Supporting Information for "Adsorption, desorption, and crystallization of aqueous solutions in nanopores"

Piyush Jain,[†] Olivier Vincent,[*,‡,§] and Abraham D. Stroock[*,‡,¶]

†*Sibley School of Mechanical and Aerospace Engineering, Cornell University, Ithaca, New York 14853, United States*

‡*Robert Frederick Smith School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, New York 14853, United States*

¶*Kavli Institute at Cornell for Nanoscale Science, Cornell University, Ithaca, New York 14853, United States*

§*Current address: University of Lyon, Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, F-69622, Villeurbanne, France*

E-mail: olivier.vincent@univ-lyon1.fr; ads10@cornell.edu

Empirical relations for LiCl and NaCl

LiCl: We have the empirical relations for surface tension of LiCl solution-vapor interface, activity of bulk LiCl solution and density of the solution at 15°C from Conde et al.[1] . Experimental data relating the activity coefficient as function of concentration is also known.[2] We performed a 5th order polynomial fit to these experimental values and extrapolated (extrapolation is limited to 20% of supersaturation for which the experimental data is available and the monotonicity is preserved for the extrapolated range of supersaturation) to predict activity coefficients for higher supersaturations.

NaCl: The empirical relation for surface tension at liquid-vapor interface is known from Derluyn,[3] the experimental values of activity of bulk NaCl solution as function of concentration is known from Olynyk et al.,[4] the experimental value of density of solution as function of concentration is known from Potter et al.[5] and an empirical relation for activity coefficient as function for supersaturated concentration is known from Steiger.[6] We made a 2nd order polynomial fit to determine the value of activity of solution at supersaturations with caution regarding the monotonicity of the fit; we used this fit to extrapolate to less than 50% of supersautration for which experimental value is known.

Surface tension at liquid-vapor interface

We use the empirical relations for surface tension of solution-vapor interface from Conde et al.[1] for LiCl and Derluyn[3] for NaCl. See Figure S1.

Activity of solution

Figure S2 is the plot of emprical relation of activity of the solution, a_{sol}, as function of dissolved mole fraction of LiCl.[1] Figure S3 is the polynomial fit to the experimental data for activity of solution, a_{sol}, as function of dissolved mole fraction of NaCl.[4]

Activity coefficient

Experimental data[2] on molal activity coefficient, ϱ, of LiCl is extrapolated for supersaturated concentrations, as shown in Figure S4. The empirical relation[6] on activity coefficient of NaCl is plotted in Figure S5. One can rearrange the molal activity coefficient, ϱ, to calculate the activity coefficient associated with mole fraction, ζ, as follows:

$$\zeta(x) = \left(\frac{\varrho}{(1-x) \times \mathrm{mw}_{\mathrm{water}}} \right) \tag{S1}$$

such that

$$\zeta(x) \times x = \varrho \times m \tag{S2}$$

where $\mathrm{mw}_{\mathrm{water}}$ is the molecular weight of water in kg/mol, x is the mole fraction and m is corresponding molality.

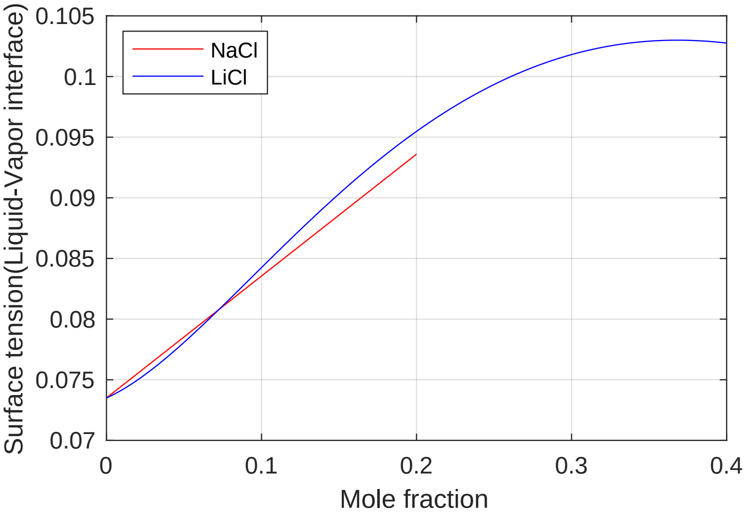


Figure S1: Plot shows the surface tension vs. mole fraction of dissolved solute. Empirical function for LiCl is from Conde et al.[1] and for NaCl is from Derluyn.[3] (Empirical relation directly available, no fitting was done here.)

