Supporting Information:

Reconciling atmospheric water uptake by hydrate forming salts

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- Calculation of sea salt composition and hygroscopicity
- Figure S1: comparison of GF and SS_{crit} between observed and modeled data.
- Hygroscopicity results from HTDMA measurements: GF and κ values from experimental data and modelled values (UManSysProp) carried out for different dry diameters and relative humidities (hydration and dehydration branch) for $MgCl_2$ and $CaCl_2$ and their hydrated form.
- Hygroscopicity results from CCNc measurements: supersaturation obtained from CCNc measurements and model output (UManSysProp) for different dry diameters of $MgCl_2$ and $CaCl_2$ and their hydrated form.
- Water activity measurements: results from the water activity meter, the ACCENT model and literature of $CaCl_2$, $CaCl_2{\cdot}4H_2O$, $MgCl_2$ and $MgCl_2{\cdot}6H_2O$ are shown.

Calculation of sea salt composition and hygroscopicity

The mass fractions of anhydrous species in sea salt were taken from the document on the standard practice for the preparation of substitute ocean water by ASTM International[(2)] and are illustrated in Table S1. We consider however only the four most abundant salts: NaCl, $MgCl_2$, Na_2SO_4 and $CaCl_2$. Volume fractions were calculated using the salt masses and densities given in Table 1. For the hydrated salt we assume that $MgCl_2$ and $CaCl_2$ were actually present as $MgCl_2{\cdot}6H_2O$ and $CaCl_2{\cdot}4H_2O$. The volume fractions of anhydrous and hydrated compounds are presented in Table 2.

Table S1: Mass concentrations c_m and mass fractions ε_m for (i) anhydrous salts only and (ii) hydrated forms of $MgCl_2$ and $CaCl_2$. Values for (i) are given by ASTM International[(2)] while those for (ii) were recalculated including the hydrated forms of $MgCl_2$ and $CaCl_2$ by using the values presented in Table 1.

Anhydrous sea salt			Partly hydrated sea salt		
Compound	c_m [g/dm^3]	ε_{ma} [%]	Compound	c_m [g/dm^3]	ε_{mh} [%]
NaCl	24.53	70.1	NaCl	24.53	58.8
$MgCl_2$	5.20	14.9	$MgCl_2{\cdot}6H_2O$	11.18	26.8
Na_2SO_4	4.09	11.7	Na_2SO_4	4.09	9.8
$CaCl_2$	1.16	3.3	$CaCl_2{\cdot}4H_2O$	1.92	4.6
mixture	34.98	100	mixture	41.72	100

