Structural–energetic heterogeneity effects
on adsorption of aromatics in silicalite

P. Szabelski and J.Narkiewicz-Michałek

Zakład Chemii Teoretycznej, Uniwersytet Marii Curie-Skłodowskiej,
Pl. M. C. Skłodowskiej 3, 20-031 Lublin, Poland

1. INTRODUCTION

Although, at present the concept of surface heterogeneity is generally accepted in the theoretical description of adsorption at solid/gas and solid/liquid solution interfaces, there is still the area of adsorption science where it has not received enough attention yet. It is the adsorption in zeolites. It was quite easy to understand that the surfaces of amorphous solids must be energetically heterogeneous. However, it was much more difficult to understand that surfaces of adsorbents such as zeolites exhibiting a high crystallographic order in the X-ray studies might be also strongly heterogeneous. The reason for that seems to be as follows: the energetic heterogeneity of the actual solid surfaces was associated intuitively with the common distortions in the geometric structure of the actual solid surfaces. Zeolites were traditionally viewed as highly organised crystallographic structures. Assuming for the time being that a zeolite has a perfect, crystallographic structure, the gas-solid potential function will commonly exhibit a variety of local minima, which will obviously be arranged in a 3-dimensional structure. Thus, from the viewpoint of statistical thermodynamics we may treat the adsorption in zeolites as that on three-dimensional lattice of energetically non-equivalent (heterogeneous) sites. This will be particularly true in the case of small molecules adsorbed in large cavities and channels.

The geometrical and energetical non-idealities of the real zeolite structures become of a special importance when the dimensions of the adsorbed molecules are comparable with the size of zeolite cavities (channels) as in the case of aromatics adsorbed in ZSM-5 zeolites.

ZSM-5 is a high silica zeolite with the framework forming an interconnecting three-dimensional channel structure [1]. There are two types of intersecting channels, both defined by 10-membered oxygen rings, in the framework of ZSM-5. The elliptical zigzag channels along the a direction have a cross section of about 0.51x0.55 nm. The straight channels along the b direction are nearly circular with the dimensions 0.54x0.56 nm. With its unique channel structure ZSM-5 zeolite has become one of the most versatile and valuable zeolites in modern petrochemical and hydrocarbon processing. The limited channel dimensions allow formation of neither aromatic compounds with more than eleven carbon atoms inside this zeolite, nor the multiple ring precursor leading to coking. Therefore, ZSM-5 is more resistant to deactivation by coke. Moreover, the interconnected channel structure also reduces the hindrance due to the counter diffusion of reaction products and reactants, as they may diffuse in and out of the channel system through different pores. This has been termed as a "molecular traffic control" mechanism.

The tight fit situation is of a crucial importance in many practical applications of aromatics/ZSM-5 zeolite systems. Aromatic molecules experience a very strong guest-host interaction in the confined pore space of ZSM-5. The strong interaction leads to high reactivity, shape selectivity and other unusual phenomena. Such a tight fit of the guest-host system is also unique for our fundamental understanding of adsorption in pores. The slight difference in size and shape ·between the zigzag and straight channels sometimes creates a large difference in the adsorption strength.

The extensive kinetic and equilibrium study of aromatic compounds in the pentasil zeolites carried out in the recent years revealed some unique behaviours of these systems which are still poorly understood. For several aromatics the isotherm shape changes from type I to type IV with the decreasing temperature [2-7]. The adsorption heats measured with different techniques exhibit sharp maxima and/or minima at the loadings near 4 molecules per unit cell and higher [4,5,7-9]. Although one unit cell of ZSM-5 can theoretically accommodate 12 molecules of benzene and 8.8 molecules of p-xylene, the experimental capacities are about 8 molecules per unit cell for both adsorbates at lower temperatures whereas at higher temperatures they level off at four molecules per unit cell.

A variety of adsorption models has been proposed to describe the very unusual behaviour of these systems. Thus, Thamm [8,9] assumed that this might be adsorption of dimers, or a cooperative redistribution of the adsorbed molecules. Guo et al. [6] and Talu et al. [7] assumed that there exist two independent types of adsorption sites in the zeolite and that the adsorption on each type of sites can be described by the Hill-de Boer isotherm equation with different temperature dependent constants. Next, they postulated that the sharp

steps observed on the benzene and p-xylene adsorption isotherms in silicalite are connected with the phase change in the adsorbed phase predicted by their model. From the adsorption isotherms measured at different temperatures they were able to determine phase boundaries for such a phase transition.

Pan and Mersmann [10,11] examined adsorption of p-xylene in silicalite by assuming that p-xylene molecules adsorb on two types of adsorption sites located in the channel intersections and the zigzag channels. The adsorption on one type of sites was described by the Langmuir isotherm whereas the quasi-chemical approximation for a two-dimensional lattice gas was adopted to describe the adsorption on the second type of sites (zigzag channels). They argued that when the molecules started to occupy the zigzag channels, a large deformation of the host structure occurred. This deformation reduced the repulsive force between the adsorbed molecules and the host structure, and could be interpreted as a long-range interaction between the adsorbed molecules. Effectively, an attractive interaction was assumed between the admolecules adsorbed on the neighbouring zigzag sites, when they were physically separated by the admolecules located at the channel intersections.