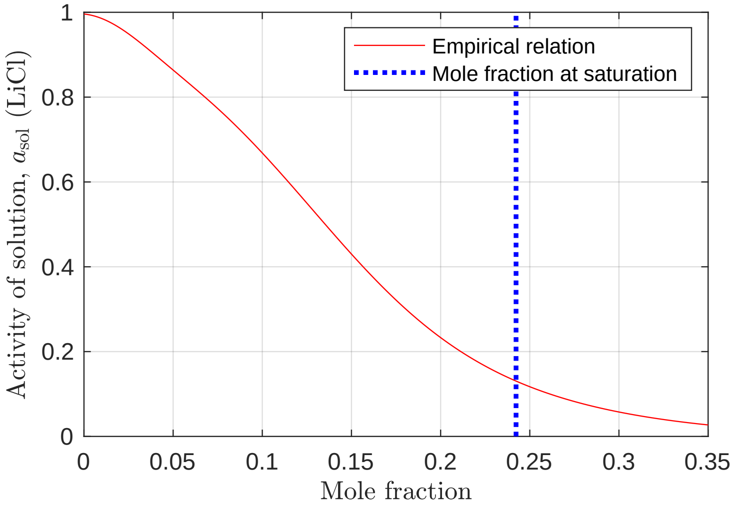


Figure S2: Plot shows the activity of the solution, a_{sol}, as function of dissolved mole fraction, x, of LiCl. Empirical relation is directly available from Conde et al.[1] (Empirical relation directly available, no fitting was done here.)

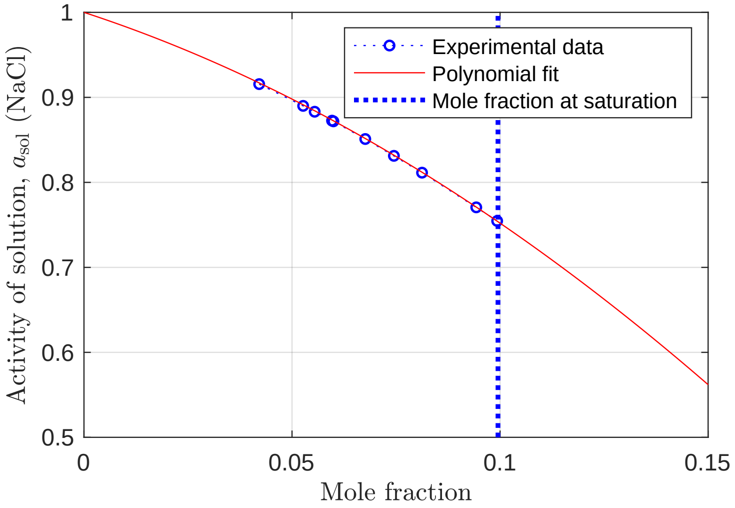


Figure S3: Plot shows the activity of the solution, a_{sol}, as function of dissolved mole fraction, x, of NaCl. Experimental data is from Olynyk et al.[4]

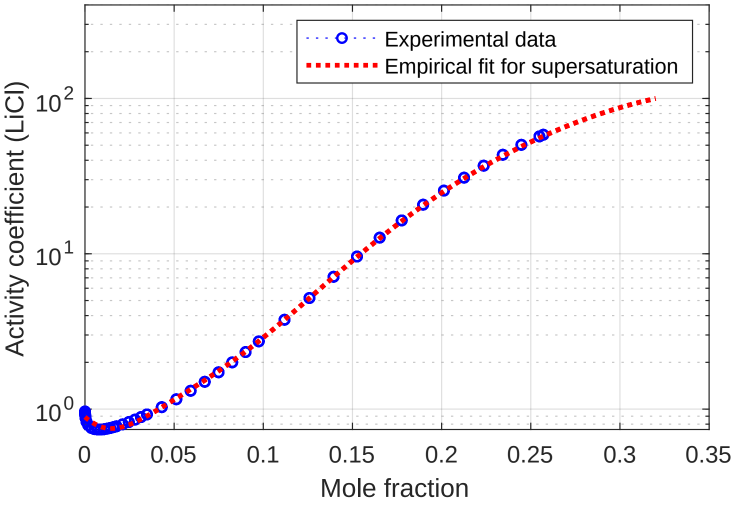


Figure S4: Plot shows the molal activity coefficient, ϱ, as function of dissolved mole fraction, x, of LiCl. Experimental data is from Hamer et al.[2]

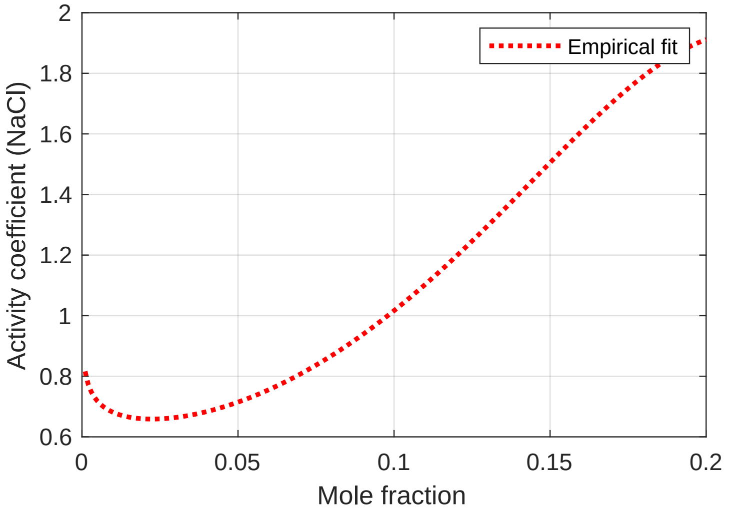


Figure S5: Plot shows the molal activity coefficient, ϱ, as function of dissolved mole fraction, x of NaCl, x. Empirical relation is from Steiger.[6]