Figure S1: Hygroscopicity and cloud activation potential

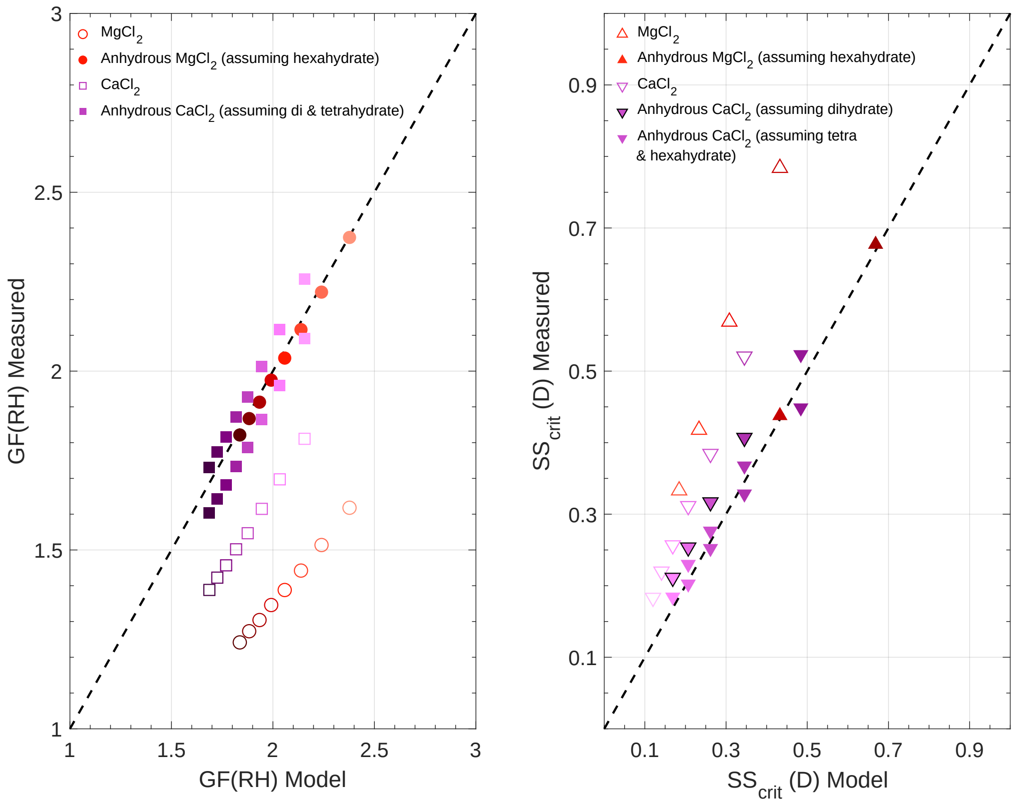

Figure S1: Comparison of measured and modelled growth factors as a function of RH (darker colours denote lower RH and lighter colours higher RH) and critical super saturations as a function of dry diameter (darker colours denote smaller diameters and lighter colours larger diameters) for particles generated from aqueous solutions of $MgCl_2$ and $CaCl_2$, respectively. The open symbols represent uncorrected data, while the filled symbols are corrected for hydrate contributions. The dashed line represents the 1:1 line.

Hygroscopicity results from HTDMA measurements

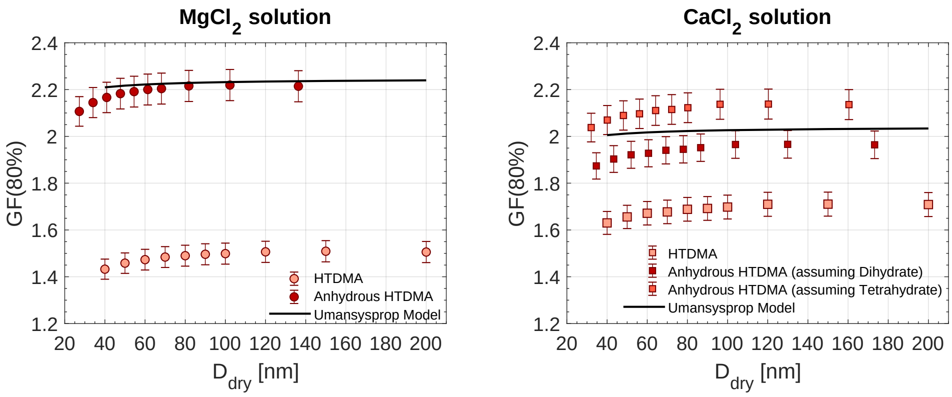

Figure S2: GF(80%) values for different dry diameters for particles generated from aqueous solutions of $MgCl_2$ (left) and $CaCl_2$ (right) together with results from the UManSysProp model.

Table S2: Dry diameters, measured GF and κ values for hydrated $MgCl_2$ at RH=80% and modelled data (UManSysProp) for anhydrous $MgCl_2$. These data are plotted in Fig. S2.

D_{set} [nm]	GF	Model GF	κ_{GF}	Model κ_{GF}
40	1.43 ± 0.03	2.21	0.58 ± 0.05	2.71
50	1.46 ± 0.03	2.22	0.60 ± 0.06	2.68
60	1.47 ± 0.03	2.22	0.62 ± 0.06	2.67
70	1.48 ± 0.03	2.23	0.63 ± 0.06	2.66
80	1.49 ± 0.03	2.23	0.63 ± 0.06	2.65
90	1.50 ± 0.03	2.23	0.63 ± 0.06	2.64
100	1.50 ± 0.03	2.23	0.63 ± 0.06	2.63
120	1.51 ± 0.03	2.23	0.64 ± 0.06	2.63
150	1.51 ± 0.03	2.24	0.64 ± 0.06	2.62
200	1.51 ± 0.03	2.24	0.63 ± 0.06	2.61

Table S3: Recalculated dry diameters, measured GF and κ values for anhydrous $MgCl_2$ at RH=80% , assuming an initially hexahydrate salt ($MgCl_2 \cdot 6H_2O$). These data are plotted in Fig. S2.

