elimelech, M. Fabrication of desalination membranes by interfacial polymerization: history, current efforts, and future directions. *Chem. Soc. Rev.* **2021**,
- (13) Li, Y.; Li, Z.; Aydin, F.; Quan, J.; Chen, X.; Yao, Y.-C.; Zhan, C.; Chen, Y.; Pham, T. A.; Noy, A. Water-ion permselectivity of narrow-diameter carbon nanotubes. *Sci. Adv.* **2020**, *6*, eaba9966.
- (14) Freger, V. Selectivity and polarization in water channel membranes: lessons learned from polymeric membranes and CNTs. *Faraday Discuss.* **2018**, *209*, 371–388.
- (15) Amiri, H.; Shepard, K. L.; Nuckolls, C. R. I. Hernández Sánchez. *Nano Lett.* **2017**, *17*, 1204–1211.
- (16) Corry, B. Designing carbon nanotube membranes for efficient water desalination. *J. Phys. Chem. B* **2008**, *112*, 1427–1434.
- (17) Song, C.; Corry, B. Intrinsic ion selectivity of narrow hydrophobic pores. *J. Phys. Chem. B* **2009**, *113*, 7642–7649.
- (18) Hummer, G.; Rasaiah, J. C.; Noworyta, J. P. Water conduction through the hydrophobic channel of a carbon nanotube. *Nature* **2001**, *414*, 188–190.

- (19) Striolo, A. The mechanism of water diffusion in narrow carbon nanotubes. *Nano Lett.* **2006**, *6*, 633–639.
- (20) Won, C. Y.; Joseph, S.; Aluru, N. Effect of quantum partial charges on the structure and dynamics of water in single-walled carbon nanotubes. *J. Chem. Phys.* **2006**, *125*, 114701.
- (21) Chaban, V. V.; Prezhdo, V. V.; Prezhdo, O. V. Confinement by carbon nanotubes drastically alters the boiling and critical behavior of water droplets. *ACS Nano* **2012**, *6*, 2766–2773.
- (22) Falk, K.; Sedlmeier, F.; Joly, L.; Netz, R. R.; Bocquet, L. Molecular origin of fast water transport in carbon nanotube membranes: superlubricity versus curvature dependent friction. *Nano Lett.* **2010**, *10*, 4067–4073.
- (23) Liu, L.; Patey, G. Simulated conduction rates of water through a (6, 6) carbon nanotube strongly depend on bulk properties of the model employed. *J. Chem. Phys.* **2016**, *144*, 184502.
- (24) Samoylova, O. N.; Calixte, E. I.; Shuford, K. L. Molecular dynamics simulations of ion transport in carbon nanotube channels. *J. Phys. Chem. C* **2015**, *119*, 1659–1666.
- (25) Tunuguntla, R. H.; Henley, R. Y.; Yao, Y.-C.; Pham, T. A.; Wanunu, M.; Noy, A. Enhanced water permeability and tunable ion selectivity in subnanometer carbon nanotube porins. *Science* **2017**, *357*, 792–796.
- (26) Tunuguntla, R. H.; Allen, F. I.; Kim, K.; Belliveau, A.; Noy, A. Ultrafast proton transport in sub-1-nm diameter carbon nanotube porins. *Nat. Nanotechnol* **2016**, *11*, 639–644.
- (27) Secchi, E.; Niguès, A.; Jubin, L.; Siria, A.; Bocquet, L. Scaling behavior for ionic

transport and its fluctuations in individual carbon nanotubes. *Phys. Rev. Lett.* **2016**, *116*, 154501.

(28) Majumder, M.; Chopra, N.; Andrews, R.; Hinds, B. J. Enhanced flow in carbon nanotubes. *Nature* **2005**, *438*, 44–44.

(29) Miller, S. A.; Young, V. Y.; Martin, C. R. Electroosmotic flow in template-prepared carbon nanotube membranes. *J. Am. Chem. Soc.* **2001**, *123*, 12335–12342.

(30) Kalra, A.; Garde, S.; Hummer, G. Osmotic water transport through carbon nanotube membranes. *PNAS* **2003**, *100*, 10175–10180.