To generalise the adsorption of aromatics in a network of heterogeneous sites in MFI zeolites, Lee et al. [12,13] proposed a lattice gas model with three types of lattice sites representing the channel intersections, the straight channels, and the zigzag channels. In their model the sites are arranged on a two dimensional array, approximating the actual three-dimensional topology of the silicalite pore system. Interactions between molecules on the various sites were modelled differently according to the kinds of sites involved. The model was solved numerically to obtain the isotherms and heats of adsorption as a function of loading for various sets of parameters and compared with the experimental data of benzene and p-xylene adsorbed in silicalite. Although this model was able to produce an isotherm with a step jump at intermediate loadings observed for the p-xylene/silicalite system, it failed to reproduce two steps observed experimentally by these authors in each adsorption isotherm of benzene in the temperature range 273 - 303 K. To arrive at a phase transition in the adsorbed phase they were forced to assume certain values of the parameters ε_s, ε_z, ε_i, and some interrelations of the gas-solid and gas-gas parameters to be fulfilled. However, the calculated isosteric heat of adsorption could not be seen as reproducing well the qualitative features of the experimental heats of adsorption reported by Thamm [8,9]. The estimated energy of adsorption ε_s was larger than ε_i, which would mean that the sites S are filled first. Meanwhile, the reported atomistic simulations suggest that channel intersections I are filled first. There are also some experimental findings that seem to support such a view.

None of the models discussed above takes the possible phase transition in the zeolite structure caused by the adsorbed molecules. Silicalite is known to exist in the three distinct phases: a monoclinic form (MONO), an orthorhombic form with Pnma symmetry (ORTHO), and an orthorhombic form with $P2_12_12_1$ symmetry (PARA) [14-16]. A reversible phase transition from the low temperature MONO to the ORTHO structure occurs around 350 K. This transition can also be brought about by the adsorption of aromatic molecules. The as-synthesised structure is known to be ORTHO. The third form PARA is observed for silicalite with high loadings of p-xylene. X-ray diffraction and NMR experimental evidence have shown that the presence of p-xylene molecules in silicalite at the loadings greater than four molecules per unit cell will induce a phase change from ORTHO to PARA [14]. This phase change is claimed to be responsible for a sharp increase in the adsorbed amount observed experimentally in this system.

A phase change of zeolite structure can be explicitly taken into account in the atomistic computer simulations. Such molecular simulations have been performed by Snurr et al. [17] for benzene and p-xylene in silicalite using the GCMC techniques. Adsorption isotherms and heats of adsorption were calculated and compared with the experimental data, however, the agreement appeared to be far from being satisfactory.

It seems, however, that combining the information obtained from the computer simulations and the conceptual progress made in the theories of gas adsorption on heterogeneous solid surfaces, it should be possible at present to provide a satisfactory theoretical description of adsorption in these systems. Developing such a theoretical description is important still for another reason. Namely, zeolites are the adsorbents which are most commonly applied in the industrial separations of gases by adsorption processes. They are also ones of the most important catalysts and catalytic supports. In the industrial processes the physical regimes may change very fast. So, it is essential to use fast methods for calculating the adsorption equilibria and kinetics. For that reason, computer simulations, which have become such a powerful tool to study the adsorption equilibria and kinetics, cannot be applied to control technological processes. Even if one uses the largest (fastest) computers, the simulation of adsorption even in a simple adsorption system is still too much time consuming to be applied in technological processes. Thus, it is not surprising that in the industrial separations of gases, very simple equations for adsorption kinetics and equilibria are used in appropriate systems of differential equations describing the dynamic separation of gases. These simple equations ignore usually the effects of zeolite heterogeneity.

As the reported simulations already provide a solid support for the three-site model, in our previous publications we proposed the improved version of this

model based on the recent experimental findings [18-20]. Like Lee et al. [12,13], we neglected the change of the energy parameters that might be caused by a possible phase transition in the zeolite structure. First, because in the case of benzene a phase transition in the zeolite structure upon adsorption is only a hypothesis at present. Second, because that hypothesis itself does not lead to predicting the two steps in the adsorption isotherm of benzene observed experimentally by Lee et al. [21]. Instead, we focused our attention on the recent discovery reported by Mentzen et al. [22-25]. They have found that two equally probable orientations of benzene molecules adsorbed in the channel intersection are possible, and that these orientations are characterised by different values of the adsorption energy ε. Thus, we assumed that these forms denoted by I1 and I2 compete for occupying the channel intersections. Next, we paid attention to the experimental heats of adsorption of benzene in silicalite measured by Thamm [8]. Strongly decreasing values of the adsorption heat observed at the lowest benzene loadings may indicate that adsorption goes on a heterogeneous surface. It is widely recognised that heats of adsorption are much more sensitive to the nature of an adsorption system than adsorption isotherms [26,27]. One can easily understand the thermodynamic reason for that. Namely, heats of adsorption are related to temperature derivatives, and temperature appears always in exponential terms. There are important features of adsorption systems, which can hardly be seen in the behaviour of adsorption isotherms, but are clearly observed on the adsorption heat curves. Surface energetic heterogeneity is one of such fundamental features. Thus, extending the three site lattice model by taking into account two different spatial locations of the aromatic molecule in the channel intersection and dispersion of the adsorption energy on the sites of the same type we arrived at a quantitative description of adsorption isotherms and accompanying heats of adsorption of benzene and p-xylene in silicalite [20].

The purpose of this work is to test our model on a set of adsorption isotherms of toluene in silicalite measured by Lee et al. [21] at different temperatures, and heats of adsorption determined calorimetrically by Thamm at 301 K [8].

