



A cluster-exact approximation study of the adsorption of binary mixtures on heterogeneous surfaces



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ABSTRACT

The adsorption of binary mixtures on heterogeneous surfaces is studied by a cluster approximation (CA), based on the exact calculation of configurations on finite cells. The substrate is characterized by n types of sites, each with different adsorption energy. The process is monitored through the total and partial isotherms. The theoretical formalism is used to model experimental data of methane–ethane mixtures adsorbed on a template-synthesized carbon. The CA results are compared with the ones corresponding to the well-known Ideal Adsorbed Solution Theory (IAST). Even though a good fitting is obtained from IAST, it is found that CA is a more accurate model to estimate the binary data on the highly heterogeneous carbon sample.

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1. Introduction

Physical adsorption is one of the basic mechanisms that are present in many molecular processes of great technological interest (catalysis, corrosion, lubrication, detergency, etc.) [1–3]. This fact, along with the intrinsic heterogeneity characterizing the real adsorbents, makes the study of adsorption on heterogeneous surfaces especially interesting and one of the most important topics of physical chemistry of surfaces [4,5].

For adsorption of single species, a seminal contribution was made by Langmuir, who derived the monolayer adsorption isotherm for a monoatomic molecule gas adsorbed on a homogeneous surface, without lateral interactions among the adsorbed molecules [6]. Later, some theories were proposed to describe multilayer adsorption [7–17]. Among them, the conventional Brunauer–Emmett–Teller (BET) [7], Guggenheim–Anderson–de Boer (GAB) [8–10] and Frenkel–Halsey–Hill [11–13] models are the simplest and provide the basis to construct more elaborate approaches. These models have played an important role in the characterization of solid surfaces by means of gas adsorption.

More recently, Dutcher et al. [18] extended the BET and GAB models to include arbitrary numbers of additional adsorbed monolayers. Using statistical mechanics, the authors derived expressions for solute and solvent activities in single-solute solutions. In Ref. [19], the model was generalized for mixtures

containing an arbitrary number of solutes. The theoretical results were applied to study osmotic coefficients and water activities of aqueous solutions.

In the case of adsorption of multicomponent gas mixtures, the problem is more demanding from a theoretical and experimental point of view [20,21]. For pure components, the number of adsorbed molecules can be accurately determined by simply measuring the weight increase of the adsorbent sample, for mixtures one has to carry out additional experiments to determine the composition in the sample. Thus, although this problem has been studied for decades [20–32], there are many aspects which are not yet completely solved. In fact, most of the studies are devoted to the adsorption of mixtures on homogeneous surfaces. On the other hand, if some sort of surface heterogeneity exists, the statistical problem becomes exceedingly difficult.

However, several attempts were done in the past in order to solve the problem of mixture adsorption on heterogeneous adsorbents. A seminal contribution to this field was done by Sircar [33–35], who developed a model, called heterogeneous Langmuir (HL) model, capable of describing the effect of surface heterogeneity on pure and multicomponent adsorption. HL model is based on two main assumptions: (1) the adsorbent can be described by a patchwise distribution of Langmuirian sites, and (2) a uniform distribution of Henry's law constants characterizes the energetic heterogeneity. Beyond this important theoretical contribution, the description of the process of adsorption in the presence of multicomponent adsorbates and heterogeneous surfaces is a complex problem that does not have yet an exact statistical mechanical treatment.

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One way of overcoming these experimental and theoretical complications is to develop simplified models. In this line, a cluster-exact approximation (CA) was presented in a recent paper from our group [36]. This theoretical approach, based on the exact calculation of configurations on finite cells, is a brute force approximation to the system partition function [37,38].

In our previous work [36], CA proved to be a very useful tool for the research of adsorption of binary mixtures on homogeneous surfaces. The results showed, in addition, that CA could be applied to model experimental data of multicomponent adsorption.¹ Here, the scheme introduced in Ref. [36] is extended to include non-regular surfaces. For this purpose, a cluster composed by m sites of n different types (heterogeneous substrate) is used to calculate the partition function of the system. In this framework, partial and total adsorption isotherms are obtained in terms of the adsorbate–substrate adsorption energies. These energies are determined by adjusting the pure component adsorption data with a weighted sum of homogeneous adsorption isotherms (each homogeneous isotherm represents the adsorption on a type of lattice site).

