Postprint: Mechanistic Study on the Effect of Sodium Halides on the Aqueous Solubility Characteristics of Malonic Acid Aerosol Particles

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Abstract

Water vapor in the atmosphere affects the growth and evolution kinetic characteristics of aerosol particles, thereby altering their environmental effects. Currently, understanding of the interaction mechanism between aerosol particles containing organic components and water remains very limited. This study establishes a molecular dynamics model for investigating the water-solubility characteristics of pure organic aerosol and organic-inorganic mixed aerosol particles, simulating the effects of different sodium halide salts (Na 工/NaCl/NaF) on the water-solubility characteristics of malonic acid (C3H40 户 clusters under different temperature conditions. The study focuses on analyzing the cluster structures and gas-particle interface characteristics under the influence of various factors. The results show that as temperature increases, the C3H404 H}O clusters successively exhibit layered structures and mixed structures. After adding 40 sodium halide molecules, the ranking of water molecule dissolution degree for the initial clusters is 40NaF<40NaCl

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Preamble

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Impact of Sodium Halides on the Water-Soluble Characteristics of Malonic Acid Aerosol Particles

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Abstract

Atmospheric water vapor influences the growth and evolution dynamics of aerosol particles, thereby altering their environmental effects. However, understanding of the interaction mechanisms between water and aerosol particles containing organic components remains limited. This study establishes molecular dynamics models to investigate the water-soluble characteristics of pure organic aerosols and organic-inorganic mixed aerosol particles. We simulate the effects of different sodium halide salts (NaI/NaCl/NaF) on the water dissolution behavior of malonic acid ($C_3H_4O_4$) clusters under various temperature conditions, with particular focus on analyzing cluster structures and gas-particle interfacial properties under different influencing factors. The results demonstrate that as temperature increases, $C_3H_4O_4$-H_2O clusters sequentially exhibit demixed structures and mixed structures. After adding 40 sodium halide molecules, the dissolution degree of the initial clusters by water molecules follows the order: 40 NaF < 40 NaCl < 0 NaX < 40 NaI, with these differences becoming more pronounced at higher temperatures. At elevated temperature (T = 300 K), the surfaces of all cluster types contain both $C_3H_4O_4$ molecules and H_2O molecules, with the hydrophobic groups of $C_3H_4O_4$ molecules oriented toward the gas phase.

Keywords: aerosol; malonic acid; sodium halide; dissolution; molecular dynamics

Introduction

Atmospheric aerosol particles significantly influence global climate conditions, atmospheric radiative forcing, and regional air quality. Ambient water vapor plays a crucial role in the growth and evolution of aerosol particles, primarily affecting their light scattering properties, cloud lifetime, and particle sedimentation rates. Organic compounds constitute a substantial fraction of aerosol particle composition, and the dynamic evolution of their interactions with water vapor has long been a focal point and challenge in aerosol research. Current investigations primarily employ experimental methods and thermodynamic classical theory-based modeling approaches, both of which have significant limitations in elucidating molecular-level mechanisms governing aerosol-water interactions. Consequently, molecular simulation techniques are necessary.

Molecular dynamics methods based on classical mechanics theory have gradually been applied to study the hygroscopic characteristics of simple-component aerosol particles. For instance, Zhang et al. used MD simulations to investigate the kinetic characteristics of newly formed clusters during homogeneous and ion-induced water vapor nucleation processes. Bahadur and Russell employed MD methods to study the deliquescence properties of NaCl particles and analyzed the variation of water molecule adsorption coefficients during hygroscopic processes. Akbarzadeh et al. investigated differences in deliquescence characteristics between NH_4Cl and NH_4NO_3 particles using MD simulations. The Picaud research group conducted MD studies on the structural evolution of binary aerosol systems involving malonic acid, formic acid, acetic acid, and propionic acid particles interacting with water molecules, analyzing the hygroscopic properties of different binary particles. Comparing their simulation results with Schill' s experimental work, they concluded that the hygroscopic characteristics of organic aerosol particles depend not only on the oxygen-to-carbon ratio of the organic compound but also on the number of carboxyl groups and the molecular structure of the organic species. The Chakraborty group subsequently investigated the structure and interfacial properties of aqueous aerosol particles coated with monocarboxylic and dicarboxylic acids. However, current research on interactions between organic-inorganic mixed aerosol particles and water vapor primarily relies on experimental methods, with molecular-level kinetic mechanisms remaining largely unexplored.

