

Supporting information

Understanding the hydration process of salts:

The impact of a nucleation barrier

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S1. Application of the Classical Nucleation Theory to hydration

The induction time τ [s] is taken as a measure of the nucleation frequency J [s⁻¹]:

$$\tau \equiv \frac{c}{J}, \quad (1)$$

where c [-] is a proportionality constant.

The generic expression for the nucleation rate J given by:¹

$$J = N_s j Z \exp\left(\frac{-\Delta G^*}{k_B T}\right) \quad (2)$$

where

N_s : number of nucleation sites [-]

j : rate at which molecules attach to the cluster causing it to grow [s^{-1}]

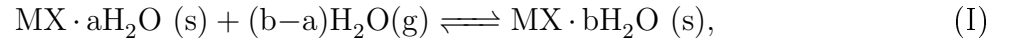
Z : Zeldovich factor [-]

ΔG^* : Formation Gibbs free energy of a critical cluster [J]

k_B : Boltzmann constant [$1.38 \cdot 10^{-23}$ J/K]

T : absolute temperature [K]

For analysis of the induction time, the theory of homogeneous nucleation as developed by Volmer and Weber² has been adapted to the generic case of hydration, where the energy barrier ΔG^* to form a critical cluster (nucleus) and the nucleus radius r^* [m] are evaluated for the generic case of hydration:



where (b-a) gaseous molecules of water bind to a unit $MX \cdot aH_2O$ to form the hydrated unit $MX \cdot bH_2O$.

We will obtain:

$$\Delta G^* = \Delta G(r^*) \quad (3)$$

by finding the maximum of the Gibbs free energy ΔG as a function of the cluster radius r [m]:

$$\left(\frac{\partial \Delta G(r)}{\partial r} \right)_T = 0. \quad (4)$$

The total formation Gibbs free energy by formation of a cluster is given by the sum of a bulk term and a surface term:

$$\Delta G = \Delta G_{bulk} + \Delta G_{surface} \quad (5)$$

$$\Delta G = (G_f - G_i) + \gamma A \quad (6)$$

where G_f [J] is the Gibbs free energy of the bulk hydrated state and G_i [J] is the Gibbs free energy of the bulk dehydrated state of the cluster, γ [J/m²] and A [m²] are the surface tension and the surface area of the cluster respectively.

The bulk term will be analysed first:

$$\Delta G_{bulk} = G_f - G_i = G_b + N_b \mu - (G_a + N_a \mu) \quad (7)$$

where G_b is the Gibbs free energy of the final solid phase ($\text{MX} \cdot b\text{H}_2\text{O}$); N_b is the final number of water molecules in the gas phase; G_a is the Gibbs free energy of the initial solid phase ($\text{MX} \cdot a\text{H}_2\text{O}$) and N_a is the initial number of water molecules in the gas phase and μ is the chemical potential of the gas phase water.

Since the reaction has the following stoichiometry with respect to the number of salt units N in the cluster:

$$N_b - N_a = -N(b - a) \quad (8)$$

the bulk term is:

$$\Delta G_{bulk} = G_b - G_a - N(b - a)\mu. \quad (9)$$

When macroscopically sized phases α and β are in equilibrium, the change in bulk Gibbs free energy should be zero:

$$\Delta G_{bulk} = 0 \quad (10)$$

$$\Delta G_{bulk} = G_b - G_a - N(b - a)\mu_{eq} = 0 \quad (11)$$

Therefore, the Gibbs free energy contributions of the solid can be expressed in the equilibrium potential μ_{eq} [J].

$$G_b - G_a = N(b - a)\mu_{eq} \quad (12)$$

That is, in equilibrium, the change in Gibbs free energy of the solid phase is compensated by the change in Gibbs free energy of the gas phase. This is the condition at the equilibrium (de)hydration temperature.

The driving force ΔG for nucleus formation is therefore:

$$\Delta G = [N(b - a)\mu_{eq} - (N(b - a)\mu)] + \gamma A \quad (13)$$

$$= -N(b - a)(\mu - \mu_{eq}) + \gamma A \quad (14)$$

$$\equiv -N(b - a)\Delta\mu + \gamma A \quad (15)$$

The number of salt units N in the cluster can be expressed as follows:

$$N = \frac{V}{v} \quad (16)$$

where V [m³] is the volume of the cluster and v is the volume of 1 hydrated salt unit $\text{MX} \cdot b\text{H}_2\text{O}$.