D_{corr} [nm]	GF	κ_{GF}
27	2.10 ± 0.04	2.46 ± 0.17
34	2.14 ± 0.04	2.52 ± 0.17
41	2.16 ± 0.05	2.55 ± 0.18
48	2.18 ± 0.04	2.57 ± 0.18
55	2.19 ± 0.04	2.57 ± 0.18
62	2.19 ± 0.04	2.58 ± 0.18
68	2.20 ± 0.04	2.58 ± 0.18
82	2.21 ± 0.05	2.59 ± 0.18
102	2.21 ± 0.05	2.58 ± 0.18
136	2.21 ± 0.05	2.53 ± 0.17

Table S4: Recalculated dry diameters, measured GF and κ values for hydrated $CaCl_2$ at RH=80% (data) and modelled data (UManSysProp) for anhydrous $CaCl_2$. These data are plotted in Fig. S2.

D_{set} [nm]	GF	Model GF	κ_{GF}	Model κ_{GF}
40	1.63 ± 0.03	2.01	0.86 ± 0.07	1.97
50	1.66 ± 0.03	2.01	0.91 ± 0.07	1.95
60	1.67 ± 0.04	2.02	0.95 ± 0.08	1.94
70	1.68 ± 0.04	2.02	0.96 ± 0.08	1.93
80	1.69 ± 0.04	2.02	0.98 ± 0.08	1.92
90	1.69 ± 0.04	2.03	0.99 ± 0.08	1.92
100	1.70 ± 0.04	2.03	1.01 ± 0.08	1.91
120	1.71 ± 0.04	2.03	1.03 ± 0.08	1.91
150	1.71 ± 0.04	2.03	1.03 ± 0.08	1.90
200	1.71 ± 0.04	2.03	1.03 ± 0.08	1.90

Table S5: Recalculated dry diameters, measured GF and κ values for anhydrous $CaCl_2$ at RH=80%, recalculated assuming an initially dihydrated salt ($CaCl_2 \cdot 2H_2O$). These data are plotted in Fig. S2.

D_{corr} [nm]	GF	κ_{GF}
35	1.88 ± 0.04	1.65 ± 0.12
43	1.91 ± 0.04	1.69 ± 0.13
52	1.93 ± 0.04	1.71 ± 0.13
61	1.94 ± 0.04	1.71 ± 0.13
69	1.95 ± 0.04	1.73 ± 0.13
78	1.95 ± 0.04	1.73 ± 0.13
87	1.96 ± 0.04	1.74 ± 0.13
104	1.97 ± 0.04	1.76 ± 0.13
130	1.98 ± 0.04	1.75 ± 0.13
173	1.97 ± 0.04	1.72 ± 0.13

Table S6: Recalculated dry diameters, measured GF and κ values for anhydrous $CaCl_2$ at RH=80%, recalculated assuming an initially tetrahydrated salt ($CaCl_2 \cdot 4H_2O$). These data are plotted in Fig. S2.

D_{corr} [nm]	GF	κ_{GF}
32	2.03 ± 0.04	2.16 ± 0.15
40	2.06 ± 0.04	2.20 ± 0.16
48	2.08 ± 0.04	2.23 ± 0.16
56	2.09 ± 0.04	2.22 ± 0.16
64	2.11 ± 0.04	2.25 ± 0.16
72	2.11 ± 0.05	2.24 ± 0.16
80	2.12 ± 0.04	2.26 ± 0.16
96	2.13 ± 0.04	2.28 ± 0.16
120	2.13 ± 0.05	2.26 ± 0.16
160	2.13 ± 0.05	2.23 ± 0.16

Table S7: Measured GF and κ values for the hydration branch of dried (hydrated) particles from $MgCl_2$ and modelled data (UManSysProp) for anhydrous $MgCl_2$ with D_{dry}=200 nm. Data is plotted in Fig. 1a in the main manuscript.