This study establishes molecular dynamics models for binary $C_3H_4O_4$-H_2O systems and ternary $C_3H_4O_4$-sodium halide (NaI/NaCl/NaF)-H_2O systems. We simulate the effects of different sodium halide types on the interaction processes between organic aerosol particles and water molecules under various temperature conditions, comparing and analyzing the structural and interfacial evolution characteristics of the particles.

1. Molecular Dynamics Simulation

The simulation system contains three molecular types: water molecules are modeled using the SPC/E model, malonic acid molecules employ potential parameters from the OPLS-AA force field, and ions from sodium halides use parameters from the literature. The potential function expression for the simulation system comprises non-bonded potential energy terms (including Lennard-Jones 12-6 potential and electrostatic potential) and intramolecular interaction potential terms (bond stretching, angle bending, and dihedral torsion). For 1-4 atomic interactions within the same molecule, $f = 0.5$; otherwise, $f = 1$. The cutoff radius for van der Waals and Coulombic forces is 1.4 nm, with long-range Coulombic forces calculated using the PPPM algorithm. Simulations employ periodic boundary conditions with a time step of 1 fs.

All simulations in this study utilize the NVT ensemble with temperature control via the Nose-Hoover thermostat. First, three clusters containing 120 malonic acid molecules ($C_3H_4O_4$) and 40 different sodium halide molecules (NaI/NaCl/NaF) are constructed to represent different organic-inorganic mixed aerosol particles, placed in a cubic box with 8 nm edge length. After 2 ns of equilibration, the clusters are transferred to the center of a new cubic box (8 nm edge length) with 360 uniformly distributed water molecules added to simulate specific humidity conditions. The system runs for 5 ns at 100 K, during which all water molecules become adsorbed onto the initial clusters. The clusters are then placed in another new cubic box (22 nm edge length) and simulated for 1 ns under different temperature conditions (100, 140, 180, 220, 260, and 300 K). Some temperature values employed in this study are below typical atmospheric tropospheric temperatures because, in molecular dynamics simulations, cluster structural and interfacial changes primarily depend on the molecular potential parameters. Since the accuracy of these parameters cannot be guaranteed, the simulation system is controlled at different temperatures —while ensuring cluster molecules do not evaporate—to capture all possible structural and interfacial characteristics. Finally, data collection is performed for 1 ns across all simulation systems.

For comparison, hygroscopicity simulations of pure malonic acid clusters (120 $C_3H_4O_4$) are conducted following the same procedure. To analyze the structural and interfacial properties of different clusters, we calculate equilibrium snapshots, cluster size distribution functions, and cluster radial distribution functions based on molecular simulation results. During analysis, the Stillinger criterion is adopted to determine whether two molecules are connected. The distance criteria for different molecular types are as follows: two malonic acid molecules are considered connected if any of these conditions are met: $r(O(C=O)\text{-}H(O\text{-}H)) \leq 0.225$ nm, $r(O(C=O)\text{-}H(C\text{-}H)) \leq 0.325$ nm, $r(O(C\text{-}O)\text{-}H(O\text{-}H)) \leq 0.225$ nm, or $r(O(C\text{-}O)\text{-}H(C\text{-}H)) \leq 0.325$ nm. For malonic acid molecules and ions: $r(Na^+\text{-}O(C=O)) \leq 0.32$ nm, $r(Cl^-\text{-}H(O\text{-}H)) \leq 0.28$ nm, $r(F^-\text{-}H(O\text{-}H)) \leq 0.19$ nm, $r(I^-\text{-}H(O\text{-}H)) \leq 0.325$ nm. For ion-ion interactions: $r(Na^+\text{-}Cl^-) \leq 0.33$ nm, $r(Na^+\text{-}F^-) \leq 0.28$ nm, $r(Na^+\text{-}I^-) \leq 0.41$ nm. These critical values correspond to the distances at the first valley of the respective radial distribution functions.

