Published in Surface Science 114, issue 1, 85-95, 1982
which should be used for any reference to this work

PHYSICAL ADSORPTION OF SIMPLE GASES ON THE (111) FACE OF SULFUR; A MODEL FOR THE ADSORPTION BY HETEROGENEOUS SURFACES, INCLUDING LATERAL INTERACTIONS

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As revealed by previous ab initio calculations, the surface of the (111) face of rhombic sulfur is characterized by heterogeneous but low adsorption energies. This implies relatively important contributions from lateral interactions in the adsorption mechanism. A theoretical model is presented for this case, also taking into account the random distribution of the sites. One assumes a local Fowler–Guggenheim isotherm and that the adsorption energies have a skew-Gaussian distribution with a non-zero minimum value. The resulting isotherm is tested in a satisfactory way with the data obtained for nitrogen, argon, methane and neopentane adsorption in the submonolayer region.

1. Introduction

This paper presents in a condensed form an investigation [1] dealing with a new equation for the adsorption by heterogeneous and non porous surfaces, taking into account lateral interactions. The study is applied to the model of a surface where the sites are randomly distributed, as far as their adsorption energies are concerned, and where relatively important adsorbate–adsorbate interactions exist. The general framework is the so-called condensation approximation (CA) [2–6] applied to the method of integral transforms, assuming a local isotherm of the Fowler–Guggenheim type and a skew-Gaussian distribution of adsorption energies.

Simultaneously, in the case of argon adsorbed on sulphur, the resulting energy distribution for the adsorption sites is compared with "ab initio"

calculations [7]. The study provides therefore a test for the improved adsorption isotherm and for the absolute values of the adsorption energies.

2. Theoretical part

In recent years, attempts have been made to describe real surfaces in terms of the integral equation

$$\theta_t(T; p) = \int_\Omega \theta_\ell(T; p; \epsilon)\, \chi(\epsilon)\, \mathrm{d}\epsilon, \tag{1}$$

where $\theta_t(T; p)$ is the overall adsorption isotherm, expressed in terms of a fractional coverage of the surface; $\theta_\ell(T; p; \epsilon)$ is the local adsorption isotherm, and $\chi(\epsilon)$ the normalized distribution function for the adsorption energy ϵ. The latter, a positive quantity, is conventionally defined as $\epsilon = -U_0 - E_v$, and corresponds to the difference between the local minimum of the adsorption potential, U_0 or ϕ_0, and the vibrational energy E_v on the site.

Eq. (1) can be solved in different ways, by assuming analytical functions for θ_ℓ and/or $\chi(\epsilon)$. A well-known example is the model of Ross and Olivier [8], based on a local isotherm of the Hill–De Boer type and a Gaussian distribution $\chi(\epsilon)$. Moreover, it is supposed that adsorption takes place on relatively large and energetically homogeneous patches. In this case, the overall adsorption isotherm $\theta_t(T; p)$ is fully defined and it leads to a good fit with experimental data only under very specific conditions implied by the model. This treatment was considered in an earlier and preliminary investigation of adsorption by sulphur [9]. A more flexible approach is the one where the form of the local isotherm alone is postulated, and the energy distribution $\chi(\epsilon)$ is recalculated from experimental data by applying various mathematical techniques.

However, as an alternative to the approach of Ross and Olivier, one may postulate in the case of localized adsorption that the local isotherm is the Fowler–Guggenheim isotherm (FG) [10],

$$\theta_{FG}(T; p; \epsilon) = \left\{1 + (K/p)\, \exp\left[-(\epsilon + zW\psi)/RT\right]\right\}^{-1}. \tag{2}$$

The parameter K is a characteristic pressure, depending on the system [11–13] and $zW\psi$ is the potential resulting from the average interaction between a given admolecule and its neighbours (z nearest neighbours). W is the interaction energy between two neighbouring admolecules and ψ is a function depending of on the topography of the surface. For the models of a patchwise homogeneous surface and of a random distribution of the sites, ψ is respectively [14,15]: $\psi = \theta_{FG}$, the coverage of the patch of energy ϵ, and $\psi = \theta_t(T; p)$, the total coverage of the surface.

