Supplementary Information

Thermodynamics of Hydrogel for Applications to Atmospheric Water Harvesting, Evaporation, and Desalination

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Flory Theory. Flory¹² developed a lattice model and arrived at expression for the entropy of mixing between a solvent and a polymer that is different from Gibbs' entropy of mixing expression. For a solution of n_1 molecules of the solvent and n_2 molecules of the polymer, the increase in entropy due to mixing is

$$\Delta S = -k_B (n_1 ln f_1 + n_2 ln f_2) \tag{S1}$$

where Δ means final minus initial values and $k_{\rm B}$ is the Boltzmann constant, and f the volume fraction of the solvent and the polymer, which can be expressed as

$$f_1 = \frac{n_1}{n_1 + Zn_2}, \qquad f_2 = \frac{Zn_2}{n_1 + Zn_2}$$
 (S2)

with Z denoting the volume ratio of the polymer molecule to the solvent molecule. Equation (S1) can also be derived from the free-volume concept.¹³ Its main difference from the classical Gibbs entropy of mixing expression is that the volume fraction is used instead of the mole fraction. Equation (S1) degenerates into the Gibbs expression if Z=1.

In addition to the entropy of mixing, the mixing of the solvent with the polymer also causes a change in the enthalpy, which can be expressed as

$$\Delta H = k_B T \chi n_1 f_2 \tag{S3}$$

where χ is a parameter depending on the solvent and the polymer. χ >0 means the mixing is endothermic and χ <0 exothermic. Most polymer-solvent mixing has χ >0. We note here that although Eq.(S3) is called the enthalpy change, no pressure effect was considered in the derivation of the above expression. Inside hydrogels, the pressure is usually much higher than the ambient pressure. This pressure effect is not included in Eq. (S3).

For a polymer, Flory's¹⁰ analysis of experimental data showed that the elasticity arises from the polymer configurational entropy change during stretching, for which Flory and Rehner¹⁴ derived the following expression

$$\Delta S = -\frac{k_B v_e}{2} \left[a_x^2 + a_y^2 + a_z^2 - 3 - \ln(a_x a_y a_z) \right]$$
(S4)

where a_x (y&z) is the stretching ratio in the direction represented by the subscript and v_e is the effective number of crosslinked units that excludes the two free ends of a polymer chain. v_e is related to the actual cross-linking units v and the number of molecules n_2 through

$$\nu_e = \nu - 2n_2 = \nu(1 - 2n_2/\nu) = \nu(1 - 2M_c/M)$$
(S5)

where M_c and M are the molecular weight of a crosslinked segment and that of the polymer molecular before crosslinking, respectively. Combining Eqs.(S1), (S3), and (S4), the total change in the Gibbs free energy for isotropic swelling is Eq. (1).

Helmholtz Free Energy of Combined System: From Eq.(6), we can express the derivative of the Helmholtz free energy of the hydrogel subsystem as

$$dF = \left[\left(\frac{\partial (\Delta F_{mix})}{\partial V} \right)_{T,\varphi,n_{j}} + \left(\frac{\partial (\Delta F_{pl})}{\partial V} \right)_{T,\varphi,n_{j}} - p \right] dV + \left[\left(\frac{\partial (\Delta F_{mix})}{\partial T} \right)_{V,\varphi,n_{i}} + \left(\frac{\partial (\Delta F_{pl})}{\partial T} \right)_{T,\varphi,n_{i}} - S_{c} \right] dT + \mu_{sl} dn_{sl} + \mu_{pl} dn_{pl} + \sum_{i} \mu_{i} dn_{i} + \sum_{i} ez_{i} n_{i} d\varphi + ez_{pl} n_{pl} d\varphi$$
(S6)

Similarly, the Helmholtz free energy of the external solution can be written as

$$dF_{e} = \left[\left(\frac{\partial (\Delta F_{mix})}{\partial V} \right)_{T,\varphi,n_{i}} - p \right]_{e} dV_{e} + \left[\left(\frac{\partial (\Delta F_{mix})}{\partial T} \right)_{V,\varphi,n_{i}} - S_{c} \right]_{e} dT + \mu_{sl,e} dn_{sl,e} + \left(\sum_{i} \mu_{i} dn_{i} \right)_{e} + \left(\sum_{i} ez_{i} n_{i} d\varphi \right)_{e}$$
(S7)

where we use subscript "e" to denote the external solution. We consider the case of constant temperature, and note that dV=- dV_o , dn_i =- $dn_{i,o}$, and dn_{si} =- $dn_{sl,o}$, and dn_{pl} =0. Thus, the total Helmholtz free energy of the combined system can be written as Eq. (7).

