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How big is the hydrated electron? Thermodynamics of electron solvation and its partial molar volume[1]

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Several models for the hydrated electron solvation structure have been proposed, which all can do a reasonable job of reproducing the room temperature optical spectrum. As Larsen, Glover and Schwartz [1] demonstrated, tweaking the electron-water pseudopotential can completely change the structure from a cavity to a non-cavity geometry. Deciding between the competing models then requires comparison with other observables. The resonance Raman spectrum and the temperature dependence of the optical spectrum can be cited as evidence in favor of a non-cavity structure [2]. In the present work we will re-examine the thermodynamics of hydration [3]. In particular, we will present new experimental and simulation results for the partial molar volume, which can bear directly on the cavity vs. non-cavity controversy.

[1] Larsen, R.E., W.J. Glover, and B.J. Schwartz, Does the Hydrated Electron Occupy a Cavity? Science, 2010. 329(5987): p. 65-69.

[2] Casey, J.R., A. Kahros, and B.J. Schwartz, To Be or Not to Be in a Cavity: The Hydrated Electron Dilemma. Journal of Physical Chemistry B, 2013. 117(46): p. 14173-14182.

[3] Bartels, D.M., et al., Pulse radiolysis of supercritical water. 3. Spectrum and thermodynamics of the hydrated electron. Journal of Physical Chemistry A, 2005. 109(7): p. 1299-1307.

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