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NUMERICAL SIMULATION OF POLYMOLECULAR ADSORPTION

P. V. Koshkin and A. V. Tvardovskii

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A model of the polymolecular adsorption on homogeneous and inhomogeneous surfaces in the absence of lateral interactions and also with their allowance for the case of the homogeneous surface is presented. A procedure to calculate isotherms on the basis of statistical data on the substance distribution over the surface is suggested. The calculated dependences of the differential adsorption energy on the degree of filling and the isotherms are compared with the experimental data for the system benzene vapor–graphitized soot.

The aim of the present work is to calculate the isotherms and dependences of the differential adsorption energy on the degree of filling on the basis of the statistical data on substance distribution over the surface of an adsorbent obtained by the presently widely adopted Monte Carlo method (for instance, [1–3]) for a canonical Gibbs ensemble.

Model. We have chosen a three-dimensional grid model as the basic one. It is assumed that the near-surface nodes of the grid correspond to the minimum energies of binding of molecules to the surface of a model adsorbent and represent the centers of localized adsorption on which vertical associates are formed. The influence of a substrate is considered only for the molecules of a monolayer because of a drastic decrease in the field with distance. Interactions between the adsorbate molecules are taken into account by the Lennard-Jones potential for the first coordination sphere. On the system the Ising boundary conditions are imposed (geometrically, these boundary conditions transform a plane into a torus surface).

Simulation of Adsorption. In simulation, the Monte Carlo method for a canonical ensemble was employed. The probability of adsorption of the molecule w_i^{a} on the ith center (or complex) is expressed as follows:

$$w_i^{\mathrm{a}} = \frac{\exp\left(-\frac{U_i}{kT}\right)}{\sum_i \exp\left(-\frac{U_i}{kT}\right)}, \tag{1}$$

Here, in the denominator summation is carried out over all centers.

Calculation of the Quantities. The differential adsorption energy for a particular degree of filling was determined as

$$Q = \sum_i U_i w_i^{\mathrm{a}}, \tag{2}$$

Summation was carried out over all centers.

To determine the relative vapor pressure p/p_{s}, we will consider a complex consisting of m molecules. In this case, the mth molecule can exist in one of two states, namely, adsorbed or desorbed (i.e., in an equilibrium gas phase). The probability of the latter is

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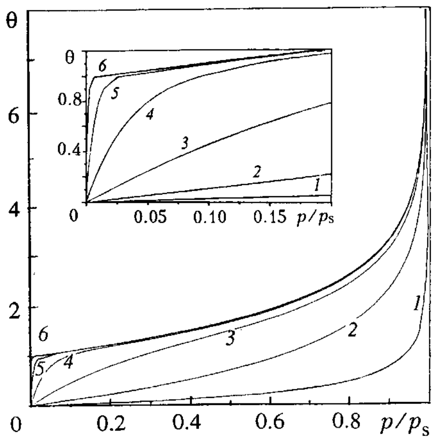


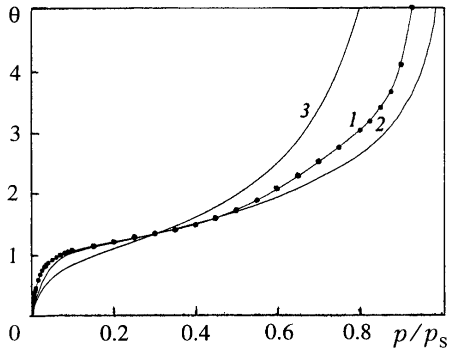


Fig. 1. Adsorption isotherms at different energetics of the model system.

