

ADSORPTION OF WATER VAPOR BY SOILS: INVESTIGATIONS OF THE INFLUENCE OF ORGANIC MATTER, IRON, AND ALUMINUM ON ENERGETIC HETEROGENEITY OF SOIL CLAYS

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Abstract—Water vapor adsorption isotherms were measured for samples of loessial soil clays modified by removing organic matter and Fe and Al compounds. The isotherms were analyzed by the exponential adsorption isotherm equation. The distribution functions of adsorption energy, average adsorption energies, and surface areas were evaluated simultaneously. The surface areas were the highest for samples after organic matter removal and the lowest when all considered components were removed. Values of the average adsorption energies decreased consecutively after each of the subsequent removal steps while the energy distributions became narrower, indicating in general less variety in surface adsorbing centers.

Key Words—Soil constituents, Surface heterogeneity, Water adsorption.

INTRODUCTION

Surfaces of natural adsorbents, soils and clay minerals, are highly heterogeneous. This fact is obviously connected with their complex chemical composition and the irregularities of their physical structure. Consequently, the simple models of adsorption, based upon the assumption of energetic homogeneity of all adsorbing centers, seems to be inadequate to describe adsorption processes taking place on their surfaces (Ościk, 1982).

In our previous work (Sokołowska *et al.*, 1988; Sokołowska, 1989a, 1989b, 1989c; Patrykiewicz *et al.*, 1990; Sokołowska *et al.*, 1992), we have advocated the use of isotherm equations based on the concept of energetic heterogeneity. This concept takes into account the fact that the distribution of adsorbing centers with their energy should be described by a continuous function. This function, called the energy distribution function, provides a global characteristic of energetic heterogeneity of adsorbing surfaces.

The approach we use has an additional advantage. The coefficients entering the isotherm adsorption equation, called the heterogeneity coefficients, define the energy distribution function. Thus, their evaluation by fitting the isotherm equation to the experimental data gives directly the distribution function. Its knowledge can be useful to assess significance of subsequent adsorbing centers appearing on a given surface (Sokołowska *et al.*, 1988; Sokołowska, 1989a, 1989b, 1989c;

Patrykiewicz *et al.*, 1990; Jaroniec *et al.*, 1975; Jaroniec *et al.*, 1976; Jaroniec, 1983; Jaroniec and Bräuer, 1986; Koopal and Vos, 1985; House and Jaycock, 1978; House *et al.* 1981; Cerofolini, 1972).

The main purpose of this study is to investigate the influence of organic matter and Fe and Al compounds on the energetics of the adsorption process of water vapor on soil clays.

THEORY

Because methods of evaluation of the adsorbent heterogeneity from measured adsorption isotherms have been widely discussed in the literature, we present here only a short outline of the theory (for details, see Jaroniec and Bräuer, 1986; Koopal and Vos, 1985).

The energetic heterogeneity of an adsorbing surface is characterized by the distribution function $\chi(\epsilon)$, defined in such a way that $\chi(\epsilon)d\epsilon$ gives the ratio of adsorbing centers having adsorption energies in the range $[\epsilon, \epsilon + d\epsilon]$. Provided that adsorption equilibrium at a pressure p on adsorbing sites having adsorption energy equal to ϵ is described by the local isotherm, $\theta_1(p, \epsilon)$, the overall, fractional coverage of an adsorbent, $\theta_1(p)$, is described by the following equation:

$$\theta_1(p) = N(p)/N_m = \int_{\Delta} \theta_1(p, \epsilon) \chi(\epsilon) d\epsilon. \quad (1)$$

In the above, N_m denotes the monolayer capacity, $N(p)$ is the experimentally measured total amount of adsorbed gas, and $\Delta = [\epsilon_{\min}, \epsilon_{\max}]$ is the range of possible variations of ϵ . For multilayer adsorption, the lowest value of energy of adsorption, ϵ_{\min} , is usually assumed to be equal to the energy of condensation of an adsorb-

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Table 1. Selected properties of investigated soils.

