Supplement of Atmos. Chem. Phys., 24, 11717–11725, 2024
https://doi.org/10.5194/acp-24-11717-2024-supplement

Atmospheric Chemistry and Physics Open Access

Supplement of

Predicting hygroscopic growth of organosulfur aerosol particles using COSMOtherm

Zijun Li et al.

Correspondence to: Zijun Li (zijun.li@qut.edu.au) and Noora Hyttinen (noora.hyttinen@fmi.fi)

Table S1. Summary of selected organosulfur (OS) compounds. The molecular weight (MW) is given in g/mol and the density (ρ) in g/cm^3. The liquid-phase densities have been estimated using the COSMO*therm* program.

Name	Abbreviation	MW	Molecular Formula	ρ
Sodium OS				
Methyl sulfate	NaMS	134.09	CH_3SO_4Na	1.95
Hydroxymethanesulfonate	NaHMS	134.09	CH_3SO_4Na	1.97
Ethyl sulfate	NaES	148.11	$C_2H_5SO_4Na$	1.46
2-hydroxyethylsulfonate	NaHES	148.11	$C_2H_5SO_4Na$	1.73
Potassium OS				
Glycolic acid sulfate	KGAS	194.20	$C_2H_3SO_6K$	1.81
Hydroxyacetone sulfate	KHAS	192.23	$C_3H_5SO_5K$	1.65
2-butenediol sulfate	KBS	206.26	$C_4H_7SO_5K$	1.54
4-hydroxy-2,3-epoxybutane sulfate	KHEBS	222.26	$C_4H_7SO_6K$	1.64
Ammonium OS				
2-hydroxyethyl-sulfonate	NH_4HES	143.16	$C_2H_5SO_4NH_4$	1.59
(2R,3S)-1,3,4-trihydroxy-2-methylbutan-2-yl sulfate	NH_4TMS (a)	233.24	$C_5H_{11}SO_7NH_4$	1.42
(2R,3R)-2,3,4-trihydroxy-2-methylbutyl sulfate	NH_4TMS (b)	233.24	$C_5H_{11}SO_7NH_4$	1.42

S1 COSMO*therm* Parametrizations

Three parametrizations of the COSMO*therm* program were tested for the water activity calculations: BP_TZVPD_FINE_21 (abbreviated FINE), BP_TZVP_21 (abbreviated TZVP) and BP_TZVP_ELYTE_21 (abbreviated ELYTE).

The FINE parametrization utilizes BP/def2-TZVPD-FINE//BP/def-TZVP level of theory quantum chemistry input, while TZVP and ELYTE use BP/def-TZVP level of theory input. The highest level of theory parametrization, FINE, works poorly with the strong charges of small ions, such as atomic ions and strong small semi-spherical ions (such as SO_4^{2-}, NH_4^+) (BIOVIA COSMO*therm*, 2021). For this reason, the electrolyte parametrization, ELYTE, was recently developed to better describe the interactions between ions. However, the ELYTE parametrization is only recommended for up to 6 molal solutions, corresponding to around 0.1 mole fraction of salt in water (BIOVIA COSMO*therm*, 2021). A comparison between experimental and COSMO*therm*-derived water activities in ammonium sulfate solutions showed that the ELYTE and TZVP parametrizations lead to equally good agreement with experiments, while FINE significantly overestimates the experiments (Hyttinen, 2023). However, FINE was recommended for other ammonium and sulfate salts (Hyttinen, 2023).

In this study, we investigate salts containing two different atomic ions, Na^+ and K^+. We therefore tested the three different COSMO*therm* parametrizations for the studied salts. Fig. S1 shows a comparison of the parametrizations of one of the studied anions, hydroxyacetone sulfate, as an example. Water activities were computed for all three cations: a) Na^+, b) K^+ and c) NH_4^+. Generally, water activity estimates are lowest with ELYTE and highest with FINE. For the recommended concentration for ELYTE (< 6 mol kg^{-1}, right side of the grey lines), all parametrizations give similar results for the sodium (a) and ammonium (c) salts. On the contrary, water activities in the potassium solutions computed using the FINE parametrization are significantly higher than those computed using the two other parametrizations.

