Article

Importance of the Number of Acid Molecules and the Strength of the Base for Double-Ion Formation in (HSO)·Base·(HO) Clusters

Kelly E. Anderson, J. Ilja Siepmann, Peter H. McMurry, and Joost VandeVondele

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

Importance of the Number of Acid Molecules and the Strength of the Base for Double-Ion Formation in $(H_2SO_4)_m \cdot Base \cdot (H_2O)_6$ Clusters

Kelly E. Anderson,[†] J. Ilja Siepmann,*,[†] Peter H. McMurry,[†] and Joost VandeVondele[‡]

Departments of Chemistry and of Mechanical Engineering, University of Minnesota, 207 Pleasant Street SE, Minneapolis, Minnesota 55455, and Institute of Physical Chemistry, University of Zurich, Winterthurerstrasse 190, 8057 Zurich, Switzerland

Received March 17, 2008; E-mail: siepmann@umn.edu

Abstract: Sulfuric acid and water clusters are important for new particle formation in the atmosphere. Recent experimental studies demonstrate that critical clusters in diverse atmospheric environments contain two acid molecules and may also include additional N-containing molecules (i.e., a base). We use first-principles molecular dynamics simulations to show that the presence of two sulfuric acid molecules in $(H_2SO_4)_m \cdot base \cdot (H_2O)_6$ clusters is always sufficient to form a double ion, whereas a single acid molecule, even in the presence of a base, is not.

Atmospheric aerosol particles exert a considerable impact on global climate through the scattering of solar radiation and the involvement in cloud condensation. The formation of new aerosol particles by nucleation of gas-phase species remains the least understood of the steps influencing aerosol concentration.[1] Recent experimental atmospheric observations demonstrate that critical clusters found in diverse continental and marine environments contain two sulfuric acid (H_2SO_4) molecules.[2] Variations in the kinetic prefactor with environment suggest that additional conucleating species may be present in the critical cluster.[2] This is consistent with comparisons of particle formation rates obtained by classical nucleation theory to experimental observation, which show that basing aerosol formation solely on H_2SO_4 + H_2O reactions does not adequately explain atmospheric nucleation.[3–5] Instead, nucleation mechanisms that include additional species, such as ammonia (NH_3), may play a significant role in atmospheric new particle formation.

Many theoretical studies have used ab initio techniques to examine proton transfer in small clusters of H_2SO_4 and H_2O, as well ternary clusters with ammonia.[6–15] These studies explored the clusters either at 0 K or included temperature effects via the harmonic approximation including zero-point energy effects, i.e., a cluster is viewed as a solid-like entity whose properties are determined by a single or a few configurations. In general, these static calculations indicate that for $H_2SO_4 \cdot (H_2O)_n$, acid dissociation occurs and a double-ion cluster is formed for $n \geq 3$.[8,11,13] In the presence of a single ammonia molecule, acid dissociation was found even for $n = 1$.[9,14] To some extent, these theoretical predictions of double-ion formation for clusters with a single acid molecule disagree with the experimental observation that critical nuclei contain two acid molecules.[2] Furthermore, the static calculations indicate that for clusters with two acid molecules both of them tend to deprotonate.[10,14]

Several studies have used first-principles molecular dynamics (FPMD) simulations to investigate atmospherically relevant small molecules in aqueous clusters and at interfaces. These simulations view the system as a liquid-like entity whose phase space needs to be sampled, albeit this is commonly done based on classical mechanics. Both experiment[16] and simulation[17] support the liquid-like character of the critical cluster for nucleation of neat water over the atmospherically relevant temperature range. Tobias et al. showed that a chloride ion prefers surface locations in a $Cl^- \cdot (H_2O)_6$ cluster, making the ion available for heterogeneous reactions at the air/water

[†] University of Minnesota.

[‡] University of Zurich.
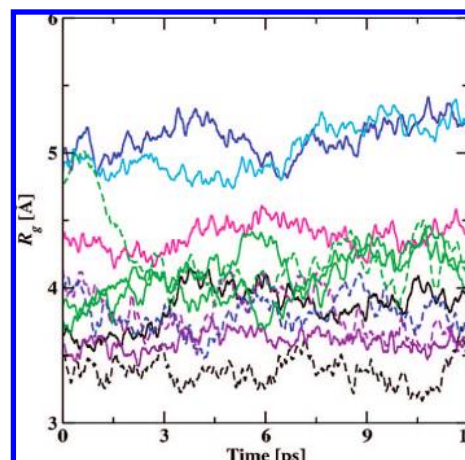
(1) Kulmala, M. *Science* **2003**, *302*, 1000–1001.

