PAPER

A semiempirical model for adsorption of binary mixtures†

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The statistical thermodynamics of polyatomic species mixtures adsorbed on two-dimensional lattices was developed based on generalization of the semiempirical approximation for the adsorption of single components [Romá, F. et al., Langmuir, 2006, 22, 3192–3197]. In this scheme, the partial adsorption isotherms are obtained using a correction function $\tilde{C}$, which relates to the conditional probability of finding the ith empty site to a lattice with $i-1$ already vacant sites. This approximation allows us to write a new theoretical model using a combination of the correction functions corresponding to exact 1-D calculations and the Guggenheim–DiMarzio approach. Finally, comparisons with MC simulations and experimental data of methane–ethane and ethane–propylene mixtures on activated carbon are used to test the accuracy and reliability of the proposed model. The obtained results indicate that the new thermodynamic description is significantly better than the existing theoretical models developed to treat adsorption of interacting binary mixtures of polyatomics.

1 Introduction

The separation of multicomponent gas mixtures *via* an adsorption process is of major importance for both environmental and economic reasons. It is vitally important, for example, to develop a viable adsorption method based on separation technologies to reduce carbon dioxide emissions that cause global warming and removal of carbon dioxide from natural gas for efficient recovery of pure components of oil products.[1,2]

For multicomponent systems, it is difficult to obtain accurate experimental data by simply measuring the weight increase on the surface and usually requires additional experiments to determine the composition of each adsorbed component. Frequently, the practical way of estimating multicomponent adsorption is to predict mixture isotherms from single component isotherms. An early seminal contribution to this subject was made by Prausnitz and Myers[3] in 1965 with their work on the ideal adsorbed solution theory (IAST). The IAST model has been successfully used to evaluate and validate experimental data for adsorption equilibria of gas mixtures.[4–7]

Although the IAST model is independent of the mechanism proposed for physical adsorption, it also requires the knowledge of the amount adsorbed *versus* the system pressure. From a theoretical point of view, this can be done using Langmuir type

equations, losing in many cases, important information about the characteristics of the system (surface topography, lateral interactions, *etc.*).[8,9] On the other hand, the resultant equations are non-linear and involve integrals that cannot be solved analytically for most of the pure component isotherm equations.[10]

In order to describe real multicomponent adsorption systems, it is necessary to take into account three main properties on the calculation of the thermodynamic quantities: energetic surface topography; the type of interactions between adsorbed particles; and finally, relative molecular sizes of the components of the mixture. Most of the studies on mixture adsorption have only been focused on the first two aspects, considering equal sizes of the components and hence discarding the polyatomic character of the molecules.[11,12] The difficulty in the analysis of polyatomic adsorbates is mainly associated with three factors, which differentiate the multisite statistics from the usual single-particle statistics. They are as follows: (i) no statistical equivalence exists between particles and vacancies; (ii) the occupation of a given lattice site ensures that at least one of its nearest-neighbor sites is also occupied; and (iii) an isolated vacancy cannot serve to determine whether that site can ever become occupied.

Recently, two new theories to describe adsorption of binary mixtures with multisite occupancy have been introduced. The first one, denoted EA approximation,[13] develops an exact model to study the adsorption of linear adsorbates on homogeneous surfaces in one dimension. This model can be extended to higher dimensions using a connectivity ansatz.[14] The second one is a generalization of the Guggenheim–DiMarzio (GD) theory,[15,16] in which an approximate method of counting the number of ways to pack together a mixture of molecules of arbitrary shape and orientations is obtained.[17,18]

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In the case of single-component adsorption, the classical theories fail to reproduce adsorption results for high values of adsorbate sizes. Detailed comparisons between theoretical and simulation data showed that the GD approach fits the numerical points at low coverage very well and the EA model behaves excellently at high coverage. On the basis of these findings, the semiempirical model for the adsorption of polyatomics (SE) was developed.[19] The results obtained in ref. 19 indicated that the SE model performs significantly better than the other existing approaches. In this line, the main objective of the present paper is to extend the semiempirical model to account for the presence of multicomponent adsorbates. This article is organized as follows: the theoretical formalism is presented in Section 2. Section 3 is devoted to describing the MC simulation scheme. In Section 4, analytical results are compared with Monte Carlo simulations and experimental data. Finally, the conclusions are drawn in Section 5.

