Response to Referee #1 (*italic*):

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.

We thank Referee 1 for the careful reading of the manuscript and the helpful suggestions and comments. Below are detailed answers to the reviewer comments with the locations of the incorporated changes in the revised manuscript.

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?

Koop et al. (2000) claimed that homogeneous ice nucleation in aqueous solutions does not depend on the specific nature of the solute but only on water activity. So far, no system was found that disproved this water activity criterion for homogeneous ice nucleation. On the other hand, water activity as a function of temperature depends on the specific nature of solute and is the scope of this paper. To validate the water activity criterion for homogeneous ice nucleation given by Koop et al., the relationship between solution composition and water activity has to be known. One objective of this study was to acquire additional data for such a validation.

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?

The applicability of single particle techniques for water activity measurements is indeed limited by the volatility of the substances under investigation. Vapor pressure of semivolatile substances strongly decreases with decreasing temperature, which enlarges the range of substances that can be investigated at low temperature. Since in our electrodynamic balance particles are injected under ambient conditions (room temperature and laboratory relative humidity) particles may totally evaporate before the (low) measurement temperature is reached. Modification of the setup for direct injection at low temperature would extend the range of substances that can be investigated.
We added the following sentence to the manuscript (page 12690, line 21):
“The applicability of single particle techniques for water activity measurements is limited by the volatility of the substances under investigation. The range of substances that may be investigated is enlarged at low temperature since vapor pressure strongly decreases with decreasing temperature. To take full advantage of this, injection of particles should occur at the measurement temperature to avoid complete evaporation before the measurement temperature is reached.”

Section 4.2 The discussion of hydrogen 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.

We modified the manuscript according to the referee’s suggestions:
We added the following statement to the beginning of section 4.2 (page 12691, line 22):
“This section is intended to interpret the strong change of water activity with decreasing temperature observed for some investigated substances. In this context we discuss changes in hydrogen bonding, which play an important role. Hydrogen bonding increases with decreasing temperature and might become more influential at low temperature”.

We changed the sentence on pages 12692-12693:
“This interplay of entropic and enthalpy contributions to the Gibbs energy leads to a closed loop miscibility gap at elevated temperature (353.15–523.15K) for aqueous PEG solutions with PEG molecular weights of 2200 g mol^{-1} *and higher (e.g., Dormidontova, 2004; Kjellander and Florin, 1981; Zobrist et al., 2003).”*

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.

This does not seem to be the case for all investigated systems. For the aqueous 1,4-butanediol solutions shown in Figure 2, the agreement at intermediate water:organic mass ratios is rather better than at low ones. We consider the bulk measurements as more reliable than the total gas phase pressure measurements, since the temperature dependence of the total gas phase pressure measurements vary quite strongly between similar solution concentrations. Unfortunately, we do not know why this is the case and were not able to improve the reproducibility of these measurements.
We have published a companion paper in ACPD (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) that presents 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.

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.

We consider the error in the total gas phase pressure measurements is 0.03 in absolute a_w. *The present study shows, that temperature dependence of water activity is indeed often strong and complex at lower temperatures typical of the upper troposphere. In the present situation, we consider the applicability of the water activity criterion (Koop et al., 2000) more reliable than extrapolation of water activity to lower temperatures for a given solution composition. We think that applying the water activity criterion to the homogeneous freezing curve measured by the DSC method leads to better prediction of water activity at homogeneous freezing temperatures than extrapolations from data acquired at higher temperatures.*

We add the following sentence to the manuscript (page 12684, line 11):
"We conservatively estimate the uncertainty in the water activity in organic solutions to be twice of that determined for pure water ice, namely ±0.03 in absolute a_w*, to account for possible artefacts by residual foaming and/or temperature gradients due to the glass beads."*

We correct the footnotes in tables12,13, 14, and 16 to:
" The accuracy of the water activity measurements is ±0.03 (absolute range) in* a_w*."*

We change the footnotes in tables 3, 4, 5, 6 to:
" The accuracy of the water activity measurements is specified by the manufacturer as ±0.015 (absolute range) in* a_w*."*

We change the footnotes in tables 7 and 8 to:
" The accuracy of the water activity measurements is specified by the manufacturer as ±0.003 (absolute range) in* a_w*."*

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.

We have published a companion paper in ACPD (see above) that presents a new, improved parameterisation of the temperature dependence of activity coefficients in the AIOMFAC model. For electrolyte-free organic and organic–water mixtures the AIOMFAC model uses a group-contribution approach based on UNIFAC. AIOMFAC contains a recently extended parameterization of organic-inorganic interactions, mainly based on room temperature data. Inorganic-organic interactions might be different at low temperatures but there is too little experimental data available that would make such a parameterization feasible at this point.
We refer in the revised manuscript to the companion paper by modifying the second section of the conclusions (page 12696, lines14-24) the following way:

“More accurate a_w data at low temperatures are needed in the context of applications of homogeneous ice nucleation theory at upper tropospheric temperatures. The experiments presented in this study provide new equilibrium data sets useful for the development and improvement of thermodynamic activity coefficient models, such as UNIFAC (UNIquac Functional group Activity Coefficients) and AIOMFAC (Aerosol Inorganic–Organic Mixtures Functional groups Activity Coefficients). For electrolyte-free organic and organic–water mixtures the AIOMFAC model uses a group-contribution approach based on UNIFAC. We present in a companion paper (Ganbavale et al., 2014) a new, improved parametrisation of AIOMFAC that makes, in addition to published data, use of the data collected in this study. In turn, improved thermodynamic models can be used for more accurate predictions of the temperature dependence of activity coefficients of water and other solution constituents, as well as equilibrium compositions of multiphase systems for mixtures and environmental conditions, for which experimental data is unavailable.”

Response to Referee #2 (*italic*):

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 a_w *but not on the nature of the solute. We can reconcile both theories (in numerical simulations not presented here) by using functions* $s(a_w)$ *and* $g(a_w)$ *with physically plausible dependencies on* a_w*."*

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 a_w *(despite sufficient supply of water from outside of the glassy phase). Koop et al. (2000) take effects of cooling rate into account, since delta(*a_w*) 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.