

SURFACE HETEROGENEITY EFFECTS IN WATER VAPOUR ADSORPTION ON CLAY MINERALS

Z. Sokołowska¹, J. Stawiński¹, S. Sokołowski²

¹ Institute of Agrophysics, Polish Academy of Sciences, Doświadczalna 4, 20-236 Lublin, Poland

² Computer Laboratory, Faculty of Chemistry, Maria Curie-Skłodowska University, Pl. Maria Curie-Skłodowska 3, 20-031 Lublin, Poland

A b s t r a c t. The paper is devoted to the problem of evaluation of energetic heterogeneity of clays and clay minerals from analysis of experimental adsorption isotherms of water vapour. The computed distribution functions of adsorption energy are next used to describe the dependence between heat of immersion and the amount of pre-adsorbed water.

INTRODUCTION

The simplest attempts to describe adsorption of gases on energetically heterogeneous surfaces have been based upon application of discrete models, in which the adsorption centres are divided into a finite number of groups, each characterized by a corresponding value of energy of adsorption [1,7,13]. The discrete models lead to the total adsorption isotherm equation being a sum of 'local' isotherms, describing equilibrium on a given kind of adsorption centres.

Because of the complex character of natural soil adsorbents, their distribution of adsorption centres with respect to adsorption energy is described by a continuous function and the overall adsorption isotherm θ is given by the integral [7]:

$$\theta_t(p) = \int \theta_1(p, \epsilon) \chi(\epsilon) d\epsilon. \quad (1)$$

In the above $\theta_1(p, \epsilon)$ is the local adsorption equation that gives the fractional coverage of adsorption centres with the energy of adsorption equal to ϵ and at the equilibrium pressure equal to p , $\theta_1(p) = N_a(p)/N_m$, where $N_a(p)$ is the total number of adsorbed molecules at the pressure p , N_m is the monolayer capacity, and the function $\chi(\epsilon)$ (called the energy distribution function) gives the fraction of adsorption centres with the energy of adsorption equal to ϵ . The physical significance of the energy distribution function $\chi(\epsilon)$ for heterogeneous adsorbents can be compared with the pore size distribution function used for characterization of material porosity [14].

The adsorption energy distributions are usually calculated by solving the integral equation of adsorption (1) [3,5-8,19]. In the case of multilayer adsorption, the local adsorption equilibrium is usually interpreted in terms of the BET model [2,5-7].

In this paper we apply calculate energy distribution functions from experimental adsorption isotherms of water vapour adsorbed on clay minerals. We also discuss the influence of energetic heterogeneity on heats of immersion.

Evaluation of the energy distribution function from measured adsorption isotherms

Let us consider Eq. (1) when the local adsorption obeys the BET model, i.e.,

$$\theta_1(p, \varepsilon) = \frac{1}{1-x} \frac{K(\varepsilon)y}{[1+K(\varepsilon)y]}, \quad (2)$$

where $y=p/(1-x)$, $x=p/p_s$, p_s is the saturated vapour pressure, $K(\varepsilon)=\exp(\varepsilon/RT)/A_0$, R is the Boltzmann constant, T is the temperature and A_0 is a constant [4].

We assume next that the measured isotherm $N_a(p) = \theta_t(p) N_m$ can be approximated [5,6,8-10] by:

$$\ln [N_a(p) (1-x)] = \sum_{j=0}^M B_j \ln^j (y/p_0), \quad (3)$$

where the B_j ($B_0 = -\ln N_m$) and p_0 are the parameters. In the case discussed here, the expression for $\chi(\varepsilon)$ evaluated from solution of Eq. (1) can be then approximated [8-10,17,18] by:

$$\chi'(\varepsilon) = \sum_{j=1}^M j B_j E^{j-1} \exp \left[\sum_{j=1}^M B_j E^j \right], \quad (4)$$

where $E = (\varepsilon_s - \varepsilon)/RT$, ε_s is the energy of condensation and $\chi'(\varepsilon) = \chi(\varepsilon)/RT$. Thus, the problem of evaluating energy distribution is reduced to approximating the experimental data $\ln [N_a(1-x)]$ by the polynomial (3). Details of the numerical technique used for this purpose can be found in our previous works [17,18].