The theoretical scheme is applied to model experimental data of methane–ethane mixtures adsorbed on a template-synthesized carbon [39]. In addition, experimental and CA results are compared with the classical Ideal Adsorbed Solution Theory (IAST) [40]. IAST has become the benchmark for studying adsorption equilibrium of gas mixtures from the isotherms of the pure components. This theory (1) is a predictive model which does not require the gas mixture data; (2) is independent of the model of physical adsorption; and (3) provides a powerful tool to compare the predictions from different adsorption models [33–35,39,41–43].

The paper is organized as follows. In Section 2, the cluster approximation for binary mixtures adsorbed on heterogeneous surfaces is developed. In order to test the applicability of the proposed model, Section 3 is devoted to (1) the analysis of experimental data for methane–ethane mixtures adsorbed on a template-synthesized carbon, and (2) the comparison with results obtained from the well-known IAST. Finally, the conclusions are drawn in Section 4.

2. Theory: cluster-exact approximation for binary mixtures adsorbed on heterogeneous surfaces

The heterogeneous surface is represented by a lattice with M_1, M_2, \dots, M_n adsorption sites of kind 1, 2, \dots, n , respectively. The total number of lattice sites M results:

$$M = \sum_{j=1}^n M_j. \quad (1)$$

To describe a system consisting of N adsorbed molecules ($N = N_a + N_b$, being $N_a[N_b]$ the number of molecules of $a[b]$ species) on a lattice of M sites at a given temperature T , the occupation variable σ_i is introduced: $\sigma_i = 0$ if site i is empty, and $\sigma_i = 1[2]$ if site i is occupied by an $a[b]$ particle. Then, in the grand canonical ensemble, the model is characterized by the Hamiltonian:

$$H = \frac{1}{2} \sum_i \sum_{l(i)} [w_{aa} \delta_{\sigma_i, \sigma_l, 1} + w_{bb} \delta_{\sigma_i, \sigma_l, 2} + w_{ab} (\delta_{\sigma_i, 1} \delta_{\sigma_l, 2} + \delta_{\sigma_i, 2} \delta_{\sigma_l, 1})] + \sum_i [\epsilon_{a,i} \delta_{\sigma_i, 1} + \epsilon_{b,i} \delta_{\sigma_i, 2}] - \sum_i [\mu_a \delta_{\sigma_i, 1} + \mu_b \delta_{\sigma_i, 2}], \quad (2)$$

¹ CA could also be applied to systems of multisolute solutions, as those studied in Refs. [18,19].

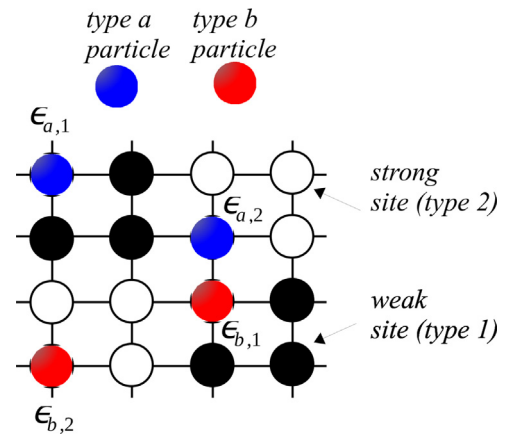


Fig. 1. Cartoon representing a cluster of size $m = 16$ with two different kinds of sites ($n = 2$), $m_1 = 8$ and $m_2 = 8$. In the figure, strong (open circles) and weak (solid circles) sites are arranged in a chessboard structure. Blue [red] circles correspond to $a[b]$ particles. (For interpretation of reference to color in this figure legend, the reader is referred to the web version of this article.)

where the summation over $l(i)$ represents a sum running over the all the nearest-neighbor sites of i ; the pairwise interactions, w_{aa}, w_{ab}, w_{bb} are assumed to occur between nearest neighbors only; the symbol δ represent the Kronecker delta; and μ_a, μ_b are the chemical potentials of both species. $\epsilon_{a[b],i}$ denotes the interaction energy corresponding to a molecule of the $a[b]$ species adsorbed on the site i . Then, $\epsilon_{a[b],i}$ can take n values $\{\epsilon_{a[b],1}, \epsilon_{a[b],2}, \dots, \epsilon_{a[b],n}\}$ according to the type of the site i .

