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

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Partitioning of nitric acid and sulfuric acid between aqueous and organic phases may play a role in the chemistry of aqueous/organic phase-separated atmospheric aerosol particles, as well as other environmental systems. To assess the extent to which these acids partition to organic phases, organic compounds with O : C ratios ranging from 0 to 0.75 were mixed with acidified aqueous phases. The organic phase was removed and its acid content quantified with a mass-based measurement. Up to 60% of the acid was observed to partition to the organic phase, present either entirely in the dissociated form, the undissociated form, or both depending on the organic phase. Values of partitioning coefficients, D_{diss} and D_{un} , corresponding to partitioning of the dissociated and undissociated acid, were determined by fitting a simple partitioning model to the data. Values of D_{un} correlated well with the O : C ratio of the organic component and to a lesser extent with the water content of the organic phase. The addition of ammonium sulfate led to an increase or decrease in partitioning of sulfuric acid to the organic phase, apparently depending on the balance between the resulting enhancement in the HSO_4^- concentration and the reduction in the water content of the organic phase. These results demonstrate that significant fractions of sulfuric and nitric acid can partition to the organic phase in phase-separated systems in undissociated and dissociated forms, and thus potentially participate in specific or general acid catalysis of organic reactions.

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Environmental significance

Aqueous/organic phase-separated systems are common to the atmosphere in the form of aerosols, but are also found in other environments such as soils and the surface microlayer of oceans and lakes. In many of these systems inorganic acids are presumed to reside predominantly in the aqueous phase, but data on this partitioning are relatively rare. Measurements of the partitioning of nitric acid and sulfuric acid between an aqueous phase and a number of model organic phases covering a range of polarity demonstrate that significant quantities of acid can partition to the organic phase, to an extent that depends on the O : C ratio of the organic phase, as well as other factors. These acids can then participate in organic reactions.

1. Introduction

Liquid–liquid phase-separated systems are prevalent in the environment, particularly in the atmosphere.^{1,2} Depending on their composition and the surrounding conditions, homogeneous aerosol particles can undergo phase separation, typically forming a phase dominated by water, inorganic species, and water-soluble organic compounds and a relatively non-polar, organic-rich phase.³ This is not a rare occurrence; recent modeling work suggests that in the southeastern United States

approximately 65% of the aerosol is phase separated.⁴ Whether aerosols are phase-separated can have dramatic impacts on properties such as cloud condensation nuclei activity,⁵ particle mass and growth,^{6,7} particle reactivity,⁸ and optical properties.⁹ Because phase-separation can so strongly influence aerosol properties, much effort has been dedicated to determining the factors that control or predict its occurrence.^{10–12} Compositionally, one of the best predictors of whether an aerosol will undergo liquid–liquid phase-separation is the ratio of oxygen to carbon atoms of the organic material (O : C ratio).¹³ This value serves as a surrogate for polarity or oxidation state, as it is readily determined by mass spectrometry in laboratory and field measurements.¹⁴

In addition to having important physical properties, atmospheric aerosols also serve as sites for condensed-phase chemical reactions, essentially acting as suspended micro-reactors. Particle-phase reactions of organic compounds can be

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initiated by OH radicals, NO₃ radicals, and O₃, similar to atmospheric gas-phase oxidation, and they can occur *via* the coupling of functional groups (such as carbonyl, hydroxyl, hydroperoxy, and carboxyl) to form oligomers.^{15,16} These oligomerization reactions can modify particle chemical and physical properties and also contribute to particle growth by reducing effective compound vapor pressures, thus drawing more mass into the particle through subsequent gas-to-particle partitioning. Like many condensed-phase reactions, a number of those that can occur in aerosol particles are catalyzed by strong acids. For example, the dehydration of alcohols, the formation of hemiacetals and hemiketals, the formation of acetals and ketals, the conversion of hydroperoxides to carbonyls, and ester formation can be significantly faster in the presence of strong acid.¹⁶ Notably, many of these reactions produce water as a product, so that in an aqueous environment there will be a strong driving force against their occurrence. But in a phase-separated system, one in which organic reactants are concentrated in an organic phase where the water content is much reduced, such reactions may be highly favorable as long as sufficient acid partitions to the organic phase to drive catalysis.

The most common inorganic acids in the atmosphere are sulfuric acid, predominantly formed from oxidation of SO₂, and nitric acid, formed from various reactions of nitrogen oxides.¹⁷ Though strong acids in aqueous solution, they may exist in either their dissociated or undissociated form in predominantly organic phases. This distinction is especially important for the catalysis of particle-phase reactions. When the solvent mixture is sufficiently polar to allow significant dissociation, the rate is likely controlled by the H⁺ concentration (referred to as specific acid catalysis). On the other hand, if the undissociated form of the acid dominates in the solution, the rate can instead be determined by the molecular form (general acid catalysis).¹⁸ Depending on the reaction and conditions, one pathway may be significantly faster than the other. It is therefore important to have some understanding of the extent to which sulfuric and nitric acid partition to organic phases, as well as the forms in which they reside.

The purpose of this study was to investigate the partitioning of sulfuric and nitric acid in model organic/aqueous phase-separated systems that were chosen to act as proxies for phase-separated aerosol. Understanding the partitioning behavior of these acids in these simple model systems can help determine the extent to which the processes discussed above are relevant to real environmental systems.

2. Materials and methods

2.1 Materials

Chemicals with purities/grade and suppliers were as follows: HPLC grade water, ACS grade nitric acid (69 ± 1 w/w% in water, <5 ppm impurities), and ACS grade hexane (a mixture of isomers, 98.5%) from Macron Fine Chemicals; ACS Plus grade sulfuric acid (96.5 ± 1.5 w/w% in water, <3 ppm impurities), ACS grade ethyl acetate (99.9%), and ammonium sulfate (99.5%) from Fisher Scientific; 2-hexanone (98%) from J&K Scientific; ACS reagent grade 2-butanone (>99.0%) and

anhydrous propylene carbonate (99.7%) from Sigma-Aldrich; ammonium bisulfate (99.9%) from Alfa Aesar; and anhydrous ammonia and ultra-high purity (UHP) nitrogen from Airgas. Chemicals were used as received, with no further purification.

