Competing Forces in Chiral Surface Chemistry: Enantiospecificity versus Enantiomer Aggregation

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Supporting information

Here we derive the expressions for the equilibrium adsorption coverage of enantiomers assuming the Langmuir-like model in which clusters of $2n$ adsorbate molecules are either homochiral or heterochiral as illustrated in Figure 5 of the main text. The primary variables are:

P_D - partial pressure of *D*- enantiomers in the gas phase

P_L - partial pressure of *L*- enantiomers in the gas phase

θ_{D_1} - fractional coverage of *D*- monomers (= 0 → 1)

θ_{L_1} - fractional coverage of *L*- monomers (= 0 → 1)

$\theta_{D_{2n}}$ - fractional coverage of homochiral D_{2n} clusters (= 0 → $\frac{1}{2n}$)

$\theta_{L_{2n}}$ - fractional coverage of homochiral L_{2n} clusters (= 0 → $\frac{1}{2n}$)

θ_{DL_n} - fractional coverage of heterochiral $(DL)_n$ clusters (= 0 → $\frac{1}{2n}$)

The primary constants are

K_a^D - equilibrium constant for *D*-enantiomer adsorption

K_a^L - equilibrium constant for *L*-enantiomer adsorption

K_c^D - equilibrium constant for *D*-enantiomer conglomerate clustering

K_c^L - equilibrium constant for *L*-enantiomer conglomerate clustering

K_r^{DL} - equilibrium constant for *DL*-racemate clustering

n - cluster size is always $2n$ adsorbate molecules

Note that K_a^D, K_a^L, K_c^D and K_c^L are enantiospecific on chiral surfaces but not on achiral surfaces. K_r^{DL} is never enantiospecific.

The coverages of monomer and clusters on the surface are given by

$$\theta_{D_1} = K_a^D P_D \delta \tag{1}$$

$$\theta_{L_1} = K_a^L P_L \delta \tag{2}$$

$$\theta_{D_{2n}} = K_c^D {\theta_{D_1}}^{2n} \tag{3}$$

$$\theta_{L_{2n}} = K_c^L {\theta_{L_1}}^{2n} \tag{4}$$

$$\theta_{DL_n} = K_r^{DL} {\theta_{D_1}}^{n} {\theta_{L_1}}^{n} \tag{5}$$

where the coverages of the monomers lie in the range $0 \leq \theta_{D_1} < 1$ (and same for θ_{L_1}) while the coverages of the clusters fall in the range $0 \leq \theta_{D_{2n}} < \frac{1}{2n}$ (and same for $\theta_{L_{2n}}$ and θ_{DL_n}). The total coverage of adsorbate molecules on the surface, $\theta^{tot} = 1 - \delta$, where the coverage of vacancies, δ, is given by

$$\delta = 1 - \theta_{D_1} - \theta_{L_1} - 2n\theta_{D_{2n}} - 2n\theta_{L_{2n}} - 2n\theta_{DL_n} \quad . \tag{6}$$

The relative pressures of enantiomers in the gas phase define the enantiomeric excess in the gas phase.

$$ee_g = \frac{P_D - P_L}{P_D + P_L} \tag{SI1}$$

$$P = P_D + P_L \tag{SI2}$$

$$ee_g \cdot P = P_D - P_L \tag{SI3}$$

Solving SI1 and SI2 for P_D and P_L yields

$$P_D = \frac{1}{2}\left(1 + ee_g\right)P \tag{SI4}$$

$$P_L = \frac{1}{2}\left(1 - ee_g\right)P \tag{SI5}$$

Expression for δ in terms of ee_g (eq. 13)

Using (6) one can find a polynomial equation for the coverage of empty sites~~,~~,

$$\delta = 1 - K_a^D P_D \delta - K_a^L P_L \delta$$

$$-2nK_c^D (K_a^D P_D \delta)^{2n} - 2nK_c^L (K_a^L P_L \delta)^{2n} - 2nK_r^{DL} (K_a^D P_D \delta)^n (K_a^L P_L \delta)^n$$

$$0 = 1 - \delta - K_a^D P_D \delta - K_a^L P_L \delta$$

$$-2nK_c^D (K_a^D P_D \delta)^{2n} - 2nK_c^L (K_a^L P_L \delta)^{2n} - 2nK_r^{DL} (K_a^D P_D \delta)^n (K_a^L P_L \delta)^n$$