Nr	Locality	Typology	Fraction %			pH		CEC	EB	Al	OM
			Sand	Silt	Clay	H ₂ O	KCl				
1	Rogóżno	Orthic luvisol	8	80	12	6.3	5.7	21.5	17.4	0.0	2.1
2	Jabłoń	Mollic gleysol	23	64	13	6.6	5.9	19.3	13.9	0.0	3.3
3	Tarnawatka	Eutric cambisol	13	77	10	5.7	4.8	10.4	6.4	0.6	2.1
4	Machnów	Stagn. phaeozem	9	77	14	7.1	6.6	21.5	17.4	0.0	3.3
5	Rudnik	Eutric cambisol	13	73	14	5.3	4.4	9.5	7.2	0.7	1.9

Abbreviations: sand = >0.05 mm; silt = 0.05–0.002 mm; clay = <0.002 mm; CEC (pH 8.2, barium triethanolamine method), meq/100 g; EB = exchangeable bases, meq/100 g, NH₄Ac pH 5 extract; Al = exchangeable Al, meq/100 g; OM = organic matter percentage, by oxidizing with dichromate.

bate, $\epsilon_{\min} = \epsilon_c$, and the upper integration limit is considered to be infinity.

The distribution $\chi(\epsilon)$ satisfies the normalization condition

$$1 = \int_{\Delta} d\epsilon \chi(\epsilon). \quad (2)$$

The adsorption energy distributions are usually calculated by solving the integral equation of adsorption (1) in which the local adsorption isotherm is assumed *a priori*. The choice of the local model isotherm function should be guided by experimental conditions. Obviously, the shape of the computed energy distribution depends slightly upon the model utilized. In the case of multilayer adsorption, the local adsorption equilibrium has often been interpreted in terms of the classical BET model (Hill, 1964):

$$\theta_i(p, \epsilon) = \frac{1}{(1-x)} \frac{c(\epsilon)y}{[1+c(\epsilon)y]}, \quad (3)$$

where $y = x/(1-x)$, $x = p/p_s$, p_s is the saturated vapor pressure, $c = \exp[(\epsilon - \epsilon_c)/RT]$, R is the Boltzmann constant, and T is the temperature.

The solution of the integral equation (1) for the local isotherm depicted by Eq. 3 and for the energy distribution function given by the following equation:

$$\tilde{\chi}(\epsilon) = \sum_{j=1}^M j B_j E^{j-1} \exp\left\{ \sum_{j=1}^M B_j E^j \right\}, \quad (4)$$

where E is dimensionless energy, $E = (\epsilon_c - \epsilon)/RT$, $\tilde{\chi}(\epsilon)$ is dimensionless distribution, $\tilde{\chi}(\epsilon) = \chi(\epsilon)RT$, and $\{B_j\}$ are so-called heterogeneity coefficients and can be approximated by the so-called exponential total adsorption isotherm (e.g., Sokołowska, 1989a-c):

$$\theta_i(p) = \exp\left\{ \sum_{j=1}^M B_j \ln^j(y/p_0) \right\} \quad (5)$$

The mathematical flexibility of function 4 makes it possible to describe situations in which energetic heterogeneity is characterized by single and by multiple maxima, corresponding to adsorbing sites of different character.

Evaluation of the heterogeneity parameters $\{B_j\}$ is based on approximation of the experimental adsorption data by the polynomial

$$\ln[N_a(p)(1-x)] = \sum_{j=0}^M B_j n^j(y/p_s), \quad (6)$$

which can be performed by using standard non-linear regression methods (IMSL Fortran Subroutine Library, 1990). We stress that the coefficient B_0 is related to the monolayer capacity via the equation

$$N_m = \exp(-B_0). \quad (7)$$

All details of the above-mentioned numerical procedures can be found elsewhere (Jaroniec, 1983; Jaroniec and Bräuer, 1986; Sokołowska *et al.*, 1992).

EXPERIMENTAL METHODS

The experiments were carried out on Na forms of clay fractions taken from humus (0–25 cm) horizons of five different loessial soils of the Lublin Upland Region: Orthic Luvisol, Mollic Gleysol, Eutric Cambisol, Stagnogleyic Phaeozem and Eutric Cambisol. Hereafter, we refer to these as soils 1, 2, 3, 4 and 5, respectively. Table 1 contains some selected characteristics of the soils.

