Reconciling atmospheric water uptake by hydrate forming salts

Bernadette Rosati,[*,†,¶] Andreas Paul,[†,§] Emil Mark Iversen,[†] Andreas Massling,[‡] and Merete Bilde[*,†]

†*Department of Chemistry, Aarhus University, Denmark*

‡*Department of Environmental Science, Aarhus University, Denmark*

¶*Faculty of Physics, University of Vienna, Austria*

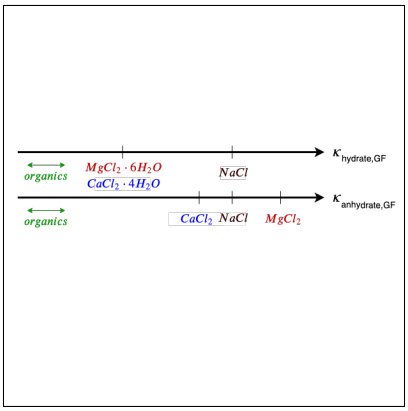
§*now at: Institute of Energy and Climate Research, Forschungszentrum Jülich, Germany*

E-mail: bernadette.rosati@chem.au.dk; bilde@chem.au.dk

Abstract

Magnesium and calcium chloride salts contribute to the global atmospheric aerosol burden via emission of sea spray and mineral dust. Their influence on aerosol hygroscopicity and cloud forming potential is important but uncertain with ambiguities between results reported in the literature. To address this, we have conducted measurements of the hygroscopic growth and critical supersaturation of dried, size selected nano-particles made from aqueous solution droplets of $MgCl_2$ and $CaCl_2$, respectively, and compare experimentally derived values with results from state-of-the-art thermodynamic modelling. It is characteristic of both $MgCl_2$ and $CaCl_2$ salts that they bind water in the form of hydrates under a range of ambient conditions. We discuss how hydrate formation affects the particles' water uptake and provide an expression for hydrate correction factors needed in calculations of hygroscopic growth factors, critical supersaturations, and κ values of particles containing hydrate forming salts. We demonstrate the importance of accounting for hydrate forming salts when predicting hygroscopic properties of sea spray aerosol.

Graphical TOC Entry



Keywords

Hydrate forming salts, hygroscopicity, cloud activation, water activity

Atmospheric aerosols containing inorganic salts are ubiquitous in the Earth's atmosphere and play a critical role in climate due to their interactions with sunlight and role in cloud formation.[1] Mineral dust is a major contributor to the atmospheric loading of inorganic salts and is mainly emitted from dry soils as a result of surface winds.[2–5] Mineral dust is dominated by almost insoluble oxides and carbonates with low hygroscopicity.[6] During atmospheric transit, surface reactions of these oxides and carbonates with acidic gases lead to the formation of $MgCl_2$ and $CaCl_2$ salts.[7–9] These salts are soluble in water and thus directly impact particle water uptake.[10] The oceans constitute another major emission source of inorganic salt, releasing so-called sea spray aerosols (SSA) through wave breaking at the ocean surface into the atmosphere.[11] SSA are comprised of a mixture of inorganic salts and organic species,[11–13] where the relative ratio varies as a function of size.[14–16] The hygroscopic nature of SSA is mainly driven by the inorganic fraction and although sodium chloride (NaCl) makes up the major inorganic compound in SSA by mass, recent work has shown that it is imperative to include the whole complexity of inorganic sea salt in assessment of its hygroscopicity[17] and cloud forming potential.[18] Rasmussen et al.[19] pointed out that sea salt contains hydrate forming salts which affect volatility and hydrated forms of $MgCl_2$ and $CaCl_2$ have been proposed to be responsible for lowering the hygroscopic potential of sea salt compared to pure NaCl.[17]

While $MgCl_2$ is typically stable and solid in its hexahydrate state ($MgCl_2{\cdot}6H_2O$) at 298 K and relative humidities (RH) above 3%,[20] the hydration state of solid $CaCl_2$ at 298 K is much less clear. The number of water molecules associated with $CaCl_2$ may be 0, 2, 4 or 6 for humidities in the range 0-28%.[20] As a further complication the tetrahydrate ($CaCl_2{\cdot}4H_2O$) can exist in two allotropic forms with different solubilities[21] and several of the hydrates may exist in meta-stable states.[22]

Several recent studies have targeted the hygroscopicity and cloud activation potential of $MgCl_2$ and $CaCl_2$ salts[6,9,23–26] revealing ambiguities in how to address and present the water uptake of hydrate forming salts. We here suggest a transparent and clear way of report-

ing hygroscopicity and cloud activation potential for hydrate forming salts of atmospheric relevance and provide a comparison to results from a state-of-the-art thermodynamic model.