(2) Kuang, C.; McMurry, P. H.; McCormick, A. V.; Eisele, F. L. *J. Geophys. Res.* **2008**, *113*, D10209.

(3) Weber, R. J.; Marti, J.; McMurry, P. H.; Eisele, F. L.; Tanner, D. J.; Jefferson, A. *Chem. Eng. Commun.* **1996**, *151*, 53–64.

(4) Korhonen, P.; Kulmala, M.; Laaksonen, A.; Viisanen, Y.; McGraw, R.; Seinfeld, J. H. *J. Geophys. Res.* **1999**, *104*, 26349–26353.

(5) Weber, R. J.; McMurry, P. H.; Mauldin, R. L.; Tanner, D. J.; Eisele, F. L.; Clarke, A. D.; Kapustin, V. N. *Geophys. Res. Lett.* **1999**, *26*, 307–310.

(6) Arstila, H.; Laasonen, K.; Laaksonen, A. *J. Chem. Phys.* **1998**, *108*, 1031–1039.

(7) Ianni, J. C.; Bandy, A. R. *J. Phys. Chem. A* **1999**, *103*, 2801–2811.

(8) Re, S.; Osamura, Y.; Morokuma, K. *J. Phys. Chem. A* **1999**, *103*, 3535–3547.

(9) Larson, L. J.; Largent, A.; Tao, F.-M. *J. Phys. Chem. A* **1999**, *103*, 6786–6792.

(10) Ding, C.-G.; Laasonen, K.; Laaksonen, A. *J. Phys. Chem. A* **2003**, *107*, 8648–8658.

(11) Ding, C.-G.; Laasonen, K. *Chem. Phys. Lett.* **2004**, *390*, 307–313.

(12) Bianco, R.; Wang, S.; Hynes, J. T. *J. Phys. Chem. B* **2005**, *109*, 21313–21321.

(13) Arrouvel, C.; Viossat, V.; Minot, C. *J. Mol. Struct. (THEOCHEM)* **2005**, *718*, 71–76.

(14) Kurtén, T.; Torpo, L.; Ding, C.-G.; Vehkamäki, H.; Sundberg, M. R.; Laasonen, K.; Kulmala, M. *J. Geophys. Res.* **2007**, *112*, D04210.

(15) Nadykto, A. B.; Yu, F. *Chem. Phys. Lett.* **2007**, *435*, 14–18.

(16) Wölk, J.; Strey, R. *J. Phys. Chem. B* **2001**, *105*, 11683–11701.

(17) Chen, B.; Siepmann, J. I.; Klein, M. L. *J. Phys. Chem. A* **2005**, *109*, 1137–1145.

interface.[18] Shamay et al. used FPMD slab simulations to show that nitric acid at the air/water interface is less likely to dissociate than in a bulk aqueous liquid, changing its chemical reactivity at the surface.[19] In this study, we use FPMD simulations to examine the effect of acid concentration and the presence of a base on proton dissociation and ionic speciation in small clusters of water and sulfuric acid.

The CP2K simulation package was used to perform the FPMD simulations.[20] The electronic structure part of CP2K uses the Gaussian plane wave (GPW) method[21] for the calculation of forces and energies. The GPW method is based on the Kohn−Sham formulation[22] of density functional theory and employs a hybrid scheme of Gaussian and plane wave functions. Previous CP2K studies have shown that the vapor−liquid equilibrium properties of water are sensitive to the choice of functional and basis set.[23,24] The BLYP functional[25] with a Gaussian triple-ζ basis set augmented by two polarization functions (TZV2P) and a charge density cutoff of 280 Ry was chosen for this study because this representation has been well characterized for both water clusters and the liquid phase.[20,23,26,27] Nine clusters of $(H_2SO_4)_m$·base·$(H_2O)_6$ were simulated where $m = 1$ or 2. Since the cluster growth rate is determined by the uptake rate of the least volatile constituent (H_2SO_4), the experimental data do not indicate the number of water molecules present in the critical nucleus, and the current choice of six was made to provide a suitable microsolvation environment and to be higher than the minimum number of water molecules observed that lead to deprotonation in the static calculations. Three N-containing bases were selected that reflect the diversity of bases in the natural environment: NH_3, methylamine (CH_3NH_2), and pyridine (C_5H_5N). For each base, three clusters were simulated, one containing one H_2SO_4 molecule and two containing two H_2SO_4 molecules, starting with and without hydrogen bonds between the acid molecules. An additional two clusters with no base present were simulated, H_2SO_4·$(H_2O)_6$ and $(H_2SO_4)_2$·$(H_2O)_6$, for comparison.