The clay fractions (<2 μm) were separated by a few cycles of sedimentation and siphoning from Na forms of soils. The resulting suspensions were coagulated with NaCl and the sediments were washed free of excess chlorides as indicated by a negative reaction with AgNO₃. Original Na-clays were then divided into four portions. The first portion remained unchanged. From the second, organic matter was removed by wet oxidation with H₂O₂ (Kunze, 1965). The third portion was treated to remove organic matter and then Fe compounds by the citrate-dithionite extraction procedure (Kunze, 1965), and the fourth was treated to remove organic matter, Fe, and then Al compounds. The Al compounds were dissolved by boiling the samples with NaOH (Jackson, 1965). Each modified sample was re-saturated with Na (1 N NaCl) and washed free of excess chlorides.

The contents of organic matter and extractable Fe and Al are presented in Table 2. Organic matter was

Table 2. Composition of investigated clay fractions.

Nr	OM %	Fe %	Al %	M	I	K
1	4.34	2.77	4.45	0	62	38
2	7.08	2.82	5.06	19	44	37
3	2.69	2.36	5.28	9	63	28
4	4.65	2.86	6.18	22	64	14
5	1.45	3.27	4.70	26	53	21

Abbreviations: samples numbered as in Table 1. OM %, Fe % and Al % = percentage of organic matter, Fe, and Al compounds (the latter calculated as Al_2O_3 and Fe_2O_3) for untreated clay samples. Percentage of clay minerals: M = smectites, I = illite, K = kaolinite and chlorite (mineralogical analysis was performed by E. Morgun from Institute of Soil Science and Photosynthesis, Puschino, Russia.)

determined by oxidizing with dichromate and iron and aluminum by citrate-dithionite and NaOH extractions, respectively (Fe-AAS, Al-eriochromocyanine). Table 2 also contains information about the mineralogical composition of the soil samples.

For all clays, the water vapor adsorption isotherms at $T = 298$ K were measured by using a vacuum microbalance technique. A detailed description of the apparatus used in our experiments has been given by Paterson and Stawiński (1979). During measurements, the temperature was kept constant with accuracy 0.1 K. The amount of soils used in experiments was about 100–200 mg. The time necessary for equilibration was dependent on the relative vapour pressure and at relative pressures higher than 0.3 the measurements lasted 48 hr. All adsorption measurements were replicated, usually three times. Analysis of the replicated data has indicated that the precision of measurement is about 0.8%.

The experimental adsorption isotherms were numerically approximated using the exponential adsorption isotherm (Eq. 5). The surface areas were determined from monolayer capacities (the latter from Eq.

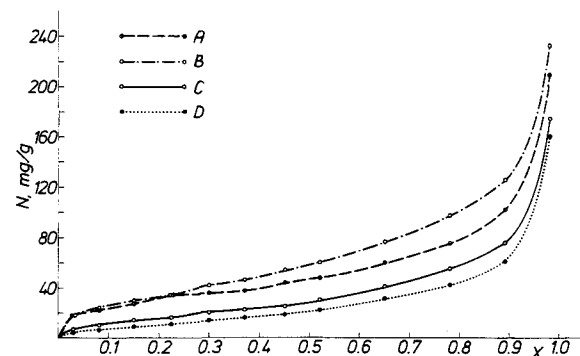


Figure 1. Adsorption isotherms of water vapour on Orthic Luvisol (sample 1) at $T = 298$ K. A = original clays; B = clays without organic matter; C = clays without organic matter and Fe; D = clays without organic matter, Fe and Al. Abbreviations for axes: N is the quantity of adsorbed water, and $x = p/p_s$ is the relative pressure.

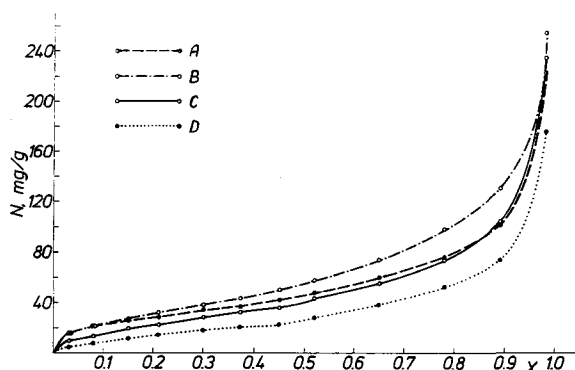


Figure 2. Adsorption isotherms of water vapour on Mollic Gleysol (sample 2) at $T = 298$ K. Abbreviations as in Figure 1.

