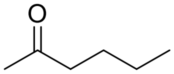
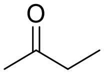
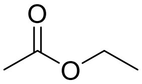
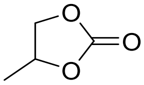
Electronic Supplementary Material (ESI) for Environmental Science: Atmospheres.

Supplementary Information

Measurements of the partitioning of nitric acid and sulfuric acid in aqueous/organic phase-separated systems

Benjamin L. Deming and Paul J. Ziemann

Table S1. Organic components in aqueous/organic phase-separated systems and their structures.

Organic Phase	O:C Ratio	Structure
Hexanes	0.00	
2-Hexanone	0.25	
2-Butanone	0.25	
Ethyl acetate	0.50	
Propylene carbonate	0.75	

1. Effect of mixing time on measured acid partitioning

For these measurements, 1.5 mL of ethyl acetate and 1.5 mL of aqueous 1 M HNO_3 or H_2SO_4 were combined in a test tube, vortexed for varying amounts of time, and centrifuged. The organic layer was removed and transferred to a pre-weighed vial, exposed to gaseous ammonia for 15 s, the solvent was evaporated under a stream of nitrogen, and then the vial was reweighed on the microbalance. Figure S2 shows that 5s of mixing is sufficient to achieve equilibrium phase partitioning, although 30 s was typically used.

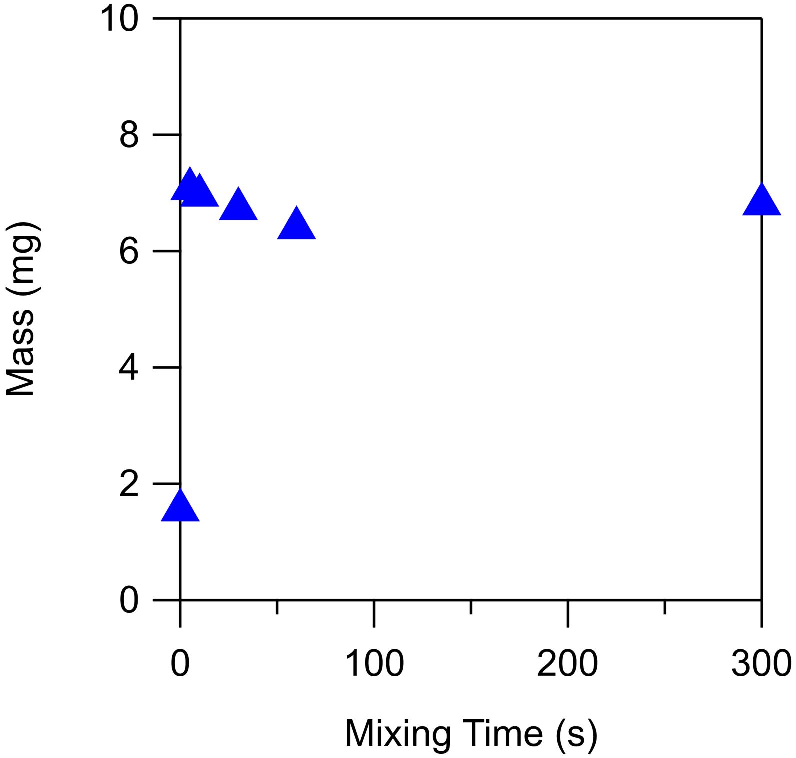


Figure S1. Effect of mixing time on measured partitioning of HNO_3 from water to ethyl acetate. The point at zero seconds indicates that some mixing occurs without vortexing.

2. Effect of exposure time to ammonia on measured acid partitioning

For these experiments the same procedure described in section 1 above was used with 30 s of vortexing and varying ammonia exposure times. As shown in Figure S2, 5 s is sufficient to convert all the acid in the organic phase to the ammonium salt, although 15 s was used in all experiments.

