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Affinity distribution functions in multicomponent heterogeneous adsorption. Analytical inversion of isotherms to obtain affinity spectra

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An analytical approach for the interpretation of multicomponent heterogeneous adsorption or complexation isotherms in terms of multidimensional affinity spectra is presented. Fourier transform, applied to analyze the corresponding integral equation, leads to an inversion formula which allows the computation of the multicomponent affinity spectrum underlying a given competitive isotherm. Although a different mathematical methodology is used, this procedure can be seen as the extension to multicomponent systems of the classical Sips's work devoted to monocomponent systems. Furthermore, a methodology which yields analytical expressions for the main statistical properties (mean free energies of binding and covariance matrix) of multidimensional affinity spectra is reported. Thus, the level of binding correlation between the different components can be quantified. It has to be highlighted that the reported methodology does not require the knowledge of the affinity spectrum to calculate the means, variances, and covariance of the binding energies of the different components. Nonideal competitive consistent adsorption isotherm, widely used in metal/proton competitive complexation to environmental macromolecules, and Frumkin competitive isotherms are selected to illustrate the application of the reported results. Explicit analytical expressions for the affinity spectrum as well as for the matrix correlation are obtained for the NICCA case. © *2004 American Institute of Physics.*
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I. INTRODUCTION

The interpretation of the interactions of small molecules with heterogeneous surfaces and/or macromolecules, both in gas and solution phase, has been the subject of intensive research for the last decades owing to its great importance in several scientific disciplines: environmental speciation studies,[1–3] gas/solid adsorption,[4,5] binding of ligands to biochemical receptors,[6] chromatographic studies,[7] polymer science,[8,9] etc. A current strategy to describe monocomponent adsorption consists in expressing the total macromolecular/surface coverage θ as a weighted superposition of local Langmuirian isotherms[1,2,10]

$$\theta(c) = \int_{-\infty}^{\infty} p'(k) \frac{kc}{1+kc} dk = \int_{-\infty}^{\infty} p(\ln k) \frac{kc}{1+kc} d \ln k,$$
(1)

where c is the concentration of the adsorbed species and $p'(k)$ is the so-called affinity distribution function or affinity spectrum, which expresses the probability density of having sites in the macromolecule/surface with binding stability constant for the adsorbed species lying in between k and $k+dk$. Usually, as indicated in Eq. (1), the affinity spectrum is represented in the logarithmic space $\ln k$, proportional to

the binding free energy. Hence, once a concrete form for the affinity spectrum is proposed, Eq. (1) produces an analytical isotherm which can further be used to fit an experimental set of coverage versus concentration data.

In other cases, one could be interested in the knowledge of the affinity spectrum underlying an empirically proposed isotherm, which successfully describes the experimental information available. This inverse problem reduces to solving the integral equation (1) for $p(\ln k)$. An inversion formula to obtain $p(\ln k)$ for a given analytical isotherm was provided by Sips in a pioneer work.[10] The formula has been widely used for a long time in the interpretation of monocomponent isotherms (such as Langmuir–Freundlich, Frumkin or Temkin) in terms of a underlying affinity distribution function.[10,11] On the other hand, several numerical methods have been applied to determine $p(\ln k)$ directly from a given set of experimental θ versus $\ln(c)$ data. Among these, the use of regularization methods to solve the integral equation (1) became the subject of many works devoted to the analysis of heterogeneous monocomponent adsorption, both in gas and in solution phase.[3,4,12]

The affinity spectrum approach can be straightforwardly extended to multicomponent competitive adsorption, by considering the macromolecular/surface coverage of each component i, $\theta_i(c_1, c_2, ..., c_N)$, dependent on the concentrations

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of all the N components of the system, as a superposition of competitive Langmuirian isotherms[13–16]

$$\theta_i(c_1,c_2,\ldots,c_N) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} p(\ln k_1, \ln k_2, \ldots, \ln k_N)$$

$$\times \frac{k_i c_i}{1 + \sum_{j=1}^{N} k_j c_j} \prod_j d\ln k_j. \tag{2}$$

Nevertheless, the main obstacle for this generalization lies in the multidimensional nature of the integral equation (2). This has resulted, in contrast with the equivalent treatment of monocomponents systems, in a lack of simple analytical results allowing an easy interpretation of empirical isotherms in terms of an underlying affinity distribution function. Regularization methods have been successfully applied to the finding of $p(\ln k_1, \ln k_2, \ldots, \ln k_N)$ for two adsorbing components in solution.[17] However, the inverse problem has not been analytically solved for the general case. A first aim of this work is to provide, in Sec. II, a general analytical solution for Eq. (2), based on Fourier analysis, and to apply it, in Sec. III, to the finding of the affinity spectrum which generates nonideal competitive consistent adsorption (NICCA) and competitive Frumkin isotherms. It is important here to note that the choice of the local competitive isotherm appearing in the kernel of Eq. (2), in the case of competitive adsorption, could be multiple. In this work we only undertake the problem of Langmuirian local adsorption, but if, for instance, the molecules of one component bind to more that one site at the same time (chelate complexation), other choices of the local adsorption isotherm would be required.[17]

Another question of interest in the characterization of the binding to heterogeneous systems is determining the minimum information needed to successfully describe a set of experimental adsorption data. This question arises from the very ill-posed nature of the integral equation (1), i.e., small changes in the affinity spectrum lead to almost the same binding curve. This means that, from a practical point of view, only a part of the information contained in the affinity spectrum is of interest in the interpretation and prediction of the empirical information for a given range of concentrations.

In the case of monocomponent systems, it has been shown that in a wide range of concentrations corresponding to intermediate coverages, only the mean μ and the variance σ^2 of each peak of the affinity spectrum are relevant in the description of the experimental binding curve (that is, different isotherms with the same μ and σ^2 can reproduce with similar accuracy the same binding curve).[18] Hence, the knowledge of μ and σ^2 is almost enough to characterize the binding properties of the heterogeneous surface.

It is therefore expected that something similar will hold for multicomponent systems, becoming relevant quantities in this case not only the mean and variance of the spectrum of the different components, but also the correlation of the binding among them. The natural mathematical description of such statistical properties is the set of mean affinities (one for each component) and the elements of the covariance matri-

ces. A procedure to obtain means and covariance matrices of multidimensional affinity spectra in terms of the parameters of competitive isotherms is given in Sec. IV, and thereafter applied to NICCA and Frumkin isotherms.

II. FOURIER ANALYSIS OF MULTICOMPONENT BINDING ISOTHERMS: AN INVERSION FORMULA TO OBTAIN THE MULTIDIMENSIONAL AFFINITY SPECTRA

A. Transformation of the integral Eq. (2) in order to apply Fourier analysis

Let us assume that the coverage of certain component i, $\theta_i(\{c_j\})$, can be expressed as a superposition of multicomponent Langmuirian isotherms, as Eq. (2) indicates. In order to apply Fourier transform techniques, it is convenient to rewrite Eq. (2) in terms of a new set of variables,

$$x_i = -\ln k_i, \tag{3}$$

$$\mu_i = \ln c_i, \tag{4}$$

where x_i is proportional to the binding free energy of component i to the site and μ_i is proportional to the chemical potential of component i. In terms of these new variables, Eq. (2) rewrites

$$\theta_i(\vec{\mu}) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} p(-\vec{x}) g_i(\vec{\mu}-\vec{x}) \prod_i dx_i, \tag{5}$$

where vectorial notation, $\vec{\mu} = (\mu_1, \mu_2, \ldots, \mu_N)$ and $\vec{x} = (x_1, x_2, \ldots, x_N)$, have been used, and

$$g_i(\vec{\mu}-\vec{x}) = \frac{e^{\mu_i - x_i}}{1 + \sum_{j=1}^{N} e^{\mu_j - x_j}}. \tag{6}$$

Thus, Eq. (5) takes the form of a convolution equation.