2. THEORY

Chemical impurities and unavoidable distortions in the structure of the prepared zeolite samples must contribute to the variety of the local minima in the gas-solid potential function [26]. Because of chemical impurities and unavoidable distortions of the zeolite structure, free energies of adsorption will vary when going from one to another site of type j. If one assumes that these local distortions have a random nature, the external force field acting on an

adsorbed molecule and created by the presence of other molecules adsorbed nearby, will be a function of the average occupation of sites of all the types, θ_{st}, θ_{zt}, θ_{i1t}, θ_{i2t}. Taking into account all possible interactions between molecules adsorbed on the neighbouring sites we can write the fractional coverage of sites of jth type, characterised by a certain value of the adsorption energy ε_j, in the following form

$$\theta_s = \frac{\lambda \exp\left\{\dfrac{E_s + \sum\limits_j \omega_{sj}\theta_{jt}}{kT}\right\}}{1 + \lambda \exp\left\{\dfrac{E_s + \sum\limits_j \omega_{sj}\theta_{jt}}{kT}\right\}} \tag{1}$$

$$\theta_z = \frac{\lambda \exp\left\{\dfrac{E_z + \sum\limits_j \omega_{zj}\theta_{jt}}{kT}\right\}}{1 + \lambda \exp\left\{\dfrac{E_z + \sum\limits_j \omega_{zj}\theta_{jt}}{kT}\right\}} \tag{2}$$

$$\theta_{i1} = \frac{\lambda \exp\left\{\dfrac{E_{i1} + \sum\limits_j \omega_{i1j}\theta_{jt}}{kT}\right\}}{1 + \lambda \exp\left\{\dfrac{E_{i1} + \sum\limits_j \omega_{i1j}\theta_{jt}}{kT}\right\} + \lambda \exp\left\{\dfrac{E_{i2} + \sum\limits_j \omega_{i2j}\theta_{jt}}{kT}\right\}} \tag{3}$$

$$\theta_{i2} = \frac{\lambda \exp\left\{\dfrac{E_{i2} + \sum\limits_j \omega_{i2j}\theta_{jt}}{kT}\right\}}{1 + \lambda \exp\left\{\dfrac{E_{i1} + \sum\limits_j \omega_{i1j}\theta_{jt}}{kT}\right\} + \lambda \exp\left\{\dfrac{E_{i2} + \sum\limits_j \omega_{i2j}\theta_{jt}}{kT}\right\}} \tag{4}$$

where

$$E_j = \varepsilon_j + kT \ln f_j \quad j = s, z, i1, i2 \tag{5}$$

f_j being the molecular partition function of the admolecules occupying sites of jth type. In the above equations λ denotes the absolute activity defined as

$$\lambda = \exp\left(\frac{\mu}{kT}\right) = p \exp\left(\frac{\mu^0}{kT}\right) \tag{6}$$

where μ is the chemical potential, μ^0 is the standard chemical potential and p is the gas pressure.

Traditionally, the surface energetic heterogeneity was viewed as the dispersion of ε-values, (the local minima at the gas - solid potential function), that dispersion not affecting f_j. In the case of aromatics/ZSM-5 systems the dispersion of E_j has to be considered because the local distortions may affect seriously the local movement of the adsorbed molecules. This is because the dimensions of the channels of ZSM-5 and of the adsorbed molecules are comparable.

Let $\chi_j(E_j)$ denote the differential distribution of the number of sites j among various values of E_j, normalised to unity. Thus, the average surface coverage of sites j, θ_{jt}, will be represented by the integral

$$\theta_{jt} = \int_{\Omega_j} \theta_j(E_j, p, T) \chi_j(E_j) dE_j \tag{7}$$

where Ω_j is a physical domain of adsorption energies E_j. Then, it seems natural to assume that the local distortions of the zeolite structure will result in a gaussian - like dispersion of E_j values

$$\chi_j(E_j) = \frac{\dfrac{1}{c_j} \exp\left(\dfrac{E_j - E_j^0}{c_j}\right)}{\left[1 + \exp\left(\dfrac{E_j - E_j^0}{c_j}\right)\right]^2} \tag{8}$$

where the heterogeneity parameter c_j characterises the width of the distribution function $\chi_j(E_j)$ and E_j^0 is the most probable value of E_j. Using the Rudziński-Jagiełło approach [26] to calculate the integral (7), we obtain the following expressions for the fractional surface coverages of the sites of each type

$$\theta_{st} = \frac{\left[\lambda\exp\left\{\frac{E_s^0 + \sum_j \omega_{sj}\theta_{jt}}{kT}\right\}\right]^{\gamma_s}}{1 + \left[\lambda\exp\left\{\frac{E_s^0 + \sum_j \omega_{sj}\theta_{jt}}{kT}\right\}\right]^{\gamma_s}} \tag{9}$$

$$\theta_{zt} = \frac{\left[\lambda\exp\left\{\frac{E_z^0 + \sum_j \omega_{zj}\theta_{jt}}{kT}\right\}\right]^{\gamma_z}}{1 + \left[\lambda\exp\left\{\frac{E_z^0 + \sum_j \omega_{zj}\theta_{jt}}{kT}\right\}\right]^{\gamma_z}} \tag{10}$$

$$\theta_{i1t} = \frac{\left[\lambda\exp\left\{\frac{E_{i1}^0 + \sum_j \omega_{i1j}\theta_{jt}}{kT}\right\}\right]^{\gamma_{i1}}}{1 + \left[\lambda\exp\left\{\frac{E_{i1}^0 + \sum_j \omega_{i1j}\theta_{jt}}{kT}\right\}\right]^{\gamma_{i1}} + \left[\lambda\exp\left\{\frac{E_{i2}^0 + \sum_j \omega_{i2j}\theta_{jt}}{kT}\right\}\right]^{\gamma_{i2}}} \tag{11}$$

$$\theta_{i2t} = \frac{\left[\lambda\exp\left\{\frac{E_{i2}^0 + \sum_j \omega_{i2j}\theta_{jt}}{kT}\right\}\right]^{\gamma_{i2}}}{1 + \left[\lambda\exp\left\{\frac{E_{i1}^0 + \sum_j \omega_{i1j}\theta_{jt}}{kT}\right\}\right]^{\gamma_{i1}} + \left[\lambda\exp\left\{\frac{E_{i2}^0 + \sum_j \omega_{i2j}\theta_{jt}}{kT}\right\}\right]^{\gamma_{i2}}} \tag{12}$$

where to the first approximation $\gamma_j < 1$ may be identified with kT/c_j.