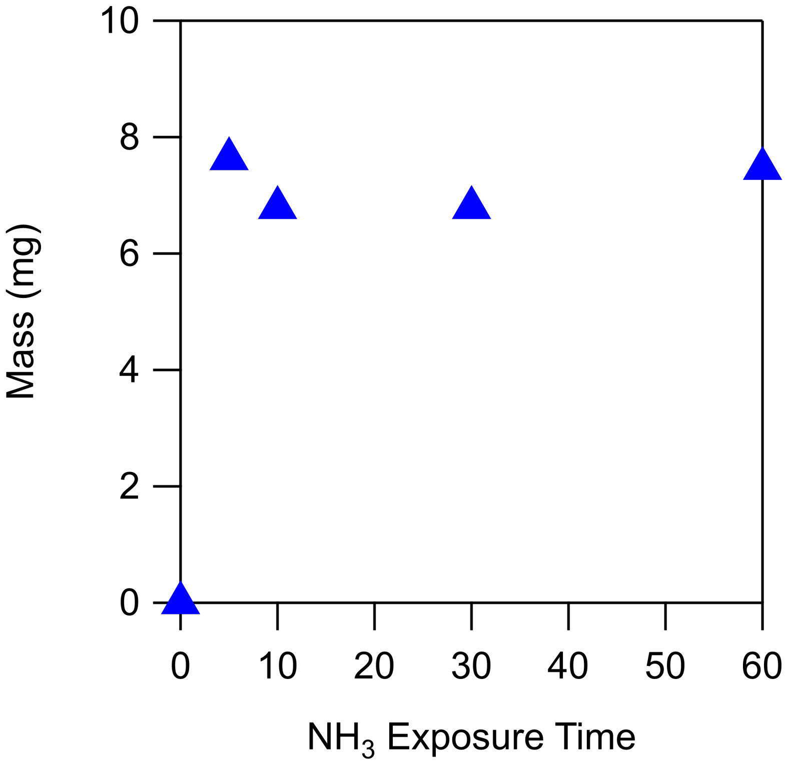


Figure S2. Effect of ammonia exposure time on measured partitioning of HNO_3 from water to ethyl acetate. The point at zero seconds indicates that no salt is formed until ammonia is added.

3. Evaluation of the possible loss of ammonium nitrate during solvent evaporation

For these experiments the same procedure described in section 1 above was used with 30 s of vortexing and 15 s ammonia exposure time, with varying solvent evaporation times after the sample was determined to be dry. The results in Figure S3 show that there is no significant loss of ammonium nitrate even after flowing nitrogen over a dried sample for 1 h.

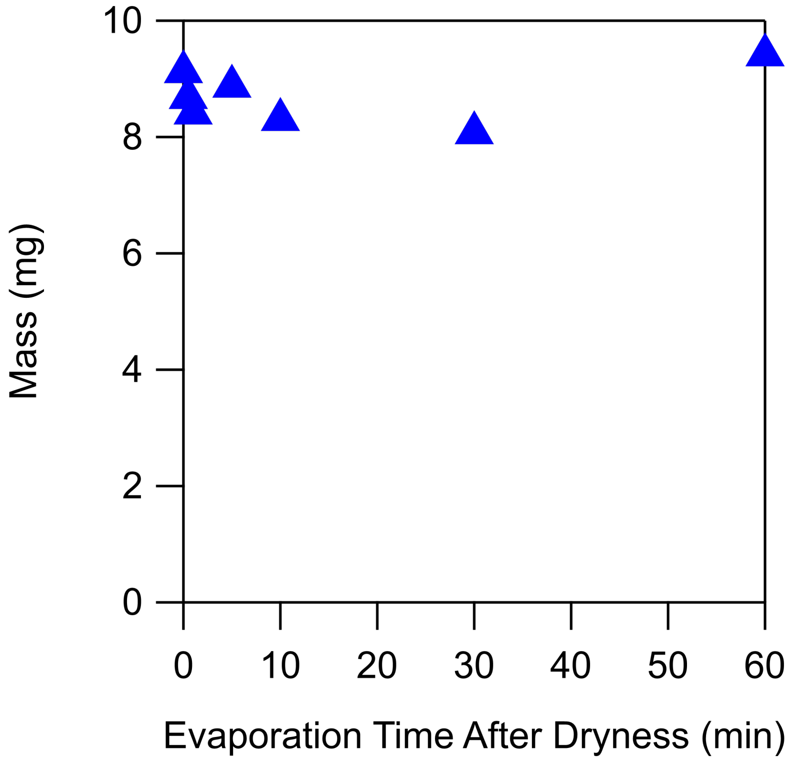


Figure S3. Effect of drying time on measured partitioning of HNO_3 from water to ethyl acetate.