Fourier analysis provides an immediate solution for the Fourier transform (FT) of the affinity spectrum. Since several definitions of FT are commonly found in the literature, we adhere to the FT definition of an arbitrary function f, as in Ref. 19,

$$\tilde{f}(\vec{\omega}) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{i(\vec{\omega}\cdot\vec{x})} f(\vec{x}) \prod_i dx_i, \tag{7}$$

where the components of vector $\vec{\omega} = (\omega_1, \omega_2, \ldots, \omega_N)$ are the variables in the Fourier space.

Bearing in mind that the FT of the convolution of two functions, is the product of their Fourier transforms and recalling that the FT of $p(-\vec{x})$ is the complex conjugate of the FT of $p(\vec{x})$, the Fourier transform of (5) leads to

$$\tilde{\theta}_i(\vec{\omega}) = \tilde{p}^*(\vec{\omega}) \tilde{g}_i(\vec{\omega}). \tag{8}$$

Nevertheless, as functions g_i and θ_i do not tend to zero in the limit $\mu_i \to \infty$, we modify Eq. (5) in such a way that Fourier analysis can be applied with well behaved functions.

From the total macromolecular coverage

$$\theta = \sum_{i=1}^{N} \theta_i \tag{9}$$

a new function B can be defined as

$$B(\vec{\mu}) = (-1)^{N+1} \frac{\partial^N \theta}{\partial \mu_1 \partial \mu_2 \cdots \partial \mu_N}. \tag{10}$$

This function, $B(\vec{\mu})$, has the properties of a density of probability if the macromolecular coverage is expressed, as in the present work, as a superposition of competitive langmuirian isotherms. As it is shown in Appendix A, $B(\vec{\mu})$ is positive for all values of μ_i,

$$B(\vec{\mu}) > 0 \quad \forall \mu_i \tag{11}$$

and its integral over all μ_i is

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} B(\vec{\mu}) \prod_i d\mu_i = 1. \tag{12}$$

As we will see, properties (11) and (12) will play an important role in Sec. III, in order to quantify the correlation in multicomponent affinity spectra.

Let us use $B(\vec{\mu})$ in solving (5). Differentiating both sides of (5) with respect to each $\mu_1, \mu_2, \ldots, \mu_N$, the integral equation becomes

$$B(\vec{\mu}) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} p(-\vec{x}) h(\vec{\mu} - \vec{x}) \prod_i dx_i, \tag{13}$$

where

$$h(\vec{\mu} - \vec{x}) = \Gamma(N+1) \frac{\prod_{i=1}^{N} e^{\mu_i - x_i}}{\left(1 + \sum_{j=1}^{N} e^{\mu_j - x_j}\right)^{N+1}} \tag{14}$$

and $\Gamma(i)$ is the gamma function.

In this way, we have transformed the integral equation (2) into another one which contain well behaved functions to apply Fourier analysis, since both B and h tend to zero when the respective variables μ_i or $\mu_i - x_i$ tend to $\pm\infty$.

B. Fourier analysis of the transformed equations: Analytical solution of Eq. (2)

Applying Fourier transform to both sides of Eq. (13) and using the FT convolution property (8),

$$\widetilde{B}(\vec{\omega}) = \widetilde{p}^*(\vec{\omega}) \widetilde{h}(\vec{\omega}). \tag{15}$$

Fortunately, the FT of function h,

$$\widetilde{h}(\vec{\omega}) = \Gamma(N+1) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{i(\vec{\omega} \cdot \vec{x})}$$

$$\times \frac{\prod_{i=1}^{N} e^{x_i}}{\left(1 + \sum_{j=1}^{N} e^{x_j}\right)^{N+1}} \prod_i dx_i, \tag{16}$$

can be computed analytically by introducing the change of variables $u_j = e^{x_j}$. Using the property,[20] $\widetilde{h}(\vec{\omega})$ can be written as

$$\widetilde{h}(\vec{\omega}) = \Gamma\left(1 - i \sum_{j=1}^{N} \omega_j\right) \prod_{j=1}^{N} \Gamma(1 + i\omega_j) \tag{17}$$

and, $\widetilde{B}(\vec{\omega})$ becomes

$$\widetilde{B}(\vec{\omega}) = \widetilde{p}^*(\vec{\omega}) \Gamma\left(1 - i \sum_{j=1}^{N} \omega_j\right) \prod_{j=1}^{N} \Gamma(1 + i\omega_j). \tag{18}$$

Notice that, regardless of the isotherm, Eq. (18) relates the macroscopic information contained in $\widetilde{B}$ (which is calculated from the competitive isotherm under study) to the microscopic information contained in the affinity spectrum. Isolating $\widetilde{p}^*$ in (18) and recalling the inverse FT of $\widetilde{p}^*$,

$$p(-\vec{x}) = \frac{1}{(2\pi)^N} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-i(\vec{\omega} \cdot \vec{x})} \widetilde{p}^*(\vec{\omega}) \prod_i d\omega_i, \tag{19}$$

we obtain for $p(\{\ln k_i\})$,

$$p(\{\ln k_i\}) = \frac{1}{(2\pi)^N} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{i\sum_{j=1}^{N} \omega_j \ln k_j}$$

$$\times \frac{\widetilde{B}(\vec{\omega})}{\Gamma\left(1 - i \sum_{j=1}^{N} \omega_j\right) \prod_{j=1}^{N} \Gamma(1 + i\omega_j)} \prod_i d\omega_i. \tag{20}$$

Equation (20) represents the sought inversion formula which provides, for a given competitive isotherm, the affinity spectrum (if it exists).

For the particular case of $N=1$, expression (20) reduces to

$$p(\ln k) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega \ln k} \frac{\widetilde{B}(\omega)}{\Gamma(1+i\omega) \Gamma(1-i\omega)} d\omega$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega \ln k} \widetilde{B}(\omega) \frac{\sinh(\pi\omega)}{\pi\omega} d\omega \tag{21}$$

which can be seen as an alternative to the classical inversion formula deduced by Sips.[10] Although we do not have a direct derivation of Sips inversion formula from the general equation (21), this expression can be easily tested, for instance, with the Langmuir–Freundlich isotherm,

$$\theta = \frac{(\bar{k}c)^m}{1 + (\bar{k}c)^m} = \frac{[e^{(\mu - \bar{x})}]^m}{1 + [e^{(\mu - \bar{x})}]^m}, \tag{22}$$

where m is the heterogeneity parameter for monocomponent systems. The Fourier transform of function $B(\mu)$ for this isotherm (as can easily be deduced from Appendix B, for the particular case of $N=1$) is

$$\widetilde{B}(\omega) = e^{+i\omega\bar{x}} \frac{\sinh \pi\omega}{m \sinh\left(\frac{\pi\omega}{m}\right)} \Gamma(1+i\omega) \Gamma(i-i\omega)$$

$$= e^{i\omega\bar{x}} \frac{\pi\omega}{m \sinh\left(\frac{\pi\omega}{m}\right)}. \tag{23}$$

Replacing (23) in (21) and using Ref. 19, the well-known Sips distribution is obtained,

$$p(\ln k) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega(\ln k - \ln \bar{k})} \frac{\sinh \pi\omega}{m \sinh\left(\dfrac{\pi\omega}{m}\right)} d\omega$$

$$= \frac{\sin(\pi m)}{2\pi(\cosh(m(\ln k - \ln \bar{k})) + \cos \pi m)}. \tag{24}$$