(31) Keerthi, A.; Geim, A.; Janardanan, A.; Rooney, A.; Esfandiar, A.; Hu, S.; Dar, S.; Grigorieva, I.; Haigh, S.; Wang, F., et al. Ballistic molecular transport through two-dimensional channels. *Nature* **2018**, *558*, 420–424.

(32) Hong, Y.; Zhang, J.; Zhu, C.; Zeng, X. C.; Francisco, J. S. Water desalination through rim functionalized carbon nanotubes. *J. Mater. Chem. A* **2019**, *7*, 3583–3591.

(33) Hou, Y.; Wang, M.; Chen, X.; Hou, X. Continuous water-water hydrogen bonding network across the rim of carbon nanotubes facilitating water transport for desalination. *Nano Res.* **2021**, 1–8.

(34) Corry, B. Water and ion transport through functionalised carbon nanotubes: implications for desalination technology. *Energy Environ. Sci.* **2011**, *4*, 751–759.

(35) Biesheuvel, P.; Bazant, M. Analysis of ionic conductance of carbon nanotubes. *Phys. Rev. E* **2016**, *94*, 050601.

(36) Uematsu, Y.; Netz, R. R.; Bocquet, L.; Bonthuis, D. J. Crossover of the power-law exponent for carbon nanotube conductivity as a function of salinity. *J. Phys. Chem. B* **2018**, *122*, 2992–2997.

- (37) Kavokine, N.; Netz, R. R.; Bocquet, L. Fluids at the nanoscale: From continuum to subcontinuum transport. *Annu. Rev. Fluid Mech.* **2021**, *53*, 377–410.
- (38) Noh, Y.; Aluru, N. R. Ion transport in electrically imperfect nanopores. *ACS Nano* **2020**, *14*, 10518–10526.
- (39) Sarkadi, Z.; Fertig, D.; Ható, Z.; Valiskó, M.; Boda, D. From nanotubes to nanoholes: Scaling of selectivity in uniformly charged nanopores through the Dukhin number for 1: 1 electrolytes. *J. Chem. Phys.* **2021**, *154*, 154704.
- (40) Yao, Y.-C.; Taqieddin, A.; Alibakhshi, M. A.; Wanunu, M.; Aluru, N. R.; Noy, A. Strong electroosmotic coupling dominates ion conductance of 1.5 nm diameter carbon nanotube porins. *ACS Nano* **2019**, *13*, 12851–12859.
- (41) Manghi, M.; Palmeri, J.; Yazda, K.; Henn, F.; Jourdain, V. Role of charge regulation and flow slip in the ionic conductance of nanopores: An analytical approach. *Phys. Rev. E* **2018**, *98*, 012605.
- (42) Gao, X. *Molecular Dynamics Study of Water and Ion Transport in Carbon Nanotubes and Slit Nanochannels*; Hong Kong University of Science and Technology (Hong Kong), 2017.
- (43) Beu, T. A. Molecular dynamics simulations of ion transport through carbon nanotubes. I. Influence of geometry, ion specificity, and many-body interactions. *J. Chem. Phys.* **2010**, *132*, 164513.
- (44) Beu, T. A. Molecular dynamics simulations of ion transport through carbon nanotubes. II. Structural effects of the nanotube radius, solute concentration, and applied electric fields. *J. Chem. Phys.* **2011**, *135*, 044515.
- (45) Ailenei, A.-E.; Beu, T. A. Ion transport through gated carbon nanotubes: molecular dynamics simulations using polarizable water. *J. Mol. Struct.* **2021**, 131022.

