Atmospheric
Chemistry
and Physics

Supplement of

Water activity and surface tension of aqueous ammonium sulfate and D-glucose aerosol nanoparticles

Eugene F. Mikhailov et al.

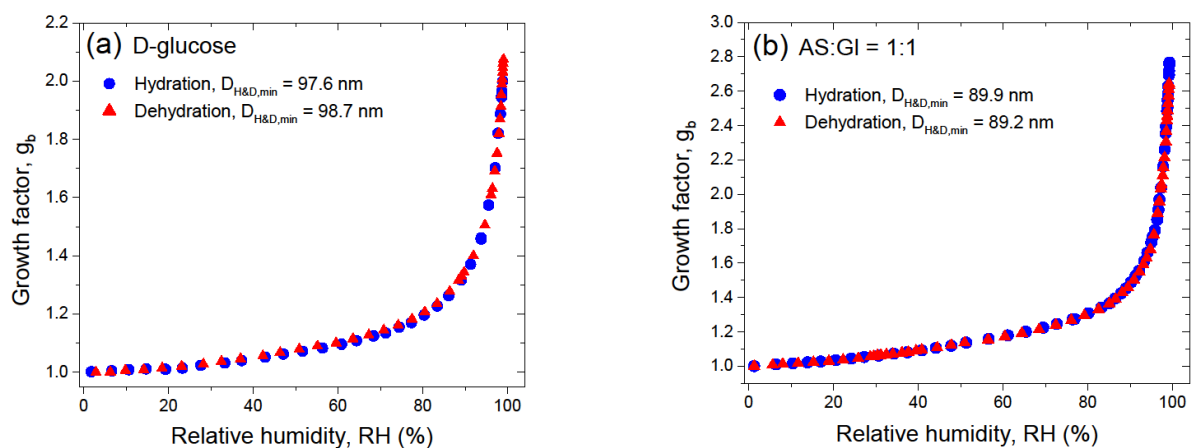*Correspondence to:* Alexei A. Kiselev (alexei.kiselev@kit.edu)

Figure S1. Growth factors observed in the hydration and dehydration experiments for the preconditioned D-glucose (**a**) and mixed AS-Gl particles with a mass ratio of 1:1 (**b**).
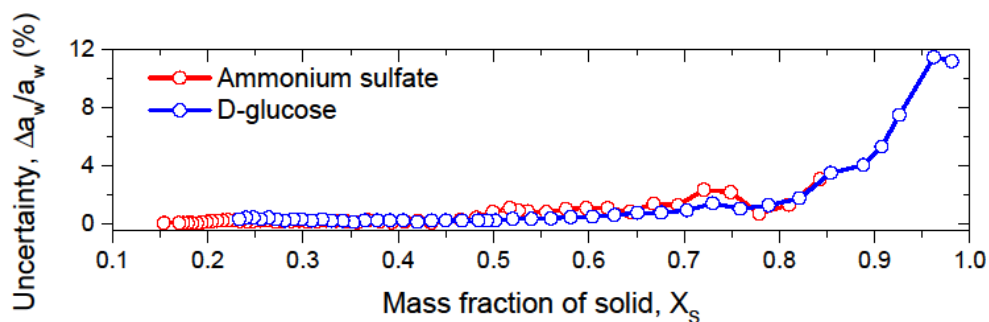

Figure S2. The relative uncertainty of water activity, a_w for pure ammonium sulfate and D-glucose aerosol particle obtained by DKA.
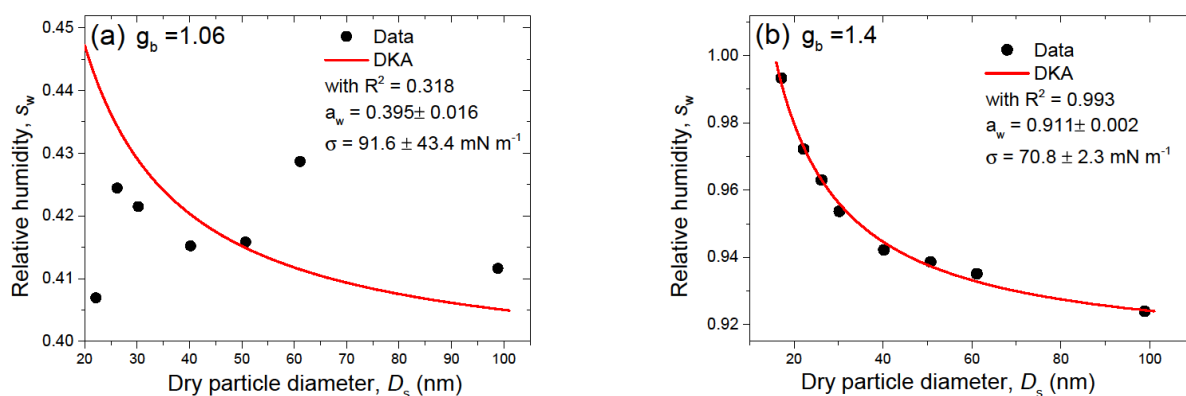