2.2 Acid partitioning measurements

The partitioning of nitric acid and sulfuric acid in organic/aqueous phase-separated systems was investigated using the shake-flask method.^{19,20} The procedures used in this work were validated in a number of experiments noted below and described in detail in the ESI along with Fig. S1–S4.† Aqueous phases consisted of either pure water or 30 w/w% = 2.27 M (mol L⁻¹) ammonium sulfate solutions that are typical for the atmosphere.²¹ Organic phases were chosen to act as proxies for organic aerosol, covering a range of O : C ratios and therefore polarities. To be compatible with the partitioning measurements they also needed to be non-reactive towards both strong acid and ammonia for the concentrations and exposure times used here. Hexane, 2-hexanone, 2-butanone, ethyl acetate, and propylene carbonate were thus used as organic phases. Other relevant organic compounds tested, notably carboxylic acids, alcohols, and aldehydes, were found to react with the ammonia and/or strong acid, and therefore could not be used. The phases and relevant properties are listed in Table 1, and the structures of the organic components are given in ESI.†

The aqueous phases were acidified to create solutions between approximately 0 and 1 M, not considering any reaction with ammonium sulfate. Aliquots (typically 1.5 mL each) of organic phase and acidified aqueous phase were added to test tubes and then mixed by vortexing for approximately 30 s, a time that is shown in the ESI† to be sufficient to establish partitioning equilibrium. The test tubes were then centrifuged and 1 mL of organic phase was transferred to a vial pre-weighed on a Mettler Toledo XS3DU Microbalance. Because the addition of acid or ammonium sulfate could change the overall volume of each phase, the total aqueous and organic volumes after mixing were measured using a syringe that is accurate to approximately 0.05 mL. The sampled organic solution was exposed to a slow stream of ammonia (~600 cm³ min⁻¹) for ~15 s, which is shown in ESI† to be sufficient to convert any nitric or sulfuric acid to the corresponding ammonium salt. This was often accompanied by the visible crystallization of these salts. Since strong acids were used, experiments were performed wearing gloves, a lab coat, and goggles. Samples were exposed to ammonia in a fume hood and remained within one for at least 10 min to allow for any residual vapor to dissipate.

With the exception of propylene carbonate, the organic phases were all sufficiently volatile to be removed *via* evaporation in a hood under a steady stream of nitrogen. Since ammonium nitrate might also evaporate during this process (it is much more volatile than ammonium sulfate), experiments described in ESI† were conducted to verify that under the conditions used here no ammonium nitrate was lost by evaporation. The vials, then containing only ammonium salt, assumed to be either ammonium sulfate or ammonium nitrate,



Table 1 Organic and aqueous phases used in these experiments and their relevant properties

| Organic or aqueous phase | O : C ratio | Molecular weight (g mol ⁻¹) | Organic phase water (vol%) | Density (g mL ⁻¹) |
|-------------------------------------|-------------|---|----------------------------|-------------------------------|
| Hexane | 0.00 | 86.2 | 0.01 | 0.66 |
| 2-Hexanone | 0.17 | 100.2 | 2 | 0.81 |
| 2-Butanone | 0.25 | 72.1 | 1 | 0.81 |
| Ethyl acetate | 0.50 | 88.1 | 3 | 0.90 |
| Propylene carbonate | 0.75 | 102.1 | 8 | 1.21 |
| Water | — | 18.0 | — | 1.00 |
| Aqueous ammonium sulfate (30%, w/w) | — | — | — | 1.17 |

were again weighed on the microbalance. The balance is accurate to ± 0.5 μg , corresponding to minimum detectable organic-phase concentrations of 6.3 μM for nitric acid and 3.8 μM for sulfuric acid. Blanks were measured for all systems by conducting identical experiments but without adding acid, and in all cases yielded negligible mass after the organic phase was dried. Samples containing propylene carbonate were dried to a constant mass with nitrogen in a hood in an attempt to remove any organic-phase water, and then weighed. The mass of propylene carbonate was corrected for by treating the samples containing no added acid as a blank. This approach worked well for nitric acid but resulted in nonphysical results (blank mass higher than sample mass) for sulfuric acid, apparently because some residual water could not be fully removed by drying when ammonium sulfate was present. The results for experiments with propylene carbonate have larger uncertainties due to these additional complications.

We note that although the assumption that the mass of salt measured in all these experiments corresponded to either ammonium nitrate (NH_4NO_3) or ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) is valid for the nitric acid experiments, since ammonium nitrate is the only possible salt, in the sulfuric acid experiments ammonium bisulfate (NH_4HSO_4), letovicite ($(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$), or ammonium sulfate hydrate ($(\text{NH}_4)_2\text{SO}_4 \cdot \text{H}_2\text{O}$) might also have formed. If the salt was one of these three instead of ammonium sulfate, then the reported concentration of sulfuric acid would be in error by -15% , -7% , and 12% , respectively. Considering the other sources of uncertainty in these measurements, these alternate forms could be present without significantly affecting the results presented here. Nonetheless, in an attempt to verify that the salt formed was ammonium sulfate, the behavior of a phase-separated salt sample and ammonium sulfate and ammonium bisulfate standards were compared when heated in an oven at 230 $^\circ\text{C}$. Although the thermal decomposition of ammonium sulfate salts is complicated,²² it is expected that ammonium sulfate would be stable at this temperature while ammonium bisulfate, letovicite, and ammonium sulfate hydrate would not. Based on the results of these experiments, which are described in ESI,[†] it appears that the phase-separated salt sample was ammonium sulfate.

The acidity of the organic phases in these systems was also measured over a larger concentration range using pH strips (Sigma Chemical Company). Aqueous phases containing

between 10^{-6} and 10 M of either HNO_3 or H_2SO_4 were prepared and then 2 mL of each aqueous phase and 2 mL of either hexane, 2-butanone, ethyl acetate, and propylene carbonate were added to a test tube and mixed by vortexing for 30 s. The organic layer was then removed using a syringe and a pH strip was submerged in the solvent. The four dye squares were compared visually to the provided key and matched to the closest pH value.