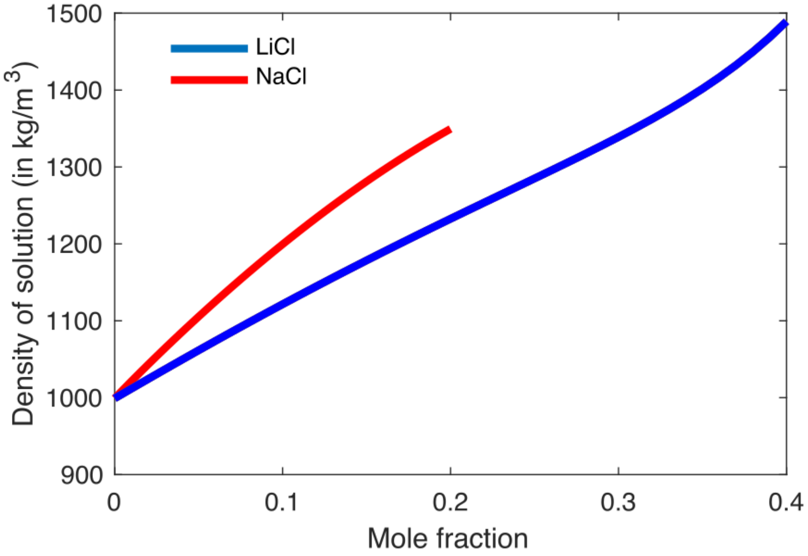


Figure S6: Plot shows the density of solution as a function of dissolved mole fraction of NaCl. Empirical relations are directly available from Conde et al.[1] for LiCl and Derluyn[3] for NaCl.

Derivation of critical radius from CNT

We consider here homogeneous salt crystallization in supersaturated solution in cylindrical pore as sketched in Figure 1(e). According to CNT, for homogeneous salt crystal nucleation in a supersaturated solution, there is a critical population of salt molecules that act as embryo for crystallization. The change in free energy,ΔG [J] for formation of a spherical crystal of radius r [m] can be derived by integrating the first law of thermodynamics for the thermodynamic potential, G, which includes two contributions, one due to the difference in chemical potential of solute between the solution and the crystal and another one associated with interfacial energy:

$$\Delta G = \frac{\frac{4}{3}\pi r^3}{v_{\mathrm{s}}^{\mathrm{c}}}(\mu_{\mathrm{s,r_p}}^{\mathrm{c}} - \mu_{\mathrm{s,r_p}}^{\mathrm{sol}}) + 4\pi r^2 \gamma_{\mathrm{cl}} \tag{S3}$$

where $v_{\mathrm{s}}^{\mathrm{c}}$ [m^3/mol] is the molar volume of salt crystal, γ_{cl} [N/m] is the surface tension at the interface of two phases (solution+crystal); $\mu_{\mathrm{s,r_p}}^{\mathrm{c}}$ [J/mol] is the chemical potential of solute crystal and $\mu_{\mathrm{s,r_p}}^{\mathrm{sol}}$ is the chemical potential of dissolved solute, in a capillary of radius, r_{p}.

The free energy, ΔG, passes through a maximum at $r = r_{\mathrm{c}}$, where r_{c} is the critical radius of nucleus which corresponds to maximum energy barrier needed to overcome for crystallization to happen in pores. Differentiating Equation S3 to find the maximum of $\Delta G(r_{\mathrm{c}})$ gives critical radius r_{c} in terms of chemical potential as

$$r_{\mathrm{c}} = \frac{-2\gamma_{\ell \mathrm{c}} v_{\mathrm{s}}^{\mathrm{c}}}{\mu_{\mathrm{s,r_p}}^{\mathrm{c}} - \mu_{\mathrm{s,r_p}}^{\mathrm{sol}}} \tag{S4}$$

We can obtain the change in molar chemical potential, both in dissolved phase and crystal phase, due to capillary stress, p_{cap} (defined later), by integrating isothermal Gibbs-Duhem equation,

$$(\mu_{\mathrm{s,r_p}}^{\mathrm{c}} - \mu_{\mathrm{s,r_p}}^{\mathrm{sol}}) = (\mu_{\mathrm{s}}^{\mathrm{c}} - \mu_{\mathrm{s}}^{\mathrm{sol}}) + p_{\mathrm{cap}}(v_{\mathrm{m,c}} - v_{\mathrm{m,l}}) \tag{S5}$$

where, $\mu_{\mathrm{s}}^{\mathrm{c}}$ and $\mu_{\mathrm{s}}^{\mathrm{sol}}$ are the chemical potential of crystal and dissolved solute in bulk solution, without any hydrostatic stress, and $v_{\mathrm{s}}^{\mathrm{sol}}$ is the molar volume of dissolved solute. Using saturated solution as reference where bulk crystal is in equilibrium with bulk solution with activity of dissolved solute given by α_{sat}, the difference in chemical potential, $\mu_{\mathrm{s}}^{\mathrm{c}} - \mu_{\mathrm{s}}^{\mathrm{sol}}$, can be written as:

$$\mu_{\mathrm{s}}^{\mathrm{c}} - \mu_{\mathrm{s}}^{\mathrm{sol}} = -RT \ln\left(\frac{\alpha_{\mathrm{th}}}{\alpha_{\mathrm{sat}}}\right) \tag{S6}$$

where α_{th} is the activity of dissolved solute for crystal nucleation in a pore of radius, r_{p}.

