Model-Independent Description of Multicomponent Adsorption from Affinity Spectrum Statistics

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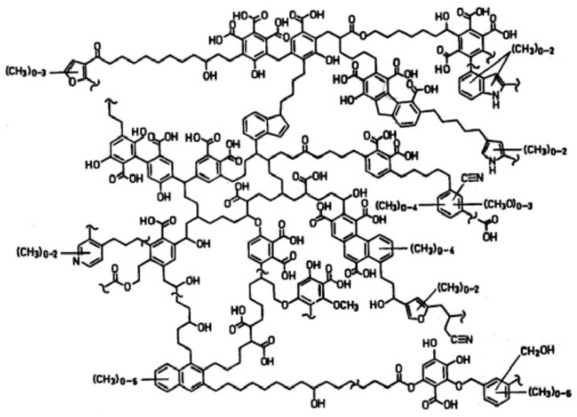
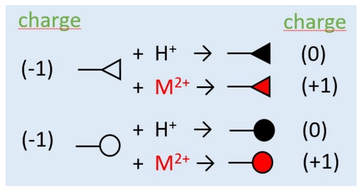
1. Motivation

Multi-cation adsorption to natural organic matter is described by an **affinity spectrum** —a density of binding free energies over all sites— showing *intrinsic* and *electrostatically induced* heterogeneity [1,2]

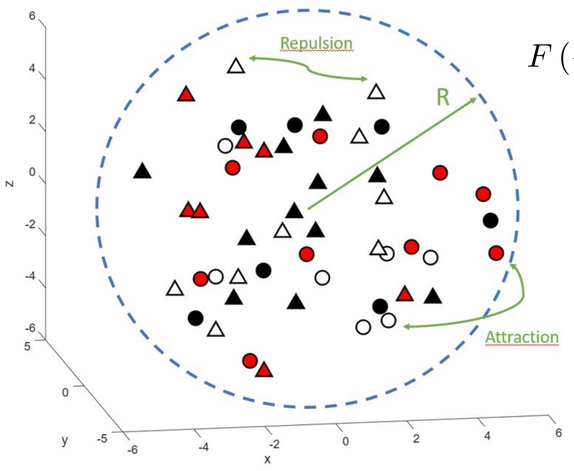




carboxylic and phenolic binding sites for H^+ and M^{2+}

2. Monte Carlo model of randomly distributed sites

Semi-grand Canonical Ensemble: proton/metal occupation numbers fluctuate at fixed H and M chemical potentials; sites interact via a screened Coulomb term:



$$F\left(\{s_i, m_i\}\right) = \sum_{i=1}^{n} \mu_{\mathrm{H},i}\, s_i + \sum_{i=1}^{n} \mu_{\mathrm{M},i}\, m_i + \sum_{j>i}^{n} \phi_{ij}^{\mathrm{int}}$$

$$\mu_{\mathrm{H},i} = \ln(10)\left(\mathrm{pH} - \mathrm{p}K_{\mathrm{a},i}\right)$$

$$\mu_{\mathrm{M},i} = \ln(10)\left(\mathrm{pM} - \mathrm{p}K_{\mathrm{M},i}\right)$$

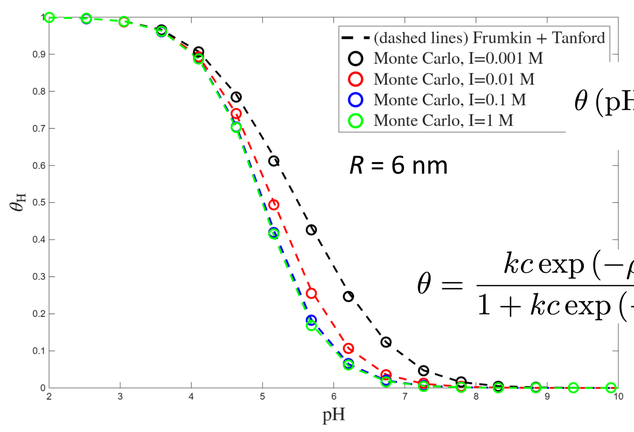
$$\phi_{ij}^{\mathrm{int}} = \frac{q_i q_j\, \ell_{\mathrm{B}}}{r_{ij}} \exp\left(-\kappa r_{ij}\right) \quad ; \quad q_i = 0, \pm 1, \pm 2, \ldots$$

