Electronic Supplementary Information

Entropy in Multiple Equilibria, Theory and Applications

Gion Calzaferri

Table of Contents

ESI1. Derivation of equation (14)

$$ZX_{rc-1} + X \rightleftarrows ZX_{rc} \quad K_{rc} \tag{S1}$$

$$K_{rc} = \frac{[ZX_{rc}] \quad c^{\emptyset}}{[ZX_{rc-1}][X]} \tag{S2}$$

$$\prod_{j=1}^{rc} K_j = \frac{[ZX_1][ZX_2]}{[Z] \ [ZX_1]} \cdot \ldots \cdot \frac{[ZX_{rc-1}] \ [ZX_{rc}]}{[ZX_{rc-2}][ZX_{rc-1}]} \cdot \left(\frac{c^{\emptyset}}{[X]}\right)^{rc} \tag{S3}$$

From this we obtain for $rc=n$ the desired expression (14):

$$Z + nX \rightleftarrows ZX_n \quad K_{tot} \tag{S4}$$

$$K_{tot} = \frac{[ZX_n]}{[Z]}\left(\frac{c^{\emptyset}}{[X]}\right)^n = \prod_{rc=1}^{n} K_{rc} \tag{S5}$$

ESI2. Derivation of equation (15)

We evaluate the product, eqn (14):

$$K_{tot}^{pd} = \prod_{rc=1}^{n} K_{rc}^{pd} \quad \text{with} \quad K_{r+1}^{pd} = K_r^{pd} \frac{r \qquad n-r}{r+1 n-r+1} \tag{S6}$$

It is convenient to introduce the following abbreviation:

$$f(r) = \frac{r \qquad n-r}{r+1 n-r+1} \tag{S7}$$

This allows us to write:

$$K_{r+1}^{pd} = K_r^{pd} f(r) \tag{S8}$$

Using this we can write the following sequence of equations, which finally lead to the desired result:

$$K_{tot}^{pd} = K_1^{pd} \cdot \ K_2^{pd} \cdot \ K_3^{pd} \cdot \ \ \cdot \ldots K_{n-2}^{pd} \cdot K_{n-1}^{pd} \cdot K_n^{pd} \tag{S9}$$

$$K_{tot}^{pd} = K_1^{pd} \cdot \ K_1^{pd} f(1) \cdot K_2^{pd} f(2) \cdot \ldots K_{n-3}^{pd} f(n-3) \cdot K_{n-2}^{pd} f(n-2) \cdot K_{n-1}^{pd} f(n-1)$$

$$K_{tot}^{pd} = \ldots$$

ESI2

$$K_{tot}^{pd} = \left(K_1^{pd}\right)^n \cdot \{ f(1) \cdot f(1)f(2) \cdot \ldots \cdot \ldots \cdot f(1)f(2)f(3)\ldots f(n-3)f(n-2)f(n-1)\}$$

$$K_{tot}^{pd} = \left(K_1^{pd}\right)^n \cdot \left\{ f(1) \cdot \prod_{r=1}^{2} f(r) \cdot \prod_{r=1}^{3} f(r) \cdot \ldots \cdot \prod_{r=1}^{n-2} f(r) \cdot \prod_{r=1}^{n-1} f(r) \right\}$$

$$K_{tot}^{pd} = \left(K_1^{pd}\right)^n \cdot \{ f(1)^{n-1} f(2)^{n-2} \ldots f(n-1)^1 \} = \left(K_1^{pd}\right)^n \prod_{r=1}^{n-1} f(r)^{n-r}$$

$$K_{tot}^{pd} = \left(\frac{K_1^{pd}}{n}\right)^n \tag{S10}$$

ESI3. Experimental equilibrium constants K_1 and K_2 of dicarboxylic acids *HOOC-(CH$_2$)$_m$-COOH*

m	0	1	2	3	4	5	6	7	8
K_1	$10^{-1.27}$	$10^{-2.85}$	$10^{-4.21}$	$10^{-4.34}$	$10^{-4.41}$	$10^{-4.5}$	$10^{-4.526}$	$10^{-4.55}$	$10^{-4.55}$
K_2	$10^{-4.27}$	$10^{-5.05}$	$10^{-5.41}$	$10^{-5.41}$	$10^{-5.41}$	$10^{-5.43}$	$10^{-5.498}$	$10^{-5.498}$	$10^{-5.498}$
PubChem CID	971	867	1110	743	196	385	10457	2266	5192

ESI4. Derivation of the equations (29) and (29A)