Fig. 2. Experimental (1), calculated (2), and theoretical (BET) (3) adsorption isotherms.

$$w_m^{\mathrm{d}} = \frac{\exp\left(\dfrac{E_{\mathrm{g}}}{kT}\right)}{\exp\left(\dfrac{E_m}{kT}\right) + \exp\left(\dfrac{E_{\mathrm{g}}}{kT}\right)} = \frac{1}{1 + \exp\left(\dfrac{E_m}{kT}\right)}, \tag{3}$$

since we assume that in the gas phase $E_{\mathrm{g}} = 0$. The probability of desorption of k molecules of the complex is

$$w_{k,m}^{\mathrm{d}} = w_m^{\mathrm{d}} w_{m-1}^{\mathrm{d}} \ldots w_{m-k+1}^{\mathrm{d}} w'_{m-k} . \tag{4}$$

Here the cofactors correspond to the probability of desorption corresponding to the index of the molecule at the moment when all molecules of the associate located above it have passed into the gas phase. With the aid of the above relations and with allowance for the binding energy of different layers of the complex we calculate the mean number of molecules desorbed from this complex $\langle n_m^{\mathrm{d}} \rangle$. With allowance for $w_i^{\mathrm{d}} + w'_i = 1$ we have

$$\langle n_m^{\mathrm{d}} \rangle = w_m^{\mathrm{d}} (1 - w_{m-1}^{\mathrm{d}}) + 2 w_m^{\mathrm{d}} w_{m-1}^{\mathrm{d}} (1 - w_{m-2}^{\mathrm{d}}) + \ldots + m w_m^{\mathrm{d}} w_{m-1}^{\mathrm{d}} \ldots w_1^{d} . \tag{5}$$

Here $\langle n^{\mathrm{d}} \rangle = \Sigma N_{\mathrm{m}} \langle n_{\mathrm{m}}^{\mathrm{d}} \rangle$. As a rule, this quantity is small as compared with the mean size of the complexes. In deriving the above relations it has been assumed that molecules can be desorbed only one at a time.

Since the number of free molecules is proportional to the vapor pressure p of the adsorbate, the dependence of the degree of filling $\theta = n^{\mathrm{a}}/N$ of the centers on $\langle n^{\mathrm{d}} \rangle$ will be identical to the adsorption isotherm. To pass to the values of p/p_{s}, it is necessary to evaluate the limiting value of $\langle n^{\mathrm{d}} \rangle$ that corresponds to the ratio $p/p_{\mathrm{s}} = 1$. Let the molecules, beginning from the kth layer, have the same binding energy E to which the probability of adsorption w corresponds. We will write (5) in the form

$$\langle n_{m+k}^{\mathrm{d}} \rangle = \Delta_m + \Delta_k . \tag{6}$$

The first term determines the magnitude of desorption only from the last m layers of the adsorbate:

$$\Delta_m = w(1 - w) + 2w^2 (1 - w) + \ldots + m w^m (1 - w) = w(1 - w)(1 + 2w + 3w^2 + \ldots + m w^{m-1}) =$$

$$= w(1 - w)(w + w^2 + w^3 + \ldots + w^m)' .$$

At $m \to \infty$, we obtain

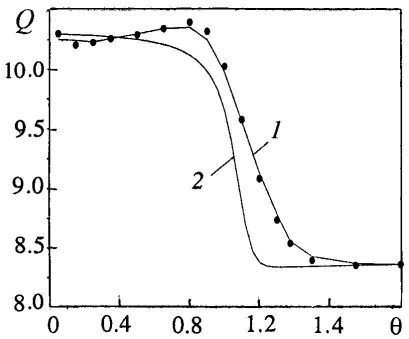


Fig. 3. Experimental (1) and calculated (2) dependences of the differential adsorption energies Q (kcal/mole) on the degree of filling.

$$\Delta_m = \frac{w}{1 - w}. \tag{7}$$

For the contribution of molecules of the first k layers to the desorption term we have

$$\Delta_k = (m + 1)\, w_{m+k} \ldots w_{k-1} (1 - w_{k-2}) + \ldots + (m + k)\, w_{m+k} \ldots w_1 < k\,(m + k)\,(w_{\max})^m,$$

where $w_{\max}$ is the highest value of w. It is obvious that with growth of m the quantity Δ_k tends to zero. Therefore for the limiting mean value of free molecules with account for the number of chains N we have

$$n_s = \frac{Nw}{1 - w}. \tag{8}$$

Correspondingly, the relative pressure is calculated as $p/p_s = \langle n^d\rangle/n_s$, where $\langle n^d\rangle$ and n_s are determined by formulas (5)–(8).

