Adsorption of Gases on Strongly Heterogeneous Surfaces. The Integral Equation Approach and Simulations

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Received: July 2, 2003; In Final Form: September 8, 2003

Adsorption of single gases and their binary mixture on a strongly heterogeneous surface is modeled using the integral equation (IE) approach. The adsorbing surface is assumed to be characterized by a rectangular distribution of the adsorption energy with respect to each component of the mixture. The influence of correlations between the distribution functions associated with different components on the corresponding adsorption isotherms and phase diagrams is discussed. The validity of the condensation approximation, which may be also applied to the model, is assessed by comparing the corresponding results with exact solutions of the IE obtained for single, as well as for mixed, adsorption. In addition, predictions of the theory are compared with the results of the grand canonical Monte Carlo (GCMC) simulations carried out for the system studied. It is shown that, in general, the IE approach gives the results that are very close to the simulation data, especially when the distribution functions have the same shape, that is, when they are highly correlated.

1. Introduction

Separation and purification of gases by adsorption processes is a versatile method that is commonly used in modern chemical industry. For example, separation of atmospheric gases or hydrocarbons is usually performed by means of such adsorption techniques such as pressure swing adsorption (PSA) or temperature swing adsorption (TSA).[1] Because of high production rates and relatively low costs, the above techniques are much more economical than the corresponding cryogenic process. Obviously, the economic costs of these methods can be substantially reduced by the effective control and optimization of the adsorption process itself.

Technological installations used for the gas separation by adsorption processes are normally controlled by computer programs that have to respond as fast as possible to the changes in the system parameters. This requires fast calculation and prediction of such quantities as surface coverage of a given component as a function of the total pressure. To achieve this goal, relatively simple methods for a theoretical prediction of the mixed-gas adsorption equilibria are indispensable. Because the experimental studies of the multicomponent systems are difficult and time-consuming, usually the knowledge about the adsorption of single gases is used to predict also adsorption of their mixtures. This approach has been found to be very useful for many gas mixtures[2] and is still successfully used in chemical engineering.

As it can be expected, the surface of adsorbents commonly used in the separation processes may be highly disordered. This effect, caused by, for example, structure defects or impurities built into the structure, is responsible for energetic heterogeneity of the adsorbent. If so, theoretical description of the heterogeneous adsorption becomes sometimes difficult even for single-component systems. Of course, the situation is even more complex when two or more gases adsorb simultaneously. For this reason, simple expressions describing the mixed adsorption that can be easily implemented into computer programs are really necessary.

Different theories of the mixed adsorption based on the properties of the associated single-component systems have been proposed so far. These include, for example, the ideal adsorbed solution (IAS) theory formulated by Myers and Prausnitz[3] and further generalized for the case of heterogeneous surfaces by Myers,[4] the vacancy solution theory (VST) developed by Suwanayuen and Danner,[5] the potential theory (PT) proposed by Polyanyi and further generalized by Moon,[6] Grant,[7] Mehta, and Danner,[8] or finally the (IE) approach developed, among others, by Rudzinski,[2] Jaroniec,[8−14] and Wojciechowski.[15] The IE approach has been also recently applied to the adsorption of gas mixtures on heterogeneous surfaces by Nieszporek.[16−18] The results obtained in the last case included phase diagrams and isosteric heats of adsorption in a binary system. Unfortunately, because of lack of adequate experimental data only model studies have been carried out. This obstacle motivated us to verify the proposed theory in an independent way by using computer simulations.

The main objective of the present paper is to compare the derived analytical expressions with the corresponding data obtained from the Monte Carlo (MC) simulations. In particular, we study the integral equation approach coupled with a rectangular adsorption energy distribution, which is the simplest version of the IE that may be applied to calculate the mixed-gas adsorption equilibria. To predict the mixed adsorption isotherms and phase diagrams, we assume as a first approximation that the interactions between molecules are negligible. As we show, strict conformity between the presented equations and the simulation data is achieved for most of the cases studied.

2. Analytical Solutions

The integral equation (IE) method is one of the most popular approaches used to study adsorption of gases on heterogeneous

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solid surfaces.[19] According to the IE formalism, the adsorption isotherm for a heterogeneous surface in a one-component system can be expressed by the following fundamental equation:

$$\theta_{it}(p,T) = \int_{\Omega} \Theta(p,T,\epsilon)\chi(\epsilon) \, d\epsilon \tag{1}$$

where ϵ is the adsorption energy in the interval Ω, $\chi(\epsilon)$ is the distribution function of the adsorption energy, and Θ is the local model of the adsorption isotherm. In principle, eq 1 can be solved for arbitrary functions Θ and χ. However, analytical solutions of eq 1 are known only for a few pairs $\Theta-\chi$.[20] The vast majority of applications of the IE relates to the local model of adsorption that is given by the Langmuir equation (LA). This local model, combined with different distribution functions χ, leads to expressions for θ_{it} that are well-known empirical isotherm equations inherent to adsorption on heterogeneous surfaces. Some of them (e.g., Freundlich, Temkin, or Langmuir−Freundlich) can only be derived by means of eq 1 using suitable approximations such as the condensation approximation (CA) or the Rudziński−Jagiełło (RJ) expansion.[20] On the other hand, in the case of, for example, a rectangular distribution of ϵ, which corresponds to the Temkin isotherm, an exact solution of eq 1 is also obtainable. We take advantage of this unique property in the following discussion.

