

# Statistical Thermodynamics Models for Polyatomic Adsorbates: Application to Adsorption of *n*-Paraffins in 5A Zeolite

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Experimental adsorption isotherms of five *n*-paraffins (ethane, propane, butane, pentane, and hexane) in 5A zeolite were described by means of a statistical thermodynamics model for linear adsorbates (MLA) developed by Ramirez-Pastor et al. (1999) and compared with the well-known multisite Langmuir model (MSL) of Nitta et al. (1984). The experimental data, obtained by different authors in a wide range of temperatures and pressures, were correlated by using an algorithm of multiple fitting. Two main conclusions were drawn from the analysis of experimental data: (i) for small molecules (ethane, propane), MLA is the more accurate model, validating the hypothesis of the linear rigid character of the adsorbate and reinforcing previous results obtained from the analysis of computational experiments developed for dimers and linear trimers; (ii) for large molecules (*n*-butane, *n*-pentane, *n*-hexane), the better performance of the MSL model suggests that the admolecules adsorb in a nonlinear structure. The isosteric heat of adsorption dependence on the number of carbons obtained from our study, ranging between 23.84 kJ/mol for ethane and 59.26 kJ/mol for hexane, showed a very good agreement with previous results reported in the literature, confirming the consistency of our analysis.

## 1. Introduction

The problem of interpreting experimental data of adsorption by using different theoretical models has been considered repeatedly.<sup>1–5</sup> However, the number of adjustable parameters required for accurate information to be derived from such an analysis still an open question.

The history of the problem leads us to Langmuir,<sup>1</sup> who considered that the adsorbent is represented by a homogeneous lattice of adsorption sites and developed the following essential assumption: *each molecule of adsorbate occupies one adsorption site of the surface*. On the basis of the dynamic equilibrium between adsorbed and gas phases and discarding chemical dissociation, Langmuir derived the well-known equation for studying localized adsorption without adsorbate–adsorbate lateral interactions

$$K_e = \frac{1}{p} \frac{\theta}{(1 - \theta)} \quad (1)$$

where  $K_e = k_e \exp(H_{st}/RT)$  is the equilibrium constant, being  $k_e$  the preexponential factor,  $H_{st}$  the isosteric heat of adsorption, and  $R$  the ideal gas law constant. The relation between  $H_{st}$  and the adsorption energy of the sites,  $\epsilon_o$ , follows from equipartition considerations and contains information about the degrees of freedom available to the molecules in both the gas phase and the adsorbed phase. In the case of a monatomic gas and localized adsorption, the isosteric heat results in  $H_{st} = -\epsilon_o - (1/2)RT$ .<sup>6</sup> The

coverage  $\theta$  represents the amount adsorbed  $Q$ , in terms of the maximum amount adsorbed  $Q_{max}$  ( $\theta = Q/Q_{max}$ ). Here,  $Q_{max}$  is temperature independent.<sup>7</sup> In this scheme, a set of isotherms for different temperatures can be correlated by using only one value of  $Q_{max}$  and a temperature dependent  $K_e(T)$  as adjustable parameters, with the restriction that  $\ln K_e(T) \propto H_{st}/T$ .

Later on, Nitta et al.<sup>2,3</sup> modified eq 1, including multisite-occupancy adsorption, that is, assuming that the adsorbate can occupy  $k$  sites on the surface. On the basis of this consideration, the energy involved in the adsorption of one molecule (or one  $k$ -mer) is  $k\epsilon_o$ , and eq 1 results in the multisite Langmuir (MSL) isotherm<sup>3</sup>

$$K_e = \frac{1}{p} \frac{\theta}{(1 - \theta)^k} \quad (2)$$

As a consequence of taking into account the effect of adsorbate size, a new adjustable parameter  $k$  was included in the MSL model, with respect to the original Langmuir model.

More recently, Ramirez-Pastor et al.<sup>8–10</sup> presented a model to study adsorption of linear adsorbates on homogeneous surfaces. The model, hereafter denoted by MLA, is based on exact forms for the thermodynamic functions of linear adsorbates in one dimension and its generalization to higher dimensions. The resulting equation for the adsorption isotherm is<sup>8–10</sup>

$$K_e = \frac{1}{p} \frac{\theta \left[ 1 - \frac{(k-1)}{k} \theta \right]^{k-1}}{(1 - \theta)^k} \quad (3)$$

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(7) Some experimental data have been correlated by using the temperature-dependent parameter  $Q_{max}(T)$ . However, this hypothesis lacks physical meaning.

As can be noticed, MLA and MSL have the same number of adjustable parameters. The MLA model was obtained from exact calculations in one dimension. For this reason, it is expected that eq 3 provides a good description for adsorption of linear  $k$ -mers. On the other hand, the MSL model for homogeneous surfaces can be obtained from Flory's theory<sup>11,12</sup> for polymer solutions when the solvent is monomeric with unitary molar volume. This is isomorphous with the case analyzed here, where empty sites and  $k$ -mers formally correspond to solvent and polymers (in Flory's solution), respectively. Although MSL was developed for studying adsorption of flexible  $k$ -mers,<sup>13</sup> the model includes the case of linear  $k$ -mers as a particular case. Beyond the structure of the adsorbate, the main difference between both models concerns the degree of approximation as the way of accounting for the total number of distinguishable arrangements for distributing identical  $k$ -mers on a surface.