In Equation S6, $\alpha_{\mathrm{th}} = (\zeta(x_{\mathrm{c,th}})x_{\mathrm{c,th}})^{\nu}$ where $\zeta(x)$ is the activity coefficient associated with mole fraction as defined earlier, and $x_{\mathrm{c,th}}$ is the mole fraction of dissolved solute sufficient for crystallization, and $\alpha_{\mathrm{sat}} = (\zeta_{\mathrm{sat}} x_{\mathrm{sat}})^{\nu}$, where ζ_{sat} equals molar activity coefficient at saturation, x_{sat} is the mole fraction at saturation and ν is the number of ions per unit neutral salt (Here, for both NaCl and LiCl, $\nu = 2$). This formulation of activity is similar to the one used in the literature.[3,6] Hence, Equation S6 can be written as:

$$\mu_{\mathrm{s}}^{\mathrm{c}} - \mu_{\mathrm{s}}^{\mathrm{sol}} = -\nu RT \ln\left(\frac{\zeta(x_{\mathrm{c,th}})x_{\mathrm{c,th}}}{\zeta_{\mathrm{sat}}x_{\mathrm{sat}}}\right) \tag{S7}$$

In order to find the pressure of solution for a given imposed vapour pressure, the chemical equilibrium relates the chemical potential of water in solution and vapor, while mechanical equilibrium relates the pressure of solution due to imposed vapor pressure, accounting for the capillary pressure. This capillary pressure, accounting for difference in pressure at the liquid vapor meniscus is given by Young-Laplace:

$$p_{\mathrm{cap}} \approx -\frac{2\gamma_{\mathrm{sol}}\cos(\theta_{\mathrm{sol}})}{r_{\mathrm{p}}}, \tag{S8}$$

where γ_{sol} is the surface tension at the solution vapor interface. Since the solution is assumed to be under maximum tension prior to crystallization, we can assume $\theta_{\mathrm{sol}} \approx \theta_{\mathrm{rec}}$. Substituting Equation S5, S7 and S8 in Equation S4, we obtain the critical radius in terms of measurable and known parameters as:

$$r_{\mathrm{c}} = \frac{-2\gamma_{\ell\mathrm{c}}}{\left(\frac{v_{\mathrm{s}}^{\mathrm{sol}} - v_{\mathrm{s}}^{\mathrm{c}}}{v_{\mathrm{s}}^{\mathrm{c}}}\right)\frac{2\gamma_{\mathrm{sol}}\cos(\theta_{\mathrm{rec}})}{r_{\mathrm{p}}} - \frac{\nu RT}{v_{\mathrm{s}}^{\mathrm{c}}}\ln\frac{\zeta(x_{\mathrm{c,th}})x_{\mathrm{c,th}}}{\zeta_{\mathrm{sat}}x_{\mathrm{sat}}}} \tag{S9}$$

This critical radius should be less than or equal to the pore radius, r_{p}, for nucleation to happen inside the porous substrate because of steric effects. The empirical data on molar volume of solution, v_{sol}, is used to to find the molar volume of dissolved solute using the relation:

$$v_{\mathrm{s}}^{\mathrm{sol}} = \frac{v_{\mathrm{sol}}(x) - (1-x)v_{\mathrm{w}}^{\mathrm{liq}}}{x} \tag{S10}$$

where $v_{\mathrm{sol}}(x)$ is the molar volume of solution at concentration, x, and $v_{\mathrm{w}}^{\mathrm{liq}}$ is the molar volume of liquid water and is assumed to be independent of x.

We use the empirical relations for density of solutions, ρ_{sol} [kg/m^3], from Conde et al.[1]

for LiCl and Derluyn[3] for NaCl to calculate $v_{\text{sol}}(x)$ as follows:.

$$v_{\text{sol}} = \frac{x \times \text{mw}_{\text{salt}} + (1-x) \times \text{mw}_{\text{water}}}{\rho_{\text{sol}}} \tag{S11}$$

where mw_{salt} and mw_{water} are the molecular weight of salt and water in kg/mol respectively. Figure S7 is the plot of the coefficient of the first term of the denominator of Equation S9.

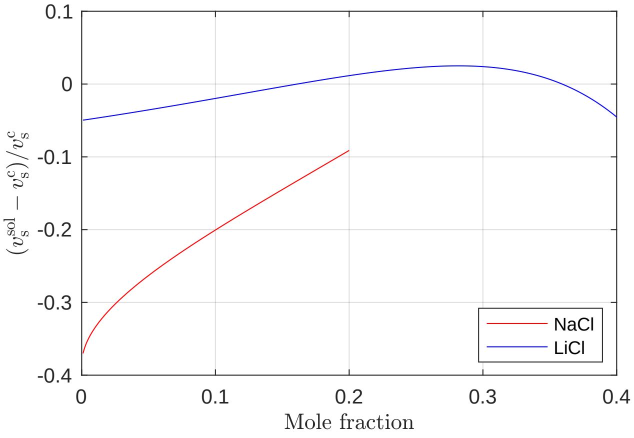


Figure S7: Normalized difference in molar volume of dissolved solute and crystal for NaCl and LiCl solution[1,5]