The initial structure of each cluster was optimized using CP2K, followed by 20 ps (C_5H_5N) or 30 ps (NH_3, CH_3NH_2) of MD simulation using a time step of 0.5 fs. A temperature of 250 K was chosen because it reflects the (reduced) temperature where multicomponent nucleation of neutral gas-phase species is believed to be the dominant process for atmospheric nucleation (after taking into account the calculated critical temperature for the BLYP representation of water[23]). The temperature was controlled by Nose−Hoover chain thermo-

(18) Tobias, D. J.; Jungwirth, P.; Parrinello, M. *J. Chem. Phys.* **2001**, *114*, 7036–7044.
(19) Shamay, E. S.; Buch, V.; Parrinello, M.; Richmond, G. L. *J. Am. Chem. Soc.* **2007**, *129*, 12910–12911.
(20) VandeVondele, J.; Krack, M.; Mohamed, F.; Parrinello, M.; Chassaing, T.; Hutter, J. *Comput. Phys. Commun.* **2005**, *167*, 103–128.
(21) Lippert, G.; Hutter, J.; Parrinello, M. *Mol. Phys.* **1997**, *92*, 477–487.
(22) Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, 1133–1138.
(23) McGrath, M. J.; Siepmann, J. I.; Kuo, I.-F. W.; Mundy, C. J.; VandeVondele, J.; Hutter, J.; Mohamed, F.; Krack, M. *J. Phys. Chem. A* **2006**, *110*, 640–646.
(24) McGrath, M. J.; Siepmann, J. I.; Kuo, I.-F. W.; Mundy, C. J. *Mol. Phys.* **2006**, *104*, 3619–3626.
(25) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.
(26) Kuo, I.-F. W.; Mundy, C. J.; McGrath, M. J.; Siepmann, J. I.; VandeVondele, J.; Sprik, M.; Hutter, J.; Chen, B.; Klein, M. L.; Mohamed, F.; Krack, M.; Parrinello, M. *J. Phys. Chem. B* **2004**, *108*, 12990–12998.
(27) McGrath, M. J.; Siepmann, J. I.; Kuo, I.-F. W.; Mundy, C. J.; VandeVondele, J.; Hutter, J.; Mohamed, F.; Krack, M. *ChemPhysChem* **2005**, *6*, 1894–1901.

Figure 1. Radii of gyration for the final 12 ps of each simulation. Colors are as follows: C_5H_5N (green), NH_3 (purple), CH_3NH_2 (blue), and base-free (black), with $m = 1$ clusters shown as dashed lines. The darker and lighter color shades indicate simulations started with and without hydrogen bonds between the two acid molecules.

Table 1. Speciation within Clusters as a Fraction of First Dissociable H_2SO_4 Protons[a]

	no base		C_5H_5N		NH_3		CH_3NH_2	
pK_a			5.22		9.25		10.66	
$(H_2SO_4)_m$	1	2	1	2	1	2	1	2
H_2SO_4	1.00	1.09	0.01	0.99	1.00	1.00	0.00	0.98
HB^+			0.00	1.00	0.00	1.00	1.00	1.00
H_3O^+	0.00	0.70	0.84	0.00	0.00	0.00	0.00	0.00
H_4SO_5	0.00	0.19	0.08	0.01	0.00	0.00	0.00	0.02
$H_5O_2^+$	0.00	0.01	0.07	0.00	0.00	0.00	0.00	0.00

