

Assessment of the conditions for the formation of organic-mineral complexes in soils on the basis of surface properties

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A b s t r a c t. In this study the author made an attempt at the determination of the character of the surface of humus acid and clay mineral complexes, with iron and calcium acting as bonding agents, taking into account the soil pH, by means of methods based on water vapour adsorption. For the purpose, under laboratory conditions, humus acid preparations (humic acid and β -humus fulvic acid fraction) were made, at various quantitative ratios, with clay minerals (micromontmorillonite, Na-montmorillonite, kaolinite), in the presence of Fe and Ca, at pH 4 and 2.5. (i.e., at pH values close to humus acids precipitation from the solution). The nature of the surface of the preparations was characterized by means of analysis of the shapes of water vapour adsorption isotherms at 20 and 40°C, and by analyzing such physical parameters as the specific surface area and the molar energy of adsorption, those properties perfectly characterizing the surface of an organic-mineral adsorbent.

K e y w o r d s: mineral-organic complexes, humus acids, specific surface area, molar energy of adsorption, water vapour adsorption isotherms

INTRODUCTION

The problem of humus substance complexes with clay minerals remains unsolved. Investigation of the complexes in unaltered form, directly as extracted from the soil, is very difficult due to the dispersing effect of all extraction agents which usually break up the complexes and destroy their natural properties. However, in spite of the difficulties involved, such studies have been conducted. It is much easier to conduct experiments on organic-mineral complex preparations artificially obtained under laboratory conditions. Model studies in this field, conducted by various authors [9,12-14,16,21,22], confirmed the possibility of formation of clay-humus complexes in soils in two manners:

- as complexes of the external surfaces of silicates with organic humus compounds;

- as intramicellar forms of organic humus substance complexes between the crystalline grid planes of clay minerals.

Only surface bonds between humic acids and clay minerals are possible, while fulvic acids and simple organic compounds can penetrate the interpacket spaces of clay minerals. Humus compounds are sorbed on mica-type clay minerals in the presence of polyvalent metals (Fe, Ca, Al, Mg and others) [2,7,17,21,22]. The presence of montmorillonite or of clay minerals with mixed structures, capable of swelling, enables their bonding with fulvic acids of simpler structure, as well as lateral radicals of humic acids between the crystalline grid planes of those minerals [4,6-8,12,13,17,21,22].

To prove or disprove those theoretical considerations, the author made, under laboratory conditions, preparations of complexes of humus acids and minerals, at various quantitative ratios (10, 5, 2.5%), in the presence of Fe and Ca and at pH 4 and 2.5 as close to the precipitation of those preparations from the solution. The nature of the surface of the preparations under study was characterized through analysis of the shape of adsorption isotherms at 20 and 40°C, and by means of parameters calculated on the basis of the isotherms, such as the specific surface area and the molar energy of adsorption. The obtained shapes of water vapour adsorption isotherms and the varied results of specific surface area and molar energy of adsorption are due to the varied structure of clay minerals and humus acids, and to the related varied character of humus substance and clay mineral complexes.

MATERIALS AND METHODS

The material used in making the preparations was clay minerals from the USA - mica-montmorillonite, Na-montmorillonite, kaolinite, and humus acids fractions such as humic acids and b-humus fulvic acid fraction, extracted from chernozem using the Schnitzer's and Stevenson's method, as well as salts - iron sulfate and calcium chloride. Suspensions of the preparations were prepared, at a ratio of 1:10 with a solution of NaOH, and then humus acid fractions were added at varied rates, i.e., 10, 5, and 2.5%, together with iron sulfate and calcium chloride at 2.5%. The suspensions were then brought to the required pH level, i.e., 4 and 2.5 (to pH levels close to precipitation of the fractions from the solution) and shaken, stirring occasionally, then left for 24 h for re-reaction according to Mortland [14]; pH was checked and adjusted daily until equilibrium was reached, i.e., for 5 days. Next, the preparations were washed with distilled water until the chloride reaction ceased, then centrifuged and oven dried at 30°C under vacuum. In this manner ready preparations of organic-mineral complexes were obtained, with participation of iron and calcium, combinations of which are presented in Tables 1-3.

