Supplement of Atmos. Chem. Phys., 17, 4369–4385, 2017
http://www.atmos-chem-phys.net/17/4369/2017/
doi:10.5194/acp-17-4369-2017-supplement

Atmospheric Chemistry and Physics Open Access EGU

Supplement of

Hygroscopic properties of aminium sulfate aerosols

Grazia Rovelli et al.

Correspondence to: Jonathan P. Reid (j.p.reid@bristol.ac.uk)

Supplementary Information outline:

- **Table S1:** List and description of the uncertainties taken into account when calculating the hygroscopicity properties of aerosols from comparative kinetics experiments in a CK-EDB.
- **Table S2:** Measured densities and refractive indices of aminium sulphates solutions.
- **Table S3:** 3rd order polynomial fitted parameters for densities, calculated melt densities and melt refractive indices calculated with molar refraction mixing rule for the six considered aminium sulphates.
- **Table S4:** Comparison of pure melt densities from this work and from Clegg et al. (2013) and solid densities from Qiu and Zhang (2012).
- **Table S5:** Coefficients of the fitted equations of the measured apparent molar volumes.
- **Table S6:** Extended ZSR fitted coefficients at two fixed water activities (a_w, 0.80 and 0.925) for mixtures of aminium sulphate salts and sulphuric acid.

- **Figure S1:** Schematics of the EDB experimental setup used in this work.
- **Figure S2:** Measured densities of aminium sulphates solutions and 3rd order polynomial fittings of data and measured refractive indices as a function of mass fraction and the corresponding molar refraction mixing rule fitting.
- **Figure S3:** Comparison of measured GF_r from CK-EDB experiments and GF_r data from H-TDMA measurements by Qiu and Zhang (2012)
- **Figure S4:** Measured and fitted apparent molar volumes of aminium sulphates in aqueous solutions from this work and from Clegg et al. (2013).

Table S1: List and description of the uncertainties taken into account when calculating the hygroscopicity properties of aerosols from comparative kinetics experiments in a CK-EDB.

Quantity	Symbol/Formula	Uncertainties
Water activity	a_w	- a_w: uncertainty from RH determination in the EDB measurements (Davies et al., 2013): - RH>80% (pure water used as a probe): $RH = RH_{w}{}^{+(0.169RH_w{}^2-0.364RH_w+0.194)}_{-(-0.020RH_w+0.021)}$ - RH<80% (NaCl used as a probe): $RH = RH_{eq}{}^{+(-0.0175RH_{eq}{}^2-0.0005RH_{eq}+0.017)}_{-(-0.0266RH_{eq}{}^2+0.0086RH_{eq}+0.017)}$
Radial growth factor	$GF_r = \frac{a}{a_{dry}}$	- a (measured)*:* ±100 nm (Davies, 2014), <1% for droplets bigger than 10 µm.[(a)] - a_{dry}: uncertainty on the initial radius extrapolation at t_0 ($a_{dry}{}^{+150\,nm}_{-100\,nm}$); uncertainty on the initial solution concentration.
Mass fraction	$mfs = \frac{m_{solute}}{m_{tot}}$	- m_{solute} (dry mass from the initial concentration): $a_{dry}{}^{+150\,nm}_{-100\,nm}$; uncertainty on the initial solution concentration.[(b)] - m_{tot}: uncertainty from radius determination.
Mole curves	$\frac{n_{\mathrm{water}}}{n_{solute}}$	- n_{water}, calculated from $m_{water} = m_{tot} - m_{solute}$ (see uncertainties indicated above for *mfs*).
Stoichiometric osmotic coefficient	$\phi_{st} = \frac{-\ln(a_w)}{(m_{st} \cdot M_w/1000)}$	- m_{st} (stoichiometric molality): uncertainties on n_{solute} and m_{water} (see uncertainties indicated for *mfs* and for n_{water}/n_{solute}).

Symbols: a_w; water activity; GF_r – radial growth factor; a – droplet radius; a_{dry} – dry particle radius; mfs – mass fraction of solute; m_{solute} – mass of solute in the particle; m_{tot} – total particle mass; n_{water} – moles of water; n_{solute} – moles of solute; ϕ_{st} – stoichiometric osmotic coefficients; m_{st} – stoichiometric molality; M_w – molecular mass of water.