Latent Heat of Evaporation. We consider hydrogel is at equilibrium with saturated water vapor outside at pressure p_s . Inside hydrogel, water is at different pressure p. Using Eq. (23), we can write the water molar entropy as

$$s_{w}(T,p) = -\left(\frac{\partial \mu_{w}}{\partial T}\right)_{p,n_{i}}$$

= $s_{w}^{*}(T,p) - R\left[ln(1-f_{2,eq}) + f_{2,eq} + \chi f_{2,eq}^{2}\right] - RTf_{2,eq}^{2}\frac{\partial \chi}{\partial T}$ (S8)

where $s_w^*(T, p)$ is the entropy of pure water at pressure T and p. The $\frac{\partial \chi}{\partial T}$ term arises because entropy caused by molecular configuration change around the contacting region between water and polymer molecules is also included in Eq.(S3). In an ideal mixing model,¹⁰ this term cancels the χf_2^2 term in the square brackets so that only mixing of entropy term is left. The latent heat of evaporation is

$$L = h_{w,v}^{*}(T, p_{s}) - h_{w}(T, p) = T [s_{w,v}^{*}(T, p_{s}) - s_{w}(T, p)]$$

= $L_{o} + RT [ln(1 - f_{2,eq}) + f_{2,eq} + \chi f_{2,eq}^{2}] + RT^{2} f_{2,eq}^{2} \frac{\partial \chi}{\partial T}$ (S9)

where additional subscript "v" is used to represent the vapor phase, and $L_o = h_{w,v}^*(T, p_s) - h_w^*(T, p_s)$ is latent heat of evaporation of pure water at temperature T and p_s. In deriving the above expression, we took $s_w^*(T, p_s) - s_w^*(T, p) = 0$, which can be justified by the Maxwell relationship $(\partial s^*/\partial p)_T = -(\partial v^*/\partial T)_p$ by neglecting the thermal expansion of pure water.

Freezing Point Depression and Boiling Point Elevation. First, let's examine the melting point depression. We assume pure ice is formed inside the hydrogel, whose chemical potential can be written as

$$d\mu_{ice} = v_{ice}dp - s_{ice}dT + RTdln(a_{ice}) = v_{ice}dp - s_{ice}dT$$
(S10)

From Eq.(23), the change in the chemical potential of water can be written as

$$d\mu_w = v_w^* dp - s_w^* dT + RTd[ln(1 - f_2) + f_2 + \chi f_2^2]$$
(S11)

Note T in the last term on the right-hand side is outside the differentiation as the derivative is taken with (p,T) kept constant by definition. At the freezing equilibrium, we have

$$v_{ice}dp - s_{ice}dT_{fz} = v_w^*dp - s_w^*dT_{fz} + \mathsf{R}T_{fz}\mathsf{d}[ln(1-f_2) + f_2 + \chi f_2^2]$$
(S12)

where T_{fz} represents the freezing point. For typical mixture analysis, the pressure does not change. However, in hydrogels, as f_2 increases from 0 (at which it is normal ice-water at the ambient pressure) to a finite value, the pressure inside the hydrogel increases. If we assume that ice forms inside hydrogel and experience same pressure as water, we should include the pressure change as f_2 increases. With the above argument, we get

$$(s_w^* - s_{ice})dT_{fz} = \mathsf{R}T_{fz}\mathsf{d}[ln(1 - f_2) + f_2 + \chi f_2^2] + (v_w^* - v_{ice})dp$$
(S13)

