Supplement of Atmos. Chem. Phys. Discuss., 15, 17317–17365, 2015
http://www.atmos-chem-phys-discuss.net/15/17317/2015/
doi:10.5194/acpd-15-17317-2015-supplement

Atmospheric Chemistry and Physics
Discussions
Open Access

Supplement of

Hygroscopic properties and cloud condensation nuclei activation of limonene-derived organosulfates and their mixtures with ammonium sulfate

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Supplementary information

1 Limonene organosulfates of MW 250 Da

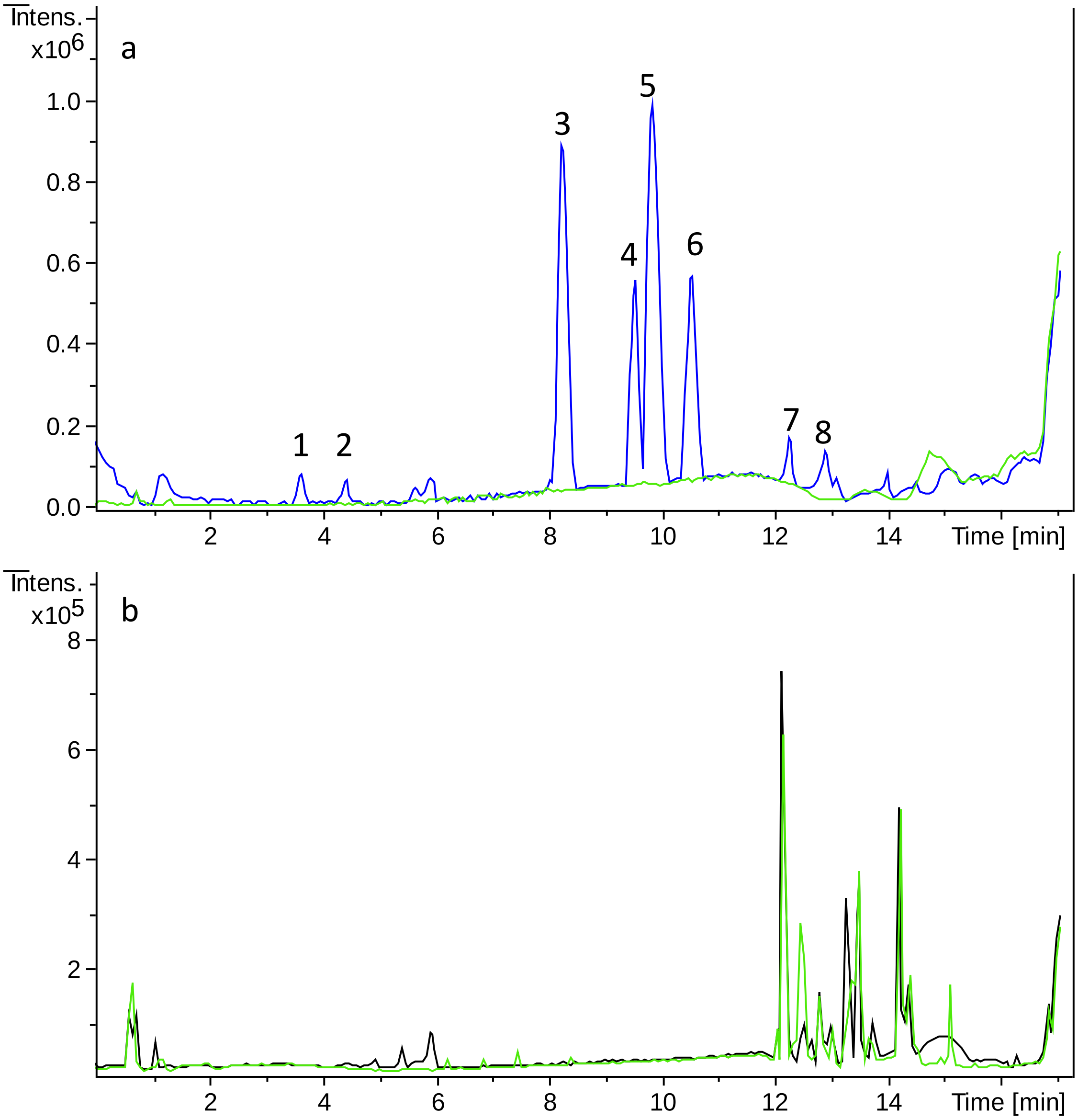


Figure 1: Base peak chromatograms of the purified limonene OS250 sample (blue) and a blank sample (green) using negative ionisation analysis (a) and positive ionisation analysis (b). peak 1: and 2: OS 286 (m/z 267.09), peak 3 to 6: OS 250 (m/z 249.08) and peak 7 and 8: OS 384 (m/z 383.19).

Figure 1 shows base peak chromatograms from UHPLC-ESI-q-TOF-MS analysis of the purified organosulfate 250 sample using negative (a) and positive (b) ionisation. The purified organosulfate 250 sample does not show any additional compounds from the positive ionisation analysis and only a small signal from an organosulfate with MW 268 (peak 1 and 2) and an organosulfate with MW 384 (peak 7 and 8) is observed.

In Table 1 below the chemical formulas (based on suggestions from smart formula in the program “data analysis” from Burker Daltonics) and suggested structures for the observed organosulfates are given.

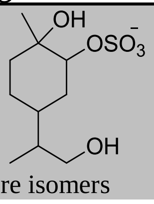
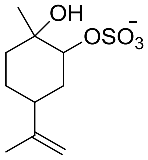
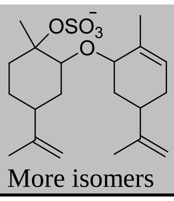
	m/z	RT [min]	msms fragments	Molecular formula	Suggested structure
OS 268	267.09	4.4; 5.9	96.96, 79.95	$C_{10}H_{19}O_6S$	 More isomers
OS 250	249.08	8.2; 9.5; 10.3	95.95	$C_{10}H_{17}O_5S$	 More isomers
OS 384	383.19	15.4	158.94, 116.92, 96.96	$C_{20}H_{31}O_5S$	 More isomers