The majority of real surfaces seem to belong rather to the model of a random topography of sites, graphitized carbon [8,16] being an exception, It

follows that

$$\theta_{\mathrm{FG}}^{(\mathrm{r})}(T;p;\epsilon)=\left\{1+(K/p)\exp\left[-(\epsilon+zW\theta_{\mathrm{t}})/RT\right]\right\}^{-1}. \tag{3}$$

The choice of the FG isotherm (3), rather than the Langmuir expression, is justified by the relatively important part played by lateral interactions in the case of adsorption on sulphur (see below, section 4).

The corresponding energy distribution $\chi(\epsilon)$ could, formally, be recalculated by inversion of eq. (1). Alternatively, simple analytical expressions can be postulated "a priori", such as the simple skew-Gaussian

$$\chi(\epsilon)=2B(\epsilon-\epsilon_0)\exp\left[-B(\epsilon-\epsilon_0)^2\right] \quad (\epsilon>\epsilon_0), \tag{4}$$

previously used in the literature [1,6,13,15].

Simple physical considerations show that there always exists a minimum adsorption energy $\epsilon_0 \neq 0$. However, for mathematical convenience, one often considers distributions which extend from 0 to $+\infty$, an assumption which is physically incorrect [13,17].

Earlier "ab initio" calculations of the local minima U_0 or ϕ_0 of the adsorption potential of argon of the (111) face of rhombic sulphur [7] revealed that the sites were randomly distributed over the surface of the unit cell. Their values range from 4 to 13 kJ/mole. The calculations were based on summations of pair-potentials of the Lennard-Jones type [16], carried out over the nearest 100–150 neighbouring atoms of a given site. A total of 249 sites was

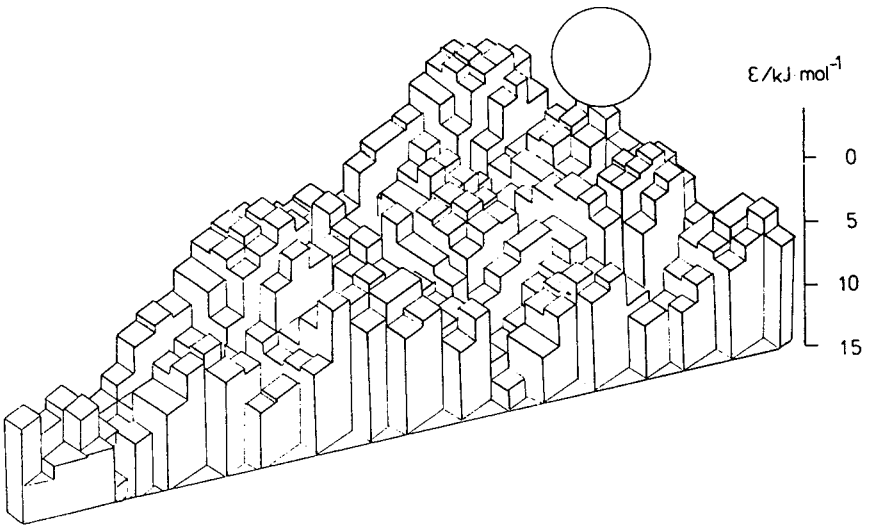

Fig. 1. Distribution of the adsorption energies of Ar on 249 sites of the (111) face of rhombic sulphur. The vertical scale corresponds to the energy $\epsilon=-U_0-E_{\mathrm{v}}$. The sphere represents an atom of Ar, drawn to scale.

considered. Fig. 1 shows the distribution of the adsorption sites on the unit cell of the (111) face itself. It can be seen that their distribution has a random character.

From the shape of the local adsorption potentials $U(z)$, it is possible to derive the force constant k_z of the vibration normal to the site considered and the frequency itself [16],

$$k_z = \left(\partial^2 U(z)/\partial z\right)_{z_{\min}}, \tag{5}$$

$$\nu_\perp = (1/2\pi)\sqrt{k_z/m}, \tag{6}$$

m being the mass of the adsorbate.