4. Evaluation of the ammonium sulfate salts formed in partitioning experiments

For these experiments the same procedure described in section 1 above was used with 30 s of vortexing and 15 s ammonia exposure time, but with sulfuric acid. The dried sample was then placed in an oven at 230°C along with samples of ammonium sulfate and ammonium bisulfate standards for varying lengths of time. Figure S4 shows that the ammonium salt sample obtained following phase partitioning of sulfuric acid and the ammonium sulfate standard did not lose mass over 100 min, whereas the ammonium bisulfate standard lost mass continuously over this period. Although we did not have letovicite or ammonium sulfate hydrate standards to test, it seems likely that these also would have decomposed under these conditions by loss of water. Ammonium sulfate is expected to begin to decompose at ~250°C.[1] This result suggests that the samples obtained in these studies by exposing sulfuric acid to ammonia were ammonium sulfate rather than other salts.

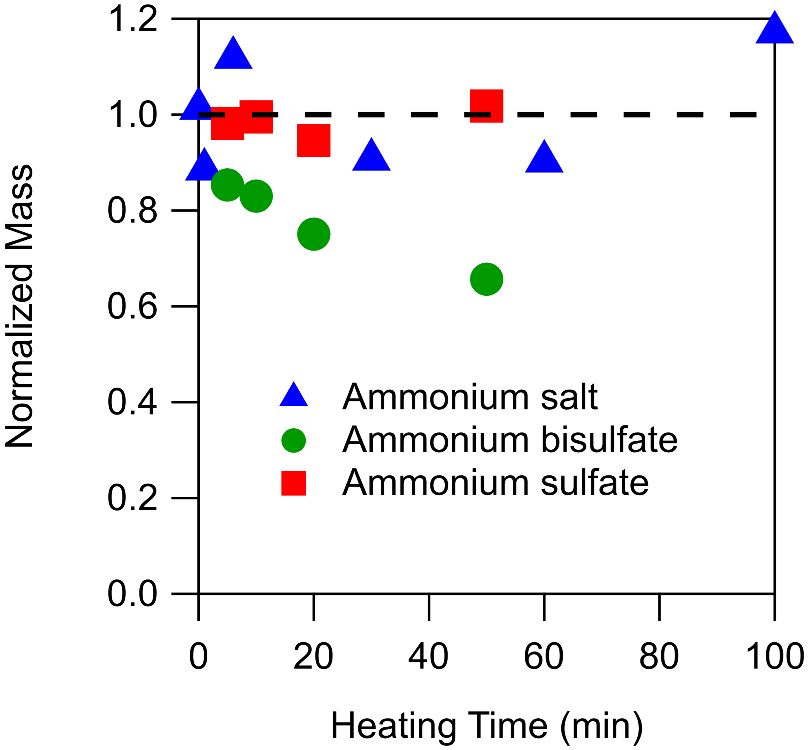


Figure S4. Effect of heating at 230°C on the mass of ammonium salt obtained following phase partitioning of H_2SO_4 from water to ethyl acetate and the mass of ammonium sulfate and ammonium bisulfate standards.

5. Derivations considering the second dissociation of sulfuric acid

The derivations outlined in the main body of this work only consider a single dissociation step of the inorganic acid. While this is valid for nitric acid, it is not necessarily true for sulfuric acid. For sulfuric acid, we instead define T_{aq} as

$$T_{aq} = H_2SO_{4\,aq} + HSO_{4\,aq}^{-} + SO_{4\,aq}^{2-} \approx HSO_{4\,aq}^{-} + SO_{4\,aq}^{2-} \tag{S1}$$

where it is assumed that the concentration of $H_2SO_{4\,aq}$ is negligible. The ratio of aqueous phase sulfate to bisulfate