2 Model and theory

We consider the adsorption of a binary mixture of N_k and N_l of hard rigid rods of length-to-breadth ratio k and l, respectively (the constant bond length is equal to the lattice constant). The adsorptive surface is represented by M equivalent adsorption sites arranged on a two-dimensional lattice with connectivity γ and periodic boundary conditions. In this paper, we only consider hardcore exclusion interaction between different rods, *i.e.*, no site can be occupied by more than one particle.

The main equilibrium adsorption properties in the lattice-gas approximation can be obtained from the grand canonical partition function,[20]

$$\Xi = \sum_{N_k} \sum_{N_l} q_k(T)^{N_k} q_l(T)^{N_l} \Omega(M, N_k, N_l)$$
$$\times \exp[\beta(\mu_k N_k + \mu_l N_l - E(N_k, N_l))], \quad (1)$$

where the quantities q_i and μ_i represent the single partition function and chemical potential of the adsorbed species i, $\{i = k, l\}$. Here, $\beta = 1/k_B T$ (k_B being the Boltzmann constant and T the temperature) and $E(N_k, N_l)$ is the interaction energy between the adsorbate and the substrate, which can be written as, $E(N_k, N_l) = \varepsilon_k N_k + \varepsilon_l N_l$, where ε_i represents the adsorption energy of an i-mer unit $\{i = k, l\}$. The function $\Omega(M, N_k, N_l)$ denotes the number of ways to pack N_k rigid rods of length to breadth ratio k; and N_l rigid rods of length-to-breadth ratio l on a lattice of M sites and connectivity γ.

In the grand canonical ensemble, the mean number of particles in the adlayer $\bar{N}_i$ and the chemical potential μ_i are related through the following general relationship,

$$\bar{N}_i = \lambda_i \left[\frac{\partial \ln \Xi(M, \lambda_k, \lambda_l)}{\partial \lambda_i} \right]_M \quad \{i = k, l\}, \quad (2)$$

with $\lambda_i = q_i(T) \exp[\beta(\mu_i - \varepsilon_i)]$. As in ref. 21 and 22, the solution of eqn (2) for λ_i gives us the balance of occupancy for the system,

$$\lambda_i^{-1} = \frac{R_i(M, \lambda_k, \lambda_l)}{\bar{N}_i} \quad \{i = k, l\}, \quad (3)$$

where $R_i(M, \lambda_k, \lambda_l)$ can be interpreted as the number of states available for adsorbing a particle of species i when the chemical potentials at the surface are μ_k and μ_l. These states can be written as,

$$R_i(M, \lambda_k, \lambda_l) = \left(\frac{\gamma}{2} M\right) \prod_{j=1}^{i} P_j \quad \{i = k, l\}. \quad (4)$$

The term between parentheses corresponds to the total number of i-uples on the surface. These i-uples can be separated into three different groups: (1) full i-uples (occupied by i-mers); (2) empty i-uples (available for adsorption), and (3) frustrated i-uples (partially occupied or occupied by segments belonging to different adsorbed i-mers). However, the additional factor represents the probability of having an empty linear i-uple. As in ref. 19, we suppose that this probability can be written as a product of i conditional probability functions, $\mathscr{P}_j$ that represents the probability of finding the j-th empty in the lattice with $j - 1$ already vacant sites. The first of these functions, $j = 1$, represents the probability of finding an empty site when $N = N_k + N_l$ adsorbed molecules already exist on the lattice,

$$\mathscr{P}_1 = 1 - \theta, \quad (5)$$

in which $\theta = \theta_k + \theta_l$ is the total surface coverage and $\theta_i = iN_i/M$ is the surface coverage of each species i.