We start with the hypothesis that eqns (21,23) are equivalent to Langmuir's isotherm equation and we test if this hypothesis is valid. For this we write:

$$\frac{[X]A}{1+[X]B} = \frac{[X]\frac{1}{n}K_1 + [X]^2\frac{2}{n}K_1K_2 + \ldots + [X]^nK_1K_2\ldots K_n}{1+[X]K_1+[X]^2K_1K_2+\ldots+[X]^nK_1K_2\ldots K_n} = \frac{[X]\left(\frac{1}{n}K_1 + [X]\frac{2}{n}K_1K_2 + \ldots + [X]^{n-1}K_1K_2\ldots K_n\right)}{1+[X]\left(K_1+[X]^2K_1K_2+\ldots+[X]^{n-1}K_1K_2\ldots K_n\right)} \tag{S11}$$

Using $\kappa_i = K_1K_2\ldots K_i$ we write:

$$\frac{[X]A}{1+[X]B} = \frac{[X]\left(\frac{1}{n}\kappa_1 + [X]\frac{2}{n}\kappa_2 + \ldots + [X]^{n-1}\kappa_n\right)}{1+[X]\left(\kappa_1+[X]^2\kappa_2+\ldots+[X]^{n-1}\kappa_n\right)} \tag{S12}$$

The following relation must hold if the hypothesis is correct:

$$\frac{[X]A}{1+[X]B} = \frac{[X]K_L}{1+[X]K_L} \tag{S13}$$

We multiplying (S13) with $(1+[X]B)(1+[X]K_L)$:

$$[X]K_L + [X]^2K_LB = [X]A + [X]^2K_LA \tag{S14}$$

Multiplying this with $\frac{1}{[X]}$ leads to:

$$K_L + [X]K_LB = A + [X]K_LA \tag{S15}$$

We insert the expressions for A and B from (S12):

$$K_L + [X]K_L\left(\kappa_1+[X]^2\kappa_2+\ldots+[X]^{n-1}\kappa_n\right) =$$
$$\left(\frac{1}{n}\kappa_1 + [X]\frac{2}{n}\kappa_2 + \ldots + [X]^{n-1}\kappa_n\right) + [X]K_L\left(\frac{1}{n}\kappa_1 + [X]\frac{2}{n}\kappa_2 + \ldots + [X]^{n-1}\kappa_n\right) \tag{S16}$$

Equation (S16) can be rearranged in order to obtain (S17):

$$K_L - \frac{1}{n}\kappa_1 = [X]\frac{2}{n}\kappa_2 + ... + [X]^{n-1}\kappa_n + [X]K_L\left(\kappa_1\left(\frac{1}{n} - 1\right) + [X]^2\left(\frac{2}{n} - 1\right)\kappa_2 + ... + [X]^{n-2}\left(\frac{n-1}{n} - 1\right)\kappa_{n-1}\right) \tag{S17}$$

Ordering (S17) according to the power of [X]:

$$K_L - \frac{1}{n}\kappa_1 = [X]\left(\frac{2}{n}\kappa_2 + \kappa_1\left(\frac{1}{n} - 1\right)K_L\right) + [X]^2\left(\frac{3}{n}\kappa_3 + \left(\frac{2}{n} - 1\right)\kappa_2 K_L\right)... + [X]^{n-1}\left(\kappa_n + \left(\frac{n-1}{n} - 1\right)\kappa_{n-1}K_L\right) \tag{S18}$$

Equation (S18) hold for all physically accessible and reasonable concentration values of [*X*]. This is only possible if the right side of (S18) is equal to zero. From this we know that eqn (S18) holds for:

$$K_L - \frac{1}{n}\kappa_1 = 0 \tag{S19}$$

This result means that we can write eqn (S20) which corresponds to the eqns (29) and (29A):

$$\Theta = \frac{K_L[X]}{1 + K_L[X]} \quad \text{with} \quad K_L = \frac{1}{n}K_1 \tag{S20}$$

ESI5. Comparison oft the Langmuir isotherm with the sum of the concentrations of bound *X*

We graphically compare equations (21)-(23) with Langmuir's eqn (29,29A) for *n* = 48 equilibrium reactions and two different values for K_l. It is no surprise that they mach perfectly well because (29) is a consequence of (21)-(23).

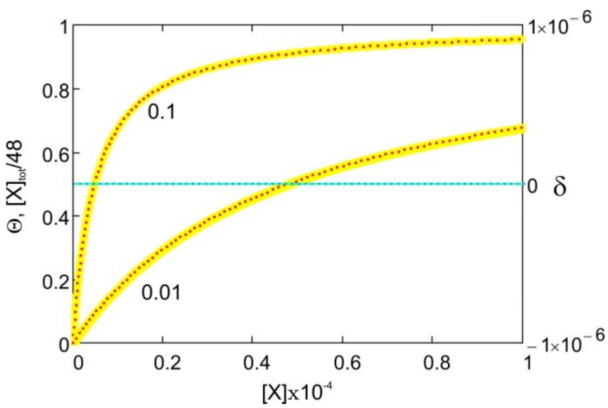

Fig. S1 Comparison of the Langmuir isotherm eqn (29) (yellow solid) and with the sum of the concentrations of bound *X*, eqns (21)-(23), (red, dots) as a function of the concentration of free *X*, shown for 48 equilibria, hence, *n*=48, and for two values of K_l, namely 0.1 and 0.01. $[X]_{tot}$ is divided by 48 in order to scale it to the value range of the Langmuir function Θ. δ indicated the difference between the numerical values of Θ([X]) and $[X]_{tot}([X])$.