[a] For $m = 2$ and base present, the values given are the averages of the two simulations with different initial structures.
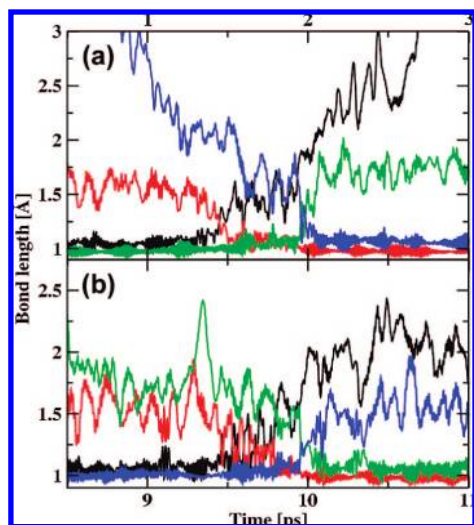
stats.[28] The structural analysis was carried using the last 12 ps of each run. Figure 1 depicts the evolution of the radius of gyration for the 11 clusters during the analysis period. The large fluctuations reflect structural rearrangements of the clusters (molecules moving from one H-bond arrangement to another) and demonstrate the liquid-like behavior of these small clusters.

The most important observation of this study is that the presence of two acid molecules is always sufficient to form a double ion, whereas a single acid molecule, even in the presence of a base, is not. With one exception, the deprotonation in the two-acid cluster already occurs during the initial geometry optimization, and in the other case, it occurs after about 1.5 ps. It appears likely that the growth of such a double-ion cluster can proceed without encountering any nucleation free energy barrier.[29] Thus, our simulations support the experimental observation that critical clusters for atmospheric nucleation contain two sulfuric acid molecules.[2]

The speciation found for the 11 clusters is summarized in Table 1. In these acidic clusters, a proton can exist in multiple types of cations, such as an Eigen ion (H_3O^+), a Zundel ion ($H_5O_2^+$), a protonated base (HB^+), or a Zundel-type complex $HSO_3O\cdots H\cdots OH_2$ (H_4SO_5). In this analysis, a hydrogen atom is considered bound to an atom X if $r_{XH} \leq 1.3$ Å, where X =

(28) Martyna, G. J.; Klein, M. L.; Tuckerman, M. *J. Chem. Phys.* **1992**, *97*, 2635–2643.
(29) Kathmann, S. M.; Schenter, G. K.; Garrett, B. C. *Phys. Rev. Lett.* **2005**, *94*, 116104.
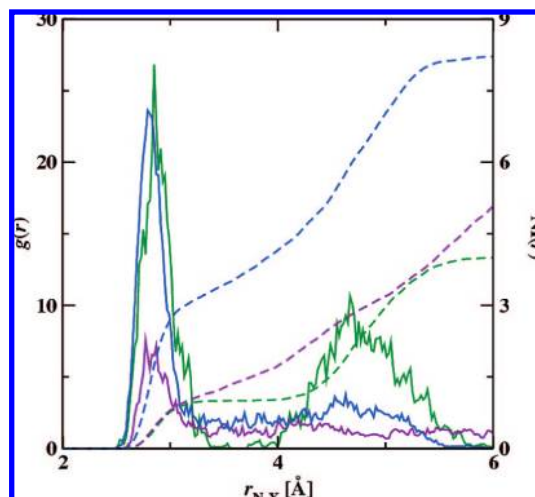
Figure 2. Trajectories of proton coordination for (a) $H_2SO_4 \cdot CH_3NH_2 \cdot (H_2O)_6$ and (b) $H_2SO_4 \cdot C_5H_5N \cdot (H_2O)_6$. Colors are as follows: $O_{acid}-H_1$ (black), $O_{wat}-H_1$ (red), $O_{wat}-H_2$ (green), $N-H_2$ or $O_{sec}-H_2$ (blue) where O_{wat} and O_{sec} are the oxygen atoms belonging to the first water molecule hydrogen-bonded to the acid and a next-nearest neighbor water molecule.
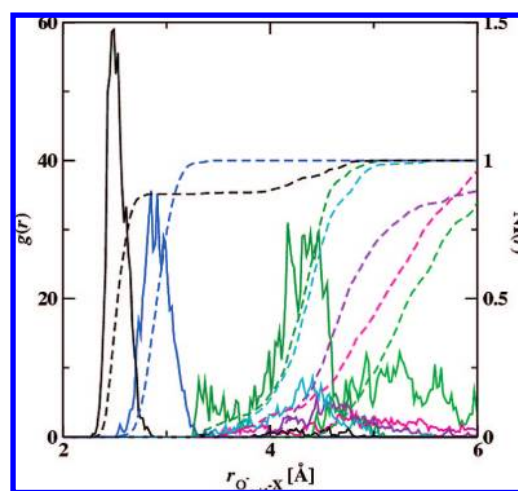
O, N, S, or C. For all clusters with two sulfuric acid molecules and a base present, the base is protonated (HB^+) throughout the entire analysis period. In the base-free cluster with $m = 2$, one acid molecule is preferentially dissociated and the movable proton is found mostly as an Eigen ion with the Zundel-type H_4SO_5 as minor species.

