Deuterium Isotope Effects on the Limiting Molar Conductivities of Strong Aqueous Electrolytes from 25 °C to 300 °C at 20 MPa

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The differences between the transport properties of strong electrolytes in H2O and D2O have long been of interest as a tool for probing the nature of the so-called “structure-making” and “structure breaking” hydration effects of ions at temperatures near 25 °C. Recently, our group has measured deuterium isotope effects on the molar conductivity (L°) and limiting ionic molar conductivity (l°) of strong electrolytes at temperatures approaching 300 °C, as a means of exploring solvation effects under hydrothermal conditions (Erickson et al., J. Phys. Chem B. 2011, 115, 3038-3151). In the present paper, we report experimental values of L° for NaCl, KCl, HCl/DCl, NaOH/NaOD, KOH/KOD, NaCH3COO, KI, CsI and KH2PO4/KD2PO4 in H2O and D2O; and the corresponding values of l° values for each of the ions from 25 to 300 °C at p = 20 MPa. Simple correlations as a function of solvent viscosity have been found to reproduce the temperature- and density-dependence of L° and l° in both solvents. The temperature dependence of the Walden product ratio, (8 °η)D2O/(8 °η)H2O, indicates a change in the relative hydration behaviour of ions, whereby the apparent Stokes radii of "structure-breaking" ions in D2O relative to H2O reverse above ~423 K. This effect is particularly evident for NaOD(aq) and KOH(aq), suggesting that the proton hopping mechanism in D2O, which is less efficient than that in H2O at ambient conditions, becomes more efficient at temperatures above about 548 K.