Nanopore Array Interactions Weak Dependence On Pore Length

DaVante Cain[1]

[1]University of California, Irvine

Abstract

There has been a great amount of interest in nanopores as the basis for sensors and templates for preparation of biomimetic channels as well as model systems to understand transport properties at the nanoscale. The presence of surface charges on the pore walls has been shown to induce ion selectivity as well as enhance ionic conductance compared to uncharged pores. Here, using three-dimensional continuum modeling, we examine the role of length of charged nanopores as well as applied voltage for controlling ion selectivity and ionic conductance of single nanopores and small nanopore arrays. First, we present conditions where the ion current and ion selectivity of nanopores with homogeneous surface charges remain unchanged even if the pore length decreases by a factor of 6. This length-independent conductance is explained through the effect of ion concentration polarization (ICP) that modifies local ionic concentrations not only at the pore entrances but also in the pore in a voltage-dependent manner. We describe how voltage controls ion selectivity of nanopores with different lengths and present conditions when charged nanopores conduct less current than uncharged pores of the same geometrical characteristics. The manuscript provides different measures of the extent of the depletion zone induced by ICP in single pores and nanopore arrays including systems with ionic diodes. The modeling shown here will help design selective nanopores for a variety of applications where single nanopores and nanopore arrays are used

Reference

References
1. Schoch, R. B.; Han, J. Y.; Renaud, P., Transport phenomena in nanofluidics. Rev Mod Phys 2008, 80 (3), 839-883.
2. Daiguji, H.; Yang, P.; Majumdar, A., Ion Transport in Nanofluidic Channels. Nano Lett 2004, 4 (1), 137-142.
3. Stein, D.; Kruithof, M.; Dekker, C., Surface-charge-governed ion transport in nanofluidic channels. Phys Rev Lett 2004, 93 (3), 035901.
4. Plecis, A.; Schoch, R. B.; Renaud, P., Ionic transport phenomena in nanofluidics: Experimental and theoretical study of the exclusion-enrichment effect on a chip. Nano Lett 2005, 5 (6), 1147-1155.
5. Lee, C.; Joly, L.; Siria, A.; Biance, A.-L.; Fulcrand, R.; Bocquet, L., Large Apparent Electric Size of Solid-State Nanopores Due to Spatially Extended Surface Conduction. Nano Lett 2012, 12 (8), 4037-4044.
6. Green, Y., Ion transport in nanopores with highly overlapping electric double layers. The Journal of Chemical Physics 2021, 154 (8).
7. Su, S.; Zhang, Y.; Peng, S.; Guo, L.; Liu, Y.; Fu, E.; Yao, H.; Du, J.; Du, G.; Xue, J., Multifunctional graphene heterogeneous nanochannel with voltage-tunable ion selectivity. Nat Commun 2022, 13 (1), 4894.
8. Zhu, Z.; Wang, D.; Tian, Y.; Jiang, L., Ion/Molecule Transportation in Nanopores and Nanochannels: From Critical Principles to Diverse Functions. J Am Chem Soc 2019, 141 (22),