For $m = 1$, the speciation varies. The acid molecule remains protonated throughout the entire simulation for the base-free and the NH_3-containing clusters. On the other side, a proton dissociates from the acid after about 1.5 and 9.5 ps for the methylamine- and pyridine-containing clusters. In the former case, the dissociation leads to the formation of $CH_3NH_3^+$, whereas an Eigen ion is the dominant protonated species in the latter case. The parts of the trajectories during which the initial proton transfers occur for the $m = 1$ clusters are shown in Figure 2. It is interesting to note that in both cases the initial transfer of the proton is induced by the formation of H_4SO_5, followed by a bound Eigen ion ($HSO_4^- \cdot H_3O^+$) that is stable for only 0.2−0.5 ps before the proton is transferred again either to the base or to a second water molecule. Although dissociation is not observed in the current simulations for the $H_2SO_4 \cdot NH_3 \cdot (H_2O)_6$ and $H_2SO_4 \cdot (H_2O)_6$ clusters, it needs to be cautioned that the 30 ps time scale of the simulations may not be sufficient to explore all important regions of phase space.

In the following, a brief structural analysis of the $(H_2SO_4)_m \cdot base \cdot (H_2O)_6$ clusters is provided. First of all, at 250 K, these clusters are dynamic entities that undergo significant structural changes associated with hydrogen-bond formation/breaking throughout the 12 ps analysis period (see Figure 1). Selected radial distribution functions and the corresponding number integrals are shown in Figures 3 and 4. For the $m = 1$ clusters, we observe that $CH_3NH_3^+$ is well solvated and acts as donor for about three H-bonds of which ≈ 2.2 are with H_2O and the remainder with HSO_4^-. The neutral ammonia molecule is involved in about 1.1 H-bonds, whereas a neutral water molecule participates in 1.7 H-bonds on average. Pyridine is not well solvated, and it accepts slightly less than one H-bond and

Figure 3. Radial distribution functions (solid) and number integrals (dashed) for $m = 1$ clusters. Solvation of base indicated by N−X pairs, where $X = O_{wat}$ or O_{acid}. Color scheme follows that of Figure 1.

Figure 4. Radial distribution functions (solid) and number integrals (dashed) for $m = 2$ clusters. The ion pair structure is indicated by $O^-_{acid}-X$ ion pairs, where X is either the N in HB^+ or the O in H_3O^+. Color scheme follows that of Figure 1.

dangles at the surface of the cluster. In this case, there is a well-defined minimum in the radial distribution function and the corresponding potential of mean force yields a barrier of ≈ 11 kJ/mol. Here, it should be noted that the pK_a values of the conjugate acids of pyridine, ammonia, and methylamine are 5.23, 9.25, and 10.66, respectively, i.e., methylamine is the strongest base and its enhanced solvation environment may justify the use of pK_a as an explanation for the proton transfer in this case.

For the $m = 2$ clusters, that all contain two ions, an important question is whether these are present as contact or solvent-separated ion pairs because the growth rate is likely to be higher for the latter. Figure 4 illustrates that a contact ion pair (with a direct H-bond) is present in the base-free cluster for about 90% of the time when the acid is deprotonated. For the HB^+-containing clusters, only one out of six cases shows a contact ion pair, whereas acid and base are separated by one or two water molecules in the other cases. In contrast, many of the static calculations indicate direct H-bonding between the acid and base.[7,10,13−15]

In conclusions, our FPMD simulations indicate the importance of two sulfuric acid molecules for the formation of double ions in $(H_2SO_4)_m \cdot base \cdot (H_2O)_6$ clusters at 250 K. For $m = 2$, one acid molecule is mostly deprotonated even when no base is present. In most of these clusters, the deprotonated acid and protonated base are separated by one or two water molecules. Further simulations are necessary to map out the free energy surface and to evaluate the importance of nuclear quantum effects for nucleation in these ternary systems.[30]

(30) Nellas, R. B.; Chen, B.; Siepmann, J. I. *Phys. Chem. Chem. Phys.* **2007**, *9*, 2779–2781.