Notes:

(a) The optical phase function measurements in the CK-EDB used to estimate the size of a levitated droplet are taken at a wavelength of 532 nm; however, the wavelength dependence of refractive index was considered negligible (e.g. for pure water m=1.333 at 589 nm and m=1.335 at 532 nm) and introduced negligible error in the determination of droplet size when compared with other experimental uncertainties that must be accounted for (Rovelli et al., 2016).

(b) No uncertainties on the applied density parameterisations are taken into account. However, the sensitivity of the hygroscopic properties retrieved by means of CK-EDB measurements to potential uncertainties in the parameterisation of solution density have been evaluated in Section III.d of the main manuscript.

Table S2: Measured densities and refractive indices of aminium sulphates solutions.

MMAS

mfs			ρ (kg m^{-3})	σ	*m*	σ
0	±	0	998.1	0	1.333	-
0.0021	±	8.90E-06	999.0	0.1	1.3334	-
0.0070	±	3.00E-05	1001.4	0.1	1.3342	-
0.0178	±	0.0001	1006.3	0.1	1.3359	-
0.0406	±	0.0002	1016.8	0	1.3394	-
0.0675	±	0.0003	1028.8	0.1	1.3436	-
0.1061	±	0.0005	1045.8	0.2	1.3494	-
0.1487	±	0.0006	1064.8	0.1	1.3561	-
0.1995	±	0.0009	1087	0	1.3638	-
0.2579	±	0.0011	1111.5	0.4	1.3724	-
0.3002	±	0.0013	1127.6	0.1	1.3778	5.77E-05
0.3657	±	0.0016	1154.7	0.1	1.3872	5.77E-05
0.4411	±	0.0019	1186.8	1.2	1.3981	-
0.5482	±	0.0023	1231.3	0.6	1.4145	1.53E-04

MEAS

mfs			ρ (kg m^{-3})	σ	*m*	σ
0	±	0	998.2	0.1	1.333	-
0.0073	±	3.00E-05	1000.6	0.1	1.3342	-
0.0129	±	5.30E-05	1002.8	0.1	1.3350	-
0.0345	±	0.0001	1010.6	0.1	1.3382	5.77E-05
0.0776	±	0.0003	1026.1	0	1.3444	-
0.1393	±	0.0006	1047.3	0.2	1.3531	-
0.2087	±	0.0009	1071.1	0.4	1.3632	5.77E-05
0.3097	±	0.0013	1107.1	0.1	1.3778	-
0.4178	±	0.0017	1144.2	0.2	1.3934	1.15E-04
0.5295	±	0.0022	1180.6	0.2	1.4091	5.77E-05
0.7687	±	0.0031	1247.6	1.2	1.4413	2.00E-04

DMAS

mfs			ρ (kg m^{-3})	σ	*m*	σ
0	±	0	998.5	0.1	1.333	-
0.0108	±	0.0001	1001.8	0.1	1.3345	-
0.0643	±	0.0005	1019.1	0.1	1.3421	-
0.1232	±	0.0010	1037.6	0.1	1.3502	-
0.1742	±	0.0015	1052.9	0.6	1.3573	-
0.2351	±	0.0020	1071.9	0.1	1.3657	1.53E-04
0.2956	±	0.0025	1088.9	1.2	1.3737	2.65E-04
0.3557	±	0.0031	1104.3	4.7	1.3823	2.00E-04
0.4082	±	0.0035	1124.5	0.4	1.3898	5.77E-05
0.4699	±	0.0040	1143.4	0.4	1.3985	5.77E-05
0.5330	±	0.0045	1156.0	1.1	1.4067	1.15E-04