2. Results and Discussion

2.1 Cluster Structure

Qualitative structural information for clusters in different simulation systems can be obtained from simulation snapshots. This study tracks structural changes of various cluster types under different temperature conditions. Figure 1 shows structural snapshots of pure $C_3H_4O_4$ clusters and $C_3H_4O_4$+NaI/NaCl/NaF clusters after interacting with water at two temperatures (140 K and 300 K). For binary $C_3H_4O_4+H_2O$ clusters, increasing temperature leads to sequential appearance of demixed structures (water molecules wrapping the $C_3H_4O_4$ cluster as a shell) and mixed structures (water molecules penetrating inside the $C_3H_4O_4$ cluster). This behavior of binary $C_3H_4O_4+H_2O$ clusters matches simulation results from the literature, qualitatively validating the simulation methodology employed in this study.

When sodium halides are added, ternary $C_3H_4O_4$+NaI/NaCl/NaF+H_2O clusters exhibit different structures compared to binary $C_3H_4O_4+H_2O$ clusters as temperature increases. Specifically, clusters with NaI and NaCl show both demixed and mixed structures, while clusters with NaF exhibit only demixed structures.

[Figure 1: see original paper]

2.2 Cluster Size Distribution Function

Quantitative description of structural changes in binary $C_3H_4O_4+H_2O$ clusters and ternary $C_3H_4O_4$+NaI/NaCl/NaF+H_2O clusters under different temperature conditions can be obtained by calculating the size distribution functions of $C_3H_4O_4$ clusters or $C_3H_4O_4$+NaI/NaCl/NaF clusters in the simulation systems. Corresponding to Figure 1, Figure 2 lists the size distribution functions of different cluster types at two temperatures (140 K and 300 K) (a–d). Figure 2 also shows the positions of the second peaks in the size distribution functions for different cluster types at 300 K (e). For convenient comparison, in Figure 2(e) all sizes of $C_3H_4O_4$ clusters in the binary system are multiplied by 5/3.

For $C_3H_4O_4$ clusters in the binary $C_3H_4O_4$+H_2O system, the size distribution functions under different temperatures (140 K and 300 K) both exhibit two peaks (at n 1 and n 120), corresponding to two primary cluster sizes present in the system. The cluster size of approximately 1 corresponds to molecules slightly exceeding the distance judgment criteria defined in this study. As temperature increases, the first peak grows while the second peak decreases, indicating that water molecules penetrate the initial $C_3H_4O_4$ cluster and partially dissolve it. This phenomenon occurs because enhanced molecular thermal motion creates numerous cavities within the malonic acid cluster, allowing water molecules to infiltrate.

After adding sodium halide salts, the number of peaks and variation trends in the size distribution functions of $C_3H_4O_4$+NaX clusters at both temperatures are essentially identical to those of $C_3H_4O_4$ clusters in the binary system. However, Figure 2(e) reveals that the size values corresponding to the second peaks of the four cluster distribution functions follow the order: 40 NaI < 0 NaX < 40 NaCl < 40 NaF, indicating that sodium halide addition alters the dissolution degree of the initial $C_3H_4O_4$ cluster by water, and this alteration depends on the sodium halide type. These results quantitatively validate the conclusions from the cluster snapshot analysis above.

To more intuitively demonstrate the effects of different factors on the dissolution degree of initial $C_3H_4O_4$ clusters and $C_3H_4O_4$+NaI/NaCl/NaF clusters in the simulation systems, this study calculates the change rate (N/N_0) of the largest cluster size (N) relative to the initial size (N_0) as a function of temperature. The results are shown in Figure 3.