In the context of the lattice-gas approximation, the state of the system is characterized only by the occupation numbers (σ_i with $i \in 1, 2, \dots, M$). To calculate the coverage of each system state and the thermodynamic quantities of the system, a cluster approximation has been developed. The cluster consists of m ($m \ll M$) sites, arranged in a given geometry, and forming a sub-system with m_1, m_2, \dots, m_n adsorption sites of kind 1, 2, \dots, n , respectively ($m = \sum_{j=1}^n m_j$). In the calculations, periodic boundary conditions are considered. As an example, Fig. 1 shows a cluster of size $m = 16$ with two different kinds of sites ($n = 2$), $m_1 = 8$ and $m_2 = 8$. In the figure, strong (open circles) and weak (solid circles) sites are arranged in a chessboard structure.

The exact grand partition function for the cluster can be written as follows:

$$\Xi = 1 + \sum_{N_a, N_b = 0}^m \lambda_a^{N_a} \lambda_b^{N_b} \left\{ \sum_E g(E, N_a, N_b) \exp(-E/k_B T) \right\}, \quad (3)$$

$1 \leq N_a + N_b \leq m$

where k_B is the Boltzmann constant and $\lambda_a \equiv \exp(\mu_a/k_B T)$ [$\lambda_b \equiv \exp(\mu_b/k_B T)$] is the activity of the $a[b]$ species. $g(E, N_a, N_b)$ is the number of configurations corresponding to N_a adsorbed a -particles and N_b adsorbed b -particles having the same energy E , being

$$E = w_{aa} N_{aa} + w_{ab} N_{ab} + w_{bb} N_{bb} + \sum_{j=1}^n (N_{a,j} \epsilon_{a,j} + N_{b,j} \epsilon_{b,j}), \quad (4)$$

where N_{aa}, N_{ab} and N_{bb} represent the number of aa, ab and bb pairs, respectively, on the cluster; and $N_{a[b],j}$ denotes the number of $a[b]$ particles adsorbed on sites type j .

The partial adsorption isotherm corresponding to the $a[b]$ species can be obtained from Eq. (3) [44],

$$\theta_{a[b]} = \frac{k_B T}{m} \left(\frac{\partial \ln \Xi}{\partial \mu_{a[b]}} \right)_{T, \mu_{b[a]}}. \quad (5)$$

Finally, the total coverage is $\theta = \theta_a + \theta_b$.

In this paper, we restrict to the case of negligible lateral interactions ($w_{aa} = w_{ab} = w_{bb} = 0$). Under this condition, the calculations in Eqs. (3)–(5) only require the knowledge of the complete set of adsorbate–substrate adsorption energies $\{\epsilon_{a[b]j}\}$'s, where j runs over the n different class of adsorptive sites. These quantities can be determined by adjusting the pure components isotherms with some adequate function. We have chosen to approximate this function by a weighted sum of homogeneous isotherms. The model is described in the following.

Using the formalism of the integral equation of the adsorption isotherm [4], the adsorption isotherm equation corresponding to a pure species adsorbed on a substrate with a discrete number n of different types of sites can be written as:

$$\theta^{a[b]} = \sum_{j=1}^n f_j \theta_{\text{loc}}^{a[b]}(\epsilon_{a[b]j}), \quad (6)$$

where $\theta^{a[b]}$ denotes the coverage obtained from the adsorption of each pure species (in contrast to $\theta_{a[b]}$ that indicates the $a[b]$ coverage in the adsorbed mixture); f_j is the fraction of sites type j on the surface; and $\theta_{\text{loc}}^{a[b]}(\epsilon_{a[b]j})$ represents the local adsorption isotherm corresponding to an adsorptive energy $\epsilon_{a[b]j}$. This local isotherm can be well approximated by using the Langmuir adsorption isotherm associated to an homogeneous surface with an adsorption energy equal to $\epsilon_{a[b]j}$. Thus,