2.3 Data analysis

We consider four potential states of the strong acids, as shown in Fig. 1: undissociated acid ($\text{HA} = \text{HNO}_3$ or H_2SO_4) and dissociated acid (H^+ and $\text{A}^- = \text{NO}_3^-$ or HSO_4^-) in both the aqueous and organic phases. In the figure and throughout the text, the subscript “org” refers to a species in the organic phase, while the subscript “aq” refers to one in the aqueous phase. Note that this framework only considers the first dissociation of sulfuric acid, and that the consequences of this assumption will be discussed in detail below.

The dissociation of these acids in the aqueous phase is well understood and the corresponding values of the acid dissociation constants for the aqueous and organic phases, $K_{\text{a,aq}}$ and $K_{\text{a,org}}$, are defined using the species concentrations as

$$K_{\text{a,aq}} = \frac{[\text{H}_{\text{aq}}^+][\text{A}_{\text{aq}}^-]}{[\text{HA}_{\text{aq}}]} \quad (1)$$

and

$$K_{\text{a,org}} = \frac{[\text{H}_{\text{org}}^+][\text{A}_{\text{org}}^-]}{[\text{HA}_{\text{org}}]} \quad (2)$$

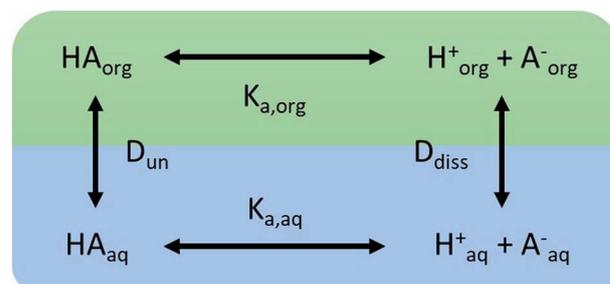


Fig. 1 The four states of strong acids and the parameters controlling their equilibrium.



Concentrations are designated in units of moles of species per liter of the noted phase (either organic or aqueous). The partitioning of undissociated and dissociated acid between the organic and aqueous phases is quantified by the distribution coefficients, D_{un} and D_{diss} , defined as

$$D_{\text{un}} = \frac{\text{HA}_{\text{org}}}{\text{HA}_{\text{aq}}} \quad (3)$$

$$D_{\text{diss}} = \frac{\text{A}_{\text{org}}^-}{\text{A}_{\text{aq}}^-} \quad (4)$$

Small distribution coefficients indicate that acid (in either the dissociated or undissociated form) prefers the aqueous phase over the organic phase. Eqn (1)–(4) and the equations $\text{H}_{\text{aq}}^+ = \text{A}_{\text{aq}}^-$ and $\text{H}_{\text{org}}^+ = \text{A}_{\text{org}}^-$ can also be combined to obtain

$$K_{\text{a,org}} = \frac{D_{\text{diss}}^2 K_{\text{a,aq}}}{D_{\text{un}}} \quad (5)$$

and since the methodology described above measures the total concentration of undissociated and dissociated acid in the organic phase, we denote T_{org}

$$T_{\text{org}} = \text{HA}_{\text{org}} + \text{A}_{\text{org}}^- \quad (6)$$

and determine the total concentration of acid in the aqueous phase, T_{aq} , by difference

$$T_{\text{aq}} = \text{HA}_{\text{aq}} + \text{A}_{\text{aq}}^- = \frac{\text{mol}_T - T_{\text{org}} V_{\text{org}}}{V_{\text{aq}}} \quad (7)$$

where mol_T is the total moles of acid added to the system, V_{org} is the measured volume of the organic phase after partitioning, and V_{aq} is the measured volume of the aqueous phase. Note that the majority of the acid remains in the aqueous phase, meaning

$T_{\text{aq}} \approx \frac{\text{mol}_T}{V_{\text{aq}}}$. Lastly, we define the ratio of total acid in the organic phase to the total in the aqueous phase, R , as

$$R = \frac{T_{\text{org}}}{T_{\text{aq}}} = \frac{\text{HA}_{\text{org}}}{T_{\text{aq}}} + \frac{\text{A}_{\text{org}}^-}{T_{\text{aq}}} \quad (8)$$

Because nitric and sulfuric acid are strong acids, they are almost entirely dissociated in the aqueous phase. Using values of $K_{\text{a,aq}}$ of 40 M for nitric acid and 10^4 M (a lower limit) for sulfuric acid,²³ at most 3% and 0.01% of each should be in the undissociated form in the aqueous phase in these experiments.

Assuming that $T_{\text{aq}} \approx \text{A}_{\text{aq}}^- = \text{H}_{\text{aq}}^+$ and that $\text{HA}_{\text{aq}} \approx \frac{T_{\text{aq}}^2}{K_{\text{a,aq}}}$, eqn (8)

becomes

$$R = \frac{\text{HA}_{\text{org}}}{\text{HA}_{\text{aq}}} \frac{T_{\text{aq}}}{K_{\text{a,aq}}} + \frac{\text{A}_{\text{org}}^-}{\text{A}_{\text{aq}}^-} \quad (9)$$

Substituting in the equations defining D_{un} and D_{diss} , this becomes

$$R = \frac{D_{\text{un}}}{K_{\text{a,aq}}} T_{\text{aq}} + D_{\text{diss}} \quad (10)$$

Plotting values of R as a function of T_{aq} should therefore result in straight lines. The slope of the line corresponds to $\frac{D_{\text{un}}}{K_{\text{a,aq}}}$ and the y-intercept is equal to D_{diss} .

