Adsorption (2014) 20:855–862
DOI 10.1007/s10450-014-9627-7

Adsorption of binary mixtures on two-dimensional surfaces: theory and Monte Carlo simulations

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Received: 17 November 2013 / Revised: 24 June 2014 / Accepted: 27 June 2014 / Published online: 18 July 2014

Abstract The adsorption of binary mixtures on square lattices is studied by combining theoretical modeling and Monte Carlo (MC) simulations in grand canonical ensemble. The adsorption thermodynamics is analyzed through the total and partial isotherms. Two theoretical models have been used in the present study: (i) the first, which we called cluster approximation (CA), is based on exact calculations of configurations on finite cells. An efficient algorithm allows us to calculate the detailed structure of the configuration space for $m = l \times l$ cells; and (ii) the second is a generalization of the classical quasi-chemical approximation (QCA) in which the adsorbate is a binary mixture of species a and b. Adsorbate–adsorbate lateral interactions are incorporated in the context of the two mentioned approximations. Results from CA and QCA are compared with MC simulations. Close agreement between simulated and theoretical data supports the validity of the theoretical models to describe the adsorption of mixed gases on two-dimensional surfaces.

Keywords Adsorption · Binary mixtures · Monte Carlo simulations · Quasi-chemical approximation

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1 Introduction

In the context of surface adsorption, the study of the adsorbate–adsorbate interactions in adsorbed films on regular substrates has its own interest (Hill 1960; Clark 1970; Steele 1974) due, particularly, to the emerging adsorbate structures that arise on the surface. These structures have an effect on microelectronics fabrication, catalyst surfaces, chemical sensors and electrodes, surfaces undergoing corrosion (Rupprechter et al. 2004; Matsushima 2004), etc.

Various theoretical approaches have been taken to describe monolayer adsorption in the context of the lattice-gas model (Hill 1960; Clark 1970; Binder and Landau 1980; Landau 1983; Tovbin 1991; Patrykiejew et al. 2000). For ideal, non-interacting particles, the systems are quite simple and usually analytically solved (Hill 1960).

Very simple interactions like excluded volume (also called rigid spheres) can also be analytically studied. However for the simplest adsorbate–adsorbate interactions that involve nearest neighbors, complexity grows in such a way that the partition function can only be exactly (and analytically) expressed in very few cases (Ramirez-Pastor et al. 2000; Romá and Ramirez-Pastor 2004; Pinto et al. 2011; Phares and Wunderlich 1985, 1995, 1997, 1999, 2000, 2001).

In the case of multicomponent adsorbates, the problem is even more complex because the large number of parameters involved, such as: interaction energies intra- and inter- species, chemical potentials of each species, molar fractions, etc. A number of contributions have been devoted to the adsorption and separation of binary mixtures (Blume et al. 1971; Phares et al. 1997; Dávila et al. 2009). One the seminal works in this field corresponds to the Blume–Emery–Griffiths (BEG) model (Blume et al. 1971), which is a very general model used in a variety of phenomena ranging from liquid helium phase separation to phase transitions in adsorbed films (Blume et al. 1971; Berker et al. 1978; Hoston and Berker 1991; Ekiz and Keskin 2002; Keskin and Erdin 2004; Freire et al. 2005; Rżysko et al. 2005). In another work, Phares et al. (Phares et al. 1997) have studied the structural ordering at low temperature and its relation with the phase diagram for a system of two interacting monomeric species on square lattice.

Adsorption of mixtures is also a much demanding problem from the experimental point of view (Dunne et al. 1996; Li et al. 2013; Smit and Maesen 2008). Whereas for pure components the number of adsorbed molecules can be determined accurately 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.

One way of overcoming these experimental and theoretical complications is to use Monte Carlo (MC) simulation method (Smit and Maesen 2008; Binder 1997; Binder and Heermann 1988; Ungerer et al. 2005; García et al. 2012; Dunne et al. 2003; Verma et al. 2013; Liu and Smit 2009; Babarao et al. 2007), and approximations such as Bragg–Williams approximation (BWA) (Hill 1960), quasi-chemical approximation (QCA) (Hill 1960) and cluster approximation (CA) (Belardinelli et al. 2003; Romá et al. 2003). Each one having its advantages and disadvantages.