The organic-mineral preparations obtained as described above were then used for the determination of selected physico-chemical properties:

- water vapour adsorption isotherms were determined at 20 and 40°C gravimetrically (by weight), using a vacuum drier in a temperature-controlled room according to Stawiński [20];
- specific surface area was determined on the basis of the initial fragment of the water vapour adsorption isotherm at 20°C within adsorbate relative pressure range of $0 < P/P_0 < 0.35$ (on the basis of 4 measurement points) on the basis of the Brunauer, Emmett and Teller equation (BET) [1,16,20];
- the least square method and the 'loo' computer program were used to determine the BET adsorption equation parameters, i.e., the mono-layer capacity A_m and the correlation coefficient R^2 (which defines curve fitting between points). Linear shape of the BET function indicated the correctness of the analysis. The tests were performed according to the requirements of the Polish Standard No. PrPN-Z-19010-1 'Determination of specific surface area of soils' by Stawiński;
- molar energy of water vapour adsorption was determined with the help of the water vapour adsorption isotherms at 20 and 40°C for a mono-layer of every organic-mineral adsorbent studied (eg., see Fig. 1) [11,16]. The following data were necessary for the calculations:
 - values of $P_0 = f(T)$ H₂O, for the two temperatures respectively; 293 K=17.535 and 316 K=64.800;
 - absolute temperatures $1/T$ (0.00341, 0.00316);
 - values of A_m (monolayer capacity) for the organo-mineral complexes under study;

- values of P/P_0 - taken from the isotherm graphs;
- values of P and $\log P$ - calculated;
- $(\log P \text{ to } 1/T) \text{ tg } \alpha$ relation - taken from the graph.

The molar energy of adsorption for the monolayers (m) was calculated according to the formula for molar enthalpy (H^s):

$$\Delta aH_m^s = 2.3038 R_0 \text{tg } \alpha \quad (1)$$

where R_0 - gas constant = $8.3143 \cdot 10^7 \text{ erg (K mol)}^{-1}$.

Data from the calculations were compared with the value of molar enthalpy of evaporation $L = \Delta H^0_{373} = 40.72 \text{ kJ mol}^{-1}$.

The values of the molar energy of adsorption (for the monolayer) of particular fractions of organo-mineral complexes are in agreement with the theory, i.e., they are always higher than the values of molar heat of evaporation (condensation) [11,16].

RESULTS AND DISCUSSION

Investigation of the character of mineral and organic substance complexes in soils is very difficult. This results from problems of a technical nature, related to the identification of the compounds in situ, as well as with the possibility of their extraction from the soils. Therefore, when undertaking this study, the author decided to conduct model studies in the laboratory, taking into account the type of clay minerals used in the study and their varied structure, as well as the rather complex structure of humus substances. Subjecting the organic-mineral preparations, obtained in the course of the study, to physico-chemical tests, primarily surface tests, permitted the formulation of hypotheses concerning the character of the surface of such organic-mineral complexes.

Surface phenomena take place on the interphase surface of the solid-soil solution division and are subject to the effect of surface forces, mainly related to the character and structure of the dual electric layer [16]. One of the fundamental surface phenomena is adsorption, consisting in an increase in concentration at the boundary area of the system phases. Surface particles or atoms are in a different state of energy than the internal particles of the phase. That additional energy, known as the surface energy, causes a number of specific properties of the surface zone, considerably differing from the properties of the internal portions of the phase.

A basic characteristic of all adsorbents, including humus acids and organic-mineral complexes, is the isotherm of water vapour adsorption. It permits the determination of such important parameters as the specific surface area, the molar energy of adsorption, and the distribution of micropores [2,16]. Knowledge of adsorption isotherms at several different temperature levels permits the calculation of the molar energy of adsorbate adsorption. Due to the specific

Table 1. Surface properties of humus acids (humic acids and β -humus) and mica-montmorillonite complexes in the presence of Fe and Ca

