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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Experimental determination of the temperature dependence of water activities for a selection of aqueous organic solutions" *by* G. Ganbavale et al.

Anonymous Referee #1

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The paper is novel in bringing together different methods for deriving temperature dependent water activities. Deriving the data is difficult clearly as multiple factors have to be taken into account (the potential for viscous solutions for example). The authors have clearly thought about detailed considerations on presentation of the results. The paper should certainly be published after some minor points are addressed.

Page 12674, line 9 'does not depend on the specific nature of the solute'. This seems a little circular as this study shows the specific nature of the solute does influence the change in water activity and thus one needs to know the composition to predict this?

Section 4.1 A potential problem which doesn't seem to be considered is the loss of semi-volatile gases from the suspended particle techniques. I would presume that, whilst the drop to temperatures relevant for homogeneous freezing might decrease the volatility of the organics sufficiently enough, how do you cover a wide enough range of vapour pressures (or volatility) and ensure this does not pose a problem?

Section 4.2 The discussion of hygrogen bonding is very interesting, but it would benefit from a rationale right at the start rather than the end. Line 1 page 12693 the authors mention a 'close loop miscibility gap'. It would be very helpful to expand this slightly as it is not 100% clear, nor are the 'elevated temperatures' discussed.

Figures 2 – 4. The difference between the bulk and total pressure derived water activity seem to differ most at intermediate water:organic mass ratios. Is this expected based on the appropriate interactions in solution and how does it relate to the potential error in both methods? Would it be possible to show how current group contribution methods perform on these graphs? Presently it is not clear how 'bad' they are.

Section, page 12695, line 16. The authors state how a change in aw by 0.025 can result in a change in rate coefficients by 6 orders of magnitude. On revisiting the description of the experimental methods, i find that the expected error in the gas phase pressure measurements, for example, is 0.015. Does this mean that the minimum error in J might be 3 orders of magnitude? In addition, in the text for figure 2, the 'uncertainty of the method' is noted to be 0.03? This is repeated in other figure captions.

Are the range of studied functionality enough to suit an improved thermodynamic model? It would be good to know how much more effort is needed to extend this list. It would also be useful for the authors to comment on whether interactions with inorganic components are needed in this regards. There are statements throughout the document as to the inorganic-organic interactions but i don't have a feel for the need for studying mixtures in this effect. Based on the experimental data from the total pressure measurements it seems this would be tricky. This makes the fitting of a group contribution method with highly resolved temperature data in regions which can be probed by the EDB all the more attractive.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 12673, 2014.