Thus, even though the BWA has proven to be a simpler way to deal with interactions than the QCA, the last has always proven to be closer to the MC simulation results than the BWA. Even more, in some lattice systems the QCA has yielded results that are indistinguishable from the MC results (Pinto et al. 2011; Bulnes et al. 2007; García et al. 2009).

On the other hand, CA is a *brute force* approximation to the system's partition function. This theoretical approach, based on the exact calculation of configurations on small cells, represents an important tool to obtain the main thermodynamic functions of the system, like total coverage, differential heat of adsorption, etc.

In this context, the main objectives of this work are: (*i*) to apply a generalization of the classical quasi-chemical approximation to study a binary mixture of species a and b; (*ii*) to develop a theoretical model based on exact calculations of the detailed structure of the configuration space for $m = l \times l$; and (*iii*) to carry out a thorough comparison between theoretical data and MC simulation results. It is expected that the study will provide a useful starting point and valuable information about the applicability of simple theoretical models to address a problem whose experimental realization is very complex.

The present work is ordered in the following way. Section 2 is dedicated to the model and basic definitions. Sections 3 and 4 have the details of the analytical approximations. Section 5 describes the Monte Carlo (MC) simulation methodology. Section 6 presents and discusses the results, and the final section gives the conclusions.

2 The model

The substrate has been represented by a two-dimensional square lattice of $M = L \times L$ adsorption sites with periodic boundary conditions.

To describe the 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 the lattice at a given temperature T, the occupation variable σ_i was 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:

$$\begin{aligned} H = &\frac{1}{2}\sum_i^M \sum_{l(i)} \big[w_{aa}\delta_{\sigma_i,\sigma_l,1} + w_{bb}\delta_{\sigma_i,\sigma_l,2} \\ &+ w_{ab}\left(\delta_{\sigma_i,1}\delta_{\sigma_l,2} + \delta_{\sigma_i,2}\delta_{\sigma_l,1}\right)\big] \\ &+ \sum_i^M \left[\epsilon_a \delta_{\sigma_i,1} + \epsilon_b \delta_{\sigma_i,2}\right] \\ &- \sum_i^M \left[\mu_a \delta_{\sigma_i,1} + \mu_b \delta_{\sigma_i,2}\right], \end{aligned} \tag{1}$$

where the symbol δ represent the Kronecker delta; μ_a, μ_b are the chemical potentials of both species; $\epsilon_{a[b]}$ denote the interaction energy with the substrate. 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.

3 Quasi-chemical approximation for binary mixtures with lateral interactions

The partition function of N_a atoms of species a and N_b atoms of species b on a regular substrate consisting of M sites is given by the form (Hill 1960),

$$\begin{aligned} Q = &q_a^{N_a} q_b^{N_b} \sum_{N_{aa}} \sum_{N_{ab}} \sum_{N_{bb}} \Omega(N_a, N_b; N_{aa}, N_{ab}, N_{bb}; M) \\ &\times e^{-\beta(w_{aa}N_{aa} + w_{ab}N_{ab} + w_{bb}N_{bb} + N_a\epsilon_a + N_b\epsilon_b)}, \end{aligned} \tag{2}$$

where $q_{a[b]}$ is the partition function for a single adsorbed $a[b]$-molecule; $\Omega(N_a, N_b; N_{aa}, N_{ab}, N_{bb}; M)$ is the number of ways to array $N_a + N_b$ particles on M sites with (N_{aa}, N_{ab}, N_{bb}) pairs of occupied sites and $\beta = 1/k_B T$ (k_B is the Boltzmann constant). The lattice allows a total number of pairs equal to $zM/2$ (z is the connectivity).

The interaction pairs (N_{aa}, N_{ab}, N_{bb}) must satisfy the following constrains:

$$\begin{cases} 2N_{aa} + N_{ab} + N_{a0} = zN_a \\ 2N_{bb} + N_{ab} + N_{b0} = zN_b \\ 2N_{00} + N_{a0} + N_{b0} = z(M - N_a - N_b), \end{cases} \tag{3}$$

where N_{x0} is the number of pairs consisting in an atom of species x and an adjacent empty site. Thus, only three of these numbers are independent (i.e. N_{aa}, N_{bb} and N_{ab}).