Effect of surface tension on predicted a_{at} and a_{dt}

Equation 18 (Main text) relates the evolution of a_{at} and a_{dt} as a function of concentration. It accounts for the variation in surface tension of solution with concentration relative to pure water. Here, we show the role played by surface tension by plotting Equation 14 with a simplifying assumption that $\gamma_{\text{sol}} \approx \gamma_{\text{w}}$, i.e,

$$a_{\text{at(dt)}} = a_{\text{s}} \times a_{\text{w,at(dt)}}. \tag{S12}$$

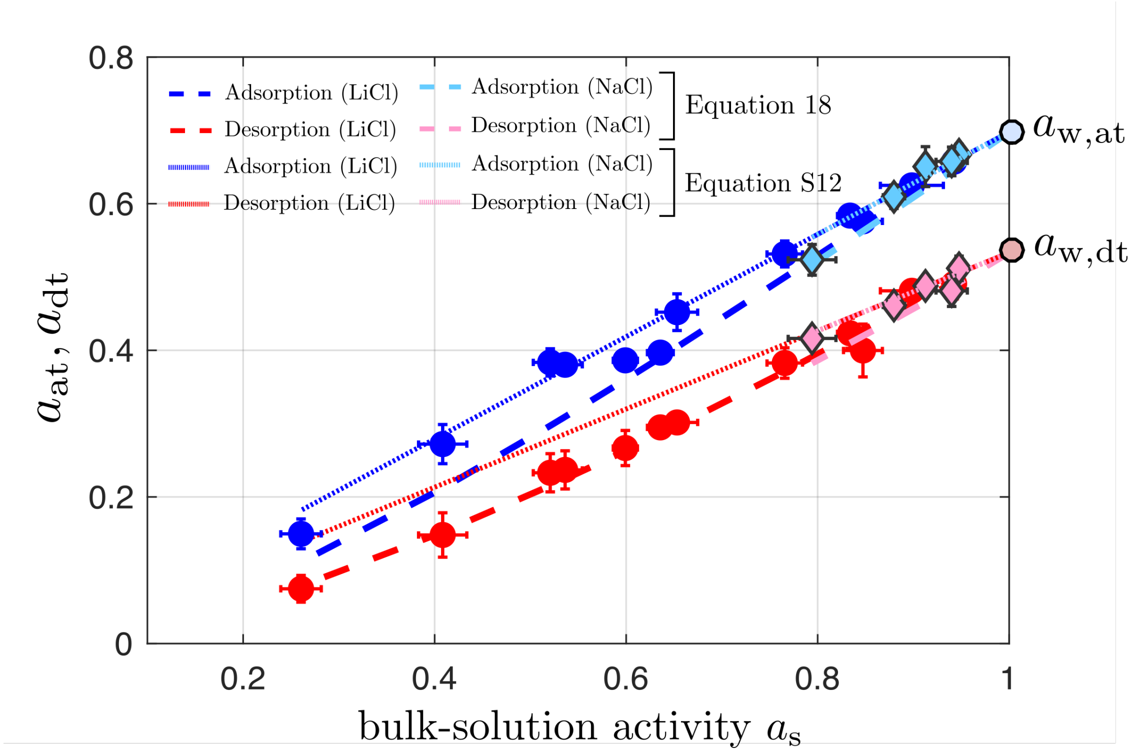


Figure S8: Adsorption-tension activity, a_{at} (completion of pore filling), and desorption-tension activity, a_{dt} (onset of pore emptying) from isotherms as in Figure 3 and 4 (Main text). Vapor activities for solution as predicted from Kelvin equation upon assuming concentration dependent surface-tension (Equation 14) and upon neglecting the effect of surface tension (Equation S12) are shown in dashed lines for LiCl and NaCl solutions. Experimental values of a_{at} and a_{dt} from isotherms as in Figures 3 and 4 (Main text) are shown for LiCl as solid circles (●, ●) and for NaCl as translucent diamonds (◆, ◆). Adsorption-tension activity and desorption-tension activity for pure water, i.e., $a_{\mathrm{w,at}}$ and $a_{\mathrm{w,dt}}$, as extracted from Figure 2 (Main text), are plotted as solid circles (●, ●). Error bars for a_{s}, a_{at} and a_{dt} represent the uncertainty in experimental values extracted from the isotherm (see Methods). In Equation 14, surface tension of solution as function of NaCl and LiCl concentration is reported in SI (Figure S1) and surface tension for pure water is taken to be 73.5 mN/m at 15°C.

Effect of contact angle and pore radius on theoretical supersaturation for crystallization

The effect of contact angle on theoretical supersaturation for the onset of crystallization, $x_{\mathrm{c,th}}/x_{\mathrm{sat}}$, found from the classical nucleation theory (Equation 21) is shown in Figure S9.