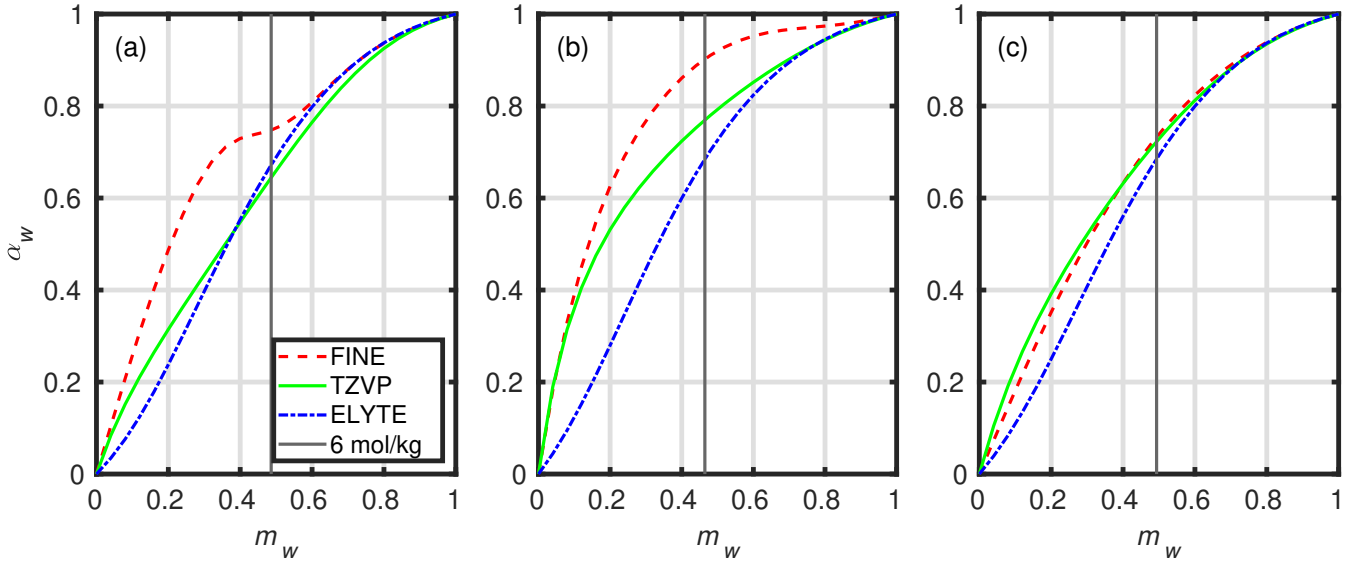

Figure S1. COSMO*therm*-estimated water activities (α_w) in a) sodium, b) potassium and c) ammonium hydroxyacetone sulfate salts at 295 K as a function of water mass fraction (m_w).

Fig. 2 in the main article shows how the hygroscopic growth factors (HGF) calculated using the FINE parametrization agree well with experiments. For some salts, it is possible to obtain even better agreement with experiments using either TZVP or ELYTE. However, without additional experiments we are not able to make more detailed recommendations on when the use of the other two parametrizations would be more appropriate. For this reason, as well as previous recommendations and simplicity in selecting parametrizations for future calculations, we have chosen to use the FINE parametrization in all of our calculations that do not contain ammonium sulfate.

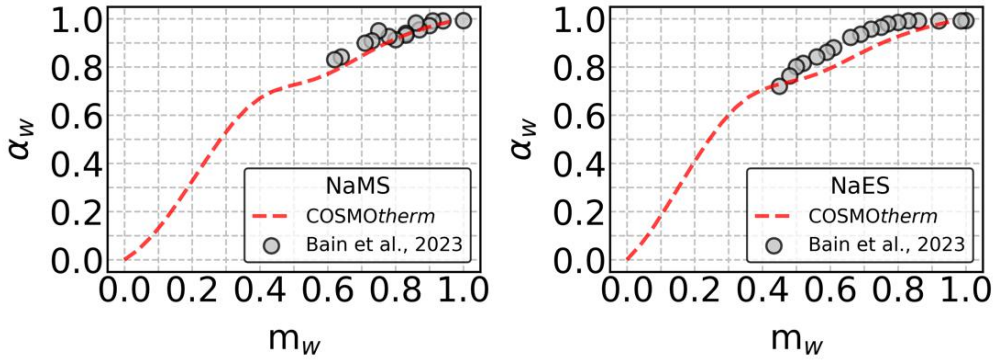

Figure S2. Comparisons between the COSMO*therm*-predicted water activities (α_w) and literature data (Bain et al., 2023) for NaMS and NaES.