III. DETERMINATION OF THE AFFINITY SPECTRUM UNDERLYING SOME ISOTHERMS

A. Affinity spectrum underlying NICCA isotherm

One of the most used multicomponent isotherms, especially in the field of environmental chemistry, is the NICCA (nonideal competitive consistent adsorption) isotherm, which can be written as[21]

$$\theta_i = \frac{n_i}{n_H} \frac{(\bar{k}_i c_i)^{n_i}}{\displaystyle\sum_{j=1}^{N} (\bar{k}_j c_j)^{n_j}} \frac{\left[\displaystyle\sum_{j=1}^{N} (\bar{k}_j c_j)^{n_j}\right]^p}{1 + \left[\displaystyle\sum_{j=1}^{N} (\bar{k}_j c_j)^{n_j}\right]^p} \tag{25}$$

or, in terms of the variable $\mu_i = \ln c_i$, as

$$\theta_i = \frac{n_i}{n_H} \frac{e^{n_i(\mu_i - \bar{x}_i)}}{\displaystyle\sum_{j=1}^{N} e^{n_j(\mu_j - \bar{x}_j)}} \frac{\left[\displaystyle\sum_{j=1}^{N} e^{n_j(\mu_j - \bar{x}_j)}\right]^p}{1 + \left[\displaystyle\sum_{j=1}^{N} e^{n_j(\mu_j - \bar{x}_j)}\right]^p}, \tag{26}$$

where $\bar{x}_i = -\ln \bar{k}_i$ and $\bar{k}_i$, n_i, and p are parameters of the isotherm. NICCA has been widely used to discuss the cation binding to humic substances. It accounts for heterogeneous competitive binding, being $\bar{k}_i$ related to the median affinity for ion i, p describing a common distribution of affinities seen by all the ions and n_i taking into account an ion specific heterogeneity. The factor n_i/n_H, where H refers to the proton, was introduced as a more general way to keep thermodynamic consistency from a previous expression of the isotherm[22] which required equal n_i values for all the ions in order to satisfy thermodynamic consistency. In the current generalized way, the maximum binding capacity is ion dependent which could reflect some degree of multidentism. As this effect suggests the use of local isotherms other than the competitive Langmuirian one considered in this work, we will restrict ourselves to the case $n_H = n_i$, $\forall i$.

Let us then apply the inversion formula (20) to a bicomponent system ($N = 2$) described by NICCA isotherm with $n_1 = n_2 = n$. Computing the total coverage θ and performing the derivatives involved in (10), $\tilde{B}$ corresponding to a bicomponent NICCA isotherm [see Appendix B, Eq. (B12)] becomes

$$\tilde{B}(\omega_1, \omega_2) = e^{i(\omega_1 \tilde{x}_1 + \omega_2 \tilde{x}_2)} \frac{\sinh[\pi(\omega_1 + \omega_2)/n]}{p \sinh[\pi(\omega_1 + \omega_2)/np]}$$

$$\times \Gamma(1 + i\omega_1/n)\Gamma(1 + i\omega_2/n)$$

$$\times \Gamma(1 - i(\omega_1 + \omega_2)/n). \tag{27}$$

Replacing this expression into Eq. (20) and using the relationship $\Gamma(1 + z) = z\Gamma(z)$,[20] we obtain

$$p(\ln k_1, \ln k_2)$$

$$= \frac{1}{(2\pi)^2} \frac{1}{n^3 p} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{i(\omega_1(\ln k_1 - \ln \bar{k}_1) + \omega_2(\ln k_2 - \ln \bar{k}_2))}$$

$$\times \frac{\sinh[\pi(\omega_1 + \omega_2)/n]}{\sinh[\pi(\omega_1 + \omega_2)/np]}$$

$$\times \frac{\Gamma(i\omega_1/n)\Gamma(i\omega_1/n)\Gamma(-i(\omega_1 + \omega_2)/n)}{\Gamma(i\omega_1)\Gamma(i\omega_2)\Gamma(-i(\omega_1 + \omega_2))} d\omega_1 d\omega_2. \tag{28}$$

Recalling now the Dirac δ-function, whose integral representation can be written as

$$\delta(q - (\omega_1 + \omega_2)) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i(q - (\omega_1 + \omega_2))u} du, \tag{29}$$

Eq. (28) rewrites

$$p(\ln k_1, \ln k_2) = \int_{-\infty}^{\infty} \phi(\ln k_1 - \ln \bar{k}_1 - u)$$

$$\times \phi(\ln k_2 - \ln \bar{k}_2 - u)\psi(u)du, \tag{30}$$

where ϕ and ψ are real-valued functions, defined as

$$\phi(u) = \frac{1}{(2\pi)n} \int_{-\infty}^{\infty} e^{iuq} \frac{\Gamma(iq/n)}{\Gamma(iq)} dq \tag{31}$$

and

$$\psi(u) = \frac{1}{(2\pi)np} \int_{-\infty}^{\infty} e^{iuq} \frac{\Gamma(-iq/n)}{\Gamma(-iq)} \frac{\sinh(\pi q/np)}{\sinh(\pi q)} dq. \tag{32}$$

