Competitive Isotherm Prediction under Polanyi-Based Modeling Assumptions

Shown herein are equations for predicting the adsorbed-phase concentrations of two competing adsorbates in a water/sorbent system. These equations allow the prediction of the complete competitive adsorption isotherm for a sorbate of primary interest ("solute 1"), at any given known initial concentration of co-solute ("solute "2"), and for any given values of sorbent mass and water volume. It is assumed that the Polanyi-Manes modeling approaches described in our previous publication (*5*) apply, that single-solute isotherm parameters for both solutes have been previously determined on the same sorbent, and that non-sorption "losses" of sorbate 2 are proportional to final liquid concentration, with a known coefficient of proportionality (previously determined from blank samples). The equations shown here apply under the six conceptual assumptions cited above Equation (4) in the main text -- *i.e.*, the "uniform adsorbate" assumptions of Greenbank and Manes (*36*) and, for solid-liquid systems, the "immiscible model" assumptions of Greenbank and Manes (*37*).

The predictive modeling equations under the above assumptions are given below. (Minor modifications for some alternative assumptions for liquid-solid systems are given in the main text.)

$$C_1^b = z_1 C_1^s \tag{S-1}$$

$$C_2^b = z_2 C_2^s \tag{S-2}$$

$$z_1 + z_2 = 1 \tag{S-3}$$

$$q_T^{b\,\prime} = \frac{q_1^{s\,\prime}}{\eta_{p,1}} = \frac{q_2^{s\,\prime}}{\eta_{p,2}} = Q_o \times 10^{\left[a_i{}^{\prime}\left(\frac{\varepsilon_{sw,i}^s}{V_{s,i}}\right)^{b_i{}^{\prime}}\right]} \tag{S-4}$$

$$q_T^{b\,\prime} = q_1^{b\,\prime} + q_2^{b\,\prime} \tag{S-5}$$

$$q_1^{b\,\prime} = q_T^{b\,\prime} \times \frac{z_1 V_{s,1} / \eta_{p,1}}{z_1 V_{s,1} / \eta_{p,1} + z_2 V_{s,2} / \eta_{p,2}} \tag{S-6}$$

$$q_2^{b\,\prime} = q_T^{b\,\prime} \times \frac{z_2 V_{s,2} / \eta_{p,2}}{z_1 V_{s,1} / \eta_{p,1} + z_2 V_{s,2} / \eta_{p,2}} \tag{S-7}$$

where C_1^b and C_2^b are the equilibrium concentrations of solute 1 and 2 in the binary solute systems, respectively; $q_T^{b'}$ is the total adsorption volume; C_1^s and C_2^s are the hypothetical aqueous concentrations for the single solute systems with the same total adsorption volume ($q_T^{b'}$); q_1^s and q_2^s are the adsorption volume for solute 1 and 2 in single solute systems with the hypothetical aqueous concentrations (C_1^s and C_2^s), respectively; $q_1^{b'}$ and $q_2^{b'}$ are the adsorption volume for solute 1 and 2 in binary solute systems, respectively; z_1 and z_2 are the molar fractions for solute 1 and 2, respectively; Q_o' is the maximum adsorption volume for all liquid adsorbates; a_i', b_i' are the single solute isotherm parameters; $V_{s,i}$ is the molar volume (of pure chemical); and $\eta_{p,i}$ is the packing efficiency, defined as the ratio of maximum adsorbed volume of a solid chemical to that for liquid chemicals. Note that $\eta_{p,i}$ will be equal to 1 for all chemicals that are normally liquids at the temperature of adsorption, and that $\eta_{p,i}$ values for solid chemicals will be as independently estimated on the basis of single solute isotherms. $V_{s,i}/\eta_{p,i}$ may be referred to as the adsorbed molar volume.

From Equation (S-4), we obtain:

$$Q_o' \times 10^{[a_1'(\frac{\varepsilon_{sw,1}^s}{V_{s,1}})^{b_1'}]} = Q_o' \times 10^{[a_2'(\frac{\varepsilon_{sw,2}^s}{V_{s,2}})^{b_2'}]} \tag{S-8}$$

Then,

$$a_1'(\frac{\varepsilon_{sw,1}^s}{V_{s,1}})^{b_1'} = a_2'(\frac{\varepsilon_{sw,2}^s}{V_{s,2}})^{b_2'} \tag{S-9}$$

$$(\frac{\varepsilon_{sw,2}^s}{V_{s,2}}) = [\frac{a_1'}{a_2'}(\frac{\varepsilon_{sw,1}^s}{V_{s,1}})^{b_1'}]^{\frac{1}{b_2'}} = \{\frac{a_1'}{a_2'}[\frac{2.303RT}{V_{s,1}} \times \log(\frac{z_1 S_{w,1}}{C_1^b})]^{b_1'}\}^{\frac{1}{b_2'}} \tag{S-10}$$

According to the definition of adsorption potential for solute 2 and Equation (S-2), we can have the following equation.

$$(\frac{\varepsilon_{sw,2}^s}{V_{s,2}}) = \frac{2.303RT}{V_{s,2}} \times \log(\frac{z_2 S_{w,2}}{C_2^b}) \tag{S-11}$$

$$\frac{z_2 S_{w,2}}{C_2^b} = 10^{(\frac{\varepsilon_{sw,2}^s}{2.303RT})} \tag{S-12}$$

$$C_2^b = z_2 S_{w,2} \times 10^{(-\frac{\varepsilon_{sw,2}^s}{2.303RT})} = (1-z_1) \times S_{w,2} \times 10^{(-\frac{\varepsilon_{sw,2}^s}{2.303RT})} \tag{S-13}$$

A mass balance conducted for solute 2 with initial concentration C_2^o gives

$$q_2^{b\prime} \times \rho_2 = \frac{VC_2^o}{M} - (\frac{V+X}{M} + K_{p,2})C_2^b \qquad \text{(S-14)}$$

Here, V is the solution volume in the sorption vial; M is the sorbent mass; $K_{p,2}$ is the partition coefficient for the co-solute; and X is an effective volume increment, used to account for solute loss when these are proportional to the final aqueous concentration. X is an empirical term that is estimated from separate experiments with blank samples.

By replacing $q_2^{b\prime}$ with Equations (S-7) and (S-4), and C_2^b with Equation (S-13), the final equation is obtained.

$$\frac{(1-z_1)V_{s,2}/\eta_{p,2}}{z_1 V_{s,1}/\eta_{p,1} + (1-z_1)V_{s,2}/\eta_{p,2}} \times Q_o \times 10^{[a_2\prime(\frac{\varepsilon_{sw,2}^s}{V_{s,2}})^{b_2\prime}]} \times \rho_2 -$$

$$\frac{VC_2^o}{M} + (\frac{V+X}{M} + K_{p,2})(1-z_1) \times S_{w,2} \times 10^{[-\frac{\varepsilon_{sw,2}^s}{2.303RT}]} = 0 \qquad \text{(S-15)}$$

in which, ρ_2 is the density of co-solute 2, and $\varepsilon_{sw,2}^s$ is given by Equation (S-7). For any given C_1^b, z_1 can be solved, and C_1^s then can be calculated from Equation (S-1). Predictive values of adsorbed volumes then can be determined using Equations (S-4) through (S-7). With the addition of the unaffected linear partitioning component, the overall sorption isotherms can be predicted.