Furthermore, the $\mathscr{P}_j$ functions can be written as,[19]

$$\mathscr{P}_j = (1 - \theta)C_j, \quad (6)$$

where C_j are the undetermined correction functions that must satisfy $C_1 = 1$ and $C_j \to 1$ as $\theta \to 0$. From eqn (4) and (6), we obtain

$$R_i(M, \lambda_k, \lambda_l) = \frac{\gamma}{2} M(1 - \theta)^i \prod_{j=2}^{i} C_j = \frac{\gamma}{2} M(1 - \theta)^i \tilde{C}^{i-1}, \quad (7)$$

and

$$\tilde{C} = \left(\prod_{j=2}^{i} C_j \right)^{\frac{1}{i-1}} \quad \{i = k, l\}, \quad (8)$$

where $\tilde{C}$ being the geometric mean of the C_js. Now, the adsorption isotherms can be easily calculated from eqn (3) and (7),

$$\lambda_i^{-1} = \frac{\gamma}{2} i \frac{(1 - \theta)^i \tilde{C}^{i-1}}{\theta_i} \quad \{i = k, l\}, \quad (9)$$

or

$$\beta(\mu_i - \ln K_i) = \ln\left(\frac{\theta_i}{i}\right) - i\ln(1 - \theta) - \ln\left(\frac{\gamma}{2}\right) - (i - 1)\ln \tilde{C}, \quad (10)$$

where $K_i = q_i(T)\exp(-\beta i \varepsilon_i)$ is the equilibrium constant for the species i.

In general, the calculation of the adsorption isotherms requires the knowledge of an analytical expression for $\tilde{C}$ [see, eqn (8)]. Now, let us consider the simplest approximation

within this scheme, namely, $\tilde{C} = 1$, for all k and l. Then, from eqn (7) we obtain,

$$R_i(M, \lambda_k, \lambda_l) = \frac{\gamma}{2} M (1 - \theta)^i. \tag{11}$$

Eqn (11) represents the Flory–Huggins (FH) limit[23,24] for the adsorption of noninteracting binary mixtures of linear species adsorbed on homogeneous surfaces (see Appendix). For single adsorption, eqn (11) reduces to the classical Flory–Huggins isotherm for non-interacting linear adsorbates on homogeneous surfaces.[19]

In the case of EA and GD approximation, the comparison between eqn (10) and the expressions in the Appendix allows us to obtain

$$\tilde{C} = \left[1 - \frac{(k-1)}{k} \theta_k - \frac{(l-1)}{l} \theta_l \right] \quad \text{(EA)}, \tag{12}$$

and

$$\tilde{C} = \left[1 - \frac{(k-1)}{k} \frac{2\theta_k}{\gamma} - \frac{(l-1)}{l} \frac{2\theta_l}{\gamma} \right] \quad \text{(GD)}. \tag{13}$$

As was shown in the case of single-component adsorption, an excellent approximation can be obtained by combining exact calculations in 1D and the GD approximation with adequate weights.[19] Extending these arguments to the case of multi-component adsorption and using the structure proposed in eqn (10), a new semiempirical adsorption isotherm for mixtures of polyatomics can be built:

$$
\begin{aligned}
\beta(\mu_i - \ln K_i) =\ & \ln\left(\frac{\theta_i}{i}\right) - i\ln(1-\theta) - \ln\left(\frac{\gamma}{2}\right) \\
& - (1-\theta)(i-1)\ln\left[1 - \frac{(k-1)2\theta_k}{k}\frac{}{\gamma} - \frac{(l-1)2\theta_l}{l}\frac{}{\gamma} \right] \\
& - \theta(i-1)\ln\left[1 - \frac{(k-1)}{k}\theta_k - \frac{(l-1)}{l}\theta_l \right], \\
& i = \{k, l\}.
\end{aligned} \tag{14}
$$

The last equation can be interpreted as follows. The first line includes three terms that are identical in both EA and GD. The second and third lines represent a combination of the average correction functions corresponding to GD and EA, with $(1 - \theta)$ and θ as weights, respectively.