Figure 1 depicts the affinity spectrum corresponding to NICCA isotherm as a function of $\log(k_1)$ and $\log(k_2)$ (we take decimal logarithms, as it is usually done in the literature) with parameters $n = p = 0.5$ and $\bar{k}_1 = \bar{k}_2 = 1$. The distribution basically corresponds to that obtained numerically in Ref. 13 by using regularization methods, this supporting the suitability of the numerical methods in the obtention of multicomponent affinity spectra. Notice that the spectrum obtained is symmetrical with respect to the line $x_1 - \bar{x}_1 = x_2 - \bar{x}_2$, something that is directly shown by Eq. (30), which remains invariant under the change $x_1 - \bar{x}_1 \leftrightarrow x_2 - \bar{x}_2$. The spectrum is clearly elongated along this line, evidencing the fact that NICCA isotherm implies nonzero correlation between the binding energy of both components. Conversely, this elongation is greatly reduced when the p value is equal to 1, see Fig. 2, indicating that this parameter plays an important role in the binding correlation of the two components, as was previously reported by Ref. 13. This result agrees with the classical meaning given to p, $0 \leq p \leq 1$, which relates this parameter with a common distribution of affinities seen by all the ions,[21,22] decreasing the width of the distribution as p approaches 1.
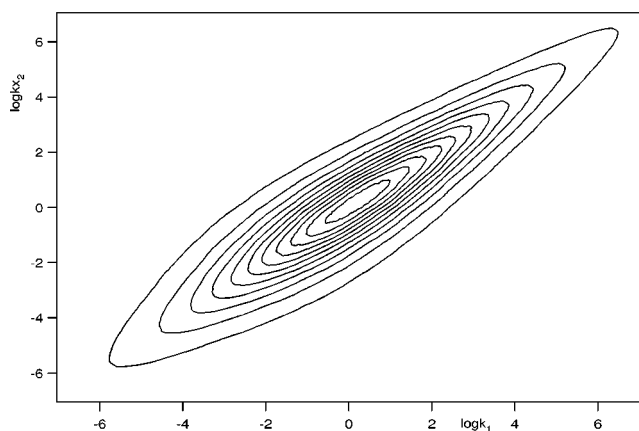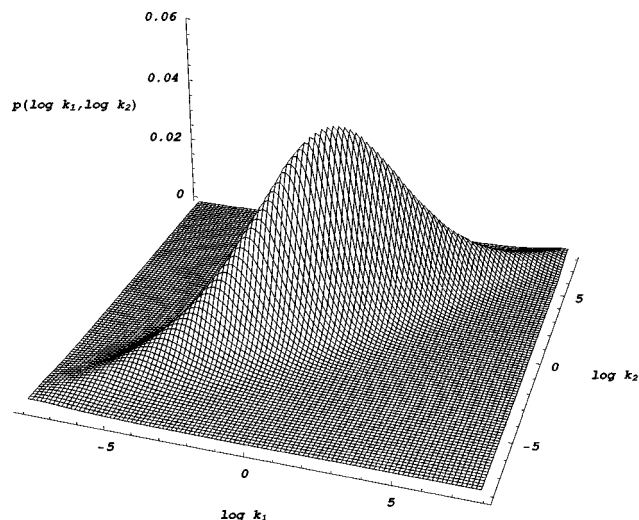
FIG. 1. Two-dimensional affinity spectrum underlying NICCA isotherm for $n = p = 0.5$, $\bar{k}_1 = \bar{k}_2 = 1$ shown as a relief plot (a) or as a contour plot (b).
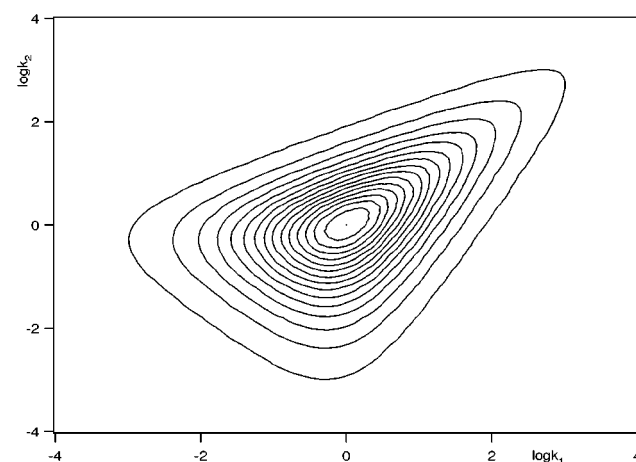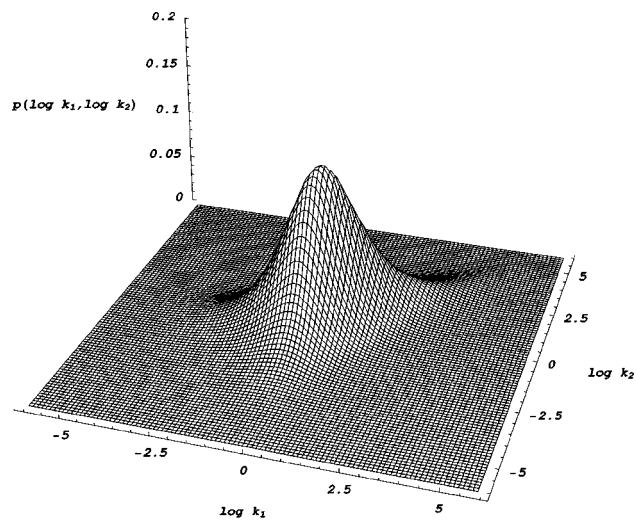

FIG. 2. Two-dimensional affinity spectrum underlying NICCA isotherm for $n = 0.5$, $p = 1$, and $\bar{k}_1 = \bar{k}_2 = 1$ shown as a relief plot (a) or as a contour plot (b).

B. Affinity spectrum underlying the multicomponent Frumkin isotherm

The inversion formula (20) can also be used to obtain the spectrum corresponding to other multicomponent isotherms. Among them, we have chosen the competitive Frumkin isotherm, which for a system of two components reads[1]

$$\theta_1 = b_1 c_1 (1 - \theta_1 - \theta_2) \exp(\rho_{11}\theta_1 + \rho_{12}\theta_2),$$
$$\theta_2 = b_2 c_2 (1 - \theta_1 - \theta_2) \exp(\rho_{22}\theta_2 + \rho_{12}\theta_1), \tag{33}$$

where b_i and ρ_{ij} are parameters of the isotherm.

Unfortunately, the FT of function B cannot be obtained analytically, so that we have to compute numerically the FT's appearing in the inversion formula (20) to obtain the spectrum. The result is shown in Figs. 3(a) or 3(b), where parameters $b_1 = b_2 = 1$, $\rho_{11} = \rho_{22} = 1$, and $\rho_{12} = 0.5$ have been used. In this case, an ellipsoidal oblate shape is obtained for the resulting spectrum. It can be observed that spurious oscillations appear, especially close to the top of the oblate which we expect to be of a smoothed form with a maximum. It is likely that these oscillations come from the fact that the affinity distribution of the Frumkin isotherm is nonzero only over a finite domain of $\ln k$. This behavior has also been found in the inversion of the monocomponent Frumkin isotherm.[23]

Notice also that the average $\log k$ along each axis of the spectrum of Fig. 3 is not zero [see Fig. 3(b)] although $b_1 = b_2 = 1$ ($\log b_1 = 0, \log b_2 = 0$) in parallel to what happens in the monocomponent Frumkin isotherm, whose mean binding energy does not coincide with the logarithm of the parameter b appearing in the isotherm.

IV. CENTRAL MOMENTS OF A MULTIDIMENSIONAL AFFINITY SPECTRUM

As it has been commented above, the integral equation (2) is an ill-posed problem for $p(\{\ln k_i\})$. This means that the coverage predicted by different isotherms can be almost the same over decades of the free metal concentration or, in other words, the description of the binding does not require all the information contained in the affinity spectrum. We can say that there is a great instability in the recovered affinity spectrum from (20) since the binding data do not contain enough information for a precise recovering of $p(\{\ln k_i\})$.

A robust strategy in these conditions is the determination of the first central moments of the spectrum, which actually
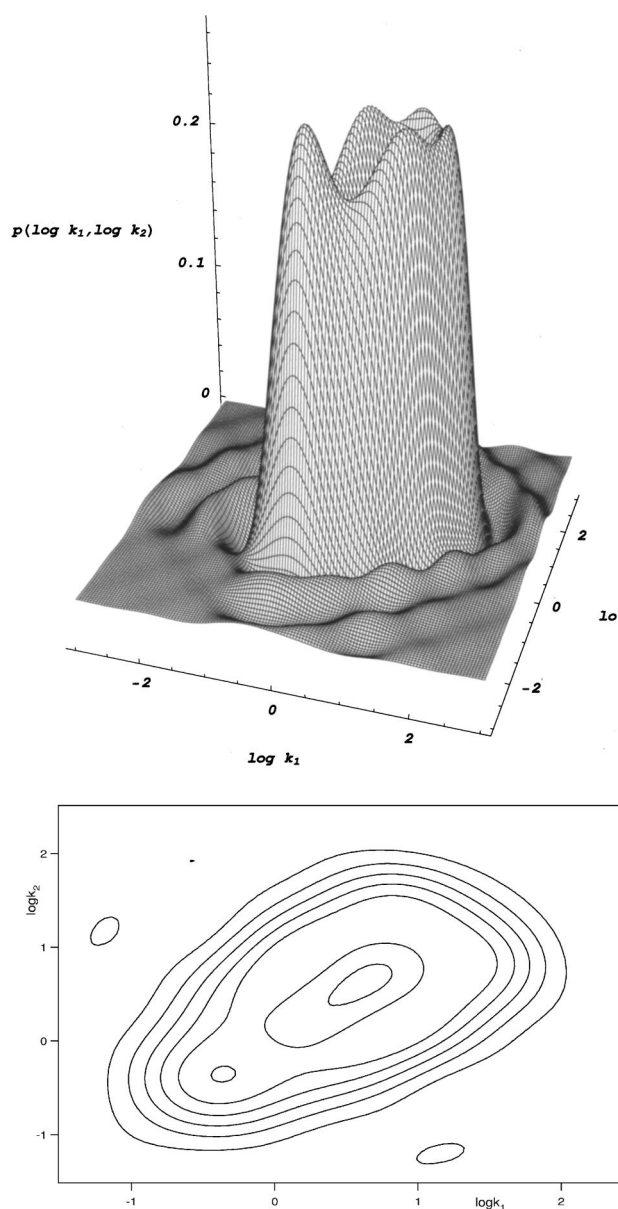
FIG. 3. Two-dimensional affinity spectrum shown as a relief plot (a) or as a contour plot (b) corresponding to the Frumkin isotherm obtained by numerically computing Eq. (18). The parameters are $b_1 = b_2 = 1$, $\rho_1 = \rho_2 = 1.5$, $\rho_{12} = 0.5$.