By using the standard formalism of the QCA, the number of ways of assigning a total of $zM/2$ independent pairs to the six categories aa, ab, bb, $a0$, $b0$ and 00, with any number 0 through $zM/2$ per category consistent with the total, is

$$\tilde{\Omega}(N_a, N_b; N_{aa}, N_{ab}, N_{bb}; M) = \frac{\left(\frac{zM}{2}\right)!}{\left[\left(\frac{N_{a0}}{2}\right)!\right]^2 \left[\left(\frac{N_{b0}}{2}\right)!\right]^2 \left[\left(\frac{N_{ab}}{2}\right)!\right]^2 N_{aa}! N_{bb}! N_{00}!}. \tag{4}$$

This cannot be set equal to $\Omega(N_a, N_b; N_{aa}, N_{ab}, N_{bb}; M)$ in Eq. (2), because treating the pairs as independent entities leads to some unphysical configurations [see Ref. (Hill 1960)]. Thus $\tilde{\Omega}$ overcounts the number of configurations. To take care of this, we must normalize $\tilde{\Omega}$

$$\Omega(N_a, N_b; N_{aa}, N_{ab}, N_{bb}; M) = C(N_a, N_b; M)\ \tilde{\Omega}(N_a, N_b; N_{aa}, N_{ab}, N_{bb}; M) \tag{5}$$

and

$$\Omega(N_a, N_b; M) = C(N_a, N_b; M) \times \sum_{N_{aa}} \sum_{N_{ab}} \sum_{N_{bb}} \tilde{\Omega}(N_a, N_b; N_{aa}, N_{ab}N_{bb}; M). \tag{6}$$

Here $\Omega(N_a, N_b; M)$ is the number of ways to arrange N_a and N_b particles of species a and b, in M sites. In the present case, this number can be exactly calculated.

From expressions (3), (5) and (6) the partition function (2) can be simplified by the usual method of the maximum term. This method takes only the largest term corresponding to the values N^*_{aa}, N^*_{bb} and N^*_{ab} [see Ref. (Hill 1960)], obtained from the equations,

$$\begin{cases} \dfrac{N^2_{a0}}{4N_{aa}N_{00}} = e^{-\beta w_{aa}} \\ \dfrac{N^2_{b0}}{4N_{bb}N_{00}} = e^{-\beta w_{bb}} \\ \dfrac{N_{a0}N_{b0}}{2N_{ab}N_{00}} = e^{-\beta w_{ab}}. \end{cases} \tag{7}$$

Then, the chemical potential of the adsorbed species $a[b]$ can be calculated as (Hill 1960)

$$\mu_{a[b]} = -\frac{1}{\beta}\left(\frac{\partial \ln Q}{\partial N_{a[b]}}\right)_{N_{b[a]}}. \tag{8}$$

The complete set of Eqs. (7) and (8) can be (numerically) solved to obtain the macroscopic thermodynamic quantities such as the total and partial adsorption isotherms of the system.

4 Cluster approximation

In the context of the lattice-gas approximation, the state of the system is characterized only by the occupation numbers (σ_i with $i \in 1, 2, \ldots, M$). 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 $m\,(m \ll M)$ adsorptive sites forming a $l \times l$ square sub-system (in the present paper, we use $l = 4$), with adsorption energy $\epsilon_{a[b]}$ for $a[b]$-particles. As before, only nearest–neighbor lateral interaction energies and periodic boundary conditions are considered.

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

$$\Xi = 1 + \sum_{\substack{N_a, N_b = 0 \\ 1 \le N_a + N_b \le m}}^{m} \lambda_a^{N_a} \lambda_b^{N_b} \times \left\{ \sum_E g(E, N_a, N_b) \exp\left(-E/k_B T\right) \right\}, \tag{9}$$

where $\lambda_a \equiv \exp(\mu_a/k_B T)[\lambda_b \equiv \exp(\mu_b/k_B T)]$ is the activity of the species $a[b]$ and $g(E, N_a, N_b)$ is the number of configurations corresponding to N_a adsorbed a-particles and N_b adsorbed b-particles having the same energy E (E depends on N_a, N_b and the number of aa, ab and bb pairs on the cluster). $g(E, N_a, N_b)$ can be calculated exactly by means of a computer algorithm.