The simplest version of the IE + LA that can be used to model single- and mixed-gas adsorption equilibria on heterogeneous surfaces involves the rectangular distribution function mentioned previously and given by

$$\chi_i(\epsilon_i) = \begin{cases} \dfrac{1}{\epsilon_i^m - \epsilon_i^l}, & \epsilon_i^l \le \epsilon < \epsilon_i^m \\ 0, & \text{elsewhere} \end{cases} \tag{2}$$

where, for a pure component i, ϵ_i^l and ϵ_i^m are the lower and upper limit of the adsorption energy interval, respectively. In the case of the single-component adsorption on the surface with χ defined in eq 2, the CA approach leads to the Temkin isotherm

$$\theta_{it} = \frac{kT}{\Delta\epsilon_i} \ln \lambda_i \tag{3}$$

where k and T have their usual meanings, λ_i is the absolute activity of the adsorbate and $\Delta\epsilon_i = \epsilon_i^m - \epsilon_i^l$. The Temkin isotherm is frequently used to fit experimental data of adsorption of gases on strongly heterogeneous surfaces. This is because of extremely simple, linear dependence of θ_{it} on $\ln \lambda_i$ that is predicted by eq 3. However, the major drawback of eq 3 is its range of applicability, that is, limited to approximately $0.2 < \theta_{it} < 0.8$.[20] In other words, the Temkin isotherm fails when $\lambda_i \to 0$, as well as when $\lambda_i \to \infty$. These problems can, however, be easily avoided by solving the IE equation in an exact way. This yields the Temkin isotherm in a full form

$$\theta_{it} = \frac{kT}{\Delta\epsilon_i} \ln \left[\frac{1 + \lambda_i \exp\left\{\dfrac{\epsilon_i^m}{kT}\right\}}{1 + \lambda_i \exp\left\{\dfrac{\epsilon_i^l}{kT}\right\}} \right] =$$

$$\frac{kT}{\Delta\epsilon_i} \ln \left[\frac{1 + \lambda_i \exp\left\{\dfrac{\epsilon_i^l + \Delta\epsilon_i}{kT}\right\}}{1 + \lambda_i \exp\left\{\dfrac{\epsilon_i^l}{kT}\right\}} \right] \tag{4}$$

which now fulfills the necessary conditions $\lim_{\lambda_i \to 0} \theta_{it} = 0$ and $\lim_{\lambda_i \to \infty} \theta_{it} = 1$. Furthermore, this exact solution allows us also to develop the IE theory of mixed adsorption that is free from errors introduced by the CA.

Another useful quantity that characterizes the adsorption process is the isosteric heat of adsorption as a function of coverage, defined by

$$q_i = -k\left[\frac{\partial \ln \lambda_i}{\partial(1/T)}\right]_{\theta_{it}} + \Omega \tag{5}$$

where Ω is a coverage-independent term related to the standard chemical potential of the adsorbate. For the sake of simplicity, we consider only the behavior of the first, coverage-dependent term on the right-hand side (rhs) of eq 5 and call it further the isosteric heat of adsorption, q_i^{st}. This approach makes it possible to compare the theory with the simulations in quite a general case, without going into details related to the molecular structure of the adsorbate.

As it is known, the isosteric heat is much more sensitive to the nature of the adsorption system (heterogeneity of the surface, intermolecular interactions, steric effects) than the corresponding isotherms.[21,22] Thus, it is reasonable to test the adsorption model also by studying its ability to reproduce the enthalpic effects accompanying the adsorption. In the case of the single-component adsorption described by the Temkin isotherm, eq 5 gives the following simple relation

$$q_i^{st} = -kT \ln(\lambda_i) = -\Delta\epsilon_i \theta_{it} \tag{6}$$

while for the isotherm defined in eq 4, one obtains the following approximate expression:

$$q_i^{st} = \left(\Delta\epsilon_i \frac{1 + e^{\Delta\epsilon_i/(kT)}}{1 - e^{\Delta\epsilon_i/(kT)}} + 2kT \right) \theta_{it} + $$

$$\left(\frac{\epsilon_i^m \, e^{\Delta\epsilon_i/(kT)} - \epsilon_i^l}{e^{\Delta\epsilon_i/(kT)} - 1} - kT \right) \tag{7}$$

Let us now focus on a more complex case involving the multicomponent system. The following theory refers to the binary mixture, but it can be easily extended to the case when the adsorbate consists of more than two gases.[18] The IE approach applied to the adsorption of a mixture containing components 1 and 2 leads to different results depending whether the adsorption energies ϵ_1 and ϵ_2 are correlated or not. In the first case, a special situation involving highly correlated energies can be indicated, namely,

$$\epsilon_2 = \epsilon_1 + \Delta_{12} \tag{8}$$

which means that the associated distribution functions are only horizontally shifted along the energy axis, one with respect to the other. The above assumption may refer to the adsorption of mixtures on selective adsorbents where specific interactions with the surface (e.g., enantioselective interactions) are much stronger for one component than for the other. When the energies are correlated in the way adopted here, the IE method gives the following equations that describe the adsorption of a single component from the mixture.[18] The approximate solution, involving eq 3, reads

$$\theta_i = \left(\frac{kT}{\Delta\epsilon_i}\right)\frac{\lambda_i}{\sum_j \lambda_j \exp\left\{\dfrac{\Delta_{ij}}{kT}\right\}}\ln\left[\sum_j \lambda_j \exp\left\{\frac{\Delta_{ij}}{kT}\right\}\right]$$

$$\text{for}\quad i,j = 1,2 \quad (9)$$

while the exact solution, obtained with the help of the Temkin isotherm in a full form, eq 4, is given by