We performed two series of experiments focusing on water uptake by nano-meter sized aerosol particles at sub- and supersaturated conditions of water vapor, respectively. These were complemented by bulk water activity measurements. A full description of the experiments and tabular values of experimental results are provided in the supplementary information (SI). In short, aerosol particles were generated from aqueous salt solutions ($CaCl_2$(aq) or $MgCl_2$(aq)) using an atomizer and dried by dilution with dry clean air and passage through diffusion dryers (RH<10%). Water uptake was probed using a Humidified Tandem Differential Mobility Analyzer (HTDMA) and a Cloud Condensation Nucleus counter (CCNc).

The hygroscopic growth factors (GF(RH); defined as the ratio between humidified and dry particle diameter) were determined directly by HTDMA measurements and indirectly from measurements on bulk solution using a water activity meter. Figures 1a and 1c, present measured GFs as a function of RH for $MgCl_2$ and $CaCl_2$ particles generated from $MgCl_2$ and $CaCl_2$ aqueous solutions, respectively, with initial dry diameters of 200 nm. For comparison, experimental values reported in the literature deploying a similar aerosol generation technique and measurement principle for 100 nm[9] and 50 nm[25] particles are shown. The results from this work confirm previously published values; at RH=80% Guo et al.[9] report GF=1.46 and Park et al.[25] GF=1.47, while we find GF=1.50 for $MgCl_2$, thus agreeing within the estimated uncertainty in GF of 3%. For $CaCl_2$, the discrepancies are larger yielding GF values of 1.51,[9] 1.48[25] and 1.69 (this study). All experimental studies show gradual increase in GF(RH) with increasing RH and gradual decrease with decreasing humidity. The lack of clear deliquescence and efflorescence indicates that the particles exist in an amorphous solid phase state after drying.[9] Interestingly, clear deliquescence has been reported for larger (micro-meter sized) particles[24,27,28] of $MgCl_2$ and $CaCl_2$ and measuring the mass of a bulk sample as function of RH.[9] This confirms particle size to be a critical parameter in the phase state behavior of atmospheric aerosol particles.[29] If particle size is a determining parameter,

the actual size needed for crystal formation and thus deliquescence and efflorescence behavior of $MgCl_2$ and $CaCl_2$ particles is yet to be uncovered.