Results. On the basis of the above procedure we have carried out simulation of the polymolecular adsorption.

For the case of a homogeneous surface without allowance for lateral interactions, a strictly definite value of energy can be assigned to each layer. Calculated isotherms 1–6 (the energy for the first layer is 7, 8, ..., 12 kcal/mole, respectively, for the subsequent layers, 8 kcal/mole, temperature is $T = 300$ K) sufficiently adequately display a variety of the dependences characteristic of this model (Fig. 1). The insert in the figure shows in detail the process of filling the monolayer.

Figure 2 presents experimental 1, model 2, and theoretical 3 isotherms corresponding to the vapor adsorption of benzene on the surface of graphitized soot [4]. Isotherm 2 is obtained for the homogeneous surface with adsorption energies of 10.3 kcal/mole (the first layer) and 8.3 kcal/mole (the subsequent layers). Curve 3 is calculated at the same data according to the BET (Brunauer–Emmett–Teller) theory by the formula

$$\theta = \frac{\exp\left(\frac{\Delta Q}{RT}\right)\frac{p}{p_s}}{\left(1 - \frac{p}{p_s}\right)\left\{1 + \left[\exp\left(\frac{\Delta Q}{RT}\right) - 1\right]\frac{p}{p_s}\right\}},$$

where ΔQ is, correspondingly, equal to 2 kcal/mole. As is seen from the figure, even in the absence of lateral interactions the isotherm obtained within the framework of the model agrees better with experiment than the BET isotherm does.

Experimental 1 and calculated 2 dependences of the differential adsorption energy on the degree of filling (Fig. 3) correspond to isotherms 1 and 2 (Fig. 2).

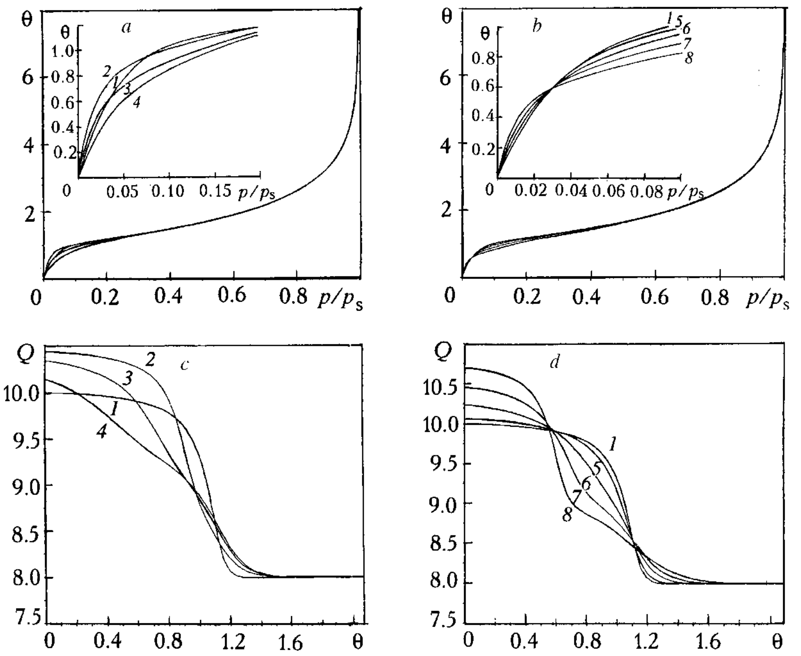
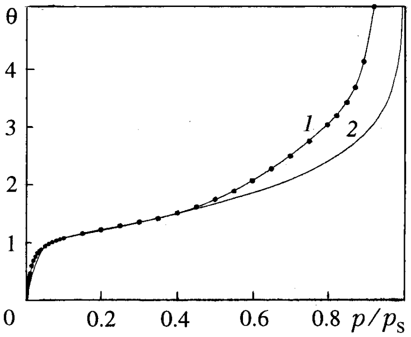