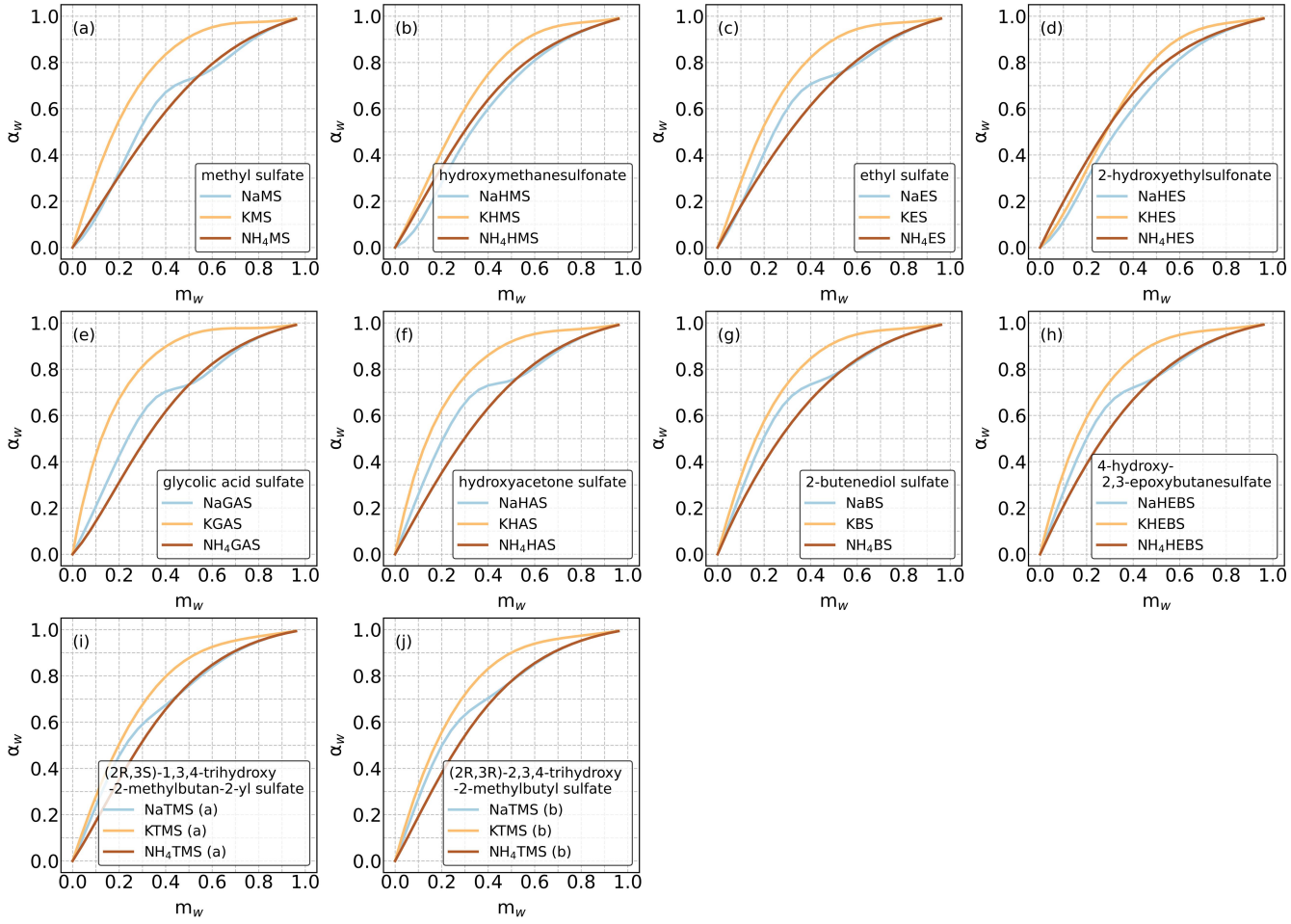

Figure S3. COSMO*therm*-derived water activities (α_w) in aqueous solutions of OS as a function of water mass fraction (m_w) at 295 K using the FINE parameterization. The sodium, potassium, and ammonium OS salts are correspondingly shown in blue, yellow, and red curves.