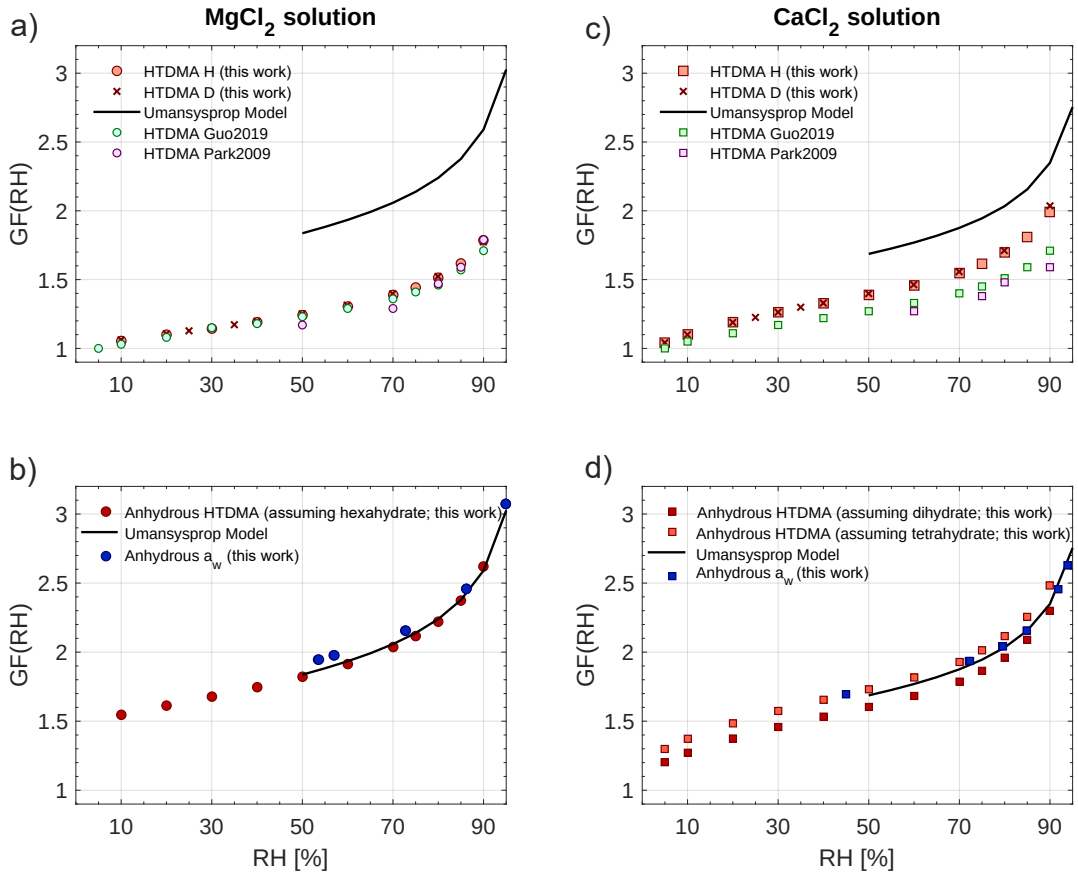


Figure 1: Hygroscopic growth factors vs. RH for dried particles made from aqueous solution of $MgCl_2$ and $CaCl_2$ salts. Panels a) and c) show experimental values from this work and literature.[9,25] Regarding HTDMA results from this work, crosses indicate values recorded during dehydration (HTDMA D) while all other values stem from hydration branch measurements (HTDMA H). Panels b) and d) show HTDMA results (this work) after correction for hydrates along with GFs obtained from bulk water activity measurements (this work), derived following Zamora et al.[30] Solid lines represent model[31] predictions for anhydrous salts (D_{dry}=200 nm).

Predictions from a state-of-the-art thermodynamic model (UManSysProp[31]) are also displayed in Fig. 1. The model runs were executed assuming that the particles consisted of $MgCl_2$ and $CaCl_2$, respectively, in their anhydrous states. Figure 1a and 1c reveal a considerable gap between observed and predicted GFs. We argue that water bound as hydrates in the dry salts is responsible for this difference. It was recently pointed out that airborne

aqueous solution droplets containing $MgCl_2$ and/or $CaCl_2$ can form stable hydrates upon drying.[19] The number of water molecules associated with the dried salt depends on temperature and RH[20,22] and hence the hydration state of the salt dissolved in the aqueous solution is not necessarily representative for the hydration state of the dried nano-particles generated from the aqueous solution.

For $MgCl_2$ the stable hydration state at RH in the range 3-33% and a temperature of 298 K is $MgCl_2{\cdot}6H_2O$.[20] The dry particle diameter as selected by the first DMA in the HTDMA system at these conditions is thus not representative of an anhydrous particle but a particle containing $MgCl_2{\cdot}6H_2O$. To obtain the diameter (D_p(RH,a)) and growth factor (GF(RH,a)) of the anhydrous salt particle, we correct the selected dry diameter in the first DMA (D_p(RH,h)) to account for hydrate water by applying a hydrate correction factor (c_H):

$$\begin{aligned} D_p(RH,a) &= c_H \cdot D_p(RH,h), \\ GF(RH,a) &= \frac{GF(RH,h)}{c_H}, \end{aligned} \tag{1}$$

where GF(RH,h) is the observed (hydrated) growth factor. As derived in the SI the hydrate correction factor c_H is calculated by assuming spherical particles with a specific molar mass (M) and density (ρ):

$$c_H = \left(\frac{M_a \cdot \rho_h}{M_h \cdot \rho_a} \right)^{1/3}. \tag{2}$$

Here the subscripts a and h refer to the anhydrous and hydrated salt, respectively. As seen in Fig. 1b, HTDMA and modeled data agree almost perfectly (within 1%) for $MgCl_2$ when the GF(RH) values are corrected for contributions of hydrate water. This result is further supported by the good agreement between GFs for the anhydrous salt derived from water activity (a_w) measurements (this work) following the procedure described in Zamora et al.[30]