We stress that although the solution (4) is only an approximation and that it can sometimes lead to excessive smoothing of the computed distribution function by neglecting small local minima and maxima in $\chi(\varepsilon)$, numerous results reported in the literature [7,8]) have indicated that well-established peaks on $\chi(\varepsilon)$ curves evaluated according to Eq. (4) do really correspond to different groups of adsorption centres. Con-

sequently, in our opinion, Eq. (4) provides the simplest and instantaneously accurate method for estimating energetic heterogeneity of adsorbents, and energy distributions obtained from this equation may be a very valuable source of information about the nature of adsorption systems.

Results of calculations of the energy distribution functions

The following systems were analysed:

(i) Adsorption of water vapour at $T=293$ K on Li- and Ca-saturated montmorillonite (Wyoming bentonite). Figure 1 shows results obtained by using the experimental technique of Paterson and Stawiński [15].

(ii) Adsorption of water vapour at $T=298$ K on Na- and Ca-saturated montmorillonite and on montmorillonite saturated with a mixture of Na and Ca ions at different equivalent fractions of exchangeable sodium ions (EFES = 0, 0.4, 0.6 and 1), [11,12].

(iii) Adsorption of water vapour at $T=302.45$ K on Li- and Ca-saturated kaolinite degassed at $T=306$ K and evaluated by using a vacuum microbalance technique.

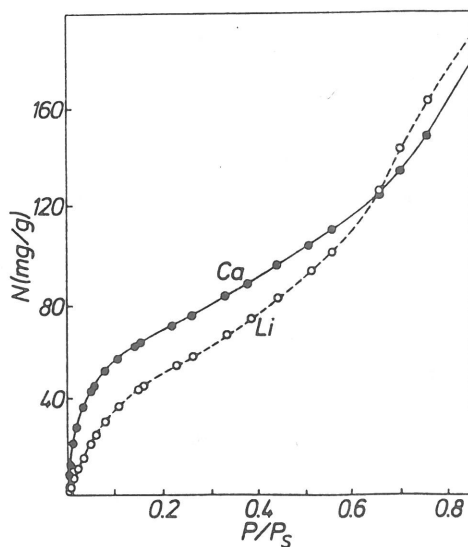


Fig. 1. Adsorption isotherms of water vapour on Li-montmorillonite (Li) and Ca-montmorillonite (Ca) at $T=293$ K.

The adsorption data (ii) were taken from the literature allowing a comparison of the results obtained in this work with those gained previously [12].

The analysis of each isotherm was made as described above by fitting Eq. (3) to the experimental data. A detailed description of the numerical method used is given by Sołowska *et al.* [18].

The curves $\chi(\epsilon)$ for the systems (i) are given in Fig. 2. They are 'skewed', non-Gaussian in shape and exhibit three main peaks, corresponding to three distinct groups of adsorption centres on the surfaces of Li- and Ca-saturated montmorillonite. The last, high energy peak in Fig. 2b with maximum occurring near $\epsilon - \epsilon_s = 12.5$ kJ/mol, can, in our opinion, be associated with the most energetic centres of original substrate and with the presence of calcium ions. On the other hand, the lithium ions seem to be responsible for the appearance of the maximum of $\chi(\epsilon)$ at $\epsilon - \epsilon_s = 6.5$ kJ/mol (see Fig. 2a). One should take into account, however, that the accuracy of the evaluated energy distribution functions are strongly dependent on the accuracy of adsorption data. In particular, a correct evaluation of the contributions due to the most energetic centres

requires highly precise data from the region of extremely low pressures. It is well known that experimental work under such conditions is inevitably connected with many difficulties. Therefore, the evaluated energy distribution functions might be slightly different depending on the accuracy of experimental measurements of adsorption isotherms [5-8].

The one of the adsorbents (Ca-montmorillonite) investigated by Keren and Shainberg [11,12] is similar but, of course, not identical with that used in our experiments. Consequently, the energy distribution $\chi(\epsilon)$ evaluated for this system (Fig. 3) differs slightly from that presented in Fig. 2b. Three remaining curves in Fig. 3 are for water vapour adsorbed on Na-montmorillonite and on montmorillonite saturated with mixtures of Na and Ca ions at EFES equal to 0.4 and 0.6. The most interesting feature is the systematic change of the shape of the distribution functions with the increase of EFES. For higher values of EFES, the second maximum observed on $\chi(\epsilon)$ curves becomes less pronounced, whereas the height of the first peak increases and attains its maximum value at EFES=1. The difference between the values of e at which both maxima $\chi(\epsilon)$ curves are located is approximately equal to 3.7 kJ/mol. The last