- (46) Li, Z.; Li, Y.; Yao, Y.-C.; Aydin, F.; Zhan, C.; Chen, Y.; Elimelech, M.; Pham, T. A.; Noy, A. Strong Differential Monovalent Anion Selectivity in Narrow Diameter Carbon Nanotube Porins. *ACS Nano* **2020**, *14*, 6269–6275.
- (47) Neklyudov, V.; Freger, V. Water and Ion Transfer to Narrow Carbon Nanotubes: Roles of Exterior and Interior. *J. Phys. Chem. Lett.* **2020**, *12*, 185–190.
- (48) Grosjean, B.; Pean, C.; Siria, A.; Bocquet, L.; Vuilleumier, R.; Bocquet, M.-L. Chemisorption of hydroxide on 2D materials from DFT calculations: graphene versus hexagonal boron nitride. *J. Phys. Chem. Lett.* **2016**, *7*, 4695–4700.
- (49) Beckstein, O.; Sansom, M. S. The influence of geometry, surface character, and flexibility on the permeation of ions and water through biological pores. *Phys. Biol.* **2004**, *1*, 42.
- (50) Waghe, A.; Rasaiah, J. C.; Hummer, G. Entropy of single-file water in (6, 6) carbon nanotubes. *J. Chem. Phys.* **2012**, *137*, 044709.
- (51) Agrawal, K. V.; Shimizu, S.; Drahushuk, L. W.; Kilcoyne, D.; Strano, M. S. Observation of extreme phase transition temperatures of water confined inside isolated carbon nanotubes. *Nat. Nanotechnol* **2017**, *12*, 267–273.
- (52) Zhan, C.; Aydin, F.; Schwegler, E.; Noy, A.; Pham, T. A. Understanding Cation Selectivity in Carbon Nanopores with Hybrid First-Principles/Continuum Simulations: Implications for Water Desalination and Separation Technologies. *ACS Appl. Nano Mater.* **2020**, *3*, 9740–9748.
- (53) Dilger, J. P.; McLaughlin, S.; McIntosh, T. J.; Simon, S. A. The dielectric constant of phospholipid bilayers and the permeability of membranes to ions. *Science* **1979**, *206*, 1196–1198.

- (54) Aydin, F.; Moradzadeh, A.; Bilodeau, C. L.; Lau, E. Y.; Schwegler, E.; Aluru, N. R.; Pham, T. A. Ion Solvation and Transport in Narrow Carbon Nanotubes: Effects of Polarizability, Cation- π Interaction, and Confinement. *J. Chem. Theory Comput.* **2021**, *17*, 1596–1605.
- (55) Levy, A.; de Souza, J. P.; Bazant, M. Z. Breakdown of electroneutrality in nanopores. *J. Colloid Interface Sci.* **2020**, *579*, 162–176.
- (56) Dellago, C.; Naor, M. M.; Hummer, G. Proton transport through water-filled carbon nanotubes. *Phys. Rev. Lett.* **2003**, *90*, 105902.
- (57) Grosjean, B.; Bocquet, M.-L.; Vuilleumier, R. Versatile electrification of two-dimensional nanomaterials in water. *Nat. Commun.* **2019**, *10*, 1–8.
- (58) Freger, V. Ion partitioning and permeation in charged low- T^* membranes. *Adv. Colloid Interface Sci.* **2020**, *277*, 102107.
- (59) Tomasi, J.; Mennucci, B.; Cammi, R. Quantum mechanical continuum solvation models. *Chem. Rev.* **2005**, *105*, 2999–3094.
- (60) Gillan, M.; Alfe, D. and A. Michaelides. *J. Chem. Phys.* **2016**, *144*, 130901.
- (61) Li, F.; Wang, L.; Zhao, J.; Xie, J. R.-H.; Riley, K. E.; Chen, Z. What is the best density functional to describe water clusters: Evaluation of widely used density functionals with various basis sets for $(\text{H}_2\text{O})_n$ ($n = 1-10$). *Theor. Chem. Acc.* **2011**, *130*, 341–352.
- (62) Temelso, B.; Archer, K. A.; Shields, G. C. Benchmark structures and binding energies of small water clusters with anharmonicity corrections. *J. Phys. Chem. A* **2011**, *115*, 12034–12046.
- (63) Mejias, J.; Lago, S. Calculation of the absolute hydration enthalpy and free energy of H^+ and OH^- . *J. Chem. Phys.* **2000**, *113*, 7306–7316.