The hydration state of $CaCl_2$ in dried particles is more difficult to infer as several possibilities are plausible. Small changes in RH, e.g. from 9-21% to 21-28%, can change $CaCl_2{\cdot}4H_2O$

to $CaCl_2 \cdot 6H_2O$[20] at 298 K, and a change in temperature from 298 to 303 K can induce a hydration change from $CaCl_2 \cdot 6H_2O$ to $CaCl_2 \cdot 4H_2O$.[20,32] It is thus challenging to access the hydration state of $CaCl_2$ particles generated by drying of aqueous solution droplets as in this work, in literature[6,9,23,25,26] and in the atmosphere. Figure 1d shows GF(RH) for $CaCl_2$ corrected assuming dihydrate ($2 \cdot H_2O$) and tetrahydrate ($4 \cdot H_2O$) states. It is clear that a correction is needed to reach agreement with the model output for anhydrous salt particles but it is not possible to infer the actual hydration state as the best correlation depends on the actual RH. This result likely reflects that we cannot exclude that individual particles may contain several hydration states of the salt. Additionally, Fig. 1d shows GF(RH) values retrieved from a_w providing excellent agreement with model data. For completeness, GF(80%) was measured as a function of initial dried particle diameter (40-200 nm) for both salts and in all cases agreement with the model was only reached after application of the hydrate correction factors (see SI).

Table 1 provides hydrate correction factors (c_H) for the different hydration states of $MgCl_2$ and $CaCl_2$. Since in the atmosphere hydrate forming salts are likely present in their hydrated state, modelled hygroscopic growth factors based on the assumption of anhydrous salts should be corrected to account for the effect of hydrates using c_H.

Table 1: Hydrate correction factors for the atmospherically relevant hydration states of $MgCl_2$ and $CaCl_2$, assuming spherical particles at T=298.15 K. Densities and molar masses used for this calculation can be found in the SI.

Compound	c_H
$MgCl_2 \cdot 6H_2O$	0.68
$CaCl_2 \cdot 2H_2O$	0.87
$CaCl_2 \cdot 4H_2O$	0.80
$CaCl_2 \cdot 6H_2O$	0.74

The particle ability to act as cloud condensation nuclei (CCN) is also affected by the salt hydration state. Figure 2 shows critical supersaturation (SS_{crit}) vs. dry particle diameter for $MgCl_2$ and $CaCl_2$ particles, respectively. As in the case of the HTDMA experiments, the dried particle diameter likely represents the diameter of a particle containing hydrated

salts. The hydrate correction factor, introduced in Eq. 2 and presented in Table 1, can be used to calculate the diameter of the anhydrous particle from the diameter of the hydrated particle (and vice versa). SS_{crit} measured for dried particles made from $MgCl_2$ and $CaCl_2$ aqueous solutions, respectively, are in relatively good agreement with previous findings[6,23,26] (Fig. 2a and c). For hydrated $MgCl_2$ particles with a diameter of 50 nm we find SS_{crit}=0.57 (κ=0.34[33]), while Gaston et al.[23] found SS_{crit}=0.48 for the same size (κ=0.47). For hydrated $CaCl_2$ Gaston et al.[23] report SS_{crit}=0.24 for particles with a diameter of 75 nm (κ=0.56), while Sullivan et al.[6] find SS_{crit}=0.265 (κ=0.46). We obtained SS_{crit}=0.275 (κ=0.42) which is in best agreement with Sullivan et al.[6] (see Fig. 2b). The most striking feature is again the significant divergence in observed CCN activity of dried salt particles and model results assuming anhydrous salts. Both literature studies assumed that $CaCl_2$ particles were present in their dihydrate state, while $MgCl_2$ was in its hexahydrate state.[6,23]