The partial adsorption isotherm corresponding to the $a[b]$-species can be obtained from Eq. (9) (Hill 1960),

$$\theta_{a[b]} = \frac{k_B T}{m}\left(\frac{\partial \ln \Xi}{\partial \mu_{a[b]}}\right)_{T, \mu_{b[a]}}. \tag{10}$$

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

5 Monte Carlo simulation

The binary mixture adsorption is simulated by assuming an ideal a-b gas at fixed T, μ_a and μ_b. In equilibrium there are two ways to perform a change of the system state: adsorbing (desorbing) one molecule onto (from) the surface. So, an elementary MC simulation step (MCS) can be detailed as follows:

1. Set μ_a, μ_b, T, and an initial state by placing randomly N molecules on the lattice.
2. Choose randomly one of the components of the mixture X ($X \equiv a$ or b).
3. Choose randomly one site i; generate a random number $\xi \in [0,1]$. (i) If the site i is empty, and $\xi \le W_{ads}$, then an X particle is adsorbed on i. Otherwise, the transition is rejected. W_{ads} is the transition probability from a state with N particles to a new state with $N+1$ particles. (ii) If the site i is occupied by an X particle, and $\xi \le W_{des}$, then the X particle is desorbed from i. Otherwise, the transition is rejected. W_{des} is the transition probability from a state with N particles to a new state with $N-1$ particles.
4. Repeat from step 2 M times.

W_{ads} and W_{des} are calculated following the Metropolis scheme (Metropolis et al. 1953).

The equilibrium state is reached after discarding the first 10^6 *MCS*, afterwards measurement averages were taken over other 10^6 successive configurations (*MCS*). Thermodynamic quantities, such as the total (θ) and partial isotherms (θ_a and θ_b) are obtained as simple averages:

$$\begin{aligned} \theta(\mu_a,\mu_b) &= \frac{\langle N\rangle}{M}, \\ \theta_a(\mu_a,\mu_b) &= \frac{\langle N_a\rangle}{M}, \\ \theta_b(\mu_a,\mu_b) &= \frac{\langle N_b\rangle}{M}, \end{aligned} \tag{11}$$

where θ, θ_a and θ_b are the total and partial surface coverages; the thermal average, $\langle\cdots\rangle$, means the time average throughout the Monte Carlo simulation.

The simulations were done for lattices of $L = 96$ and periodic boundary conditions. With this lattice size we verified that finite size effects are negligible. The chemical potential of one of the components (namely b component) is fixed through the process, $\mu_b = 0$, while the other one is variable.

6 Results and discussion

In order to simplify the analysis of the whole phase space, which includes a wide range of values of w_{aa}/k_BT, w_{bb}/k_BT and w_{ab}/k_BT, this section is divided in three subsections: the first deals with $w_{aa}/k_BT \ge 0$ and $w_{bb}/k_BT = w_{ab}/k_BT = 0$, the second deals with $w_{bb}/k_BT \ge 0$ and $w_{aa}/k_BT = w_{ab}/k_BT = 0$, and the third analyzes the case corresponding to $w_{ab}/k_BT \ge 0$ and $w_{aa}/k_BT = w_{bb}/k_BT = 0$. A similar scheme was used in Ref. (García et al. 2012) to depict the configurational structures that arise in the adsorbed phase. The cases where two or more interactions are non-zero can be understood as a combination of the three cases described in the paragraph above.

In addition, because the surface is assumed to be homogeneous, the interaction energy between the adsorbed particles and the sites is set to zero for the sake of simplicity $\epsilon_a = \epsilon_b = 0$.

The differences between numerical and theoretical results can be much easily rationalized with the help of the following relative error definition, ε, which is defined as:

$$\varepsilon = \left| \frac{\theta^{theor} - \theta^{sim}}{\theta^{sim}} \right|_{\mu} \tag{12}$$

where θ^{sim} (θ^{theor}) represents the coverage obtained by using MC simulation (analytical approach). Each pair of values ($\theta^{sim}, \theta^{theor}$) is obtained at fixed μ. We also define the integral error ε^i,

$$\varepsilon^i = \int_0^1 \varepsilon \, d\theta \tag{13}$$

which takes into account the differences between theoretical and simulation data in all range of coverage.

6.1 Case 1: $w_{aa}/k_BT \ge 0, w_{ab}/k_BT = w_{bb}/k_BT = 0$

In Fig. 1 we present the partial isotherms for $w_{bb}/k_BT = w_{ab}/k_BT = 0$ and various values of w_{aa}/k_BT. As it can be seen, the CA results (corresponding to solid lines) show a excellent agreement with the MC data (symbols) over the entire range of w_{aa}/k_BT. On the other hand, the behavior of the QCA curves (corresponding to dashed lines) can be explained as follows. There is a good agreement at low values of interaction energy, showing, for increasing values of w_{aa}/k_BT, a deviation from the MC data, but still reproducing the qualitative aspects, performing well at low and high coverage, and outlining the plateau at half coverage corresponding to the formation of a c(2×2) structure in the adsorbed species a. All this can be evaluated quantitatively from the absolute and integral error curves (see Figs. 2 and 3).