8658-8669.
9. Zhang, S.; Wang, J.; Yaroshchuk, A.; Du, Q.; Xin, P.; Bruening, M. L.; Xia, F., Addressing Challenges in Ion-Selectivity Characterization in Nanopores. J Am Chem Soc 2024, 146 (16), 11036-11042.
10. Cao, L.; Wen, Q.; Feng, Y.; Ji, D.; Li, H.; Li, N.; Jiang, L.; Guo, W., On the Origin of Ion Selectivity in Ultrathin Nanopores: Insights for Membrane-Scale Osmotic Energy Conversion. Adv Funct Mater 2018, 28 (39), 1804189.
11. Ma, L.; Li, Z.; Yuan, Z.; Wang, H.; Huang, C.; Qiu, Y., High-performance nanofluidic osmotic power generation enabled by exterior surface charges under the natural salt gradient. Journal of Power Sources 2021, 492, 229637.
12. Vlassiouk, I.; Smirnov, S.; Siwy, Z., Ionic selectivity of single nanochannels. Nano Lett 2008, 8 (7), 1978-1985.
13. Feng, J. D.; Graf, M.; Liu, K.; Ovchinnikov, D.; Dumcenco, D.; Heiranian, M.; Nandigana, V.; Aluru, N. R.; Kis, A.; Radenovic, A., Single-layer MoS2 nanopores as nanopower generators. Nature 2016, 536 (7615), 197-+.
14. Siria, A.; Poncharal, P.; Biance, A. L.; Fulcrand, R.; Blase, X.; Purcell, S. T.; Bocquet, L., Giant osmotic energy conversion measured in a single transmembrane boron nitride nanotube. Nature 2013, 494 (7438), 455-8.
15. Tsutsui, M.; Hsu, W.-L.; Garoli, D.; Leong, I. W.; Yokota, K.; Daiguji, H.; Kawai, T., Gate-All-Around Nanopore Osmotic Power Generators. Acs Nano 2024, 18 (23), 15046-15054.
16. Zhang, Z.; Wen, L.; Jiang, L., Nanofluidics for osmotic energy conversion. Nat Rev Mater 2021, 6 (7), 622-639.
17. Zhang, Z.; He, L.; Zhu, C.; Qian, Y.; Wen, L.; Jiang, L., Improved osmotic energy conversion in heterogeneous membrane boosted by three-dimensional hydrogel interface. Nat Commun 2020, 11 (1), 875.
18. Xie, G. H.; Wen, L. P.; Jiang, L., Biomimetic smart nanochannels for power harvesting. Nano Res 2016, 9 (1), 59-71.
19. Wang, L.; Wang, Z.; Patel, S. K.; Lin, S.; Elimelech, M., Nanopore-Based Power Generation from Salinity Gradient: Why It Is Not Viable. Acs Nano 2021, 15 (3), 4093-4107.
20. Han, W.; Chen, X., A review: applications of ion transport in micro-nanofluidic systems based on ion concentration polarization. Journal of Chemical Technology & Biotechnology 2020, 95 (6), 1622-1631.
21. Green, Y.; Shloush, S.; Yossifon, G., Effect of geometry on concentration polarization in realistic heterogeneous permselective systems. Phys Rev E 2014, 89 (4), 043015.
22. Zangle, T. A.; Mani, A.; Santiago, J. G., Theory and experiments of concentration polarization and ion focusing at microchannel and nanochannel interfaces. Chem Soc Rev 2010, 39 (3), 1014-1035.
23. Freger, V., Selectivity and polarization in water channel membranes: lessons learned from polymeric membranes and CNTs. Faraday Discuss 2018, 209 (0), 371-388.
24. Siwy, Z. S.; Bruening, M. L.; Howorka, S., Nanopores: synergy from DNA sequencing to industrial filtration – small holes with big impact. Chem Soc Rev 2023, 52 (6), 1983-1994.
25. Siwy, Z. S.; Howorka, S., Engineered Voltage-Responsive Nanopores. Chem. Soc. Rev. 2010, 39, 1115.
26. Daiguji, H.; Oka, Y.; Shirono, K., Nanofluidic Diode and Bipolar Transistor. Nano Lett. 2005, 5, 2274.
27. Lucas, R. A.; Lin, C.-Y.; Baker, L. A.; Siwy, Z. S., Ionic amplifying circuits inspired by electronics and biology. Nat Commun 2020, 11 (1), 1568.
28. Ni, Z.; Qiu, H.; Guo, W., Electrically Tunable Ion Selectivity of Charged Nanopores. The Journal of Physical Chemistry C 2018, 122 (51), 29380-29385.
29. Cao, E.; Cain, D.; Silva, S.; Siwy, Z. S., Ion Concentration Polarization Tunes Interpore Interactions and Transport Properties of Nanopore Arrays. Adv Funct Mater n/a (n/a), 2312646.
30. Liu, S.; Zhang, X.; Yang, Y.; Hu, N., Ion Transport in Multi-Nanochannels Regulated by pH and Ion Concentration. Anal Chem 2024, 96 (14), 5648-5657.