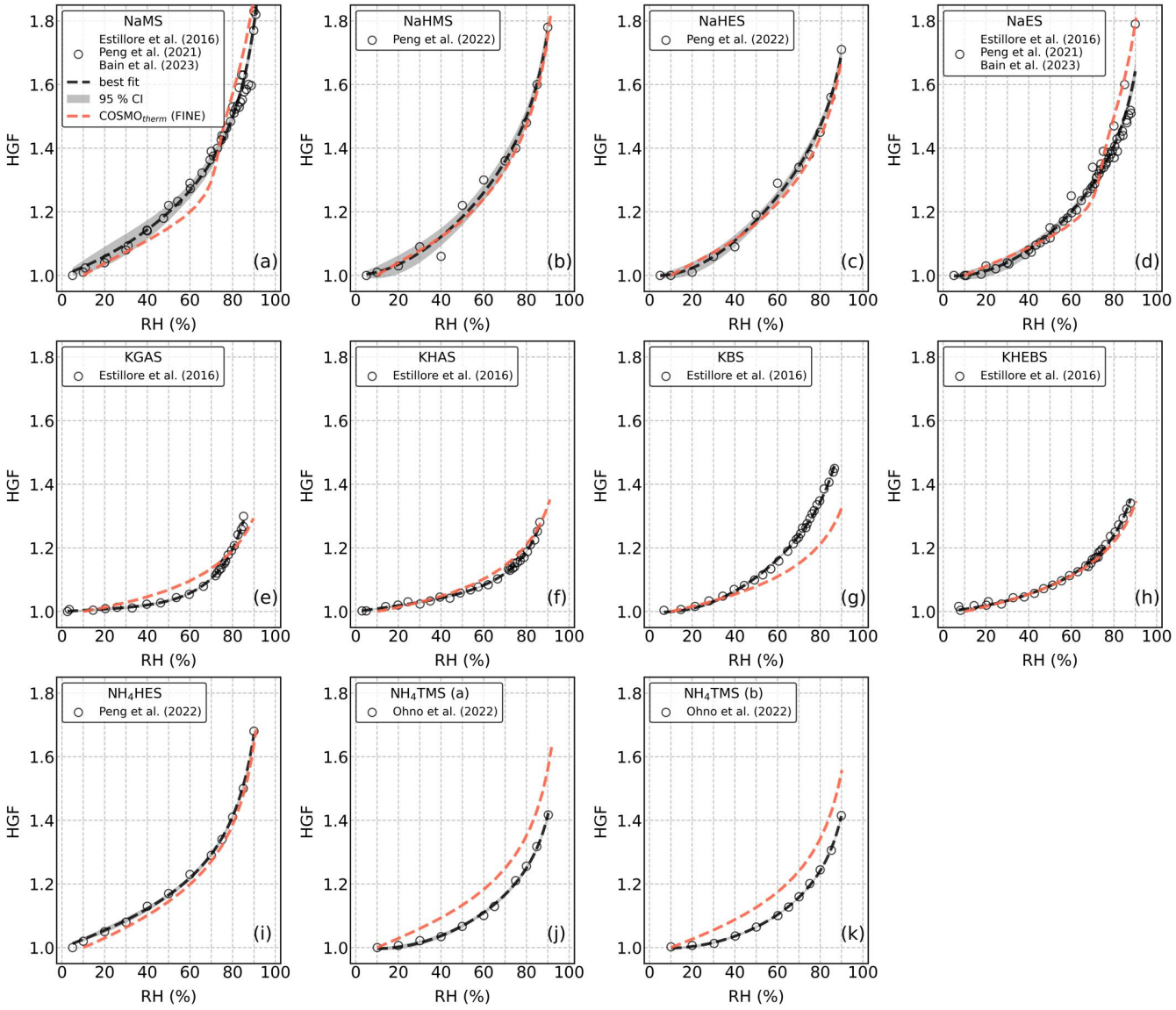

Figure S4. Hygroscopic growth factors (HGFs) of all OS particles as a function of RH at 295 K. The computed HGFs were estimated on the basis of the COSMO*therm*-derived water activities that used the FINE parameterization and are present in red dashed lines. The HGF measurement data from the literature are present in open circles in grey, with the best fit (black dashed lines) and 95% confidence intervals (95% CIs; shaded areas in grey).

