A STUDY OF THE INFLUENCE OF THE MODIFICATION OF A SOIL'S CONSTITUENT SURFACE ON ITS SORPTION AND ENERGETIC PROPERTIES

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A b s t r a c t. A synthesis of the results of a long-term investigations concerning surface free energy of soils is presented. The material included is discussed from the point of view of the influence of different factors modifying the surface of soil constituents on the dispersive and non-dispersive free energy components and on aggregation and water properties of soils. The methodical aspects of free energy measurements as well as some numerical data for minerals and soils are presented as well.

INTRODUCTION

One of the fundamental factors in the agroecology function of a soil is water management.The wettability and percolation of water through a bed of soil depend on its structure and surface properties [8,21-24]. In addition, the soil structure is closely connected with the stability of soil aggregates. The bonding of the soil's mineral constituent particles into larger aggregates occure as a result of the attractive van der Waals and the attractive or repulsive electrostatic forces, as well as from the chemical bond between the mineral and high-molecular organic compounds [25]. The magnitude of the forces acting between two particles of the soil's constituent minerals, and between the surface of these constituents and organic matter, could be predicted on the basis of the values of their surface free energies.

According to Fowkes [6], the surface free energy of a solid and liquid can be treated as the sum of several components due to dispersion interactions (London forces) - γ^d, dipole-dipole interactions - γ^p, induced dipole-dipole interactions - γ^i, hydrogen bonding - γ^h, π -bonding - γ^π, electrostatic interactions - γ^e and acceptor-donor interactions - γ^{ad} .

From the practical point of view, the surface free energy can be divided into two components-dispersion (γ^d) and nondispersion (γ^n). The dispersion component results from London's dispersion forces and, partially, from induced dipole interactions [7]. The appearing nondispersion component, however, may be the sum of several components due to specific polar intermolecular interactions [6]. Soil, with both its mineral and organic constituents, allows for a highly complex composition. Therefore, the nondispersion component of the surface free energy of a soil and its constituents results, in effect, from all the various types of specific intermolecular interactions. This results in soil with a high affinity to water. The water film adsorbed on the constituents' surfaces seem to have a strongly oriented structure, as evidenced by the higher viscosity

of water film than of bulk water [9-11]. Sometimes this leads to a solution whose soil mineral constituents form an ice-like structure within the water film in its first and second monolayers [26,28]. Properties of the water film present on the mineral constituents' surface, as well as the wettability and structure of the soil, could be predicted if one knew the surface free energy that results from the mineral and organic constituents of the soil. Thus, studies examining the components, both dispersion and nondispersion, of the surface free energy of different soil constituents were carried out. In addition, the influence of the different kinds of ionic, natural organic matter, and organic substances (which improve the soil structure) on the surface free energy and water vapour adsorption were studied.

<div align="center">METHODS, MATERIALS, RESULTS AND DISCUSION</div>

Components of the surface free energy of the mineral constituents of the soil

Determination of the dispersion and nondispersion components of the surface free energy of the soil's mineral constituents is difficult because of two principal reasons: first, their surface free energy results from almost all types of intermolecular interactions [26], and secondly, the polar liquids penetrate very easily into the bed of soil minerals, causing them to swell [25]. To minimize the possibility of error when determining the surface free energy determinations, two independent methods were used, based on the contact angle [9,13,18] and adsorption of n-alkane and water vapour [4,5] measurements. In the first method, the liquids for contact angle measurements were carefully selected. The following liquids were used: formamide, ethylene glycol, water, glycerol, diiodomethane and n-alkanes [9,13,18]. The contact angles on kaolinite, montmorillonite, bentonite, quartz, marble and aluminium oxide were measured [9,13,18]. The obtained results were analyzed on the basis of our

modifications [9,13,18] and the Girifaclo-Good-Fowkes-Kaelble-Young equation (GGFKY equation) [6,7,9,13,18,20].

The analysis proved that, by selecting a suitable pair of liquids, and by measuring the contact angles on the surface of a given mineral, it is possible to make a simultaneous determination of the dispersion and nondispersion components of the mineral surface free energy in four cases. Namely: 1) no liquid is used to form the film around its drop and, therefore, the surface free energy of the mineral does not change; 2) for the pair of liquids chosen, the film pressure for the first liquid is zero and for the second liquid is equal to the difference between the mineral surface free energy and the surface tension of the liquid; 3) the film pressure of the first liquid reduces the surface free energy of the mineral to a value equal to its surface tension, while the film pressure of the second liquid is zero; 4) the film pressure for both liquids changes the surface free energy of mineral up to the value of surface tension of the used liquid, respectively.