The expression for ΔG is thus:

$$\Delta G = -\frac{V}{v}(b-a)\Delta\mu + \gamma A \quad (17)$$

The critical cluster size r^* is obtained by application of equation 4 using the volume V and surface area A of a 2D-disc, 3D-sphere and 3D-hemisphere in terms of the radius r :

$$V_{2D(\text{disc})} = \pi r^2 h ; A_{2D} = 2\pi r h \quad (18)$$

$$V_{3D(\text{sphere})} = \frac{4}{3}\pi r^3 ; A_{3D} = 4\pi r^2 \quad (19)$$

$$V_{3D(\text{hemi-sphere})} = \frac{2}{3}\pi r^3 ; A_{3D} = 2\pi r^2, \quad (20)$$

which yields:

$$r_{2D(\text{disc})}^* = \frac{v\gamma}{(b-a)\Delta\mu} \quad (21)$$

$$r_{3D(\text{sphere})}^* = r_{3D(\text{hemi-sphere})}^* = \frac{2v\gamma}{(b-a)\Delta\mu} \quad (22)$$

The corresponding energy barriers ΔG^* are found by substituting equations 21 and 22 in equation 17:

$$\Delta G_{2D}^* = \frac{h\pi v\gamma^2}{(b-a)\Delta\mu} \quad (23)$$

$$\Delta G_{3D}^* = \frac{\eta\pi v^2\gamma^3}{(b-a)^2(\Delta\mu)^2} \quad (24)$$

with $\eta = 16/3$ in case of a sphere and $8/3$ in case of half a sphere (hemisphere).

Via the ideal gas law μ and μ_{eq} can be coupled with the respective water vapour pressures:

$$\mu = \mu_0 + k_B T \ln \frac{p}{p_0} \quad (25)$$

$$\mu_{eq} = \mu_0 + k_B T \ln \frac{p_{eq}}{p_0} \quad (26)$$

in which p is the partial water vapour pressure [Pa], p_0 is the reference pressure in standard conditions [10^5 Pa] and μ_0 is the chemical potential of the gas molecules in standard conditions [J].

Therefore:

$$\Delta\mu = k_B T \ln \frac{p}{p_{eq}}. \quad (27)$$

The following expressions for the nucleation frequency are obtained when the full expression of ΔG^* is substituted in the generic nucleation rate (equation 2):

$$J_{2D} = \kappa \exp \left(\frac{-h\pi v \gamma^2}{(k_B T)^2 (b-a) \ln p/p_{eq}} \right) \quad (28)$$

$$J_{3D} = \kappa \exp \left(\frac{-\eta\pi v^2 \gamma^3}{(k_B T)^3 (b-a)^2 (\ln p/p_{eq})^2} \right) \quad (29)$$

with the pre-exponential factor κ [s^{-1}]

$$\kappa = N_s j Z. \quad (30)$$

References

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S2. Deliquescence humidities of K₂CO₃ and MgCl₂·4H₂O

Direct measurements of the solubilities and deliquescence humidities (DRH) of the α -phases K₂CO₃ and MgCl₂·4H₂O at low temperatures are not available and had to be calculated. The DRH of a crystalline phase equals the equilibrium vapor pressure above its saturated solution. Therefore, the DRH can be calculated if the solubility and the water activity a_w of the saturated solution are known. The water activity is given as $a_w = p/p_0$, where p is the vapor pressure above the saturated solution and p_0 is the saturation water vapor pressure. The thermodynamic solubility product K of a salt hydrate $M_mX_x \cdot aH_2O$ with either 1–2 or 2–1 stoichiometry ($m = 1, x = 2$ or vice versa) is given by

$$\ln K = 3\ln(4^{1/3}m/m^\circ) + 3\ln\gamma_\pm + a\ln a_w \quad (S1)$$

where m is the saturation molality, $m^\circ = 1 \text{ mol kg}^{-1}$ and γ_\pm is the mean activity coefficient of the saturated solution. Also, the water activity is related to the osmotic coefficient ϕ :

$$\ln a_w = -3m\phi/m_w \quad (S2)$$

where $m_w = 55.50844 \text{ mol kg}^{-1}$ is the molality of water.

In lack of solubility data, the thermodynamic solubility product K_α of the lower hydrated phase (the α -phase with a mol H₂O) can be calculated from the solubility product K_β of the higher hydrated phase (the β -phase with b mol H₂O) using the following equation:¹

$$\ln K_\alpha = \ln K_\beta - (b - a)\ln(p_{\text{eq}}/p_0) \quad (S3)$$

where p_{eq} is the equilibrium vapor pressure of the hydration transition of the respective salt pair.