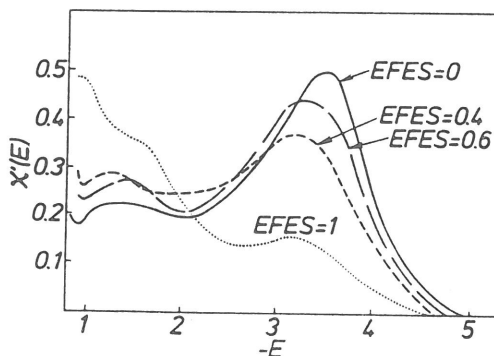
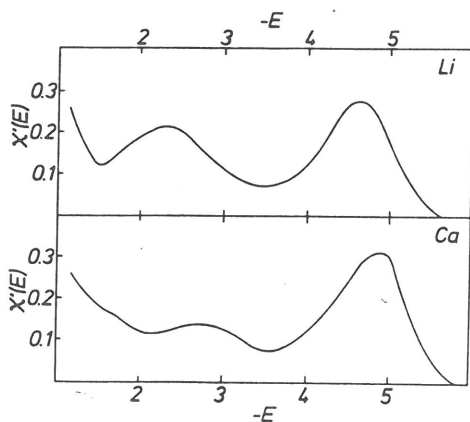


Fig. 2. Energy distribution functions for the systems (a) evaluated from eq. (4) for Li- and Ca-montmorillonite.

Fig. 3. Energy distributions for the systems (b). The curves are labelled by corresponding values of EFES.

value is close to the difference in adsorption energies for Na- and Ca-saturated montmorillonites computed according to the ion-dipole model by Keren and Shainberg [11]. Thus, one can associate the high energy peaks on the curves $\chi(\epsilon)$ evaluated for the montmorillonites saturated with Ca-ions and with mixtures of Na and Ca ions with the interactions of adsorbate particles with Ca cations and with the most energetic centres of the initial surface of montmorillonite. Similarly, because the low energy peak is evident for the system with EFES=1, and it is much less visible for all remaining systems (ii), its presence can be connected with the adsorption on Na cations. Figure 4 compares the energy distribution functions computed for Ca- and Li-saturated kaolinite (the systems (iii)). As in the case of the systems (i), the maxima at the highest values of ϵ can be attributed to adsorption of water vapour on metal ions.

Evaluation of the energy distribution functions may be of great importance and lead to characterization of adsorbing surfaces. It seems particularly important for such complicated materials as soils, because we do not have any other method enabling the determination of energetic characterization of their surfaces. Of course, the correct interpretation of the peaks appearing on

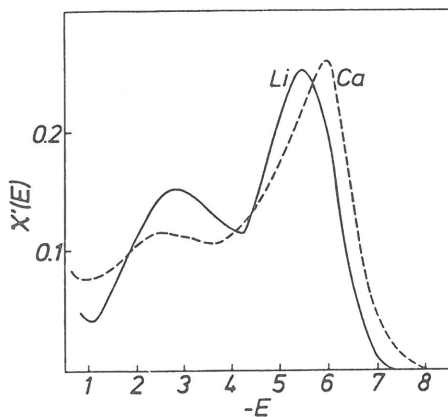


Fig. 4. Energy distributions for the systems (c). Ca - Ca-kaolinite, Li - Li-kaolinite.

$\chi(\epsilon)$ requires additional information concerning the structure of adsorbing surface.

Influence of surface heterogeneity on heat of immersion

The heat of immersion of a solid surface Q by a single liquid is composed of two terms [16,20]: a work term W , associated with formation of a semi-infinite liquid bulk phase and a potential term U , connected with the potential field created by the solid adsorbent

$$Q = W + U. \quad (5)$$

To a good approximation the term U can be identified with the energy of adsorption.

Interactions of fluid molecules with a solid surface obviously cause some perturbation in the structure of the surface liquid, as compared with its bulk structure. Consequently, the term W also depends slightly on the adsorption energy [3,11,12,16-18]. However, this effect is commonly expected to be small and will be neglected in our treatment.

