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Interactive comment on “Derivation of the stoichiometric coefficient of water (ν_w) to account for water uptake by atmospheric aerosols” by S. Metzger et al.

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1 Reply

We thank Referee 2 for his review. We believe, however, that the recommendation to reject the manuscript is unfounded for the reasons detailed in our response to R. Lescroart’s (Referee 1) criticisms (which this referee agrees on), and for the reasons outlined in the following:

- No aspect of the derivation is borrowed from the solution chemistry literature, nor

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does the derivation itself results in dimensionally incorrect and seemingly non-sensical equations like (10f), if interpreted correctly. We admit, however, that we accidentally referred to the molar concentration of water ($55.51 \text{ mol/kg}(\text{H}_2\text{O})$), which causes the inconsistency in the units for Eq. (A8). However, this number 55.51 should be interpreted as a dimensionless quantity, e.g. the inverse mass fraction of 1 mol of bound water in 1 kg of initially free water (molarity scale), by which we mean $55.51 = 1 \text{ kg}(\text{H}_2\text{O}) / (1 \text{ mol}(\text{H}_2\text{O}) * 0.01815 \text{ kg/mol})$, where the denominator refers to the mass of 1 mol of bound water (considering stoichiometry) that will be eventually be consumed during solute dissolution / dissociation. And this interpretation is more consistent with our mass fraction solubility based approach. Also, Eq. (A8) actually refers to an activity rather than molality, since it obviously compares to water activity measurements and not to the solute molality.

This inconsistency in our definitions (including in ML07) and all related ones (e.g. equations depending on Eq. (A8)) will be clarified in the revised manuscript together with some further (apparently missing) model description / explanations.

Thus, it rather seems that our approach is misunderstood.

- For example, the stoichiometric coefficient of water ν_w is not restricted to hydration, as explained in the manuscript on page 8167 line 24 up to page 8168 line 10. We refer to the consumed amount of water, e.g. hydration or other processes.
- Its true, however, that we have not related our work to established theory, and particularly to the Gibbs-Duhem equations and the known relationship between water activities and solute activity coefficients. This will be done and in the revised manuscript. And we can show within the same model that the two are consistent, i.e. one can calculate one from the other.
- Nevertheless, based on our understanding, which is supported by many results (including also the many publications that successfully applied previous EQSAM versions), the standard definition of activity coefficients are not needed

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for solid/liquid equilibrium, at least not for non-volatile compounds. The ratio of v_w/v_e is a valid correction factor that can be used instead of the standard definition of activity coefficients, with the advantage that it is of the form $a x^a$, so that only one parameter instead of solution dependent parameters is required in our concept. This has not been recognized.

- This can be easily verified with the example program to calculate the RHD and hygroscopic growth of NaCl from RHD up to conditions close to those of water vapor saturation, without any activity coefficient. Note that the example program can be easily extended to other compounds; and that it is provided in the supplement of the reply to R. Lescoat.
- Note further that at equilibrium a solution is always saturated, and that our approach does not only work for single solutes – it even works well for complex mixed solutions as our comparison results with E-AIM (Fig. 2 g,h), and the associated application paper of Xu et al. (<http://www.atmos-chem-phys-discuss.net/9/9551/2009/>), clearly demonstrate. However, this will be further clarified in the revised manuscript.
- Finally, note that we have improved the key equation of single solute molality to account for a better water uptake at high RH (> 95% – below results remain unchanged). Thus, osmotic coefficients of NaCl are now also right at dilute solutions, as it will be additionally demonstrated in the revised manuscript.
- Nevertheless, let's assume our model is both misconceived and in any case flawed in its derivation - how can it then be possible that we can predict complex solution properties such as activities and water in a much much easier way than established models?
Until we find consensus, let's simply call it a parameterization.

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