contain the relevant information for the binding description. Let us now solve this problem with a method that avoids the recovering of $p(\{\ln k_i\})$ from (20).

We begin recalling that the mean binding energy of component i is proportional to

$$\langle \ln k_i \rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \ln k_i\, p(\{\ln k_j\}) \prod_j d\ln k_j, \quad (34)$$

where the symbol $\langle\ \rangle$ indicates average over the distribution p. Likewise, the variance and covariance of the binding energy between two components is quantified by the so-called covariance matrix, $\mathbf{C}$ of the probability distribution p, whose components are defined as

$$C_{ij} = \langle \ln k_i \ln k_j \rangle - \langle \ln k_i \rangle \langle \ln k_j \rangle. \quad (35)$$

Obviously, C_{ii} is the variance of the binding energy of component i,

$$C_{ii} = \langle \ln k_i^2 \rangle - \langle \ln k_i \rangle^2 = \sigma_i^2, \quad (36)$$

while C_{ij} is the covariance between the binding energy of component i and j. The covariance quantifies to which extent an increase of the affinity of a particular site for one component, implies an increase of the affinity of such a site for the others components.[13,21,22] Two limiting cases can be considered: when we have full correlation, for any site, there is a fixed shift, α, between the binding energy of component 1 and the binding energy of component 2 at the same site, so that the multicomponent affinity spectrum takes the form

$$p(\ln k_1, \ln k_2) = p_1(\ln k_1)\, \delta(\ln k_2 - \ln k_1 - \alpha). \quad (37)$$

In this case, the one-dimensional affinity spectrum for both components has the same shape while they may differ in the location along the $\ln k$ axis. This situation is also called congruent adsorption.

When the affinity spectrum is fully uncorrelated, $C_{ij} = 0$ for $i \neq j$; for a given site, there is no relation between the affinity for component 1 and component 2, $\ln k_1$ and $\ln k_2$ are statistically independent variables and the affinity spectrum reads

$$p(\ln k_1, \ln k_2) = p_1(\ln k_1)\, p_2(\ln k_2). \quad (38)$$

For the most general case, some correlation is present and no factorization of $p(\ln k_1, \ln k_2)$ is possible. A dimensionless measure of the correlation between the binding energy of component i and j is the correlation coefficient, R_{ij},

$$R_{ij} = \frac{C_{ij}}{\sigma_i \sigma_j} \quad (i \neq j). \quad (39)$$

Obviously, for a two-component system, there is only one correlation coefficient which we will label as $R = R_{12} = R_{21}$.

On the other hand, for a given probability distribution function, p, the mean and the covariance matrix can be understood as particular cases of the so-called cumulants of the distribution function. The cumulant generating function, K, for a given distribution p can be written as[24]

$$K(\vec{\omega}) = \ln \tilde{p}(\vec{\omega})$$
$$= \ln\left[\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{i\sum_{j=1}^{N} \omega_j \ln k_j}\, p(\{\ln k_i\}) \prod_i d\ln k_i \right]. \quad (40)$$

The cumulants, $\kappa_{jkl...}$, of the distribution $p(\{\ln k_i\})$, are defined as the coefficients appearing in the series expansion of $K(\vec{\omega})$,

$$K(\vec{\omega}) = i\sum_j \kappa_j \omega_j + \frac{i^2}{2} \sum_{jk} \kappa_{jk} \omega_j \omega_k$$
$$+ \frac{i^3}{3!} \sum_{jkl} \kappa_{jkl} \omega_j \omega_k \omega_l + \cdots. \quad (41)$$

Although a general relationship between cumulants and central moments is not simple, it is a well-known result of probability theory that κ_i, the first order cumulant, is the average of the distribution function,

$$\kappa_i = \langle \ln k_i \rangle, \tag{42}$$

while κ_{ij}, the cumulants of second order, are the elements of the covariance matrix

$$\kappa_{ij} = C_{ij} = \langle \ln k_i \ln k_j \rangle - \langle \ln k_i \rangle \langle \ln k_j \rangle. \tag{43}$$

A practical fact on the computation of the central moments of the multidimensional distribution functions defined as indicated in Eq. (2) can be noticed: if we are interested in the first and second order moments, the knowledge of the full affinity spectrum is not necessary. One only needs the spectrum of simpler systems where only one or two components are present. This is easily shown by observing that, for instance,

$$\langle \ln k_i \ln k_j \rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \ln k_i \ln k_j p(\{\ln k_l\}) \prod_l d\ln k_l$$

$$= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \ln k_i \ln k_j q(\ln k_i, \ln k_j)$$

$$\times d\ln k_i d\ln k_j, \tag{44}$$

where

$$q(\ln k_i, \ln k_j)$$

$$= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} p(\{\ln k_l\}) d\ln k_1 \cdots d\ln k_{i-1}$$

$$\times d\ln k_{i+1} \cdots d\ln k_{j-1} d\ln k_{j+1} \cdots d\ln k_N \tag{45}$$

indicating that the computation of $\langle \ln k_i \ln k_j \rangle$ does not require the knowledge of the full spectrum $p(\{\ln k_i\})$, but of only $q(\ln k_i, \ln k_j)$. Due to the particular form of the kernel of Eq. (2), $q(\ln k_i, \ln k_j)$ is the affinity distribution function that is found by taking in the multicomponent local isotherm all the concentrations equal to zero except those of components i and j. In effect

$$\theta_i(0,0,...,0,c_i,0,...,0,c_j,...,0)$$

$$= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} p(\{\ln k_l\}) \frac{k_i c_i}{1 + k_i c_i + k_j c_j} \prod_l d\ln k_l$$

$$= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} q(\ln k_i, \ln k_j) \frac{k_i c_i}{1 + k_i c_i + k_j c_j} d\ln k_i d\ln k_j. \tag{46}$$

This means that obtaining the mean and covariance matrix for multicomponent systems can be done from the study of all the monocomponent systems and from the study of the bicomponent systems where only the different couples of components are present.