3 Monte Carlo simulation

In order to test the applicability of the new theoretical model we perform numerical simulations using hyper-parallel tempering Monte Carlo (HPTMC).[25,26] The HPTMC method consists of generating a compound system of R non-interacting replicas of the system under study. Each replica is associated with a gas pressure P_i, taken from a set of properly selected pressures $\{P_i\}$.[27,28] Once the values of the gas mixture pressure and molar fractions $y_{k(l)}$ are set, the chemical potential of each species is obtained using the ideal gas mixture approximation,

$$\mu_{k(l)} = \mu_{k(l)}^0 + \ln y_{k(l)} P, \tag{15}$$

where $\mu_{k(l)}^0$ is the standard chemical potential at temperature T.

Under these considerations, the simulation process consists of two major subroutines: replica-update and replica-exchange.

3.1 Replica-update

The adsorption–desorption procedure is as follows: (i) one out of R replicas is randomly selected. (ii) a linear $k(l)$-uple of nearest-neighbor sites is selected. Then, if the $k(l)$ sites are empty, an attempt is made to deposit a rod with probability $W_{\text{ads}} = \min\{1, \exp(\beta\mu_{k(l)})\}$; if the $k(l)$ sites are occupied by units belonging to the same $k(l)$-mer, an attempt is made to desorb this $k(l)$-mer with probability $W_{\text{des}} = \min\{1, \exp(-\beta\mu_{k(l)})\}$ and otherwise, the attempt is rejected. In addition, displacement (diffusional relaxation) of adparticles to nearest-neighbor positions, by either jumps along the $k(l)$-mer axis or repetition by rotation around the $k(l)$-mer end, must be allowed in order to reach equilibrium in a reasonable time.

3.2 Replica-exchange

Exchange of two configurations X_i and X_j, corresponding to the i-th and j-th replicas, respectively, is tried and accepted with probability, $W_{\text{accep}}(X_i \to X_j) = \min\{1, \exp(-\beta\Delta)\}$, where Δ in a nonthermal grand canonical ensemble is given by,

$$\Delta = [\mu_k(j) - \mu_k(i)][N_k(j) - N_k(i)] + [\mu_l(j) - \mu_l(i)][N_l(j) - N_l(i)] \tag{16}$$

The complete simulation procedure is the following: (1) replica-update, (2) replica-exchange, and (3) repeat from step (a) $R \times M$ times. This is the elementary step in the simulation process or Monte Carlo step (MCs). Typically, the equilibrium state can be well reproduced after discarding the first $r' = 10^6$ MCs. Then, the next $r = 10^6$ MCs are used to compute averages.

For each value of pressure P_i, the corresponding surface coverage $\theta_i(P_i)$ is determined through simple averages over the r samples,

$$\theta_i(j) = \frac{1}{r} \sum_{t=1}^{r} \theta_i[X_j(t)] \quad \{i = k, l\}, \tag{17}$$

where $X_j(t)$ represents the state of the replica j-th at the Monte Carlo time t.

4 Results

In this section, we analyze the main characteristics of the new adsorption isotherm given in eqn (14), in comparison with MC simulation results, experimental data and the main theoretical approximations developed for the study of binary mixtures.

Let us consider a gas mixture of rigid rods of length k and l with equal molar fractions of each component in the gas phase. The adsorption takes place on a regular homogeneous lattice with connectivity $\gamma = 4$ (square lattice) and 6 (triangular lattice). For simplicity, we consider the standard chemical potentials equal to zero and the equilibrium constants $K_i = 1$ for all the species.
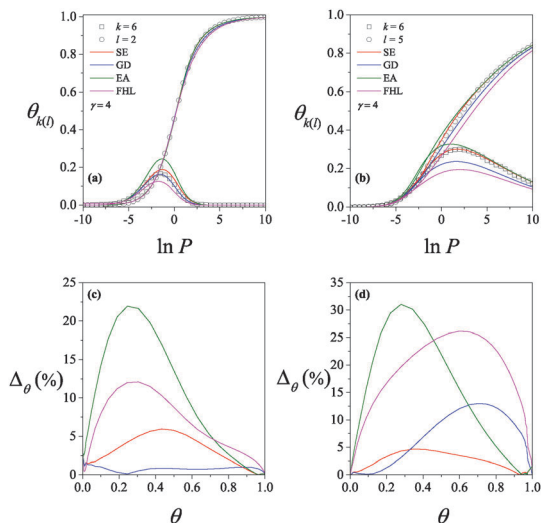
Fig. 1 Adsorption isotherms for rigid molecules on a square lattice: (a) $k = 6$ and $l = 2$; (b) $k = 6$ and $l = 5$. (c) and (d) Reduced coverage error Δ_θ (%) vs. the total surface coverage for the data in (a) and (b). Symbols represent MC results, and lines correspond to different theoretical approaches as indicated.