DEAS

mfs			ρ (kg m^{-3})	σ	*m*	σ
0	±	0	998.1	0.1	1.333	-
0.0024	±	4.70E-05	998.3	0.1	1.3335	5.77E-05
0.0124	±	2.50E-04	1000.5	0.1	1.3347	5.77E-05
0.0291	±	0.0006	1004.1	0.1	1.3371	-
0.0690	±	0.0014	1012.7	0.1	1.3426	-
0.1126	±	0.0022	1026.7	0.1	1.3518	-
0.2094	±	0.0041	1043.3	0.1	1.3629	1.15E-04
0.3061	±	0.0061	1064.9	0.1	1.3773	5.77E-05
0.4292	±	0.0085	1092.2	0.1	1.3962	1.15E-04
0.5622	±	0.0111	1117.3	1.4	1.4152	9.87E-04
0.6667	±	0.0132	1134.5	0.2	1.4309	4.16E-04

TMAS

mfs			ρ (kg m^{-3})	σ	*m*	σ
0	±	0	998.0	0.1	1.333	
0.0017	±	1.70E-05	998.5	0	1.3334	-
0.0039	±	3.70E-05	999.2	0.1	1.3336	-
0.0109	±	0.0001	1001.2	0.1	1.3346	-
0.0197	±	0.0002	1003.5	0.1	1.3359	-
0.0331	±	0.0003	1007.3	0.1	1.3378	-
0.0515	±	0.0005	1012.1	0.2	1.3404	-
0.0786	±	0.0007	1019.4	0.1	1.3444	-
0.1027	±	0.0010	1025.7	0.1	1.3477	5.77E-05
0.1303	±	0.0012	1032.9	0.1	1.3517	-
0.1450	±	0.0014	1036.8	0.1	1.3539	5.77E-05
0.1828	±	0.0017	1046.6	0.2	1.3593	5.77E-05
0.2104	±	0.0020	1053.4	0.1	1.3634	-
0.2557	±	0.0024	1065.3	0.1	1.3701	-
0.3074	±	0.0029	1078.6	0.2	1.3778	5.77E-05
0.3638	±	0.0035	1094.0	0.2	1.3864	-
0.4580	±	0.0044	1118.1	1.6	1.4006	1.53E-04

TEAS

mfs			ρ (kg m^{-3})	σ	*m*	σ
0	±	0	998.0	0.2	1.333	
0.0025	±	3.20E-04	998.5	0.1	1.3336	-
0.0129	±	7.30E-04	1001.3	0.1	1.3354	5.77E-05
0.0335	±	0.0012	1006.9	0.2	1.3392	-
0.0637	±	0.0016	1014.9	0.2	1.3447	-
0.1236	±	0.0023	1030.8	0.1	1.3558	-
0.1884	±	0.0028	1048.9	0.1	1.3683	1.53E-04
0.2747	±	0.0034	1075.1	0.1	1.3864	-
0.3807	±	0.0040	1104.8	1.2	1.4082	1.00E-04
0.4999	±	0.0046	1135.6	1.6	1.4298	1.18E-03
0.6008	±	0.0050	1158.2	1.8	1.4480	4.54E-03

Symbols: *mfs* – mass fraction of solute; ρ – measured density of solution; *m* – measured refractive index of solution; σ – standard deviation arising from the averaging of three repeated measurements.

Table S3: 3rd order polynomial fitted parameters for densities (ρ), calculated melt densities (ρ_{melt}) and melt refractive indices (m_{melt}) calculated with molar refraction mixing rule for the six considered aminium sulphates.

	a_0	a_1	a_2	a_3	ρ_{melt} (kg m^{-3})	m_{melt}
MMAS	998.10	5.12	447.11	-40.19	1410.1	1.4771
DMAS	998.47	-2.55	341.03	-51.91	1285.0	1.4725
TMAS	998.03	4.64	252.17	4.82	1259.7	1.4921
MEAS	998.17	-19.25	459.22	-127.00	1311.1	1.4708
DEAS	998.10	-10.09	285.60	-82.47	1191.1	1.4810
TEAS	998.50	-25.09	378.58	-100.86	1251.1	1.5357

Parameterisations used:

3rd order polynomial parameterization for densities (ρ) as a function of the square-rooted mass fraction (*mfs*) of solute:

$$\rho = a_0 + a_1(mfs^{0.5}) + a_2(mfs) + a_3(mfs^{1.5}) \quad \text{Eq. S1}$$

Molar refraction mixing rule for the representation of the refractive index (m) of a solution. The molar refraction (R) of a species is defined as (Liu and Daum, 2008):

$$R = \frac{(m^2-1)M}{(m^2+2)\rho} \quad \text{Eq. S2}$$

where M is the compound's molecular mass and ρ is its pure density (melt density in case of a solute, pure liquid density in the case of the solvent, i.e. water). The molar refraction for a mixture of different components is defined as the sum of the molar refractions of each compound (i) weighted by their mole fractions (x_i):

$$R = \sum_i x_i R_i \quad \text{Eq. S3}$$

Therefore, in the case of a binary solution composed of water and a generic solute:

$$\frac{({m_{solution}}^2-1)M_{solution}}{({m_{solution}}^2+2)\rho_{solution}} = x_{H_2O}\frac{({m_{H_2O}}^2-1)M_{H_2O}}{({m_{H_2O}}^2+2)\rho_{H_2O}} + x_{solute}\frac{({m_{melt}}^2-1)M_{solute}}{({m_{melt}}^2+2)\rho_{melt}} \quad \text{Eq. S4}$$

where $m_{solution}$ and $\rho_{solution}$ are measured, $M_{solution}$ is calculates as $M_{solution} = \sum_i x_i M_i$ (Liu and Daum, 2008), the mole fractions of water and solute are known from the concentration of the prepared solution, density and refractive index of pure water are known, ρ_{melt} is calculated from the density parameterisation at *mfs*=1. Therefore, the only unknown is m_{melt} and a least squares fit of the experimental refractive index data is performed with Eq. S4 to calculate it.

When correcting the obtained radius vs. time data from CK-EDB experiments, the iterative procedure proposed in a previous work (Davies et al., 2012) is applied, but the variation in refracting index with the variation of the solution concentration is calculated with the molar refraction mixing rule.

Table S4: Comparison of pure melt densities (ρ_{melt}) from this work and from Clegg et al. (2013) and solid densities (ρ_{solid}) from Qiu and Zhang (2012).

Compound	ρ_{melt} **(this work)** ($g\ cm^{-3}$)	ρ_{melt} **(Clegg et al., 2013)** ($g\ cm^{-3}$)	ρ_{solid} **(Qiu and Zhang, 2012)** ($g\ cm^{-3}$)
MMAS	1.410	1.451 (±0.0029)	1.485 ± 0.089
DMAS	1.285	1.278 (±0.0022)	1.408 ± 0.084
TMAS	1.259	1.289 (±0.0031)	1.342 ± 0.081
MEAS	1.311	-	-
DEAS	1.191	1.212 (±0.0030)	1.268 ± 0.076
TEAS	1.251	1.190 (±0.0018)	1.247 ± 0.075

Table S5: Values of the coefficients of the fitted equations of measured apparent molar volumes (V^{ϕ}) of aminium sulphates in aqueous solutions (displayed in Figure S3). The used fitting equation is the same used by Clegg et al. (2013):

$$V^{\phi} = V^{\phi\infty} + a_1 \cdot (wt\%)^{0.5} + a_2 \cdot (wt\%)^{0.75} a_3 \cdot (wt\%) + a_3 \cdot (wt\%)^{1.5}$$

where $V^{\phi\infty}$ is the apparent molar volume of the aminium salt taken from literature (as in Clegg et al.) and *wt%* is the weight percentage of salt in solution. Note that the fitted equation is constrained at *wt%* = 0 to the $V^{\phi\infty}$ literature value.