In previous works, the MSL model has been successfully used to describe different adsorption systems such as adsorption of  $O_2$ <sup>3,14</sup> in 5A and 10X zeolite,  $n$ -paraffins<sup>4,15-17</sup> in 5A zeolite, and  $n$ -paraffins<sup>5</sup> in 13X zeolite, among others. However, the information obtained about size and structure of the adsorbate is very limited. In this sense, a comparison of computer experiments (obtained from computational simulations), where the structure of the adsorbate is controlled, can help to establish criteria to interpret the fitting results.

In this context, the aim of the present work is to present an exhaustive study about the applicability of eqs 2 and 3, to describe experimental data of multisite-occupancy adsorption. This study consists of two different parts: in the first part, theoretical models are analyzed in comparison with numerical adsorption isotherms of dimers and linear trimers on discrete lattices obtained by using Monte Carlo (MC) simulations in the grand canonical ensemble. As mentioned before, the simulation scheme provides a test of the analytical model's predictability. In the second one, experimental isotherms for ethane,<sup>18,19</sup> propane,<sup>20</sup> butane,<sup>21</sup>  $n$ -pentane,<sup>16</sup> and  $n$ -hexane<sup>17</sup> adsorbed in 5A zeolite, as well as the adsorption heats, are used to test the accuracy of the theoretical models. The combination of MC simulations, the MSL model (developed for flexible  $k$ -mers), the MLA model (treating with linear  $k$ -mers), and experimental results from different authors allows light to be shed on the spatial configuration of a polyatomic molecule in the adsorbed state.

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(13) Flexible  $k$ -mer is a chain of adjacent monomers with the following sequence: once the first monomer is in place, the second monomer occupies one of the  $c$  nearest-neighbor sites of the first monomer. Third and successive monomers occupy one of the  $c - 1$  nearest-neighbor sites of the preceding monomer. This process continues until  $k$  monomers are placed without overlapping.

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The paper is organized as follows: in section 2, the fitting method is presented and contrasted against controlled computational experiments from MC simulations. Once the method is validated, section 3 is devoted to analyze experimental results for adsorption of  $n$ -paraffins in 5A zeolite, by using MSL and MLA models. Finally, general conclusions are given in section 4.

## 2. Modeling of Data: Least-Squares Fitting and Comparison with Monte Carlo Simulation in Grand Canonical Ensemble

In fitting experimental data, we considered the least-squares statistic.<sup>22</sup> Thus, we assume that  $n$  data points  $(x_i, y_i, z_i; i = 1, \dots, n)$ , are being fitted to a model that has  $m$  adjustable parameters  $a_j, j = 1, \dots, m$ . The model predicts a functional relationship between the measured independent and dependent variables

$$z(x,y) \equiv z(x,y; a_1, \dots, a_m) \quad (4)$$

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  $a_j$  values? The first thing that comes to mind is the familiar least-squares fit, minimized over  $a_1, \dots, a_m$

$$\sum_{i=1}^n [z_i - z(x_i, y_i; a_1, \dots, a_m)]^2 \quad (5)$$

The parameters of the model are then adjusted to achieve a minimum in function 5, yielding best-fit parameters. The adjustment process turns into a minimization in many dimensions.

In this work, the least-squares estimation of the isotherm parameters was performed for each adsorbate by minimizing the sum of the square difference between the experimental pressure and the predicted pressure, over all  $n$  data points corresponding to the complete set of isotherms. That is, the function  $p(\theta, T) \equiv p(\theta, T; k, H_{st}, Q_{max})$  (from eqs 2 and 3) corresponds to  $z(x, y) \equiv z(x, y; a_1, \dots, a_m)$ , being  $(\theta, T)$  and  $(k, H_{st}, Q_{max})$ , the dependent variables and fitting parameters, respectively.

To test the fitting procedure, numerical simulations are used as computer experiments. In this sense, the adsorption process is simulated through a grand canonical ensemble Monte Carlo method.<sup>23,24</sup> For a given value of the temperature  $T$  and chemical potential  $\mu$ , an ideal gas phase of linear polyatomic molecules is put in contact with a square lattice of  $M \rightarrow \infty$  adsorption sites. Under these conditions, the Hamiltonian of the system is given by

$$H = (\epsilon_0 - \mu) \sum_{i=1}^M c_i \quad (6)$$

where  $c_i$  is the occupation variable, which can take the values  $c_i = 0$  or 1, if the site  $i$  is empty or occupied by a  $k$ -mer unit, respectively.