$$\theta_i = \left(\frac{kT}{\Delta\epsilon_i}\right)\frac{\lambda_i}{\sum_j \lambda_j \exp\left\{\dfrac{\Delta_{ij}}{kT}\right\}}\ln\left[\frac{1 + \left(\sum_j \lambda_j \exp\left\{\dfrac{\Delta_{ij}}{kT}\right\}\right)\exp\left\{\dfrac{\epsilon_i^m}{kT}\right\}}{1 + \left(\sum_j \lambda_j \exp\left\{\dfrac{\Delta_{ij}}{kT}\right\}\right)\exp\left\{\dfrac{\epsilon_i^l}{kT}\right\}}\right]$$

$$(10)$$

and in both equations

$$\Delta_{ij} = \begin{cases} -\Delta_{ji}, & i \neq j \\ 0, & i = j \end{cases} \quad (11)$$

Recall that the first isotherm equation corresponds to the CA, while the latter was derived with no auxiliary assumptions.[18] Obviously, the accuracy of the obtained results will depend on whether the CA-based or the exact isotherms for the single-component adsorption are used in the calculations. We will come back to this question in the next section.

The second extreme case related to the mutual relationship between the distribution functions involves a complete lack of correlations. In consequence, the two-dimensional distribution function $\chi_{ij}(\epsilon_i,\epsilon_j)$, which corresponds to the adsorption of the binary mixture, may be expressed by the following simple product: $\chi_i(\epsilon_i)\chi_j(\epsilon_j)$. If so, the adsorption isotherm for a given component of the mixture, presuming the Langmuir isotherm as a local model of adsorption, reads[20]

$$\theta_i = \frac{kT}{\Delta\epsilon_i \Delta\epsilon_j}\int\!\!\int_D \frac{\lambda_i \exp(\epsilon_i/(kT))}{1 + \lambda_i \exp(\epsilon_i/(kT)) + \lambda_j \exp(\epsilon_j/(kT))}\,d\epsilon_i\,d\epsilon_j$$

$$(12)$$

where the domain of integration, D, is a Cartesian product (a rectangle) of the intervals $(\epsilon_i^l, \epsilon_i^m)$ and $(\epsilon_j^l, \epsilon_j^m)$. Unfortunately, an exact calculation of the integral on the rhs of eq 12 is, in general, not possible. In particular, the solution of eq 12 includes a polylogarithm function, which involves summation of an infinite series. Thus, suitable approximate methods are necessary to make the problem tractable. For example, in the case when the adsorption energies are not correlated at all, the IE approach may be also coupled with the idea proposed by Wojciechowski.[15] In particular, Wojciechowski's approach assumes that the presence of the second component affects the adsorption of the first one only by random blocking of the adsorption sites and that the blocking effect is proportional to the coverage of the second component.[15] It is worth noting that this approximation is quite general and can be applied to the energy distribution functions of an arbitrary shape (also when the energies are correlated), as well as to multicomponent systems. Taking into account the above assumption, the corresponding adsorption isotherms for the binary system can be expressed by

$$\theta_i = \frac{\dfrac{kT}{\Delta\epsilon_i}\ln(\lambda_i)\left[\dfrac{kT}{\Delta\epsilon_j}\ln(\lambda_j) - 1\right]}{\dfrac{kT}{\Delta\epsilon_i}\ln(\lambda_i)\dfrac{kT}{\Delta\epsilon_j}\ln(\lambda_j) - 1}\quad \text{for}\quad i,j = 2 \quad (13)$$

in the CA-based case and by a more complicated equation

$$\theta_i =$$

$$\frac{\dfrac{kT}{\Delta\epsilon_i}\ln\left(\dfrac{1 + \lambda_i \exp(\epsilon_i^m/(kT))}{1 + \lambda_i \exp(\epsilon_i^l/(kT))}\right)\left[\dfrac{kT}{\Delta\epsilon_j}\ln\left(\dfrac{1 + \lambda_j \exp(\epsilon_j^m/(kT))}{1 + \lambda_j \exp(\epsilon_j^l/(kT))}\right) - 1\right]}{\dfrac{kT}{\Delta\epsilon_i}\ln\left(\dfrac{1 + \lambda_i \exp(\epsilon_i^m/(kT))}{1 + \lambda_i \exp(\epsilon_i^l/(kT))}\right)\dfrac{kT}{\Delta\epsilon_j}\ln\left(\dfrac{1 + \lambda_j \exp(\epsilon_j^m/(kT))}{1 + \lambda_j \exp(\epsilon_j^l/(kT))}\right) - 1}$$

$$\text{for}\quad ij = 2 \quad (14)$$

for the single-component Temkin isotherm in a full form.[18]

In the following, we assume that the difference between the standard chemical potentials of the components is negligible, that is, the components have very similar physical properties, for example, a pair of enantiomers. In consequence, eqs 9, 10, and 12−14) can be treated as functions of the total absolute activity (pressure), λ, which makes it possible to substitute λ_i ($i = 1, 2$) by λy_i, where y_i denotes the mole fraction of the component i and, obviously, $y_1 + y_2 = 1$.