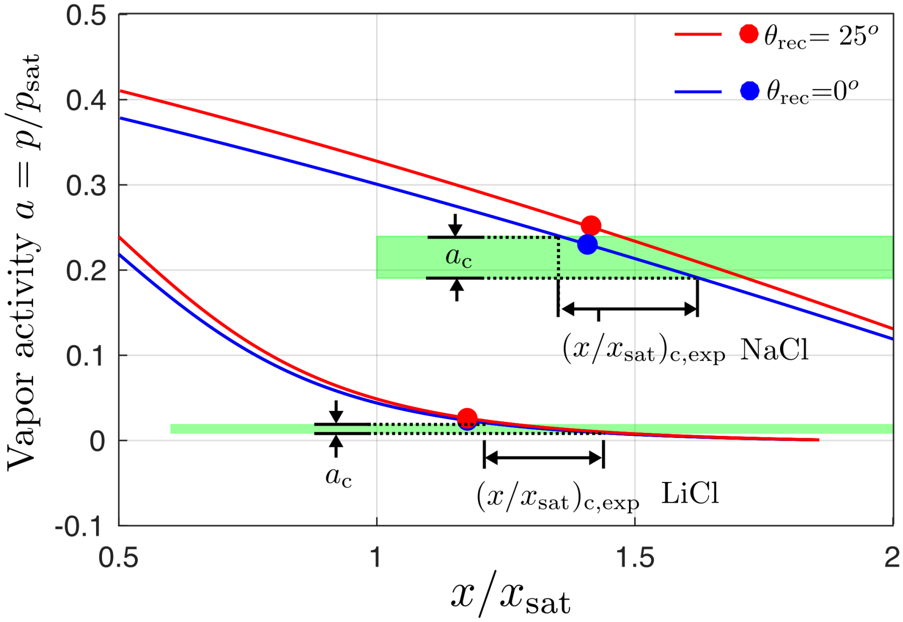


Figure S9: Difference in x/x_{sat} on assuming $\theta_{\mathrm{rec}} = 25°$ or $\theta_{\mathrm{rec}} = 0°$: The solid red and blue lines are the equilibrium vapor activity vs supersaturation for $r_{\mathrm{p}} = 1.4$ nm for NaCl and LiCl solutions as indicated. The blue dots are the values of theoretical supersaturation for the onset of crystallization, $x_{\mathrm{c,th}}/x_{\mathrm{sat}}$, found from the classical nucleation theory for $r_{\mathrm{c}} = r_{\mathrm{p}}$ (Equation 21) and correspond to $r_{\mathrm{p}} = 1.4$ nm assuming $\theta_{\mathrm{rec}} = 0°$ and $\theta_{\mathrm{rec}} = 25°$. The shaded green is the range of averaged experimental vapor activity, a_{c} (same as in Figure 6(a)). $(x/x_{\mathrm{sat}})_{\mathrm{c,exp}}$ is the supersaturation associated with a_{c} (obtained experimentally) for onset of crystallization.

We here describe the effect of pore size on supersaturations estimated from experiments. The effect of pore size on theoretical supersaturation for the onset of crystallization, $x_{\mathrm{c,th}}/x_{\mathrm{sat}}$, found from the classical nucleation theory (Equation 21) is shown in Figure S10 by comparing $r_{\mathrm{p}} = 1.2$ nm and 1.6 nm and $r_{\mathrm{p}} = 1.4$ nm (Figure 6, Main text). At $r_{\mathrm{p}} = 1.2$ nm, $x_{\mathrm{c,th}}/x_{\mathrm{sat}} = 1.492$ for NaCl and $x_{\mathrm{c,th}}/x_{\mathrm{sat}} = 1.199$ for LiCl, at $r_{\mathrm{p}} = 1.4$ nm, $x_{\mathrm{c,th}}/x_{\mathrm{sat}} = 1.408$ for NaCl and $x_{\mathrm{c,th}}/x_{\mathrm{sat}} = 1.176$ for LiCl, at $r_{\mathrm{p}} = 1.6$ nm, $x_{\mathrm{c,th}}/x_{\mathrm{sat}} = 1.349$ for NaCl and $x_{\mathrm{c,th}}/x_{\mathrm{sat}} = 1.151$

for LiCl and is plotted as blue dots in Figure S10 and Figure 6 (Main text). We obtain $(x/x_{\mathrm{sat}})_{\mathrm{c,exp}}$ assuming crystallization in pore of radius $r_{\mathrm{p}} = 1.2$ nm and $r_{\mathrm{p}} = 1.6$ nm in a similar manner as shown for $r_{\mathrm{p}} = 1.4$ nm in Figure S10. Corresponding to $r_{\mathrm{p}} = 1.2$ nm, $(x/x_{\mathrm{sat}})_{\mathrm{c,exp}} = 1.09 - 1.39$ for NaCl and $(x/x_{\mathrm{sat}})_{\mathrm{c,exp}} = 1.17 - 1.43$ for LiCl, at $r_{\mathrm{p}} = 1.4$ nm, $(x/x_{\mathrm{sat}})_{\mathrm{c,exp}} = 1.35 - 1.61$ for NaCl and $(x/x_{\mathrm{sat}})_{\mathrm{c,exp}} = 1.22 - 1.47$ for LiCl, and at $r_{\mathrm{p}} = 1.6$ nm, $(x/x_{\mathrm{sat}})_{\mathrm{c,exp}} = 1.51 - 1.73$ for NaCl and $(x/x_{\mathrm{sat}})_{\mathrm{c,exp}} = 1.26 - 1.50$ for LiCl.