Sample	S ($\text{m}^2 \text{g}^{-1}$)	A_m (g g^{-1})	R^2	E (kJ mol^{-1})
Humic acids (HA_s)	240.0	0.0700	0.9900	58.6
β -humus	319.4	0.0900	0.9990	120.7
Mica-montmorillonite	129.0	0.0356	0.9972	60.0
Mica-mont + 10% HA_s , pH4	241.0	0.0670	0.9999	70.0
Mica-mont + 10% HA_s +Fe, pH4	179.0	0.0495	0.9968	68.0
Mica-mont + 10% HA_s + Ca, pH4	164.0	0.0453	0.9964	67.0
Mica-mont + 5% HA_s , pH4	152.0	0.0421	0.9939	77.0
Mica-mont + 5% HA_s + Fe, pH4	172.0	0.0467	0.9960	63.0
Mica-mont + 5% HA_s + Ca, pH4	163.0	0.0453	0.9948	66.0
Mica-mont + 5% HA_s +5% β -humus + Fe, pH4	155.0	0.0430	0.9986	65.0
Mica-mont + 5% HA_s +5% β -humus + Ca, pH4	182.0	0.0503	0.9987	62.0
Mica-mont + 2.5% HA_s + Fe, pH4	169.0	0.0469	0.9924	48.0
Mica-mont + 2.5% HA_s + Ca, pH4	155.0	0.0430	0.9907	54.0
Mica-mont + 5% HA_s + Fe, pH 2.5	161.0	0.0450	0.9969	59.0
Mica-mont + 5% HA_s + Ca, pH 2.5	195.5	0.0541	0.9978	71.0
Mica-mont + 5% HA_s +5% β -humus, pH 2.5	142.0	0.0390	0.9978	54.7
Mica-mont + 5% HA_s +5% β -humus +Fe, pH 2.5	93.4	0.0258	0.9964	63.7
Mica-mont + 5% HA_s +5% β -humus +Ca, pH 2.5	174.8	0.0480	0.9989	55.0
Mica-mont + 2.5% HA_s , pH 2.5	173.9	0.0480	0.9935	62.2
Mica-mont + 2.5% HA_s , +Fe, pH 2.5	186.5	0.0520	0.9931	51.0
Mica-mont + 2.5% HA_s , +Ca, pH 2.5	161.4	0.0450	0.9945	63.7

HA_s - Humic acids, S - specific surface area; A_m - mono-layer capacity, R^2 - correlation coefficient, E - molar energy of adsorption for the mono-layer.

Table 2. Surface properties of humus acids (humic acids and β -humus) and kaolinite complexes in the presence of Fe and Ca

Sample	S ($\text{m}^2 \text{g}^{-1}$)	A_m (g g^{-1})	R^2	E (kJ mol^{-1})
Kaolinite	9.2	0.0027	0.9614	63.8
Kaolinite + 10% HA _s , pH 2.5	38.6	0.0106	0.9993	55.6
Kaolinite + 10% HA _s + Fe, pH 2.5	49.0	0.0135	0.9996	58.5
Kaolinite + 10% HA _s + Ca, pH 2.5	37.6	0.0104	0.9993	43.5
Kaolinite + 5% HA _s , pH 2.5	23.6	0.0065	0.9646	66.4
Kaolinite + 5% HA _s + Fe, pH 2.5	31.2	0.0086	0.9962	25.1
Kaolinite + 5% HA _s + Ca, pH 2.5	25.8	0.0070	0.9786	70.8
Kaolinite + 2.5% HA _s , pH 2.5	16.5	0.0046	0.9805	85.7
Kaolinite + 2.5% HA _s + Fe, pH 2.5	23.4	0.0065	0.9644	86.8

Explanations as in Table 1.

properties of humus acids and clay minerals, the best adsorbate for the characterization of their surface properties is water vapour [3,16,20]. Therefore, this study employs methods based on water vapour adsorption.

Considering the size of humus compound molecules, the literature of the subject [10,14,16,20,21] suggests that since fulvic acid molecules of $2\text{-}6 \cdot 10^{-9}$ m in diameter, according to Chan, apart from spherical forms have also flake forms of approximately 10^{-9} m in diameter, they can penetrate between the planes of swelling minerals into the interpacket spaces of clay minerals, while humic acids cannot penetrate the interpacket spaces but get surface-bonded with clay minerals to form complexes [4-6,9,18,19].

Subsequently to the reaction of the surface of soil clay minerals with humus substances through exposed carboxyl, phenol and amino groups belonging to aminoacids or other compounds, various types of complex clay-humus compounds can be formed [8,12,13]. The results concerning the surface properties of the organic-mineral complex preparations are presented in Tables 1-3 below.