3. The MC Simulations

To assess the validity of the equations derived in the previous section, we employed the grand canonical MC (GCMC) simulations that were carried out on a square $L \times L$ lattice of discrete sites. The method discussed below corresponds to the adsorption of a binary mixture, but it can be easily adapted to the single-component system by setting $y_i = 1$. In practice, the simulations of mixed adsorption were organized as follows. In the first step preceding the actual simulation, the lattice with a rectangular distribution of the adsorption energy was prepared. To this purpose, for each component of the mixture ($i = 1, 2$), a uniformly distributed adsorption energy, $\epsilon_i \in (\epsilon_i^l, \epsilon_i^m)$ was sampled and attributed to every lattice site. In consequence, every site was characterized by two, generally different, values of the adsorption energy, ϵ_1 and ϵ_2.

The MC simulation starts with a random selection of a lattice site. Next, depending on whether the site is empty ($s = 0$, $i = 0$) or it is occupied ($s = 1$, $i = 1$ or 2), an event attributed to this site is selected. In the first case, the type of the molecule to be adsorbed is chosen at random. To this purpose, a uniformly distributed random number $0 < \xi < 1$ is sampled, and when it is less than y_1, a molecule of type 1 is attempted to adsorb. In the opposite case, the adsorption of a molecule of type 2 is tested. In both cases, the adsorption event occurs with a probability

$$p_{ai} = \min(1, \lambda \exp(\epsilon_i)) \quad (15)$$

To decide whether the adsorption event is successful, ξ is sampled again. If it is less than p_{ai}, the molecule adsorbs. Then, s is set to 1, and i is appropriately updated. Otherwise, the trial ends. In the case when the selected site is occupied by a molecule of type i, the residing molecule is attempted to desorb with a probability $p_{di} = 1/p_{ai}$. In this case, the decision is made by applying the rule based on ξ, which was defined previously. When the molecule is chosen to be desorbed, then s and i are both set to 0. In the opposite case, the molecule remains

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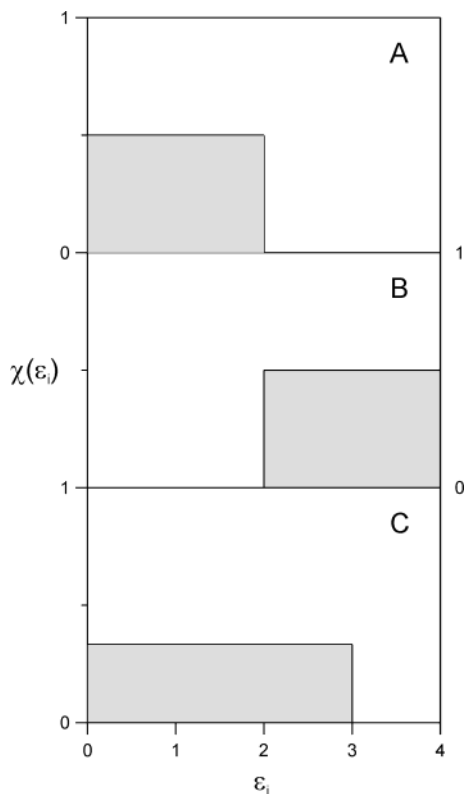*J. Phys. Chem. B, Vol. 107, No. 44, 2003* **12299**

Figure 1. The rectangular distribution functions of the adsorption energy used for the calculation of the single and mixed adsorption data.

adsorbed on the surface. The procedure described above corresponds to a single simulation step, which is repeated several times, typically $10^4 L^2$ for each λ (constant gas-phase composition) or each y_i (constant pressure). When the system reaches a steady state, that is, when the numbers of the adsorbed molecules, N_1 and N_2, remain approximately constant in the course of the simulation, the average values are calculated. To that purpose, the last $10L^2$ values of N_i are averaged, and the resulting values are divided by L^2. This yields the fractional coverage of the surface, θ_i, at a given λ or y_i. The mole fraction of the component i in the adsorbed phase, x_i, is defined as usual, that is, $x_i = \theta_i/(\theta_1 + \theta_2)$. All of the simulations described in this work were performed for $L = 100$. The results presented in the following sections are averages over 20 independent runs.

The isosteric heats of adsorption in one-component systems were calculated using the relation between the average potential energy of the adsorbed phase, U, and the fractional coverage, θ_{it}. In particular, the function $U(\theta_{it})$ obtained from the simulations was approximated by a fourth-degree polynomial and differentiated with respect to θ_{it}. This method revealed to be more accurate than the method based on the fluctuation theorem (FT)[23] applied also for comparison. Unfortunately, the FT method was found to generate large fluctuations in q_i^{st} when θ_{it} is close to 0, as well as when it is close to saturation.