Solving the system of equations (9-12), one will obtain the fractional surface coverages θ_{jt} for $j = s, z, i1, i2$, and the overall adsorption isotherm θ_t will be given as,

$$\theta_t = \frac{1}{3} \sum_{j=s,z,i1,i2} \theta_{jt} \tag{13}$$

At appropriate values of the interaction parameters ω_{jm}, (j,m=s,z,i1,i2), or at the suitably low temperature T_c, the μ/kT considered as a function of θ_t will show a critical point at which,

$$\frac{\partial \mu}{\partial \theta_t} = 0 \quad \text{and} \quad \frac{\partial^2 \mu}{\partial \theta_t^2} = 0 \tag{14}$$

and next a non-physical loop at still lower temperatures. In such a case, one has to perform the Maxwell construction to arrive at the physical isotherm, represented by a straight line fulfilling the following conditions,

$$\mu_M = \int_{\theta_{tG}}^{\theta_{tL}} \frac{\mu(\theta_t) d\theta_t}{\theta_{tL} - \theta_{tG}} \tag{15}$$

and

$$\mu_M = \mu(\theta_{tG} - \theta_{tL}) \tag{16}$$

Now, let us investigate the related behaviour of the heat of adsorption. To that purpose we rewrite eqs. (9-12) to the following form,

$$F_s = \frac{\mu_s - \mu}{kT} = \frac{1}{\gamma_s} \ln \frac{\theta_{st}}{1 - \theta_{st}} - \frac{E_s^0}{kT} - \sum \frac{\omega_{sj}}{kT} \theta_{jt} - \ln \lambda = 0 \tag{17}$$

$$F_z = \frac{\mu_z - \mu}{kT} = \frac{1}{\gamma_z} \ln \frac{\theta_{zt}}{1 - \theta_{zt}} - \frac{E_z^0}{kT} - \sum_j \frac{\omega_{zj}}{kT} \theta_{jt} - \ln \lambda = 0 \tag{18}$$

$$F_{i1} = \frac{\mu_{i1} - \mu}{kT} = \frac{1}{\gamma_{i1}} \ln \frac{\theta_{i1t}}{1 - \theta_{i1t} - \theta_{i2t}} - \frac{E_{i1}^0}{kT} - \sum_j \frac{\omega_{i1j}}{kT} \theta_{jt} - \ln \lambda = 0 \tag{19}$$

$$F_{i2} = \frac{\mu_{i2} - \mu}{kT} = \frac{1}{\gamma_{i2}} \ln \frac{\theta_{i2t}}{1 - \theta_{i1t} - \theta_{i2t}} - \frac{E_{i2}^0}{kT} - \sum_j \frac{\omega_{i2j}}{kT} \theta_{jt} - \ln \lambda = 0 \tag{20}$$

where μ_j, (j = s,z,i1,i2), are the chemical potentials of the molecules adsorbed on sites j. Let $Q_j(\{\theta_{mt}\})$ denote the molar differential heat of adsorption on the sites of type j, at a certain set of the (average) surface coverages $\{\theta_{mt}\}$. It is given by,

$$Q_j(\{\theta_{mt}\}) = -k \frac{\partial}{\partial(1/T)} \left(\frac{\mu_j - \mu}{kT} \right)_{\{\theta_{mt}\}} \tag{21}$$

Thus, Q_j's take the following explicit forms,

$$Q_s(\{\theta_{mt}\}) = Q_s^0 + \varsigma_s \ln\frac{\theta_{st}}{1-\theta_{st}} + \sum_j \omega_{sj}\theta_{jt} \tag{22}$$

$$Q_z(\{\theta_{mt}\}) = Q_z^0 + \varsigma_z \ln\frac{\theta_{zt}}{1-\theta_{zt}} + \sum_j \omega_{zj}\theta_{jt} \tag{23}$$

$$Q_{i1}(\{\theta_{mt}\}) = Q_{i1}^0 + \varsigma_{i1} \ln\frac{\theta_{i1t}}{1-\theta_{i1t}-\theta_{i2t}} + \sum_j \omega_{i1j}\theta_{jt} \tag{24}$$

$$Q_{i2}(\{\theta_{mt}\}) = Q_{i2}^0 + \varsigma_{i2} \ln\frac{\theta_{i2t}}{1-\theta_{i1t}-\theta_{i2t}} + \sum_j \omega_{i2j}\theta_{jt} \tag{25}$$

where

$$Q_j^0 = k\frac{d}{d(1/T)}\left(\frac{E_j^0 + \mu^0}{kT}\right) \tag{26}$$

and

$$\varsigma_j = -k\frac{d(1/\gamma_j)}{d(1/T)} \tag{27}$$

An incremental increase in μ, $d\mu$, will result into an incremental increase of θ_t, $d\theta_t$, represented by,

$$d\theta_t = \sum_j \left(\frac{\partial\theta_{jt}}{\partial\mu}\right)d\mu \tag{28}$$

That incremental increase will be accompanied by a heat effect dQ_t,

$$dQ_t = \sum_j Q_j^0\left(\frac{\partial\theta_{jt}}{\partial\mu}\right)d\mu \tag{29}$$

Thus, the overall (measured) differential heat of adsorption $Q_t(\{\theta_{mt}\})$ will be given by,

$$Q_t = \frac{\sum_j Q_j^0\left(\frac{\partial\theta_{jt}}{\partial\mu}\right)}{\sum_j\left(\frac{\partial\theta_{jt}}{\partial\mu}\right)} \tag{30}$$