Using for contact angle measurements such liquids as formamide, ethylene glycol, glycerol and water with only diiodomethane can be useful for determining the surface free energy components of soil minerals [9,13,18].

The second method for determining the dispersion and nondispersion components is based on measurements of the adsorption isotherms of water and n-alkane vapours. Using the Bangham-Razouk equation, the film pressure of water and n-alkane from these isotherms has been calculated [4,5]. The main problem in using this method for determining the dispersion and nondispersion components is to conform the proper value of film pressure of adsorbed vapour of a given liquid to value of the work of proper wettability processes [4,5].

The dispersion and nondispersion components of surface free energy of kaolinite, montmorillonite, bentonite, quartz, marble and aluminium oxide were calculated, taking into account the values of the contact angles for four pairs of liquids [9,13,18]. It is assumed that the pressure of the diiodomethane film at the interface mineral-air is zero and pressure of the other liquid of a given pair decreases the value of mineral surface free energy to its surface tension. Calculated in this way, the values of the surface free energy components are close to those determined from the adsorption isotherms [4,5]. The dispersion component of the mineral constituents of the soil, calculated from the contact angles of a particular pair of liquids and from the adsorption isotherms, is evidently lower than that calculated from the contact angles measured in the system mineral-water drop-n-alkane [13]. The differences result from the presence of a stable water film on the soil mineral constituents' surface [18]. Application of the method based on the contact angle measurements for the chosen pair of liquids on the mineral surface in air, and of the method based on measurements of adsorption isotherms of water and n-alkane vapours, allow us to calculate the components of surface free energy of a mineral covered with water film [4,5,18]. However, the method based on the contact angles measurements for water drops on the surface of a given mineral immersed in two different n-alkanes allows us to calculate the dispersion component of the surface free energy of the mineral without water film [18].

This conclusion has been proved by calculations of the dispersion component of the mineral, based on the assumption that on the mineral surface the water film is present, and that the pressure of this film is equal to the work of spreading. Taking into account the values of the dispersion component, determined from the contact angles measured in the system mineral-water drop-n-alkane, and assuming that on the mineral surface there is a water film whose pressure is equal to work of spreading, the values of the dispersion component were calculated. These values are close to those determined from contact angles measured in the system mineral-liquid drop-air [9,13,18].

The total surface free energy of minerals studied (the sum of the components) is about 200 mJ/m^2, and 60-70 % of this energy results from nondispersion intermolecular interactions (dipole-dipole, induced dipole-dipole, ion-dipole of water, hydrogen bond).

However, as present in the natural environment, the water film on the mineral surface reduces value of its energy by 20 % to 40 %. The water film properties depend, among other things, on the kind of exchangeable ion. This has been proved for kaolinite and bentonite by studies examining different ions [15,17].

The values determined for the surface free energy of Me-kaolinite and Me-bentonite, both from the contact angles measured for the mineral-glycerol drop-air and mineral-diiodomethane drop-air (second case of GGFKY equation solutions) and from adsorption isotherms of water and n-alkane vapours, depend on the type of exchangeable ion. Considering, however, the particular components, it can be stated that the dispersion component does not actually depend on the type of exchangeable ion. The nondispersion component varies greatly, depending on this ion. There is an almost linear relationship between the nondispersion component and the entropy of ion hydration [15,17]. The values of the nondispersion component for K-kaolinite, K-bentonite, Ba-kaolinite and Ba-bentonite are somewhat scattered from a straight-line relationship, what can be connected with higher radii of the potassium and barium ions than for other cations studied. The nondispersion component values are connected to the adsorption capacity of the samples. There is also a straight-line relationship between the zeta potential and the entropy of ion hydration.

The values of surface free energy of the mineral constituents of soil can be decreased by adsorption of an organic compound, such as dodecylammonium hydrochloride (DDACl).
From conducted studies, the influence on energetic and sorption properties of kaolinite results that covering kaolinite surface with DDACl up to amounts corresponding to statistical monolayer causes a decrease of the dispersion component value from 39.8 for natural kaolinite to 25.4 mJ/m^2 for the sample covered with a statistical monolayer of DDACl. The non-dispersion component value, however, assumes a minimum DDACl coverage of 0.125 statistical monolayer and is equal to 15.8 mJ/m^2. For natural kaolinite, the value of the nondispersion component is equal to 23.6 mJ/m^2. Further coverage of the kaolinite surface with DDACl causes an increase of this component to a value approaching that for natural kaolinite. This may result from a reorientation of the adsorbed DDACl molecules. The decrease in kaolinite surface free energy by DDACl proves that the soil surface free energy value is lower than that for the mineral constituents of the soil because of the presence of different types of natural organic matter. This conclusion is proven by studies on the surface free energy of the soil and its changes under the influence of dodecylammonium hydrochloride (DDACl), oleic acid (OA), and Magnafloc 455.