31. Liu, Y.; Sairi, M.; Neusser, G.; Kranz, C.; Arrigan, D. W. M., Achievement of Diffusional Independence at Nanoscale Liquid–Liquid Interfaces within Arrays. Anal Chem 2015, 87 (11), 5486-5490.
32. Liu, Y.; Holzinger, A.; Knittel, P.; Poltorak, L.; Gamero-Quijano, A.; Rickard, W. D. A.; Walcarius, A.; Herzog, G.; Kranz, C.; Arrigan, D. W. M., Visualization of Diffusion within Nanoarrays. Anal Chem 2016, 88 (13), 6689-6695.
33. Green, Y.; Abu-Rjal, R.; Eshel, R., Electrical Resistance of Nanochannel-Microchannel Systems: An Exact Solution. Physical Review Applied 2020, 14 (1), 014075.
34. Kwok, H.; Briggs, K.; Tabard-Cossa, V., Nanopore Fabrication by Controlled Dielectric Breakdown. Plos One 2014, 9 (3).
35. Yanagi, I.; Fujisaki, K.; Hamamura, H.; Takeda, K., Thickness-dependent dielectric breakdown and nanopore creation on sub-10-nm-thick SiN membranes in solution. J Appl Phys 2017, 121 (4).
36. Hall, J. E., Access Resistance of a Small Circular Pore. J. Gen. Physiol. 1975, 66, 531.
37. Smeets, R. M. M.; Keyser, U. F.; Krapf, D.; Wu, M. Y.; Dekker, N. H.; Dekker, C., Salt dependence of ion transport and DNA translocation through solid-state nanopores. Nano Lett 2006, 6 (1), 89-95.
38. Melnikov, D. V.; Hulings, Z. K.; Gracheva, M. E., Concentration Polarization, Surface Charge, and Ionic Current Blockade in Nanopores. The Journal of Physical Chemistry C 2020, 124 (36), 19802-19808.
39. Vlassiouk, I.; Siwy, Z. S., Nanofluidic Diode. Nano Lett. 2007, 7, 552.