In adsorption-desorption equilibrium there are two elementary ways to perform a change of the system state, namely, adsorbing one molecule onto the surface (adding one molecule into the adsorbed phase volume  $M$ ) and desorbing one molecule from the adsorbed phase (removing

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one molecule from the volume  $M$ ). The algorithm to carry out an elementary step in Monte Carlo simulation (1 MCS), is as follows:

Given a square lattice of  $M$  adsorption sites with energies already assigned, (i) Set the value of  $\mu$  and temperature  $T$ . (ii) Choose randomly one of the linear  $k$ -uples on the lattice and generate a random number  $\xi \in [0,1]$

\* if the  $k$  sites are empty, then adsorb a molecule if  $\xi \leq W(H_i \rightarrow H_f)$ .

\* if the  $k$  sites are occupied by atoms belonging to the same molecule, then desorb the molecule if  $\xi \leq W(H_i \rightarrow H_f)$ .

\* otherwise, the attempt is rejected.

$W(H_i \rightarrow H_f)$  is the transition probability given by the Metropolis<sup>25</sup> rule

$$W(H_i \rightarrow H_f) = \min\{1, \exp(-\beta\Delta H)\} \quad (7)$$

where  $\beta = 1/k_B T$ ,  $k_B$  being the Boltzmann constant, and  $\Delta H = H_f - H_i$  is the difference between the Hamiltonians of the final and initial states. (iii) Repeat from step ii  $M$  times.

The equilibrium state can be well reproduced after discarding the first  $r' = 10^5 - 10^6$  MC simulations. Then, averages are taken over  $r = 10^5 - 10^6$  successive configurations.

The adsorption isotherm, or mean coverage as function of the chemical potential  $[\theta(\mu)]$ , is obtained as a simple average

$$\theta(\mu) = \frac{1}{M} \sum_{i=1}^M \langle c_i \rangle = \frac{k\langle N \rangle}{M} \quad (8)$$

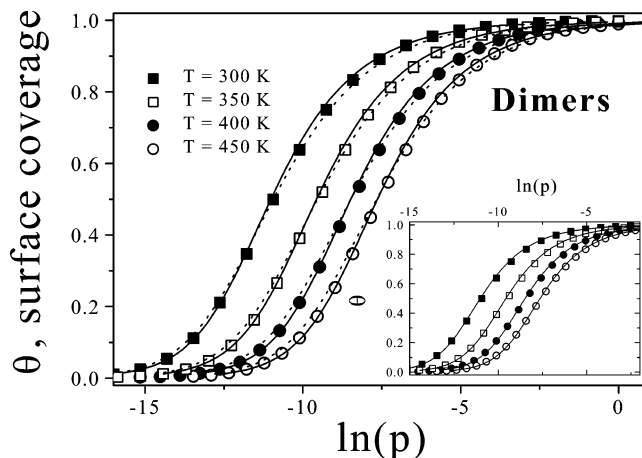
where  $\langle N \rangle$  is the mean number of adsorbed particles, and  $\langle \dots \rangle$  means the time average over the  $r$  Monte Carlo simulation runs.

The simulations have been developed for square  $L \times L$  lattices, with  $L = 72$ ,  $\epsilon_0 = -12.55$  kJ/mol, and periodic boundary conditions. With this lattice size we verified that finite size effects are negligible. In addition, a set of isotherms (at different temperatures) have been obtained for each type of ad-molecule (dimer/trimer).

Figure 1 presents a comparison between simulated adsorption isotherms (coverage vs  $\ln p$ ) and the corresponding ones obtained from the analytical approaches of eqs 2 and 3 for dimers adsorbed at different temperatures. In fitting the simulation data, theoretical models were used with the adsorbate size set equal to 2 ( $k = 2$ ). The values obtained for  $H_{st}$  and  $Q_{max}$  are listed in Table 1 and are in good agreement with those used in the numerical simulations. Given that the adsorption energy of the dimers on the homogeneous surface,  $2\epsilon_0$ , is the only one interaction in the system, the isosteric heat of adsorption can be written as  $H_{st} = -2\epsilon_0 = 25.10$  kJ/mol.<sup>26</sup> In addition,  $Q_{max} = (72 \times 72)/2 = 2592$ . As expected for small molecules, the hypothesis of linear adsorbate holds true and the MLA model seems to be the more accurate description with a dispersion of  $D = 0.09$  in comparison with the corresponding ones obtained from the MSL model,  $D = 0.21$ . In addition, the MLA model shows a closer agreement between the values of  $H_{st}$  and  $Q_{max}$  incoming from fitting and the one established "a priori" in the computer

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(26) The (vibrational) translational, vibrational, and rotational degrees of freedom available to the diatomic molecules in the (adsorbed) gas phase are not considered in the simulations. Consequently, the isosteric heat of adsorption does not present a term  $RT$ .



