Reply to CC:

Referee report for “Surface tension and hygroscopicity analysis of aerosols containing organosulfate surfactants”

The manuscript provides surface tension measurements of a series of sodium alkyl sulfates (SMS, SES, SOS, SDeS and SDS) in binary and ternary (mixtures with citric acid or NaCl) performed using electrodeformation of optically trapped droplets probed with Raman spectroscopy. The measured values are used to infer the hygroscopic growth factors and kappa-parameters. As the members of the studied series are often used proxies for real atmospheric surfactants – also others than atmospheric organosulfates, as SDS has been used in this context at least since Li et al. (1998) – and also the citric acid can be seen as a proxy various highly-oxidised organic molecules, the reported measurements are relevant for the readers of this journal and especially the study of a series of homologous molecules provides molecular-level insight. The manuscript is well written and suitable for publication in ACP after following comments have been considered.

The major concern comes from the stated purities of the compounds used, especially SMS (>92%) and SOS (>95%): as even a small amount of, say, SDS could significantly affect the surface tensions here, can it be confirmed that no strongly surface-active impurities are present?

The potential impact of impurities on surface active molecules should always be considered. As is pointed out, the stated purities of sodium methyl sulfate (SMS, >92%) and sodium octyl sulfate (SOS, >95%).

Based on product specifications, SMS may contain trace amounts of residual alcohols from synthesis. However, such volatile impurities will evaporate rapidly during droplet generation, especially given the use of a nebulization or spraying step. For SOS, a small amount (up to 1%) of 1-octanol may be present due to partial hydrolysis. In our experiments, the sodium octyl sulfate is mixed with citric acid at a 1:100 molar ratio, meaning the resulting 1-octanol concentration is approximately 10^{-4} M. At this level, the influence of 1-octanol on the surface tension is expected to be negligible. This estimation is supported by prior studies; for example, see references: Langmuir 1997, 13, 15, 4064–4068 and J. Colloid Interface Sci. 2017, 488, 1–10.

Additionally, our measured surface tension values for sodium octyl sulfate are in good agreement with those reported in the literature, further suggesting that the effect of potential impurities is minimal. See, for example: J. Phys. Chem. B 1996, 100, 50, 19634–19640.

With respect to sodium dodecyl sulfate (SDS), we are aware that commercial SDS can contain dodecanol as an impurity, which is strongly surface-active. However, our surface tension measurements are consistent with values reported in the literature for purified SDS samples in which such impurities have been largely removed. This comparison is supported by the findings of the following study: Langmuir 2022, 38, 22, 6794–6801.

Overall, these observations suggest that any surface active impurities present in our samples are at concentrations low enough to have a negligible impact on the reported surface tension values (or simply evaporate prior to the start of the measurement).

Minor issues:

1. Line 5 (abstract): “the surface tension continues decrease” – I assume that this refers to the hydrocarbon length, but I can be wrong as well. Please reformulate this sentence to be less ambiguous.

The sentence refers to the behavior of short-chain organosulfates, whose surface tension continues to decrease with decreasing relative humidity, even under highly viscous and dry conditions. This suggests that surface adsorption persists without reaching a plateau, in contrast to the behavior typically observed for organic acids.

However, the original sentence was awkwardly written. We have revised the sentence in the abstract as follows:

“For droplets containing short-chain OSs, the surface tension decreases as relative humidity (RH) decreases, even under dry and highly viscous conditions.”

2. Line 20: Perhaps the most recent IPCC assessment report could be cited instead?

We have added a citation to the IPCC’s sixth assessment report (2023).

3. Line 39: Study of Li and Jang (2013) did not pass the peer review for ACP (as apparent from the reference), please reconsider this.

We removed this reference.

4. Line 56: For Kelly et al. (2009), please cite the corresponding GMD article instead of the preprint, if there is no special reason for the latter.

Fixed.

5.Line 96: For consistency, please indicate also the instrument(s) used for gravimetry.

We just weigh 5 mL of each sample using a micropipette (Sartorius AG, Germany) and a balance (Sartorius AG, Germany).