4. Results and Discussion

Let us start this section with the discussion of the results obtained for the single-component systems. In this case, to match the simulation data, two sets of expressions can be used: eq 3 or eq 4 for the adsorption isotherms and eq 6 or eq 7 for the isosteric heats, respectively. The validity of these equations was tested by comparing their predictions with the corresponding data simulated for a few typical examples of χ. For the sake of convenience, in further discussion, we express all of the
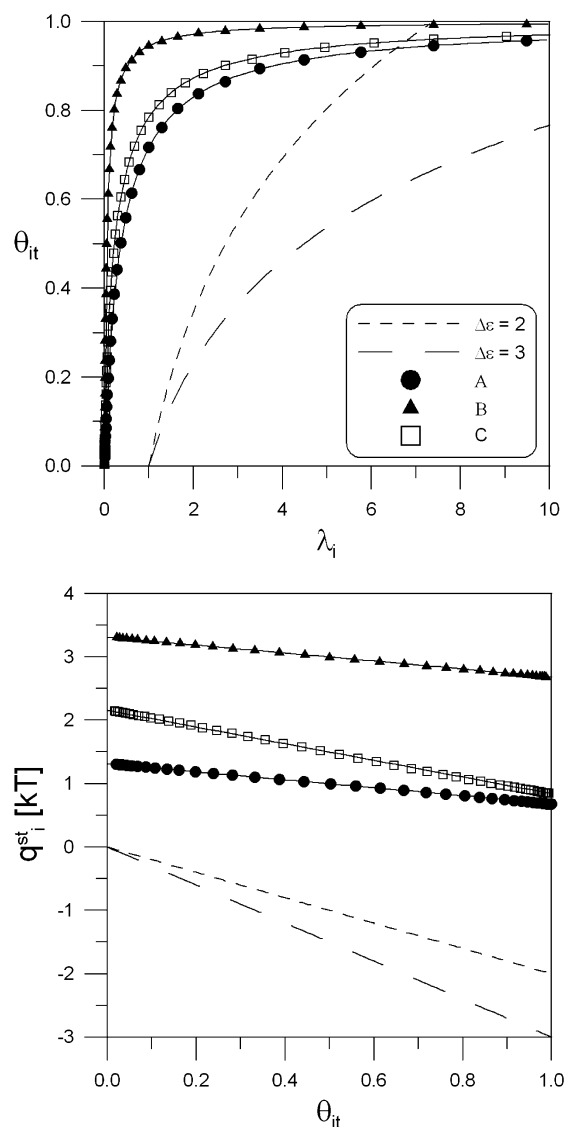

Figure 2. The single-component adsorption isotherms (top panel) and the isosteric heats of adsorption (bottom panel) obtained for the distribution functions shown in Figure 1. The solid and dashed lines in both panels denote the exact results (eqs 4 and 7), while the dashed lines are the data calculated using the CA (eqs 3 and 6). The symbols in the figure represent the corresponding results of the MC simulations.

adsorption energies in kT units. Accordingly, the simulations were performed for the surfaces characterized by the following rectangular distributions of the adsorption energy: (A) $\epsilon_i^l = 0$, $\epsilon_i^m = 2$; (B) $\epsilon_i^l = 2$, $\epsilon_i^m = 4$ (the same width of the distribution functions, $\Delta\epsilon_i = 2$); (C) $\epsilon_i^l = 0$, $\epsilon_i^m = 3$ ($\Delta\epsilon_i = 3$). Figure 1 illustrates this situation. This particular choice allows us to study the effect of the correlations between the distribution functions on the mixed adsorption.

Figure 2 shows the adsorption isotherms (top part) of single components calculated using eq 3 (solid lines) and eq 4 (dashed lines) set against the corresponding MC data. As it can be easily seen, the isotherms derived using the CA are completely different from the results obtained by means of the simulations. In particular, the theoretical isotherms are substantially underestimated at low pressures, but they also violate the condition $\lim_{\lambda_i \to \infty} \theta_{it} = 1$. The latter effect can be easily noticed for the distributions A and B. Note also that the isotherms calculated for these two distributions, using the CA, overlap entirely. This effect originates from the fact that eq 3 involves only the
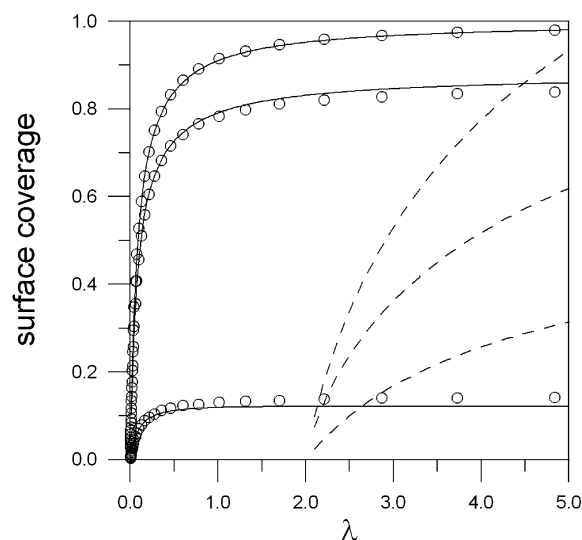
Figure 3. The adsorption isotherms obtained for the equimolar mixture of components 1 and 2 that are characterized by the uncorrelated distribution functions A and B, respectively (see Figure 1). The solid and dashed lines are the results calculated without the CA (eq 14) and with the CA (eq 13). The lines from the top to the bottom denote θ, θ_2, and θ_1, respectively. The results of the MC simulations are also shown for comparison (○).

difference $\Delta\epsilon_i$, which is identical in both cases, but not ϵ_i^l and ϵ_i^m themselves, which are different for A and B. On the other hand, the Temkin isotherm in a full form gives the results that coincide exactly with the simulations, regardless of the parameters used. A similar conclusion can be drawn while considering the isosteric heats of adsorption displayed in Figure 2 (bottom part). In this case, the isosteric heats predicted by eq 7 are straight lines with a slope that depends on $\Delta\epsilon_i$ only and with an intercept being a function of $\Delta\epsilon_i$, as well as of ϵ_i^l and ϵ_i^m. In consequence, the isosteric heats plotted against θ_{it} for A and B are parallel lines that are vertically shifted, one with respect to the other. This behavior agrees entirely with the predictions of the Monte Carlo method. As it can be also seen in Figure 2, the CA leads to serious discrepancies between the theory and simulations. In this case, like for the adsorption isotherms, it is observed that eq 6 predicts two instead of three different curves for the considered distributions. Obviously, the reason for that is the same as it is for the adsorption isotherms discussed earlier (see eqs 3 and 6).

