Atmospheric
Chemistry
and Physics
Discussions

Open Access

Interactive comment on "Quantifying water diffusion in high-viscosity and glassy aqueous solutions using a Raman isotope tracer method" by H. C. Price et al.

Anonymous Referee #1

Received and published: 20 December 2013

The authors report water diffusion data for aqueous solutions of atmospheric relevance. They use a Raman microscopic technique utilizing isotopic labeling following the approach pioneered by Zhu et al. (2011). They adapted the technique for studying atmospheric relevant aqueous solutions at different water activities. The paper is well written, the experimental procedure is clearly outlined and the results are presented comprehensibly. It is well suited for ACP and should be published after some revision. I list the points where I feel revision is needed below:

- one concern relates to the fits given in Fig. 6: Here the authors present their measured diffusion constants of water into different aqueous matrices, with fits for each

matrix to a Vogel-Fulcher-Tamman expression. First, I feel the authors should show the whole water activity range (i.e. from 0.0 to 1.0) on the x-axis. Obviously, the fits for all substances need to converge into the diffusion constant for water in water at a water activity of 1.0. My impression from what is presented in the figure is that this is not being the case now and refitting is needed. It is more difficult to do a reasonable fit to water activities approaching a water activity of 0, since the measurement with the technique used by the authors limit the accessible range to water activities of about 0.2 and higher. However, it is clear that even in a matrix containing no water at all, there will be a finite diffusion constant of water. Thus the authors have to check whether their fits lead to unreasonable low water diffusion constants for the pure substances. This seems especially critical for the fit of levoglucosan. In addition, I feel strongly that the authors should provide the reader with the coefficients of the fit (I suggest giving this in an appendix).

- My next major concern applies to Eq. (4) on page 29390: This equation hold only for the case of linear diffusion, i.e. if the diffusion constant is **independent** of concentration, but not for the cases studied in this paper! Hence, also the data presented in Fig. 8 as well as the discussion up to line 7 on page 29290 is not correct. In order to calculate a time scale for diffusion where the diffusing species acts a plasticizer you need always to specify the conditions from which you start to the ones where you wait to come into equilibrium again. These means that you have to take into account the history of relative humidity and temperature changes, since those will be manifesting themselves in concentration gradients within the particle. But even when you start with a homogeneous particle at the beginning and do a step change in relative humidity you need to solve the full non-linear equation to calculate time scales. This may be best illustrated using an example: I presume the authors mean in their sentence (line 5, page 29390): *"Figure 8a shows these timescales for water diffusing into sucrose, levoglucosan and raffinose/M5AS aqueous spherical droplets of radii between 100nm and 1 μm at 20% RH."* actually the half time needed to reach equilibrium upon a change from a homogeneous particle at 0% RH exposed to rapid change to 20% RH. Here

neither the diffusion constant at aw=0.0 (what constant would the authors use as they provide no fit down to aw=0?) nor the diffusion constant at aw=0.2 allows to calculate the time response, but you need to put the concentration dependence of the diffusion constant into a model like KM-GAP (Shiraiwa et al., 2012) or the one used by Zobrist et al., 2011 to get the time response right. If you use simply eq. (4) and the diffusion constant at aw=0.2 you can easily be orders of magnitude to fast (depending on the magnitude of the diffusion constant at aw=0.0) and if you would use the one at aw=0.0 and put it into eq. (4) you may be orders of magnitudes to slow. Of course the problem of applying Stokes-Einstein is an independent one from using wrongly eq. (4) and correctly discussed by the authors. The authors have to rethink how they want to discuss the problem of Stoke-Einstein. Easiest would be to compare just the diffusion constants measured with those derived via Stokes-Einstein. However, the numbers given in Fig. 8 need to be corrected, most significantly for the lower range in RH.

- The authors provide the value of the diffusion constant of aqueous sucrose in the abstract, but do not state the water activity for this diffusion constant (presumably 0.2?).

- In the paragraph starting on line 21 on page 29377 Zobrist et al., 2011 should be cited as well as Koop et al. 2011, since experimental evidence of the core-shell structure has been given in this paper already.

- In line 8, page 29379: I feel the citation of Bones et al., 2012 is inappropriate since those authors also measured essentially water diffusion and not viscosity.

- Section starting line 26, page 29379: I think the technique used by Zobrist et al., 2011 allows the determination of density as shown in the paper of Lienhard et al., 2012 of the same group. They seemed to have used literature data for the study of Zobrist et al., 2011 simply because literature data were available.

- Sentence starting line 3, page 29380: Zhu et al., 2011 deserve a citation at this point, I feel the authors should acknowledge explicitly that they are adapting the Zhu et al. approach right at the beginning of the paragraph and not somewhere hidden later in

the paragraph. In the context I also feel that the statement in the summary on line 25 page 29392 (*".. we describe a new experimental system..."*) should be changed to something like: "we adapted the technique pioneered by Zhu et al. to an experimental system allowing measuring aqueous solutions of atmospheric relevance at different water activities...".

- Fig. 7 and discussion of this figure: Again, the authors should plot the full range of water activity, i.e. from aw=0 to aw=1. Then it should be noted that Zobrist et al., 2011 estimates that their parameterization at room temperature carries an uncertainty of a factor of three below a water activity of 0.6 and about 30% for aw larger than 0.6. That means that there is agreement within uncertainty with the Zobrist et al. parameterization, but not with the He et al., 2006 parameterization for the driest data point. This discussion needs to be made carefully, since it influences strongly the estimate of the diffusion constant at aw=0. Also note that the parameterization of the authors has a point of inflection at about aw=0.8. Do the authors think that is real? In addition, I feel it would make sense to add the data of Zhu et al., 2011 and the ones of Parker and Ring, 1995 and Tromp et al., 1997 to this figure even though those measured water diffusion in maltose and not sucrose. From a first rough view those seem to strongly support the data of the present paper.

- Section 3.4: The authors show interesting morphology maps for the gel of $MgSO_4$. Do they believe their finding also hold for accumulation mode size particles?

References:

Bones et al.: PNAS, 109, 11613-11618 (2012).

He et al.: J. Appl. Phys., 100, 074702-074711 (2006).

Lienhard et al.: J. Phys. Chem. A, 116, 9954-9968 (2012).

Parker and Ring: Carbohydr. Res., 273, 147-155 (1995).

Shiraiwa et al.: ACP, 12, 2777-2794 (2012).

Tromp et al.: Carbohydr. Res., 303, 199-205 (1997).

Zobrist et al.: PCCP, 13, 3514-3526 (2011).

Zhu et al.: J. Phys. Chem. B, 115, 5849-5855 (2011).

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 29375, 2013.