The results of specific surface area and molar energy of adsorption indicate that for all the combinations of organic-mineral preparations there was an increase in the specific surface area due to the addition of humus acid fractions to clay minerals. The minerals themselves had much lower

values of specific surface area. Mica-montmorillonite had a specific surface area of $130.6 \text{ m}^2 \text{ g}^{-1}$, while after the addition of humus fractions the corresponding values were from 139 to $241 \text{ m}^2 \text{ g}^{-1}$. The specific surface area of Na-montmorillonite was $89.3 \text{ m}^2 \text{ g}^{-1}$, while after the addition of humus fractions it increased to $115.9\text{-}210.3 \text{ m}^2 \text{ g}^{-1}$. Likewise, the specific surface area of kaolinite was $9.5 \text{ m}^2 \text{ g}^{-1}$, while after the addition of humus fractions it increased to $16.5\text{-}49 \text{ m}^2 \text{ g}^{-1}$. This indicates a differentiated degree of clay mineral reaction with humus fractions. The differences among the specific surface area values of kaolinite and montmorillonites with the humus fractions are probably due to the different structure of those minerals, as well as to the specific and characteristic type of bonds in the complexes they form with the humus fractions. Clay minerals from the montmorillonite group, i.e., Na-montmorillonite and mica-montmorillonite are characterized by a similar type of crystalline grid structure of the type 1 to 2, and therefore their packets adsorb water vapour in a similar manner. Kaolinite, on the other hand, has a crystalline grid of the type 1 to 1, which has a considerable effect on its different adsorption of water vapour, as the kaolinite grid is rigid and does not expand when wetted. Cations and water do not permeate between the structural units forming the colloid micelles. The specific surface area of kaolinite is limited to just the

Table 3. Surface properties of humus acids (humic acids and β -humus) and Na-montmorillonite complexes in the presence of Fe and Ca

Sample	S ($\text{m}^2 \text{g}^{-1}$)	A_m (g g^{-1})	R^2	E (kJ mol^{-1})
Na-montmorillonite	89.5	0.0247	0.9964	60.5
Na-mont. + 10% HA_s , pH4	174.5	0.0483	0.9988	64.5
Na-mont. + 10% HA_s + Fe, pH4	122.2	0.0338	0.8969	64.9
Na-mont. Na + 10% HA_s + Ca, pH4	226.6	0.0627	0.9989	47.1
Na-mont. + 5% HA_s , pH4	133.0	0.0368	0.9981	76.5
Na-mont. Na + 5% HA_s + Ca, pH4	201.7	0.0559	0.9976	55.5
Na-mont. Na + 5% HA_s + 5% β -humus, pH4	175.4	0.0485	0.9988	73.8
Na-mont. Na + 5% HA_s + 5% β -humus + Fe, pH4	178.0	0.0450	0.9984	73.3
Na-mont. + 5% HA_s + 5% β -humus + Ca, pH4	210.3	0.0582	0.9981	58.9
Na-mont. + 2.5% HA_s , pH4	115.9	0.0321	0.9959	43.5
Na-mont. + 2.5% HA_s + Fe, pH4	174.4	0.0483	0.9982	66.7
Na-mont + 2.5% HA_s + Ca, pH4	184.3	0.0510	0.9975	54.7
Na-mont Na+ 10% HA_s pH 2.5	179.5	0.0497	0.9992	68.3
Na-mont Na+ 10% HA_s + Fe, pH 2.5	159.8	0.0442	0.9912	76.5
Na-mont Na + 5% HA_s pH 2.5	184.3	0.0510	0.9986	66.6
Na-mont Na+ 5% HA_s + Fe, pH 2.5	185.1	0.0512	0.9985	66.5
Na-mont Na + 5% HA_s + Ca, pH 2.5	223.6	0.619	0.9994	66.5
Na-mont Na + 2.5% HA_s , pH 2.5	197.9	0.0548	0.9997	64.8
Na-mont Na+ 2.5% HA_s , + Fe, pH 2.5	183.5	0.0508	0.9985	53.1
Na-mont Na + 2.5% HA_s , + Ca, pH 2.5	169.3	0.0469	0.9924	48.1

Explanations as in Table 1.