	$V^{\phi\infty}$	a_1			a_2			a_3			a_4		
MMAS	86.27	-0.542	±	0.276		0		0.792	±	0.099	-0.0507	±	0.00882
DMAS	123.83	2.039	±	0.150		0			0		0.00266	±	0.00367
TMAS	159.47	-8.051	±	0.962	6.866	±	0.883	-1.318	±	0.201		0	
MEAS	120.8	-1.043	±	0.238	1.062	±	0.088		0			0	
DEAS	191.91		0			0		0.115	±	0.009		0	
TEAS	256.16	-22.759	±	1.264	7.080	±	0.495		0			0	

Table S6: Extended ZSR fitted coefficients (Eq. 3 in Sauerwein et al. (2015)) at two fixed water activities (a_w, 0.80 and 0.925) for mixtures of aminium sulphate salts and sulphuric acid, as in Figure 7 in the main manuscript. The coefficients refer to the ZSR fitting of data from Sauerwein et al. (2016) together with the CK-EDB datapoint (red dashed lines in Figure 7 in the main manuscript). Symbols: w^o_a – water associated to H_2SO_4 in an aqueous solution at the same water activity as the mixture; w^o_{as} – water associated to the aminium salt in an aqueous solution at the same water activity as the mixture; A^o – fitted empirical parameter.

a_w = 0.80

	w^o_a	w^o_{as}			A^o		
MMAS	0.2682	0.2501	±	0.0092	-0.3218	±	0.0447
DMAS	0.2682	0.3072	±	0.0047	-0.4272	±	0.0240
TMAS	0.2682	0.3782	±	0.0112	-0.6147	±	0.0388
MEAS	0.2682	0.2747	±	0.0076	-0.3733	±	0.0256
DEAS	0.2682	0.3299	±	0.0195	-0.4655	±	0.0882

a_w = 0.925

	w^o_a	w^o_{as}			A^o		
MMAS	0.5641	0.6035	±	0.0194	-0.6155	±	0.0934
DMAS	0.5641	0.6997	±	0.0248	-0.7095	±	0.1273
TMAS	0.5641	0.8143	±	0.0215	-1.0166	±	0.0749
MEAS	0.5641	0.6587	±	0.0140	-0.6166	±	0.0476
DEAS	0.5641	0.8472	±	0.0325	-1.0603	±	0.1233

Figure S1: Schematics of the EDB experimental setup used in this work (view from top).

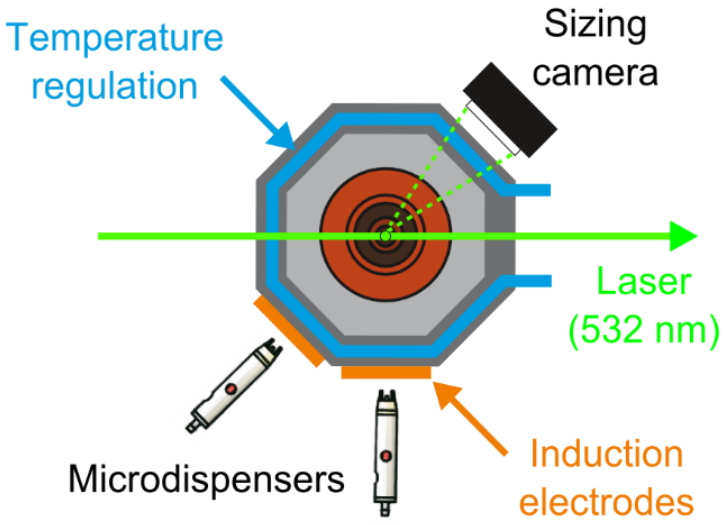
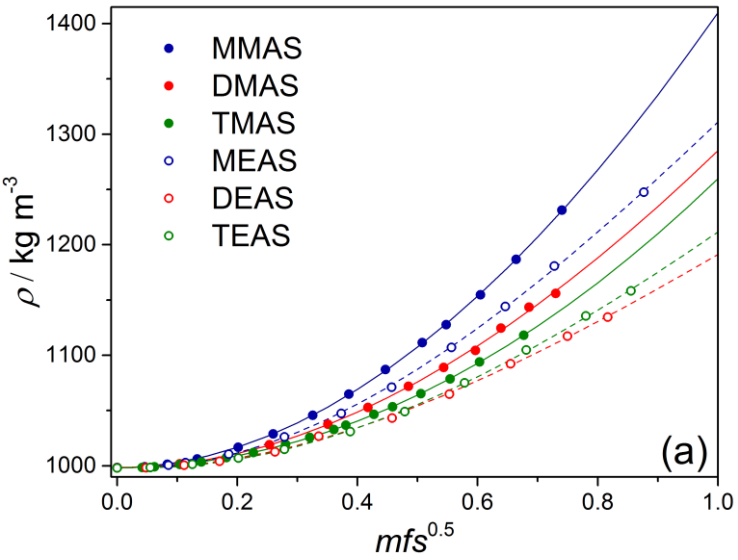
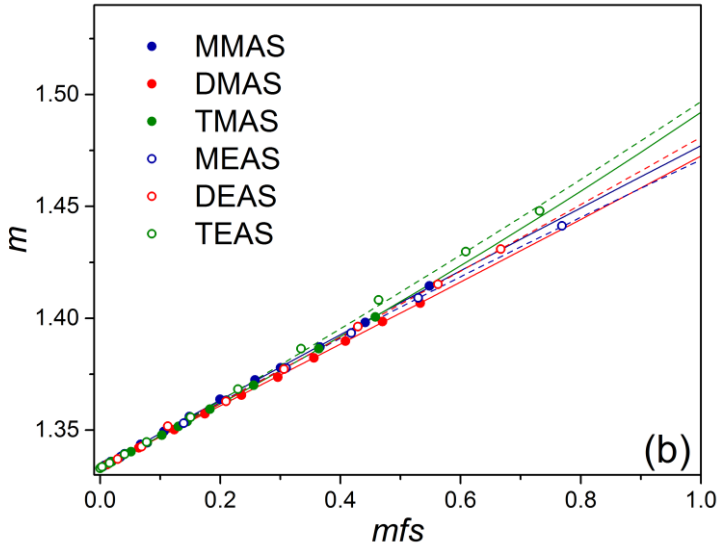