The derivatives $\partial\theta_{jt}/\partial\mu$, $(j = s,z,i1,i2)$, can be evaluated from the equation system (17-20). It can be done as follows. Let G_j denote F_j multiplied by kT. Then

$$\frac{\partial G_j}{\partial\mu} = 1 + \sum_m\left(\frac{\partial G_j}{\partial\theta_{mt}}\right)\left(\frac{\partial\theta_{mt}}{\partial\mu}\right) = 0 \quad \text{for } j,m = s,z,i1,i2 \tag{31}$$

The derivatives $\partial\theta_{mt}/\partial\mu$, $(m = s,z,i1,i2)$, are found by solving this system of four linear equations. Let G_j^m denote the derivative,

$$G_j^m = \frac{\partial G_j}{\partial \theta_{mt}} \qquad j,m = s,z,i1,i2 \tag{32}$$

The solution of the equation system (31) reads,

$$\frac{\partial \theta_{mt}}{\partial \mu} = \frac{D_m}{D} \tag{33}$$

where

$$D = \begin{vmatrix} G_s^s & G_s^z & G_s^{i1} & G_s^{i2} \\ G_z^s & G_z^z & G_z^{i1} & G_z^{i2} \\ G_{i1}^s & G_{i1}^z & G_{i1}^{i1} & G_{i1}^{i2} \\ G_{i2}^s & G_{i2}^z & G_{i2}^{i1} & G_{i2}^{i2} \end{vmatrix} \tag{34}$$

and the determinant D_m can be obtained from the determinant D by replacing the m-th column by the column of constants from equation system (31).

Within the range of the surface coverages corresponding to the phase transition region, the heat of adsorption becomes independent of the surface coverage, and is given by,

$$Q_t = \frac{1}{\theta_{tL} - \theta_{tG}} \int_{\theta_{tG}}^{\theta_{tL}} Q_t(\theta_t) d\theta_t \tag{35}$$

From eqs. 30 and 33 one can evaluate the heat of adsorption as a function of loading of zeolite channels. These equations correspond to the so-called "heterogeneous three-site model". Putting in the above equations $\gamma_j=1$ and $\zeta_j=0$, (j=i1, i2, s, z), one arrives at the equations corresponding to the so-called "homogeneous three-site model", discussed in our previous publication and describing the adsorption in the case when all adsorption sites of the same type have the same energy of adsorption.

3. RESULTS AND DISCUSSION

In our previous publications [19,20] we discussed the influence of the structural and energetic heterogeneity effects on adsorption of benzene and p-xylene in silicalite by fitting simultaneously the theoretical equations of our extended three-site lattice model to the experimental adsorption isotherms and isosteric heats of adsorption. As a conclusion, we stated that the sharp changes in the adsorption isotherms and local minima and maxima observed on the adsorption heat curves are due to rapid changes in the occupation of various adsorption sites. We called these changes - the cooperative redistribution of adsorbed molecules. Our theoretical calculations showed that the adsorption of benzene and p-xylene in silicalite is governed by a delicate balance between the adsorbate-solid and adsorbate-adsorbate interactions, and that the effects of

dispersion of adsorption energies on different kinds of adsorption sites are much more pronounced in the case of smaller benzene molecules adsorption.

The adsorption isotherms of toluene in silicalite at the temperatures -10, 0, 10 and 30°C reported by Lee et al. [21] have only one plateau at a loading of 4 M/u.c. and do not level out, even after a relative pressure of 0.2. As in the case of benzene, the calorimetric heat of toluene adsorption determined by Thamm at 301 K [8] decreases appreciably as the amount adsorbed increases at low loadings, remains constant up to 4 molecules per unit cell and passes through a minimum when the sorbed amount is further increased. Contrary to benzene, however, the minimum in the heat curve for toluene is followed up by a second plateau, which extends from moderate pore fillings up to the maximum sorbed amount.

The behaviour of the experimental adsorption isotherms and accompanying heats of adsorption of toluene in silicalite suggests that the effect of the dispersion of Ej's values in this system will be intermediate between that for benzene and p-xylene, especially at low loadings. Thus, in this paper we decided to check first which agreement of the theoretical predictions with the experimental results can be obtained using the simpler "homogeneous" model. Firstly, because the "heterogeneous" version of our model leads to a much more complicated set of equations involving four best-fit parameters more than "homogeneous" one. Secondly, because the behaviour of the toluene adsorption heat in silicalite at the loadings > 4 molecules per unit cell resembles that of p-xylene, for which the effects of the energetic heterogeneity of the sites of the same type were found to be of minor importance [20].

The most serious disadvantage of lattice models is a large number of interaction parameters to be fitted. If, however, one looks at the complicated shape of the adsorption isotherms and of the related heat of adsorption curves, and realises that we fit them simultaneously by using the same set of parameters, one can see a thin margin for an arbitrary choice of these parameters. As a matter of fact, we have performed numerous model calculations, which proved that the calculated data are very sensitive to a particular choice of these parameters.

The strategy of our calculations was the same as in our previous publications. First, we tried to fit simultaneously the experimental adsorption isotherm and the heat of adsorption of toluene in silicalite at 303 K with the smallest possible number of ω_{jm}, (j,m = i1, i2, s, z) parameters. Next, we used these parameters to predict the adsorption isotherms at different temperatures. For this purpose, the temperature dependence of the free energy of adsorption on different types of sites should be known. In the simplest case, one may treat the parameters of lateral interactions ω_{jm} as temperature independent and

assume the free energy change upon adsorption on a jth type of site, - $RT\ln K_j = -(E_j' + \mu^0)/kT$, to be a linear function of temperature,

$$- \Delta A_j = RT \ln K_j = \varepsilon_j + \alpha_j T \qquad (34)$$

where the parameter α_j denotes the entropy change upon adsorption on the site of jth type.