Taking into account the above remarks, one may expect that the CA should produce substantial errors also in the quantities inherent to the mixed adsorption. To illustrate this, we calculated the adsorption isotherms for the equimolar mixture the components of which are associated with the distributions A and B (see Figure 1). We call this case briefly A + B. Moreover, we assumed no correlations between the distributions. This choice was based on general properties of eqs 13 and 14 that, to some extent, embrace also the case when the distributions are correlated. Consequently, these properties can be treated as representative for all of the CA-based formulas for the mixed adsorption used in this work. The results obtained by means of both eqs 13 and 14 are compared with the simulations in Figure 3. As seen in this figure, the CA fails completely because eq 13 (dashed lines) predicts the isotherms that are different even qualitatively from the simulations. On the other hand, the isotherms calculated using eq 14 (solid lines) nearly overlap with the simulated curves. For these reasons, in the following, we focus exclusively on the theory that does not involve the
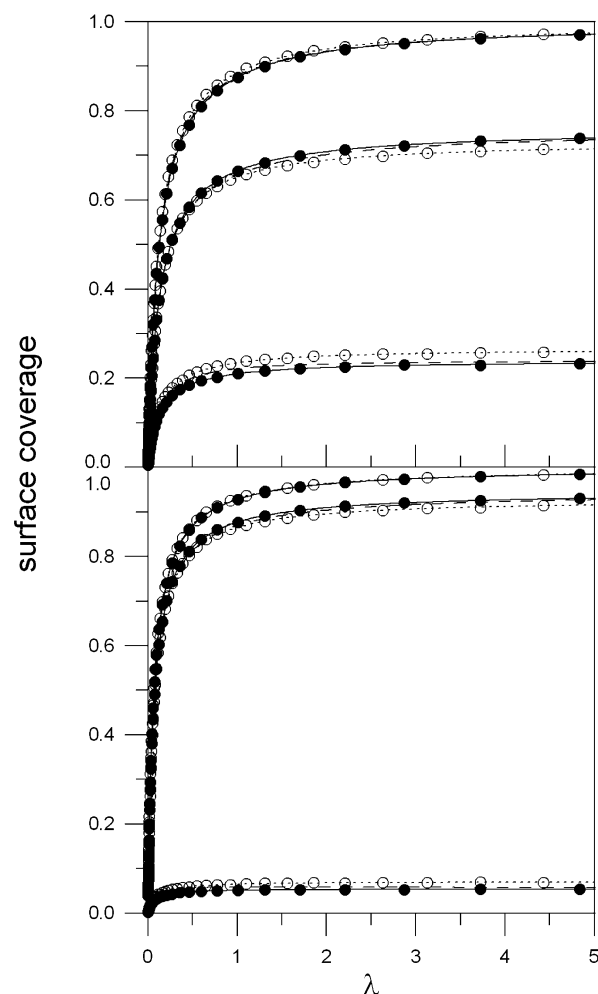

Figure 4. The adsorption isotherms obtained for the mixture of components 1 and 2 that are characterized by the distribution functions A and B, respectively. The top part corresponds to $y_1 = 0.7$, while the bottom part corresponds to $y_1 = 0.3$. The solid and dashed lines are the results calculated using eq 10 (existence of the correlations) and eq 13 (lack of the correlations). In both parts, the lines from the top to the bottom denote θ, θ_2, and θ_1, respectively. The symbols are the MC data obtained for the correlated (●) and uncorrelated (○) distributions. The additional dotted lines represent the isotherms obtained by numerical integration of eq 12.

CA which, as we demonstrated, leads to entirely erroneous results for single, as well as mixed, adsorption.

As we mentioned before, eq 14, which refers to the uncorrelated distributions, has a more universal character than eq 10 because it can be, in principle, used also in the case when the distributions are correlated. To test the above hypothesis, we simulated the mixed adsorption isotherms for the correlated and uncorrelated distributions A + B for two different mole fractions of the first component (in the following, the first component always corresponds to the first distribution in the above sum), that is, $y_1 = 0.7$ and $y_1 = 0.3$. The top part of Figure 4 presents the results obtained for the first value, while the bottom part corresponds to the latter. The symbols in both parts denote the MC data. As it follows from Figure 4, in general, the partial isotherms θ_1 simulated for the uncorrelated distributions (open symbols) run above the analogous curves obtained for the correlated distributions (filled symbols). Simultaneously, an opposite tendency can be observed for θ_2. However, despite noticeable differences between the partial isotherms, the total isotherms, $\theta = \theta_1 + \theta_2$, obtained for the correlated and uncorrelated distributions overlap.
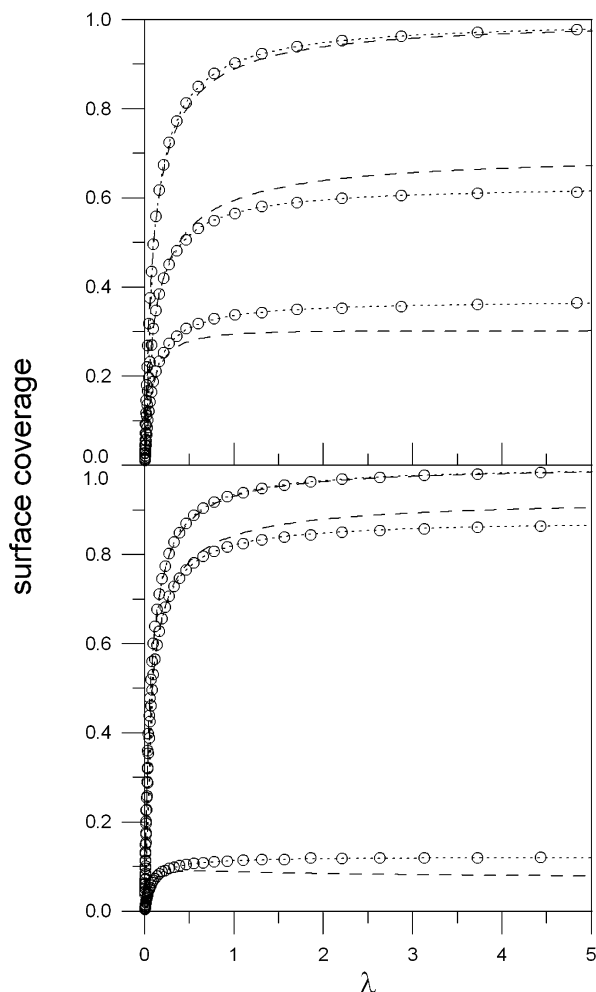
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Figure 5. The adsorption isotherms obtained for the mixture of components 1 and 2 that are characterized by the distribution functions C and B, respectively. The top part corresponds to $y_1 = 0.7$, while the bottom part corresponds to $y_1 = 0.3$. The solid and dashed lines are the results calculated using eq 10 (existence of the correlations) and eq 13 (lack of the correlations), respectively. In both parts, the lines from the top to the bottom denote θ, θ_2, and θ_1. The symbols are the MC data obtained for the correlated (●) and uncorrelated (○) distributions. The additional dotted lines represent the isotherms obtained by numerical integration of eq 12.

