

## Supplementary Material

Given the brevity of the original HG14 paper, herein we present a detailed derivation of the intermolecular contribution to the equilibrium vapor pressure over a curved brine surface,  $\frac{p_\zeta}{p_r}$  in Eq. (8).

Consider the limiting cases of the solvating particle system as presented in the main text's Fig. 1: (1) a charged spherical particle covered by a thick brine layer in contact with the solute's vapor and (2) a charged spherical particle covered by a thin brine layer in contact with the solute's vapor (Fig. S1). As the solid core disappears, the thickness of the brine layer  $l$  approaches  $R_{\text{DRH}}$ , and the strength of interfacial potential also vanishes. Thus the equilibrium vapor pressure for system (1) is that of a solution-only droplet,  $p_r$ . Conversely if  $l$  is small, the strength of the intermolecular forces might compete with the water activity and/or the curvature effect and thus contribute significantly to the free energy of the system. The equilibrium vapor pressure over system (2) is  $p_\zeta$ .

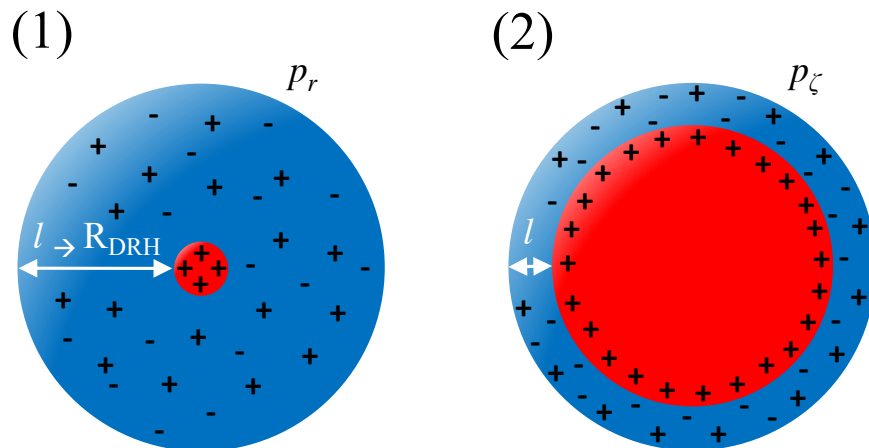


Figure S1: Limiting cases of the solvating particle system as described in the text.

In both cases the Gibbs free energy per unit area of the system  $G$  is given by the sum of contributions of the individual components,

$$G(T, p, N_{liq}, N_v) = \mu_{liq}(T, p)N_{liq} + g_{mix}(T)N_{liq} + \mu_v(T, p)N_v + \zeta(l), \quad (\text{S1})$$

where  $\mu_{liq}$  and  $\mu_v$  correspond to the chemical potentials per mole of the liquid (*liq*) and vapor (*v*), respectively, and  $N_{liq}$  and  $N_v$  are the number of moles per unit area in the liquid and vapor phases. The energy of ideal mixing is given by  $g_{mix}(T)N_{liq}$ , and the interfacial free energy per unit area resulting from the intermolecular interactions in the system is  $\zeta(l)$ . The exchange of molecules at the solution – vapor interface sets a condition for thermodynamic equilibrium,

$$\frac{\partial G}{\partial N_{liq}} = \frac{\partial G}{\partial N_v}. \quad (\text{S2})$$

Thus in the limit of system (1) when  $\zeta(l) \rightarrow 0$ ,

$$\mu_{liq}^r(T, p) + g_{mix}(T) = \mu_v^r(T, p). \quad (\text{S3})$$

Alternatively, in the limit of system (2)

$$\mu_{liq}^\zeta(T, p) + g_{mix}(T) + \zeta'(l)v_{sol} = \mu_v^\zeta(T, p), \quad (\text{S4})$$

where in the case of a liquid solution the equivalency  $N_{liq} = \rho_{sol}l$  is exploited and the interfacial term emerges from differentiating using the chain rule, such that

$$\frac{\partial G}{\partial N_{liq}} = \frac{\partial G}{\partial(\rho_{sol}l)} = \frac{1}{\rho_{sol}} \frac{\partial G}{\partial l} \quad (\text{S5})$$

and knowing  $\rho_{sol} = 1/v_{sol}$ . Given that  $\mu_{liq}^\zeta = \mu_{liq}^r$ , the difference between Eq. (S3) and Eq. (S4) becomes,

$$\mu_v^\zeta - \mu_v^r = v_{sol}\zeta'(l). \quad (\text{S6})$$

Alternatively, using the ideal gas law  $\mu_v^r$  and  $\mu_v^\zeta$  can be expressed as a departure from a

reference chemical potential  $\mu_\theta$ ,

$$\mu_v^r = \mu_\theta + R_g T \ln(p_r), \quad (\text{S7})$$

and,

$$\mu_v^\zeta = \mu_\theta + R_g T \ln(p_\zeta). \quad (\text{S8})$$

Replacing the reference chemical potential,  $\mu_\theta$ , from (S8) with  $\mu_\theta = \mu_v^r - R_g T \ln(p_r)$  from (S7) yields,

$$\mu_v^\zeta = \mu_v^r - R_g T \ln(p_r) + R_g T \ln(p_\zeta), \quad (\text{S9})$$

$$\mu_v^\zeta = \mu_v^r + R_g T \ln\left(\frac{p_\zeta}{p_r}\right). \quad (\text{S10})$$