In Fig. 2 the difference between the QCA and MC simulation is clearly shown. This plot indicates that the error is zero for three limiting cases: $\theta = 0$, $\theta = 0.5$ and $\theta = 1$. It also shows that the maximum error is in the neighborhood of the $\theta = 0.5$ plateau, for all values of w_{aa}/k_BT. This extreme in the error is, for all studied values of w_{aa}/k_BT (always considering case 1), in the interval $\theta \in [0.4; 0.6]$ and never larger than 25 % (relative to θ^{sim}).

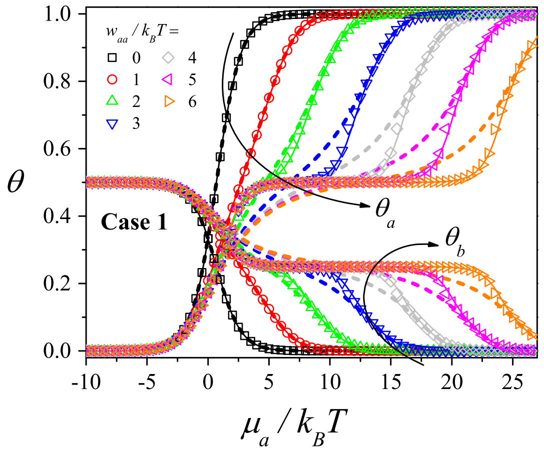

Fig. 1 Case 1: partial isotherms for the case $w_{aa}/k_BT = 0, 1, 2, 3, 4, 5$ and 6, and $w_{bb}/k_BT = w_{ab}/k_BT = 0$. *Symbols*, *solid lines* and *dashed lines* represent MC simulations, CA results and QCA data, respectively

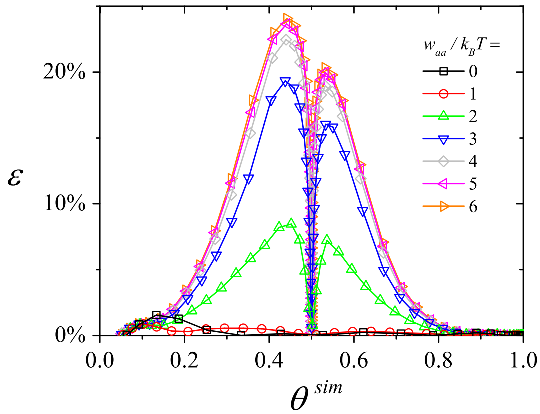

Fig. 2 Case 1: relative errors of QCA against the MC data as was defined in Eq. (12). The results correspond to the partial isotherm of species *a*

Another feature of the behavior of the QCA is the monotonic error growth with increasing w_{aa}/k_BT; this can be more clearly seen in Fig. 3. Regarding the CA, the integral error (ε^i) is plotted in Fig. 3. There, one can see that the error is about one order of magnitude smaller than the QCA in spite of the small size of the sub-system considered in the CA.

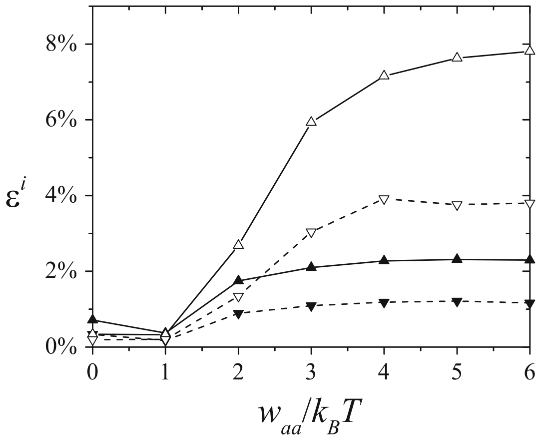

Fig. 3 Case 1: integral errors for QCA (*open symbol*) and CA (*full symbol*). Triangles up (*down*) correspond to the partial isotherms of species *a*[*b*]