Fig. 2 ame as Fig. 1 for triangular lattices.

The partial adsorption isotherms for $\gamma = 4$, $k = 6$ and two values of $l = (2, 5)$ are shown in Fig. 1(a) and (b), respectively. Symbols represent MC data and lines correspond to different approaches as indicated. A typical feature in binary mixtures of polyatomic species can be seen in both figures, namely the displacement of the smaller species by the other species at higher pressures. This phenomenon, known as adsorption preference reversal (APR), can be understood from the entropic competition between the adsorbed species. A comprehensive study of the APR phenomenon in terms of the difference in the size of the adsorbed molecules can be found in the ESI.†

In Fig. 1(a), the major deviations between simulation and theoretical results are present in the partial adsorption isotherm of the bigger species. As is clearly shown in Fig. 1(b), these differences depend on the degree of approximation used in $\tilde{C}$.[19]

In order to compare simulation and analytical data, the reduced coverage error is defined as[22]

$$\Delta_\theta(\%) = 100 \times \left| \frac{\theta_{MC} - \theta_{appr}}{\theta_{MC}} \right|, \tag{18}$$

where $\theta_{MC}(\theta_{appr})$ represents the value of the total coverage obtained by using the MC simulation (analytical approach). Each pair of values $(\theta_{MC}, \theta_{appr})$ is obtained at fixed P.

The results of eqn (18) are presented in Fig. 1(c) and (d). In Fig. 1(c), the better agreement between simulation and analytical data occurs for concentrations higher than $\theta \approx 0.6$. This is due to the fact that only dimers are present on the surface at that coverage, and all theoretical approaches fit very well in this case.[29] However, in the case of large adsorbates, the classical approaches fail to reproduce adsorption results for all ranges of coverage, as can be seen in Fig. 1(d). On the other hand, the semiempirical approximation provides good results with an error less than 7% in both cases.
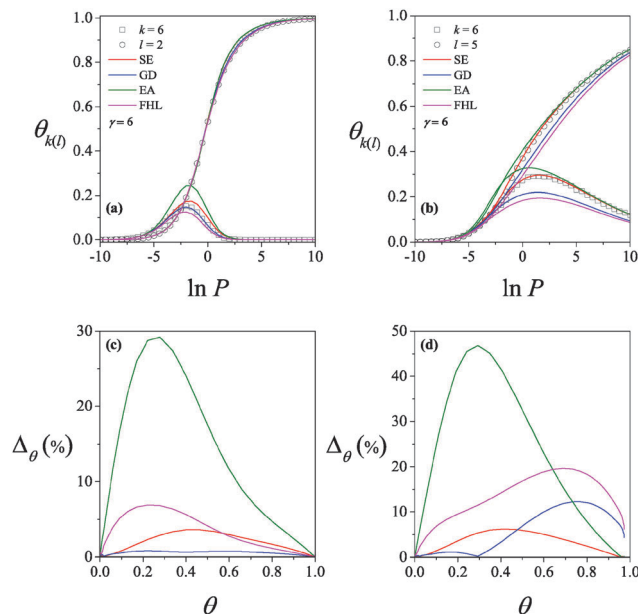
The same procedure given in Fig. 1 is repeated for triangular lattices. The results are presented in Fig. 2. In most of the cases, the error increases with the lattice connectivity. In contrast, the SE remains under 7%, which implies that SE is an extremely good approximation for representing binary mixture adsorption with multisite occupancy, at least for the sizes considered here.

To complete our study, partial isotherms for mixtures with different sizes of l and a constant value of $k = 6$ are compared. For each pair of values (k, l), the differences between theoretical and simulation data can be easily rationalized with the help of the average error over the total range of coverage, which can be defined as

$$\bar{\Delta}_\theta = \frac{1}{R} \sum_\theta \Delta_\theta(\%), \tag{19}$$

where R is the number of adsorption isotherm points (or the number of replicas as described in Section 3).