RH [%]	GF	Model GF	κ_{GF}	Model κ_{GF}
10.04 ± 0.21	1.05 ± 0.02	-	1.55 ± 2.10	-
20.11 ± 0.12	1.10 ± 0.02	-	1.33 ± 1.05	-
30.03 ± 0.14	1.14 ± 0.02	-	1.17 ± 0.69	-
40.04 ± 0.14	1.19 ± 0.02	-	1.04 ± 0.50	-
50.04 ± 0.13	1.24 ± 0.03	1.84	0.93 ± 0.38	5.26
60.04 ± 0.15	1.30 ± 0.03	1.93	0.83 ± 0.29	4.22
70.06 ± 0.19	1.39 ± 0.03	2.06	0.74 ± 0.23	3.37
75.01 ± 0.20	1.44 ± 0.03	2.14	0.69 ± 0.20	2.99
79.99 ± 0.23	1.51 ± 0.03	2.24	0.64 ± 0.18	2.62
84.99 ± 0.21	1.62 ± 0.03	2.37	0.60 ± 0.16	2.27
89.96 ± 0.19	1.79 ± 0.04	2.58	0.56 ± 0.14	1.90

Table S8: Measured GF and κ values for the dehydration branch of dried (hydrated) particles made from $MgCl_2$ with D_{dry}=200 nm. Data is plotted in Fig. 1a in the main manuscript.

RH [%]	GF	κ_{GF}
9.98 ± 0.07	1.06 ± 0.02	1.81 ± 0.67
19.98 ± 0.06	1.11 ± 0.02	1.43 ± 0.34
24.98 ± 0.08	1.13 ± 0.02	1.32 ± 0.27
29.98 ± 0.09	1.15 ± 0.02	1.22 ± 0.22
34.99 ± 0.07	1.17 ± 0.02	1.15 ± 0.19
39.96 ± 0.09	1.20 ± 0.02	1.09 ± 0.16
49.96 ± 0.09	1.25 ± 0.03	0.98 ± 0.12
59.88 ± 0.14	1.31 ± 0.03	0.87 ± 0.10
69.93 ± 0.07	1.40 ± 0.03	0.76 ± 0.08
79.94 ± 0.12	1.52 ± 0.03	0.66 ± 0.06
89.95 ± 0.23	1.78 ± 0.05	0.54 ± 0.06

Table S9: Measured GF and κ values for the hydration branch of dried (hydrated) particles made from solution of $CaCl_2$ and modelled data (UManSysProp) for anhydrous $CaCl_2$ with D_{dry}=200 nm. Data is plotted in Fig. 1c in the main manuscript.

RH [%]	GF	Model GF	κ_{GF}	Model κ_{GF}
4.95 ± 0.20	1.04 ± 0.03	–	2.54 ± 1.90	–
10.06 ± 0.25	1.10 ± 0.02	–	3.03 ± 0.82	–
20.02 ± 0.16	1.19 ± 0.02	–	2.78 ± 0.43	–
30.03 ± 0.15	1.26 ± 0.03	–	2.39 ± 0.30	–
40.02 ± 0.12	1.33 ± 0.03	–	2.04 ± 0.22	–
50.38 ± 0.14	1.39 ± 0.03	1.69	1.70 ± 0.17	3.84
60.05 ± 0.16	1.46 ± 0.03	1.77	1.42 ± 0.13	3.06
70.04 ± 0.20	1.55 ± 0.03	1.88	1.18 ± 0.11	3.60
75.00 ± 0.16	1.61 ± 0.03	1.95	1.10 ± 0.09	3.96
80.01 ± 0.19	1.70 ± 0.03	2.03	1.00 ± 0.08	4.45
84.96 ± 0.20	1.81 ± 0.04	2.16	0.91 ± 0.07	5.20
89.94 ± 0.16	1.99 ± 0.04	2.35	0.81 ± 0.06	6.56

Table S10: Measured GF and κ values for the dehydration branch of dried (hydrated) particles made from $CaCl_2$ with D_{dry}=200 nm. Data is plotted in Fig. 1c in the main manuscript.

RH [%]	GF	κ_{GF}
4.98 ± 0.06	1.04 ± 0.02	2.51 ± 1.38
9.98 ± 0.05	1.10 ± 0.02	3.00 ± 0.77
19.99 ± 0.04	1.19 ± 0.02	2.76 ± 0.43
24.99 ± 0.06	1.23 ± 0.03	2.55 ± 0.36
29.98 ± 0.06	1.26 ± 0.03	2.40 ± 0.31
34.98 ± 0.07	1.30 ± 0.03	2.24 ± 0.26
39.96 ± 0.08	1.33 ± 0.03	2.06 ± 0.23
49.98 ± 0.05	1.40 ± 0.03	1.76 ± 0.17
59.92 ± 0.10	1.46 ± 0.03	1.45 ± 0.14
69.95 ± 0.04	1.56 ± 0.03	1.22 ± 0.11
79.92 ± 0.12	1.71 ± 0.04	1.04 ± 0.10
90.01 ± 0.23	2.04 ± 0.07	0.87 ± 0.11