Table 1: Information on the organosulfates observed in the purified limonene organosulfate sample. Molecular formulas are suggested based on smart formula analysis in the program “data analysis” from Burker Daltonics.

2 CCN Calibration

During measurements with the CCNc, the supersaturation (SS) was entered to be in the range of 0.1 to 1.3% increasing in steps of 0.1%. Measurement of ammonium sulfate (AS) hence resulted in 13 appurtenant critical particle diameters (d50). The 13 measured d50-values for AS was used to correct the SS in the CCNc by calibration with theoretical SS for ammonium sulfate, using the Köhler equation (Seinfeld and Pandis, 2006):

$$SS(D_p) = \left(exp\left(\frac{4M_w\sigma_w}{RT\rho_w D_p} - \frac{6n_s M_w}{\pi\rho_w D_p^3} \right) - 1 \right) \cdot 100\% \tag{1}$$

where M_w is the molecular weight of water (18.0153 g/mol), σ_w is the surface tension of water (0.07286 J/m^2), R is the gas constant (8.314 J/kg K), T is the temperature (298.15 K), ρ_w is the density of water (997.1 kg/m^3), Dp is the droplet diameter, and ns is given below:

$$n_s = \frac{v\pi d_s^3 \rho_s}{6M_s} \tag{2}$$

where ν is the van Hoff factor, ρ_s is the density of AS (1770 kg/m^3), d_s is the diameter of the dry AS particle (here the measured d50) and M_s is the molecular weight of AS (132.1395 g/mol).

The van Hoff factor was calculated with the following parametrisation as suggested by (Prisle, 2006):

$$v = -0.002 * c_{AS}^5 + 0.032c_{AS}^4 - 0.197C_{AS}^3 + 0.5997C_{AS}^2 - 0.8431c_{AS} + 2.3552 \tag{3}$$

For each of the 13 measured d50-vlaues a Köhler curve was modelled by setting d_s to d50 and calculating SS while increasing D_p in steps of 1.01. The critical supersaturation (SS50) was then found as the top of the Köhler curve. Figure 2 shows the modelled Köhler curve for ds = 133.34 nm.