As seen in Figure 4, the behavior of the isotherms simulated for the correlated distributions is perfectly reproduced by the theory (solid lines). This refers to the partial, as well as to the total, adsorption isotherms obtained for $y_1 = 0.7$ and $y_1 = 0.3$. Obviously, the observed agreement is not surprising because eq 10 is an exact solution of eq 12 with the condition $\epsilon_2 = \epsilon_1 + \Delta_{12}$. On the other hand, a more interesting situation can be encountered in the case of the uncorrelated distributions. Here, the behavior of the partial isotherms calculated using eq 14 (dashed lines) resembles much more closely the behavior of the isotherms simulated for the correlated than for the uncorrelated distributions. As it can be noticed in the bottom part of Figure 4, the discrepancies between the simulations and the theory are somewhat smaller for $y_1 = 0.3$ than for $y_1 = 0.7$. Of course, the observed effect originates from the fact that eq 14 was derived using the approximation proposed by Wojciechowski.[15] However, an exact solution can be obtained by direct numerical calculation of the double integral on the rhs of eq 12. Effect of this procedure is also shown for comparison in Figure 4 (dotted lines). In this case, the theory agrees fully with the simulations.
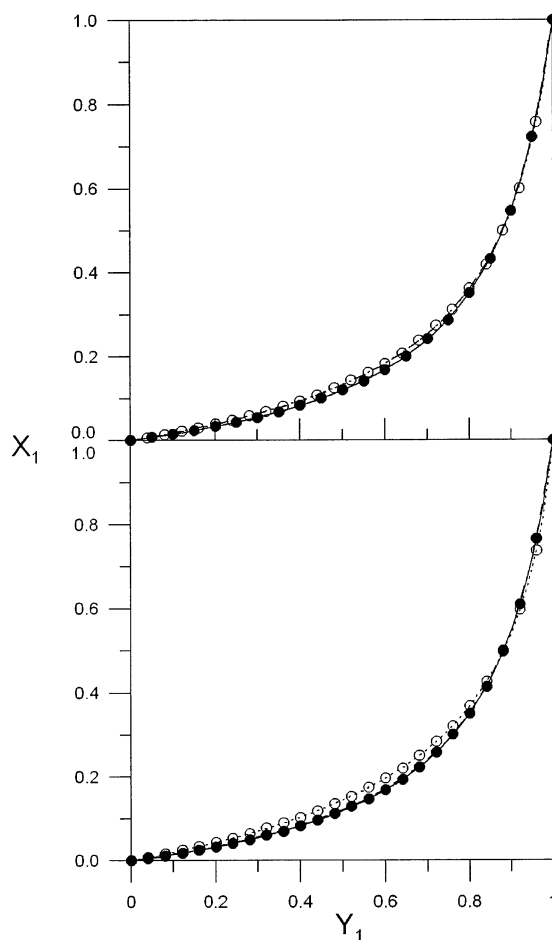

Figure 6. The phase diagrams obtained for the mixture of components 1 and 2 that are characterized by the distribution functions A and B, respectively. The top part corresponds to $\lambda = 0.1$, while the bottom part corresponds to $\lambda = 10$. The notation used in the figure is the same as that for the adsorption isotherms.

The above discussion refers to the case when the distribution functions are exactly the same in shape but they are only horizontally shifted along the energy axis. Another possibility involves a more general situation, that is, when the distributions are both rectangular but they have different widths. In this case, to match the simulations, only the approximate eq 14 can be used as an analytical solution of the problem. The results obtained using eq 14 for the case C + B are compared with the simulations in Figure 5. The top part corresponds to $y_1 = 0.7$, while the bottom part shows analogous data but plotted for $y_1 = 0.3$. Here we observe that Wojciechowski's approximation leads to much greater discrepancies than those observed for the correlated distributions (compare with Figure 4). As it can be easily noticed in both parts of Figure 5, the theoretical partial isotherms (dashed lines) are considerably overestimated for the second component and underestimated for the first one. This effect, like in the case of the correlated distributions, is more profound for $y_1 = 0.7$ than for $y_1 = 0.3$. In consequence, one may conclude that eq 14, although derived for the distributions of different widths, describes the mixed adsorption process in a more accurate way when the distributions functions are very similar in shape.