For argon on sulphur, $\nu_\perp$ is found to be in the range of $(0.5\text{–}1.5) \times 10^{12}\ \mathrm{s}^{-1}$ [1]. The corresponding energies E_0^ν vary from (0.13–0.30)kJ/mole, which is small when compared with ϕ_0. Using eq. (1), an approximate distribution curve can be obtained for the 249 sites by considering energy intervals of 1 kJ/mole (fig. 5).

Following Harris [2] and Cerofolini [3–6], the problem of the exact integration of eq. (1) could be solved in a satisfactory way by the so-called condensation approximation (CA). In this method, the local isotherm $\theta_\ell(T; p;\ \epsilon)$ is replaced by a step-wise "condensation isotherm" $\theta_c(T; p_c; \epsilon)$, for which adsorption is assumed to occur at a critical pressure $p_c = p_c(\epsilon)$. The best fit between θ_ℓ and θ_c is obtained by minimizing either the Lagrangian distance between the two isotherms, or the socalled $L^2(0; +\infty)$ metric, both procedures leading to the same result [3]. As a consequence the following condition must be fulfilled

$$\theta_\ell(T; p_c; \epsilon) = 1/2. \tag{7}$$

This equation provides a relation between the condensation pressure p_c on a patch/site and its adsorption energy ϵ, through the chosen local isotherm.

The condensation approximation also implies that integral (1) reduces to the simpler form

$$\theta_t(T; p) = \int_{\epsilon_0}^{\infty} \chi_c(\epsilon_c)\, \mathrm{d}\epsilon, \tag{8}$$

or conversely

$$\chi_c(\epsilon_c) = -\partial\theta_t/\partial\epsilon_c. \tag{9}$$

The distribution $\chi_c(\epsilon_c)$ is slightly broader than the exact distribution $\chi(\epsilon)$ appearing in integral transform (1). The relation between the two is discussed in the literature [5].

Combining eqs. (3) and (7), one finds that for a random distribution of sites following the Fowler–Guggenheim isotherm (3), CA leads to [15]

$$p_c(\epsilon) = K \exp\left[-(\epsilon_c + zW\theta_t)/RT\right], \tag{10}$$

or inversely

$$\epsilon = RT \ln(K/p) - zW\theta_t. \tag{11}$$

The subscripts referring to the condensation may be omitted, since eqs. (10) and (11) provide unique relations between p and ϵ, generally valid for the overall isotherm.

In the present study, it was found that in the case of adsorption by sulphur the experimental data could not be fitted in a satisfactory way to an overall equation of the Dubinin–Radushkevich type [18] suggested by Kaganer for non-porous solids [19],

$$\theta_t(T; p) = \exp\left\{-B\left[RT \ln(p_0/p)\right]^2\right\}, \tag{12}$$

where p_0 denotes the vapour pressure of the adsorptive at temperature T. A more flexible modification of eq. (12) where p_0 is replaced by an adjustable pressure p_m,

$$\theta_t(T; p) = \exp\left\{-B\left[RT \ln(p_m/p)\right]^2\right\}, \tag{13}$$

as used by different authors [5,13,17,20], did not lead to a satisfactory fit over the whole range of experimental data. An alternative adsorption equation was therefore considered, based on the following assumptions:

(1) the local isotherm is of the FG type (3);

(2) in the framework of CA, this implies relations (10)–(11) between pressure and energy;

(3) the adsorption energy distribution $\chi_c(\epsilon)$, closely approximating the true distribution $\chi(\epsilon)$ of eq. (1) is given by the displaced skew-Gaussian (4), a reasonable first choice for a heterogeneous surface, as discussed above.