Replacing $(s_w^* - s_{ice})$ on the left hand side by L_m/T_{fz} , where L_m is the latent heat of melting. We can also approximate $v_w^* \approx v_{ice}$ and neglect the last term. This approximation allows integration of Eq. (S12), leading to Eq. (26). At the boiling point, the chemical potential equals the pure vapor chemical potential. We can follow similar steps as in the freezing point depression, replacing "ice" subscript in Eq. (S13) by "v" for vapor. We consider the boiling happens on surface of hydrogel so that the outside vapor phase is at a constant pressure while the liquid phase pressure inside the hydrogel depends on f_2 . Equation (S13) becomes

$$-[s_{w,v}(T_{bp}, p_v) - s_w^*(T_{bp}, p)]dT_{bp} + v_{w,v}dp_v = \mathsf{R}T_{bp}\mathsf{d}[ln(1 - f_2) + f_2 + \chi f_2^2] + v_w^*dp \quad (S14)$$

where T_{bp} is the boiling point. The outside vapor pressure p_v does not change during measurement. The first term again can be related to latent heat of evaporation (the entropy dependence on pressure for water is small). Using Eq. (13) for pressure change, we can write the above equation into

$$-\left[L_o/R + KT_{bp}\left(f_2^{1/3} - \frac{f_2}{2}\right)\right]\frac{dT_{bp}}{T_{bp}^2} = d\left[ln(1 - f_{2,eq}) + f_{2,eq} + \chi f_{2,eq}^2\right] + K d\left(f_2^{1/3} - \frac{f_2}{2}\right)$$
(S15)

The second term inside the square bracket on the left-hand side arises from temperature dependence of pressure in Eq.(13), but its value is small relative to the latent heat of evaporation as we discussed. We can neglect this term and arrive at Eq. (27).

Salt Content Inside Hydrogel in Equilibrium with Salty Water Outside. Adding up Eqs. (30) and (31) and using charge neutrality $x_{Na+} = x_{Cl-}$, we get

$$\mu_{NaCl} = \mu_{NaCl}^{o} + v_{NaCl}(p - p_o) + 2RT[ln(1 - f_2) + f_2 + \chi f_2^2] + RTln(\gamma_{NaCl} x_{NaCl})^2$$
(S16)

where $\gamma_{NaCl} = \sqrt{\gamma_{Na+}\gamma_{Cl-}}$ is the activity coefficient of NaCl, and $v_{NaCl} = v_{Na+} + v_{Cl-}$ is the molar volume of NaCl. For water and ions outside hydrogel, we have

$$\mu_{w,e} = \mu_w^o + RT ln(\gamma_w x_w)_e \tag{S17}$$

$$\mu_{Na+,e} = \mu_{Na+}^o + RT ln(\gamma_{Na+} x_{Na+})_e$$
(S18)

$$\mu_{Cl-,e} = \mu_{Cl-}^{o} + RT ln(\gamma_{Cl-} x_{Cl-})_e$$
(S19)

$$\mu_{NaCl,e} = \mu_{NaCl}^o + RTln[(\gamma_{NaCl}x_{NaCl})^2]_e$$
(S20)

From Eqs. (S16) and (S20), we get Eq. (32). From Eq.(S17) and Eq. (23), we get Eq. (33).

Also, in this case, a membrane potential might exist. To show this possibility, we start with the chemical potential balance of individual ion species:

$$v_{Na+}(p-p_o) + F\varphi + RT[ln(1-f_2) + f_2 + \chi f_2^2 + ln(\gamma_{Na+}x_{Na+})] = RTln(\gamma_{Na+}x_{Na+})_e$$
(S21)
$$v_{Cl-}(p-p_o) - F\varphi + RT[ln(1-f_2) + f_2 + \chi f_2^2 + ln(\gamma_{Cl-}x_{Cl-})] = RTln(\gamma_{Cl-}x_{Cl-})_e$$
(S22)

If the activity coefficients of the ions are equal, subtracting the above two equations leads to Eq. (34).