[Figure 2: see original paper]

Figure 3 reveals that at low temperatures ($T \leq 180$ K), the dissolution degree of initial clusters by water is nearly zero in all simulation systems. As temperature increases, the size of initial clusters decreases in all systems. Under the same temperature conditions, the change rate of cluster size (N/N_0) follows the order: 40 NaF > 40 NaCl > 0 NaX > 40 NaI. This demonstrates that sodium halide addition changes the stability of initial clusters, and the difference in the degree of influence of various sodium halides on malonic acid cluster stability increases with temperature.

[Figure 3: see original paper]

2.3 Cluster Radial Distribution Function

The distribution of different components in clusters under humid conditions can be obtained from radial distribution functions of representative atoms in the corresponding molecules. Since calculation of component radial distribution functions requires approximately spherical clusters, this study only calculates radial distribution functions of $C_3H_4O_4$ molecules, H_2O molecules, Na^+, and X^- in $C_3H_4O_4$+H_2O clusters and $C_3H_4O_4$+NaI/NaCl/NaF+H_2O clusters at

T = 180 K and T = 300 K. Here, O(C=O) and H(C-H) represent $C_3H_4O_4$ molecules, while O(H_2O) represents H_2O molecules. The results are shown in Figure 4.

[Figure 4: see original paper]

Figure 4 shows that for all simulation systems, sodium halide ions are located inside the clusters. At lower temperature (T = 180 K), water molecules wrap around the initial $C_3H_4O_4$ clusters and $C_3H_4O_4$+NaI/NaCl/NaF clusters. As temperature increases (T = 300 K), water molecules diffuse into the cluster interior, but the diffusion degree differs among cluster types. Notably, the diffusion degree of water molecules in malonic acid clusters containing NaCl/NaF is smaller than in pure malonic acid clusters and those containing NaI. At higher temperature (T = 300 K), the gas-particle interface of both binary $C_3H_4O_4+H_2O$ clusters and ternary $C_3H_4O_4+H_2O$+NaX clusters consists of malonic acid molecules and water molecules, with the hydrophobic groups (-CH_3) of malonic acid molecules oriented toward the gas phase and hydrophilic groups (-COOH) oriented toward the particle interior.

The area ratio of different components at the gas-particle interface and the morphology of organic molecules affect the accommodation coefficient of water vapor molecules on the cluster surface from the gas phase, thereby influencing the hygroscopic growth characteristics of the cluster. Through this simulation analysis, we can obtain variation patterns of the relative content of different components on the surfaces of pure malonic acid and malonic acid-sodium halide mixed aerosol particles, as well as the molecular morphology of surface organic components. This will lay the foundation for the quantitative description of water molecule adsorption coefficients on aerosol particle surfaces in future work.

3. Conclusions

This study employs molecular dynamics methods to simulate the water-soluble characteristics of pure malonic acid organic aerosol particles and malonic acid-sodium halide mixed aerosol particles. Through analysis of simulation snapshots and calculations of cluster size distributions, maximum cluster size change rates, and cluster radial distribution functions, we investigate the influence patterns and microscopic mechanisms of temperature and sodium halide type (NaI/NaCl/NaF) on the water-soluble characteristics of malonic acid ($C_3H_4O_4$) aerosol particles from both qualitative and quantitative perspectives. The main conclusions are as follows:

Under humid conditions, as temperature increases, water molecules gradually dissolve the initial $C_3H_4O_4$ clusters. Binary $C_3H_4O_4+H_2O$ clusters sequentially exhibit demixed structures (water molecules wrapping the initial cluster) and mixed structures (water molecules penetrating inside the $C_3H_4O_4$ cluster).

The addition of different sodium halide salts produces varying effects on the stability of initial clusters (their susceptibility to dissolution by water molecules), with stability following the order: 40 NaF > 40 NaCl > 0 NaX > 40 NaI. Consequently, clusters containing NaI and NaCl exhibit both demixed and mixed structures with increasing temperature, while clusters containing NaF show only demixed structures. Moreover, these differences in dissolution degree become more pronounced at higher temperatures.

At high temperature (T = 300 K), the surfaces of all cluster types studied consist of malonic acid molecules and water molecules, with the hydrophobic groups of malonic acid molecules oriented toward the gas phase.

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