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Water dynamics in concentrated electrolytes: Local ion effect on hydrogen-bond jumps rather than collective coupling to ion clusters

Guillaume Stirnemann^{a,1}, Pavel Jungwirth^{b,1}, and Damien Laage^{c,1}

Zhang et al. (1) suggest that water rotational dynamics slows down in all concentrated ionic solutions mostly because of a collective effect due to the coupling between water dynamics and the motion of large ion clusters. These conclusions were based on simulations of aqueous NaSCN and KSCN salts, with a focus on extremely concentrated solutions (5–15 M). While a collective viscosity effect can play a role in some very specific concentrated salts, it is important to stress that this cannot be a general explanation for the slowdown observed in all concentrated electrolytes.

We have shown (2) that the extended jump model (3) can be effectively used to determine how ions affect water reorientation dynamics. Within this approach, which was subsequently followed by Zhang et al. (1), water can reorient either via the jump of a water OH group between hydrogen-bond (HB) acceptors or by the tumbling of the local frame of an intact HB between two successive jumps. The resulting reorientation rate is summed over these two distinct mechanisms,

$$\frac{1}{\tau_{reor}} = \frac{1}{\tau_{reor}^{jump}} + \frac{1}{\tau_{reor}^{frame}} \quad [1]$$

In 300-K bulk water (4), $\tau_{reor}^{jump} \approx 3.6$ ps and $\tau_{reor}^{frame} \approx 5.6$ ps. Zhang et al. (1) claim that the slowdown in all concentrated ion solutions arises primarily from the slower frame reorientation and not from a more local ion effect on jumps. However, the frame reorientation brings only a minor contribution to the slowdown of water reorientation dynamics. It follows directly from Eq. 1 that suppressing frame reorientation entirely would lead to a maximum slowdown of only $(3.6^{-1} + 5.6^{-1}/3.6^{-1}) \approx 1.6$, while larger

retardations are found for many concentrated electrolyte solutions (2, 5, 6), including, for example, the most concentrated NaSCN solution studied in ref. 1.

Zhang et al. (1) suggest that the strong frame retardation originates from the slowed-down motions of water molecules slaved to large ion clusters. However, in very concentrated NaSCN and KSCN solutions, ions form a percolating network, and not ion clusters (7); water molecules are thus rather affected by the confinement within the ion network pores. We also note that while Zhang et al. (1) use well-established approaches (2, 8), several of their results are inconsistent with the literature, which casts some doubts on their implementation. These inconsistencies include, for example, their τ_{reor}^{frame} depending on the subsequent jump and not only on the HB acceptor (2) or their non-Poissonian HB hop-time distributions (8). Finally, we mention in passing that the very high concentrations studied in ref. 1 (5–15 M) are extreme cases, which are not relevant for biological processes at physiological conditions (0.15 M).

Zhang et al. (1) speculate that ions and biomolecules slow down water dynamics in the same collective fashion. However, our prior studies (9, 10) had established the opposite. While in all cases the dominant effect is local (i.e., on the HB jumps) and not collective, ions and biomolecules affect water dynamics differently. This is confirmed by temperature-dependent studies showing that the slowdown effect of ions is mostly enthalpic due to the water–ion interaction, while that of proteins and DNA is mostly entropic due to an excluded-volume effect (10).

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