

Interactive comment on “A study of the phase transition behavior of mixed ammonium sulfate – malonic acid aerosols” by C. F. Braban and J. P. D. Abbatt

C. F. Braban and J. P. D. Abbatt

Received and published: 12 July 2004

Responses to Referee 1’s specific comments are in italics below the original comment:

Introduction, paragraphs 2–3 and also later in text: ...binary AS-dicarboxylic acid mixtures at 3 compositions... and ...detailed case studies of a three-component aerosol...: it is not clear to me how the authors use the terms binary and ternary. In one case, they seem to treat water as a component, in the other, they do not. They should make the manuscript more consistent in this respect.

The reviewer’s point here is well taken and is to some extent true, and I will go through and check for consistency.

Introduction, paragraph 3: the authors should also mention the works by Wise et

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al.[2003] and Marcolli et al. [2004].

This is true and these references will be added in.

Section 3.2, paragraph 1: ...the lowest RH...can be calculated and measured...: the authors should specify what kind of calculation they mean.

The theoretical calculation for the deliquescence of multicomponent aerosol solutions is described in Seinfeld and Pandis p.514 – 519 and references therein. As none of these types of calculations was performed during this work, the methods were not discussed. However a reference will be inserted into the paper for further information.

Section 3.2, paragraph 1: the authors should specify how they predicted EDRH = 73% for the AS-MA system. They should discuss the accuracy of the prediction. They should also give the measured DRH values for pure AS and MA at 283 K (indicated by the arrows 1 and 2 in Figure 3A).

The predicted EDRH was obtained from interpolation of the data from Brooks et al. (2003) and Choi and Chan (2002). A re-evaluation of this data in preparing these comments leads me to think a value of predicted EDRH = 72% is more accurate from the interpolation. There is significant scatter in the room temperature therefore a reasonable estimate of the error in this number is 2-3%.

Section 3.2.2, Figure 3B: Between EDRH and the RH of full deliquescence, crystalline and dissolved AS should coexist in the same particle, giving rise to two ammonium peaks at 1422 cm⁻¹ and 1455 cm⁻¹. However, according to Figure 3B, a continuous shift of the ammonium band is observed. Is this a problem of resolution? The authors should comment on this.

In Figures 2 and 3 the transition between the dry AS peak position and the aqueous position does occur more gradually (over a range of ~ 5% RH) than in the pure AS experiment, suggesting that dissolution is occurring. However, the two peaks are not well-resolved. One potential approach would be to use a fitting procedure involving

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two overlapping peaks. This might be able to deconvolute the two phases, but was not attempted as part of this study.

Section 4.1: For mixtures of miscible components, deliquescence starts at the EDRH and ends at a higher RH. The results should be discussed in this respect. Specifically, the second sentence of paragraph 1 should be reformulated. Full deliquescence should occur at the EDRH only for the eutonic composition.

These reviewer comments are correct, and the sentence in Section 4.1 will be modified to "deliquescence commenced at the eutonic".

The authors should try to indicate also the completion of deliquescence as Choi and Chan [2002] have done.

The onset of deliquescence is fairly clear for the compositions for which either malonic acid or ammonium sulfate are the minor components ($f_{MA} < 0.25$ and $f_{MA} > 0.9$). However due to the large changes in the IR, in particular the broadening of most of the modes and the change in scattering as a function of RH, we do not think it is possible to state the end of deliquescence with as much certainty. In general, we can say that it appears as though all systems have fully deliquesced by at least 82% RH, if not at a somewhat lower RH.

The sentence In particular it only requires a very low level of AS or MA to shift deliquescence to the EDRH... should be reformulated to: ...to shift the starting point of deliquescence to the EDRH. But this is true for any system.

We agree that the sentence should be modified, and technically it is true for any system. However we do not think it is clear from the literature the concentration at which an "impurity" begins to act as a second component and shifts the transition of the major component. It strikes us as important to stress this point because in the atmosphere the organic component may have a significant effect when present in low fractions.

Section 4.1, paragraph 2, Figure 5: The first hypothesis can not explain the observa-

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tions: if crystalline AS was present, it should not go into solution below EDRH, which is at 73 % according to the manuscript and between 70.9 and 71.7 % RH according to Brooks et al. [2002]. The Figure caption saying AS observed to go into solution is misleading: In the text it is assumed that AS remains at least partly liquid.

We believe the first hypothesis is valid because if full efflorescence has not occurred, there will be a metastable supersaturated solution present. The solution is hypothesized to be mostly malonic acid, but potentially a non-stoichiometric solution of malonate, malonic acid, ammonium, sulfate and hydrogen ions (see response to comment of S. Martin). It is not known if AS (or letivocite) has an appreciable solubility in that liquid but it probably does, given that it is a highly soluble salt. If so, the AS (or letivocite) solubility would change as a function of the degree of supersaturation of the aqueous phase.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 2949, 2004.

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