Table 1. Parameters found by fitting simultaneously the experimental isotherms and heats of adsorption of toluene in silicalite by the equations corresponding to the "homogeneous three-site model" ($\gamma_j=1$, $\zeta_j=0$ for $j=i_1,i_2,s,z$). The parameters ω_{jm} which were found to be zero for both adsorbates are not listed. The Henry constant K_j is defined as $\exp((E_j + \mu^0)/kT)$

Homogeneous three-site model					
($\gamma_j=1$, $\zeta_j=0$ for $j=i1,i2,s,z$)					
$RT\ln K_{i1}$ (kJ/mol)	$RT\ln K_{i2}$ (kJ/mol)	$RT\ln K_s$ (kJ/mol)	$RT\ln K_z$ (kJ/mol)	ω_{i1i1} (kJ/mol)	ω_{i1s} (kJ/mol)
-7.9	-15.0	-11.8	-10.7	6.5	-6.0
ω_{i1z} (kJ/mol)	ω_{i2s} (kJ/mol)	ω_{i2z} (kJ/mol)	ω_{ss} (kJ/mol)	ω_{zz} (kJ/mol)	ω_{sz} (kJ/mol)
-7.4	-5.8	-0.7	0.0	5.0	-13.0
Q_{i1}^0 (kJ/mol)	Q_{i2}^0 (kJ/mol)	Q_s^0 (kJ/mol)	Q_z^0 (kJ/mol)	-	-
65.0	85.0	47.0	69.0	-	-

Table 2. The entropies and energies of adsorption on different kinds of adsorption sites found by fitting our equations for the "homogeneous three site model" to the experimental isotherms of adsorption of toluene in silicalite at different temperatures. The potential energies of gas-solid interaction ε_j's were calculated from the Henry's constants K_j's at 303 K given in Table 1

Homogeneous three-site model			
(($\gamma_j=1$, $\zeta_j=0$ for $j=i1,i2,s,z$)			
ΔS_{i1} (kJ/mol K)	ΔS_{i2} (kJ/mol K)	ΔS_s (kJ/mol K)	ΔS_z (kJ/mol K)
-0.133	-0.174	-0.216	-0.228
ε_{i1} (kJ/mol)	ε_{i2} (kJ/mol)	ε_s (kJ/mol)	ε_z (kJ/mol)
32.4	37.9	53.7	58.4

Table 1 collects the values of the parameters found by computer, while fitting simultaneously the experimental adsorption isotherm and the corresponding isosteric heat of adsorption of toluene in silicalite at 303 K by the equations corresponding to the "homogeneous three-site model". Having the values K_j and ω_{jm} at 303 K we had to find four additional parameters α_j (j=i1,i2,s,z) while fitting best the experimental adsorption isotherms of toluene in silicalite at different temperatures. The values of these parameters are given in Table 2.

Figure 1 shows graphically the agreement between the experimental adsorption isotherm of toluene in silicalite at 303 K and the theoretical one calculated using the parameters collected in Table 1. In Figure 2 the comparison between the experimental and theoretical heats of adsorption is presented. Figure 3 shows the ability of our model to predict the temperature dependence of toluene adsorption in silicalite.
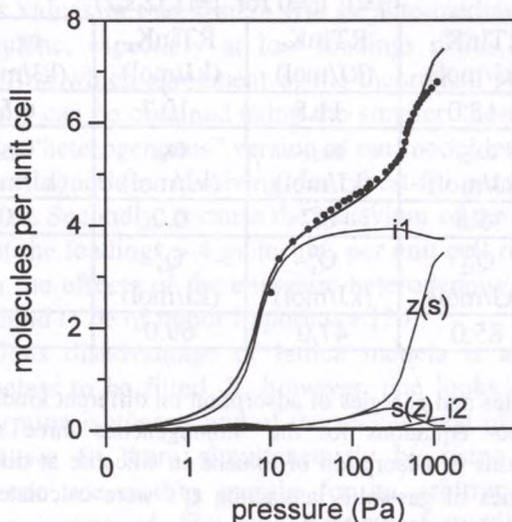

Figure 1. Comparison of the experimental isotherm of toluene adsorption in silicalite (•) measured by Lee et al. [21] at 303 K with the theoretical one (—) calculated for the "homogeneous three-site model" using the parameters collected in Table 1. The solid lines denoted by i1, i2, z(s) and s(z) are the occupancies of sites I in two different orientations, and Z and S sites (or vice versa), respectively

One can see that our model predicts well the behaviour of the adsorption isotherm of toluene in silicalite at 303 K (Figure 1) and the temperature dependence of adsorption in the region of low and intermediate loadings (Figure 3). At the highest loadings, however, a discrepancy is observed between the theory and experiment. The calculated adsorption isotherms predict a saturation of approximately 7.5 molecules per unit cell, whereas it follows from

the experiment that only 6.8 molecules of toluene per unit cell can be accommodated at the highest investigated pressures.

Valuable information on the mechanism of pore filling can be obtained by examining the contributions from the adsorption on various adsorption sites shown in Figure 1. Because of the symmetry of eqs. 1 and 2 it is impossible to judge which of the calculated solid lines means the occupancy of Z or S sites. The discrimination between calculated contributions should be made on a rational physical basis. So far, however, there has been insufficient experimental evidence to make an unequivocal assignment in the case of toluene adsorption. That is why we used the symbols z(s) and s(z) to denote the occupancy of channel sites predicted by our model.