Components of the soil surface free energy

The studies on the surface free energy of soil have been carried out through measurements of the contact angles for cis-decalin, diiodomethane, and glycerol and the adsorption isotherms for water. The values of the surface free energy components were calculated from the GGFKY equation [6,7,9,20], which was solved using the 'geometric mean' from the dispersion and nondispersion interfacial interactions approach.
From a detailed analysis of this equation, it has been assumed for the calculations that at the interface soil-air, the pressure of both

the diiodomethane and glycerol films is zero. Calculated in this way, the dispersion component of the surface free energy, e.g., for chernozem from Werbkowice, is equal to 43.3 mJ/m^2, but the nondispersion component is only 10.8 mJ/m^2 [16]. These values were verified by an analysis of the maximum pressure of the water film on the soil surface, which was calculated from the Bangham-Razouk equation using the adsorption isotherm of water [16]. The surface free energy of soil can be changed under the influence of the different types of organic compounds covering the soil surface. The dispersion component of the soil covered with DDACl, which is within a range of 0 to 6 mg/g, practically does not change, but the nondispersion component decreases from 10.8 mJ/m^2 almost to zero [16]. The coverage of the soil with OA in a range of concentration from 0 to 6 mg/g caused a slight decrease in the dispersion component to within the range of 43.3 to 40.0 mJ/m^2 and strong decrease in the nondispersion component (from 10.8 to 0.0 mJ/m^2) [12].

In the case of the soil covered with Magnafloc 455, its dispersion component does not actually change for the range of concentrations studied; simultaneously, the nondispersion component increases from 10.8 to 17.7-18.5 mJ/m^2 [10].

The prominent influence of organic matter on surface free energy of soil has been examined in studies of the adsorption of water vapour and wettability of clay fraction in soils of different origins [4,18]. The same influence has been found in instances of the clay fraction of soil from which organic, iron and aluminium compounds have been removed. It has been proven that the maximum pressure of the water film corresponds to the pressure of the water film of three statistical monolayer thicknesses.

The statistical monolayers were calculated on the assumption that the water molecule occupied an area equal to 10.8 Å^2 [27]. It was found that an increase in the concentration of the organic matter in the clay fraction

causes a linear decrease in the water film pressure. However, if the organic matter has been removed from a given sample, then a decrease in the water film pressure, contrary to expectation, is observed. This conclusion has been derived from studies on the clay fraction of the soil from various localities; Jabłoń, Machnów, Rogóźno, Tarnawatka and Rudnik. The clay fraction from Bukowina is an exception.

The water film pressure also depends on the content of the iron and aluminium compounds in the clay fraction of the soil. After removal of the organic matter from the clay fraction, an inverse relationship was found between the water film pressure and the sum of content of iron and aluminium compounds in the clay fraction.

However, there is a direct proportional relationship between the water film pressure and the aluminium content for the clay fraction in which the organic matter and iron compounds were removed. Of course, the water film pressure on surface of the clay fraction is related to the surface free energy of the clay fraction of the soil.

The surface free energy of the clay fraction and its components, both dispersion and nondispersion, were determined from contact angle values measured in these systems: clay fraction-cis-decalin-air, clay fraction-diiodomethane-air and clay fraction-water-air [18,19]. The components were determined using the GGFKY equation [6,7,9,20], in which the pressure of the cis-decalin film was assumed to be equal to the difference between the dispersion component of the clay surface free energy and the cis-decalin surface tension. However, in the use of diiodomethane and water, the pressure of their film was assumed to be equal to zero.

The dispersion component value of the surface free energy of the clay fraction of the Na-soil from Jabłoń, Machnów, Tarnawatka, Rogóźno and Rudnik lie in a range from 38.3 to 42.2 mJ/m^2, and the nondispersion component from 13.0 to 22.1 mJ/m^2. In the case of the clay fraction of Na-soil from

Bukowina, the values of the dispersion component lie in a range from 27.2 to 41.3 mJ/m^2, and the nondispersion component from 12.7 to 20.4 mJ/m^2. For the clay fraction of the Ca-soil, the dispersion and nondispersion component values ranged from 35.9 to 38.7 mJ/m^2, and from 17.3 to 25.4 mJ/m^2, respectively.

