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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 #2

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In this interesting and important work, the authors experimentally measured the temperature dependence of water activities for several aqueous organic solutions by four different methods and discussed the intrinsic link between water activity and hydrogen bonding effects. The authors also found the better water-activity scaling of homogeneous nucleation temperature by considering the temperature dependence of the activities. The experimental results shown in this manuscript are clearly represented and have important implication for not only atmospheric science but also physics of supercooled water and aqueous solutions, especially for our understanding of the low temperature phase behavior of water (for example, see K. Murata and H. Tanaka, Nat.

Commun. 4, 2844 (2013), and G. Bullock and V. Molinero, Faraday Discuss. 167, 371 (2013)). Hence, this work is deserving of eventual publication. However there are several points, as outlined below, the authors need to be addressed before publication.

*Specific comments:

(1) In Section 4.2, the authors pointed out that competition among organic-organic, organic-water and water-water interactions is responsible for the temperature behavior of water activity. I agree this authors' interpretation for aqueous organic solutions. However such competition is not limited to aqueous organic solutions but rather general in usual binary mixtures (solute-solute, solute-solvent, solvent-solvent interactions), of course including aqueous "inorganic" solutions (so-called hydration or ion-dipole interaction) according to the classical mixture model. As is mentioned in this manuscript, the temperature dependence of the water activities of the aqueous inorganic solutions is more moderate in contrast to that of the aqueous organic solutions. What is the difference in the temperature behavior between them? Does the difference come from just a different temperature sensitivity in the interaction parameter, or is there a distinct difference in the interaction mechanism between water and organic/inorganic solute in the microscopic point of view? I believe that this point is also crucial in discussing the nature of the hydrogen bonding state in general aqueous solutions.

(2) In section 4.2, the authors speculated that the strong increase of the water activities with decreasing temperature in aqueous M5 and 2-(2-ethoxyethoxy)ethanol is due to approaching upper critical solution temperature (or a low temperature miscibility gap) hidden by ice crystallisation, enhancing the interaction between the same component (water-water and organic-organic). This explanation looks reasonable and attractive because the critical fluctuation, as is well known, strongly affects thermodynamic quantities in the system. It is stated that "At the onset of liquid-liquid phase separation water activity lines of different concentration converge at a high aw value." by reference to the work by Ciobanu et al. (page 12693, line 13). Does the onset in this sentence mean the critical point or the binodal line (the boundary between the one phase and

the phase separated region)? Is there any experimental or numerical (theoretical) evidence supporting the authors' scenario, or any data of water activity near the critical point?

(3) It is not clear to me why the homogeneous nucleation temperature is so clearly scaled by water activity although many experimental studies, including this work, have revealed this scaling so far. Different from the melting point (or water-ice equilibrium) defined thermodynamically, and whose scaling is so-called melting point depletion, the homogeneous freezing point is determined not thermodynamically but rather kinetically. In other words, the freezing point depends on a thermodynamic path (for example, cooling rate) and viscosity since the ice nucleation potentially occurs at any temperature in the metastable (supercooled) state. Note that the word "thermodynamic" that I use here means equilibrium (coexistence or binodal) or spinodal line, defined by the Gibbs free energy. In this sense, it is surprising for me that the homogeneous nucleation of ice can be scaled solely by the genuine thermodynamic parameter, water activity. In my opinion, a thermodynamic parameter (here water activity) naturally corresponds to the temperature characterized thermodynamically (coexistence and spinodal line), which implies the possible existence of another metastable phase (for example, liquid-liquid transition, see K. Murata and H. Tanaka, Nat. Commun. 4, 2844 (2013), and G. Bullock and V. Molinero, Faraday Discuss. 167, 371 (2013)) hidden by homogeneous nucleation of ice. Although this issue would not be a main focus of this manuscript, it would be nice if you discuss and make a comment about this question.

*Technical corrections:

(1) Page 12677, line 23: I would use not "from the peer-reviewed literature" but "to the best of our knowledge" in this context.

(2) Page 12684, line 23: "ob tained" Please delete the blank.

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