AIP | The Journal of Chemical Physics

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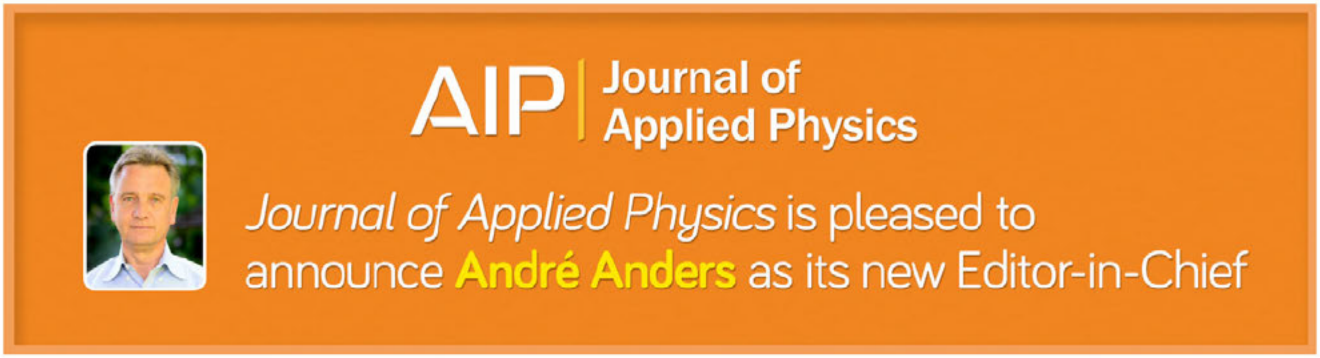
Citation: The Journal of Chemical Physics **139**, 036102 (2013); doi: 10.1063/1.4811294
View online: http://dx.doi.org/10.1063/1.4811294
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/139/3?ver=pdfcov
Published by the AIP Publishing



THE JOURNAL OF CHEMICAL PHYSICS **139**, 036102 (2013)

Note: Recombination of H^+ and OH^- ions along water wires

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(Received 25 March 2013; accepted 3 June 2013; published online 18 July 2013)

[http://dx.doi.org/10.1063/1.4811294]

Dissociation[1] and recombination[2] of H_3O^+ and OH^- ions are fundamental properties of the ionization of water and the chemistry of acids and bases. The small dissociation constant of liquid water (10^{-14} M^2) implies that dissociation is rare. Classic experiments by Eigen and De Maeyer have shown that recombination is fast.[3,4] Little is known about the corresponding events in narrow channels, except for a recent study of the relative rates of diffusion.[5] We present here the results of molecular dynamics simulations of proton transfer (PT) in the transport and recombination of free H^+ and OH^- ions in open chains of water molecules filling carbon nanotubes (CNTs) of diameter 8.1 Å and lengths ranging from ∼29.6 to 174.8 Å containing from 12 to 72 water molecules using a dissociating water model.[6] The events leading to the neutralization of a pair of hydrogen and hydroxide ions along a water wire in a narrow pore are discussed and compared with a recent study in bulk water.[2]

The dissociating water model used in our study was obtained by scaling the potential derived by Ojam*ä*e, Shavitt, and Singer (OSS2) from *ab initio* studies at the MP2 level of neutral and protonated water clusters,[7] as described in our work on hydrogen and hydroxide ions in bulk water.[6] The original OSS2 model is unsuitable for the bulk liquid since it represents a supercooled or glassy state with a negligible diffusion coefficient.[8] A scaling parameter $\lambda = 0.53$ was chosen to optimize agreement between the simulations and experimental atom-atom distribution functions, diffusion coefficients, and the rotational autocorrelation functions of liquid water at 298 K.[6] The charges q_i on the hydrogen or oxygen atoms scale as $\lambda^{1/2}$ with $q_H = 0.728e$ where e is the electronic charge. Hydronium and hydroxide ions in the tube were modeled as a water molecule with an extra proton (H_3O^+) or a missing proton (OH^-).[6] Although nuclear quantum effects were ignored, excellent agreement was obtained with the experimental mobilities of the hydrogen and hydroxide ion in bulk water[6] and with the solvation structure and mechanism of PT proposed in earlier *ab initio* CP-MD studies.[9,10] Classical simulations with the scaled OSS2 (or sOSS2) potential based on MP2 calculations provide greater convenience and ease of application to PT in larger systems. The same sOSS2 force field was used for the water-water and ion-water interactions in the nanotube. The interactions between nanotube and water were treated as Lennard-Jones interactions between the carbon atoms of the nanotube and the oxygen atoms of the ions and water molecules.[11]