Figure S2: Measured densities of aminium sulphates solutions and 3rd order polynomial fittings of data (Panel (a)). Measured refractive indices as a function of mass fraction and the corresponding molar refraction mixing rule fitting (Panel (b)).





5

Figure S3: Comparison of measured GF_r from CK-EDB experiments and GF_r data from H-TDMA measurements by Qiu and Zhang (2012).

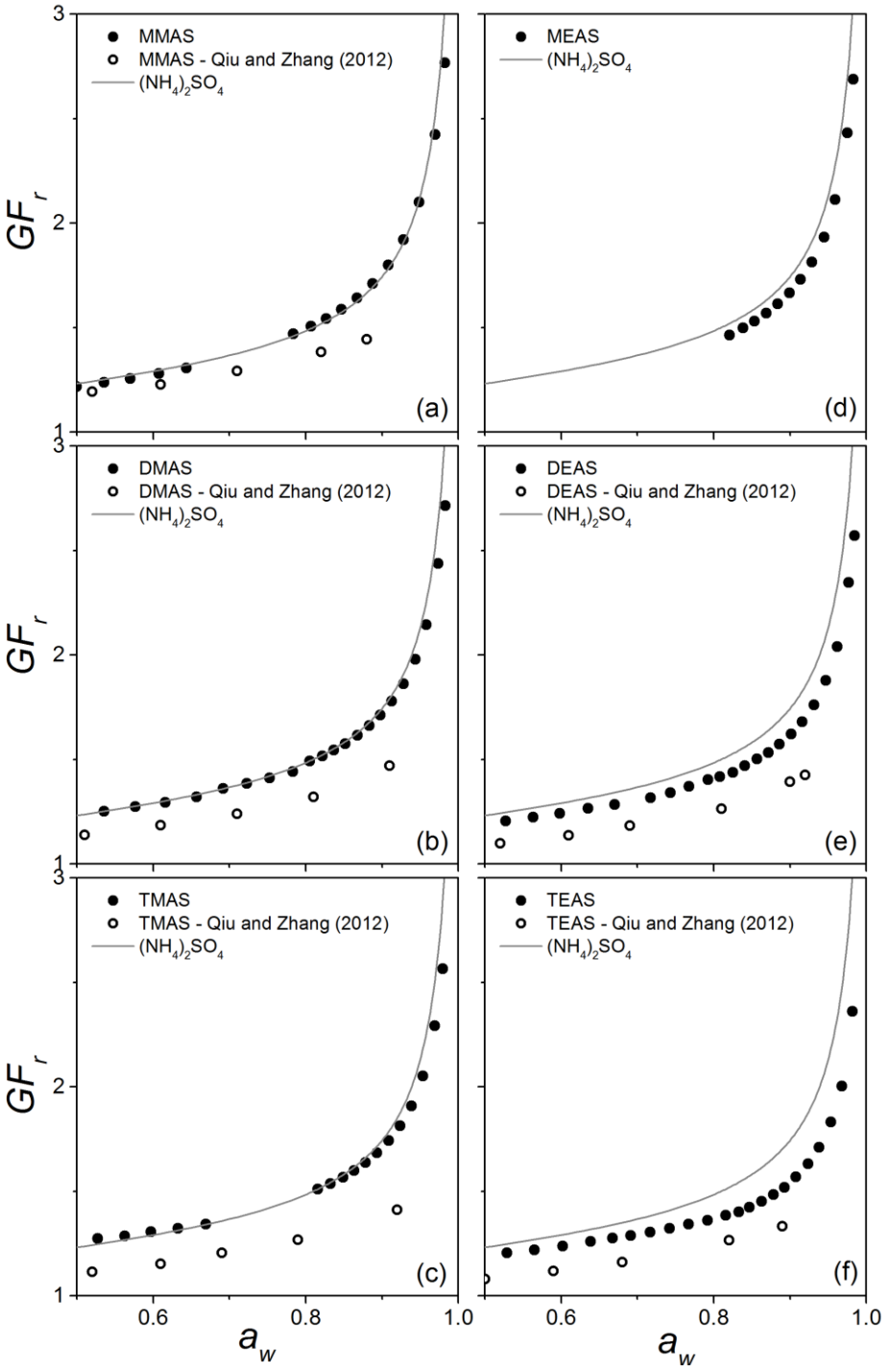
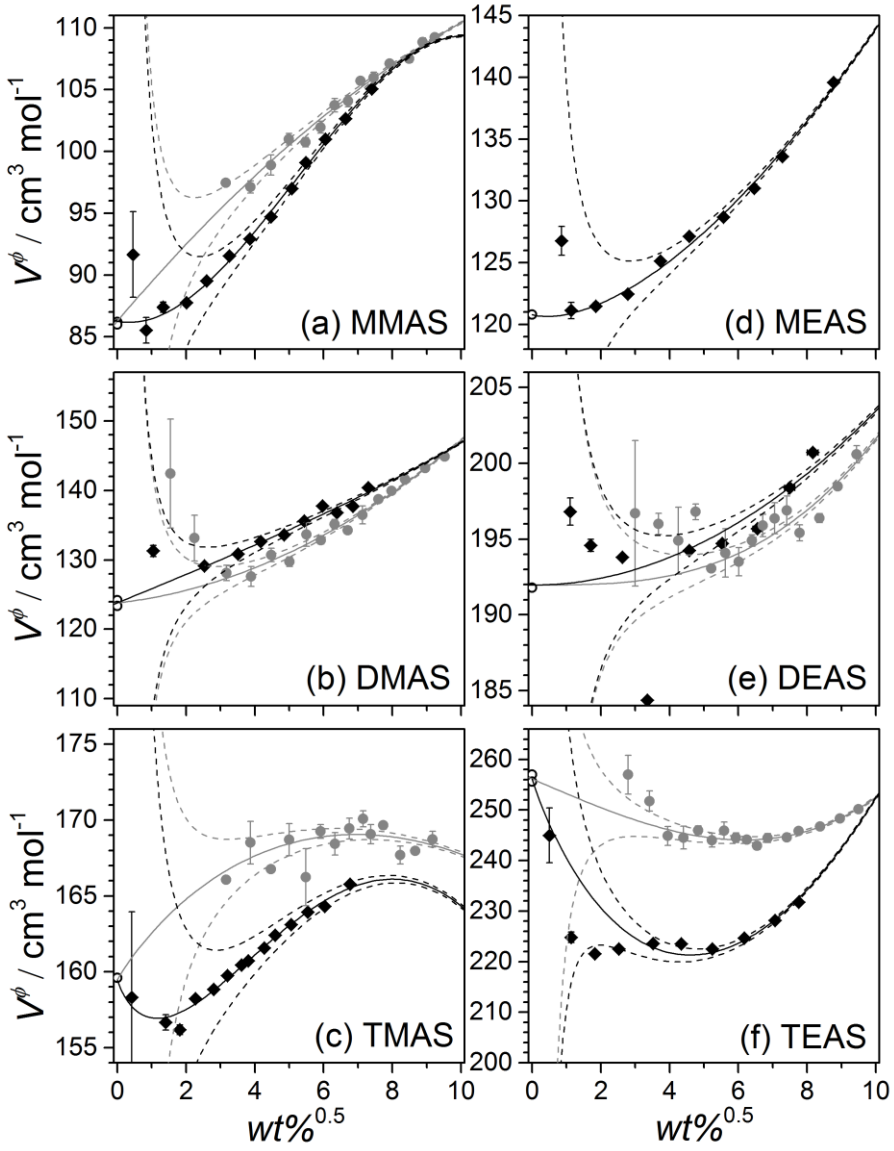