Figures used in the abstract

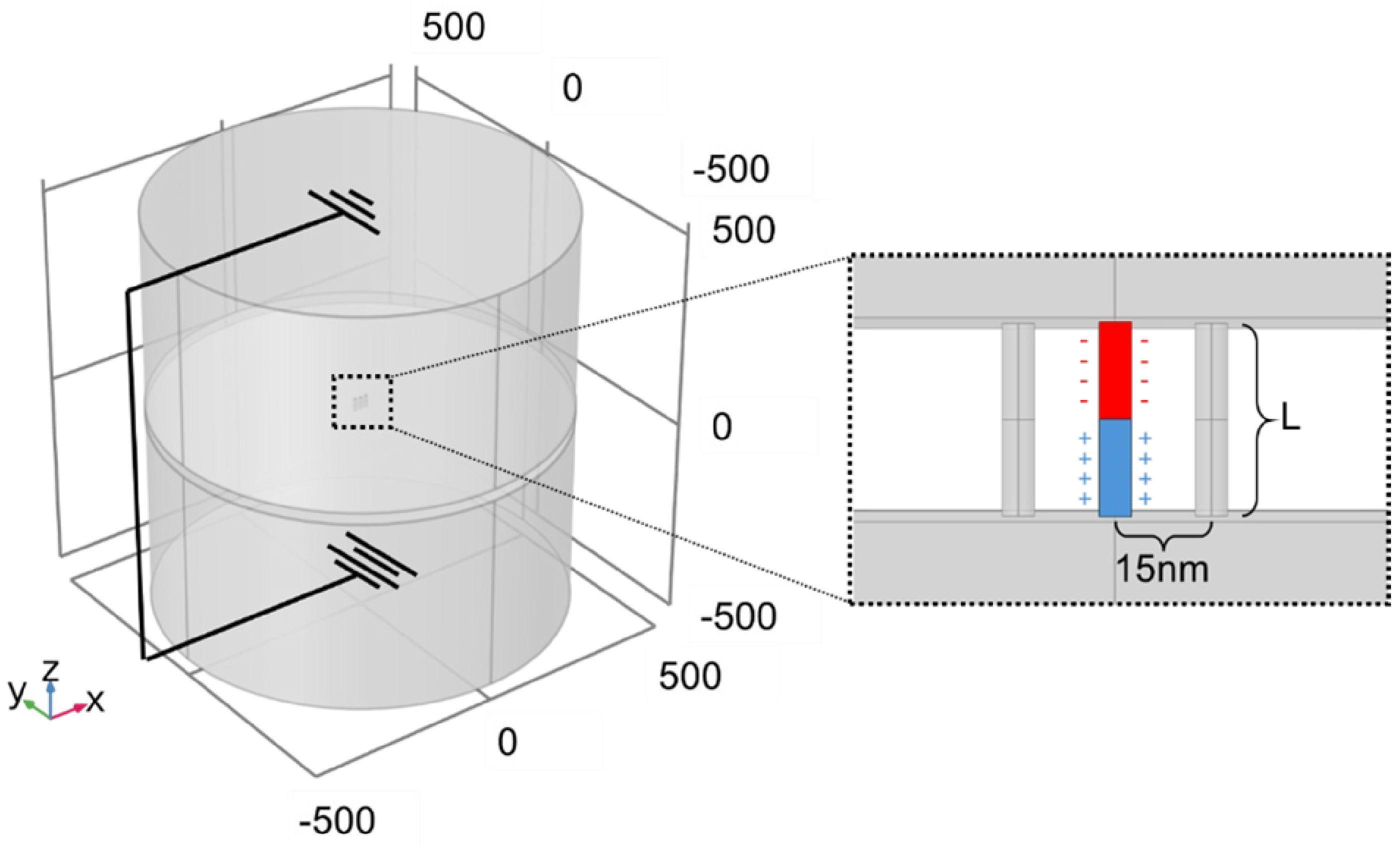

Figure 1 : Scheme 1: Geometrical setup for nanopore array modeling. Cylindrical reservoirs of 0.5 m radius and 0.5 m height are connected with a membrane containing a single nanopore or 3-nanopore array with the pore-to-pore distance set to 15 nm. The nanopore dia