Let us consider wetting by liquid adsorbate of a sample containing known amount N_a of pre-adsorbed particles and let the adsorption isotherm pressure corresponding to N_a be equal to p . According to the approach discussed in the preceding section, the distribution of adsorption energy is described by the function $\chi(\epsilon)$. If the adsorbent surface is 'dry', i.e., $N_a = 0$, then, obviously $U = \int \chi(\epsilon) d\epsilon$. The average number of occupied sites 'i', having adsorption energy equal to ϵ_i , is $N_m \theta_1(p, \epsilon_i) \chi(\epsilon_i)$ and the energy of interaction of these molecules with the surface is equal to $N_m \theta_1(p, \epsilon_i) \chi(\epsilon_i) \epsilon_i$. Assuming that the energy of adsorption of molecules in the second and subsequent layers is constant and equal to the energy of condensation ϵ_s , we obtain the following equation

$$Q(N_a = 0) - Q(N_a) =$$

$$N_m \int (\epsilon - \epsilon_s) \theta_1(p, \epsilon) \chi(\epsilon) d\epsilon, \quad (6)$$

describing the shift in the heat of immersion with the change of amount of pre-adsorbed fluid N_a .

In Fig. 5 we compare the heats of immersion of Na/Ca montmorillonites (the systems (ii)) equilibrated with different amounts of water in adsorbed phase. The solid lines denote the results of experimental measurements by Keren and Shainberg [11,12] and the dashed lines are the results obtained via Eq. (6). The constants B_j defining the distribution functions (4) are collected in Table 1, and the energy of condensation of water at $T = 298$ K is approximately equal to 42.5 kJ/mol [11,12]).

Up to N_a equal approximately to the monolayer capacity N_m ($N_m = \exp(B_0)$), the agreement between computed and experimental curves is very good. Unfortunately, at higher values of N_a , the discrepancies between theoretically predicted and experimental curves increase rapidly. There are several reasons for such behaviour. Firstly, the local BET model used in our calculations is inaccurate at higher relative pressures p/p_s . The BET Eq. (2) predicts formation of an infinite number of adsorbed layers at the relative pressure $p/p_s=1$.

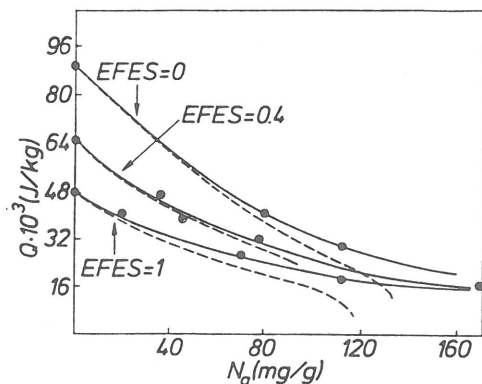


Fig. 5. Dependence of the heat of immersion (Q) on amount of pre-adsorbed water (N_a) determined from the systems (b). Solid lines and points denote the experimental results, and dashed lines were evaluated according to Eq. (6). The curves are labelled by the values of EFES.

Table 1. Energy distribution parameters for water vapour adsorbed on Ca-montmorillonite, Na-montmorillonite and montmorillonite saturated with a mixture of Ca and Na ions in the ratio 4:6

B_j	EFES=0	EFES=0.4	EFES=1
B_0	-4.624	-4.317	-3.688
B_1	-0.199	-0.0695	0.330
B_2	-0.311	-0.274	-0.220
B_3	0.0249	-0.0135	0.0954
B_4	0.0448	0.0422	0.0989
B_5	0.0119	0.0112	0.0192

Because of a finite c -spacing of montmorillonite, the BET equation fails in the region of higher relative pressures. Secondly, the surface field of the solid has been shown to influence not only the structure of the first adsorbed layer, but also the next two or three layers, which means that the energy of adsorption is not equal to ϵ_s for molecules adsorbed in these layers [1]. Moreover, our calculations of the energy distribution functions have neglected effects of mutual interactions between adsorbed molecules. It is obvious that the errors from neglecting these interactions become more significant when more molecules are adsorbed. Despite all the above inaccuracies, our results clearly demonstrate importance of heterogeneity effects in calculations of the heat of immersional wetting of soil samples.

CONCLUSIONS

The main part of this work has been devoted to evaluation of energy distribution functions from experimentally measured adsorption isotherms. We have demonstrated that such calculations can be useful in analysis of experimental adsorption data. However, the physicochemical meaning of different peaks observed on $\chi(\epsilon)$ curves may be difficult to interpret and such interpretation requires additional information about nature of active centres occurring on the surface. We also stress, that the accuracy of calculations of the energy distribution functions

depends strongly upon the accuracy of measured adsorption data.

