Review of ACPD 11-24813-2011
Metzger et al.

Addendum

For the parameterization of bulk solution water activity (no Kelvin term), the relevant equation is equation 17c, which truly is a single-parameter equation. Since the quantity of interest is the water content, we can rearrange the equation as follows, replacing molality with the following (see Metzger et al.'s equation (2), which assumes volume additivity):

$$\mu_s = \frac{V_s}{V_w} \frac{\rho_s}{\rho_w} \frac{1}{M_s}$$
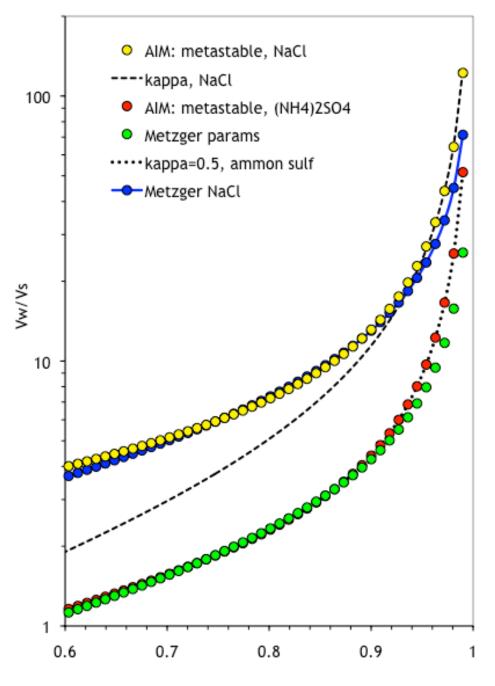
to yield this version of Eq. 17c:

$$\frac{V_w}{V_s} = \left(\frac{a_w}{1-a_w}\right)^{1/\nu_i} \left[\frac{\rho_s}{\rho_w M_s}\right] \left[M_w \nu_i\right]^{1/\nu_i}$$

Compare with the equation proposed by PK2007:

$$\frac{V_w}{V_s} = \left(\frac{a_w}{1-a_w}\right)\kappa$$

The parameter ν_i plays a role similar to kappa, in that it is specific to the solute being studied and serves as a scaling factor on an assumed function of water activity. The advantage to the formulation presented here is that the water activity function is raised to a power that can vary according to the solute, whereas in PK2007 the shape of the function relating water activity to solution composition is fixed and is simply scaled up or down through the selected value of κ. For NaCl and Na_2SO_4, as shown by Kreidenweis et al. (2008), the $(a_w/(1-a_w))$ function simply does not well represent the actual functional dependency well below water saturation.

As can be seen in the figure below, the parameterization proposed in this manuscript corrects the functional dependence on a_w for NaCl, yielding water contents much closer to the AIM values over a large range of a_w. However, the PK2007 formulation, for a choice of κ that optimizes the fit near ~95% RH, appears to do a better job at representing the AIM water contents at high relative humidity. The Metzger et al. parameterization for high RH may correct the underrepresentation at high RH, but I did not try it (see review).