Hygroscopicity results from CCNc measurements

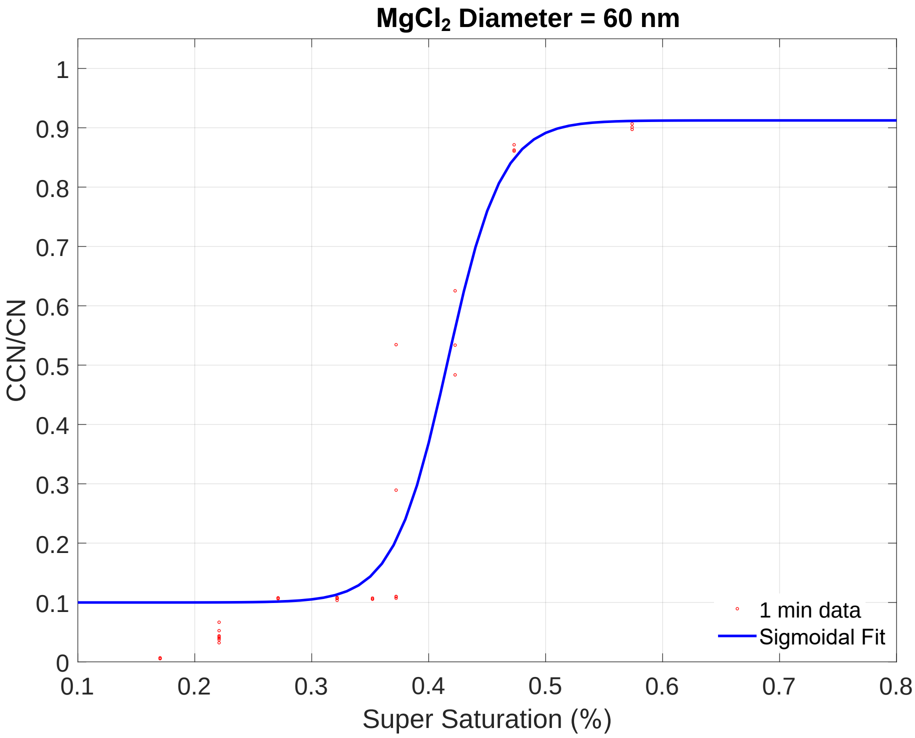

Figure S3: Example activation curve of $MgCl_2$ in the CCNc: the 1-minute averaged data and sigmoidal fit used to retrieve the SS_{crit} are illustrated.

Table S11: Measured $MgCl_2$ CCNc data corresponding to Fig. S3 together with model data (UManSysProp). D_{set} corresponds to the diameter selected in the DMA, while D_{corr} denotes the diameter after hydrate correction assuming $MgCl_2 \cdot 6H_2O$. The κ values are only presented for anhydrous $MgCl_2$, i.e. using D_{corr}.

D_{set} [nm]	D_{corr} [nm]	SS_{crit}	Model SS_{crit} (D_{set})	Model SS_{crit} (D_{corr})	κ_{CCN}	Model κ_{CCN}
40	27.27	0.784	0.433	0.783	1.103	1.117
45	30.67	0.651	0.362	0.657	1.124	1.119
50	34.08	0.569	0.308	0.563	1.072	1.122
60	40.90	0.418	0.266	0.411	1.151	1.130
70	47.71	0.333	0.184	0.328	1.141	1.138

Table S12: Measured $CaCl_2$ CCNc data. D_{set} corresponds to the diameter selected in the DMA, while D_{corr} denotes the diameter after different hydrate corrections (either $CaCl_2 \cdot 2H_2O$, $CaCl_2 \cdot 4H_2O$ or $CaCl_2 \cdot 6H_2O$).