$$\theta_{\text{loc}}^{a[b]}(\epsilon_{a[b]j}) = \frac{\chi_{a[b]j} P}{1 + \chi_{a[b]j} P} \quad (7)$$

where P is the gas pressure, $\chi_{a[b]j} = \exp[-(\epsilon_{a[b]j} - \mu_{a[b]}^0)/k_B T]$ and $\mu_{a[b]}^0$ is standard chemical potential of the $a[b]$ species. Eqs. (6) and (7) allow us to study the adsorption of pure component gases on heterogeneous surfaces.

As an example, let us consider the single adsorption of a particles on a bivariate heterogeneous surface, where strong and weak sites are spatially distributed with fractions f_1 and f_2 , respectively. In this case, Eq. (6) adopts the form,

$$\theta^a = f_1 \frac{\chi_{a,1} P}{(1 + \chi_{a,1} P)} + f_2 \frac{\chi_{a,2} P}{(1 + \chi_{a,2} P)}. \quad (8)$$

In the case of b particles,

$$\theta^b = f_1 \frac{\chi_{b,1} P}{(1 + \chi_{b,1} P)} + f_2 \frac{\chi_{b,2} P}{(1 + \chi_{b,2} P)}. \quad (9)$$

Finally, the theoretical procedure can be described as follows:

- (1) By adjusting the $a[b]$ pure isotherms with Eq. (6), the complete set of adsorbate–substrate adsorption energies $\{\epsilon_{a[b]j}\}$'s (or $\{\chi_{a[b]j}\}$'s) are obtained.
- (2) The values of the adsorption energies $\{\epsilon_{a[b]j}\}$'s are introduced in Eqs. (3)–(5). Then, by simple algebra, the partial and total concentrations of the adsorbed mixture are determined.

The items (1) and (2) are summarized in the following scheme:

$$a[b] \text{ pure isotherm} + \text{Eq. (6)} \rightarrow \{\epsilon_{a[b]j}\}'s \Rightarrow \{\chi_{a[b]j}\}'s + \text{Eqs. (3)–(5)} \rightarrow \theta_a, \theta_b, \theta \quad (10)$$

The scheme shown in (10) can be easily generalized to (i) more complex adsorbates and (ii) more general heterogeneous surfaces. In the first case, the model allows to incorporate ternary, quaternary and n -component mixtures, and also mixtures of polyatomics (extended molecules occupying more than one lattice site). For extended adsorbates, the pure component isotherms can

be adjusted by using the Fermi–Dirac (FD) approach for k -mers adsorption [45–47]. With respect to non-homogeneous substrates, approximations such as detailed mean field approximation [48] and effective substrates approximation [49,50] can be used to fit the pure isotherms, and thus to extend the analysis to correlated heterogeneous surfaces and n different kinds of adsorptive sites.

The advantages of using this simple description as a tool for modeling binary mixtures adsorption on heterogeneous surfaces, will be shown in the next section by analyzing experimental data of methane–ethane mixtures adsorbed on a template-synthesized carbon.

3. Applications: adsorption of methane–ethane mixtures on a template-synthesized carbon

In this section, analysis of experimental results has been carried out in order to determine the reaches and limitations of the theoretical model discussed here. The experimental data were taken from the work by Chen et al. [39]. In Ref. [39], a system of methane–ethane adsorbed on a template-synthesized carbon was studied. Pure component isotherms of methane and ethane gases were measured for three different temperatures: 263 K, 273 K and 303 K. Binary adsorption equilibria were obtained using a fixed bed rig operated at atmospheric pressure. Interested readers are referred to Refs. [39,41,42,51,52] for a more complete description of the sample preparation, characterization, and experimental procedure.