Substituting $K_a^D = \Delta_a K_a$ (eq. 8) and $K_a^L = \Delta_a^{-1} K_a$ (eq. 9) yields

$$0 = 1 - \delta - \Delta_a K_a P_D \delta - \Delta_a^{-1} K_a P_L \delta$$

$$-2nK_c^D (\Delta_a K_a P_D \delta)^{2n} - 2nK_c^L (\Delta_a^{-1} K_a P_L \delta)^{2n}$$

$$- 2nK_r^{DL} (\Delta_a K_a P_D \delta)^n (\Delta_a^{-1} K_a P_L \delta)^n$$

Substituting $P_D = \frac{1}{2}(1 + ee_g)P$ (eq. SI4) and $P_L = \frac{1}{2}(1 - ee_g)P$ (eq. SI5) yields

$$0 = 1 - \delta - \Delta_a K_a \tfrac{1}{2}(1 + ee_g)P\delta - \Delta_a^{-1} K_a \tfrac{1}{2}(1 - ee_g)P\delta$$

$$-2nK_c^D \left(\Delta_a K_a \tfrac{1}{2}(1 + ee_g)P\delta\right)^{2n} - 2nK_c^L \left(\Delta_a^{-1} K_a \tfrac{1}{2}(1 - ee_g)P\delta\right)^{2n}$$

$$- 2nK_r^{DL} \left(\Delta_a K_a \tfrac{1}{2}(1 + ee_g)P\delta\right)^n \left(\Delta_a^{-1} K_a \tfrac{1}{2}(1 - ee_g)P\delta\right)^n$$

$$0 = 1 - \left\{1 + \tfrac{1}{2} K_a P \Delta_a (1 + ee_g) + \tfrac{1}{2} K_a P \Delta_a^{-1} (1 - ee_g)\right\} \delta$$

$$-2n \left(\tfrac{K_a P}{2}\right)^{2n} \left\{K_c^D \left(\Delta_a (1 + ee_g)\right)^{2n} + K_c^L \left(\Delta_a^{-1} (1 - ee_g)\right)^{2n}\right.$$

$$\left. + K_r^{DL} \left(\Delta_a (1 + ee_g)\right)^n \left(\Delta_a^{-1} (1 - ee_g)\right)^n\right\} \delta^{2n}$$

Substituting $K_c^D = x\Delta_c K_c$ (eq. 10), $K_c^L = x\Delta_c^{-1} K_c$ (eq. 11), and $K_r^{DL} = (1 - x)K_c$ (eq. 12)

$$0 = 1 - \left\{1 + \tfrac{K_a P}{2} \Delta_a (1 + ee_g) + \tfrac{K_a P}{2} \Delta_a^{-1} (1 - ee_g)\right\} \delta$$

$$-2n\left(\frac{K_aP}{2}\right)^{2n}\left\{x\Delta_cK_c\left(\Delta_a(1+ee_g)\right)^{2n}+x\Delta_c^{-1}K_c\left(\Delta_a^{-1}(1-ee_g)\right)^{2n}\right.$$

$$\left.+(1-x)K_c\left(\Delta_a(1+ee_g)\right)^{n}\left(\Delta_a^{-1}(1-ee_g)\right)^{n}\right\}\delta^{2n}$$

Which yields eq. 13

$$0=1-\left\{1+\frac{K_aP}{2}\Delta_a(1+ee_g)+\frac{K_aP}{2}\Delta_a^{-1}(1-ee_g)\right\}\delta$$

$$-2n\left(\frac{K_aP}{2}\right)^{2n}K_c\left\{x\Delta_c\left(\Delta_a(1+ee_g)\right)^{2n}+x\Delta_c^{-1}\left(\Delta_a^{-1}(1-ee_g)\right)^{2n}\right.$$

$$\left.+(1-x)(1+ee_g)^{n}(1-ee_g)^{n}\right\}\delta^{2n}$$

Expression for ee_s in terms of δ (eq. ~~13~~)