Fig. 4. Adsorption isotherms (a, b) and the dependence of the differential adsorption energy on the degree of filling (c, d) for the adsorbent surface containing two types of active centers with the following quantitative ratio: 1) the homogeneous surface with a binding energy of the first layer of 10 kcal/mole (100%); 2) 10.5 (75%) and 9.5 (25%); 3) 10.5 (50%) and 9.5 (50%); 4) 10.5 (25%) and 9.5 (75%); 5) 10.2 (50%) and 9.8 (50%); 6) 10.4 (50%) and 9.6 (50%); 7) 10.6 (50%) and 9.4 (50%); 8) 10.8 (50%) and 9.2 (50%). The adsorption energy of the subsequent layers is 8 kcal/mole.



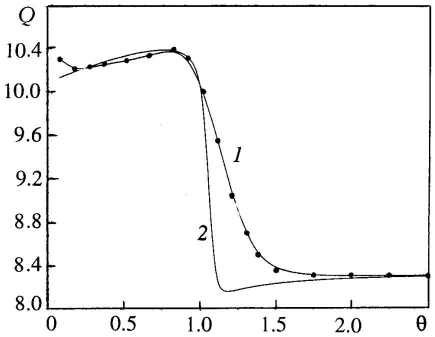
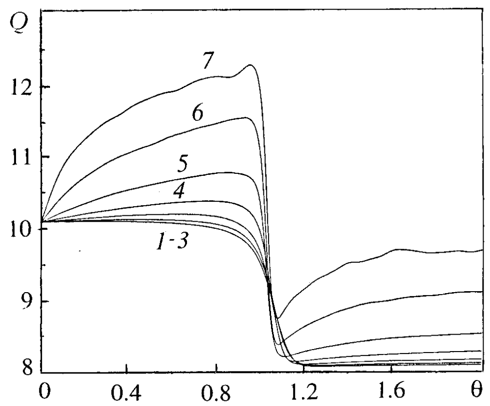


Fig. 5. Experimental (1) and calculated (2) adsorption isotherms.

Fig. 6. Experimental (1) and calculated (2) dependences of the differential adsorption heat on the degree of filling.

Figure 4 shows the influence of the energy inhomogeneity of the adsorbent surface on the isotherms and the dependences of the differential adsorption energy on the degree of filling. The introduced inhomogeneity corresponds to the assumption that the adsorbent surface contains two types of active centers with their quantitative ratio being different.

The discrepancy of the experimental and calculated data on the differential heat of adsorption in the field of filling the monolayer is caused by the absence of lateral interactions. This is attributable to the fact that for the reported data the center-to-center distances were substantially larger than the distances (corresponding to the minimum Lennard-Jones potential) between neighboring molecules in the vertical associate. After substitution into the



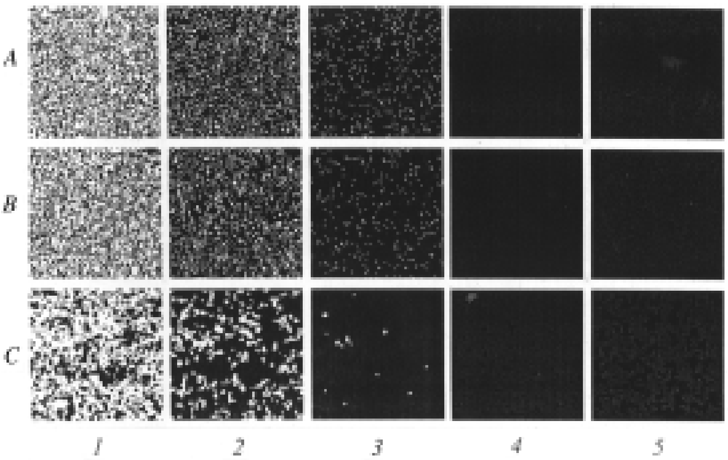


Fig. 7. Influence of the lateral interactions on the form of the dependence of the differential adsorption energy on the degree of filling.