3. Mono-component Affinity Spectrum

Frumkin isotherm describes both intrinsic and electrostatically induced heterogeneity of MC data. No fitting is required with the Tanford interaction energy [3]:

$$\rho_{\mathrm{Tanford}} = 3n\,\frac{\ell_{\mathrm{B}}}{R}\left\{\frac{1}{y^2} - \frac{3}{2y^5}\left[y^2 - 1 + (1+y)^2\exp\left(-2y\right)\right]\right\}$$

$$y = R/\ell_{\mathrm{D}}$$

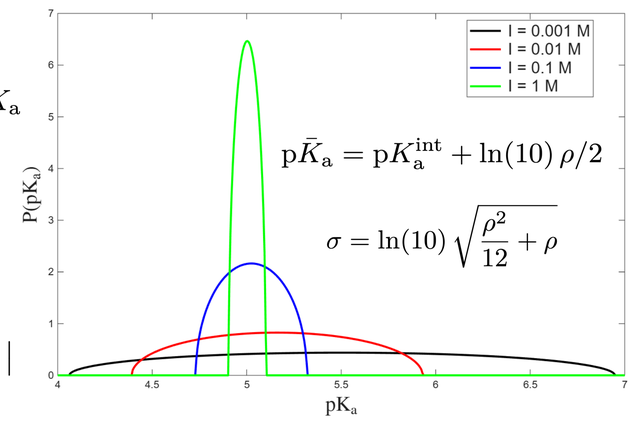


$$\theta\left(\mathrm{pH}\right) = \int_{-\infty}^{\infty} P\left(\mathrm{p}K_{\mathrm{a}}\right)\frac{1}{1+10^{\,\mathrm{pH}-\mathrm{p}K_{\mathrm{a}}}}\,d\mathrm{p}K_{\mathrm{a}}$$

$$\theta = \frac{kc\exp\left(-\rho\theta\right)}{1+kc\exp\left(-\rho\theta\right)}$$

$P(\mathrm{p}K_a)$ spectra are recovered from θ(pH) by analytical inversion [4,5]

$$P\left(\mathrm{p}K_{\mathrm{a}}\right) = \frac{\ln(10)}{\pi}\left|\mathrm{Im}\left[\theta\left(-10^{\,\mathrm{p}K_{\mathrm{a}}}\right)\right]\right|$$



$$\mathrm{p}\bar{K}_{\mathrm{a}} = \mathrm{p}K_{\mathrm{a}}^{\mathrm{int}} + \ln(10)\,\rho/2$$

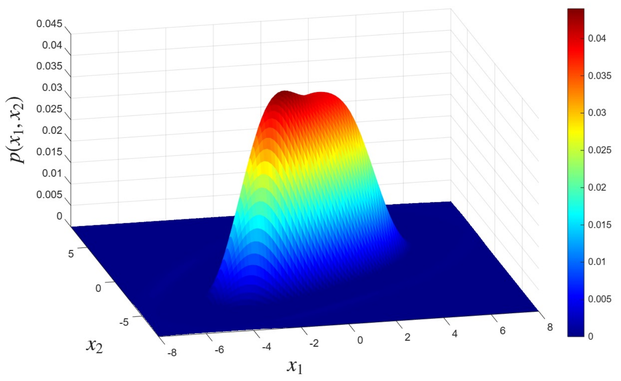
$$\sigma = \ln(10)\sqrt{\frac{\rho^2}{12} + \rho}$$

4. Multi-component Affinity Spectrum (Frumkin)

$$\theta_1\left(c_1, c_2\right) = \frac{k_1 c_1 \exp(-\rho_{11}\theta_1 - \rho_{12}\theta_2)}{1 + k_1 c_1 \exp(-\rho_{11}\theta_1 - \rho_{12}\theta_2) + k_2 c_2 \exp(-\rho_{12}\theta_1 - \rho_{22}\theta_2)}$$

$$\theta_2\left(c_1, c_2\right) = \frac{k_2 c_2 \exp(-\rho_{21}\theta_1 - \rho_{22}\theta_2)}{1 + k_1 c_1 \exp(-\rho_{11}\theta_1 - \rho_{12}\theta_2) + k_2 c_2 \exp(-\rho_{21}\theta_1 - \rho_{22}\theta_2)}$$

Analytical Inversion [4]



For any given first and second moments of the spectrum (mean $\bar{x}_i$, marginal widths σ_{ii}, and correlation coefficient R_{C}) there is always an associated Frumkin isotherm:

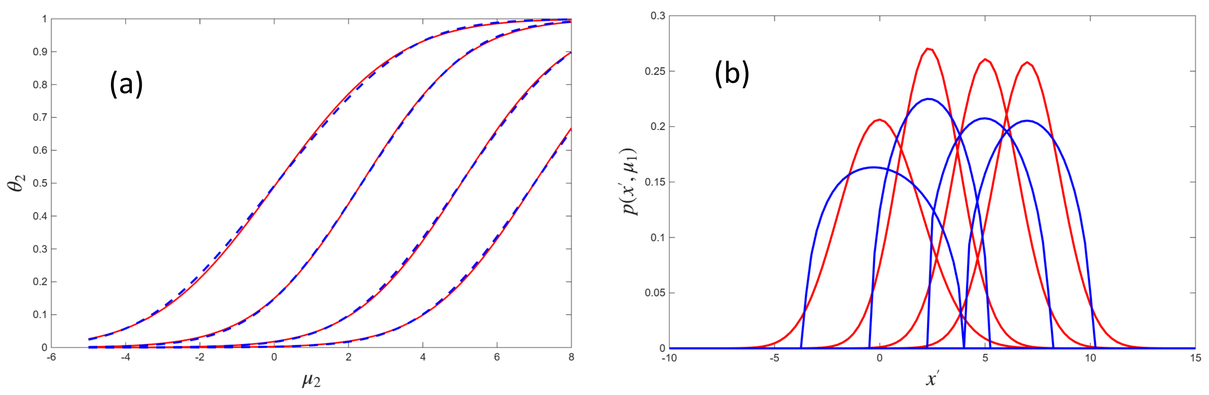
$$\rho_{ii} = -1 + \sqrt{1 + \frac{\sigma_{ii}^2}{3}} \qquad \ln k_i = -\bar{x}_i + \rho_{ii}/2$$

$$\rho_{12} = \frac{(\rho_{11} + \rho_{22} - \tilde{\rho})}{2} \quad \text{with} \quad \tilde{\rho} = -1 + \sqrt{1 + \frac{\tilde{\sigma}^2}{3}}$$

$$\text{and} \qquad \tilde{\sigma}^2 = \left(\frac{\sigma_{11}}{\sigma_{22}} + \frac{\sigma_{22}}{\sigma_{11}} - 2R_{\mathrm{C}}\right)\sigma_{11}\sigma_{22}$$

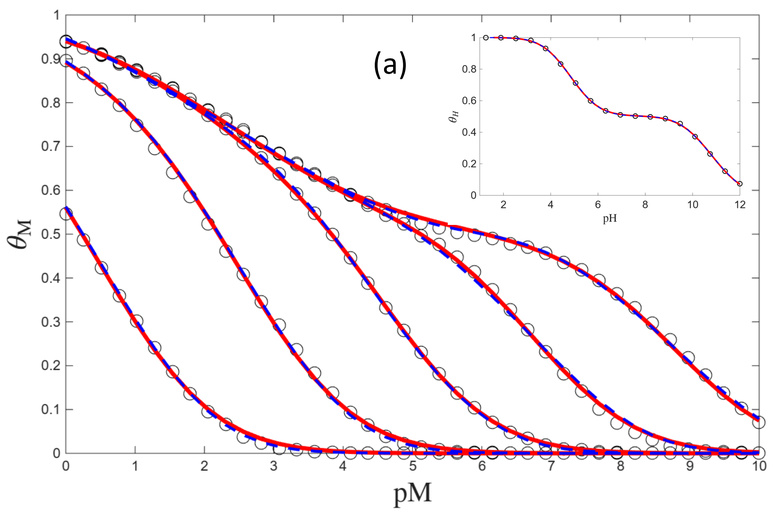
5. Primacy of the lowest cumulants

Only the lowest cumulants matter: affinity spectra with the same average and variance give almost identical isotherms