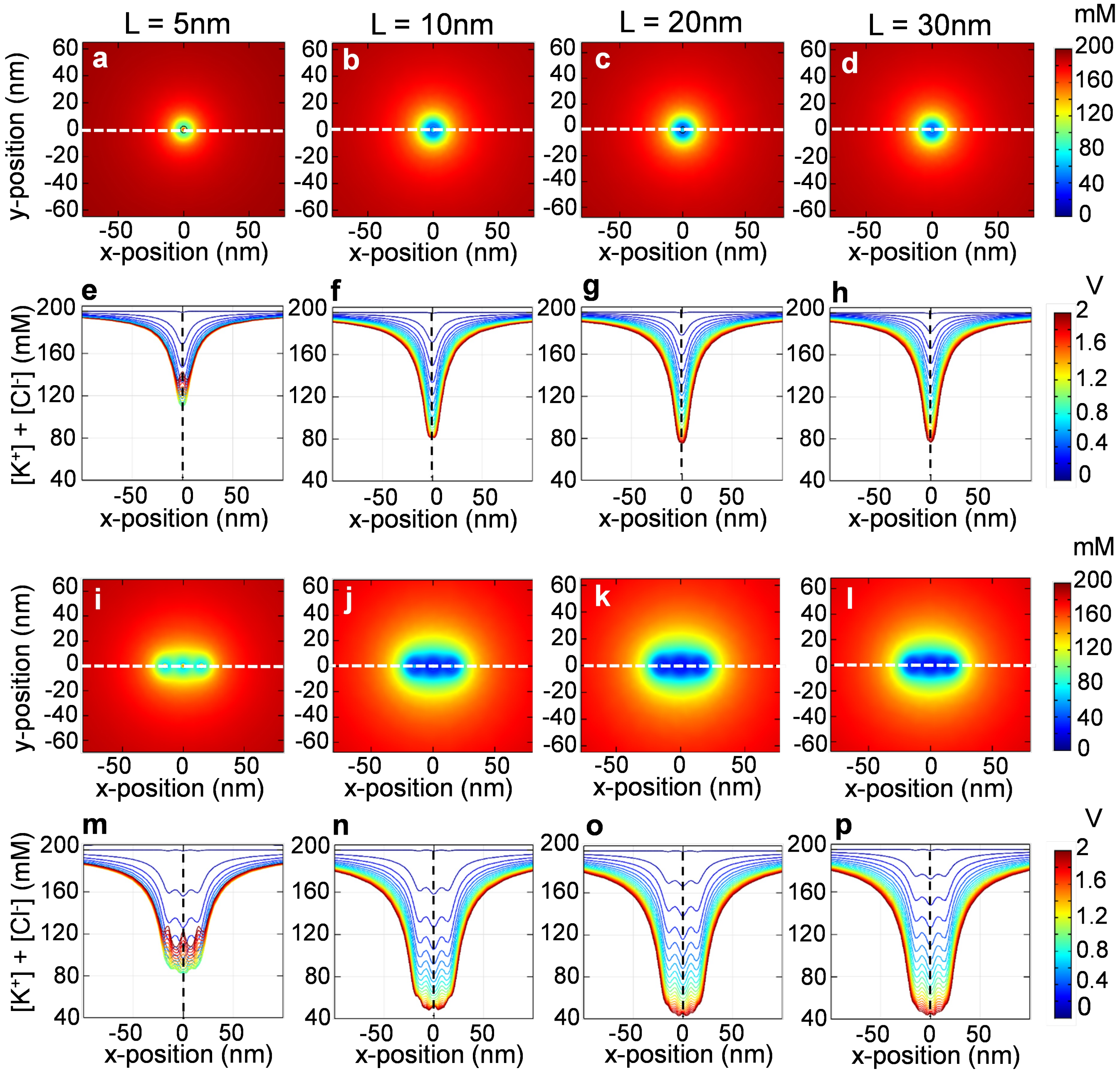

Figure 2 : Figure 1. Ionic depletion caused by ion concentration polarization in single nanopores (a-h) and in nanopore arrays with 3 pores (i-p) in 100 mM bulk KCl concentration as a function of pore length and voltage. Results for 5, 10, 20 and 30 nm long pores ar

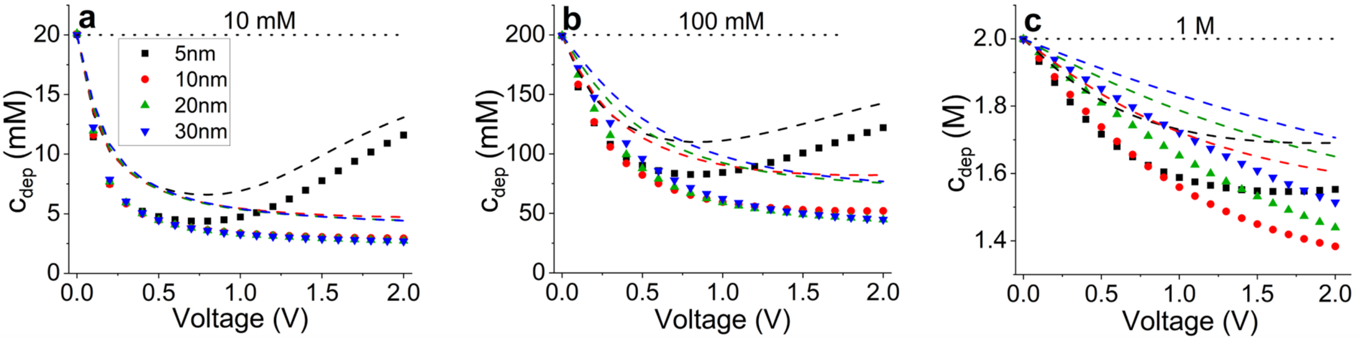

Figure 3 : Figure 2. The total ionic concentration, called cdep, in the middle of single nanopores (dashed lines) and the middle of the center pore in the arrays (symbols) as a function of pore length and voltage. This graph shows concentrations at the vertical dash