The dependence of $\bar{\Delta}_\theta$ with the l-mer size and the geometry is shown in Fig. 3 for the different theoretical approaches
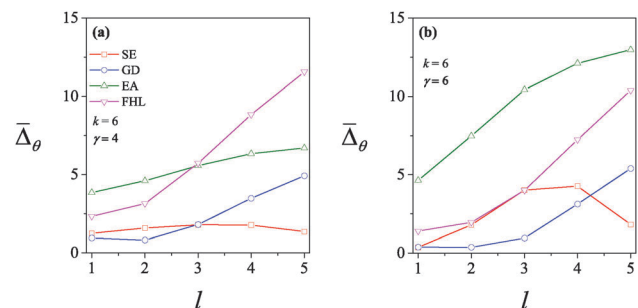

Fig. 3 Average error $\bar{\Delta}_\theta$ for fixed k and different values of l: (a) square lattice, $\gamma = 4$ and (b) triangular lattice, $\gamma = 6$. The meaning of the lines is indicated in the figure.

considered in the present work. As can be seen, $\bar{\Delta}_\theta$ increases monotonically showing that the disagreement between MC and analytical data is more evident for large adsorbates. In contrast, the SE approximation remains almost constant at around 1.8% for square lattices and 4.3% for triangular lattices. The agreement between the new theoretical approach and the simulation data is excellent in all ranges of l. These findings demonstrate that accurate calculation of the correction function [eqn (8)] is crucial to understand the adsorption process of rigid rod mixtures.

Finally, analysis of experimental results extracted from ref. 30 has been carried out in order to test the applicability of the proposed model. For this purpose, experimental adsorption isotherms of hydrocarbon mixtures of methane–ethane and ethane–propylene on activated carbon (AC-40) at 20 °C were analyzed using the semiempirical adsorption model presented here. Given that the experimental data were reported in the adsorbed amount (moles g^{-1} adsorbed) as a function of pressure (in mmHg units), the theoretical isotherms were rewritten in terms of pressure P and the adsorbed amount g as fitting quantities.

Thus, assuming that the adsorbed phase is in equilibrium with an ideal gas phase mixture, the chemical potentials $\mu_{k(l)}$ are related to P and the molar fractions as in eqn (17). In addition, $\theta = g/g_{max}$, where g_{max} represents the maximum adsorbed amount in the surface.

As is common in the literature, a "bead segment" chain model of the molecules was adopted, in which each CH$_n$ group (bead) occupies one adsorption site on the surface. Under this consideration, C$_m$ is set in the fitting data as $k(l) = m$.[31]

In this scheme, a set of isotherms of methane–ethane and ethane–propylene on activated carbon (AC-40) at 20 °C for different values of molar fraction were correlated by using only one value of g_{max} and a temperature dependent $K_{k(l)}(T)$ as adjustable parameters. The results are presented in Fig. 4 and the fitting parameters are listed in Table 1. A very good agreement between experimental (symbols) and theoretical (lines) data is observed.

5 Conclusions

A new theoretical approach to treat the statistical thermodynamics of polyatomic species mixtures adsorbed on two-dimensional lattices has been presented. The formalism, based on generalization of the semiempirical approximation for single-component adsorption, is capable of including the main theories of multisite occupancy adsorption as particular cases. In this framework, a simple semiempirical adsorption isotherm was obtained by combining exact calculations in 1D and the GD approximation with adequate weights.

The reaches and limitations of the theory were analyzed by comparing with MC simulations in square and triangular lattices. The obtained results showed that the SE model represents a significant qualitative advance with respect to existing theoretical models developed to treat the problem of mixture adsorption of long straight rigid rods.

Finally, experimental data of methane–ethane and ethane–propylene mixtures adsorbed on activated carbon were very well fitted by using the new model. Even though further comprehensive analysis of experimental isotherms needs to be done, the SE theory seems to be a promising approach toward a more accurate description of the adsorption thermodynamics of interacting polyatomic species.