So called intrinsic κ values can be calculated as:[23]

$$\kappa_{int} = \frac{\nu \cdot \rho_s \cdot M_w}{\rho_w \cdot M_s}, \tag{3}$$

where ν is the number of ions, ρ_s and ρ_w are the densities of solute and water and M_w and M_s are the molecular weights of solute and water. κ_{int} for $CaCl_2 \cdot 2H_2O$ is 0.68 while experimental results assuming $CaCl_2 \cdot 2H_2O$ are notably lower.[6,23] Gaston et al.[23] accounted for solution non-idealities using the van't Hoff factor and report on this basis a κ value of 0.589 for $CaCl_2 \cdot 2H_2O$. This is closer to their experimental result (0.56) but still higher than results from Sullivan et al.[6] and from this study .

Applying the hydrate correction factors to the dry diameters from our study yield the results presented in Fig. 2b and 2d. In case of $MgCl_2 \cdot 6H_2O$ we obtain excellent agreement with model data. In the case of $CaCl_2$ the tetrahydrate or hexahydrate hypothesis leads to the best agreement. In comparison, the HTDMA results where best agreement was obtained assuming dihydrate or tetrahydrates and could be caused by slightly differing RH when the aerosols were size selected. Nevertheless, the results emphasize that including some hydration

even if the precise state is not known still yields a smaller error than assuming anhydrous particles.