It is worth considering some limiting cases of this relationship in order to orient one to the figures that follow. As noted above, the values of $K_{\text{a,aq}}$ for nitric and sulfuric acid are 40 and $>10^4$, so that these acids are predominantly dissociated in water. If D_{un} is on the order of 1 or less, indicating that undissociated nitric and sulfuric favor the aqueous phase over the organic phase, then $\frac{D_{\text{un}}}{K_{\text{a,aq}}} \approx 0$. Eqn (10) will therefore reduce to $R = D_{\text{diss}}$

and the plots will appear as flat, straight lines with y-intercepts equal to D_{diss} . In this case, the fraction of total acid in the organic phase is constant and does not depend on how much acid is present. Furthermore, since

$$R = \frac{T_{\text{org}}}{T_{\text{aq}}} = D_{\text{diss}} = \frac{\text{A}_{\text{org}}^-}{\text{A}_{\text{aq}}^-} \quad (11)$$

and $T_{\text{aq}} \approx \text{A}_{\text{aq}}^-$, $T_{\text{org}} \approx \text{A}_{\text{org}}^-$. A flat line thus also indicates that the acid is mostly dissociated in the organic phase. Conversely, if the acid in the organic phase is instead predominantly in the undissociated form, then $D_{\text{diss}} \approx 0$, and the plot will have a non-zero slope of $\frac{D_{\text{un}}}{K_{\text{a,aq}}}$ and a y-intercept ≈ 0 . In cases when signif-

icant fractions of the acid in the organic phase are present in the undissociated and dissociated forms, then the plot will have a non-zero slope and y-intercept. We note here that the inclusion of the second dissociation of sulfuric acid has a slight effect on this framework, as shown by derivations in the ESI† that take this dissociation into account. Under the assumption that SO_4^{2-} does not significantly partition to the organic phase (discussed in more detail in Section 3.4 and the ESI†), these considerations result in correction factors of 1.11 and 1.46 applied to the derived values of D_{un} and D_{diss} , respectively.

2.4 Liquid–liquid equilibrium model of acid partitioning

A number of thermodynamic models can be used to predict the partitioning of inorganic acids in liquid–liquid phase-separated systems. In this work, the algorithm described in Zuend and Seinfeld (2013)²⁴ was used to predict the composition of each phase given the composition of the system as a whole. Briefly, the algorithm generates a series of initial guesses based on the idea that one phase will contain mostly water and inorganic species, while the other will consist mostly of organic compounds. The activity coefficients for all species are then calculated using the group-contribution model AIOMFAC (Aerosol Inorganic–Organic Mixtures Functional groups Activity Coefficients) described in Zuend *et al.* (2008, 2011).^{25,26} At equilibrium, the activity of each species should be the same in each phase, so the activity coefficients can be used to adjust the modeled phase-separation. Activity coefficients are then calculated for the adjusted system, allowing the initial guesses to be iteratively improved. Importantly, the model allows for inorganic species to exist in the predominantly organic phase, although it considers them to be totally dissociated (with the



exception of the bisulfate ion, for which the partial dissociation is solved explicitly using ion activities and known equilibrium constants).

AIOMFAC is available for download (<https://github.com/andizuend/AIOMFAC>), and here the liquid–liquid equilibrium model was built on top of it using Zuend and Seinfeld (2013)²⁴ as a guide. To ensure that this version of the model performs as expected, Fig. 5d in Zuend and Seinfeld (2013)²⁴ was captured using the “IgorThief” tool in Igor Pro and compared with the

corresponding model outputs. This figure was chosen because it most closely resembles the kinds of systems and results the model was used for in this work. The comparison, shown in Fig. S5,[†] indicates that this version of the model adequately reproduces those results. In addition to using AIOMFAC for the partitioning modeling, it also was used to calculate the equilibrium concentrations of species in aqueous sulfuric acid and sulfuric acid/ammonium sulfate solutions.