A. Calculation of the mean and covariance matrix of the spectrum associated to a competitive isotherm

We can now take advantage of Eq. (18) to carry out the calculation of the cumulants of multicomponent affinity spectra. Taking logarithms at both sides of (18) we obtain

$$\ln \tilde{p}^*(\vec{\omega}) = \ln \tilde{B}(\vec{\omega}) - \sum_{j=1}^{N} \ln \Gamma(1 + i\omega_j)$$

$$- \ln \Gamma\left(1 - i\sum_{j=1}^{N} \omega_j\right). \tag{47}$$

Recalling that $\ln \tilde{p}^* = (\ln \tilde{p})^*$, the left-hand side of (47) can be related to the cumulants of p as

$$\ln \tilde{p}^*(\vec{\omega}) = -i\sum_j \kappa_j \omega_j + \frac{i^2}{2} \sum_{jk} \kappa_{jk} \omega_j \omega_k$$

$$- \frac{i^3}{3!} \sum_{jkl} \kappa_{jkl} \omega_j \omega_k \omega_l + \cdots. \tag{48}$$

On the other hand, B has all the properties of a distribution function, as pointed out in Sec. II A. Thus, Eq. (47) simply expresses the fact that the complex conjugate of the cumulant generating function of $p(\{\ln k_i\})$, is the cumulant generating function of B plus a function independent of the particular isotherm under study. We can now expand both sides of (47) in terms of the Fourier set of variables, w_i. Expansion of the left-hand side (lhs) of (47) leads to the cumulants of $p(\{\ln k_i\})$, Eq. (48), and the expansion of the first term on the right-hand side (rhs) of (47) leads to the cumulants of B,

$$\ln \tilde{B}(\vec{\omega}) = i\sum_i \kappa_i^B \omega_i + \frac{i^2}{2} \sum_{ij} \kappa_{ij}^B \omega_i \omega_j$$

$$+ \frac{i^3}{3!} \sum_{ijk} \kappa_{ijk}^B \omega_i \omega_j \omega_k + \cdots, \tag{49}$$

where the superscript B recalls that these cumulants refer to the B distribution at the same time that it allows to differentiate both cumulants.

The expansion of the second term of the rhs of (47) can be done using[20]

$$\ln \Gamma(1 + z) = -Cz + \sum_{j=2}^{\infty} \frac{(-z)^j}{j} \zeta(j), \tag{50}$$

where C is the Catalan constant and $\zeta(z)$ is the Riemann's zeta function. Identifying in the resulting equation the terms of the same power on w_i, for the first two cumulants of the affinity spectrum (mean and covariance matrix) we obtain

$$\kappa_i = \langle \ln k_i \rangle = -\kappa_i^B = -\int_{-\infty}^{\infty} \mu_i B^{(i)}(\mu_i) d\mu_i, \tag{51}$$

where $B^{(i)}(\mu_i)$ is the function B corresponding to the monocomponent system obtained by taking all the concentrations equal to zero except that of component i.

Proceeding analogously, the covariance matrix is

$$\kappa_{ij} = C_{ij} = \kappa_{ij}^B - \frac{\pi^2}{6} = C_{ij}^B - \frac{\pi^2}{6} \quad (i \neq j) \tag{52}$$

and

$$\kappa_{ii} = C_{ii} = \kappa_{ii}^B - \frac{\pi^2}{3} = C_{ii}^B - \frac{\pi^2}{3} \quad (i=j), \tag{53}$$

where the elements C_{ij}^B are

$$C_{ij}^B = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \mu_i \mu_j B^{(ij)}(\mu_i, \mu_i) d\mu_i \, d\mu_j - \kappa_i^B \kappa_j^B, \tag{54}$$

where $B^{(ij)}(\mu_i, \mu_i)$ is the function B corresponding to the two-component system obtained by taking all the concentrations equal to zero except those of components i and j.

Equations (51)–(53) give the mean binding energy and the elements of the covariance matrix underlying any competitive isotherm in terms of the isotherm parameters through B, obtained from the derivatives of the isotherm, and without requiring the knowledge of the affinity spectrum.

B. Binding correlation in NICCA and Frumkin isotherms

First we are going to use the results presented above to obtain the mean and the correlation matrix corresponding to NICCA isotherm with $n_1 = n_2 = n$. Performing the corresponding integrals we obtain

$$\kappa_i = \langle \ln k_i \rangle = \ln \bar{k}_i \tag{55}$$

and

$$C_{ii} = \sigma_i^2 = \frac{\pi^2}{3} \left(\frac{1 - n^2 p^2}{n^2 p^2} \right) = \frac{\pi^2}{3} \left(\frac{1-m^2}{m^2} \right), \tag{56}$$

$$C_{ij} = \frac{\pi^2}{6} \left(\frac{2 - p^2 - n^2 p^2}{n^2 p^2} \right) \quad (i \neq j), \tag{57}$$

the correlation coefficient becoming

$$R = R_{ij} = \frac{2 - p^2 - n^2 p^2}{2(1 - n^2 p^2)} = \frac{2 - p^2 - m^2}{2(1 - m^2)}. \tag{58}$$

The diagonal elements of the correlation matrix, C_{ii} give the variance of a Sips distribution with heterogeneity parameter $m = np$,[18] in agreement with the fact that NICCA isotherm reduces to a Langmuir–Freundlich isotherm when only one component is present. This means that $m = np$ is the responsible of the heterogeneity of adsorbate i, a heterogeneity that is also present even in absence of the rest of components.

In Fig. 4, the correlation coefficient, given by (58), is plotted as a function of the parameter p for different values of m. Notice that R is always positive ranging between 0.5 and 1, corresponding these limiting cases to $p=1$ and $p = m$, respectively. For $p=1$, NICCA isotherm reduces to the so-called Langmuir–Freundlich generalized isotherm

$$\theta_i = \frac{\sum_{j=1}^{N} (\bar{k}_j c_j)^m}{1 + \sum_{j=1}^{N} (\bar{k}_j c_j)^m} \tag{59}$$

for which (58) prescribes $R = 1/2$, independently of the m value. This fact corresponds to the situation of minimum
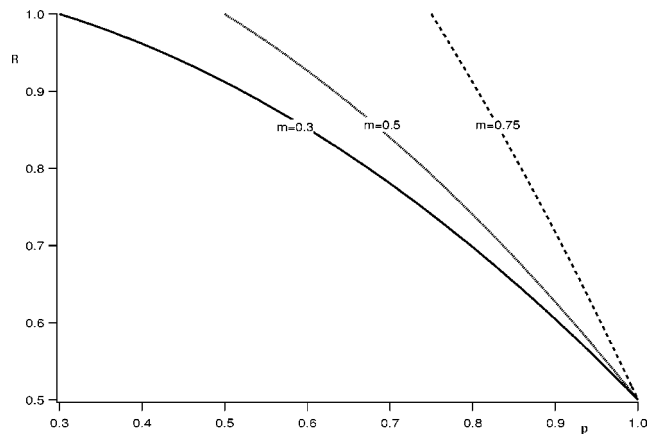

FIG. 4. Correlation coefficient corresponding to NICCA isotherm as a function of parameter p, for different values of intrinsic heterogeneity parameter $m = np$: $z = 0.3$ (continuous line); $m = 0.5$ (dotted line); $m = 0.75$ (dashed line).

correlation of binding between the different components allowed by this isotherm. For $p = m$, i.e., $n = 1$, we have $R = 1$, i.e., a situation of fully correlation, in agreement with the original consideration of p as a measure of the heterogeneity of the ligand, in contrast with m, a parameter ion dependent which reflects the deviation of the local binding from the ideal case ($n = 1$).[21,22] Thus, if $n = 1$, the only one source of heterogeneity comes from the ligand and is common for all the ions (described by p) leading to fully correlation or congruent binding.