7), assuming the area occupied by a water molecule is equal to 10.8 \AA^2 . The values of average energies of adsorption $\langle \epsilon \rangle$ were computed according to the equation:

$$\langle \epsilon \rangle = \int \chi(\epsilon) \epsilon d\epsilon, \quad (8)$$

with the energy distribution function being evaluated according to Eq. 4.

RESULTS

In Figures 1 through 5 we have displayed experimental adsorption isotherms (points), together with the results of their numerical approximation *via* the exponential isotherm Eq. 5. In general, the shape of all the isotherms is similar; however, the course of the particular curves differs among each other.

Table 3 presents the values of surface area and average energies of adsorption, computed according to Eqs. 7 and 8, respectively. The surface areas range from $43 \text{ m}^2/\text{g}$ to $111 \text{ m}^2/\text{g}$, and the adsorption energies, $\langle \epsilon \rangle - \epsilon_c$, are in the range characteristic for soils and clays (Sokołowska, 1989c), from 1.5 kcal/mol to 3.2 kcal/mol. At $T = 298$ K the value of ϵ_c equals 10.5 kcal/mol (Keren and Shainberg, 1979).

The results of calculations of the energy distribution functions are presented in Figures 6 through 10. In all

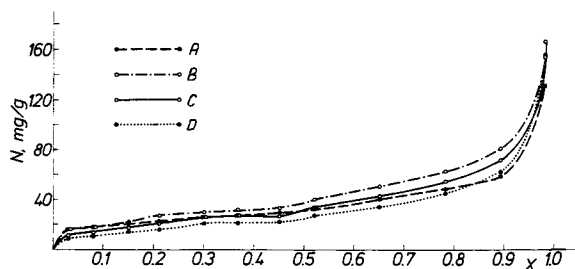


Figure 3. Adsorption isotherms of water vapour on Eutric Cambisol (sample 3) at $T = 298$ K. Abbreviations as in Figure 1.

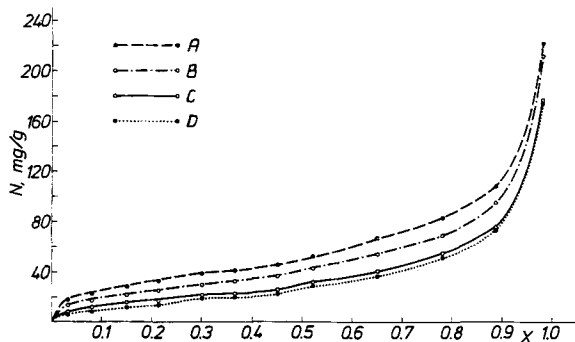


Figure 4. Adsorption isotherms of water vapour on Stagnogleyic Phaeozem (sample 4) at $T = 298$ K. Abbreviations as in Figure 1.

but one case (clay 4 with OM and Fe removed) the distributions exhibit one or two maxima of various widths and heights. If more than one maximum appears, the best developed is that with the highest energy.

Obviously, the method based on the exponential isotherm (Eq. 5) is an approximate one. The energy distributions obtained by using more refined approaches (House and Jaycock, 1978) may also show more details than the distributions computed from Eq. 4. In general, accuracy of the evaluated energy distributions is dependent on the accuracy of adsorption data and this problem was discussed by Jaroniec and Bräuer (1986) and by Sokołowska *et al.* (1992).