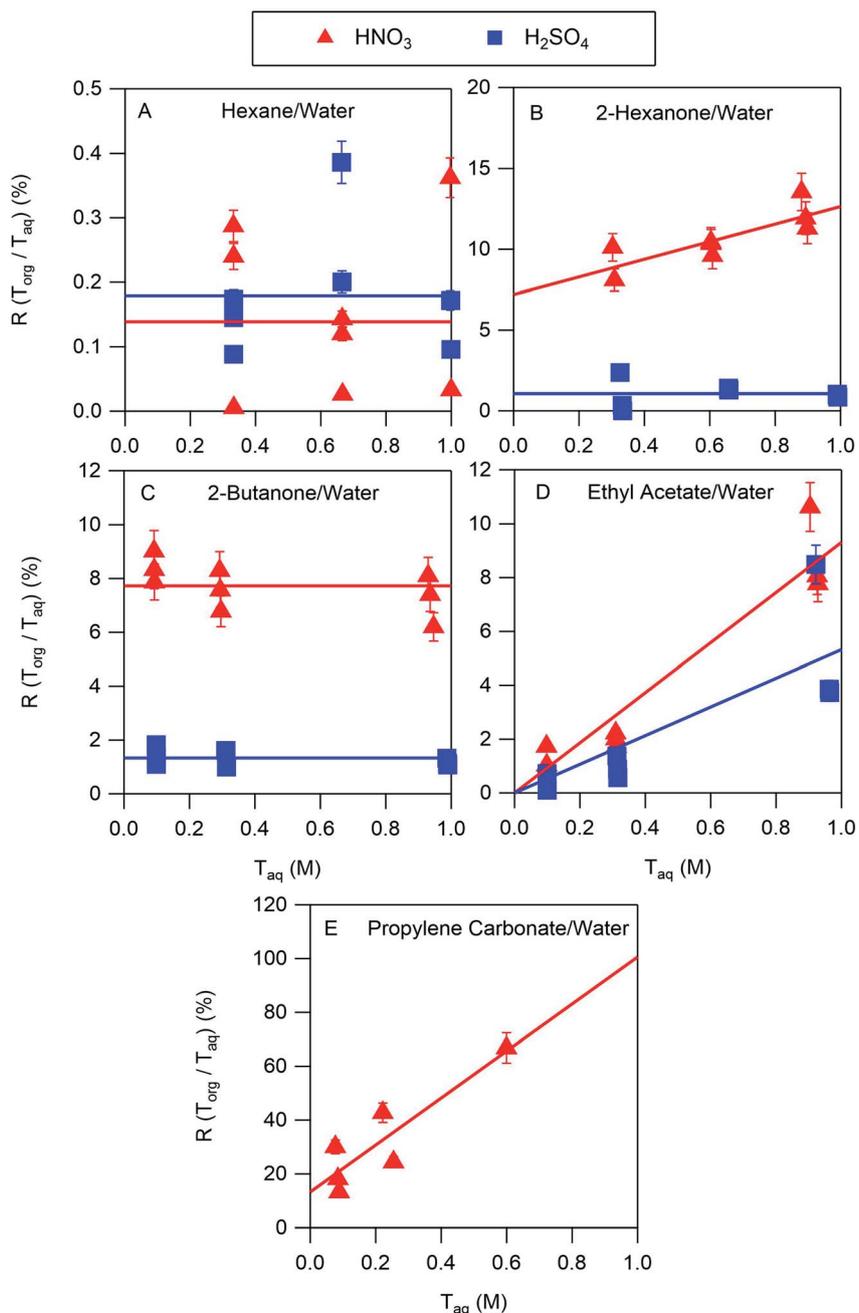


Fig. 2 Ratios of organic-phase acid/aqueous-phase acid, $R(T_{org}/T_{aq})$, measured for HNO_3 and H_2SO_4 as a function of the aqueous-phase acid concentration, with (A) hexane, (B) 2-hexanone, (C) 2-butanone, (D) ethyl acetate, and (E) propylene carbonate as the organic phase. Lines are linear least squares fits to the data, with slopes set to zero when the uncertainty exceeds the value and y -intercepts set to zero when values are negative. The error bars correspond to \pm one standard deviation calculated from the expected uncertainties in the mass and volume measurements, and in many cases fall within the symbol.



3. Results & discussion

3.1 Partitioning of acid between aqueous and organic phases

The results of the nitric and sulfuric acid partitioning measurements are shown in Fig. 2 for phase-separated aqueous/organic systems containing water and either hexane, 2-hexanone, 2-butanone, ethyl acetate, or propylene carbonate. From Table 1, the O : C ratios of these organic components are 0.0, 0.17, 0.25, 0.50, and 0.75, respectively, indicating that the polarity increases in the order shown. This trend is also roughly reflected in the vol% water in these components of 0.01, 2, 1, 3, and 8, respectively. One can expect that the addition of water to the organic phase will increase the polarity of the resulting solution, thus enhancing the extent to which both the undissociated and dissociated forms of the acid can be solvated and increasing partitioning of both species to the organic phase. In the figures, values of $R(T_{\text{org}}/T_{\text{aq}})$ are plotted against T_{aq} , as suggested by the discussion above and eqn (10). Least-squares lines were first fit to the data, and then because of the significant scatter, in cases where the uncertainty in the slope was greater than the value the slope was set to zero. And in one case where the y -intercept was slightly negative, and thus nonphysical, that value was also set to zero. Visual inspection of the resulting lines indicates that this approach is reasonable, and it allows the profiles to be classified according to zero or positive slope and zero or positive y -intercept, thus simplifying the data interpretation and comparisons between systems.

The ratio $T_{\text{org}}/T_{\text{aq}}$ is approximately 0.001 for hexane; 0.01–0.1 for 2-hexanone, 2-butanone, and ethyl acetate; and 0.1–1 for propylene carbonate. These values correlate better with the vol% water for each group of 0.01, 1–3, and 8 than with the O : C ratios of 0.0, 0.17–0.5, and 0.75, although in either case there is clear evidence that partitioning increases with increasing polarity of the organic phase. The results also indicate that nitric acid partitions more strongly to the organic phase than sulfuric acid. As discussed in Section 2.3, the presence of three types of lines: (1) zero slope and positive y -intercept, (2) positive slope and zero y -intercept, and (3) positive slope and positive y -intercept are indicative of acids being fully dissociated, undissociated, and partially dissociated, respectively, in the organic phase. In addition, the y -intercept gives the value of the D_{diss} , the distribution coefficient for NO_3^- or HSO_4^- , and the slope gives the value of $\frac{D_{\text{un}}}{K_{\text{a, aq}}}$, the ratio of the

distribution coefficient for HNO_3 or H_2SO_4 divided by its acid dissociation constant in water. Values of D_{diss} and D_{un} determined from the lines are given in Table 2, although for lines with zero slope the value of D_{un} cannot be determined. The uncertainties were taken from the fits to the data as output by Igor Pro. Values of D_{diss} and D_{un} range from approximately 0.001–0.1 and 2–60, respectively, indicating that larger fractions of undissociated acid partition to the organic phase than dissociated acid. It should be remembered, however, that for values of $K_{\text{a, aq}}$ of 40 M for nitric acid and 10^4 M for sulfuric acid (Levanov *et al.*, 2018)²³ at most about 3% and 0.01% of these acids should be undissociated in the aqueous phase. As a result, except in the case of ethyl acetate, a significant fraction of the acid present in the organic phase is always dissociated. When both D_{diss} and D_{un} are known, $K_{\text{a, org}}$ can be calculated using eqn (5). This is only possible with this data set for nitric acid in 2-hexanone and propylene carbonate, resulting in values of 0.11 M and 0.022 M, respectively. Unsurprisingly, the dissociation of nitric acid is therefore significantly reduced in predominantly organic phases as compared to the aqueous phase. Although the values of D_{diss} and D_{un} indicate that in some systems the undissociated form of the acid dominates, in others the dissociated form does, and in still others both forms are significantly present in the organic phase, one could expect that for the complex mixture of oxidized organic compounds present in SOA, that significant amounts of both undissociated and dissociated forms of nitric and sulfuric acid should be present. This should allow for the occurrence of both specific and general acid catalysis in the organic phase, even though reactions in the aqueous phase are probably limited to specific acid catalysis.