**Figure 1.** Adsorption isotherms ( $\theta$  vs  $\ln p$ ) for dimers adsorbed on a square lattice at different temperatures as indicated. Symbols represent MC results and (dashed) solid lines correspond to the (MSL) MLA model with  $k = 2$ . Comparison between simulated (symbols) and MLA (solid lines) results with all free parameters is shown in the inset. The parameters used in the theoretical models and in the simulation runs are listed in Table 1.

experiment. The differences<sup>27</sup> are as much as 0.16% and 0.11%, respectively, whereas those for the MSL model are significantly larger (2.8% and 0.3%).

In the study of Figure 1, we set  $k = 2$ . This strategy diminishes considerably the computational cost of the theoretical calculations. However, it is of interest to evaluate the capabilities of the theory for describing experiments involving adsorbates of unknown size. For this purpose, we repeat the procedure of Figure 1 by using the crude MLA model with all adjustable parameters ( $k$ ,  $H_{st}$ , and  $Q_{max}$ ). The resulting curves are shown in the inset, and the values of the parameters are given in Table 1. A similar study was done by applying the MSL model (the curves are not shown in the inset for sake of simplicity). Even though a good fitting is found from the MSL model, MLA results are more accurate for the case of dimers.

In many cases, sorption experimental results are plotted as a function of pressure. Formally, fitting data in a pressure scale implies the use of new forms as adjusting functions (in comparison with the analysis in Figure 1). Its consequences on the fitting procedure are evaluated in Figure 2, where simulation and theoretical isotherms are presented in a pressure scale. As observed from Figure 2 and Table 1, data can be fitted correctly, with differences of 5.0 [9.5]% and 0.15 [0.19]% (for  $H_{st}$  and  $Q_{max}$ , respectively), for the MLA [MSL] model. As remarked before, the MLA model provides more accurate results.

Figure 3 (4) shows adsorption isotherms for trimers as a function of  $\ln p$  ( $p$ ) at different temperatures (notation is as in Figures 1 and 2). The results are analogous to those obtained for the case of dimers. Namely, with the MLA model the fitting parameters ( $H_{st}$ ,  $Q_{max}$ , and  $D$ ) are much more satisfactory (see Table 1), reinforcing the arguments given in the explanation of Figures 1 and 2.

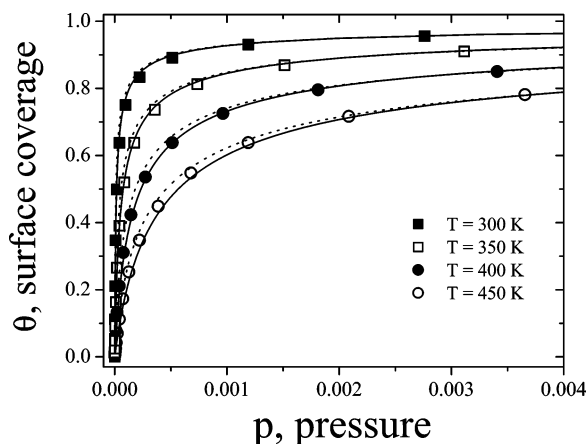
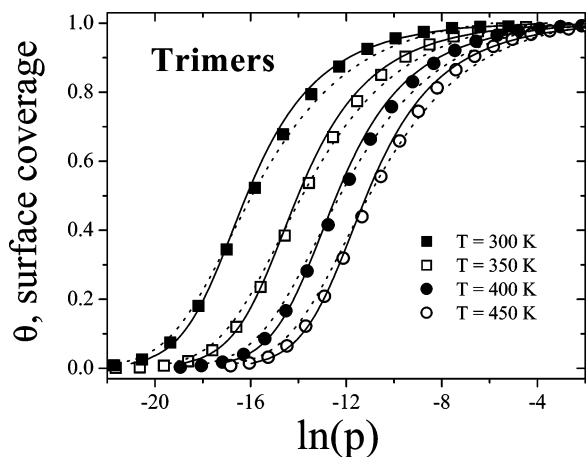
The exhaustive analysis of Figures 1–4 allows us to conclude that the MLA model appears as a very good tool in order to interpret data of adsorption of small adsorbates. In addition, the excellent correlation of simulational data by using simultaneous fitting in a single regression and MLA model demonstrates the robustness and consistency of our technique.

(27) For a given parameter  $X$ , the differences between simulation ( $X_{sim}$ ) and theoretical ( $X_{theo}$ ) predictions can be much easily rationalized with the help of the expression  $100 \times |(X_{theo} - X_{sim})/X_{sim}|$ .