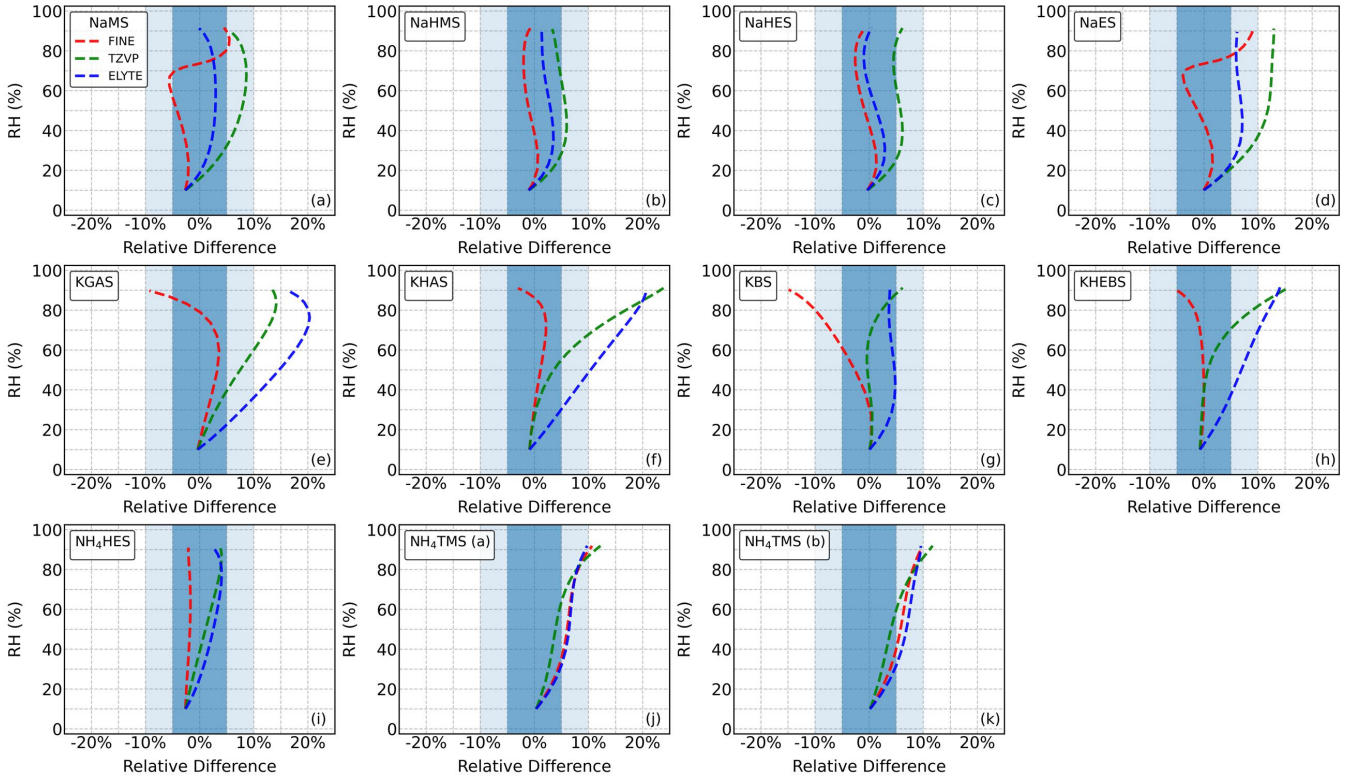

Figure S5. Relative differences between observed and model-simulated hygroscopicity growth factor for all OS particles at different RH at 295 K, with colors indicating FINE (red), TZVP (green), and ELYTE (blue) parametrizations.