To compare the experimental results with those obtained from CA, the scheme in (10) was used. Then, as a first step, the $\{\chi_{a[b]j}\}$'s were determined by fitting the pure component isotherms with the function given in Eq. (6).² Based on previous work [39], the template-synthesized carbon was modeled as a bivariate heterogeneous surface composed by two types of sites with equal concentration. Accordingly, Eqs. (8) and (9) were used as fitting functions (with $f_1 = f_2 = 0.5$).

Before starting the comparison, and given that the experimental data are presented in units of amount of adsorbed gas (mmol/g), it is convenient to write the theoretical densities θ^a [Eq. (8)] and θ^b [Eq. (9)] in a more appropriate form

$$\theta^a = \frac{Q^a}{Q_{\text{max}}^a} \quad \text{and} \quad \theta^b = \frac{Q^b}{Q_{\text{max}}^b}, \quad (11)$$

where $(Q_{\text{max}}^{a[b]}) Q^{a[b]}$ represents the (maximum) amount of adsorbed $a[b]$ gas on the surface.

For the fittings, the least-squares statistics was considered [53]. Thus, suppose that n data points $(x_i, y_i, z_i; i = 1, \dots, n)$ are being fitted to a model that has L adjustable parameters $(a_j; j = 1, \dots, L)$. The model predicts a functional relationship between the measured independent and dependent variables,

$$z(x, y) \equiv z(x, y; a_1 \dots a_L) \quad (12)$$

where the dependence on the parameters is indicated explicitly on the right-hand side. What, exactly, do we want to minimize to get fitted values for the a_j 's? The first thing that comes to mind is the familiar least-squares fit, minimize over $a_1 \dots a_L$:

$$\sum_{i=1}^{n_m} [z_i - z(x_i, y_i; a_1 \dots a_L)]^2 \quad (13)$$

² As it will be seen below, the adsorbate concentrations analyzed here are sufficiently low to satisfy the assumption of negligible lateral interactions.

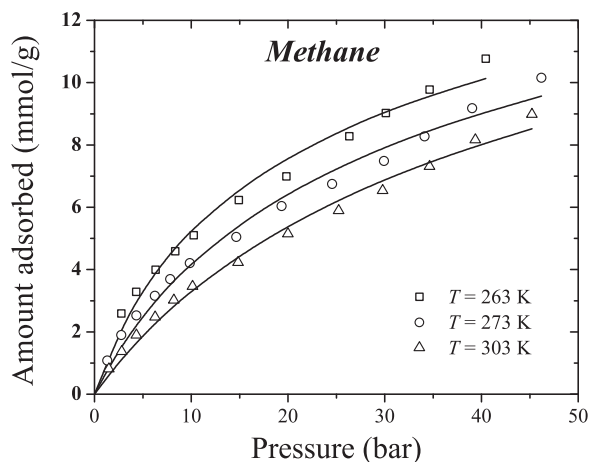


Fig. 2. Adsorption isotherms of methane on the template-synthesized carbon for three different temperatures as indicated. Symbols correspond to experimental data from Ref. [39], and lines represent fitting curves obtained by a weighted sum of local isotherms as discussed in the text. The fitting parameters are collected in Table 1.

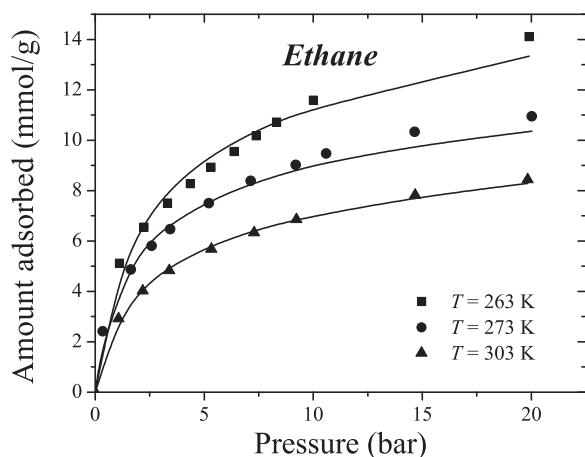


Fig. 3. As Fig. 2 for ethane on the template-synthesized carbon.

The parameters of the model are then adjusted to achieve a minimum in function (13), yielding best-fit parameters. The adjustment process is thus a problem in minimization in many dimensions.