From eq. (8) it follows that the overall isotherm θ_t corresponding to this model is

$$\theta_t(T; p) = \exp\left[-B(\epsilon - \epsilon_0)^2\right], \tag{14}$$

and using condition (11)

$$\theta_t(T; p) = \exp\left\{-B\left[RT \ln(K/p) - \epsilon_0 - zW\theta_t\right]^2\right\}. \tag{15}$$

This equation can be expressed in the more convenient form

$$\ln p = -\frac{1}{RT\sqrt{B}}\left(\ln\frac{1}{\theta_t}\right)^{1/2} + \ln(K') - \frac{zW\theta_t}{RT}, \tag{16}$$

where

$$K' = K \exp(-\epsilon_0/RT). \tag{17}$$

It is important to note that, owing to the presence of the variable quantity $zW\theta_t/RT$ in the exponent, eq. (15) is formally not compatible with DRK expressions like (12) or (13), with constants p_0 or p_m.

In the present model, this feature is a direct consequence of the random distribution of the sites, introducing θ_t in the right-hand side of the FG isotherm (3). On the other hand, if one considers patchwise adsorption, one arrives at an equation of type (13) [15].

Table 1
Best fit values of experimental data in eq. (15), obtained for the adsorption of Ar, N_2, CH_4 and neopentane on $S_\alpha(111)$; the limits for θ_t correspond to the best fit

Adsorptive	T (K)	θ_t	B (10^{-2} kJ^{-2} mol^2)	zW (kJ mol^{-1})	$2\alpha/\beta$ on P-33 [8] (kJ mol^{-1})	K' (Torr)	ϵ_0 (kJ mol^{-1})
Ar	76.9	1×10^{-3}–0.8	6.161	3.20	3.87 (77.5 K)	2.539×10^4	5.38
	85.6		5.517		3.90 (90.1 K)	5.959×10^4	5.56
N_2	76.9	2×10^{-3}–0.8	6.841	2.37	2.64 (77.5 K)	1.974×10^4	5.22
	85.7		6.014		2.62 (90.1 K)	5.829×10^4	5.18
CH_4	76.8	2×10^{-3}–0.8	8.915	2.00	5.5 (calc. [8])	96.9	8.07
	79.5		8.286			165.0	8.06
neo-C_5H_{12}	253.1	2×10^{-3}–0.8	1.278	6.65	12.2 (calc. [8])	4530	27.5
	263.1		1.246			6258	28.0
	273.1		1.121			9791	28.1

As seen in section 4, the experimental data obtained for the adsorption on sulphur follow eq. (16) in a very satisfactory way and over a large range of surface coverages (table 1).

3. Experimental part

Adsorption experiments were carried out volumetrically on crystallites of rhombic sulphur, by using the following gases: N_2 and Ar (76.9 and 85.6 K), CH_4 (76.8 and 79.5 K) and neopentane (253.1, 263.1 and 273.1 K). For the first three gases, the temperature of the liquid nitrogen/oxygen baths was controlled with an argon vapour pressure manometer.

Pressures were read with transducer gauges (Barocel 570 A) covering the ranges 10^{-3}–10 and 1–1000 Torr, with an accuracy of $\pm 0.5\%$, or better. Thermal transpiration was accounted for by applying the relations of Weber and of Miller [21].

Small crystallites of suplphur were prepared in successive batches, by adding 50 ml of chloroform to 100 ml of a solution of sulphur in CS_2, at 23°C. As indicated by Kitchener et al. [22], this procedure favours the precipitation of rhombic sulphur crystallites with a predominance of the (111) faces. Optical and electronic microscopy confirmed by the bi-pyramidal shape of the crystallites. The collected material was dried under vacuum and sieved (5–100 μm). Adsorption was carried out on 103.02 g of crystallites having a total surface area $S_m(N_2;\ 76.9\ K) = 5.99 \times 10^{-2}\ m^2/g$ as obtained from the BET plot [23].

For every isotherm, a total of approximately 50 points was measured in the range $10^{-3} < \theta < 1$, the coverage being expressed conveniently with respect to the BET monolayer capacity.

4. Results and discussion

The new overall isotherm (15) was tested in its logarithmic form (16) by using experimental data obtained for the submonolayer region. The isotherms are found to be of type II, according to the so-called BET classification [23], which denotes the formation of multilayers at higher pressures. However, one may assume that in the submonolayer region considered here ($10^{-3} < \theta_t < 0.8$), multilayer effects can be neglected.