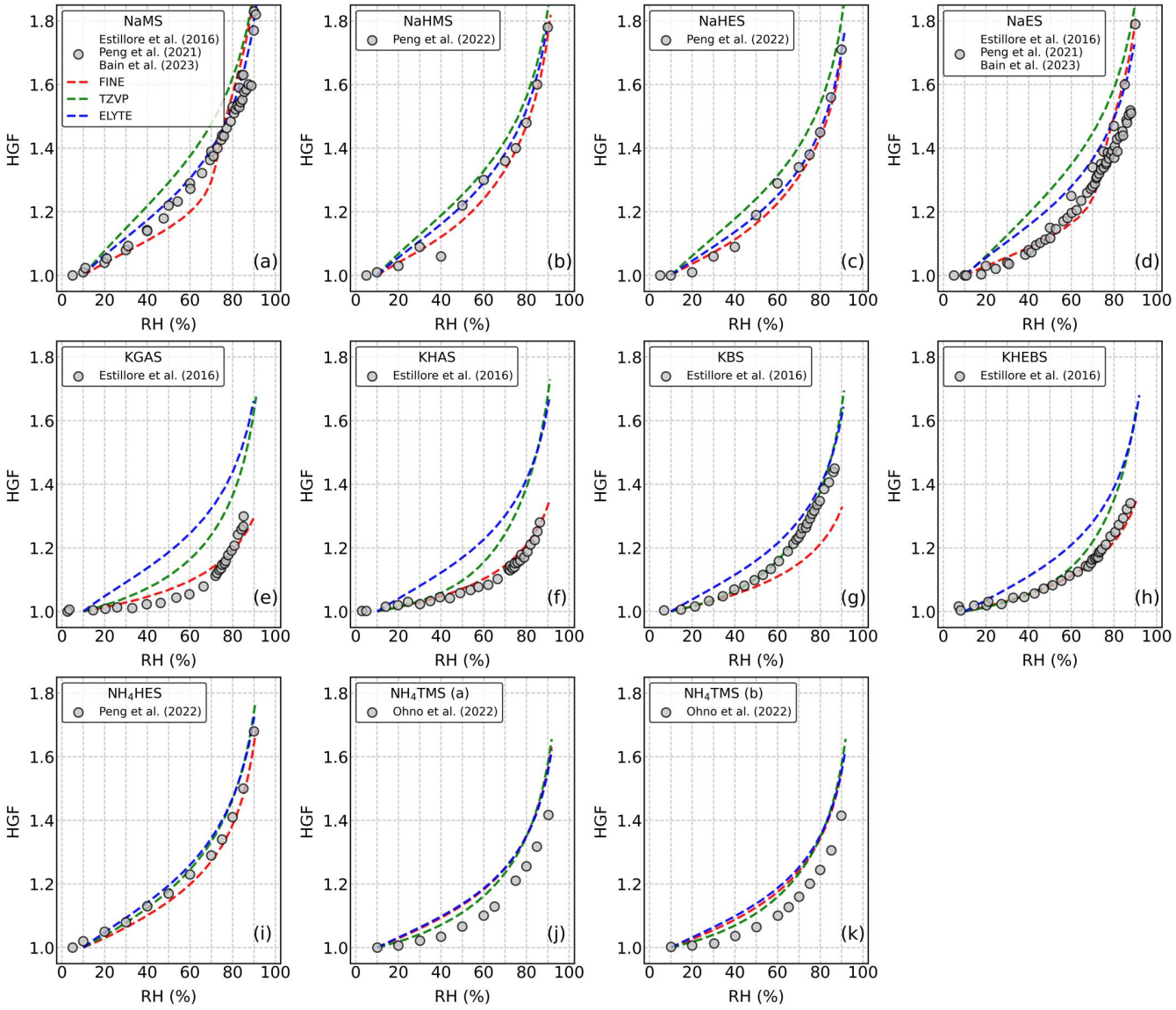

Figure S6. Hygroscopic growth factors (HGFs) of all OS particles as a function of RH at 295 K. The HGF derived from the COSMO*therm*-derived water activities are in dashed lines for FINE (red), TZVP (green), and ELYTE (blue) parameterizations. The HGF measurement data from the literature are present in filled circles in grey.