D_{set} [nm]	D_{corr} ($2 \cdot H_2O$) [nm]	D_{corr} ($4 \cdot H_2O$) [nm]	D_{corr} ($6 \cdot H_2O$) [nm]	SS_{crit}
47.25	40.92	37.90	34.90	0.573
53.16	46.04	42.67	39.27	0.460
59.06	51.15	47.38	43.63	0.391
75.00	64.96	60.17	55.40	0.275
100.00	86.61	80.22	73.87	0.183

Table S13: Modelled critical super saturations for $CaCl_2$ corresponding to the set and corrected diameters presented in Table S12. $SS_{crit,obs}$ represents the results direclty measured with the CCNc (same as SS_{crit} entries in Table S12).

SS_{crit} D_{set}	SS_{crit} D_{corr} ($2 \cdot H_2O$)	SS_{crit} D_{corr} ($4 \cdot H_2O$)	SS_{crit} D_{corr} ($6 \cdot H_2O$)	$SS_{crit,obs}$
0.376	0.468	0.525	0.595	0.573
0.315	0.394	0.439	0.498	0.460
0.268	0.334	0.375	0.425	0.391
0.186	0.232	0.261	0.295	0.275
0.120	0.149	0.168	0.191	0.183

Water activity measurements

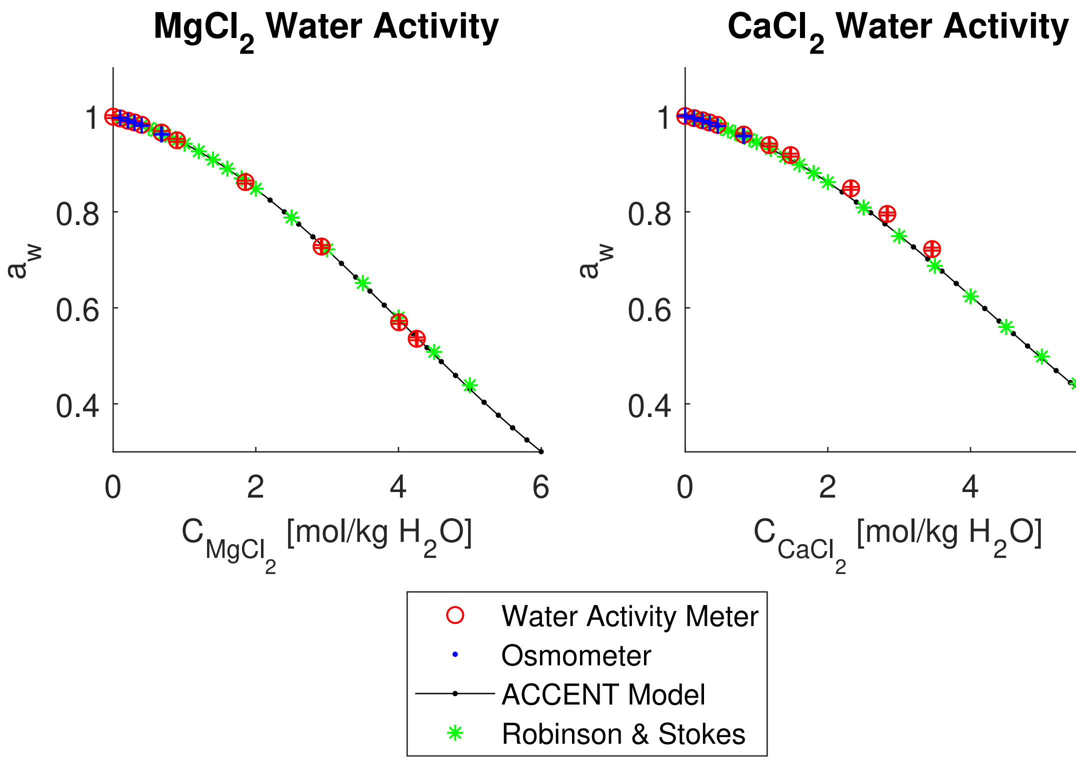

Figure S4: Water activities of solutions of $MgCl_2 \cdot 6H_2O$ and $CaCl_2 \cdot 4H_2O$ measured with the water activity meter and the osmometer as a function of molality. Note that the shown molalities are of the anhydrous salts. Furthermore, modeled values from the ACCENT model(1) and table values from Robinson and Stokes(3) are plotted.

Table S14: Water activity measurements on solutions of $CaCl_2 \cdot 4H_2O$.