The correlation coefficient corresponding to a two-component Frumkin isotherm is plotted as a function of the interaction parameter ρ_{12}, for different values of ρ_{11} and ρ_{22} in Fig. 5. Notice that, while in the NICCA isotherm considered above ($n_1 = n_2 = n$) we have only two parameters (n and p) to reproduce three independent statistical properties of the spectrum (for instance, the two variances and the correlation coefficient), in this case we have three parameters to describe them. In this sense, the present situation is more flexible, which can be seen for instance in the values scanned by the correlation coefficient, depicted in Fig. 5. Since an analytical expression for the correlation coefficient is not available for the two-component Frumkin isotherm, we have calculated it from (54) and (39), performing the integrals numerically.
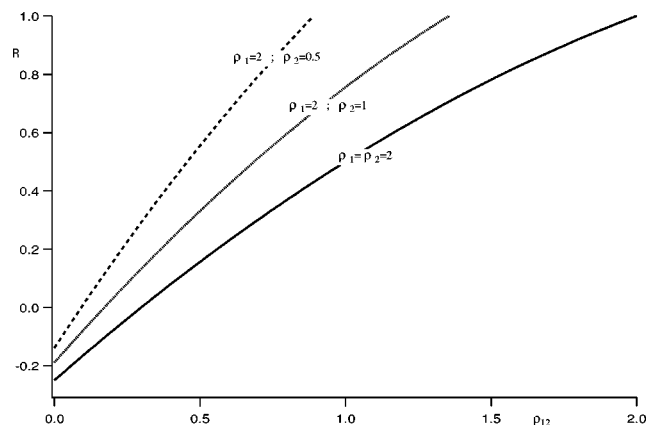

FIG. 5. Correlation coefficient corresponding to Frumkin isotherm as a function of ρ_{12}, for $\rho_1 = 2$ and $\rho_2 = 2$ (continuous line); $\rho_1 = 2$ and $\rho_2 = 1$ (dotted line); $\rho_1 = 2$ and $\rho_2 = 0.5$ (dashed line).

Notice that, via a suitable selection of the parameters, any value of the correlation coefficient can be achieved in this case, according to the more flexible situation that we are considering. On the other hand, although we do not have a general condition for the achievement of the maximum level of correlation ($R=1$), we can see that for $\rho_{12}=\rho_{11}=\rho_{22}$, $R=1$. In effect, when all the interaction parameters are equal, all the components of the system behave likely from the point of view of heterogeneity.

V. CONCLUDING REMARKS

We have undertaken the problem of obtaining the affinity spectrum underlying multicomponent adsorption isotherms. The main difficulty lies in the fact that the integral equation to be solved involves the integration over several variables (as many as number of components can be adsorbed). Nevertheless, by rewriting the integral equation in a suitable manner, a general analytical solution can be found. This implies the definition of a new function, B, basically a Nth derivative of the total macromolecular coverage, which has the properties of a probability distribution function. By further applying Fourier transform techniques, we have been able to provide an inversion formula, which is the counterpart to that given by Sips for one-component systems.

The analytical solution obtained has been applied to NICCA isotherm, commonly used in environmental water studies and an analytical expression for the underlying spectrum has been derived. The resulting spectrum agrees with that obtained numerically in the literature by using least-square regularization methods. The spectrum associated to Frumkin isotherm is also computed, although in this case numerical FT transform techniques have been used and some spurious oscillations remain.

On the other hand, a method to obtain the main statistical properties of multicomponent affinity spectra underlying competitive isotherms as a function of the isotherm parameters is presented. An expression for the cumulants of the affinity spectrum in terms of the cumulants of the function B has been reported. These results lead to analytical expressions for the mean and covariance matrix of NICCA isotherm, and, by performing the suitable numerical integrations, to those of Frumkin isotherm. These results allow to quantify the level of binding correlation among the different adsorbing molecules.

ACKNOWLEDGMENTS

APPENDIX A: THE FUNCTION $B(\vec{\mu})$ CAN BE CONSIDERED A PROBABILITY DISTRIBUTION FUNCTION

The function $B(\vec{\mu})$ is defined as

$$B(\vec{\mu})=(-1)^{N+1}\frac{\partial^N \theta}{\partial \mu_1 \partial \mu_2 \cdots \partial \mu_N}, \tag{A1}$$

where $\theta=\Sigma_{i=1}^N \theta_i$ is the total macromolecular coverage and $\mu_i=\ln c_i$. If the macromolecular coverage can be expressed by means of certain affinity spectrum $p(\{\ln k_i\})$ we have

$$\theta(\vec{\mu})=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}p(\{\ln k_i\})$$
$$\times\frac{\sum_{i=1}^N e^{\ln k_i+\mu_i}}{\left(1+\sum_{j=1}^N e^{\ln k_j+\mu_j}\right)^{N+1}}\prod_i d\ln k_i. \tag{A2}$$

Performing the derivatives indicated in (A1), $B(\vec{\mu})$ becomes

$$B(\vec{\mu})=\Gamma(N+1)\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}p(\{\ln k_i\})$$
$$\times\frac{\prod_{i=1}^N e^{\ln k_i+\mu_i}}{\left(1+\sum_{j=1}^N e^{\ln k_j+\mu_j}\right)^{N+1}}\prod_i d\ln k_i. \tag{A3}$$

Since all the terms in the integrals appearing in (A3) are positive, we have $B(\vec{\mu})>0$ for all the μ_i values.

On the other hand, the integration of both sides of (A3) with respect $\mu_1,\mu_2,\ldots,\mu_N$,

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}B(\vec{\mu})\prod_j d\mu_j$$
$$=\Gamma(N+1)\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}p(\{\ln k_i\})$$
$$\times\left\{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\frac{\prod_{i=1}^N e^{\ln k_i+\mu_i}}{\left(1+\sum_{j=1}^N e^{\ln k_j+\mu_j}\right)^{N+1}}\prod_j d\mu_j\right\}$$
$$\times\prod_i d\ln k_i \tag{A4}$$

taking into account that

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\frac{\prod_{i=1}^{N}e^{\ln k_i+\mu_i}}{\left(1+\sum_{j=1}^{N}e^{\ln k_j+\mu_j}\right)^{N+1}}\prod_{j}d\mu_j$$

$$=\frac{1}{\Gamma(N+1)} \tag{A5}$$

the normalization condition of the affinity spectrum, leads to

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}B(\vec{\mu})\prod_{j}d\mu_j=1 \tag{A6}$$

which is the normalization condition for B.

APPENDIX B: FT OF FUNCTION $B(\mu_1,\mu_2)$ FOR THE NICCA ISOTHERM

The Fourier transform of function B for the two-component NICCA isotherm can be written as

$$\tilde{B}(\omega_1,\omega_2)=-\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}e^{i(\omega_1\mu_1+\omega_2\mu_2)}\frac{\partial^2}{\partial\mu_1\partial\mu_2}$$
$$\times\left\{\frac{[e^{n(\mu_1-\bar{x}_1)}+e^{n(\mu_2-\bar{x}_2)}]^p}{1+[e^{n(\mu_1-\bar{x}_1)}+e^{n(\mu_2-\bar{x}_2)}]^p}\right\}d\mu_1\,d\mu_2, \tag{B1}$$

where the definition of B, Eq. (10), the expression of the NICCA isotherm, Eq. (26) with $n_H=n_1=n_2$, and the definition of FT, Eq. (7), have been used.

Introducing the change of variables $y_1=n(\mu_1-\bar{x}_1)$ and $y_2=n(\mu_2-\bar{x}_2)$ the integral becomes

$$\tilde{B}(\omega_1,w\omega_2)=e^{i(\omega_1\bar{x}_1+\omega_2\bar{x}_2)}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}e^{i[y_1(\omega_1/n)+y_2(\omega_2/n)]}$$
$$\times F(y_1,y_2)dy_1\,dy_2$$
$$=e^{i(\omega_1\bar{x}_1+\omega_2\bar{x}_2)}\tilde{F}\left(\frac{\omega_1}{n},\frac{\omega_2}{n}\right), \tag{B2}$$

where

$$F(y_1,y_2)=-\frac{\partial^2}{\partial y_1\partial y_2}\left\{\frac{[e^{y_1}+e^{y_2}]^p}{1+[e^{y_1}+e^{y_2}]^p}\right\}. \tag{B3}$$

and $\tilde{F}(\omega_1/n,\omega_2/n)$ is the FT of $F(y_1,y_2)$ when ω_i/n label the variables in the Fourier space.