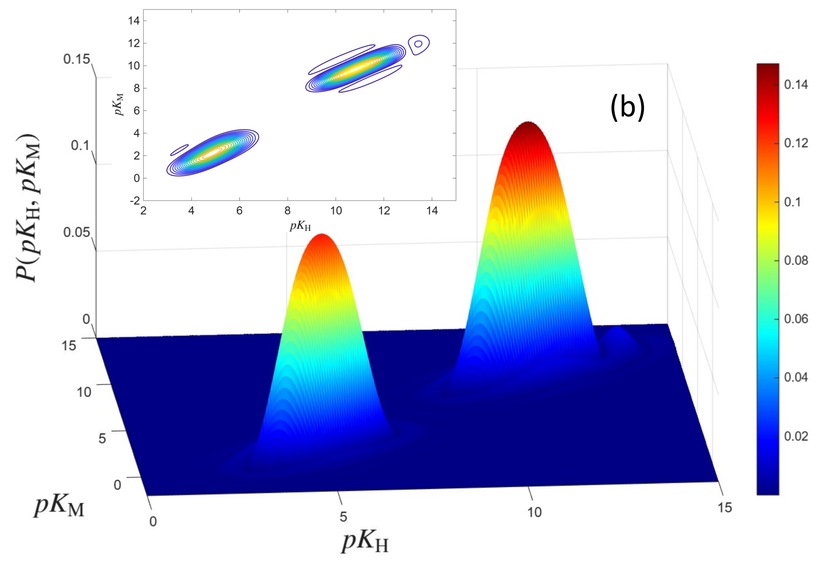
Blue = **Frumkin** isotherm ; *Red* = isotherm from **Gaussian** spectrum, both with $\sigma_{11} = \sigma_{22} = 2$, $R_{\mathrm{C}} = 0.7$, $\bar{x}_1 = \bar{x}_2 = 0$ and fixed $\mu_1 = -4, 2, 5, 7$; (a) Isotherms (b) Conditional Affinity Spectrum [5]. Note that the Gaussian and Frumkin isotherms almost overlap

6. Monte Carlo validation (bimodal distribution)



Fitting results (Frumkin and Gaussian models):

	Mode 1 (Frum.)	Mode 1 (Gauss)	Mode 2 (Frum.)	Mode 2 (Gauss)
$\mathrm{p}K_{\mathrm{a}}^{\mathrm{av}}$	4.91	4.90	10.88	10.88
$\mathrm{p}K_{\mathrm{M}}^{\mathrm{av}}$	2.26	2.27	9.73	9.68
σ_{H}	0.68	0.70	0.78	0.83
σ_{M}	1.75	1.98	1.70	1.80
R_{c}	0.85	0.90	0.98	0.96
Q_i	0.49	0.50	0.50	0.49



(a) Markers: MC simulations of metal titration curves at fixed pH = 2, 4, 6, 8, 10. I = 0.01 M, $\mathrm{p}K_{\mathrm{a},1}^{\mathrm{int}} = 4.5$,$\mathrm{p}K_{\mathrm{M},1}^{\mathrm{int}} = 2$, (abundance $Q_1 = 0.5$); $\mathrm{p}K_{\mathrm{a},2}^{\mathrm{int}} = 9.6$, $\mathrm{p}K_{\mathrm{M},2}^{\mathrm{int}} = 8$, R = 4 nm ($Q_2 = 0.5$). Inset: proton titration. *Blue*/*red*=best-fit bimodal Frumkin and Gaussian models. **(b)** Bimodal Frumkin competitive spectrum: electrostatics induce positive H-M binding correlation

Take-home message

- **The lowest cumulants of the affinity spectrum (mean and covariance matrix) capture most of the information provided by the binding isotherms**, as illustrated with multicomponent Gaussian and Frumkin spectra. This suggests a model-independent way to standardize experimental binding data.
- **The Frumkin isotherm reproduces multicomponent MC simulations for both intrinsic and electrostatic heterogeneities**. Its underlying affinity spectrum has a well-defined mean and covariance, and does not require numerical calculation of multiple integrals —unlike the Gaussian model.

[1] Gledhill, M., Gosnell, K., Humphreys, M. P., Delaigue, L., Helle, N., Zhu, K., Lodeiro, P., Rey-Castro, C., Achterberg E. P. (2026) *Nature Communications 17, 3533;* **[2]** Lodeiro, P., Rey-Castro, C., David, C., Humphreys, M. P., Gledhill, M. (2023). *Environ. Sci. Technol.*, *57 (*50), 21136-21144; **[3]** Tanford, C. (1961). *Physical Chemistry of Macromolecules*. New York: John Wiley & Sons, Chapter 7; **[4]** Garcés J. L., Mas, F., Puy J. (2004) *J. Chem. Phys.* 120 (19) 9266-76; **[5]** Garcés J. L., Mas, F., Puy J. (2006) *J. Chem. Phys.* 124, 044710

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