Let us now present the phase diagrams obtained for the systems discussed above. They were calculated for two markedly different values of λ, that is, 0.1 (low pressures) and 10 (high pressures). Figure 6 shows the results calculated for the case A + B, assuming existence of the correlations (solid lines, eq 10),
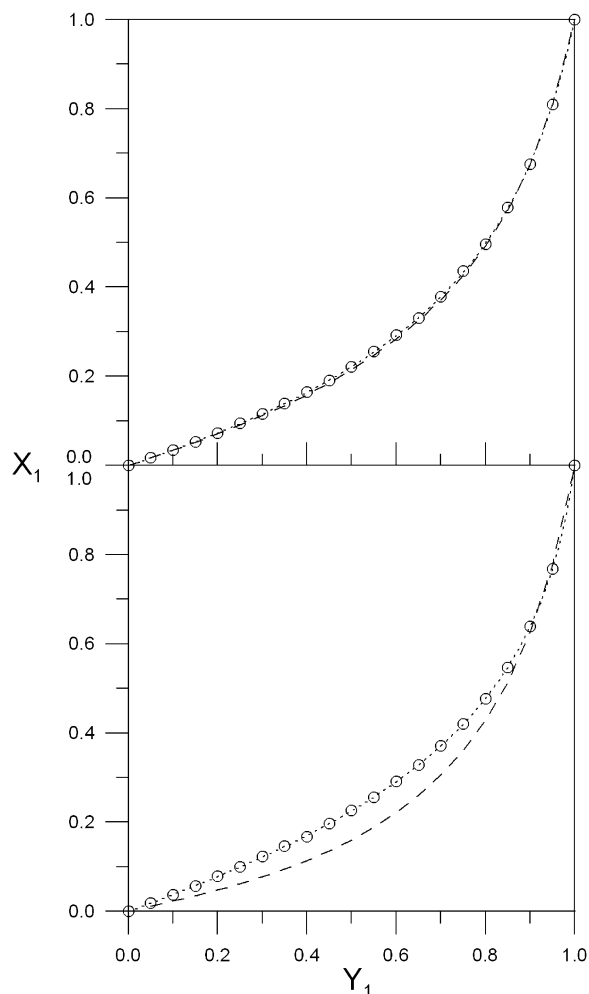
Figure 7. The phase diagrams obtained for the mixture of components 1 and 2 that are characterized by the distribution functions C and B, respectively. The top part corresponds to $\lambda = 0.1$, while the bottom part corresponds to $\lambda = 10$. The notation used in the figure is the same that as for the adsorption isotherms.

as well as lack of them (dashed lines, eq 14). The filled and open symbols in Figure 6 are the corresponding diagrams obtained from the simulations, respectively. The top part of the figure refers to $\lambda = 0.1$, while the bottom part displays the diagrams calculated for $\lambda = 10$. As seen in Figure 6, the IE predicts the phase diagrams that are, in general, consistent with the simulations, regardless of the assumed relationship between the distribution functions. The observed agreement between the theory and the MC data deteriorates somewhat for the uncorrelated case when λ is large (see the bottom part). In this case, the behavior of x_1 (dashed line) follows that of the simulated diagram obtained for the correlated distributions (filled symbols). This tendency is consistent with our earlier observations related to the adsorption isotherms (compare with Figure 4). Thus, we may conclude again that the IE, although it works perfectly for the correlated distributions, is less accurate when the distributions are exactly the same in shape but they are uncorrelated.

Figure 7 shows analogous diagrams but obtained for the uncorrelated distributions C + B. Interestingly, a good match between the theory and the simulations is observed only for low pressures (see the top part). In contrast, in the case of $\lambda = 10$, the curve predicted by eq 14 (dashed line) exhibits considerable deviation from the simulated diagram. Note that

also the partial isotherms shown in the figure follow this trend. The effects discussed above confirm again that, for the uncorrelated distributions, the proposed version of the IE works much better for low than for high pressures.

5. Concluding Remarks

The results of this work demonstrate that the IE, in general, provides a good quantitative description of the binary adsorption on strongly heterogeneous surfaces. This conclusion is firmly supported by the results of the GCMC simulations carried out for the rectangular distributions of the adsorption energy. In particular, the obtained results indicate that the IE predicts the adsorption isotherms and phase diagrams that are entirely consistent with the simulations when the distribution functions are highly correlated. When, however, the distributions are markedly different in width, the theory gives somewhat less accurate predictions because of the adopted approximations that are necessary to obtain the analytical solution of the problem. Additionally, in this case, the IE is found to describe adequately the mixed adsorption only at low pressures. Nevertheless, the observed discrepancies between the theory and simulations are minor compared to those produced by the CA.

The obtained results indicate also that the CA leads to entirely incorrect behavior of the adsorption characteristics inherent to single and mixed adsorption on strongly heterogeneous surfaces. This finding proves that to model correctly the adsorption in the binary systems studied here one should exclude application of the CA. This choice leads to a much more complicated form of the associated equations but causes the results to be consistent with the computer experiments and physically realistic.

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