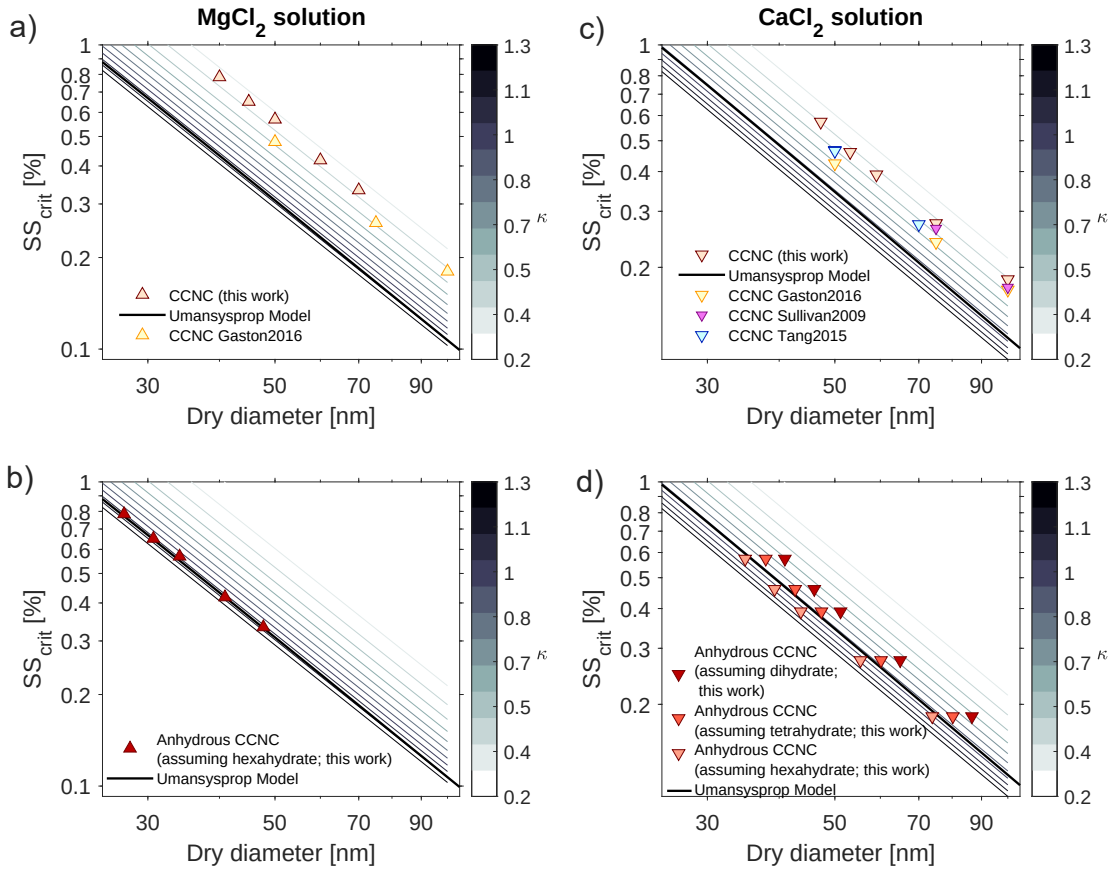


Figure 2: Critical super-saturations (SS_{crit}) as a function of size for $MgCl_2$ and $CaCl_2$ together with κ-isolines. Additionally, available literature data[6,23,26] and model data are displayed. Panels a) and c) show data as directly obtained from the measurement, while b) and d) were corrected for hydrate contributions.

To reconcile hygroscopicity data gathered at sub- and supersaturated water vapour conditions, the hygroscopicity parameter κ[33] is typically used. Figure 3 displays κ values obtained from HTDMA and CCNc measurements from this study and literature plotted vs. values calculated using the UManSysProp model. Generally, a large disagreement between experimental and modeled (assuming anhydrous particles) values is observed for both $MgCl_2$ and $CaCl_2$ (open symbols). Agreement between experimental and modelled κ values is obtained if particle diameters are modified to account for hydrate water following Eq. 2. We conclude

that the hydration state of $MgCl_2$ in dried salt nano-particles is 6 while for $CaCl_2$ hydration states in the range 2-6 are likely depending on drying procedure. Since results from subsaturated conditions suggest a hydration state of 2-4 and results from supersaturated conditions suggest a hydration state of 4-6, we suggest use of the tetrahydrate state if no firm knowledge on hydration state is available. Consistent with other studies for both organic and inorganic compounds,[33,34] there is a significant difference in κ calculated from subsaturated (GF(RH)) and supersaturated (SS_{crit}) conditions: in the case of $MgCl_2$ the model results yield κ_{GF} of 1.89, while $\kappa_{SS_{crit}}$ is merely of 1.23, similarly a κ_{GF} of 1.38 and $\kappa_{SS_{crit}}$ of 0.97 were found for $CaCl_2$.

For comparison, Fig. 3 additionally presents results for the notoriously hygroscopic NaCl salt, calculated from GF(RH) and SS_{crit} values (black symbols). It is evident that the anhydrous forms of $MgCl_2$ and $CaCl_2$ are actually extremely hygroscopic, with $CaCl_2$ reaching values close to those of NaCl ($\kappa_{GF,CaCl_2}$=1.38, $\kappa_{GF,NaCl}$=1.49) and $MgCl_2$ being much more hygroscopic than NaCl ($\kappa_{GF,MgCl_2}$=1.89, $\kappa_{GF,NaCl}$=1.49). When, however, considering the hydrated states of $MgCl_2$ and $CaCl_2$, their κ reach comparable values around 0.5. It should be noted that NaCl is typically present in its anhydrous state except at temperatures below 273 K.[22]