At low adsorbate pressures toluene molecules fill mainly the channel intersections in the location denoted by i1. As the loading approaches four molecules per unit cell the intersections are mostly filled and molecules begin to occupy the channels. At coverages above 4 molecules/u.c. we observe a sharp increase of adsorption in sinusoidal (or straight) channels, accompanied by a partial reorientation of molecules occupying the channel intersections. At the maximum loading of about 7 molecules/u.c. almost all sinusoidal (or straight) channels and channel intersections are filled by toluene molecules.
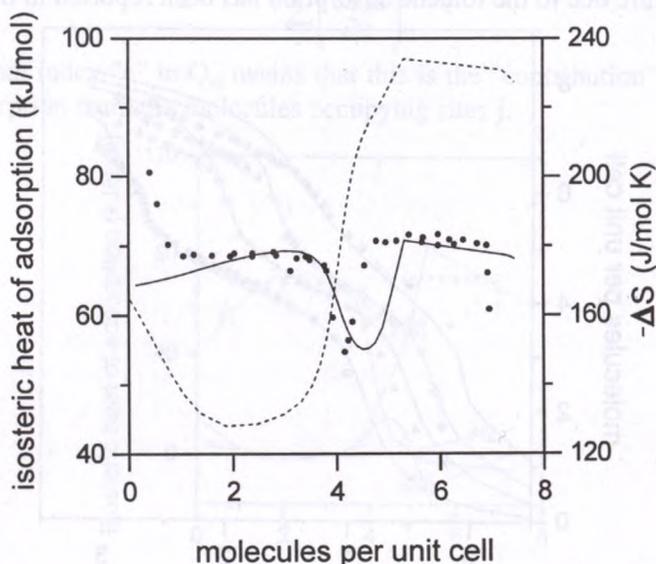

Figure 2. Comparison between the experimental differential heat of adsorption of toluene in silicalite measured by Thamm at 301 K [8] and the theoretical one (solid line) calculated for the "homogeneous three-site model" using the parameters collected in Table 1. The dashed line represents the differential entropy of adsorption

Because of a large number of interaction parameters involved in our model, their detailed discussion is difficult at present. One striking property observed is the high value of the interaction (attraction) parameters ω_{1i1} and ω_{zz} obtained for toluene adsorption. This would suggest a high positive cooperativity of adsorption on these kinds of adsorption sites. That means, the total energy of the molecules adsorbed on sites I in the orientation denoted here by i1 and on the sites Z (or S) grows rapidly with the number of molecules adsorbed on these sites. However, the calculations show that adsorption on Z (or S) sites starts rapidly only when the chemical potential of toluene in the gaseous phase is high enough to overcome the repulsive interaction between the molecules adsorbed on the adjacent adsorption sites I and Z (or S). This repulsive interaction, represented by the negative ω_{jm} values found by the computer, may simulate the geometrical restrictions imposed on two molecules to be adsorbed on the sites being nearest-neighbours, which are not explicitly taken into account in our model. It is also possible that, like for the p-xylene/ZSM-5 system, the tight-fit situation, and the tendency of the adsorbed toluene molecules to reduce the repulsive forces, may lead to the changes in the zeolite structure which, in turn, may promote the abrupt filling of the Z (or S) sites. However, contrary to the p-xylene/ZSM-5 system, no experimental evidence of the phase transition in the zeolite structure due to the toluene adsorption has been reported in literature.
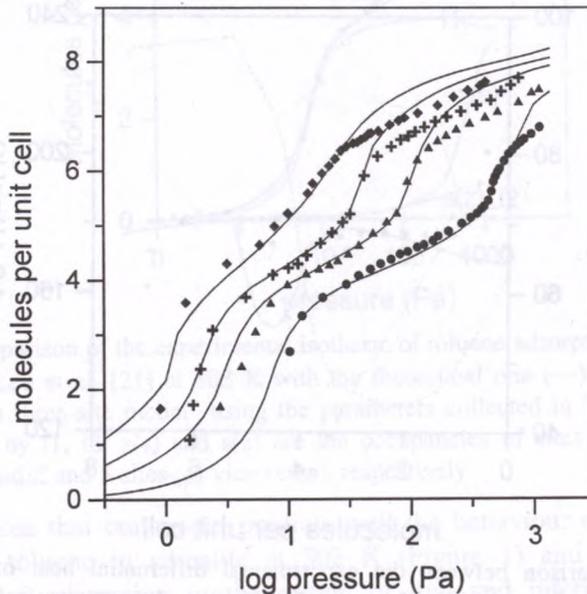

Figure 3. Comparison between the experimental adsorption isotherms for toluene in silicalite measured by Lee et al. [21] at different temperatures (♦ - 263 K, + - 273 K, ▲ - 283 K, • - 303 K), and the theoretical ones calculated for the "homogeneous three-site model" using the parameters from Tables 1 and 2

As mentioned before, the behaviour of theoretically predicted isosteric heats of adsorption is a much stronger test for the theory than the behaviour of theoretical adsorption isotherms. This is because the behaviour of the experimental heats of adsorption is much more sensitive to the nature of an experimental adsorption system. Thus, we believe that special attention should be given to the agreement between theoretical and experimental heats of adsorption.

Looking at Figure 2 one can see that the "homogeneous" version of our model is not able to reproduce the sharp decline in the heat of adsorption at small surface coverages and the constancy of the heat of adsorption at the coverages < 4 molecules per unit cell. Instead, the calculated heat of adsorption increases slowly with the increasing loading of silicalite. Before discussing the reason for this discrepancy, let us analyse Figure 4, where the contributions to the total isosteric heat of adsorption generated by the adsorption on various adsorption sites are shown. These contributions were calculated according to the equation

$$Q_{cj} = \frac{Q_j^0 \left(\dfrac{\partial \theta_{jt}}{\partial \mu} \right)}{\sum_j \left(\dfrac{\partial \theta_{jt}}{\partial \mu} \right)} \qquad (35)$$

