

Comment on acp-2020-1329

Anonymous Referee #3

Referee comment on "Energetic analysis of succinic acid in water droplets: insight into the size-dependent solubility of atmospheric nanoparticles" by Chuchu Chen et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2020-1329-RC3>, 2021

This study presents a detailed analysis of the energy profiles of a single succinic acid molecule as it is moved from the middle of a droplet to the surface. This transect is compared with the one of a flat slab. Enthalpic (split up in solvent-solvent and solute-solvent contributions) as well as entropic energy terms as a function of droplet radius and half slab thickness (both varying from 1 to 4 nm) were calculated. The results were discussed in the context with previous molecular dynamics studies and experimental work (Sayou et al., 2017; Werner et al., 2016). The authors found that the surface preference of succinic acid is stronger for a droplet than the slab of the same size, and that the surface propensity is enhanced due to the curvature effect. Moreover, they found that the surface preference is primarily an enthalpic effect, both, in the droplet and in the slab. Yet, if fluctuations are considered (Figs. 4 and 5) the surface propensity of succinic acid seems to become irrelevant compared with the huge effect of the internal bulk volume to surface ratio, which strongly increases with increasing droplet size from radii of one to four nanometers. To give relevance to their work, the authors should therefore add a statement whether the size dependence due to the enthalpic effect is relevant at all and whether it needs to be considered when analyzing surface/bulk partitioning of organic species. This question becomes even more relevant considering that the droplets under investigation are very small and thus the curvature effects are maximized. Based on their size, the droplets would be nucleation-mode aerosol particles, but considering their strong dilution, they rather represent particles during cloud droplet activation. Yet, so small particles (and such a strong curvature) is unrealistic for cloud droplet activation. The authors should therefore better motivate the relevance of the chosen system and explain for what atmospheric processes it might be relevant. Moreover, the relevance of internal pressure arising through the high curvature in small droplets could be discussed more explicitly and quantitatively. The internal pressure within the droplet could be quantified and related to the solvation energy of succinic acid. To find out whether the size dependence of the solvation energy is depending on the internal pressure, bulk systems with increasing internal pressure could be calculated as a reference. Overall, the discussion and the English should be improved to increase readability.

Specific comments

Line 15, "with the potential of mean forces method": rephrase.

Line 19: why only "may"? Please be more specific.

Line 58, "organic composition solvation": rephrase.

Line 60: By simulating only one succinic acid molecule in water, you neglect solute-solute interactions, which are highly important in aerosol particles. Please comment on this restriction.

Line 86: Having only one succinic acid molecule together with so many water molecules corresponds to very high dilution. At such high dilution succinic acid dissociation becomes relevant. Please comment on this.

Line 156: It would be interesting to relate the curvature effect to internal pressure.

Line 159–160: What is meant here? Just a surface enrichment or an increase of surface enrichment?

Line 162: Figure 3b shows the opposite or do you mean "less negative"?

Lines 174–175: Why "at the considered temperature"? For what temperature would the pressure be relevant for a flat slab?

Lines 177–179: The discussion of Fig. 3 should be improved. It should be tried to rationalize the molecular dynamics simulation rather than just describe the curves.

Line 180, "This result shows that different from thin slabs": rephrase.

Line 181: quantify the pressure.

Lines 192–194: Please explain better.

Lines 201–206: This needs to be formulated better.

Lines 216–217: rephrase.

Line 246: explain Panel 6b better.

Line 250: can you specify the long-range forces?

Figure 1: Could you add an image where the succinic acid molecule is directly on the surface to visualize surface hydration?

Figure 2: In panel (c) (3 nm) the curves of the droplet and the slab overlap at the interface, while in all other panels (1, 2, 4 nm) this is not the case. Do you have an explanation?

Figure 3: Are the points depicted in these plots averages or evaluated at the center of the slab/droplet? Can you explain the reversal of trends found in panels (a) and (b) with increasing droplet radius/slab thickness?

Figure 6: explain how t is evaluated. Are the differences relevant considering the fluctuations shown in Figs. 4 and 5?