A comparison of predicted and measured heats of immersion for adsorbents involving known amounts of pre-adsorbed water has indicated that some points of the theory presented above should be improved. In our opinion, the assumption that the local adsorption obeys the BET model, allowing for formation of an infinite number of adsorbed layers is responsible for the most of observed deviations.

REFERENCES

1. Cases J., Francois M.: Etudes des propriétés thermodynamiques de l'eau au voisinage des interfaces. *Agronomie*, 2, 931-938, 1982.
2. Cerofolini G.F.: Multilayer adsorption on heterogeneous surfaces. *J. Low Temperature Physics*, 6, 473-486, 1972.
3. Dekany I., Szanto F., Rudziński W.: Effect of surface modification on immersional wetting of organophilic kaolinite and illite derivatives. *Acta Chimica Hungarica*, 114, 283-292, 1983.
4. Hill T.L.: *An Introduction to Statistical Thermodynamics*. Mc Graw-Hill, Madison, 1964.
5. House W.A., Jaroniec M., Bräuer P., Fink P.: Surface heterogeneity effects in nitrogen adsorption on chemically modified aerosils. *Thin Solid Films*, 85, 77-86, 1981.
6. House W.A., Jaroniec M., Bräuer P., Fink P.: Surface heterogeneity effects in nitrogen adsorption on chemically modified aerosils. II: Adsorptive energy distribution functions evaluated using numerical methods. *Thin Solid Films*, 87, 323-336, 1982.
7. Jaroniec M.: Physical adsorption on heterogeneous solids. *Adv. Coll. Interface Sci.*, 18, 149-225, 1983.
8. Jaroniec M., Bräuer P.: Recent progress in determination of energetic heterogeneity of solids from adsorption data. *Surface Science Reports*, 6, 65-117, 1986.
9. Jaroniec M., Rudziński W., Sokolowski S., Smarzewski R.: Determination of energy distribution function from observed adsorption isotherms. *J. Coll. Polymer Sci.*, 253, 164-166, 1975.
10. Jaroniec M., Madey R.: *Physical Adsorption on Heterogeneous Solids*. Elsevier, Amsterdam, 1988.
11. Keren R., Shainberg I.: Water vapour isotherms and heat of immersion of Na/Ca montmorillonite system: I. Homoionic clay. *Clays and Clay Minerals*, 23, 193-200, 1979.
12. Keren R., Shainberg I.: Water vapour isotherms and heat of immersion of Na/Ca montmorillonite system: II. Mixed systems. *Clays and Clay Minerals*, 27, 145-151, 1979.
13. Koresh J., Soffer A.: Application of the two-site Langmuir isotherm to microporous adsorbents. *J. Coll. Interface Sci.*, 92, 517-520, 1983.
14. Ościk J.: *Adsorption*. Ellis Horwood Ltd., Chichester, 1982.
15. Paterson E., Stawiński J.: The use of a vacuum microbalance in the investigation of the kinetics of water vapour adsorption on soil components. *Pol. J. Soil Sci.*, 12, 105-111, 1979.
16. Rudziński W., Zajac J., Dekany I., Szanto F.: Heats of immersion in monolayer adsorption from binary liquid mixtures on heterogeneous surfaces: Equations for excess isotherms and heats of immersion corresponding to condensation approximation. *J. Coll. Interface Sci.*, 112, 473-483, 1986.
17. Sokolowska Z., Łajtar L., Patrykiewicz A., Sokolowski S.: Multilayer localized adsorption of gases on surfaces: Heats of immersion of heterogeneous solid surfaces. *Z. phys. Chem. (Leipzig)*, 270, 810-816, 1989.
18. Sokolowska Z., Sokolowski S., Ganey S., Arsova A.: Adsorption of water vapour on Eutric fluvisols as governed by energetic heterogeneity of soil samples. *Geoderma*, 52, 59-72, 1992.
19. Stawiński J., Sokolowska Z., Sokolowski S.: Adsorption de vapeur l'eau sur les constituants du sol choisis et l'hétérogénéité énergétique de leur surface. *Zesz. Prob. Post. Nauk Roln.*, 312, 375-384, 1986.
20. Zettlemoyer A.C.: Immersional wetting of solid surfaces. In: *Chemistry and Physics of Interfaces*. Am. Chem. Soc. Publ., Washington, 1969.