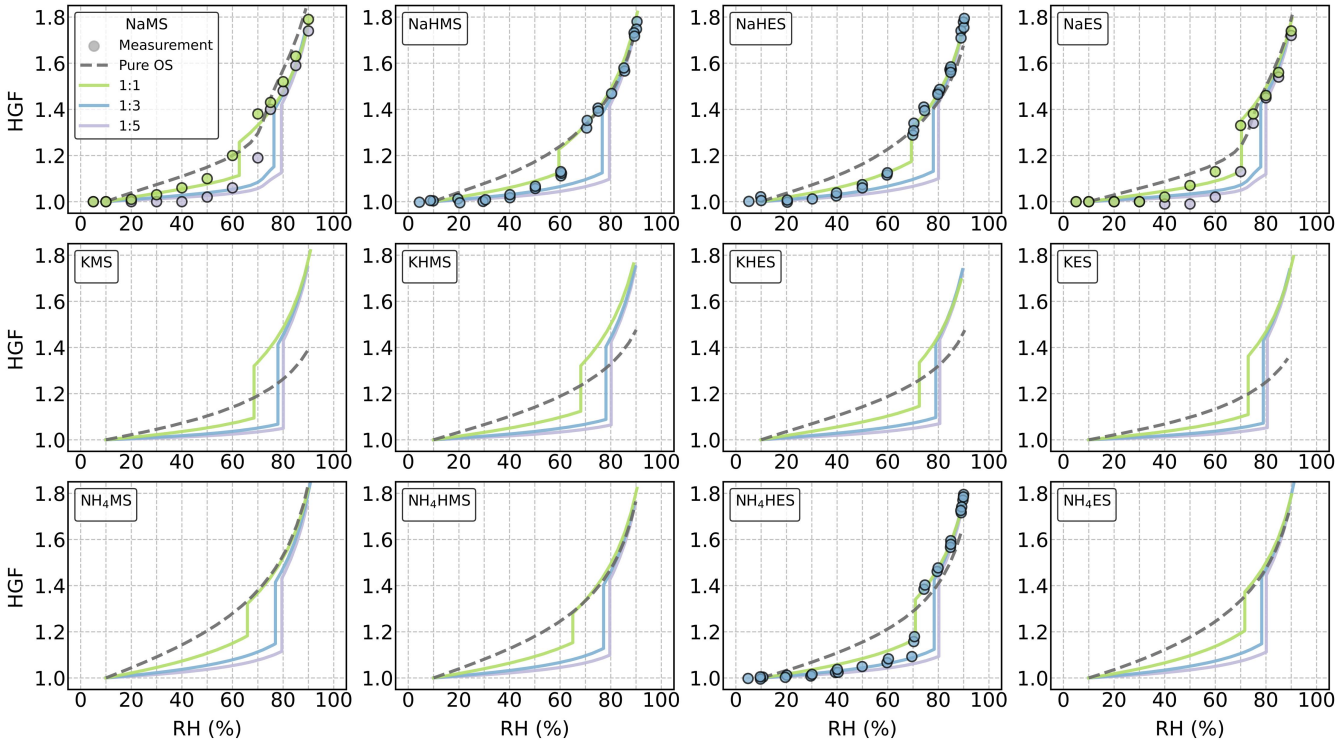

Figure S7. Hygroscopic growth factors (HGFs) for OS-AS mixture particles. The filled circles indicate the measurement data from the literature (Peng et al., 2021, 2022), with colors indicating different OS:AS mass ratios. The HGF data calculated from the COSMO*therm*-derived water activities are in dashed lines for pure organosulfur (OS) compounds and in solid lines for the OS-AS mixtures, with colors indicating different OS:AS mass ratios.

References

Bain, A., Chan, M. N., and Bzdek, B. R.: Physical properties of short chain aqueous organosulfate aerosol, Environ. Sci.: Atmos., 3, 1365–1373, https://doi.org/10.1039/D3EA00088E, 2023.

BIOVIA COSMO*therm*: Reference Manual, 2021.

Hyttinen, N.: The effect of atmospherically relevant aminium salts on water uptake, Atmos. Chem. Phys., 23, 13 809–13 817, https://doi.org/10.5194/acp-23-13809-2023, 2023.

Peng, C., Razafindrambinina, P. N., Malek, K. A., Chen, L., Wang, W., Huang, R.-J., Zhang, Y., Ding, X., Ge, M., Wang, X., Asa-Awuku, A. A., and Tang, M.: Interactions of organosulfates with water vapor under sub- and supersaturated conditions, Atmos. Chem. Phys., 21, 7135–7148, https://doi.org/10.5194/acp-21-7135-2021, 2021.

Peng, C., Malek, K. A., Rastogi, D., Zhang, Y., Wang, W., Ding, X., Asa-Awuku, A. A., Wang, X., and Tang, M.: Hygroscopicity and cloud condensation nucleation activities of hydroxyalkylsulfonates, Sci. Total Environ., 830, 154 767, https://doi.org/https://doi.org/10.1016/j.scitotenv.2022.154767, 2022.