ESI6. Derivation of equation (9)

In order to solve the eqns (33A) and (33B) we write them as differential equations with the initial condition (33C).

$$\frac{dN_0}{dn} = -p_0 N_0 \tag{S21}$$

$$\frac{dN_b}{dn} = p_{b-1}N_{b-1} - p_b N_b; \quad B \geq b \geq 1 \tag{S22}$$

We solve eq S11, using eqn (18) for b=0:

$$\int \frac{dN_0}{N_0} = -\int p_0 dn \quad \text{with} \quad p_0 = \frac{B}{BN - n} \tag{S23A}$$

The result reads as follows:

$$lnN_0 = -\int \frac{B}{BN - n} dn = Bln(BN - n) + lnC_0 \tag{S23B}$$

$$N_0 = C_0(BN - n)^B \tag{S23C}$$

The integration constant C_0 follows from the initial condition (33C).

The solution of eqn (S22) is found by first solving it for N_1 and then solving it for N_2.

The solution for the general case N_b is readily found from this.

$$\frac{dN_1}{dn} + \frac{B - 1}{BN - n} N_1 = \frac{B}{BN - n} N_0 \tag{S24}$$

We insert the result (S23C) for N_0:

$$\frac{dN_1}{dn} + \frac{B - 1}{BN - n} N_1 = \frac{B}{BN - n} C_0(BN - n)^B \tag{S24A}$$

It is convenient to write the solution of (S24A) as follows:[1S,2S]

$$N_1 = G(n)^{U(n)} \tag{S24B}$$

and then to determine $U(n)$ and $G(n)$:

$$U(n) = -\int \frac{B - 1}{BN - n} dn = (B - 1)\ln(BN - n) + C_{11} \tag{S24C}$$

$$G(n) = \int \frac{B}{BN - n} C_0(BN - n)^B e^{-(U(n)} dn \tag{S24D}$$

Rearrangement and simplification leads to (S24E) and then (S24F):

$$G(n) = BC_0 \int (BN - n)^{B - 1} e^{-(B - 1)\ln(BN - n) + C_{11}} dn \tag{S24E}$$

$$G(n) = BC_0 \int e^{-C_{11}} dn = BC_0(n + C_{10})e^{-C_{11}} \tag{S24F}$$

Inserting (S24C) and (S24F) in (S24B) leads to

$$N_1 = BC_0(n + C_{10})e^{-C_{11}} e^{(B - 1)\ln(BN - n) + C_{11}} \tag{S24G}$$

This equation simplifies to the solution (S15) we have been searching for:

$$N_1 = BC_0\left(n + C_{10}\right)(BN - n)^{(B - 1)} \tag{S25}$$

The solution (S16) for N_2 is readily found by the same procedure:

$$N_2 = BC_0(B - 1)\left(\frac{n^2}{2} + nC_{10} + C_{20}\right)(BN - n)^{(B - 2)} \tag{S16}$$

On the basis of the solution (S23C), (S25), and (S26) for N_0, N_1 and N_2 we find the general solution for N_b to read as follows:

$$N_b(n,B,N) = \frac{B!C_0}{(B-b)!}(BN-n)^{(B-b)}\sum_{i=0}^{b} C_{i0}\frac{n^{b-1}}{(b-1)!} \tag{S27}$$

Inserting the solution (S27) into (S22) we find that the initial condition (28C) is fulfilled if we use eqn (S28).

$$C_0 = \frac{B}{(BN)^b}, \quad C_{00} = 1, \; and \; \; C_{b0} = 0 \, for \, b > 0 \tag{S28}$$

$$\sum_{i=0}^{b} C_{i0}\frac{n^{b-1}}{(b-1)!} = \frac{n^b}{b!} \tag{S28A}$$

Insertion of the results (S28) and (S28A), which are a consequence of the initial condition (28C), into eqn (S27) leads readily to the eqn (9) we have been searching for.

[1S] W. I. Smirnow, Lehrgang der Höheren Mathematik, Teil II, Deutscher Verlag der Wissenschaft, Berlin **1966**.

[2S] H. G. Zachmann, Mathematik für Chemiker, VCH, Weinheim, **1990**, ISBN 3-527-25930-0.