The use of Eqs. (S1) and (S2) requires the ability to calculate osmotic and activity coefficients in the saturated solutions of the α - and β -phases. A Pitzer type ion interaction model² is appropriate for such calculations. In the present study, an extended form of the equations including $\beta^{(2)}$ and $\beta^{(3)}$ terms in the expression for the ionic strength dependence of the second virial coefficient was used.³ The model parameters have to be determined from experimental data.

S3. Ion interaction parameters

S3.1 $K_2CO_3(aq)$ at 25 °C

The parameters of the ion interaction equations for $K_2CO_3(aq)$ at 25 °C were determined from isopiestic vapor pressure measurements of Sarbar et al.⁴ Using their isopiestic molalities osmotic coefficients were calculated using appropriate equations for the reference electrolytes used in their study. Their data extend from dilute solution to saturation of $K_2CO_3 \cdot 1.5H_2O$ ($m=8.1 \text{ mol kg}^{-1}$). Since the expected solubility of the anhydrous salt, based on its solubilities at elevated temperatures,⁵ is significantly higher, the final model equation has to extend to such high concentrations. In order to obtain reasonable extrapolation behavior, additional values of estimated osmotic coefficients were used. These values were obtained using the data of Sarbar et al. together with the BET equation^{6,7} to obtain a realistic extrapolation of their data. These estimated osmotic coefficients extend to about 20 mol kg^{-1} . In order to achieve both accurate representation of the experimental data⁴ and reasonable behavior in the supersaturated region, the extended model equation including the $\beta^{(2)}$ and $\beta^{(3)}$ parameters had to be used. The final model parameters at 25 °C are listed in Table S1.

Using the model parameters in Table S1 the solubility product of $K_2CO_3 \cdot 1.5H_2O$ was calculated yielding $\ln K=6.766$ with Eq. (S1). The solubility of anhydrous K_2CO_3 was calculated from Eq. (S3) using the equilibrium vapor pressures of the present work. With the resulting solubility product of $\ln K=12.46$ at 25 °C, the solubility of anhydrous K_2CO_3 of 13.7 mol kg^{-1} and its deliquescence pressure of 6.02 mbar were obtained.

S3.2 $MgCl_2(aq)$ at 25 °C

The parameters of the ion interaction equations for $MgCl_2(aq)$ at 25 °C are largely based on the previous treatment of the $MgCl_2-H_2O$ system.⁸ However, two modifications were necessary. First, as in the case of $K_2CO_3(aq)$, the very high solubility of $MgCl_2 \cdot 4H_2O$ requires significant extrapolation to concentrations where no experimental data are available. Therefore, the same approach with extrapolated data using the BET model as described before was used again including the parameters $\beta^{(2)}$ and $\beta^{(3)}$. The resulting model parameters are listed in Table S1. Second, the solubility product of $MgCl_2 \cdot 4H_2O$ had to be recalculated as the equation reported earlier⁸ cannot be extrapolated to low temperatures.

The parameters in Table S1 together with the solubility reported in the literature ($5.814 \text{ mol kg}^{-1}$) yield a value of 10.388 for the solubility product of $MgCl_2 \cdot 6H_2O$ at 25 °C. The solubility product of $MgCl_2 \cdot 4H_2O$ was then calculated from Eq. (S3) using the equilibrium vapor pressures of both the present work and those reported by Carling⁹ yielding a value of 17.484. With this value, the solubility of 9.06 mol kg^{-1} and a deliquescence pressure of 2.61 mbar were obtained for $MgCl_2 \cdot 4H_2O$.

Table S1 Ion interaction (Pitzer) parameters for K₂CO₃(aq) and MgCl₂(aq) at 25 °C

Parameter	K ₂ CO ₃ (aq)	MgCl ₂ (aq)
α_1	1.4	1.0
α_2	0.5	0.5
α_3	0.1	0.1
$\beta^{(0)} / \text{kg mol}^{-1}$	-5.763260E-01	5.566291E+00
$\beta^{(1)} / \text{kg mol}^{-1}$	2.197031E-01	0
$\beta^{(2)} / \text{kg mol}^{-1}$	-1.192558E+00	2.977926E+00
$\beta^{(3)} / \text{kg mol}^{-1}$	1.254361E+00	-7.463355E+00
$C / \text{kg}^2 \text{mol}^{-2}$	3.285781E-03	-7.561581E-02

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