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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.

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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.

We thank Referee #2 for the careful reading of the manuscript and for pointing out the two interesting publications. Below are detailed answers to the reviewer comments with the locations of the incorporated changes in the revised manuscript.

*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.

The referee raises here very interesting questions. We write on page 12695, line 1, that the temperature dependence of many inorganic solutions is small. There are also exceptions. For example the temperature dependence of aqueous ammonium nitrate solutions is large (Koop, T.: Homogeneous ice nucleation in water and aqueous solutions, Z. Phys. Chem., 218, 1231–1258, 2004). From a thermodynamic point of view, the temperature dependence of water activity can be rationalized by Gibbs free energy, enthalpy, and heat capacity changes of water-solute systems as a function of temperature. In a companion paper (G. Ganbavale, A. Zuend, C. Marcolli, and T. Peter: Improved AIOMFAC model parameterisation of the temperature dependence of activity coefficients for aqueous organic mixtures, Atmos. Chem. Phys. Discuss., 14, 16907–16995, 2014), we have made use of these relationships to develop a new, improved parameterisation of the temperature dependence of activity coefficients in the AIOMFAC (Aerosol Inorganic–Organic Mixtures Functional groups Activity Coefficients) model applicable for aqueous as well as water-free organic solutions (see pages 16918 – 16920 of that manuscript).

(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?

We mean the binodal line. We were unsuccessful in finding direct experimental or theoretical evidence that could support the evidence of a hidden LLPS at low temperature. In the revised manuscript, we make use of the literature pointed out by the referee and add the following sentence at the end of section 4.2 (page 12693, line 18): “Low temperature liquid-liquid transitions without macroscopic phase separation have

been observed in different water-sugar and water-polyol systems (Murata and Tanaka, 2013).”

(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.

If homogeneous ice nucleation is understood in the framework of classical nucleation theory (CNT), the water activity criterion can be rationalized the following way: CNT formulates the Gibbs free energy to create a new solid phase from the liquid as the sum of a volume term accounting for the energy released when a molecule is incorporated from the liquid into the solid phase and a surface term accounting for the energy needed to build up the interface between the solid and the liquid phases. Clusters of critical size will develop to ice crystals. Since the chemical potential of water in aqueous solutions is typically lower than in pure water, the volume term for solutions is smaller than for pure water, just as for the melting point depression. Concerning the reconciliation between CNT (as kinetic concept) and the water activity criterion (as thermodynamic concept) Koop et al. (2000) noted: “This apparent contradiction is resolved when the interface energy (s) and the diffusion activation energy for a water molecule to cross the solution/ice interface (g) are assumed to depend only on aw but not on the nature of the solute. We can reconcile both theories (in numerical simulations not presented here) by using functions s(aw) and g(aw) with physically plausible dependencies on aw.”

Beyond this we are not aware of any experimental data that gives clear evidence of a dependence of homogeneous ice nucleation temperature on solution viscosity. Rather, when viscosity is too high homogeneous ice nucleation is inhibited and a glass forms (which “freezes” the molecular matrix in a state of low aw (despite sufficient supply of water from outside of the glassy phase). Koop et al. (2000) take effects of cooling rate into account, since delta(aw) refers to a specific cooling rate (see their Figure 2a).

*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.

We changed the manuscript accordingly.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/14/C6010/2014/acpd-14-C6010-2014-supplement.pdf

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