$$F = \frac{SO_{4\,aq}^{2-}}{HSO_{4\,aq}^{2-}} \tag{S2}$$

can then be assumed to be relatively constant over the range of acid concentrations investigated here (which was verified using AIOMFAC to be 0.46), and D_{SO4} is defined as the partitioning constant of SO_4^{2-}

$$D_{SO_4} = \frac{SO_{4\,org}^{2-}}{SO_{4\,aq}^{2-}} \tag{S3}$$

Substituting Equations S1–S3 into Equation 10 from the main text (here labelled as Equation S4)

$$R = \frac{D_{un}}{K_{a,aq}} T_{aq} + D_{diss} \tag{S4}$$

gives

$$R = \frac{D_{un}}{K_{a,aq}} \frac{1+2F}{(1+F)^2} T_{aq} + D_{diss} \frac{1}{1+F} + D_{SO_4} \frac{1}{1+\frac{1}{F}} \tag{S5}$$

As discussed in Section 3.4 in the main text, it was found experimentally that ammonium sulfate does not significantly partition to any of the organic phases investigated here. Assuming then that $D_{SO4} = 0$, Equation S5 reduces to

$$R = \frac{D_{un}}{K_{a,aq}} \frac{1+2F}{(1+F)^2} T_{aq} + D_{diss} \frac{1}{1+F} \tag{S6}$$

The D_{un} and D_{diss} values obtained as discussed in the main text can therefore be corrected by multiplying by a factor of $\frac{(1+F)^2}{1+2F} = 1.11$ for D_{un} and $1 + F = 1.46$ for D_{diss}.

6. Validation of liquid-liquid equilibrium model

Although the algorithm outlined in Zuend and Seinfeld[2] was used as a guide for the code in this work, it was important to verify that the model performed as expected. To validate our implementation, we reconstructed a figure in their work by using the same model inputs. Figure 5d was chosen because it most closely resembles how the model would be used here. Briefly, mixtures containing water, sodium chloride, gallic acid, sorbitol, methylglutaric acid, hydroxybenzoic acid, octanetetrol, and hydroxypinonic acid were modeled. The mole fraction of water in the total mixture was varied from 0.25 to just under 1.0. The model was used to calculate the phase partitioning of the mixture components as the partitioning vector Q_A, defined as the fraction of each componnt in the predominantly aqueous phase. The same data points from Figure 5d in Zuend and Seinfeld[2] were digitized using the "IgorThief" tool in Igor Pro. The two datasets are shown together below in Figure S1. Since the mole fraction of water in the acid partitioning measurements in this work was typically ~0.85, the range from 0.6 to 1.0 is shown. The agreement between the present results (markers) and the previous outputs (lines) suggest that our implementation of the liquid-liquid equilibrium model is working properly. Note that there is a slight, but constant, offset between the results for hydroxypinonic acid. The reason for this is unclear but may be attributable to breaking the compound into slightly different functional groups for AIOMFAC inputs.