**Table 1.** Table of Parameters Used in the Fitting of Simulated Data of Figures 1–4<sup>a</sup>

system	simulation data			MLA model				MSL model			
	$k$	$H_{st}$	$Q_{max}$	$k$	$H_{st}$	$Q_{max}$	$D$	$k$	$H_{st}$	$Q_{max}$	$D$
dimers (Figure 1)	2	25.10	2592	<b>2</b>	25.13	2595	0.09	<b>2</b>	24.38	2600	0.21
dimers (Figure 1 inset)	2	25.10	2592	2.02	25.17	2596	0.08	1.98	24.80	2598	0.19
dimers (Figure 2)	2	25.10	2592	<b>2</b>	26.35	2596	$5 \times 10^{-5}$	<b>2</b>	27.47	2597	$6 \times 10^{-5}$
trimers (Figure 3)	3	37.65	1728	<b>3</b>	37.39	1738	0.27	<b>3</b>	36.55	1768	0.52
trimers (Figure 4)	3	37.65	1728	<b>3</b>	37.60	1770	$5 \times 10^{-6}$	<b>3</b>	40.36	1776	$5 \times 10^{-6}$

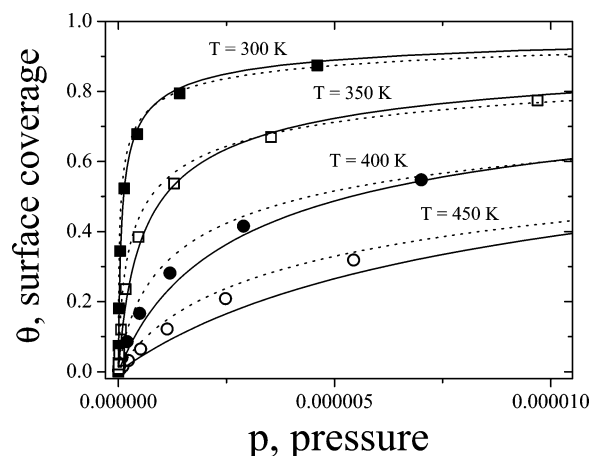
<sup>a</sup> The values shown in boldface type indicate that the corresponding parameter was fixed in the adjust.

**Figure 2.** Same as Figure 1 for  $\theta$  vs pressure  $p$ .**Figure 3.** Same as Figure 1 for linear trimers adsorbed on a square lattice at different temperatures as indicated.

Finally, it is worth emphasizing that the technique used above is valid for analyzing a set of isotherms (obtained at different temperatures). Stability of the theoretical solution increases as the number of isotherms in the simultaneous fitting increases. In the lowest limit, the methodology fails when it is applied to fit one isolated isotherm. In this case, good fittings can be obtained from several different sets of parameters ( $k$ ,  $H_{st}$ ,  $Q_{max}$ ). This crucial point has to be carefully considered for the application of the analytical isotherms to many real systems.

### 3. Comparison between Theory and Experimental Results

The aim of the present section is to test the applicability of the MLA model to the adsorption of  $n$ -paraffins in 5A zeolite. For this purpose, experimental adsorption isotherms from ethane to  $n$ -hexane, previously compiled by Silva et al.,<sup>4</sup> were analyzed in terms of MLA. Given that the experimental data are mainly for higher pressures,

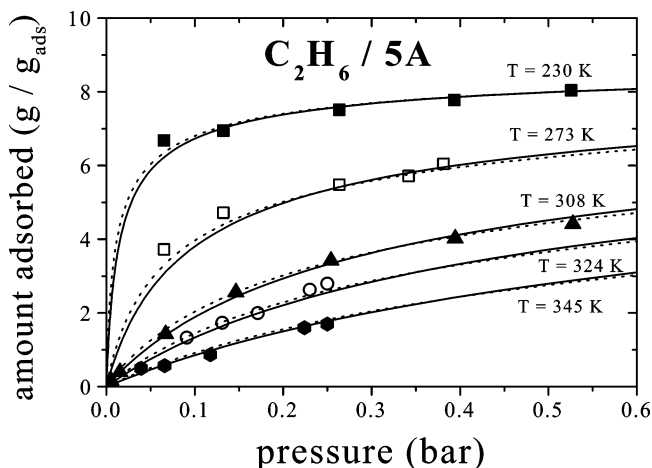
**Figure 4.** Same as Figure 3 for  $\theta$  vs pressure  $p$ .

the theoretical isotherms were obtained by using the pressure,  $p$ , as a fitting quantity.<sup>28</sup> In addition, this choice allows us a direct comparison with the results obtained in ref 4. Experimental data are reported in adsorbed amount (g/100 g adsorbed) as a function of pressure.<sup>4</sup> Two main reasons motivated the selected range ( $C_2$ – $C_6$ ): (1) the effects of multisite occupancy disappear for very small molecules as methane. In this limit ( $k \approx 1$ ), single-site occupancy is recovered and the theoretical models (MLA and MSL) provide identical results. (2) As established in a previous work,<sup>4</sup> fitting adsorption isotherms corresponding to  $n$ -paraffins with  $n > 6$  requires introduction of an attractive lateral interaction between the ad-molecules. The relative importance of attractive ad–ad interactions is still controversial and would make our analysis more cumbersome.