The least-squares procedure was performed for each set of experimental isotherms. The results are shown in Fig. 2 (methane, a species) and Fig. 3 (ethane, b species). Symbols correspond to experimental data from Ref. [39], and lines represent fitting curves. In this case, Eq. (8) [Eq. (9)] with $\theta^a = Q^a/Q_{\max}^a$ [$\theta^b = Q^b/Q_{\max}^b$] corresponds to $z(x, y) \equiv z(x, y; a_1 \dots a_L)$, being Q_{\max}^a [Q_{\max}^b], $\chi_{a,1}$ [$\chi_{b,1}$] and $\chi_{a,2}$ [$\chi_{b,2}$] the adjustable parameters. The fitting parameters are indicated in Table 1.

Based on the pure component isotherm parameters collected in Table 1, Eqs. (3)–(5) were used to predict the binary data (θ_a , θ_b , and θ). The calculations were performed for a cluster of size $m = 16$ and two types of sites ($n = 2$) with fractions $f_1 = f_2 = 0.5$. Due to the assumption of zero lateral interactions, the occupation of a given site is independent of the occupation of neighbouring sites.

Table 1

Fitting parameters corresponding to the data in Figs. 2 and 3.

	$Q_{\max}^{a[b]}$ [mmol/g]	$\chi_{a[b],1}$	$\chi_{a[b],2}$
Methane	18.23	0.061	0.013
Ethane	15.17	0.718	0.062

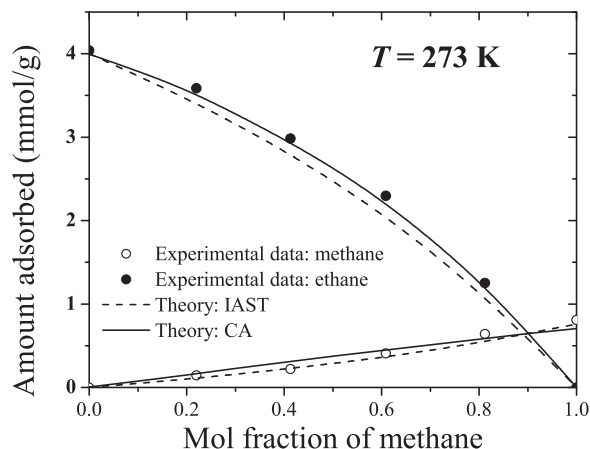


Fig. 4. Binary adsorption equilibria of methane and ethane on the template-synthesized carbon at 273 K and 1 atm. Open (solid) circles represent methane (ethane) experimental data. Solid lines and dashed lines correspond to results from CA [Eqs. (3)–(5)] and IAST [39], respectively.

Consequently, the results do not depend on the geometry and topography of the cluster.³

The number of configurations $g(E, N_a, N_b)$ [see Eq. (3)] was obtained by using a simple computer algorithm that calculates all the possible ways of arranging the particles adsorbed on the finite cell. Then, from Eqs. (3)–(5), the quantities θ_a , θ_b , and θ were determined for a temperature $T = 273$ K.

The obtained results (solid lines) are shown in Fig. 4 in comparison with experimental data (symbols) from [39]. For zero molar fraction of methane, the amount of ethane adsorbed on the surface has a maximum, and the corresponding amount of methane is zero. As the molar fraction of methane is increased, the adsorbed amount increases slowly for methane and decreases quickly for ethane. In the limit of a molar fraction of methane equal to 1, the amount of adsorbed methane has a maximum, and the corresponding amount of ethane is zero. As it can be observed, a very good agreement is obtained between experimental data and CA results.