The pH of the organic phases measured after equilibration with a series of aqueous HNO_3 or H_2SO_4 solutions ranging in concentration from 10^{-6} M to 10 M are shown in Fig. 3. It was assumed that the H^+ activity measured by the pH strips was equal to the H^+ concentration. This assumption ignores any activity effects, which are likely negligible compared to the uncertainty of the pH measurement (roughly one or two pH units), but may be important in extreme cases. These organic phase H^+ concentrations are compared with those estimated using D_{diss} values derived above and shown by the lines in Fig. 3. Note that not all systems had measurable D_{diss} values and so there is not a line for each solvent. Although there is a fair amount of scatter, the H^+ concentrations obtained from pH

Table 2 Organic/aqueous distribution coefficients determined for nitric acid and sulfuric acid from partitioning measurements with pure water and various organic phases

| Organic phase | HNO_3 | | H_2SO_4 | |
|---------------------|---------------------|-----------------|-------------------------|-----------------|
| | D_{diss} | D_{un} | D_{diss} | D_{un} |
| Hexane | 0.0014 ± 0.0004 | — | 0.0026 ± 0.0004 | — |
| 2-Hexanone | 0.072 ± 0.01 | 1.9 ± 0.6 | 0.016 ± 0.003 | — |
| 2-Butanone | 0.077 ± 0.003 | — | 0.019 ± 0.001 | — |
| Ethyl acetate | 0 | 3.3 ± 0.2 | 0 | 59 ± 10 |
| Propylene carbonate | 0.13 ± 0.06 | 31 ± 8 | — | — |



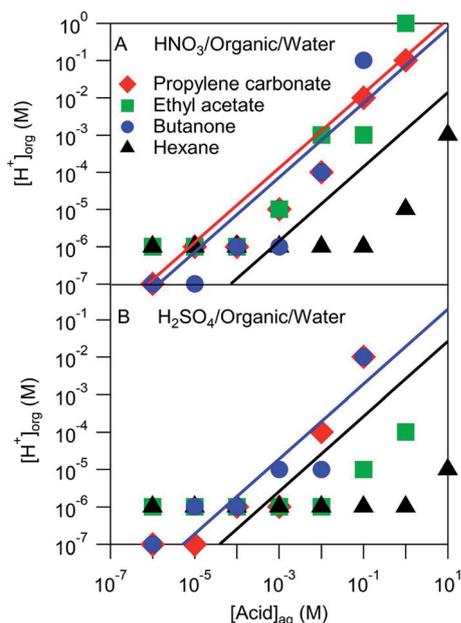


Fig. 3 Measured and modeled organic phase H^+ concentrations. Markers represent pH strip measurements and lines correspond to values derived from measured D_{diss} values.

measurements largely line up with those obtained using D_{diss} values. These results suggest that the mass-based measurements discussed above extend over a wider concentration range than measured. The notable exception is hexane, which is either overestimated by the mass-based measurements (probably because of the small amount of acid that partitioned to the organic phase) or underestimated by the pH measurements (perhaps due to activity effects or a relative lack of water in the organic phase).

3.2 Comparison of acid partitioning measurements and liquid–liquid equilibrium model results

In all cases the liquid–liquid equilibrium model underpredicts the amount of acid partitioning to the organic phase. This is perhaps not surprising, however, since the model does not consider undissociated acid, which is a significant fraction of the organic phase acid in many of the systems studied here. The model performs best for nitric acid in 2-butanone/water, as shown in Fig. 4A. The measurements indicate that the acid in the organic phase is fully dissociated, with a value of D_{diss} of 0.077 (Table 2). The model, on the other hand, predicts a value of $D_{diss} \approx 0.02$, about a factor of 4 lower than measured. As noted above, the model assumes that the acid is fully dissociated in the organic phase, leading to a relatively flat curve that for this case is consistent with the measurements. In contrast, whereas the measured value of D_{diss} is 0.072 for nitric acid in 2-hexanone/water, the model predicts a value of 0.001. Furthermore, the measurements show a significant slope for the line of 5.4, indicative of undissociated acid, which the model cannot capture since it assumes nitric acid is always fully dissociated. The model predictions for all the other systems are similar to

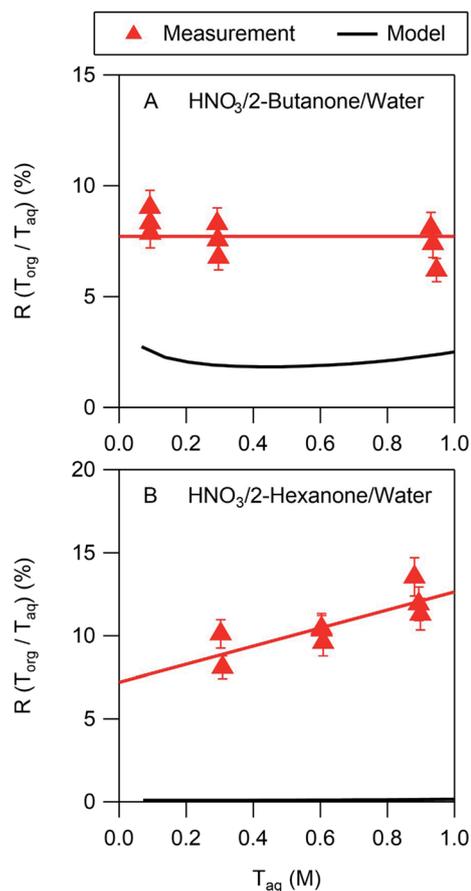


Fig. 4 Comparison of measurements and LLE model predictions for the partitioning of HNO_3 in the (A) 2-butanone/water and (B) 2-hexanone/water systems. The error bars correspond to \pm one standard deviation calculated from the expected uncertainties in the mass and volume measurements.

those shown in Fig. 4B, thus always underpredicting values of D_{diss} . Because undissociated acid is not considered, organic-phase acid in the ethyl acetate/water and propylene carbonate/water systems are similarly underpredicted. These results suggest that the presence of undissociated acid in predominantly organic phases should be included in models to more accurately describe the partitioning, although more partitioning measurements are likely needed before such inclusion is possible.