- (64) Śmiechowski, M.; Stangret, J. Hydroxide ion hydration in aqueous solutions. *J. Phys. Chem. A* **2007**, *111*, 2889–2897.
- (65) Srinivasa Rao, J.; Dinadayalane, T.; Leszczynski, J.; Narahari Sastry, G. Comprehensive Study on the Solvation of Mono-and Divalent Metal Cations: Li⁺, Na⁺, K⁺, Be²⁺, Mg²⁺ and Ca. *J. Phys. Chem. A* **2008**, *112*, 12944–12953.
- (66) Tobias, D. J.; Jungwirth, P.; Parrinello, M. Surface solvation of halogen anions in water clusters: An ab initio molecular dynamics study of the Cl-(H₂O)₆ complex. *J. Chem. Phys.* **2001**, *114*, 7036–7044.
- (67) Bajaj, P.; Riera, M.; Lin, J. K.; Mendoza Montijo, Y. E.; Gazca, J.; Paesani, F. Halide Ion Microhydration: Structure, Energetics, and Spectroscopy of Small Halide–Water Clusters. *J. Phys. Chem. A* **2019**, *123*, 2843–2852.
- (68) Frisch, M. J. et al. *Gaussian 09 Revision B.01* **2009**,
- (69) Chai, J.-D.; Head-Gordon, M. Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections. *PCCP* **2008**, *10*, 6615–6620.
- (70) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H–Pu. *J. Chem. Phys.* **2010**, *132*, 154104.
- (71) Laury, M. L.; Carlson, M. J.; Wilson, A. K. Vibrational frequency scale factors for density functional theory and the polarization consistent basis sets. *J. Comput. Chem.* **2012**, *33*, 2380–2387.
- (72) Boys, S. F.; Bernardi, F. The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors. *Mol. Phys.* **1970**, *19*, 553–566.

- (73) Barone, V.; Cossi, M. Quantum calculation of molecular energies and energy gradients in solution by a conductor solvent model. *J. Phys. Chem. A* **1998**, *102*, 1995–2001.
- (74) Cossi, M.; Scalmani, G.; Rega, N.; Barone, V. Energies, gradients, and harmonic frequencies for molecules in solution by the C-PCM solvation model. *J. Comput. Chem* **2003**, *24*, 669.
- (75) Marcus, Y.; Ben Naim, A. Solvation dynamics of nonionic solutes. *J. Chem. Phys* **1984**, *81*, 2016–2027.
- (76) Amicangelo, J. C.; Armentrout, P. Absolute binding energies of alkali-metal cation complexes with benzene determined by threshold collision-induced dissociation experiments and ab initio theory. *J. Phys. Chem. A* **2000**, *104*, 11420–11432.
- (77) Courty, A.; Mons, M.; Dimicoli, I.; Piuze, F.; Gaigeot, M.-P.; Brenner, V.; de Pujo, P.; Millié, P. Quantum Effects in the Threshold Photoionization and Energetics of the Benzene- H₂O and Benzene- D₂O Complexes: Experiment and Simulation. *J. Phys. Chem. A* **1998**, *102*, 6590–6600.
- (78) Ferretti, A.; Prampolini, G.; d’Ischia, M. Benchmarking Cation- π Interactions: Assessment of DFT and Moeller-Plesset Second Order Perturbation Theory Calculations with Optimized Basis Sets (MP2mod) for Complexes of Benzene, Phenol and Catechol with Na⁺, K⁺, Rb⁺ and Cs. *J. Phys. Chem. A* **2020**,
- (79) Upadhyay, D.; Mishra, P. Binding of benzene with water clusters (H₂O)_n, n= 1–6, in the ground and lowest singlet excited states. *J. Mol. Struct.: THEOCHEM* **2002**, *584*, 113–133.
- (80) Ma, J.; Alfè, D.; Michaelides, A.; Wang, E. The water-benzene interaction: Insight from electronic structure theories. *J. Chem. Phys.* **2009**, *130*, 154303.

- 766 (81) Schyman, P.; Jorgensen, W. L. Exploring adsorption of water and ions on carbon sur-
767 faces using a polarizable force field. *J. Phys. Chem. Lett.* **2013**, *4*, 468–474.
- 768 (82) Wheeler, S. E.; Houk, K. Are Anion/ π Interactions Actually a Case of Simple Charge-
769 Dipole Interactions? *J. Phys. Chem. A* **2010**, *114*, 8658–8664.
- 770 (83) Lucas, X.; Quinonero, D.; Frontera, A.; Deya, P. M. Counterintuitive Substituent Effect
771 of the Ethynyl Group in Ion- π Interactions. *J. Phys. Chem. A* **2009**, *113*, 10367–10375.
- 772 (84) Vlcek, L.; Chialvo, A. A. Single-ion hydration thermodynamics from clusters to bulk
773 solutions: Recent insights from molecular modeling. *Fluid Ph. Equilibria* **2016**, *407*,
774 58–75.

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