Supplement of

Energetic analysis of succinic acid in water droplets: insight into the size-dependent solubility of atmospheric nanoparticles

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S1. Gibbs energy of hydration for force field selection

We computed the hydration free energy (ΔG_{hyd}) of one single succinic acid molecule in a box of water using thermodynamic integration (TI) (Kirkwood, 1935) to choose the reasonable force fields for the following PMF calculations. Five different combinations of force fields were used. The Generalized Amber force field (GAFF) (Wang et al., 2004) with the electrostatic potential (ESP) (Case et al., 2006) calculated charges (B3LYP/aug-cc-pVTZ) for the succinic acid was combined with several force fields: SPC (Berendsen et al., 1981), SPC/E (Berendsen et al., 1987), TIP3P (Jorgensen et al., 1983), TIP4P (Jorgensen et al., 1983), and TIP4P/2005 (Abascal and Vega, 2005) for the water molecules.

The TI simulations were computed with GROMACS 2016.5 (Van Der Spoel et al., 2005) at 298.15 K following the protocol of Shirts et al. (2003). One single succinic acid molecule was set in a cubic box of the volume 27 nm^3 with 877 water molecules. Contribution of Lennard-Jones and Coulomb interactions between the succinic acid molecule and the water molecules in the box for the thermodynamic integration were carried out using an alchemical reaction coordinate λ, where $\lambda = 0$ to $\lambda = 1$ correspond to the initial and final state, respectively. The interaction range was decomposed into 21 equally spaced λ-steps, and each λ-step was initially equilibrated for 200 ps then simulated for 500 ps. The free energy differences for each step was subsequently calculated by integrating $\langle \partial \mathcal{H} / \partial \lambda \rangle$ from $\lambda = 0$ to $\lambda = 1$. $\langle . \rangle$ denotes the average computed from the respective trajectory, where $\mathcal{H}$ is the Hamiltonian of the system. ΔG_{hyd} is the sum of the free energy differences from $\lambda = 0$ to $\lambda = 1$. In the context of computer simulations, such a use of TI methods is standard (Frenkel and Smit, 2002).

The experimental free energy of hydration ($\Delta G_{\text{hyd,exp}}$) pertinent to the TI simulations with a single solute molecule was implemented as (Sander, 1999; Roeselová et al., 2004)

$$\Delta G_{\text{hyd,exp}} = \Delta G_{\text{hyd,exp}}^0 + RT \ln(\frac{p_0}{c_0 RT}) \tag{S1}$$

where $\Delta G_{\text{hyd.exp}}^0$ is the experimental hydration free energy corresponding to the standard state of $p_0 = 1$ atm gas pressure and $c_0 = 1$ mol L^{-1} aqueous concentration, R is the universal gas constant and $T = 298.15$ K for the standard state. $\Delta G_{\text{hyd.exp}}^0$ can be calculated from Henry's law constant k_{H} according to (Sander, 1999)

$$\Delta G_{\text{hyd.exp}}^0 = -RT \ln(\frac{p_0}{c_0} k_{\text{H}}) \tag{S2}$$

k_{H} ranging from $3.0*10^6$ to $4.1*10^7$ mol m^{-3} Pa^{-1} in this study was obtained as an average value from Sander (2015).

As shown in Fig. S1, ΔG_{hyd} from the combination of GAFF with ESP for the succinic acid molecule and TIP4P/2005 for water molecules is closest to $\Delta G_{\text{hyd,exp}}$ compared with the other four combinations (Zhang et al., 2018). Therefore, we selected the force field combination of GAFF with ESP for the succinic acid molecule and TIP4P/2005 for water molecules for the following calculations. In view of the approximate character of all force fields for water, discrepancies between calculation and experiment as seen in Fig.S1 are inevitable.
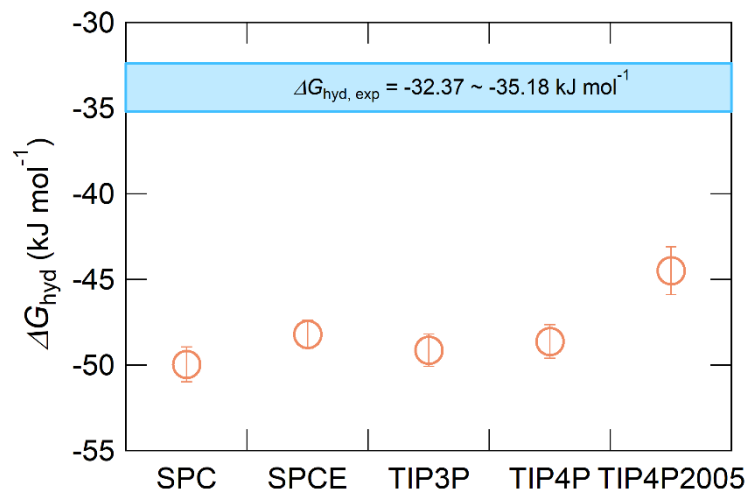
Figure S1. Gibbs energy of hydration (ΔG_{hyd})(kJ/mol) at 298.15K for succinic acid using five different force field-water model combinations. The light blue zone represents the experimental free energy of hydration ($\Delta G_{hyd,exp}$).

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