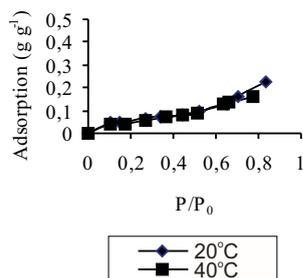


Fig. 1. Isotherms of water vapour adsorption in 20 and 40°C for mica-montmorillonite and 10% humic acids complexes in the presence of Fe, pH 4.

external part of the micelles, which is the main reason for the low sorptive capacity of kaolinite minerals [9,21]. Hence, their specific surface area as measured by means of water vapour is low, but increases when humus fractions are added. However, humus acid-kaolinite preparations are characterized by relatively lower specific surface areas when compared to similar combinations with minerals from the montmorillonite group.

Analyzing the specific surface area results presented in Tables 1-3, it was observed that increasing rate of humic acid admixture to the clay minerals (i.e., 2.5, 5, and 10% - kaolinite and montmorillonites alike) caused an increase in the specific surface area. An admixture of Fe to each of the presented combination of organic-mineral complexes with mica-montmorillonite at pH 4, and one combination with 2.5% humic acid at pH 2.5 (Table 1) caused an increase in the specific surface area as compared to the same combinations with Ca. An opposite relation was observed in the case of complexes with 5% humic acid and the combination with 5% humic acid and 5% β -humus at pH 2.5, when a greater specific surface area was displayed by combinations with Ca.

Analyzing preparations of humus acid complexes with kaolinite at pH 2.5 (Table 2) it was observed that the lower the amount of humic acid added, the lower the specific surface area (kaolinite with 10% of humic acid - $38.6 \text{ m}^2 \text{ g}^{-1}$; 5% of humic acid - $23.6 \text{ m}^2 \text{ g}^{-1}$; 2.5% of humic acid - $16.5 \text{ m}^2 \text{ g}^{-1}$). Addition of Fe to each of the combinations of organic-mineral complexes mentioned also resulted in increased specific surface area, like in the case of combinations with mica-montmorillonite.

Analysis of the results of specific surface area determinations for organic-mineral complexes with Na-montmorillonite (Table 3) showed that the greater the amount of humus acids added the greater the specific surface area. Addition of Fe to those combinations of complexes with Na-montmorillonite at pH 4 and at pH 2.5 caused a decrease in the specific surface area as compared to the same combinations with Ca.

The only exception here was the combination with Na-montmorillonite and 2.5% of humic acid at pH 2.5, where the variant with Fe had a greater specific surface area than the corresponding variant with Ca.

Analysis of the results of molar energy of adsorption for Na-montmorillonite complexes with humus fractions (Table 3) revealed that, irrespective of the pH level and of the percentage content of humic acids, there was little differentiation between combinations with humic acid only and with added Fe, while combinations with Ca showed a noticeably different tendency, with considerably lower values of the molar energy of adsorption for the mono-layer. Combinations of humus fraction complexes with mica-montmorillonite (Table 1) showed similar values of the molar energy of adsorption throughout, irrespective of the pH level, the percentage content of humic acid, and of the presence of Fe and Ca. In the case of kaolinite, insufficient number of combinations prevents the formulation of reliable conclusions, but in the case of the combination with 10% of humic acid it was observed that the addition of Ca clearly resulted in a decrease in the value of the molar energy of adsorption (Table 2).

When analyzing the shapes of water vapour adsorption isotherms at 20°C for the clay-humus complexes, attention is drawn to the fact that up to the value of P/P_0 0.7-0.73 all the isotherm curves are nearly identical; only after that value of P/P_0 is exceeded the curves diverge and certain differences can be observed (Figs 2-5). Notable differences in the shapes of the adsorption isotherms can be observed between kaolinite and montmorillonites, as well as in the case of their complexes with humus fractions. This is related to the different structure of the crystalline grid of those minerals and to the lack of expansion capability of kaolinite interpacket spaces, as well as to the easy expansion capability of the crystalline grids of montmorillonites under the effect of water.