Figure S4: Apparent molar volumes (V^{ϕ}) of aminium sulphates in aqueous solutions as a function of the square root of the solute weight percentage (*wt%*). Symbols: black diamonds – measured values, this work; black line – fitted equations (coefficients in Table S5); grey dots – measured values by Clegg et al. (2013); grey lines – fitted equations of mrasured data in Clegg et al. (2013); dashed lines – uncertainty on apparent molar volumes when a ±0.001 g cm^{-3} uncertainty on the measured density is considered; open circles – apparent molar volumes at infinite dilutions from literature (as in Fig. 1 in Clegg et al. (2013)).



References

Clegg, S. L., Qiu, C. and Zhang, R.: The deliquescence behaviour, solubilities, and densities of aqueous solutions of five methyl- and ethyl-aminium sulphate salts, Atmos. Environ., 73, 145–158, doi:10.1016/j.atmosenv.2013.02.036, 2013.

Davies, J. F.: Characterising The Impact Of Bulk, Surface And Gas-Phase Limitations On Mass Transport In Aerosol., 2014.

Davies, J. F., Haddrell, A. E. and Reid, J. P.: Time-Resolved Measurements of the Evaporation of Volatile Components from Single Aerosol Droplets, Aerosol Sci. Technol., 46(6), 666–677, doi:10.1080/02786826.2011.652750, 2012.

Davies, J. F., Haddrell, A. E., Rickards, A. M. J. and Reid, J. P.: Simultaneous analysis of the equilibrium hygroscopicity and water transport kinetics of liquid aerosol, Anal. Chem., 85(12), 5819–5826, doi:10.1021/ac4005502, 2013.

Liu, Y. and Daum, P. H.: Relationship of refractive index to mass density and self-consistency of mixing rules for multicomponent mixtures like ambient aerosols, J. Aerosol Sci., 39(11), 974–986, doi:10.1016/j.jaerosci.2008.06.006, 2008.

Qiu, C. and Zhang, R.: Physiochemical properties of alkylaminium sulfates: Hygroscopicity, thermostability, and density, Environ. Sci. Technol., 46(8), 4474–4480, doi:10.1021/es3004377, 2012.

Rovelli, G., Miles, R. E. H., Reid, J. P. and Clegg, S. L.: Accurate Measurements of Aerosol Hygroscopic Growth Over a Wide Range in Relative Humidity, J. Phys. Chem. A, 120, 4376–4388, doi:10.1021/acs.jpca.6b04194, 2016.

Sauerwein, M., Clegg, S. L. and Chan, C. K.: Water Activities and Osmotic Coefficients of Aqueous Solutions of Five Alkylaminium Sulfates and Their Mixtures with H2SO4 at 25oC, Aerosol Sci. Technol., 49(8), 566–579, doi:10.1080/02786826.2015.1043045, 2015.