Walden's Rule Revisited

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The relationship for electrolytes between the equivalent conductance at infinite dilution $\Lambda°$ and the solvent viscosity η has been recognized for decades. Reported literature values of $\Lambda°$ for NaCl(aq) between a large range of temperatures (278 and 1073 K) and pressures (0.1 and 545 MPa) when plotted as a function of η show a cusp at a viscosity of 0.0005 Poise. The low viscosity portion has a lot of scatter, possibly due to the higher uncertainties of these values in what corresponds to low-density steam. To the right of the cusp there is an exponential curve. In this work it has been found that for all salts examined to date (NaCl, LiCl, K_2SO_4, and $CaCl_2$) that this curve follows the equation

$$\Lambda° = b\, \eta^{-0.9}$$

where b is a constant that is specific to each salt found by weighted least squares regression. Results are similar for alkali halides and tetraalkylammonium bromides in methanol, with the cusp occurring at the same viscosity and the exponent being about the same. These results will be discussed in terms of Walden's Rule, Stokes Law and the Hubbard-Onsager dielectric friction theory. One deficiency of this very simple model is that it does not reproduce $\Lambda°$ with high accuracy in the low temperature, high pressure region due to the anomalous behavior of the pressure dependence of viscosity between 273 and 306 K. However, this is of little concern since the ultimate goal of this work is to find a reliable method to predict $\Lambda°$ for ions at high temperatures and pressures.