3.3 Correlation of partitioning parameters with organic phase properties

Environmental phase-separated systems are highly complex and can contain hundreds of individual components. Furthermore, they also typically contain many more (and more exotic) functional groups than the alkyl, carbonyl, and ester groups studied in this work. Relationships between general organic phase properties and partitioning parameters like the ones derived here are therefore highly desirable. The measured values of D_{un} for HNO_3 are plotted in Fig. 5 as a function of the O : C ratio of the organic phase. To supplement the



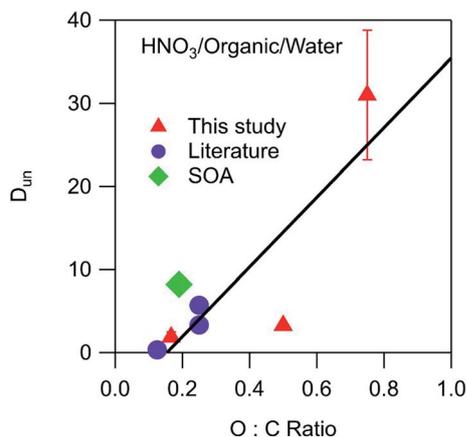


Fig. 5 Relationship between D_{un} and the O : C ratio of the organic phase for partitioning of HNO_3 . Values correspond to the following organic phase and O : C ratios: dibutyl ether (0.13),²⁷ 2-hexanone (0.17), SOA (0.19),^{29,30} ethyl ether (0.25),²⁷ diethylene glycol dibutyl ether (0.25),²⁷ ethyl acetate (0.50), and propylene carbonate (0.75). The error bars correspond to \pm one standard deviation as determined from the linear fits used to calculate D_{un} , and in most cases fall within the symbol. The line is a linear least-squares fit to the data.

measurements made here, relevant data sets from Stephen and Stephen (1963)²⁷ were also fit to eqn (10) (Fig. S6†). The values of D_{un} (including measured and literature-derived values) were found to be approximately linear with respect to the O : C ratio of the organic phase, following the equation

$$D_{un} = 42 \times (\text{O} : \text{C}) - 6 \quad (12)$$

as shown in Fig. 5. Only one value for sulfuric acid was available, and was a significant outlier from this relationship. The x-intercept of 0.14 indicates that negligible undissociated HNO_3 partitions to the organic phase below this O : C value. Also included in the plot is a value of 8.2 calculated from the Henry's law coefficients of $1.6 \times 10^5 \text{ M atm}^{-1}$ for partitioning of gaseous HNO_3 to water²⁸ and $3.7 \times 10^4 \text{ M atm}^{-1}$ for partitioning to SOA formed from the oxidation of *n*-pentadecane by OH radicals.²⁹ This SOA contained carbonyl, hydroxyl, carboxyl, ester, hydroperoxy, and peroxide groups and had an average molecular weight of 260 g mol^{-1} and an O : C ratio of 0.19.³⁰ This data point, shown as a green diamond, lies slightly above the fitted line in Fig. 5, but still suggests that the values derived in this work are relevant to real aerosol systems despite the differences

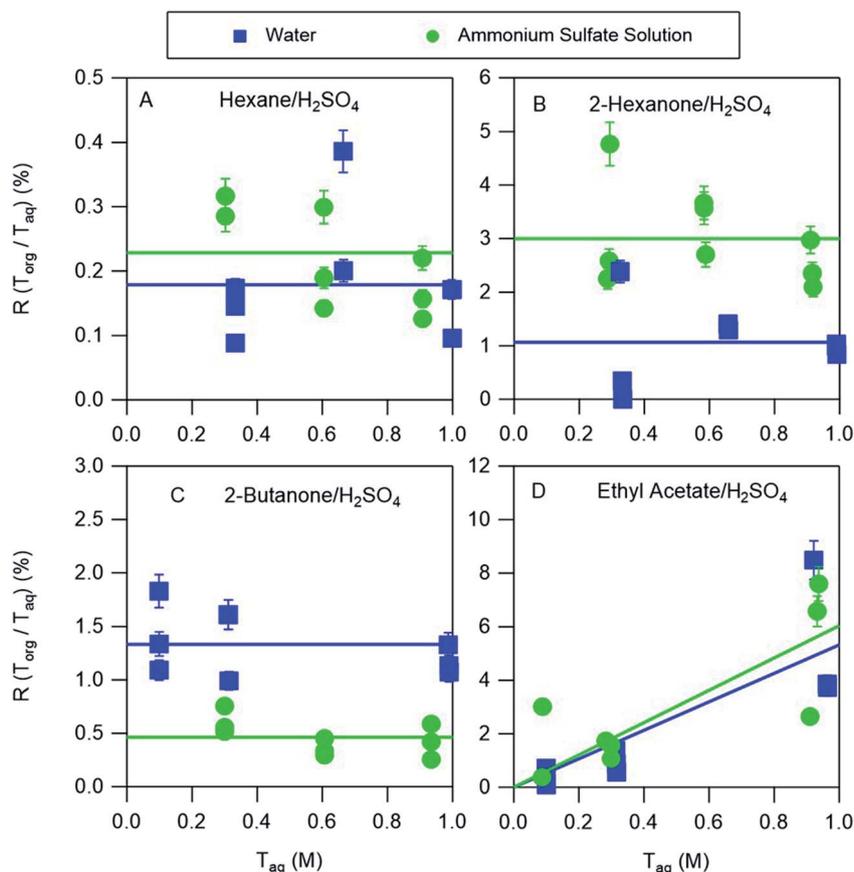


Fig. 6 Ratios R of organic-phase acid to aqueous-phase acid as a function of the aqueous-phase concentration for sulfuric acid. The aqueous phase was either water or 30% (w/w) aqueous ammonium sulfate, and the organic phases were (A) hexane, (B) 2-hexanone, (C) 2-butanone, and (D) ethyl acetate. Lines are linear least squares fits to the data, with slopes set to zero when the uncertainty exceeds the value and y-intercepts set to zero for negative values. The error bars correspond to \pm one standard deviation calculated from the expected uncertainties in the mass and volume measurements, and in many cases fall within the symbol.



in functionality and molecular weight. Unlike the case for D_{un} , values of D_{diss} do not correlate with O : C ratios, and although there is a general increase with increasing vol% water, there is too much scatter for this value to be a reliable predictor of this parameter (plots not shown).

