REPLY TO STIRNEMANN ET AL.:

Frame retardation is the key reason behind the general slowdown of water reorientation dynamics in concentrated electrolytes

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Stirnemann et al. (1) argue that the general deceleration of water reorientation dynamics in the concentrated electrolytes is not entirely due to the frame retardation, since suppressing frame reorientation entirely leads to a maximum slowdown of $\frac{\frac{1}{\tau_{reor}^{jump}}+\frac{1}{\tau_{reor}^{frame}}}{\frac{1}{\tau_{reor}^{jump}}}\approx 1.6$, smaller than the deceleration in many concentrated electrolytes. This same argument, however, can be used to reason that the general deceleration does not entirely come from the retarded jump either, since the decelerations in many concentrated electrolytes are larger than $\frac{\frac{1}{\tau_{reor}^{jump}}+\frac{1}{\tau_{reor}^{frame}}}{\frac{1}{\tau_{reor}^{frame}}}\approx 2.5$ as well (2–4). Our point in ref. 5, instead, is that at higher concentrations the ions can have nonnegligible effects on both jump and frame components. However, the effect on the jump component can be either acceleration or deceleration (e.g., figure 4 in ref. 6) for different electrolytes, while the effect on frame components is always decelerating. It is in this sense that frame retardation is the key factor behind the general deceleration.

In fact, Stirnemann et al. (6) simulated two specific electrolytes, $NaClO_4$ and Na_2SO_4, up to 8 M and drew a similar general conclusion that "a key contribution to the water reorientation slowdown at high concentrations arises from the frame retardation." The difference from ref. 5 is that they suggested the frame retardation is due to the changed hydrogen-bond (HB) switching, while we indicated that it is due to the changed water structural dynamics.

Stirnemann et al. (1) claim that the high-concentration regime (>5 M) studied in ref. 5 is not relevant for aqueous batteries or for biological processes. A recent paper (7), however, reported using the aqueous electrolytes up to 21 M in lithium-ion batteries, which enables high-voltage aqueous lithium-ion chemistries. Although concentrated electrolytes are rarely used for biological applications, concentrated solutions of molecules such as DMSO are extensively used as cosolvents therein. Intriguing nonideal water reorientation dynamics were reported for these mixtures (8), and our study provides a strong implication on the reason behind this nonideality.

The term "ion clusters" is used in ref. 5 to denote aggregates formed by associating cations and anions with various sizes and morphology. In concentrated solutions, water frame reorientation next to these aggregates is always "damped," while the jump component is affected by the complicated enthalpic and entropic factors in the local environment and is not necessarily slowed down (6).

τ_{reor}^{frame} in ref. 5 is calculated using the same approach as in ref. 6 and does not depend on the subsequent jump. The "HB hop time" refers to the waiting times before the jump obtained from the collection of successive jump events. Their distributions should be non-Poissonian (9).

The study in ref. 5 focuses on the electrolytes. Biomolecules were brought up simply to suggest how water motions can be strongly affected by large-size solutes. We would like to point out, however, that "water molecules are thus rather affected by the confinement within the ion network pores," suggested by Stirnemann et al. (1), might partly come from an entropic (steric) effect.

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1 Stirnemann G, Jungwirth P, Laage D (2018) Water dynamics in concentrated electrolytes: Local ion effect on hydrogen-bond jumps rather than collective coupling to ion clusters. *Proc Natl Acad Sci USA*, 10.1073/pnas.1803988115.
2 Bakker HJ (2008) Structural dynamics of aqueous salt solutions. *Chem Rev* 108:1456–1473.
3 Marcus Y (2009) Effect of ions on the structure of water: Structure making and breaking. *Chem Rev* 109:1346–1370.
4 Bian H, et al. (2013) Cation effects on rotational dynamics of anions and water molecules in alkali (Li+, Na+, K+, Cs+) thiocyanate (SCN^-) aqueous solutions. *J Phys Chem B* 117:7972–7984.
5 Zhang Q, Wu T, Chen C, Mukamel S, Zhuang W (2017) Molecular mechanism of water reorientational slowing down in concentrated ionic solutions. *Proc Natl Acad Sci USA* 114:10023–10028.
6 Stirnemann G, Wernersson E, Jungwirth P, Laage D (2013) Mechanisms of acceleration and retardation of water dynamics by ions. *J Am Chem Soc* 135:11824–11831.
7 Suo L, et al. (2015) “Water-in-salt” electrolyte enables high-voltage aqueous lithium-ion chemistries. *Science* 350:938–943.
8 Wong DB, et al. (2012) Water dynamics in water/DMSO binary mixtures. *J Phys Chem B* 116:5479–5490.
9 Laage D, Hynes JT (2008) On the molecular mechanism of water reorientation. *J Phys Chem B* 112:14230–14242.

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