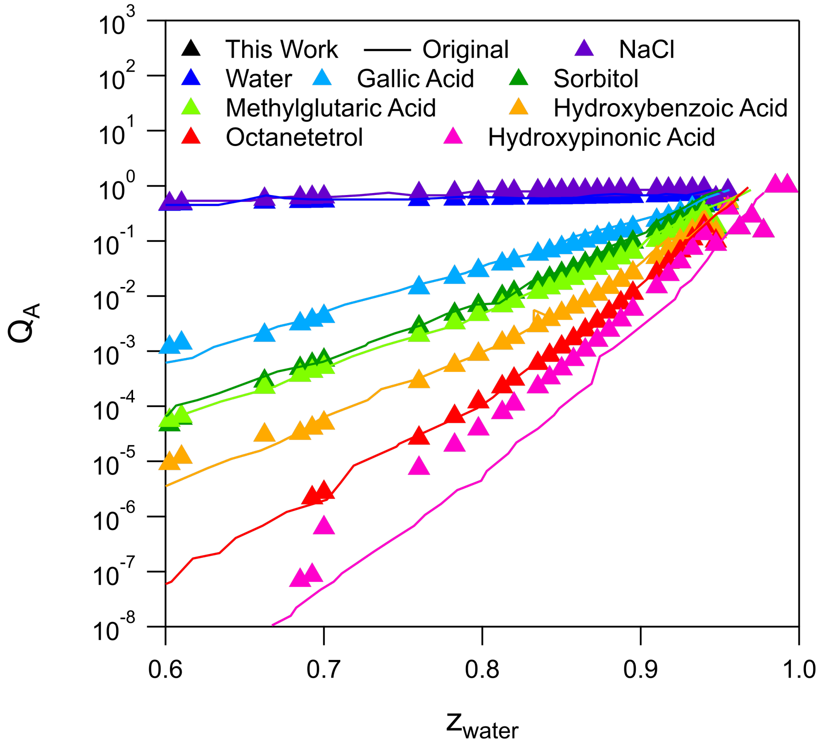


Figure S5. Comparison of LLE model outputs from this work (markers) compared with previously published results (lines). Q_A is the fraction of each species in the aqueous phase and z_{water} is the mole fraction of water in the total mixture.

7. Literature acid partitioning curves

Measurements of the partitioning of sulfuric acid and nitric acid between water and organic phases are rare. In the extensive compilation of partitioning measurements by Stephen and Stephen[3] only three relevant data sets were found. The acid partitioning measurements and fits to the data are shown below.

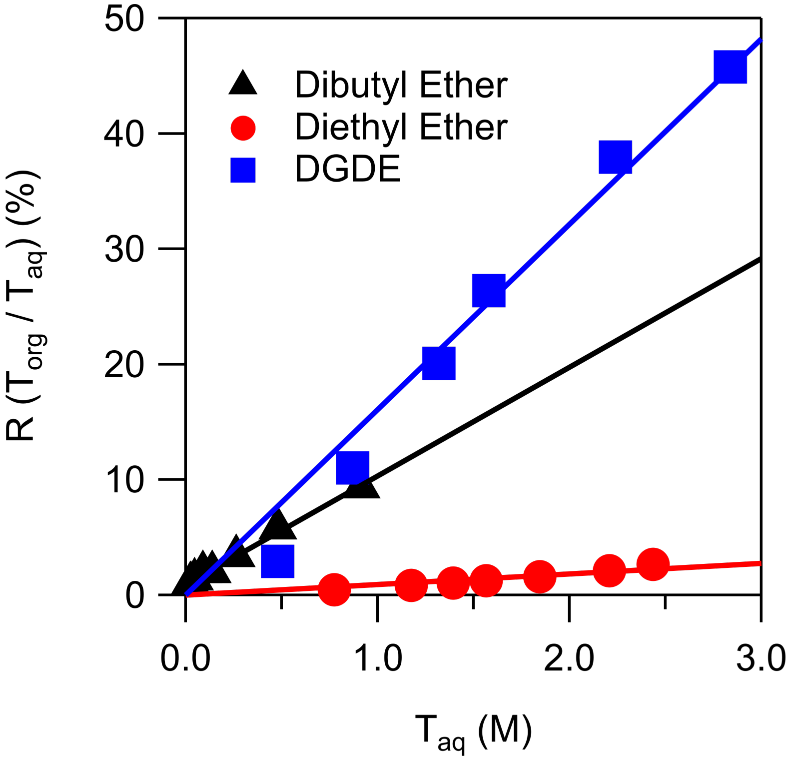


Figure S6. Partitioning of nitric acid between three solvents (dibutyl ether, diethyl ether, and diethylene glycol dibutyl ether) and water determined from literature data.[3]

References

1. Jariwala, M., J. Crawford, and D. J. LeCaptain, In situ Raman spectroscopy analysis of the regeneration of ammonium hydrogen sulfate from ammonium sulfate. Ind. Eng. Chem. Res., 46, 4900–4905.
2. A. Zuend and J. H. Seinfeld, A practical method for the calculation of liquid-liquid equilibria in multicomponent organic-water-electrolyte systems using physicochemical constraints, Fluid Phase Equilbr., 2013, 337, 201-213.
3. H. Stephen and T. Stephen, Solubilities of inorganic and organic compounds, Oxford Pergamon Press, 1963.