

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

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The work by Braban and Abbatt provides an important contribution to our understanding of the phase transitions of mixed component systems.

The purpose of this comment is to suggest that letovicite forms in the studied system. Ammonium sulfate and malonic acid can combine to form an acidic sulfate solid, namely letovicite (triammonium hydrogen disulfate).

The authors rule out the formation of letovicite on lines 24 of page 2954 through line 7 of page 2955. Principally, the authors state that bisulfate has a peak at 1300 cm^{-1} whereas the observed spectra do not show a peak in this region. In fact, the principal

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peak of bisulfate is 1200 cm^{-1} , and I will assume that the manuscript has a typo. In lines 16-18 on page 2958, the authors state that Figure 1C is similar to Figure 2C. I wish to dispute this statement, specifically in regard to the peak at 1100 cm^{-1} , which is significantly broader in Figure 1C than in Figure 2C. Moreover, shoulders are clearly apparent in Figure 1C. I suggest that the peak in Figure 1C is consistent with letovicite peaks as shoulders at 1210 cm^{-1} and 1095 cm^{-1} around a central ammonium sulfate peak at 1115 cm^{-1} .

Relevant literature on the spectroscopy of letovicite includes (a) Damak, M.; Kamoun, M.; Daoud, A.; Romain, F.; Lautie, A.; Novak, A. J. *Mol. Struct.* 1985, 130, 245-254 and (b) Kamoun, M.; Lautie, A.; Romain, F.; Novak, A. J. *Raman Spectroscopy* 1988, 19, 329-335. Moreover, we (Schlenker et al.) have a manuscript submitted showing spectral assignments of aerosol crystalline ammonium sulfate at 1115 cm^{-1} and crystalline letovicite at 1095 , 1134 , 1188 , and 1208 cm^{-1} .

The suggestion of the formation of letovicite is also consistent with the behavior seen in Figure 5. Namely, whereas pure crystalline ammonium sulfate deliquesces at 80% relative humidity, pure crystalline letovicite deliquesces at 69.5%. A step change consistent with this change in dominant solid at 10 to 30 wt% is apparent in Figure 5. Of course, this interpretation based upon pure compounds does not take into account malonic acid and hence the shift to a eutonic relative humidity, as mentioned by Braban and Abbatt.

With this comment, I wish to suggest that the evidence presented in the manuscript appears to unduly rule out the formation of letovicite. If this solid forms, some of the implications discussed by Braban and Abbatt may also be affected (e.g., lines 10-16 on page 2960).

As an example of a possible complication, consider first a solution composed of 10% nitric acid (as an analog to malonic acid) and 90% ammonium sulfate. If the only solids allowed to form are letovicite and ammonium sulfate, then both of these solids form at

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low relative humidity, and an aqueous layer of slightly acidified ammonium sulfate remains. This complex behavior is possible because the solution contains nitrate, proton, ammonium, sulfate, and water. That is, because nitric acid and ammonium sulfate dissociate, the system has five components instead of three so that solids like letovicite, which do not lie on the central axis of composition mixtures of nitric acid and ammonium sulfate, can form. When this finding is applied to a system for which malonic acid is substituted for nitric acid, it is reasonable (in the absence of a phase diagram but consistent with Gibbs phase rule) to suggest that ammonium sulfate and letovicite both crystallize and a residual aqueous layer of slightly acidified ammonium malonate remains.

The work by Braban and Abbatt is an important contribution towards understanding the phase transitions of multicomponent particles.

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