C_{CaCl_2} [mol/kg]	$a_{w,WAM}$	$a_{w,OSM}$
0	0.9995	1
0.1240	0.9951	0.9949
0.2427	0.9906	0.9900
0.3409	0.9861	0.9853
0.4548	0.9811	0.9787
0.8199	0.9608	0.9581
1.1773	0.9391	-
1.4776	0.9182	-
2.3252	0.8489	-
2.8330	0.7956	-
3.4618	0.7224	-
5.9286	0.4498	-

Table S15: Table- and model values for solutions of $CaCl_2$.

C_{CaCl_2} [mol/kg]	a_w ACCENT Model	a_w Robinson & Stokes
0.1	0.99537	0.995
0.2	0.99070	0.991
0.3	0.98587	0.986
0.4	0.98084	0.981
0.5	0.97559	0.976
0.6	0.97008	0.970
0.7	0.96431	0.964
0.8	0.95826	0.958
0.9	0.95190	0.952
1.0	0.94525	0.945
1.2	0.93100	0.931
1.4	0.91549	0.915
1.6	0.89874	0.899
1.8	0.88078	0.881
2.0	0.86166	0.862
2.2	0.84145	-
2.4	0.82021	-
2.5	-	0.8091
2.6	0.79804	-
2.8	0.77503	-
3.0	0.75126	0.749
3.2	0.72685	-
3.4	0.70189	-
3.5	-	0.6875
3.6	0.67648	-
3.8	0.65073	-
4.0	0.62475	0.624
4.2	0.59862	-
4.4	0.57246	-
4.5	-	0.5601
4.6	0.54636	-
4.8	0.52041	-
5.0	0.49470	0.499
5.2	0.46432	-
5.4	0.44430	-
5.5	-	0.4425
5.6	0.41982	-
5.8	0.39585	-
6.0	0.37248	0.392

Table S16: Water activity measurements on solutions of $MgCl_2 \cdot 6H_2O$.

C_{MgCl_2} [mol/kg]	$a_{w,WAM}$	$a_{w,OSM}$
0	0.9982	-
0.0979	0.9946	0.9956
0.2093	0.9898	0.9903
0.2967	0.9864	0.9856
0.3988	0.9813	0.9801
0.6785	0.9651	0.9615
0.8937	0.9490	-
1.8541	0.8620	-
2.9219	0.7277	-
4.0086	0.5699	-
4.2557	0.5356	-

Table S17: Table- and model values for solutions of $MgCl_2$.

C_{MgCl_2} [mol/kg]	a_w ACCENT Model	a_w Robinson & Stokes
0.1	0.99535	0.995
0.2	0.99060	0.991
0.3	0.98562	0.986
0.4	0.98037	0.980
0.5	0.97482	0.975
0.6	0.96894	0.969
0.7	0.96271	0.963
0.8	0.95613	0.956
0.9	0.94917	0.949
1.0	0.94184	0.942
1.2	0.92600	0.926
1.4	0.90861	0.909
1.6	0.88968	0.890
1.8	0.86927	0.870
2.0	0.84745	0.848
2.2	0.82430	-
2.4	0.79993	-
2.5	-	0.7881
2.6	0.77445	-
2.8	0.74798	-
3.0	0.72065	0.722
3.2	0.69260	-
3.4	0.66397	-
3.5	-	0.652
3.6	0.63491	-
3.8	0.60555	-
4.0	0.57604	0.580
4.2	0.54651	-
4.4	0.51711	-
4.5	-	0.5082
4.6	0.48797	-
4.8	0.45920	-
5.0	0.43093	0.439
5.2	0.40327	-
5.4	0.37631	-
5.6	0.35014	-
5.8	0.32484	-
6.0	0.30049	-

Bibliography

[1] S. L. Clegg, J. H. Seinfeld, and P. Brimblecombe. Thermodynamic modelling of aqueous aerosols containing electrolytes and dissolved organic compounds. *Journal of Aerosol Science*, 32:713–738, 2001.

[2] A. D1141-98. *Standard Practice for the Preparation of Substitute Ocean Water*. ASTM International, West Conshohocken, PA, USA, 2013. doi: 10.1520/D1141-98R13. URL `http://www.astm.ofg`.

[3] R. A. Robinson and R. H. Stokes. *Electrolyte Solutions*. Dover Publications, Inc., second revised edition edition, 2002.