We used the sOSS2 model to study neutralization in water wires by placing H_3O^+ and OH^- ions at the ends of four nanotubes of lengths 29.6, 58.7, 116.8, and 174.8 Å corresponding to 12, 24, 48, and 72 water molecules in open chains with the temperature controlled by a Nosé-Hoover thermostat (the Nosé-Hoover thermostat relaxation constant is given as $Q = 10\, fk_B$ with f as the number of degrees of freedom and k_B as the Boltzmann constant).[12,13] After equilibration for 20 ps, we monitored the ions as they moved towards each other and recombined to form a neutral water chain. The water dipoles are oriented in the same direction between the two ions but point away from or towards the positive and negative charges respectively, with near mirror image symmetry about a plane perpendicular to the tube axis at the position of each ion. Each ion is coordinated by two water molecules on either side of the ion, unlike in bulk water where significant differences in ion hydration and solvent reorganization contribute to differences in the diffusion coefficients of the hydrogen and hydroxide ions.[9,14] Each ion moves in the attractive Coulomb force field of the other ion that is modulated by electrostatic shielding of water dipoles in the chain.[15,16] Proton transfers occur from a hydronium ion to a neighboring hydrogen bonded water molecule and/or from a water molecule to an adjacent hydroxide ion to which it is hydrogen bonded. Several runs were also made with the Nosé-Hoover thermostat turned off after equilibration to study the effect of temperature control on neutralization.

Ion transport was followed by monitoring the changes in the index numbers O* of H_3O^{*+} and O* of O^*H^- as a function of time, see Fig. S1 in the supplementary material.[17] In general, neutralization takes place in three steps: namely, ion transport, compression of the water wire between the ions, and recombination (Figs. 1(a)–1(c)) as in bulk water.[2] However, there are significant differences between the mechanisms of recombination of H^+ and OH^- ions in bulk water[2] and in the narrow channel discussed here. The ions move towards each other at a much faster rate in the channel than in the bulk phase, until they are separated by two water molecules at a distance of ∼7 Å, followed by compression of the intervening water wire which triggers PT and neutralization in a coordinated step via the synchronized transfer of three hydrogen-bonded protons along the water chain

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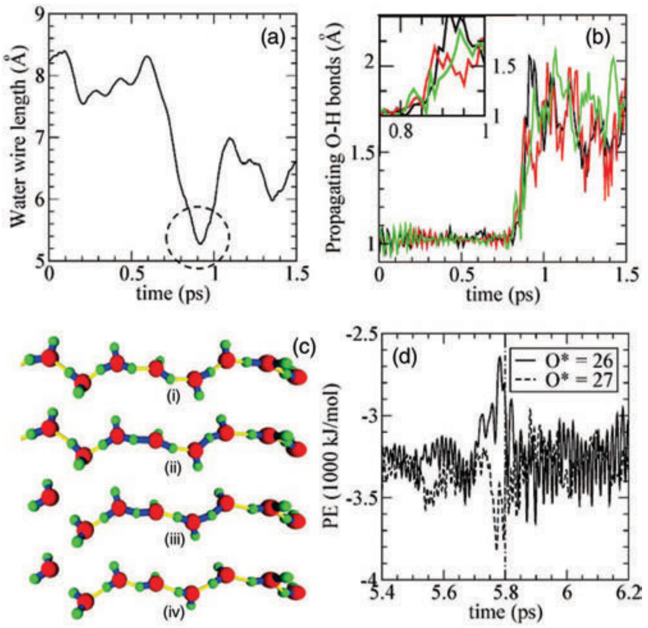