In order to reduce the number of unknows which appear in eq. (16), the surface coverage θ_t was calculated by using the BET monolayer capacity N_{am}. In spite of the shortcomings of the BET method, the quantity N_{am} often appears to give a satisfactory measure of the monolayer capactity [23]. In the present case, consistency was found between the results for the different gases.

As shown in figs. 2 and 3, which represent plots of $\ln(p) + zW\theta_t/RT$ versus $[\ln(1/\theta_t)]^{1/2}$ for various values of zW/RT, best fits of all experimental data of

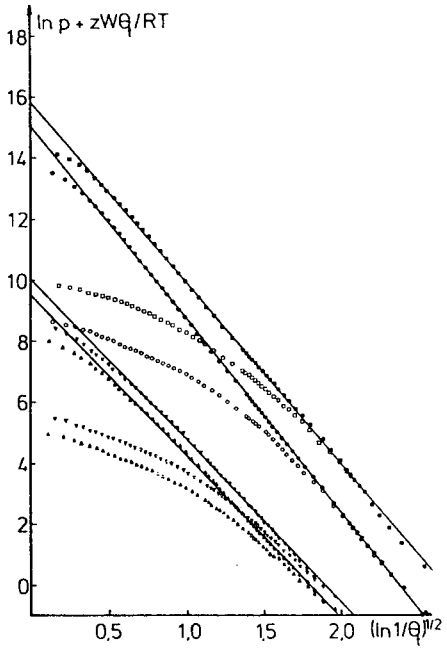

Fig. 2.Representation of $\ln p + zW\theta_t/RT$ versus $\ln^{1/2}(1/\theta_t)$, according to eq. (15), for the best fit values of the lateral interaction parameter zW and for $zW=0$: Ar (76.9 K): $zW=3.2$ kJ/mol (●) and zero (○); Ar (85.6 K) $zW=3.2$ kJ/mol (■) and zero (□); CH_4 (76.8 K): $zW=2.0$ kJ/mol (▲) and zero (△); CH_4 (79.5 K): $zW=2.0$ kJ/mol (▼) and zero (▽).

eq. (16) can be obtained. The corresponding parameters are given in table 1, with the domains of validity which appear to be larger than for the DR-based eqs. (12) and (13). The best fit values for the lateral interaction terms zW are close to $2\alpha/\beta$, the corresponding quantity appearing in the model of Ross and Olivier [8], obtained experimentally for adsorption on carbon P-33 or calculated. In the case of neopentane, however, zW is smaller than expected, although the molecular surface area $A_m(\text{neo-}C_5H_{12};\ 263\ \text{K}) = 40 \times 10^{-20}\ \text{m}^2$ is close to te value calculated from the liquid density [23].

The experimental values of K' can be used to calculate the minimum adsorption energy ϵ_0, by means of eq. (17). The specific parameter K of the FG equation (3), based on a statistical mechanical model [10], is given by the relation

$$K = \left(2\pi mkT/h^2\right)^{3/2} kT\left[1 - \exp(-h\nu_\perp/kT)\right], \tag{18}$$

if one neglects vibrations parallel to the surface. Here m is the mass of the adsorbate and $\nu_\perp$ the frequency normal to the site.

Simpler relations, discussed by Sokolowski et al. [13], have been proposed by Hobson [11] and by Adamson [12]. Their influence on the value of ϵ_0 is