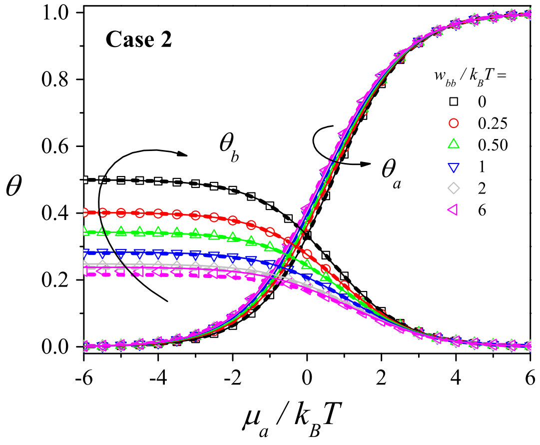

Fig. 4 Case 2: partial isotherms for the case $w_{bb}/k_BT = 0, 1, 2, 3, 4, 5$ and 6, and $w_{aa}/k_BT = w_{ab}/k_BT = 0$. *Symbols*, *solid lines* and *dashed lines* represent MC simulations, CA results and QCA data, respectively.

6.2 Case 2: $w_{bb}/k_BT \geq 0, w_{aa}/k_BT = w_{ab}/k_BT = 0$

In the case 2, as we have fixed $\mu_b = 0$, the isotherms of species *b* reach, for $\mu_a \to -\infty$, a constant value $\theta_b = 1/2$ at $w_{bb}/k_BT = 0$, corresponding essentially to randomly distributed particles (see Fig. 4). As interaction energy w_{bb}/k_BT is increased, the starting value of θ_b decreases. For increasing values of μ_a, the evolution of the isotherms shows that particles of species *a* completely displace the other species. In this case, QCA has a much better accordance with the simulation data compared with the previous case, as can be seen in the integral error one order of magnitude lower (see Fig. 5). On the other hand, the CA theoretical approach has again a good performance but quantitatively similar to the previous case. Regardless of the differences between the curves in Fig. 5, it is important to note that both approximations present errors less than 1 %, well below the errors that are usually found in experiments.

6.3 Case 3: $w_{ab}/k_BT \geq 0, w_{aa}/k_BT = w_{bb}/k_BT = 0$

In Fig. 6 we analyze the effects of the interspecies interaction w_{ab}/k_BT. For values of $\mu_a \to -\infty$ we have only the species *b* present, so there is no effect of w_{ab}/k_BT on the

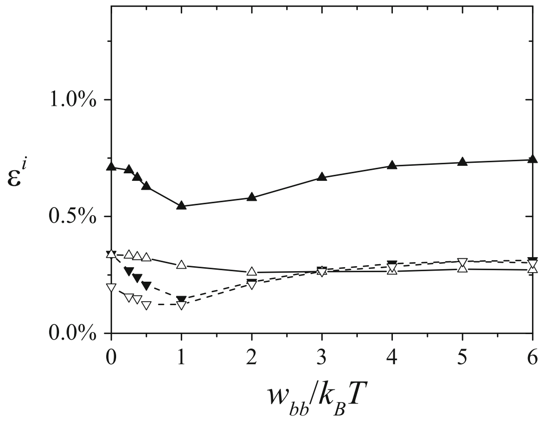

Fig. 5 Case 2: integral errors for QCA (*open symbols*) and CA (*full symbols*). Triangles up (*down*) correspond to the partial isotherms of species $a[b]$

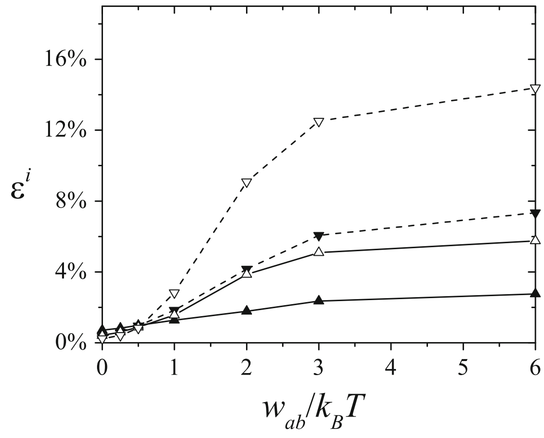

Fig. 7 Case 3: integral errors for QCA (*open symbols*) and CA (*full symbols*). Triangles up (*down*) correspond to the partial isotherms of species $a[b]$