By making  $\frac{p_\zeta}{p_r}$  the subject,

$$\frac{p_\zeta}{p_r} = e^{\frac{\mu_v^\zeta - \mu_v^r}{R_g T}}. \quad (\text{S11})$$

Knowing from Eq. (S6) that  $v_{sol}\zeta'(l)$  is the change in chemical potential resulting from the addition of intermolecular forces, Eq. (S11) can straightforwardly be rewritten as,

$$\boxed{\frac{p_\zeta}{p_r} = e^{\frac{v_{sol}\zeta'(l)}{R_g T}}}. \quad (\text{S12})$$

This expression is presented in the main text as the interfacial contribution to Eq. (10).

The interfacial term  $\zeta(l)$  that accounts for both dispersive and electrostatic interactions, which individually contribute to the stability of the pre-deliqescence layer comes from DLVO theory. The independent interaction terms are presented in the main text, while here the effects of these two interaction terms are illustrated in Fig. S2 and Fig. S3.

On the coarse scale of Fig. S2, the electrostatic and dispersive terms appear to overlap. Both contribute to the hygroscopic growth of the particle at its earliest onset, which suggests that intermolecular forces influence the stability of the first layers of water molecules condensing on the particle. A closer view of this growth near DRH (Fig. S3) shows that

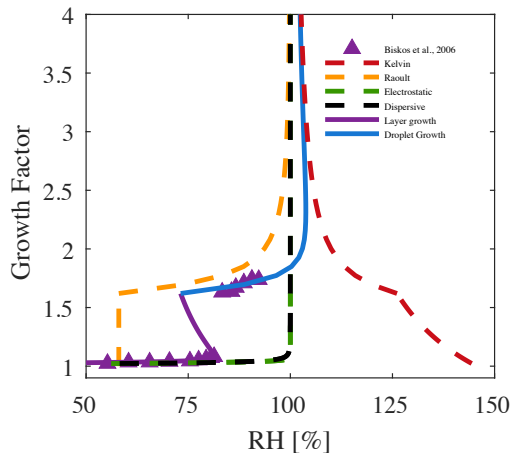


Figure S2: Figure 4 from the main text reproduced with the intermolecular term decomposed into its electrostatic (green) and dispersive (black) contributions. The curves are plotted using  $q_s = 0.4 \text{ C m}^{-2}$ ,  $A_h = -2.5 \times 10^{-20}$ , and  $C = 7620 \text{ mol m}^{-3}$

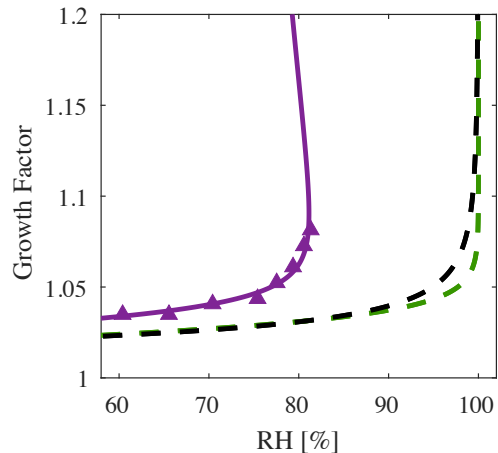


Figure S3: A zoomed-in view of the contribution of the intermolecular interaction terms near DRH. Differences between the electrostatic and the dispersive terms can be observed.

the electrostatic and the dispersive terms have distinct effects on the layer growth. For the values of surface charge ( $q_s$ ) and Hamaker constant ( $A_h$ ) used here, the dispersive term has a stronger effect at high growth factors (1.05 - 1.1). Below 1.05 both terms seem to similarly enhance the condensation of water, and above 1.1 the intermolecular forces can be neglected and both terms converge to  $RH = 100\%$ . Similar data fitting to that which is done in the main manuscript can be done using only the electrostatic or the dispersive contribution, but in these cases the fitted values of surface charge and/or Hamaker constant become more physically unrealistic. The use of both contributions, as presented in the context of DLVO theory, as we do here, yields the highest quality data fits and most physically realistic fitting parameters.