Fig. 8. Visualized representation of the adsorption process. The degree of filling characterizes the remoteness of the running adsorption centers from the substrate (the white color corresponds to the adsorbent surface).

indicated potential and passage to energetics of the system such a difference becomes even more pronounced and after calculation of the probabilities of being a molecule at one or another center expressed in terms of the exponents we arrive at the ultimately small influence of the lateral interactions on dynamics of the adsorption.

Figure 5 provides a comparison of experimental isotherm 1 and calculated isotherm 2 corresponding to the case where the contribution of the lateral interactions becomes substantial. In principle, the given procedure of calculation of the isotherms is not fully correct for this case since the energies entering into the formulas of the probabilities of molecule desorption are no longer quantities independent of the dynamics of the desorption. However, precisely the distribution of molecules with respect to the centers and associates that directly reflects the energetic structure of the system and, in particular, the contribution of lateral interactions to the adsorption process is the prevailing factor of reliability of the data. Proceeding from this, we can presume that the errors of the procedure employed in the calculations of the isotherm of such a system are not substantial.

An increase in the influence of lateral interactions leads to better coincidence of the experimental dependence of the differential heat of adsorption 1 and calculated dependence 2 in the field of monosorption (Fig. 6).

Figure 7 shows the influence of a gradual increase in the lateral interactions (curves 1–7, respectively, 0.029, 0.042, 0.070, 0.153, 0.266, 0.558, and 0.869 kcal/mole) on the form of the dependence of the differential energy of adsorption. The wavy trend of curve 7 is related to the fact that the statistics used (200 × 200 centers) are insufficient for a completely adequate description of the system with such energetics.

Finally, Fig. 8 represents a visualization of the adsorption process for the cases displayed by curves 1 (A), 3 (B), and 7 (C) (see Fig. 7). Indices 1, 2, 3, 4, and 5 correspond to degrees of filling equal to 0.4, 0.8, 1.0, 1.2, and 1.6, respectively.

NOTATION

w_i^{a}, probability of the adsorption of a molecule on the ith center (or complex); U_i, potential at the corresponding node at the running fixed distribution of the adsorbate; k, Boltzmann constant; T, absolute temperature; Q, differential adsorption energy; p, running pressure; p_{s}, saturation pressure; w_m^{d}, probability of the desorption of the upper mth, reckoned off the surface, molecule of the vertical associate; E_m and E_{g}, binding energy of the molecule in the adsorbed state and in the gas phase, respectively; $w_{k,m}^{\mathrm{d}}$, probability of the desorption of k upper molecules from m molecules of the complex; w'_{m-k}, probability of the fact that the molecule corresponding to the index remains in the adsorbed state on passage of k upper molecules from m molecules of the associate into the gas phase; $\langle n_m^{\mathrm{d}} \rangle$, mean number of desorbed molecules from the complex with size m; $\langle n^{\mathrm{d}} \rangle$, mean number of desorbed molecules at the running degree of filling; N_m, number of vertical associates consisting of m molecules; n^{a}, number of adsorbed particles; N, number of adsorption centers; E, binding energy for molecules of the upper layers; w, probability of molecule absorption at the node with binding energy E; Δ_i, contribution of the chain of i molecules of the associate to desorption; n_{s}, mean number of desorbed molecules in the case of saturation of the system; ΔQ, pure heat of adsorption; R, universal gas constant. Subscripts and superscripts: a, adsorbed state; d, desorbed state; s, saturation state; g, gas phase; max, maximum.

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