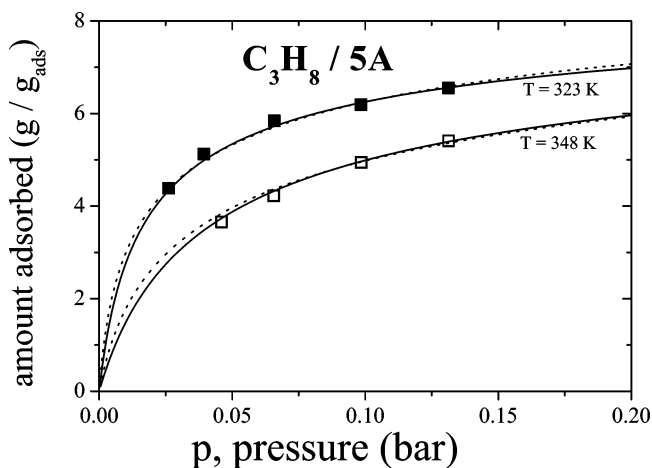
Adsorption isotherms for ethane, propane,  $n$ -butane,  $n$ -pentane, and  $n$ -hexane are shown in Figures 5–9, respectively. Symbols correspond to experimental data at different temperatures and (dashed) solid lines represent theoretical curves from the (MSL) MLA model. As is common in the literature, we adopt a “bead segment” chain model of the molecules, in which each methyl (bead) group occupies one adsorption site on the surface. Under this consideration, we set  $k = 2$ – $6$  in fitting data corresponding to  $C_2$ – $C_6$ , respectively. The values of the adjusted parameters  $H_{st}$  and  $Q_{max}$  are shown in Table 2.

Several conclusions can be extracted from Figures 5–9 and Table 2. On one hand, as it can be appreciated from the values of the dispersion, MLA model provides the more accurate results for ethane and propane, while MSL model appears more adequate to describe “long-chain” molecules as  $n$ -butane,  $n$ -pentane and  $n$ -hexane. Moreover, spurious effects appear in MLA predictions for sizes  $k > 3$ . Note for example, the decreasing observed in  $H_{st}$  for  $n$ -butane in

(28) Previous calculations for monomers (not presented here for simplicity) show that more accurate results can be obtained by using the coverage  $\theta$  as a dependent variable. However, the inherent complexity of the dependence of the coverage on the pressure,  $\theta(p)$ , represents a major difficulty in implementing this procedure for  $k > 1$ .



**Figure 5.** Comparison between experimental and theoretical adsorption isotherms ( $\theta$  vs pressure  $p$ ) for  $C_2H_6$  adsorbed in 5A zeolite. Symbols represent experimental data from refs 16 and 17 and (dashed) solid lines correspond to the (MSL) MLA model. The parameters used in MSL and MLA models are listed in Table 2.



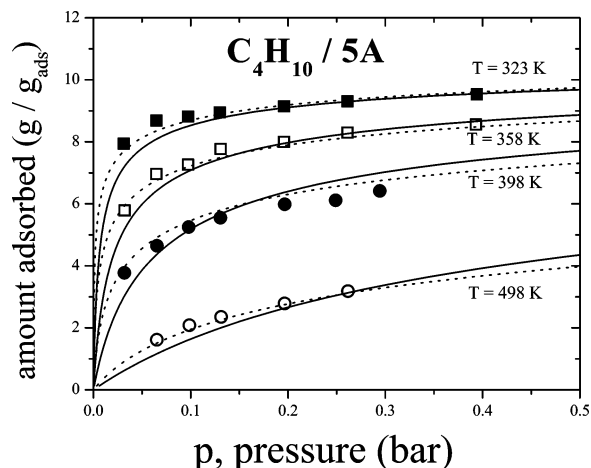
**Figure 6.** Same as Figure 5 for  $C_3H_8$  adsorbed in 5A zeolite. Symbols represent experimental data from ref 18 and (dashed) solid lines correspond to the (MSL) MLA model. The parameters used in MSL and MLA models are listed in Table 2.

comparison with the corresponding one to propane. Discrepancies between experimental and MLA results increase as the size of the adsorbate increases. In this sense, MLA isotherms are only shown in the range  $C_2$ – $C_4$  (Figures 5–7).

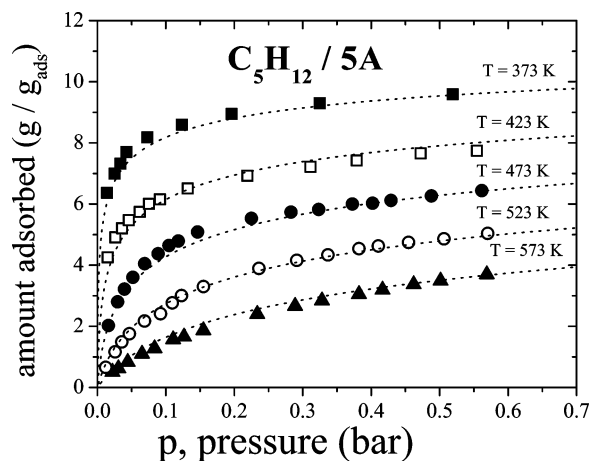
On the other hand, the values of  $Q_{\max}$  obtained from the MLA model for ethane and propane are lower than those reported in ref 4. Moreover, the regression technique used in the present paper has been shown to be an improvement over the one presented in ref 4. To confirm this statement, we used the parameters obtained in ref 4 to calculate the dispersion in the fittings. The result is shown in the last column of Table 2. As it can be noticed,  $D(\text{ref 4}) \geq D$  for all values of  $k$ .<sup>29</sup>

A possible explanation for the deviation from the MLA model observed for large molecules as  $n$ -butane,  $n$ -pentane, and  $n$ -hexane is associated with the relation of sizes of adsorbate/cage of 5A zeolite. As the length of the adsorbate is increased, the geometry of the cage forces the ad-molecule to adopt a “more compact” spatial configuration.