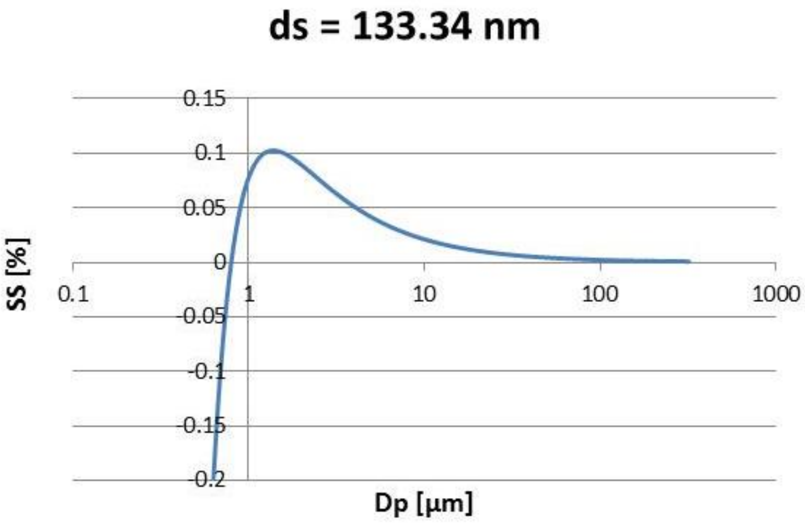


Figure 2: Köhler curve for AS with a dry particle diameter, ds, of 133.34 nm.

The theoretical SS50-values found from the Kóhler curves were then plotted against the SS entered in the CCNc (Figure 3) and the following regression line was obtained, where the uncertainties were found using the linear regression approach:

$$SS_{corrected} = 0.686\ (\pm 0.006) \cdot SS_{entered\ in\ the\ CCNc} + 0.031 (0.005) \qquad (s4)$$

The SS in the CCNC was corrected using the regression line and the entered SS, resulting in corrected SS in the range of 0.099 to 0.922%.

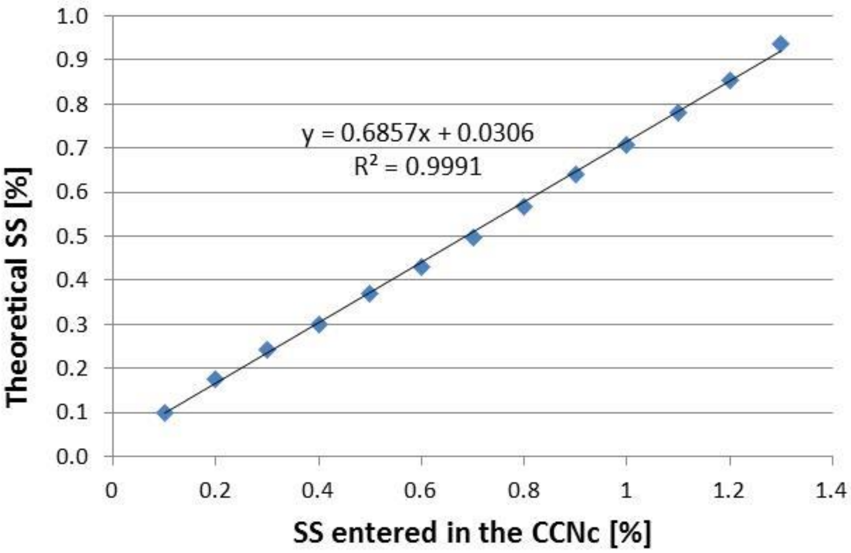


Figure 3: Calibration curve for correction of SS in the CCNC.

Prisle, N. L.: Cloud Condensation Nuclei Properties of Organic Aerosol Particles: Effects of Acid Dissociation and Surfactant Partitioning, M.Sc. Thesis, Department of Chemistry, Faculty of Science, University of Copenhagen, 2006.

Seinfeld, J. H., and Pandis, S. N.: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, Wiley, 2006.