Solubility of Salts inside Hydrogel. From Eq. (S16), we have the chemical potential of NaCl in the solution as

$$d\mu_{NaCl} = d\mu_{NaCl}^{*}(p,T) + RTd\{ln(\gamma x_{NaCl,l})^{2}\} + 2RTd\{[ln(1-f_{2}) + f_{2} + \chi f_{2}^{2}]\}$$
(S23)

when salt in solution is at equilibrium with solid salt, we have

$$d\mu_{NaCl,s}^{*}(p,T) = d\mu_{NaCl}^{*}(p,T) + RTd\{ln(\gamma x_{NaCl,l})^{2}\} + 2RTd\{[ln(1-f_{2}) + f_{2} + \chi f_{2}^{2}]\}(S24)$$

where $\mu_{NaCl,s}^*(p,T)$ is the chemical potential of pure solid salt. At the melting point (T_m=801 °C for NaCl), pure NaCl solid and liquid are at equilibrium with x_{NaCl}=1 and f₂=0. The chemical potentials of pure substance can be similarly expressed by entropy as in Eqs. (S10) and (S11), and an equation like Eq. (S13) can be integrated for temperature to change from T_m to T, x_{NaCl} from 1 to its solubility in water, and f₂ from 0 to a given value. Since the temperature range is large, the entropy change with temperature for both the solid and liquid phase may need to be included. Instead of direct integration of Eq. (S24), it is easier to use the Gibbs-Helmholtz

$$\left(\frac{\partial(\mu_i/T)}{\partial T}\right)_p = -\frac{h_i}{T^2} \tag{S25}$$

and write down the chemical potential change for pure NaCl in liquid and solid phase as

$$\frac{\mu_{NaCl,s}^{*}(T,p)}{T} - \frac{\mu_{NaCl,s}^{*}(T_{m},p)}{T_{m}} = H_{s}(T_{m},p)\left(\frac{1}{T} - \frac{1}{T_{m}}\right) - \int_{T_{m}}^{T} \left[\frac{1}{T^{2}}\int_{T_{m}}^{T} c_{p,sd}dT\right]dT$$
(S26)

$$\frac{\mu_{NaCl}^{*}(T,p)}{T} - \frac{\mu_{NaCl}^{*}(T_m,p)}{T_m} = H_l(T_m,p)\left(\frac{1}{T} - \frac{1}{T_m}\right) - \int_{T_m}^T \left[\frac{1}{T^2}\int_{T_m}^T c_{p,lq}dT\right]dT$$
(S27)

The above relation leads to

$$\mu_{s}^{*}(T,p) - \mu_{l}^{*}(T,p) = -L_{sl}\left(1 - \frac{T}{T_{m}}\right) + T\int_{T_{m}}^{T}\left[\frac{1}{T^{2}}\int_{T_{m}}^{T}\left(c_{p,l} - c_{p,s}\right)dT\right]dT$$
(S28)

where L_m is the latent heat of the solid-liquid phase transition at T_m and p. We will neglect the specific heat term, as is often done in literature. This can be justified because the specific heat difference between liquid and solid NaCl is ~50 J/kg-K,⁶⁵ while the latent heat is 1460 kJ/kg. In this case, setting the chemical of the solid and liquid phases equaling each other, and using Eq. (S28), we get Eq. (36).

Polyelectrolyte Hydrogel in Equilibrium with Salty Water. Balancing the chemical potential for each mobile species, we arrive at

$$K\left[f_2^{1/3} - \frac{f_2}{2}\right] + \left[ln(1 - f_2) + f_2 + \chi f_2^2 + ln(\gamma_w x_w)\right] = ln(\gamma_w x_w)_e$$
(S29)

$$K_{Na+}\left[f_2^{1/3} - \frac{f_2}{2}\right] + \frac{F\varphi}{RT} + \left[ln(1 - f_2) + f_2 + \chi f_2^2 + ln\gamma_{Na+}x_{Na+}\right] = ln(\gamma_{Na+}x_{Na+})_e$$
(S30)

$$K_{Cl-}\left[f_2^{1/3} - \frac{f_2}{2}\right] - \frac{F\varphi}{RT} + \left[ln(1 - f_2) + f_2 + \chi f_2^2 + ln\gamma_{Cl-}x_{Cl-}\right] = ln(\gamma_{Cl-}x_{Cl-})_e$$
(S31)

with the condition

$$x_{Na+} + x_{Cl-} + x_w = 1 \tag{S32}$$

Solving Eqs.(S29)-(S32) will give us the equilibrium volume fraction f_2 , concentrations of Na⁺ and Cl⁻ ions and water, and the Donnan potential φ . Examples of the solution are given in Fig.9.

Reference

⁶⁵ C.-J. Li, P.W. Li, K. Wang, E.E. Molina, AIMS Energy, 2014, 2, 133-157.