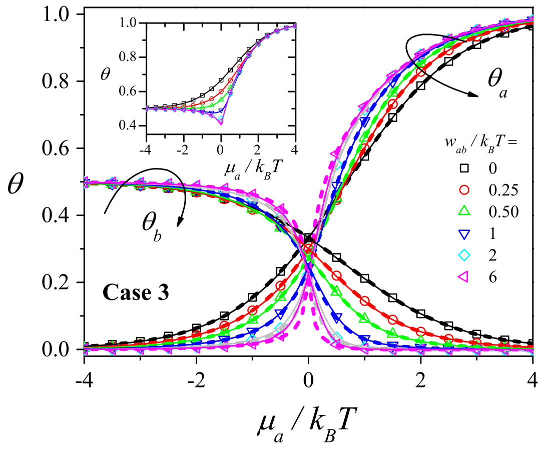

Fig. 6 Case 3: partial isotherms for the case $w_{ab}/k_BT = 0, 1, 2, 3, 4, 5$ and 6, and $w_{aa}/k_BT = w_{bb}/k_BT = 0$. *Symbols*, *solid lines* and *dashed lines* represent MC simulations, CA results and QCA data, respectively

curves. The same occurs at high values of μ_a as the species a has completely displaced the species b. In the intermediate zone both species coexist and the curves show a dependence on the interspecies lateral interaction. As can be seen from the integral errors in Fig. 7, although the CA has a better performance, both approximations are shown to be quantitatively equivalent.

In this case, an unusual feature is observed for sufficiently high values of w_{ab}/k_BT. This mixture effect can be explained as follows: as μ_a/k_BT increases and a particles start to adsorb, b particles are displaced from the surface. The repulsive character of w_{ab} leads to more b particles being displaced from the surface than a particles being adsorbed in such a way that the total coverage $(\theta_a + \theta_b)$ decreases and presents a local minimum. The inset in Fig. 6 shows this minimum from both the simulated points (symbols) and the theoretical approaches (curves). New experiments on interacting mixtures are needed in order to confirm (or discard) this theoretical prediction.

Finally, it is interesting to do some comments on the well-known *ideal adsorbed solution theory* (IAST), developed by Myers and Prausnitz (Myers and Prausnitz 1965) 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. In this context, even considering pure component isotherms that take into account the intra–species interaction, the IAST is not able to take into account the inter–species interaction effect. Thus, many features presented here, as the local minimum observed in the total coverage for high values of the intra–species interactions (Case 3), could not be predicted by the IAST.

7 Conclusions

In the present paper, two analytical approaches to the problem of adsorption of interacting binary mixtures have been analyzed. The theories addressed are the classical quasi-chemical approximation (QCA), generalized to two species, and the called cluster approximation (CA).

Both theories were systematically compared with Monte Carlo simulations. Three cases, corresponding to the presence of one of the lateral interactions at a time, were discussed. The effect of inclusion of different values for the lateral interactions can be understood as a combination of the three cases considered in details.

The theoretical results present a very good qualitative and quantitative agreement with the MC data. From the integral error curves it can be observed that, in most of the cases, the quasi chemical approximation has a slightly greater error than the cluster approximation, except for the case 2 where the agreement is better than 1 % in the entire range of parameters for both approaches.

In all the cases, the error is less than 10 %. The only exception is for the QCA in part of the case 3 for the highest values of interaction parameter (situation that does not have much correspondence with the experiment).

Considering the complexity in the experimental study of this adsorbates, it is important to note the usefulness of these theoretical approaches as a first tool to predict the behavior of a system governed by a large number of parameters. Thus, the application of QCA and CA allows (1) to identify and characterize the most prominent features of the process of adsorption of mixtures with inter– and intra–species interactions (systems where the role of the lateral interactions is relevant), (2) to draw general conclusions on the effects of the competition between two adsorbed species and (3) to provide a framework to consistently interpret experimental findings without heavy or time-consuming calculations. In this line, a comprehensive analysis of experimental data corresponding to adsorption of interacting mixtures is in progress.

Acknowledgments This work was supported in part by CONICET (Argentina) under project number PIP 112-201101-00615; Universidad Nacional de San Luis (Argentina) under project 322000; Universidad Tecnológica Nacional, Facultad Regional San Rafael, under project PID UTN 1835 Disp. 284/12; and the National Agency of Scientific and Technological Promotion (Argentina) under project PICT-2010-1466.

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