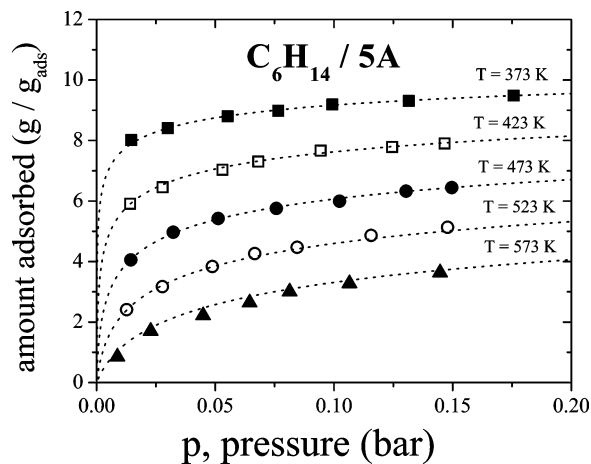
(29) An identical result is obtained by calculating the dispersion as the average of the absolute values of the difference between experimental and calculated data.



**Figure 7.** Same as Figure 5 for  $C_4H_{10}$  adsorbed in 5A zeolite. Symbols represent experimental data from ref 19 and (dashed) solid lines correspond to the (MSL) MLA model. The parameters used in MSL and MLA models are listed in Table 2.



**Figure 8.** Comparison between experimental and MSL adsorption isotherms ( $\theta$  vs pressure  $p$ ) for  $C_5H_{12}$  adsorbed in 5A zeolite. Symbols represent experimental data from ref 14 and dashed lines correspond to the MSL model. The parameters used in the MSL model are listed in Table 2.



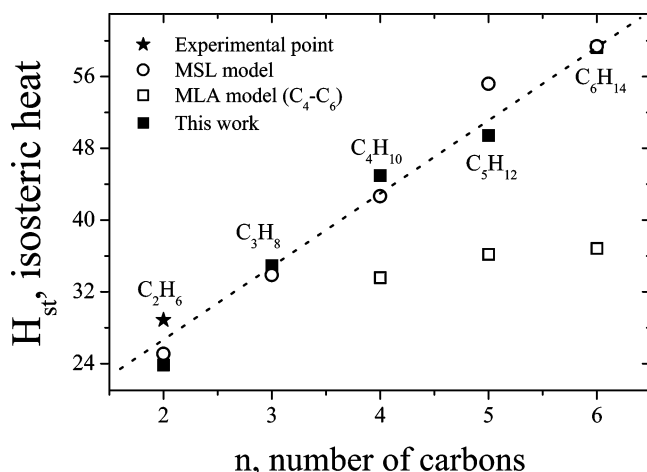
**Figure 9.** Same as Figure 8 for  $C_6H_{14}$  adsorbed in 5A zeolite. Symbols represent experimental data from ref 15 and dashed lines correspond to the MSL model. The parameters used in MSL model are listed in Table 2.

Consequently, the adsorbate departs from linearity and adsorbs as a flexible  $k$ -mer. This packing effect, which seems to be critical for  $k > 3$ , cannot be correctly taken into account with a model assuming linear adsorbates.

Table 2. Table of Parameters Used in the Fitting of Experimental Data of Figures 5 and 9<sup>a</sup>

adsorbate/5A	MLA model				MSL model				MSL model (ref 4)			
	<i>k</i>	<i>H</i> <sub>st</sub>	<i>Q</i> <sub>max</sub>	<i>D</i>	<i>k</i>	<i>H</i> <sub>st</sub>	<i>Q</i> <sub>max</sub>	<i>D</i>	<i>k</i>	<i>H</i> <sub>st</sub>	<i>Q</i> <sub>max</sub>	<i>D</i> <sup>4</sup>
C <sub>2</sub> H <sub>6</sub> (Figure 5)	<b>2</b>	23.84	9.06	0.022	<b>2</b>	25.93	9.11	0.024	2.4	25.10	11.3	0.088
C <sub>3</sub> H <sub>8</sub> (Figure 6)	<b>3</b>	34.63	9.44	0.003	<b>3</b>	34.92	11.01	0.004	3	33.87	13	0.093
C <sub>4</sub> H <sub>10</sub> (Figure 7)	<b>4</b>	33.58	11.41	0.035	<b>4</b>	44.96	12.05	0.032	4	42.66	13	0.053
C <sub>5</sub> H <sub>12</sub> (Figure 8)	<b>5</b>	36.17	12.07	0.051	<b>5</b>	49.43	13.55	0.028	5	55.20	13	0.045
C <sub>6</sub> H <sub>14</sub> (Figure 9)	<b>6</b>	36.84	11.79	0.015	<b>6</b>	59.26	12.90	0.005	6	59.38	13	0.005