Appendix: main theoretical adsorption isotherms of (k-mers–l-mers) binary mixtures adsorbed on regular lattices at the monolayer

$$\beta(\mu_k - \ln K_k) = \ln\left(\frac{\theta_k}{k}\right) - k\ln(1 - \theta_k - \theta_l) - \ln\left(\frac{\gamma}{2}\right) \quad \text{(FH)}$$

$$\beta(\mu_l - \ln K_l) = \ln\left(\frac{\theta_l}{l}\right) - l\ln(1 - \theta_k - \theta_l) - \ln\left(\frac{\gamma}{2}\right)$$

$$\beta(\mu_k - \ln K_k) = \ln\left(\frac{\theta_k}{k}\right) - k\ln(1 - \theta_k - \theta_l)$$
$$- \ln\left(\frac{\gamma}{2}\right) - (k-1)$$
$$\times \ln\left[1 - \frac{(k-1)}{k}\theta_k - \frac{(l-1)}{l}\theta_l\right] \quad \text{(EA)}$$

$$\beta(\mu_l - \ln K_l) = \ln\left(\frac{\theta_l}{l}\right) - k\ln(1 - \theta_k - \theta_l)$$
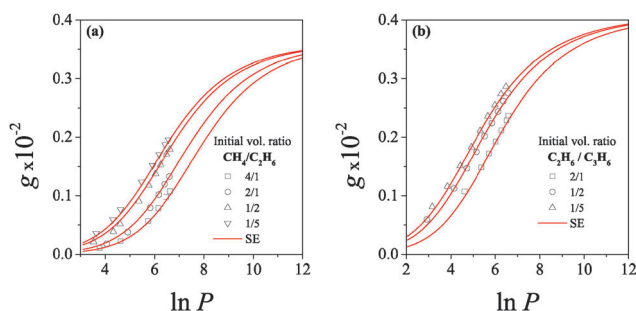$$- \ln\left(\frac{\gamma}{2}\right) - (l-1)\ln\left[1 - \frac{(k-1)}{k}\theta_k - \frac{(l-1)}{l}\theta_l\right]$$

Fig. 4 Comparison between experimental and theoretical adsorption isotherms for a binary mixture: (a) CH$_4$–C$_2$H$_6$ and (b) C$_2$H$_6$–C$_3$H$_6$ adsorbed on commercial activated carbon. Symbols represent experimental data from ref. 26 and lines correspond to results from eqn (14). The parameters used in the fitting procedure are listed in Table 1.

Table 1 Parameters used in the fitting of Fig. 4

	CH$_4$–C$_2$H$_6$	C$_2$H$_6$–C$_3$H$_6$
$g_{max} \times 10^{-2}$ (mol g^{-1})	0.41	0.41
$K_k \times 10^9$ (mmHg^{-1})	3.5	0.48
$K_l \times 10^5$ (mmHg^{-1})	1.6	0.6

$$\beta(\mu_k - \ln K_k) = \ln\left(\frac{\theta_k}{k}\right) - k\ln(1 - \theta_k - \theta_l)$$

$$- \ln\left(\frac{\gamma}{2}\right) - (k-1)$$

$$\times \ln\left[1 - \frac{(k-1)}{k}\frac{2\theta_k}{\gamma} - \frac{(l-1)}{l}\frac{2\theta_l}{\gamma}\right] \quad \text{(GD)}$$

$$\beta(\mu_l - \ln K_l) = \ln\left(\frac{\theta_l}{l}\right) - k\ln(1 - \theta_k - \theta_l)$$

$$- \ln\left(\frac{\gamma}{2}\right) - (l-1)$$

$$\times \ln\left[1 - \frac{(k-1)}{k}\frac{2\theta_k}{\gamma} - \frac{(l-1)}{l}\frac{2\theta_l}{\gamma}\right].$$

FH: Flory–Huggins's approximation (see ref. 23 and 24).

EA: Exact isotherm in 1-D and extension to higher dimensions (see ref. 14, 21, 22 and 29).

GD: Guggenheim–DiMarzio's approximation (see ref. 15 and 16).

Acknowledgements

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