The total coverages of *D*- and *L*- enantiomers on the surface are given by

$$\theta_D^{tot}=\theta_{D_1}+2n\theta_{D_{2n}}+n\theta_{DL_n} \tag{SI6}$$

$$\theta_L^{tot}=\theta_{L_1}+2n\theta_{L_{2n}}+n\theta_{DL_n} \tag{SI7}$$

The surface enantiomeric excess is given by

$$ee_s=\frac{\theta_D^{tot}-\theta_L^{tot}}{\theta_D^{tot}+\theta_L^{tot}} \tag{SI8}$$

Substituting eq. SI6 and eq. SI7 gives

$$ee_s=\frac{\theta_{D_1}+2n\theta_{D_{2n}}-\theta_{L_1}+2n\theta_{L_{2n}}}{\theta_{D_1}+2n\theta_{D_{2n}}+n\theta_{DL_n}+\theta_{L_1}+2n\theta_{L_{2n}}+n\theta_{DL_n}}$$

Substituting eq. 6 into the denominator

$$ee_s=\frac{\theta_{D_1}+2n\theta_{D_{2n}}-\theta_{L_1}-2n\theta_{L_{2n}}}{1-\delta}$$

Substituting eqs. 1-4 into the numerator

$$(1-\delta)ee_s=K_a^DP_D\delta-K_a^LP_L\delta+2nK_c^D(K_a^DP_D\delta)^{2n}-2nK_c^L(K_a^LP_L\delta)^{2n}$$

Substituting $K_a^D=\Delta_aK_a$ (eq. 8) and $K_a^L=\Delta_a^{-1}K_a$ (eq. 9) yields

$$(1-\delta)ee_s = (\Delta_a K_a P_D - \Delta_a^{-1} K_a P_L)\delta + 2n[K_c^D(\Delta_a K_a P_D)^{2n} - K_c^L(\Delta_a^{-1} K_a P_L)^{2n}]\delta^{2n}$$

Substituting $K_c^D = x\Delta_c K_c$ (eq. 10), $K_c^L = x\Delta_c^{-1} K_c$ (eq. 11),

$$(1-\delta)ee_s = K_a(\Delta_a P_D - \Delta_a^{-1} P_L)\delta + 2nK_a^{2n}[x\Delta_c K_c(\Delta_a P_D)^{2n} - x\Delta_c^{-1} K_c(\Delta_a^{-1} P_L)^{2n}]\delta^{2n}$$

Substituting $P_D = \frac{1}{2}(1+ee_g)P$ (eq. SI4) and $P_L = \frac{1}{2}(1-ee_g)P$ (eq. SI5) yields

$$(1-\delta)ee_s = K_a\left(\frac{1}{2}\Delta_a(1+ee_g)P - \frac{1}{2}\Delta_a^{-1}(1-ee_g)P\right)\delta$$

$$+ 2nK_a^{2n}\left\{x\Delta_c K_c\left[\frac{1}{2}\Delta_a(1+ee_g)P\right]^{2n} - x\Delta_c^{-1} K_c\left[\frac{1}{2}\Delta_a^{-1}(1-ee_g)P\right]^{2n}\right\}\delta^{2n}$$

Which gives eq. 14

$$(1-\delta)ee_s = \left(\frac{K_a P}{2}\right)\{\Delta_a(1+ee_g) - \Delta_a^{-1}(1-ee_g)\}\delta$$

$$+ 2n\left(\frac{K_a P}{2}\right)^{2n} K_c x\left\{\Delta_c[\Delta_a(1+ee_g)]^{2n} - \Delta_c^{-1}[\Delta_a^{-1}(1-ee_g)]^{2n}\right\}\delta^{2n}$$