3.4 Influence of ammonium sulfate on acid partitioning

The partitioning of nitric acid and sulfuric acid is likely to be perturbed by the presence of salts. Ammonium sulfate is prevalent in atmospheric aerosol and so experiments were also conducted to investigate the potential effects of this salt on acid partitioning. In the aqueous phase, the combination of ammonium sulfate and sulfuric acid produces H^+ , HSO_4^- , SO_4^{2-} , and NH_4^+ . Similarly, ammonium sulfate and nitric acid produce H^+ , HSO_4^- , SO_4^{2-} , NH_4^+ , and NO_3^- . In the nitric acid systems, it is therefore possible for both ammonium nitrate and ammonium sulfate to precipitate when ammonia is bubbled in the organic phase, complicating the interpretation of those measurements. We therefore discuss only the partitioning of sulfuric acid between organic phases and either water or ammonium sulfate aqueous phases. The equilibria between these species in aqueous solutions is well understood and may be accurately predicted using thermodynamic models such as AIOMFAC. For example, AIOMFAC calculations indicate that in a solution of ammonium sulfate in water >99% of the sulfate is present as SO_4^{2-} . Because of the difficulty of solvating this divalent ion in the organic phase little partitioning is expected, consistent with aqueous ammonium sulfate partitioning measurements that showed no measurable salt in any of the organic phases. When ammonium sulfate is added to an aqueous sulfuric acid solution the reaction of SO_4^{2-} with H^+ should increase the concentration of HSO_4^- , with AIOMFAC calculations indicating that the concentrations of HSO_4^- in 0.3 M and 1.0 M aqueous solutions of sulfuric acid (the approximate range covered in these experiments) increase from 0.23 and 0.75 to 0.43 and 1.36, respectively, when 30 w/w% = 2.27 M ammonium sulfate is added, typical of the concentration in atmospheric aerosol particles.²¹ As a result, additional HSO_4^- would be expected to partition to the organic phase. The results of the partitioning measurements shown in Fig. 6, and the distribution coefficients obtained from the fitted lines are given in Table 3. For hexane, ethyl acetate, and 2-hexanone there are enhancements in partitioning of sulfuric acid to the organic

phase compared to the ammonium sulfate-free measurements. They are relatively small for hexane and ethyl acetate but about a factor of three for 2-hexanone, and might be explained by the increase in the aqueous phase concentration of HSO_4^- . Conversely, partitioning decreases for 2-butanone, and might be attributed to reductions in the vol% water in the organic phases when ammonium sulfate is added, which was shown above to generally correlate with partitioning. In particular, as the aqueous phase becomes saturated with ammonium sulfate less water will partition to the organic phase, and so less HSO_4^- will partition. This effect can thus compensate for or even overcome the enhanced partitioning due to the increase in the aqueous phase concentration of HSO_4^- . Notably, the only organic phase for which acid partitioning decreases with the addition of ammonium sulfate is 2-butanone, which has the highest vol% water. Despite some differences, it is notable that distribution coefficients derived from systems using pure water are within a factor of three of those obtained for nearly saturated ammonium sulfate solutions. By using a thermodynamic model like AIOMFAC to understand the aqueous phase equilibria, the values derived in this work may therefore be used to predict the amount and forms of acids in the organic phases of even relatively salty aerosols.

4. Conclusions

This study sought to determine the extent to which strong acids might be present in the organic phase of environmentally important aqueous/organic phase-separated systems, and thus potentially participate in organic chemical reactions. By using a series of model organic phases with a range of polarity and a simple gravimetric analytical method it was shown that nitric and sulfuric acid, the dominant strong acids in atmospheric aerosol particles, can undergo significant partitioning to an organic phase. The extent of this partitioning tends to be greater for nitric than sulfuric acid, to increase with increasing O : C ratio and vol% water of the organic phase, and to be influenced positively or negatively by the presence of ammonium sulfate, a dominant salt in atmospheric aerosol. Since studies were conducted with organic components having O : C ratios ranging from 0 to 0.75, the results should be applicable to the atmosphere, where the O : C ratio of organic aerosol typically ranges from 0.2 to 0.8.¹⁴ By fitting the data to a simple partitioning model, values of distribution coefficients, D_{diss} and D_{un} , for partitioning of dissociated and undissociated acid to the organic phase were obtained, providing quantitative information on the amounts and form of partitioned acids. The results of this study suggest that partitioning of inorganic acids to predominantly organic phases can be significant and warrants further study. It would therefore be useful if future studies could expand on the limited selection of single organic phases employed here to include more complex mixtures and compounds with other functional groups, which might be possible by using more dilute acid solutions (which would be less likely to catalyze reactions of functional groups) and more sensitive acid detection methods such as ion chromatography or electrochemical measurements. Furthermore, it is an open

Table 3 Organic/aqueous distribution coefficients determined for sulfuric acid from partitioning measurements with pure water or an aqueous ammonium sulfate solution and various organic phases

| Organic phase | Water | | Ammonium sulfate solution | |
|---------------|-------------------|-----------------|---------------------------|-----------------|
| | D_{diss} | D_{un} | D_{diss} | D_{un} |
| Hexane | 0.0026 ± 0.0004 | — | 0.0034 ± 0.0004 | — |
| 2-Hexanone | 0.016 ± 0.003 | — | 0.0439 ± 0.0044 | — |
| 2-Butanone | 0.019 ± 0.001 | — | 0.0067 ± 0.0007 | — |
| Ethyl acetate | 0 | 59 ± 10 | — | 68 ± 11 |



question how well investigations of acidity and partitioning of the bulk solutions studied here apply to aerosol particles. For example, studies by Wei *et al.*³¹ suggest that pH gradients exist within particles, with protons accumulating at the surface and correspondingly more basic conditions towards the center of the particle. But on the other hand, studies by Dallemagne *et al.*³² showed that the pH of an organic shell in a phase-separated particle essentially matches that in the corresponding bulk solution. Comparison of the measurements made here with predictions of a liquid-liquid equilibrium model showed that the model seriously underpredicted the extent of acid partitioning to the organic phase, which was due at least in part because the model only considers the dissociated acid. The inclusion of undissociated acid should improve predictions, though more partitioning measurements are likely needed before this can be implemented. Depending on the acid and the particular model organic phase, these acids can exist primarily in either the dissociated or undissociated form, or both. One could then expect that for the complex mixture of oxidized organic compounds present in atmospheric aerosol that significant amounts of both forms of nitric and sulfuric acid should be present, allowing for the occurrence of both specific (H^+) and general (HA) acid catalysis in the organic phase, even though reactions in the aqueous phase are probably limited to specific acid catalysis.

Conflicts of interest

There are no conflicts of interest to declare.

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