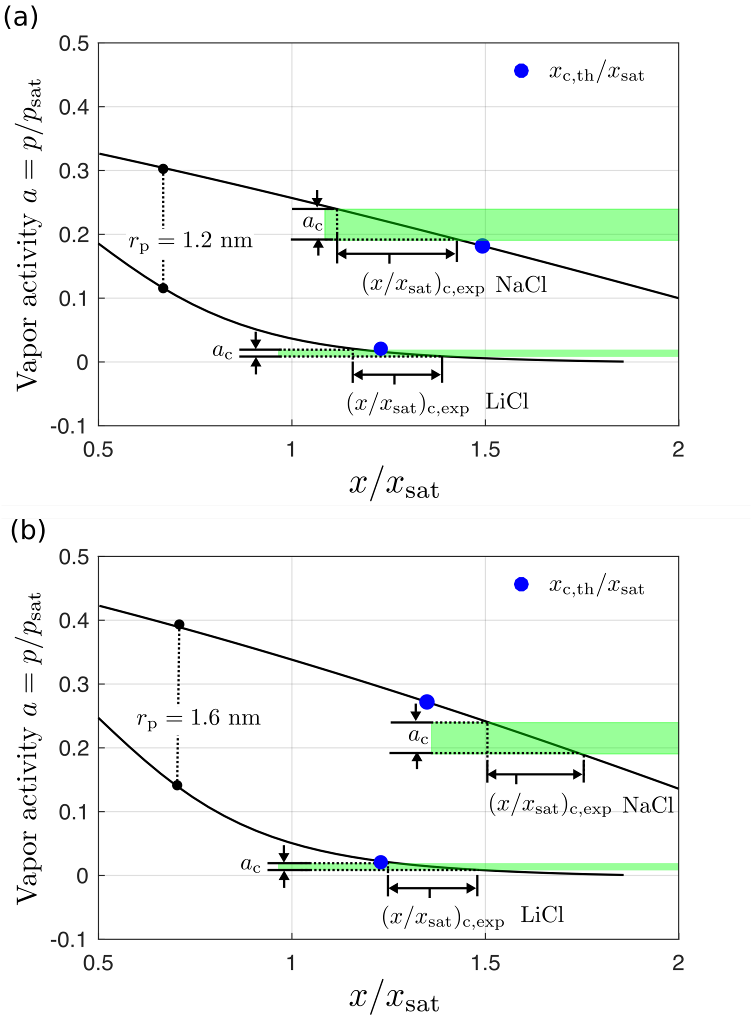
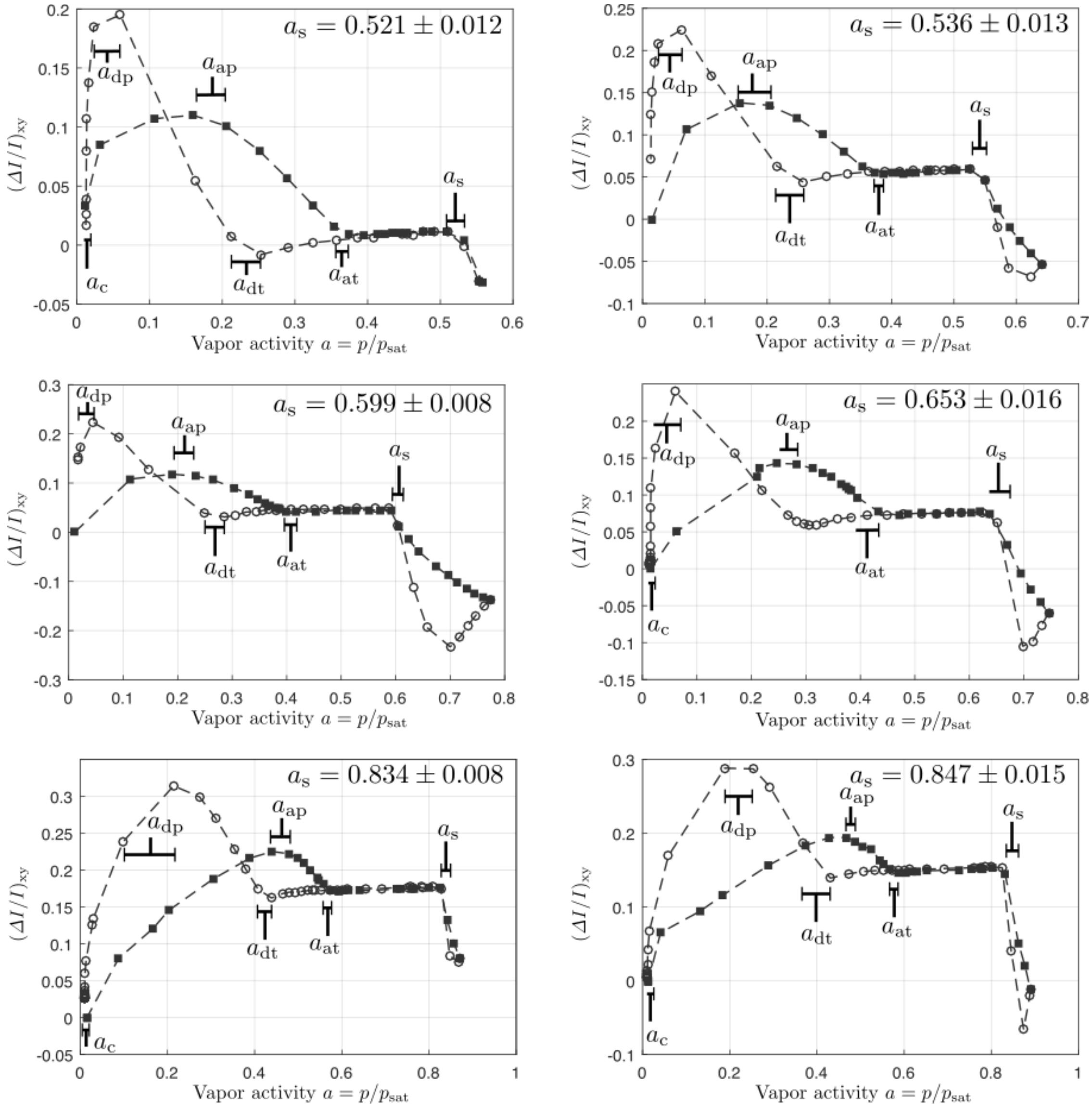
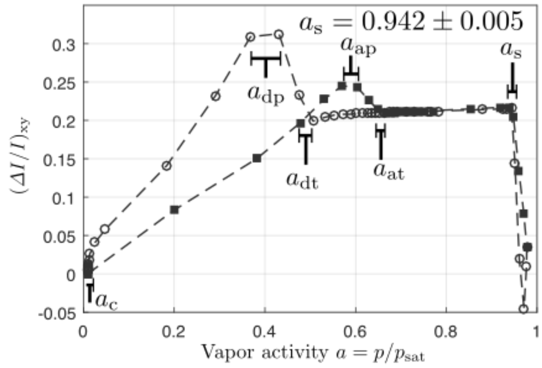