We have edited the referenced sentence to include these details:

“The density (ρ) of each bulk solution was determined gravimetrically by weighing 5 mL aliquots dispensed with a micropipette (Sartorius AG, Germany) on a digital balance (Sartorius AG, Germany) accurate to 10^{-4} mg.”

6. Equations (1)-(3) and Table 1: These kinds of data are very valuable to test different hypothesis and compare theories of CCN activation. To facilitate it, authors have kindly included the measurement data as a supplement. However, also reporting measurement uncertainties (either in the supplement or at least in Fig. 2) would further facilitate such use.

The accuracies of the instruments used to make the measurements whose fits are listed in Table 1 are now provided in the main text.

7. Line 115: Please provide also original references for the Szyszkowski-Langmuir and Eberhardt models.

References have been added.

8. Equation (5): It might be good to stress that the mole fraction here is the total mole fraction of the solution, as a similar type of equation has been used in related context (e.g. Bzdek et al., 2020) with surface mole fractions.

We now explicitly state that x_i is the bulk mole fraction of the solute.

9. Please provide a reference for Eq. (7).

Reference have been added. It is: Lac, E. and Homsy, G. Axisymmetric deformation and stability of a viscous drop in a steady electric field, J. Fluid Mech., 590, 239–264.

10. Lines 256-261: The conclusions hold, as the literature values refer either to kappas calculated assuming the surface tension of water (Han et al., 2022) or deduced directly from measured growth factors (Marsh et al., 2017). This could be spelled out clearly.

The referenced sentence has been rewritten to clarify this point. It now reads: **“At high RH, results converge to the value of $\kappa \approx 0.2$, which has been previously reported for aqueous tricarboxylic acids like CA, where these literature values were either calculated assuming the surface tension of water (Han et al., 2022) or derived directly from growth factor measurements without surface tension corrections (Marsh et al., 2017).”**

11. Figure 7 (c) and (d) and related discussion: Could at least part of the water signal originate from an adsorbed layer instead of residual water within the particle? Such adsorbed layers have been extensively studied for nanosized NaCl and NaCl-SDS particles (e.g. Harmon et al., 2010, and references therein).

In response to this comment, we have added the following to our explanation in the manuscript:

“A thin interfacial layer of strongly bound water between the NaCl core and the surfactant shell could explain this residual water signal and the retention of a near-spherical shape, consistent with hydration structures reported for NaCl–SDS core–shell systems (Harmon et al. 2010).”

Very minor issues:

Line 36: From US to China is not more than half of the Northern Hemisphere, thus “globally” sounds like an overstatement. Maybe either part of the sentence could be reworded?

We have modified the sentence as follows:

“Organosulfates (R-OSO$_3^-$, OSs) are among the primary and most abundant anionic surfactants in atmospheric aerosols and have been detected worldwide, from North and South America to Asia.”

I know that I am already presenting a minority view at this point, but I would prefer authors to make a clear distinction between “aerosol” and “aerosol particle”.

Thank you for raising this point. We agree that the distinction is important. Strictly speaking, “aerosol” refers to the suspension of particles in a gas, whereas “aerosol particle” designates the individual particulate matter within that suspension. In the laboratory, we generate surrogates that mimic atmospheric aerosols but are not perfect representations of ambient particles. Throughout this manuscript, the term “aerosol droplets” is used to describe liquid-phase particles produced in the lab (via a medical nebulizer), and we might have used it interchangeably with the term ”aerosols” multiple times.

Additional references:

Harmon, C W., R. L. Grimm, T. M. McIntire, M. D. Peterson, B. Njegic, V. M. Angel, A. Alshawa, J. S. Underwood, D. J. Tobias, R. B. Gerber, M. S. Gordon, J. C. Hemminger, and S. A. Nizkorodov, 2010: Hygroscopic Growth and Deliquescence of NaCl Nanoparticles Mixed with Surfactant SDS. J. Phys. Chem. B, 114, 2435-2449.

Li, Z., A. L. Williams, and M. J. Rood, 1998: Influence of Soluble Surfactant Properties on the Activation of Aerosol Particles Containing Inorganic Solute. J. Atmos. Sci., 55, 1859–1866.