Response to Comment on "Experimental Energy Barriers to Anions Transporting through Nanofiltration Membranes"

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Response to Smith *et al.'s* Comment on "Experimental Energy Barriers to Anions Transporting through Nanofiltration Membranes"

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The comment on our article "Experimental Energy Barriers to Transporting Anions through nanofiltration Membranes"[1] by Smith, Mukharjee and SenGupta raises an important point that requires clarification, namely the use and definition of the term 'hydrated radius'. In our article we discuss two measures of hydrated ionic radius. The first is the Stokes or hydrodynamic radius which is related to the diffusion behaviour of the ion in solution. Specifically, it reflects the radius of a hard sphere that diffuses at the same rate as the ion in question, something which will be influenced by the water molecules that move with the ion. Secondly, we describe the 'hydrated radius', which we define as the physical size of the ion plus its first hydration shell. This can be determined from the ion-water radial distribution function either from diffraction studies or molecular simulation[2], for any number of ions or environmental pollutants.

The interchangeable use of these terms in the literature has led to some confusion. In their comment and previous work[3] Smith *et al.* use the term "hydrated ionic radius" to refer the Stokes radius and not the size of the first hydration shell as meant by us, and this creates a misunderstanding in the interpretation of our work. Here we hope to clarify how the disparate use of these terms has resulted in some of the comments made by Smith *et al*. For the remainder of this article we shall use the terms 'Stokes radius' and 'First hydration shell radius' to avoid further confusion.

The first question Smith *et al*. hope to address is the link between the hydrated radius of an ion and the free energy of hydration. In Table 1 we show the hydration free energy, bare ion radius, Stokes radius and the radius of the first hydration shell for a number of well characterised monovalent cations and anions, avoiding polyatomic ions for clarity. While different studies show slightly different values, in all cases the ordering of the ions is the same so only a single data set for each value is shown.

Table 1. Properties of monovalent cations and anions.

Ion	Hydration Free energy (kcal/mol) [4]	Bare ion (Pauling) radius (Å) [5]	Stokes radius (Å) [6]	First hydration shell radius (Å) [7]
Li⁺	-113.8	0.60	2.38	1.96
Na⁺	-88.7	0.95	1.84	2.38
K⁺	-71.2	1.33	1.25	2.75
F⁻	-119.7	1.36	1.66	2.63
Cl⁻	-89.1	1.81	1.21	3.13
Br⁻	-82.7	1.95	1.18	3.41

While the Stokes radius follows the same order for the ions as the hydration free energy, there is an inverse relationship of the hydration free energy to the radius of the first hydration shell. Smith *et al.*, confuse the different definitions of these radii, yielding the erroneous conclusion that a stronger free energy of hydration means a larger first hydration shell radius and, that since F⁻ has the lowest hydrated radius of the anions reported in our paper that it should be preferred over Cl⁻ by anion exchange resins. Once the different uses of the term 'hydrated radius' are understood, the disparity between our results and the claims of Smith *et al.* evaporate.

The second point made by Smith *et al*. discusses whether there is a simpler method to predict ion rejection in the absence of data on the free energy of hydration. We agree that the results of experiments utilising ion exchange resins provide an excellent step in predicting the order of rejection of nanofiltration (NF) membranes that can successfully reproduce the permeability sequence in many cases. However, we note that they cannot account for membrane dependent differences that are apparent in our results. While the relative rejection order of the anions is the same for the two membranes in the study, the relative magnitude of the rejection differs significantly between the two membrane types as seen in Figure 1 of the original article.[1] As noted there, quantitative rejection values cannot be easily explained by ion parameters such the radius of the first hydration shell, the Stokes radius or the hydration free energy alone. This is true even for F⁻ and Cl- for which good data for the ion properties exists. Thus, we do not believe that relative rejection can simply be seen as an intrinsic property of the anions, but rather will be influenced by properties of the membrane such as pore radius, morphology and surface charge. In this case, we think that understanding the partial dehydration required for ions to enter the membranes and how this differs amongst different membrane types is important for explaining ion rejection. Furthermore, we expect this to be more important in membranes with well defined narrow pores (why? I am not convinced it is more important but well defined pores are the only way to be able to possibly be able to discriminate between any mechanisms).   For example, computational studies have suggested situations in which relative rejection orders of monatomic cations and anions can be reversed,[8] such as in narrow carbon nanotubes, something that cannot be explained by intrinsic properties of the ions without reference to properties of the pores. In these situations we believe that the concepts of hydration free energies and free energies of transport are extremely useful in tackling the mechanistic research questions presented in the original article.

The aim of our article was to clarify the molecular mechanisms yielding differential ion rejections in NF membranes, something that cannot be explained by solution diffusion models such as the Nernst-Planck equation. We hope that the quantification of the free energy barriers seen by permeating ions can assist in teasing out which effects are important in dictating ion rejection, be they intrinsic to the ion or related to properties of the membrane itself.

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