<sup>a</sup> The values shown in boldface type indicate that the corresponding parameter was fixed in the adjust. *H*<sub>st</sub> and *Q*<sub>max</sub> are expressed in (kJ/mol) and (g/100 g of adsorbent), respectively. *D* is defined as the average of the quadratic difference between experimental and theoretical results.



**Figure 10.** Isosteric heat of adsorption as a function of carbon number for C<sub>2</sub> to C<sub>6</sub> *n*-paraffins. The star corresponds to experimental data from Ruthven et al. (Ruthven, D. M.; Loughlin, K. F.; Holborow, K. A. *Chem. Eng. Sci.* **1973**, *28*, 701.); open circles correspond to the MSL model from ref 4; open squares correspond to the MLA model for C<sub>4</sub>–C<sub>6</sub>, and full squares represent the values obtained in this work by using the MLA model for ethane and propane and the MSL model for *n*-butane, *n*-pentane, and *n*-hexane.

Other effects, such as surface heterogeneity and lateral interactions may also be sources of discrepancy.

The consistency of the parameters found by the fitting of the whole set of isotherms is demonstrated in Figure 10, where the isosteric heat of adsorption is plotted as a function of the number of carbons. As observed from the figure, the isosteric heat of adsorption obtained in this work (by using the MLA model for ethane and propane and the MSL model for *n*-butane, *n*-pentane, and *n*-hexane) increases with the number of carbons, ranging from 23.84 kJ/mol for ethane to 59.26 kJ/mol for *n*-hexane. This behavior is in good agreement with the general experimental data of *n*-paraffin–zeolite systems. On the other hand, *H*<sub>st</sub> obtained in the framework of the MLA model departs from a linear increase and remains almost constant for *k* > 3. The differences between the values of *H*<sub>st</sub> from ref 4 and the corresponding ones reported in this paper for C<sub>4</sub>–C<sub>6</sub> are related with the different regression techniques used in fitting the experimental data.

#### 4. Conclusions

The adsorption isotherms of C<sub>2</sub>–C<sub>6</sub> *n*-paraffins in 5A zeolite, published in the literature from various authors and measured at several temperatures for each adsorbate, have been analyzed through two statistical models including multisite occupancy. The first one is the well-known multisite Langmuir model (MSL).<sup>3</sup> The second is a statistical thermodynamics model for linear adsorbates (MLA), derived from exact calculations in one dimension.<sup>8</sup> The range selected, from ethane to *n*-hexane, did not

require introduction of lateral interactions between the ad-molecules, minimizing the number of fitting parameters of the models.

A nonlinear regression technique was used in fitting the experimental data, where the isotherms at all temperatures were fitted simultaneously in a single regression. The fitting procedure and the theoretical isotherms were tested in comparison with Monte Carlo simulations, which allowed us to determine the conditions of applicability of the method. With respect to the analysis of experimental data, the regression technique used in the present paper has been shown to be an improvement over the one presented in ref 4.

The MSL model has been used in previous works<sup>4</sup> to interpret experimental adsorption isotherms of *n*-paraffins in 5A zeolite. Furthermore, this paper presented the first application of the MLA model to study adsorption of *n*-paraffins. The combination of MSL and MLA models, developed for studying flexible and linear *k*-mers, respectively, sheds light on the spatial configuration of the molecule in the adsorbed state. From this comparative analysis arises that small molecules (methane, ethane, propane) adsorb as a linear array of monomers in the cage of a Z5A and its isotherms are well described by the MLA model. As the length of the adsorbate is increased, the geometry of the zeolite cage forces the ad-molecule to adopt a “more compact” spatial configuration. Consequently, the adsorbate departs from linear and adsorbs as a flexible *k*-mer. Adsorption isotherms characterized by this packing effect, which seems to be critical for *k* > 3, can be accurately fitted by the MSL model.

To maintain the consistency of our study, isosteric heats of adsorption were obtained from the MLA model for C<sub>2</sub>–C<sub>3</sub> and from the MSL model for C<sub>4</sub>–C<sub>6</sub>. The resulting values increase almost linearly over the whole range of carbon numbers and are in excellent agreement with the ones reported in the literature.

The analysis presented here, where a large amount of experimental data were considered by combining theoretical modeling and Monte Carlo simulation, shows that MSL and MLA models provide a very good theoretical framework, considering the complexity of the physical situation which is intended to be described. So they appear as reliable and useful analytical models for adsorption of light hydrocarbons in zeolites where multisite occupancy takes place.

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