Model-Independent Description of Multicomponent Adsorption from Affinity Spectrum Statistics

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Understanding adsorption in heterogeneous systems remains a central challenge, particularly for multicomponent mixtures. Equilibrium adsorption isotherms are commonly interpreted in terms of an underlying affinity spectrum, defined as the probability density function of adsorption free energies over the ensemble of adsorption sites. This framework provides a natural link between macroscopic adsorption behaviour and microscopic energetic heterogeneity. [1]

In this work, we show that the macroscopic properties of adsorption are primarily governed by the main statistical features of the affinity spectrum, namely its mean values and covariance matrix. When these are fixed, different functional forms of the spectrum — including Gaussian, ellipsoidal, and Frumkin-type distributions — lead not only to very similar adsorption isotherms, but also to similar Conditional Affinity Spectra (CAS), i.e., the effective spectra obtained upon fixing the chemical potential of one component. [2-4] This indicates that the detailed shape of the spectrum plays a secondary role, and that adsorption behaviour is controlled by a small set of statistical descriptors — a result that holds even when the functional forms differ substantially at the tails of the distribution, where direct experimental determination is least reliable.

This observation enables a unified and standardized description of heterogeneous and structurally disordered natural organic matter, largely independent of the specific isotherm model employed (e.g., NICA, Frumkin, Gaussian-based approaches), which can be viewed as alternative parameterizations of the same underlying statistical structure.

We focus on the Frumkin isotherm, showing that for any prescribed set of mean affinities and covariance matrix, there exists a unique corresponding set of parameters consistent with these constraints. This highlights that the Frumkin model can effectively capture system heterogeneity beyond its traditional interpretation in terms of intermolecular interactions. [2] In contrast to NICA (Non-Ideal Competitive Adsorption), this isotherm remains linear at low concentrations (i.e., satisfies the Henry limiting law) and clearly separates stoichiometric parameters from those describing heterogeneity.

Finally, we validate these results against Monte Carlo simulations and experimental data from model systems, establishing a statistically grounded and model-independent framework for multicomponent adsorption, with direct implications for trace element cycling by natural organic matter in changing ocean and soil environments. [3]

References:

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