DISCUSSION

Despite the absence of quantitative relationships between theoretical values and the quantities characterizing soil properties, some interesting qualitative dependencies are observed. The influence of the treatment of soils on the adsorption isotherms (see Figures 1–5) was similar. Except for clay 4, the highest adsorption was observed after removal of organic matter; and, except for clay 5, the lowest adsorption occurred on

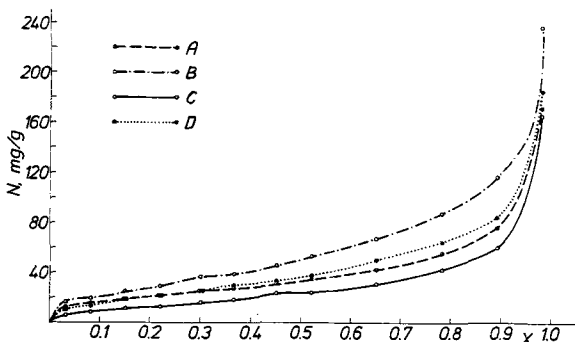


Figure 5. Adsorption isotherms of water vapour on Eutric Cambisol (sample 5) at $T = 298$ K. Abbreviations as in Figure 1.

Table 3. Surface areas and average values of adsorption energies for investigated samples of soil clays.

Soil sample	Surface area, m^2/g	$\langle \epsilon \rangle - \epsilon_0$, kcal/mole
1 A	88.4 ± 0.8	2.32 ± 0.05
1 B	111.0 ± 1.0	2.20 ± 0.05
1 C	58.0 ± 0.6	1.85 ± 0.03
1 D	43.3 ± 0.5	1.49 ± 0.03
2 A	87.2 ± 0.8	2.68 ± 0.06
2 B	106.6 ± 1.0	1.79 ± 0.04
2 C	81.0 ± 0.7	1.37 ± 0.03
2 D	53.2 ± 0.4	1.25 ± 0.02
3 A	70.5 ± 0.6	3.16 ± 0.06
3 B	74.0 ± 0.6	2.92 ± 0.06
3 C	62.4 ± 0.5	2.60 ± 0.05
3 D	51.2 ± 0.4	2.30 ± 0.05
4 A	95.7 ± 0.9	3.05 ± 0.06
4 B	76.5 ± 0.7	2.75 ± 0.05
4 C	57.3 ± 0.5	2.50 ± 0.05
4 D	54.1 ± 0.4	1.50 ± 0.03
5 A	64.8 ± 0.5	3.00 ± 0.06
5 B	96.7 ± 0.9	2.41 ± 0.05
5 C	71.6 ± 0.6	1.74 ± 0.04
5 D	46.8 ± 0.4	1.67 ± 0.03

For symbols: A, B, C and D see Figure 1.

samples obtained by removing all considered components. The same relationship, except for clay 4, holds for surface areas (Table 3).

The increase of surface area after organic matter depletion as well as the absence of its positive correlation with organic matter content is in an apparent contradiction with literature data. Some published results (Dobrzański *et al.*, 1972) suggest that the surface areas of soils are higher with higher quantities of organic matter. However, the water vapor adsorption effect

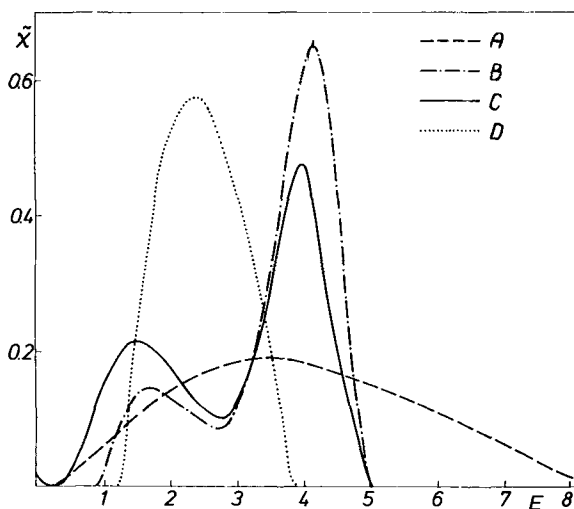


Figure 6. Energy distribution functions $\tilde{\chi}(E)$ evaluated from adsorption isotherms presented in Figure 1. Abbreviations as in Figure 1.