Figure S3. The $s_w(D_s)$ dependence of D-glucose aerosol particles and uncertainty of DKA-derived water activity, a_w and surface tension, σ at growth factor, g_b=1.06 (**a**) and g_b=1.4 (**b**).
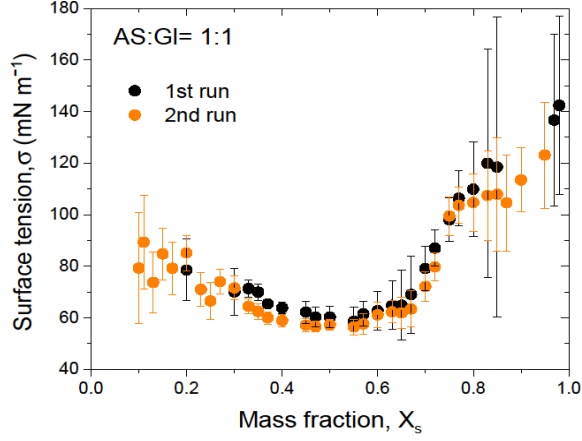
Figure S4. The DKA-derived σ based on a sequence of measurements with four (1st run) and eight (2nd run) dry diameters, D_s. For further analysis we used σ from the 2nd run with less error.

S1. Related parameters of the DKA model

The experimental $s_w(g_b)$ dependences, obtained for each dry particle diameters D_s were fitted using cubic spline interpolation. The resulting set of $s_w(D_s)$ values at given g_b was then used to determine water activity and surface tension (Eq.3) (Fig.S3). The growth factor g_b is related to the mass fraction of solute X_s, its dry density ρ_s and the density of the solution ρ_{sol} as follows:

$$g_b = \left(\frac{\rho_s}{X_s \rho_{sol}}\right)^{1/3}. \tag{S1}$$

Equation (S1) is used to calculate the desirable g_b at given value of X_s and vice versa. The concentration dependence of $\rho_{sol,AS}$ (g cm^{-3}) for ammonium sulfate aqueous solution was taken from (Tang and Munkelwitz, 1994):

$$\rho_{sol,AS} = 0.9971 + 0.592\, X_{AS} - 5.036 \cdot 10^{-4}\, X_{AS}^2 + 1.024 \cdot 10^{-6}\, X_{AS}^3 \ , \tag{S2}$$

and density for glucose solution, $\rho_{sol,Gl}$ was obtained by the polynomial fit of the experimental data from different authors (Mikhailov et al., 2020). The updated parameters were obtained after addition of glucose density at $X_{Gl}=1$:

$$\rho_{sol,Gl} = 0.9963 + 0.3998\, X_{Gl} + 0.0520\, X_{Gl}^2 + 0.0904 X_{Gl}^3 \ , \tag{S3}$$

where the standard deviation of the fit is 0.0012 g cm^{-3}. For mixed AS/Gl aerosol particles the density solution was determined using the expression from Tang (1997),

$$\rho_{sol} = \left(\frac{X_{s.AS}}{\rho_{sol.AS}} + \frac{X_{s.Gl}}{\rho_{sol,Gl}}\right)^{-1} , \tag{S4}$$

where $\rho_{sol,AS}$ and $\rho_{sol,Gl}$ are the corresponding solution densities of the binary solutions evaluated at the total mass fraction of solute in solution X_s . Thus, with an AS:Gl mass ratio of 1:1 the $X_{s.AS} = X_{s.Gl} = 0.5 X_s$. The partial molar volume of water v_w as a function of solute mass fraction and solution density was determined as (Brechtel and Kreidenweis, 2000):

$$v_w = \frac{M_w}{\rho_{sol}}\left(1 + \frac{d\ln\rho_{sol}}{X_s}\right), \tag{S5}$$

where M_w is the molecular weight of water.

S2. Normalization of solute activity coefficients

The activity and the activity coefficient are effected by the choice of standard state and by the choice of concentration scale (Robinson and Stokes, 1970; Prausnitz et al., 1999). The activity coefficients calculated from Eq. (9) are unsymmetric molality based coefficients. The activity coefficients derived from AIOMFAC for glucose and from E-AIM for ammonium sulfate are based on the mole fraction scale but use different reference state, i.e. symmetric for glucose and unsymmetric for ammonium sulfate, respectively. Thus, in order to compare AIOMFAC activities for D-glucose with whose calculated from Eq. (9), we need first converted the model activity coefficients normalized symmetrically to activity coefficients normalized unsymmetrically (Prausnitz et al. 1999):

$$\frac{f_{s,x}}{\gamma_{s,x}} = \lim_{x_i \to 0} f_{s,x} \quad, \tag{S6}$$

where $f_{s,x}$ and $\gamma_{s,x}$ are the mole fraction based activity coefficients of solute, s in symmetric and asymmetric reference state, respectively. We then converted the obtained unsymmetrically normalized mole fraction scale activity coefficients, $\gamma_{s,x}$ into molality based coefficients, $\gamma_{s,m}$ using the ratio (Prausnitz et al. 1999) :