Notice that the function $[e^{y_1}+e^{y_2}]^p/(1+[e^{y_1}+e^{y_2}]^p)$ can be expressed as

$$\frac{[e^{y_1}+e^{y_2}]^p}{1+[e^{y_1}+e^{y_2}]^p}=\int_{-\infty}^{\infty}P_{Sips}(u_1;p)\frac{e^{y_1}e^{-u_1}+e^{y_2}e^{-u_1}}{1+e^{y_1}e^{-u_1}+e^{y_2}e^{-u_1}}du_1$$

$$=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}P_{Sips}(u_1;p)\delta(u_1-u_2)$$

$$\times\frac{e^{y_1}e^{-u_1}+e^{y_2}e^{-u_2}}{1+e^{y_1}e^{-u_1}+e^{y_2}e^{-u_2}}du_1\,du_2, \tag{B4}$$

where $P_{Sips}(u;p)$ is the Sips distribution function with zero mean,

$$P_{Sips}(u;p)=\frac{\sin[\pi p]}{2\pi(\cosh pu+\cos\pi p)} \tag{B5}$$

which yields the Langmuir–Freundlich isotherm. Performing now the derivatives in (B3), the term $F(y_1,y_2)$ becomes

$$F(y_1,y_2)=2\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}P_{Sips}(u_1;p)\delta(u_1-u_2)$$
$$\times\frac{e^{y_1-u_1}e^{y_2-u_2}}{(1+e^{y_1-u_1}+e^{y_2-u_2})^3}du_1\,du_2 \tag{B6}$$

which is the convolution product of functions

$$f_1(x_1,x_2)=P_{Sips}(x_1;p)\delta(x_1-x_2) \tag{B7}$$

and

$$f_2(x_1,x_2)=\frac{2e^{x_1}e^{x_2}}{(1+e^{x_1}+e^{x_2})^3}. \tag{B8}$$

Hence, the Fourier transform of function $F(y_1,y_2)$ is the product of the Fourier transform of these last two functions,

$$\tilde{F}(\omega_1,\omega_2)=\tilde{f}_1(\omega_1,\omega_2)\tilde{f}_2(\omega_1,\omega_2), \tag{B9}$$

where

$$\tilde{f}_1(\omega_1,\omega_2)=\frac{\sinh[\pi(\omega_1+\omega_2)]}{p\sinh[\pi(\omega_1+\omega_2)/p]} \tag{B10}$$

and

$$\tilde{f}_2(\omega_1,\omega_2)=\Gamma(1+i\omega_1)\Gamma(1+i\omega_2)\Gamma(1-i(\omega_1+\omega_2)). \tag{B11}$$

Equation (B10) is the FT of the generalized Sips distribution (B5) for a two component system, and can be obtained using Ref. 19. Thus, the Fourier transform of function $B(\mu_1,\mu_2)$, Eq. (B2), becomes

$$\tilde{B}(\omega_1,\omega_2)=e^{i(\omega_1\bar{x}_1+\omega_2\bar{x}_2)}\tilde{F}\left(\frac{\omega_1}{n},\frac{\omega_2}{n}\right)$$
$$=e^{i(w_1\bar{x}_1+w_2\bar{x}_2)}\frac{\sinh[\pi(\omega_1+\omega_2)/n]}{p\sinh[\pi(\omega_1+\omega_2)/np]}$$
$$\times\Gamma(1+i\omega_1/n)\Gamma(1+i\omega_2/n)$$
$$\times\Gamma(1-i(\omega_1+\omega_2)/n). \tag{B12}$$

[1] J. Buffle, *Complexation Reactions in Aquatic Systems*, Ellis Horword series in Analytical Science (Ellis Horwood Limited, Chichester, 1988), Chap. 5.

[2] M. M. Nederlof, W. H. van Riemsdijk, and L. K. Koopal, in *Heavy Metals in the Environment, Trace Metals in the Environment*, edited by J. P. Verner (Elsevier, Amsterdam, 1991), Vol. 1, pp. 365–396.

[3] M. Cernik, M. Borkovec, and J. C. Westall, Environ. Sci. Technol. **29**, 413 (1995).

[4] M. Jaroniec and P. Bräuer, Surf. Sci. Rep. **6**, 65 (1986).

[5] M. Jaroniec and R. Madey, in *Physical Adsorption on Heterogeneous Solids* (Elsevier, Amsterdam, 1988).

[6] C. Brunni, A. Germani, G. Kochi, and R. Strom, J. Theor. Biol. **61**, 143 (1976).

[7] P. Szabelski, K. Kaczmarski, A. Cavazzini, Y. B. Chen, B. Sellergren, and G. Guiochon, J. Chromatogr. A **964**, 99 (2002).

[8] R. J. Umpleby, S. Baxter, Y. Chen, R. N. Shah, and K. D. Shimizu, Anal. Chem. **73**, 4584 (2001).

[9] T. Takeuchi, T. Mukawa, J. Matsui, M. Higashi, and K. Shimizu, Anal. Chem. **73**, 3869 (2001).

[10] R. Sips, J. Chem. Phys. **16**, 490 (1948).
[11] G. J. M. Koper and M. Borkovec, J. Chem. Phys. **104**, 4204 (1995).
[12] J. L. Garcés, F. Mas, and J. Puy, Environ. Sci. Technol. **32**, 539 (1998).
[13] U. Rusch, M. Borkovec, J. Daicic, and W. H. van Riemsdijk, J. Colloid Interface Sci. **191**, 247 (1997).
[14] K. Nieszporek and W. Rudzinski, Colloids Surf., A **196**, 52 (2002).
[15] W. Rudzinski, K. Nieszporek, H. Moon, and H.-K. Rhee, Chem. Eng. Sci. **90**, 2641 (1995).
[16] H. Moon and C. Tien, Chem. Eng. Sci. **43**, 2967 (1988).
[17] M. Cerník, M. Borkovec, and J. C. Westall, Langmuir **12**, 6127 (1996).
[18] J. L. Garcés, F. Mas, J. Cecília, E. Companys, J. Galceran, J. Salvador, and J. Puy, Phys. Chem. Chem. Phys. **4**, 3764 (2002).

[19] A. D. Polyanin and A. V. Manzhirov, *Handbook of Integral Equations* (CRC, Boca Raton, Fl, 1998), pp. 435–436 and p. 735.
[20] I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series and Products*, 4th ed. (Academic, New York, 1980), pp. 622 and 939.
[21] D. G. Kinniburgh, W. H. van Riemsdijk, L. K. Koopal, M. Borkovec, M. F. Benedetti, and M. J. Avena, Colloids Surf., A **151**, 147 (1999).
[22] L. K. Koopal, W. H. van Riemsdijk, J. C. M. de Wit, and M. F. Benedetti, J. Colloid Interface Sci. **166**, 51 (1994).
[23] M. Borkovec, U. Rusch, M. Cernik, G. J. M. Koper, and J. C. Westall, Colloids Surf., A **107**, 285 (1996).
[24] A. Rényi, *Probability Theory*, North-Holland series in Applied Mathematics and Mechanics (North-Holland, Amsterdam, 1970), Chap. 6.