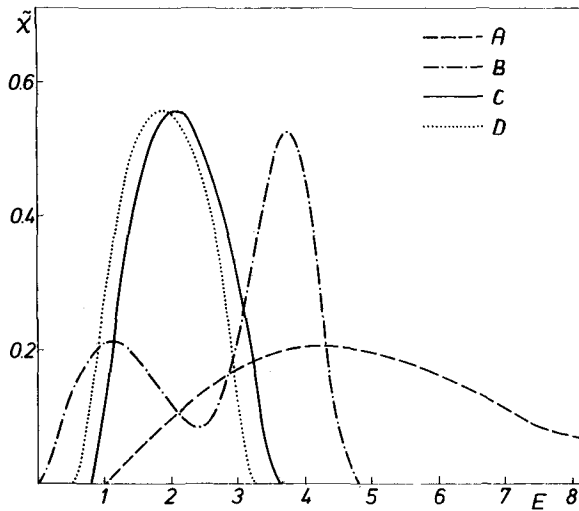


Figure 7. Energy distribution functions $\bar{\chi}(E)$ evaluated from adsorption isotherms presented in Figure 2. Abbreviations as in Figure 1.

(and also the surface area) may be attributed mainly to the presence of fulvic acids. The surface area increases if the fulvic to humic acid ratio increases too (Dobrzański, *op. cit.*). In the case of our samples fulvic acids are certainly washed out during the preparation steps. The remaining humic acids plus humines can be assumed to be bound most strongly to the mineral matrix, "gluing" the smallest surface irregularities. In addition such particles can pose even large nonpolar parts (aliphatic or aromatic chains), diminishing the surface available for water adsorption by their hydrophobic action. Thus, it is not surprising that after removal of organic matter the total surface area increases.

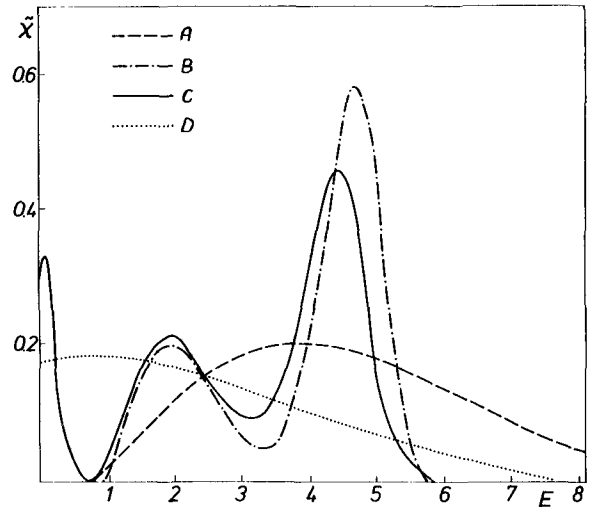


Figure 9. Energy distribution functions $\bar{\chi}(E)$ evaluated from adsorption isotherms presented in Figure 4. Abbreviations as in Figure 1.

The further decrease of the surface area after removing the Fe and Al compounds is easier to explain. When existing as separate particles, Fe and Al compounds have their own surface area. Fe and Al compounds also conglomerate the clay minerals (Brogowski *et al.*, 1979). Their removal disrupts small intergrain pores and the surface of clay minerals becomes "smoother." Consequently the surface area decreases.

The average energies of water adsorption by the original clays (Table 3) were the highest in all cases. It appears that the most energetic centers for water vapor adsorption are probably still connected with organic

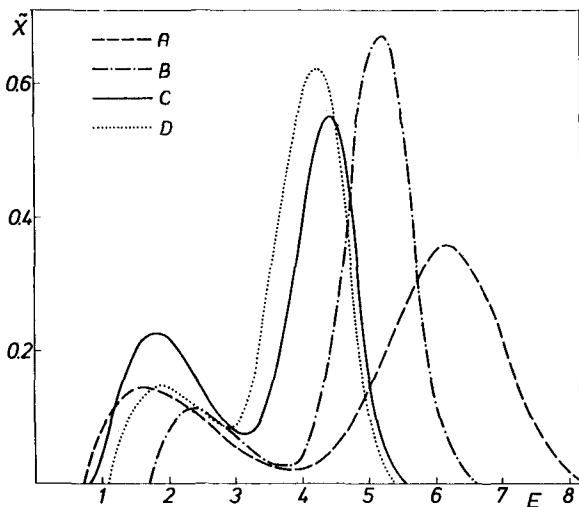


Figure 8. Energy distribution functions $\bar{\chi}(E)$ evaluated from adsorption isotherms presented in Figure 3. Abbreviations as in Figure 1.