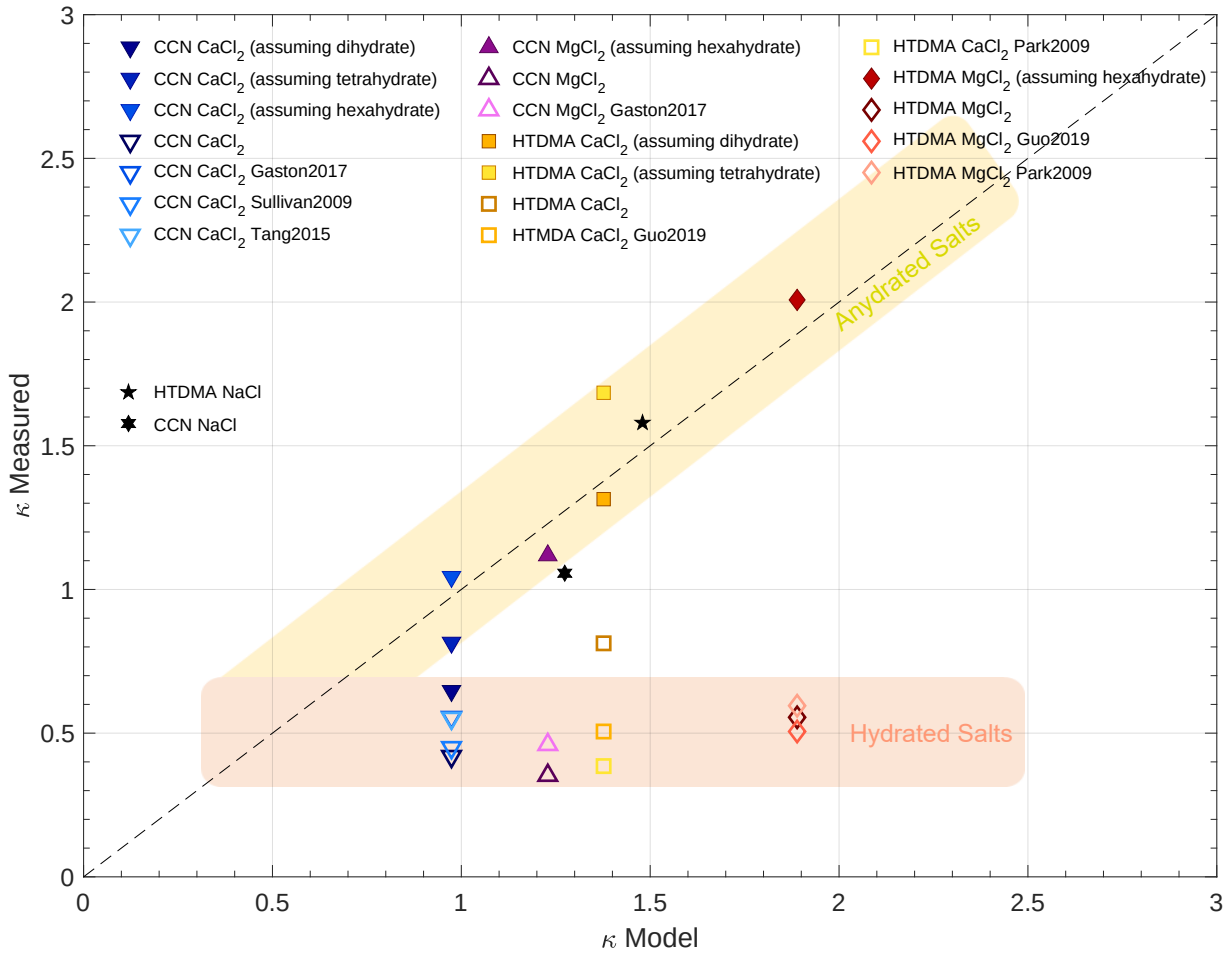


Figure 3: Hygroscopicity parameter κ: Comparison of κ values as calculated from HTDMA (taken at RH=90%) and CCNc (calculated as mean over all sizes, see SI) as well as literature data[6,9,23,25,26] for $MgCl_2$ and $CaCl_2$. The κ-Model data were obtained using the UManSysProp model. The dashed line represents the 1:1 line. All filled symbols were corrected for hydrates, while open symbols represent uncorrected data. Additionally, results for NaCl as measured and modeled from HTDMA and CCNc data are illustrated.

Figure 3 demonstrates the importance of hydrates for correct interpretation and prediction of hygroscopic growth and cloud droplet activation and shows that closure between experimental data and state-of-the-art model predictions can be achieved when hydrates are considered. These findings also underline that hygroscopicity of complex aerosols containing hydrate forming salts (such as sea salt) cannot be directly predicted by using models that combine properties of anhydrous salts as this approach leads to an overestimation of the hygroscopic growth as was shown in previous studies.[17]