It is interesting to compare the present approach with the standard Ideal Adsorbed Solution Theory (IAST), developed by Myers and Prausnitz [40] to predict multicomponent adsorption equilibria. The IAST, which is widely used in engineering models, is based on the assumption that the adsorbed phase can be treated as an ideal solution of the adsorbed components. The basic equation of IAST theory is the analogue of Raoult's law for vapour–liquid equilibrium,

$$Py_i = P_i^0(\pi)x_i \quad (14)$$

where P is the total pressure, and $P_i^0(\pi)$ is the pressure for sorption of every pure component i , which yields the same spreading pressure, π , as that for the mixture. y_i and x_i are the mole fractions of component i in the fluid and the adsorbed phase, respectively. Thus,

$$x_i = \frac{\theta_i}{\sum_j \theta_j}, \quad (15)$$

where the sum runs over the number of components of the mixture. In the case of a binary mixture, $x_{a[b]} = \theta_{a[b]}/(\theta_a + \theta_b)$.

³ In the particular case studied in this article, the 4×4 cluster ($m = 16$) was modeled as a collection of homogeneous 2×2 patches arranged in a chessboard-like structure (see in Fig. 1).

The spreading pressure is defined by the Gibbs adsorption isotherm

$$\frac{\pi}{k_B T} = \int_{P=0}^{P=P_i^0} \frac{\theta^i(P)}{P} dP, \quad (16)$$

where $\theta^i(P)$ is the pure component isotherm, given by, for example, the function in Eq. (6). The total isotherm is obtained from

$$\theta = \sum_j \theta_j = \frac{1}{\sum_j x_i / \theta^i(P_i^0)}. \quad (17)$$

The set of Eqs. (14)–(17) (along with an adequate function for the pure component isotherm) need to be solved numerically to obtain the concentrations of the individual components in the mixture. In the present paper, the IAST results were taken from Ref. [39]. The curves for $T=273$ K are shown in Fig. 4 as dashed lines.

The behavior of IAST and CA can be explained as follows. In the case of the curve corresponding to methane (open circles), IAST (dashed line) and CA (solid line) provide good approximations with very small differences between experimental and theoretical results. In the case of ethane (solid circles), appreciable differences can be seen between IAST and CA, with CA being the most accurate approximation. Even though a good fitting is obtained from IAST, this approach misestimates the value of the experimental points over all the range.

The system of Fig. 4 was also studied in previous research [39] using IAST and the extended Sips model [54]. Chen et al. found that the prediction of IAST is superior to the extended Sips model.

The study in Fig. 4, along with the results reported in Ref. [39], indicate that (1) the template-synthesized carbon can be well modeled as a heterogeneous substrate, and (2) CA is a more accurate model to describe adsorption of binary mixtures on heterogeneous surfaces. CA is a very good approximation considering the complexity of the physical situation which is intended to be represented.

Finally, it is important to note the usefulness of CA as a starting point to predict the behavior of a system governed by a large number of parameters, without heavy or time-consuming calculations. As an example, it took approximately 60 s to solve Eqs. (3)–(5) and to obtain the theoretical points in Fig. 4 on one node of the BACO parallel cluster.⁴ A similar study, using standard Monte Carlo simulations [36], should take about 12 h.

4. Conclusions

A cluster-exact approximation (CA) has been presented to study the adsorption of binary mixtures on heterogeneous surfaces. The formalism is based on exact calculations of configurations on a finite cell (cluster). The cluster is composed by m sites of n different types (heterogeneous substrate). In this scheme, partial and total adsorption isotherms are obtained in terms of the adsorbate–substrate adsorption energies. These energies are determined by adjusting the pure component adsorption data with a weighted sum of homogeneous adsorption isotherms (each homogeneous isotherm represents the adsorption on a type of lattice site).

The theoretical results were applied to analyze experimental data of methane–ethane mixtures adsorbed on a template-synthesized carbon. In this case and following previous work [39], the substrate was modeled as a bivariate heterogeneous surface composed by two kinds of sites. Experimental data were also compared with the classical Ideal Adsorbed Solution Theory. Even

though a good fitting is obtained from IAST, it is found that CA is a more accurate model to estimate the binary data on the highly heterogeneous carbon sample.

In summary, the proposed theoretical model is simple, mathematically handable, and seems to be a promising way toward a more accurate description of the adsorption thermodynamics of binary mixtures on heterogeneous surfaces. In this sense, future efforts will be directed to (1) introduce nearest-neighbor lateral interactions in the adsorbed layer; and (2) extend the calculations to new low-dimensional materials such as carbon nanotubes.

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