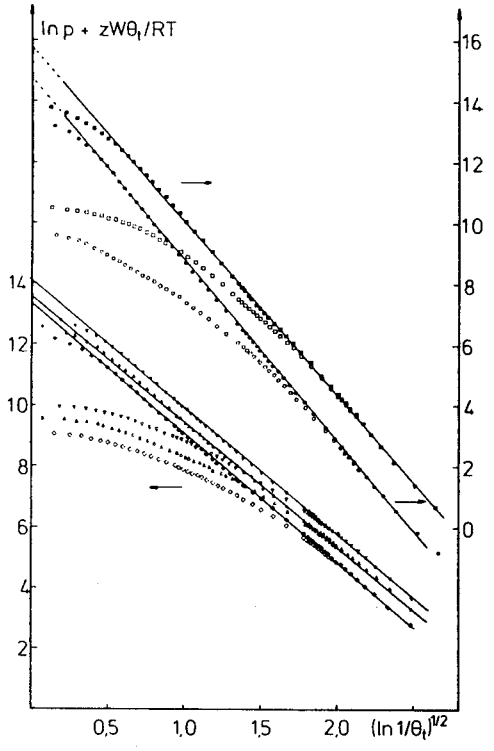

Fig. 3. Same representation as in fig. 2 for neopentane and nitrogen (left and right hand ordinates respectively): neopentane (253.1 K): $zW=6.65$ kJ/mol (◆) and zero (◇); neopentane (263.1 K): $zW=6.65$ kJ/mol (▲) and zero (△); neopentane (273.1 K): $zW=6.65$. kJ/mol (▼) and zero (▽); N_2 (76.9 K): $zW=2.37$ kJ/mol (●) and zero (○); N_2 (85.7 K): $zW=2.37$ kJ/mol (■) and zero (□).

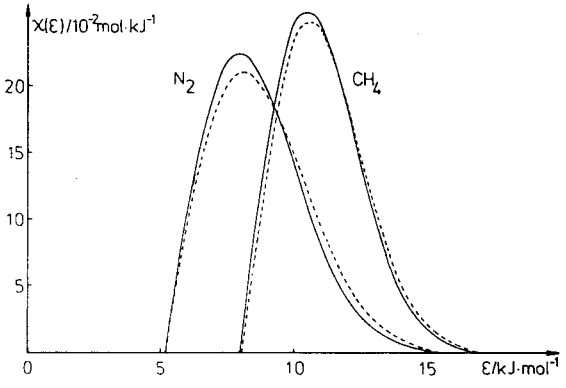

Fig. 4. Calculated adsorption energy distribution, following eq. (4) for nitrogen (76.9 and 85.7 K) and methane (76.8 and 79.5 K). The full lines correspond to the lower temperatures.

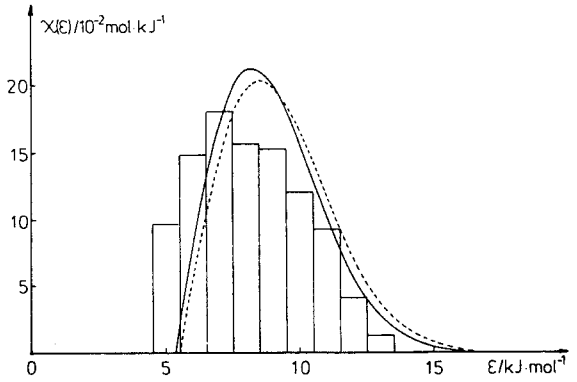

Fig. 5. Comparison of the adsorption energies of argon on $S_a(111)$ obtained from eq. (4) for 76.9 K (full line) and 85.6 K (broken line) and calculated ab initio [7] (histogramme).

relatively small. Fig. 5 shows the good agreement found between the adsorption energy distribution $\chi_c(\epsilon)$ obtained for argon by using eq. (4) and the distribution calculated "ab initio" [7]. This agreement may be regarded as a further test for the consistency of the model presented here, in the form of eq. (15), as well as an illustration of the validity of the "ab initio" calculations of this type [16].

Finally, inspection of the values of parameter B shows that in the case of eq. (15) there no longer exists a shifting (or similarity) coefficient β, as it is the case in the original DR equation [18]. The latter is valid for the filling of micropores and it has the analytical form (12), θ_t representing the fraction of the micropores filled at $(T; p)$. The absence of a simple adsorbate dependent shifting factor in eq. (15) is not too surprising since eqs. (12) and (15) correspond to different physical situations. Their comparison may, however, lead to a better understanding of the model for adsorption in microporous solids [24]. As opposed to the case of a heterogeneous and open surface examined here, micropores may be considered as a collection of sites or small homogeneous regions, which are physically isolated by the walls of the pores

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