$$\gamma_{s,m} = \gamma_{s,x}/(1 + 0.001\nu_s M_w m_s), \tag{S7}$$

where ν_s and m_s are the stoichiometric dissociation number and molality of the solute (mol kg^{-1} of water), M_w is the molecular mass of water (g mol^{-1}). The corresponding activities were then calculated using Eq. (7). Note that the above described normalisation of the activity coefficients was done for both water-dissociating ammonium sulfate and non-dissociating glucose. For dissociating ammonium sulfate we have : $\gamma_{s,x} = \gamma_{\pm,x} = \left(\gamma_{NH4+}^2 \gamma_{SO4^{2-}}\right)^{1/3}$, where the ion activity coefficient γ_{NH4+} and $\gamma_{SO4^{2-}}$ in mole fraction scale are taken from E-AIM III. For simplicity, in Eq. (6-9) we omit the subscripts m and s, i.e. instead of $\gamma_{s,m}$ for ammonium sulfate and glucose we use $\gamma_{\pm}$ and γ, respectively.

Table S1. The polynomial coefficients (A_n) of a_w in the aqueous solution droplets of pure ammonium sulfate and D-glucose and their mixture with mass ratio of AS:Gl = 4:1 and 1:1, respectively as a function of the mass fraction of the solute (X_i). R^2 is the coefficient of determination of the fit.

Polynomial fit function: $a_w = 1.0 + \sum_{n=1}^{n} A_n X_i^n$

Species	A_1	A_2	A_3	A_4	A_5	R^2	X_i range
Ammonium sulfate (AS)	-0.38778	1.12310	-4.34221	3.25940	-0.56537	0.9998	0.15-0.81
D-glucose (Gl)	0.19415	-2.52973	6.66509	-7.48629	2.19748	0.9996	0.18-0.98
AS:Gl = 4:1	-0.29223	0.252707	-1.00143	-0.649429	0.88262	0.9999	0.08-0.92
AS:Gl = 1:1	-0.15441	-0.75355	3.18257	-5.57340	2.70432	0.9996	0.08-0.98

Table S2. Polynomial coefficients (A_n) of ammonium sulfate, a_{AS} and glucose, a_{Gl} activity in the water as a function of the mass fraction (X_i). R^2 is the coefficient of determination of the fit.

Polynomial fit function: $a_i = \sum_{n=0}^{n} A_n X_i^n$

Activity	A_o	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	R^2	X_i range
a_{AS}	0.47838	-33.2125	650.3282	-6135.45	33279.56	-110597.1	229537.2	-289688.0	203350.6	-60541.04	0.9999	0.15-0.81
a_{Gl}	36.478	-743.879	6455.583	-30372.93	86029.497	-150369.9	159374.20	-94172.59	24029.23		0.9999	0.18-0.98

Table S3. The saturated surface adsorption, Γ_s^{w0} (mol cm^{-2}) and the adsorption equilibrium constant, K_s as the best fit parameters of Eq. (12).

Species	Γ_s^{w0}	K_s	a_s range	n	R^2
Ammonium sulfate	-6.04 ($\pm$ 0.29) 10^{-10}	1.99 $\pm$ 0.30	0.05-63.5	51	0.966
D-glucose	-2.91 ($\pm$ 1.02) 10^{-10}	0.05 $\pm$ 0.03	2.5-144.7	31	0.804

References

Brechtel, F. J., and Kreidenweis, S. M.: Predicting particle supersaturation from hygroscopic growth measurements in the Humidified TDMA. Part I: Theory and sensitivity studies, J. Atmos. Sci., 57, 1854–1871, https://doi.org/10.1175/1520-0469(2000)057<1854:PPCSFH>2.0.CO;2, 2000.

Mikhailov, E. F. and Vlasenko, S. S.: High-humidity tandem differential mobility analyzer for accurate determination of aerosol hygroscopic growth, microstructure, and activity coefficients over a wide range of relative humidity, Atmos. Meas. Tech., 13, 2035–2056, https://doi.org/10.5194/amt-13-2035-2020, 2020.

Prausnitz, J. M., Lichtenthaler, R. N., and de Azevedo, E. G. (1999). Molecular Thermodynamics of Fluid-Phase Equilibria. Prentice Hall, Upper Saddle River, New Jersey, USA, p. 226.

Robinson, R. A. and Stokes, R. H.: Electrolyte solutions, 2nd ed., Butterworths, London, 1970.

Tang, I. N. and Munkelwitz, H. R.: Water activities, densities, and refractive indices of aqueous sulfates and sodium nitrate droplets of atmospheric importance, J. Gephys. Res., 99, 18801–18808, https://doi.org/10.1029/94JD01345, 1994.

Tang, I.N.: Thermodynamic and optical properties of mixed-salt aerosols of atmospheric importance, J. Geophys. Res. Atmos. 102(D2), 1883-1893, https://doi.org/10.1029/96JD03085, 1997.