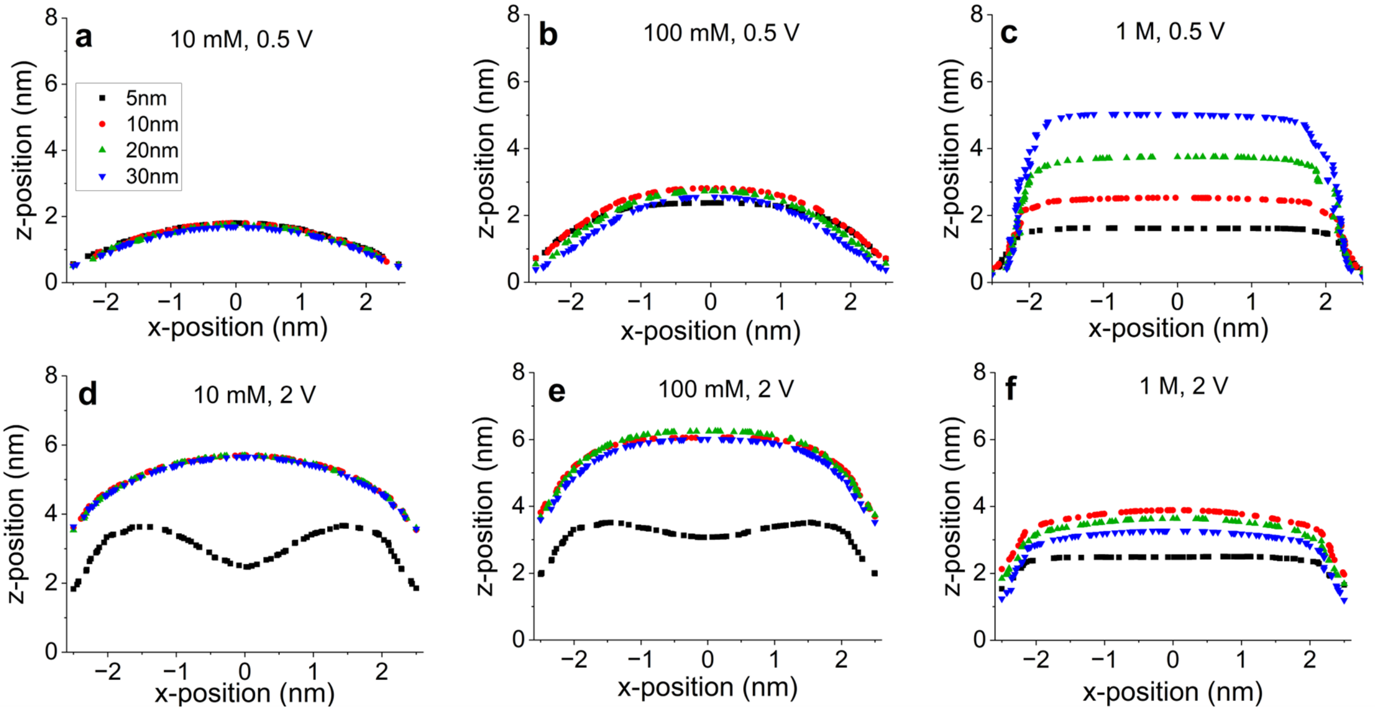

Figure 4 : Figure 5. Contours of the position in the xz-plane inside the pore where the total ionic concentration reaches 95% of the bulk total concentration. x = 0 nm indicates the middle of the center pore in 3-nanopore arrays of all lengths. The y-axis indicates