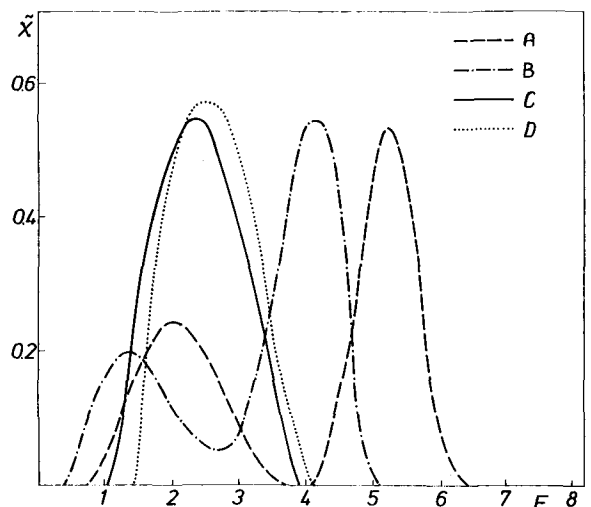


Figure 10. Energy distribution functions $\bar{\chi}(E)$ evaluated from adsorption isotherms presented in Figure 5. Abbreviations as in Figure 1.

matter and not with the mineral (even porous) network. These centers are likely to be connected with the highly polar organic functional groups (e.g., carboxyls, enols, ketones). The decrease of (ϵ) values after subsequent removal of organic matter, Fe, and Al can be attributed to the consequent disappearance of small surface irregularities.

The original clays are characterized by broad distribution functions, indicating the existence of different groups of adsorption centers of different chemical character (Figures 6–10). After removing components, the distribution function became narrower and shifted in the direction of lower adsorption energies. For three clays (soils 1, 2, and 4), the distribution functions have one broad peak shape; however, for two others (clays 3 and 5), two peaks are observed. This difference can be connected to the different composition of organic matter in these soils. In Eutric Cambisols (soils 3 and 5), organic matter is more oxidized and may have only two dominating adsorption centers. In other soils, the organic matter is less decomposed having a wider variety of functional groups, and their connections with matric chains are of more various chemical character—what gives the broadening of the energy distribution peaks. However, it is also possible that, due to the lower content of organic matter in Eutric Cambisols, the larger part of mineral surface is not covered with organic matter and it is exposed for water vapor adsorption, thus contributing more to adsorption energy distribution.

After organic matter removal the energy distribution functions have, in all cases, similar shapes. When Fe compounds are removed, further changes in energy distribution functions may be due to aluminum as well as to the clay minerals' status in soils. We could not find any correlation between mineralogical composition of investigated clays (see Table 2) and the final energy distribution. For clays 1 and 5, the final peaks coincide well with the shape of energy distribution function for pure illite (Sokołowska, 1989c), the dominant mineral in all clays studied.

The question concerning the chemical character of adsorbing sites corresponding to subsequent peaks on the $\chi(\epsilon)$ curves appears to be difficult to answer and requires additional experiments (e.g., spectroscopic measurements as in Tarasevich and Ovscharenko, 1975). Also, the physicochemical meaning of the changes in energy distribution after subsequent modification steps is difficult to interpret.

This analysis of adsorption data has concentrated on the role of energetic heterogeneity, neglecting the role of geometric irregularities of the surfaces. Due to different pedogenetical conditions, the geometrical irregularities may be different for the same minerals coming from different soils. The geometrical irregularities influence the energetic conditions and, thus, are also responsible for the shape of energy distribution functions

(Sokołowska, 1989a, 1989b). The problem concerning the influence of organic matter, Fe, and Al compounds on geometrical heterogeneity of soils (e.g., on the pore size distribution) is currently studied by the authors.

CONCLUSIONS

The presence of humic acids and humines in soils leads to diminishing of soil surface area despite the fact that the most energetic adsorption centers are connected with organic material. The subsequent removal of organic matter, Fe, and Al compounds caused the decrease of the average adsorption energy. The distribution of adsorption energy can not be directly related to soil chemical features and the presence of particular soil constituents.

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