The additional index "c" in Q_{cj} means that this is the "contribution" to the total heat of adsorption from the molecules occupying sites j.
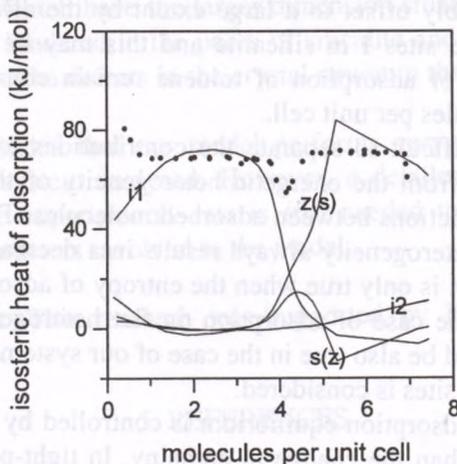

Figure 4. The contributions Q_{jc}'s to the total isosteric heat of adsorption of toluene in silicalite, calculated for the "homogeneous three-site model" using the parameters collected in Table 1. These contributions are denoted in the same way as the contributions to the total adsorption isotherm from various sites, shown in Figure 1. The black circles (•) are the experimental data reported by Thamm [8]

Looking at Figure 4, one can see that the contribution to the total theoretical isosteric heat of adsorption predicted by the "homogeneous three-site model" and coming from form I in the orientation denoted by i1 increases at low loadings. Such an increase of the adsorption heat curve is a result of the attractive interaction between molecules adsorbed on these sites, predicted by our model. This prediction does not agree with the experimental heat of adsorption of toluene, which, after the initial sharp decline, remains constant up to 4 molecules per unit cell. Thamm [8] interpreted this constancy of the heat of adsorption as the evidence that there is no interaction between the toluene molecules adsorbed on the adjacent I sites. However, from the length of the toluene molecule, which is comparable to the channel sections within 1/4 unit cell one would expect the toluene molecules sorbed on the adjacent I sites to interact with each other. The value of the parameter ω_{1i1} predicted by our model and equal to 6.0 kJ/mol confirms this expectation. The existence of strong sorbate/sorbate interaction in the p-xylene/silicalite system leading to the formation of double complexes has been identified recently from the double peaks in the DTG curves and thermal effects in the DTA curves [27]. The increasing heat of adsorption of p-xylene in silicalite observed up to the loading of 4 molecules per unit cell also confirms the existence of strong sorbate/sorbate interactions between the p-xylene molecules adsorbed on the adjacent sites I.

Thus, it is possible that similar attractive interaction exists between toluene molecules adsorbed on the sites I in the location dented by i1. This attractive interaction is probably offset to a large extent by the effects of the energetic heterogeneity of the sites I in silicalite and this may be the reason why the experimental heats of adsorption of toluene remain constant at the loadings lower than 4 molecules per unit cell.

Usually, it is difficult to separate the contributions to the total energy of adsorption coming from the energetic heterogeneity of the adsorbent surface and the lateral interactions between adsorbed molecules. The statement that the energetic surface heterogeneity always results in a decrease of the differential energy of adsorption is only true when the entropy of adsorption is comparable on all sites, as in the case of adsorption on flat heterogeneous surfaces or in large pores. It should be also true in the case of our system when the adsorption on the same type of sites is considered.

As known, the adsorption equilibrium is controlled by the change in Gibbs free energy rather than the change in enthalpy. In tight-pore systems, such as aromatics in ZSM-5 zeolites, the entropic term is as important as the enthalpic contribution. Thus, it may happen that the sites with a higher adsorption potential will also have higher entropy of adsorption, and whether they are preferential or not will depend on the temperature of a system according to the

relation $\Delta A = \Delta H - T\Delta S$. In other words, when the sites of a different type in silicalite are concerned, the sites characterised by lower adsorption potential may be filled preferentially. From Table 2 it follows that sites I, which are filled first, have the lowest adsorption potential and the highest entropy of adsorption, whereas the channel sites Z and S are characterised by higher energy and entropy of adsorption. Thus at 303 K the preferential sites are the sites with higher entropy of adsorption and in consequence the differential entropy of adsorption decreases with increasing loading, as shown in Figure 2.

4. CONCLUSIONS

The three-site lattice model for adsorption of aromatics in ZSM-5 zeolites has been developed and used to predict semi-quantitatively the adsorption isotherms and isosteric heats of adsorption of toluene in silicalite. Fitting best the experimental data by our theoretical expressions it is possible to elucidate how sorbate sitting within the zeolite varies with loading and how this affects the isotherms and accompanying isosteric heats of adsorption. The predictions of our model concerning the location of toluene molecules at low and high loadings are in accordance with those obtained by us for the p-xylene/silicalite system. The discrepancy between the experimental and calculated isosteric heat of adsorption observed at the loadings < 4 molecules per unit cell may be due to the fact that we used the simplified version of our model neglecting the energetic heterogeneity of the sites of the same type. It is possible that the toluene molecules, which have the larger dimension smaller than the p-xylene molecules, are less hindered in the pores of silicalite and because of this they are more sensitive to the defects in the crystal structure than the larger p-xylene molecules.

It may be concluded that our model performs very well considering the complexity of the system analysed. However, a detailed analysis of a large number of accurate experimental data is still needed to clarify the physical meaning of the parameters involved in the model.

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CURRICULA VITAE

Paweł Szabelski Born in Lublin in Poland in 1972. Studies of chemistry in the Faculty of Chemistry, Maria Curie-Skłodowska University in Lublin 1991-1996. Individual course of studies supervised by Professor Władysław Rudziński. Scholarship awarded by the Minister for National Education in 1996. Ph.D. student in the Faculty of Chemistry, UMCS (presentation of Ph.D. thesis scheduled for 2000). Main field of interest is theoretical description of adsorption of aromatic compounds in zeolites.

Jolanta Narkiewicz-Michałek, received her M.S. and Ph.D. in physical and theoretical chemistry from the University of Maria Curie-Skłodowska in Lublin in 1976 and 1980, respectively. At present she is an Assistant Professor in the Department of Theoretical Chemistry at this University. Her research concerns the theory of adsorption at solid/gas and solid/solution interfaces.