Figure S10: Difference in x/x_{sat} on assuming (a) $r_{\mathrm{p}} = 1.2$ nm and (b) $r_{\mathrm{p}} = 1.6$ nm: The solid black line are the equilibrium vapor activity vs supersaturation for NaCl and LiCl solutions as indicated. The blue dots are the values of theoretical supersaturation for the onset of crystallization, $x_{\mathrm{c,th}}/x_{\mathrm{sat}}$, found from the classical nucleation theory for $r_{\mathrm{c}} = r_{\mathrm{p}}$ (Equation 17, 18) and correspond to $r_{\mathrm{p}} = 1.2$ and 1.6 nm assuming $\theta_{\mathrm{rec}} = 0°$. The shaded green is the range of averaged experimental vapor activity, a_{c} (same as in Figure 6(a)). $(x/x_{\mathrm{sat}})_{\mathrm{c,exp}}$ is the supersaturation associated with a_{c} (obtained experimentally) for onset of crystallization.





a_s	x_s
0.260 ± 0.016	$0.1855 - 0.1980$
0.408 ± 0.020	$0.1492 - 0.1603$
0.521 ± 0.012	$0.1274 - 0.1347$
0.536 ± 0.013	$0.1241 - 0.1315$
0.599 ± 0.008	$0.1122 - 0.1175$
0.635 ± 0.008	$0.1042 - 0.1100$
0.653 ± 0.016	$0.0986 - 0.1080$
0.765 ± 0.014	$0.0721 - 0.0816$
0.834 ± 0.008	$0.0548 - 0.0622$
0.847 ± 0.015	$0.0489 - 0.0604$
0.898 ± 0.028	$0.0306 - 0.0495$
0.942 ± 0.005	$0.0238 - 0.0304$

Figure S11: Some reflectance isotherms for LiCl solutions with bulk-solution activity, a_s, and corresponding mole fraction, x_s, as indicated in legend. Closed squares and open circles represent adsorption branch and desorption branch respectively.

References

(1) Conde, M. R. Properties of aqueous solutions of lithium and calcium chlorides: Formulations for use in air conditioning equipment design. *International Journal of Thermal Sciences* **2004**, *43*, 367–382.

(2) Hamer, W. J.; Wu, Y. Osmotic Coefficients and Mean Activity Coefficients of Uni-univalent Electrolytes in Water at 25 degrees Celsius. *Journal of Physical and Chemical Reference Data* **1972**, *1*, 1047–1100.

(3) Derluyn, H. Salt transport and crystallization in porous limestone: neutron-X-ray imaging and poromechanical modeling. **2012**, 248.

(4) Olynyk, P.; Gordon, A. R. The Vapor Pressure of Aqueous Solutions of Sodium Chloride at 20, 25 and 30° for Concentrations from 2 Molal to Saturation. *Journal of the American Chemical Society* **1943**, *65*, 224–226.

(5) Potter, R.; Brown, D. L. The volumetric properties of aqueous sodium chloride solution from 0° to 500°C at pressures up to 2000 bars based on a regression of available data in the literature. *Geological Survey Bulletin* **1977**, *5*, C1–C36.

(6) Steiger, M. Crystal growth in porous materials - I: The crystallization pressure of large crystals. *Journal of Crystal Growth* **2005**, *282*, 455–469.