

D₂O Isotope Effects on Proton Hopping in High Temperature Aqueous Solutions by AC Conductivity

Hugues Arcis^{C,S}, Jeff Plumridge and Peter Tremaine
Dept. of Chemistry, University of Guelph, Guelph, ON, Canada
harcis@uoguelph.ca

Deuterium solvent isotope effects on the contribution of proton hopping to molar conductivities at temperatures above 318 K have been determined for the first time. Limiting molar conductivities, Λ° , of potassium hydroxide and hydrochloric acid have been measured from $T = 298$ K to $T = 598$ K at $p \sim 20$ MPa in both H₂O and D₂O, using a unique high-precision flow-through AC electrical conductance instrument. From these results, single ion limiting conductivities, $\lambda^\circ(\text{H}_3\text{O}^+)$, $\lambda^\circ(\text{D}_3\text{O}^+)$, $\lambda^\circ(\text{OH}^-)$ and $\lambda^\circ(\text{OD}^-)$ have been derived using new single ion values for $\lambda^\circ(\text{Cl}^-)$ reported recently by our group [1]. Walden products ($\lambda^\circ\eta$) for each ion were found to be simple exponential functions of temperature and solvent density. Walden product ratios for the deuteron/proton and deuterioxide/hydroxide, $(\lambda^\circ\eta)_{\text{D}_2\text{O}}/(\lambda^\circ\eta)_{\text{H}_2\text{O}}$, showed a clear difference between light and heavy water, with a more efficient transport mechanism in light water over the entire temperature range. The H₃O⁺ and OH⁻ ions and their deuterated counterparts are known to move through solution by diffusion through the bulk solvent or through proton hopping. To determine the excess limiting ionic conductivity arising from proton hopping, we have adopted the method used by Tada *et al.* [2,3] who postulated that the contribution to the experimental conductivities of the hydronium and hydroxide ions from diffusion, $\lambda^\circ(\text{H}_3\text{O}^+, \text{diff.})$ and $\lambda^\circ(\text{OH}^-, \text{diff.})$, can be assumed to be the same as those for K⁺ and Cl⁻, respectively:

$$\lambda^\circ(\text{H}_3\text{O}^+, \text{hopping}) = \lambda^\circ(\text{H}_3\text{O}^+, \text{exp.}) - \lambda^\circ(\text{H}_3\text{O}^+, \text{diff.}) \approx \lambda^\circ(\text{H}_3\text{O}^+, \text{exp.}) - \lambda^\circ(\text{K}^+, \text{exp.}) \quad (1)$$

$$\lambda^\circ(\text{OH}^-, \text{hopping}) = \lambda^\circ(\text{OH}^-, \text{exp.}) - \lambda^\circ(\text{OH}^-, \text{diff.}) \approx \lambda^\circ(\text{OH}^-, \text{exp.}) - \lambda^\circ(\text{Cl}^-, \text{exp.}) \quad (2)$$

From 298 to 598 K, ionic transport due to proton hopping was found to be greater for H₃O⁺/D₃O⁺ than for OH⁻/OD⁻. This mechanism became less important as temperature increased.

References

- [1] Plumridge, J., Arcis, H., Tremaine, P.R. *J. Solution Chem.* **2014** (in press.)
- [2] Tada, Y., Ueno, M., Tsuchihashi, N., Shimizu, K. *J. Solution Chem.* **1992**, *21*, 971-985.
- [3] Tada, Y., Ueno, M., Tsuchihashi, N., Shimizu, K. *J. Solution Chem.* **1993**, *22*, 1135-1149.