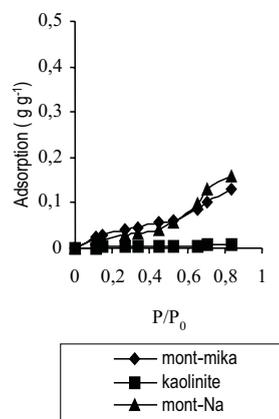


Fig. 2. Isotherms of water vapour adsorption in 20°C for mica-montmorillonite, Na-montmorillonite and kaolinite.

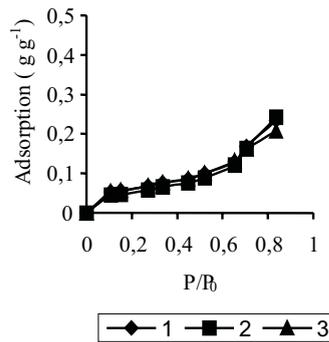


Fig. 3. Isotherms of water vapour adsorption in 20°C for: 1) mica-montmorillonite and 2.5% humus acids complexes, pH 2.5, 2) mica-montmorillonite and 2.5% humus acids complexes in the presence of Fe, pH 2.5, 3) mica-montmorillonite and 2.5% humus acids complexes in the presence of Ca, pH 2.5.

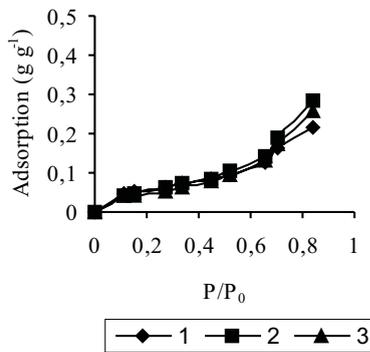


Fig. 4. Isotherms of water vapour adsorption in 20°C for: 1) Na-montmorillonite and 10% humic acids complexes, pH 2.5, 2) Na-montmorillonite and 10% humic acids complexes in the presence of Fe, pH 2.5, 3) Na-montmorillonite and 10% humic acids complexes in the presence of Ca, pH 2.5.

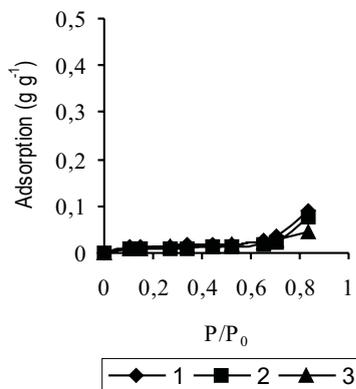


Fig. 5. Isotherms of water vapour adsorption in 20°C for: 1) kaolinite and 10% humic acids complexes, pH 2.5, 2) kaolinite and 5% humic acids complexes, pH 2.5, 3) kaolinite and 5% humic acids complexes in the presence of Fe, pH 2.5.

CONCLUSIONS

1. Addition of humus acids to clay minerals resulted in an increase in the specific surface area of all the preparations of organic-mineral complexes.

2. Differences in the specific surface area of kaolinite and montmorillonites, as well as their complexes with humus acids, are probably related to the differing structure of those minerals and to the characteristic types of their bonds. The specific surface area of kaolinite complexes with humus acids falls within the range of 16.5 to 49 m² g⁻¹, while that of montmorillonite complexes with humus acids within the range of 241 to 93.4 m² g⁻¹.

3. Increasing amounts of humus acids (2.5, 5, and 10%) added to clay minerals, i.e., kaolinite and montmorillonites, result in an increase in their specific surface area.

4. In most combinations of the organic-mineral complexes with mica-montmorillonite and with kaolinite, an admixture of Fe resulted in an increase in the specific surface area as compared to the combinations with Ca. An opposite relation was observed in the case of combinations with Na-montmorillonite.

5. In most combinations of the organic-mineral complexes an admixture of Ca resulted in a decrease in the value of the molar energy of adsorption.

6. The notable differences in the shapes of water vapour adsorption for kaolinite and montmorillonites, as well as their complexes with humus acids, are probably due to the different structures of the crystalline grids of those minerals, and therefore with their different capability to adsorb water vapour.

7. The shapes of the adsorption isotherms of the organic-mineral preparations are very similar and nearly identical up to the value of $P/P_0=0.73$; once that value is exceeded certain differences can be observed.

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