

Are Ionic Stokes Radii of Any Use?

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The pioneering attempts by Einstein [1] and Walden [2] to estimate the sizes of solute particles in solution by means of Stokes' law are acknowledged. However, since x-ray and neutron diffraction have provided accurate measures of these sizes for ions, r_i , such attempts, in terms of ionic Stokes radii, r_{iSt} , are obsolete.

The Stokes radius of an ion is obtained from its limiting conductivity λ_i^∞ in a solvent of shear viscosity η^* as:

$$r_{iSt}/nm = 8.201 |z_i| / (\eta^*/mPa \cdot s) (\lambda_i^\infty / S \cdot cm^2 \cdot mol^{-1})$$

The numerical coefficient assumes "stick" boundary conditions for Stokes' law. The theoretical indecision ([3, 4] and references therein) concerning the use of "stick" or "slip" boundary conditions for ions having sizes commensurate with those of the solvent molecules is deplorable but has not been resolved so far. It is difficult to envisage hydrated ions "slipping" through water without water molecules "sticking" to the bare ion and to the water molecules in its hydration sphere.

The fact that some ionic Stokes radii r_{iSt} , even for the "slip" values (50% larger than for "stick" values [3]), are smaller than the crystal ionic radii (e.g., for Br⁻ and I⁻) deprives them of physical significance. This is in particular noted when ion solvation numbers h_i are to be calculated from the difference between r_{iSt}^3 and r_i^3 :

$$h_i = (4\pi N_A/3)(r_{iSt}^3 - r_i^3)/V_W$$

where V_W is the solvent molar volume in the solvation shell. Unreasonable h_i values result from such calculations. The criticism by Fernandez-Prini and Atkinson [5] of this practice has not been heeded by some subsequent workers.

The "correction" of Stokes radii according to Nightingale [6] is empirical and plausible, but does not seem to have been consistently applied since then. Theoretical corrections consider the addition of dielectric friction to the hydrodynamic friction [5,7], but they require solvent physical quantities not readily available, and, of course, the decision concerning the boundary condition has not been settled.

Ionic mobilities (conductivities) are readily measured accurately and valid derivation of the infinite dilution values, λ_i^∞ , is possible. There is, therefore, no incentive to estimate such values from ionic radii in solution, r_i , according to the Stokes-Einstein-Nernst relationship. The approximate validity of Walden's rule: $\eta^* \lambda_i^\infty = const$ for a given ion, should permit estimation of the conductivity in one solvent given that in another solvent if no direct measurement could be carried out.

The conclusion is that the concept of an ionic Stokes radius is devoid of physical meaning and should be scrapped altogether.

References

- [1] Einstein, A, *Ann. Phys.* **1906**, *19*, 289.
- [2] Walden, P., *Z. Anorg. Allgem. Chem.* **1920**, *113*, 125.
- [3] Pau, P. C. F., Berg, J. O., McMillan, W. G., *J. Phys. Chem.* **1990**, *94*, 2671.
- [4] Schmidt, J. R., Skinner, J. L., *J. Chem. Phys.* **2003**, *119*, 8062.
- [5] Fernandez-Prini, R., Atkinson, G., *J. Phys. Chem.* **1971**, *75*, 239.
- [6] Nightingale, E. R. Jr., *J. Phys. Chem.* **1959**, *63*, 1381.
- [7] Ibuki, K., Nakahara, M., *J. Phys. Chem.* **1986**, *90*, 6362.