FIG. 1. (a) The collective compression of the water wire between H_3O^+ and OH^- at ~7 Å in a typical trajectory is illustrated by the sum of the three O–O distances as a function of time. (b) Changes in the three O–H bond lengths with time during synchronized proton transfer. (c) H_3O^+ and OH^- ions at 20 fs intervals along a water wire (i) before compression, (ii) and (iii) during synchronized proton transfer, and (iv) after neutralization. (d) Potential energy changes of O atoms during recombination. Vertical dashed line denotes onset of recombination.

between the two ions, as in the bulk phase.[2] Energy dissipation after recombination along a water wire is also different for the same process in bulk water.

Table I shows that the ratios of the distances traveled by O* of H_3O^+ and O* of OH^- from the tube ends before recombination are 0.79, 0.91, 0.97, and 0.98 for $N_w = 12, 24, 48$, and 72, respectively, which match the ratios (0.8, 0.91, 0.97, and 0.98) of the individual diffusion coefficients in open water wires reported in our recent study.[18] Bankura and Chandra obtained similar results for the relative rates of transport of the hydroxide and hydrogen ions in shorter nanotubes as a function of the tube length using a different water model with Quantum mechanics/Molecular mechanics (QM/MM) simulations.[5]

TABLE I. Distances travelled (Å) and elapsed times (ps) for the neutralization of an H_3O^+ and OH^- ion pair along open water chains in CNTs at 298 K in the sOSS2 model ($\lambda = 0.53$).

Length L of CNT (Å)[a]	Elapsed time (ps)	Distance (H^+)	Distance (OH^-)	Dist.(H^+)/dist.(OH^-)
29.6 (12)	0.245 ± 0.051	11.4 ± 1.7	14.4 ± 1.9	0.792
58.7 (24)	0.865 ± 0.159	26.2 ± 2.9	28.8 ± 2.9	0.910
116.8 (48)	4.32 ± 1.47	57.6 ± 8.2	55.7 ± 8.1	0.967
174.8 (72)	12.9 ± 3.8	85.8 ± 18.1	84.3 ± 17.7	0.983

[a]The number of water molecules in CNTs are in parenthesis.

The mechanism of compression and recombination illustrated in Fig. 1 from our simulations, is qualitatively similar to that proposed by Hassanali *et al.*[2] for neutralization in bulk water, where recombination also occurs along a water wire between two heavily solvated ions separated by two water molecules. Averaging over 50 trajectories we find that the recombination is fast and occurs within ~40–60 fs while compression occurs over a slightly longer time ~100 fs that is much faster than in bulk water.[2] The average times reported for recombination and compression in bulk water are 65 and 500 fs, respectively.[2]

Turning off the thermostat of the 46 water molecule-two ion system had only a small effect on the rates of transport. The average elapsed time before neutralization was unchanged within the margin of error reported in Table I. Energy dissipation after recombination along a water wire is different from the same process in bulk water. The potential energies (PE) of the oxygen atoms (index numbers 26 and 27) of the two water molecules between the hydroxide and hydronium ions (Fig. 1(d)) fluctuate normally until the water molecules are transformed, on compression and PT, into hydroxide and hydronium ions during the last 100 fs just before (vertical line) they recombine to form neutral water molecules. This is followed by rapid fluctuations in the potential energies of the same two oxygen atoms after neutralization due to energy exchange and dissipation along the chain.

S.H.L. was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (Grant No. NRF-2010-0023062) and J.C.R. was partially supported by the National Science Foundation (NSF) Grant No. CHE 0549187.

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