The results from this study can be used to predict the hygroscopicity of oceanic sea salt. The major components of dried sea salt are NaCl, $MgCl_2$, Na_2SO_4 and $CaCl_2$.[35] As discussed above, NaCl is expected to be anhydrous at most ambient conditions. Na_2SO_4 has been shown to be present both in its anhydrous and decahydrate state.[22] A previous study, however, found that suspended Na_2SO_4 microparticles are anhydrous.[36] This is supported by volatility experiments on dried mixed NaCl/Na_2SO_4 particles that did not evaporate at temperatures ranging from 50 to 300°C[19] and GF measurements for Na_2SO_4 that were well comparable to theoretical calculations assuming anhydrates and Köhler theory.[37] Thus, Na_2SO_4 is treated as anhydrous in the following. Table 2 presents estimated GF, κ_{GF} and $\kappa_{SS_{crit}}$ values for two cases: (i) assuming sea salt consists of anhydrous salts only and (ii) considering hydrated $MgCl_2$ and $CaCl_2$ salts in sea salt. By applying a volume weighted mixing rule[33] sea salt GF_a of 2.38, $\kappa_{a,GF}$=1.46 and $\kappa_{a,SS_{crit}}$=1.21 are found. When including hydrated $MgCl_2$ and $CaCl_2$, GF_h of 2.14, $\kappa_{h,GF}$=1.08 and $\kappa_{h,SS_{crit}}$=0.89 are found. GF measurements of artificial sea salt particles yielded GF(90%)=2.09 and 2.19 (κ=0.96 and 1.12) using a sea spray simulation tank and a nebulizer to generate sea salt particles, respectively,[17] while κ=0.92 was found from CCNc measurements.[38] The herein calculated sea salt results including hydrated $MgCl_2$ and $CaCl_2$ are evidently in much better agreement with the sea salt experimental data than calculations based on the anhydrous salts alone.

Table 2: Calculations of the properties of sea salt considering (i) anhydrous salts only and (ii) hydrated forms of $MgCl_2$ and $CaCl_2$. The volume fractions of the anhydrous salts ϵ_{va} are recalculated from the specifications by ASTM.[35] For case (i) anhydrous GFs, $\kappa_{a,GF}$ and $\kappa_{a,SS_{crit}}$ were calculated using the UManSysProp model. Hydrated GFs, $\kappa_{h,GF}$ and $\kappa_{h,SS_{crit}}$ were calculated assuming that NaCl and Na_2SO_4 were anhydrous, while $MgCl_2{\cdot}6H_2O$ and $CaCl_2{\cdot}4H_2O$ were present. The volume fractions of hydrated sea salt ϵ_{vh} were recalculated from the anhydrous case assuming volume additivity (see SI). GFs stem from measurements at D_{dry}=200 nm and RH=90%, while $\kappa_{SS_{crit}}$ were calculated as mean over all measured sizes.

Anhydrous sea salt					Partly hydrated sea salt				
Compound	ϵ_{va} [%]	GF_a	$\kappa_{a,GF}$	$\kappa_{a,SS_{crit}}$	Compound	ϵ_{vh} [%]	GF_h	$\kappa_{h,GF}$	$\kappa_{h,SS_{crit}}$
NaCl	72.5	2.40	1.48	1.27	NaCl	53.8	2.40	1.48	1.27
$MgCl_2$	14.3	2.59	1.89	1.16	$MgCl_2{\cdot}6H_2O$	34.1	1.79	0.56	0.35
Na_2SO_4	9.7	1.93	0.72	0.88	Na_2SO_4	7.2	1.93	0.72	0.88
$CaCl_2$	3.5	2.35	1.38	0.92	$CaCl_2{\cdot}4H_2O$	5.0	1.99	0.81	0.42
mixture	100	2.38	1.46	1.21	mixture	100	2.14	1.08	0.89

In summary, the hygroscopic and cloud activation properties of $MgCl_2$ and $CaCl_2$ are dictated by their hydration state, which substantially lowers their ability to take up water. The behavior at sub- and supersaturated water vapour conditions differs remarkably, yielding higher κ values when calculated from the hygroscopic growth compared to when calculated from the SS_{crit}. When accounting for the hydration state of the salts, very good agreement can be achieved between measured and modeled data. This work demonstrates, that it is important to account for hydrate formation when predicting hygropscopic properties of complex aerosols containing hydrate forming salts, such as sea salt aerosols.

Acknowledgement

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Supporting Information Available

The Supplementary Information is available free of charge. Details of the calculation procedure for anhydrous particle size, experimental materials and methods as well as figures and tabular values for the hygroscopicity results from HTDMA, CCNc and water activity measurements are presented.

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