The dispersion component values of the natural clay fraction do not, in fact, depend on the content of the organic matter in the clay. However, after removal of the organic matter from the clay, changes in the values of the nondispersion component of the surface free energy are observed. After removal of the organic matter from the clay fraction, its dispersion and nondispersion components decrease linearly, with an increase in the sum of the Fe and Al content in the clays. The dispersion component of the clay fraction, after removal of the organic and iron compounds, does not depend on the content of the aluminium in the clays. However, the nondispersion component increases linearly with an increase in the aluminium content in the clays.

The influence of the surface free energy of soil on wettability, adhesion and stability of the soil aggregates

The magnitude of the surface free energy of soil influences its wettability, water adhesion to the soil surface, and the stability of the soil aggregates. The coefficient of wettability, which is equal to the difference between the work of adhesion of water to the soil surface and the work of cohesion is, besides the contact angle, the measure of the soil wettability. A decrease in the wettability coefficient proves that an increase in the hydrophobicity of the soil surface has occurred. Because the work of water cohesion is a constant value at a constant temperature, in the systems studied by us the changes in the coefficient of wettability arise only from the changes in the work of adhesion. In turn, the work of adhe-

sion is a function of the surface free energy components of the soil.

Investigation of these components have indicated that the ions and organic matter have only a minor influence on the values of the dispersion component [11,19]. Thus, changes in the water adhesion of the soil surface, as influenced by different kinds of ions and organic matter, occur as a result of the changes in the nondispersion component values of the soil surface free energy [24,25]. These facts are proven by the changes in the work of water adhesion of a soil surface that has been covered with DDACl and Magnafloc 455 in the solutions of varying concentrations [10,12,20]. The work was significantly decreased for the soil surface covered with DDACl and OA solutions in concentrations ranging from 0 to 6 mg/g. However, in the case of the soil surface covered with Magnafloc 455, the work increased.

The surface free energy of the soil determines not only its wettability and adhesion of water, but also the percolation of water through a bed of soil. It has been discovered that an almost straight line relationship occurs between the surface free energy of soil and the percolation time of water through a bed of soil [3]. The same relationship also occurs between the pressure of the water film and the surface free energy of soil, as shown, for example, for the clay fraction of the soil from which the organic, iron and aluminium compounds have been removed [11,27]. The calculated immersion and adhesion works of water to the clay surface indicate that the content in the soil of organic matter, iron, and aluminium compounds influence the values of these works and that they correspond to the water film pressure. The values of the work of immersion are close to the values of a water monolayer film pressure. The work of adhesion corresponds to the water film pressure of three statistical monolayer thicknesses.

The water film properties depend on the magnitude of the surface free energy and, among other things, they are connected with the stability of the soil aggregates. Using La-place's equation, the relationship was calculated for the attractive force between two soil particles through the water phase and the surface free energy components [2,11,27]. Next, values of this force were calculated using the dispersion and nondispersion components of the clay fraction. The increase of the organic matter content in the clay caused an increase in the attractive force. However, in the case of clay from which the organic matter and iron compounds had been removed, the force would increase linearly as the aluminium increased. Of course, it must be emphasized that the forces resulting from the surface free energy are not the only forces that determine the aggregation of the soil particles. Besides these forces, there are the repulsive forces that result from the presence of an excess electrical charge on the soil surface.

CONCLUSIONS

1. The surface free energy of soil depends upon the type of exchangeable ion and on the content of the organic matter, iron, and aluminium compounds.

2. The surface free energy of the mineral constituents of soil is considerably higher than the average surface free energy of soil. The difference results, first of all, from the nondispersion component magnitudes, which, for the mineral constituents of soil, is several times higher than for the soil itself. The reason for this is the presence on the soil surface of organic matter, iron, and aluminium compounds.

3. The type of exchangeable cation and organic compound adsorbed on the mineral constituents of the soil surface exerts a major influence on the value of the nondispersion component of the surface energy.

4. The wettability, percolation, and stability of the soil aggregates are directly related to the surface free energy of the soil. Therefore, knowledge of the components of the surface free energy of the soil may allow us to predict the affinity of water to the soil surface.

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POZNANIE WPŁYWU MODYFIKACJI POWIERZCHNI SKŁADNIKÓW GLEBOWYCH NA ICH WŁAŚCIWOŚCI SORPCYJNE I ENERGETYCZNE

Przeprowadzono syntezę dotychczasowych rezultatów badań dotyczących swobodnej energii powierzchniowej gleb. Zebrany materiał przedyskutowano pod kątem wpływu różnorodnych czynników modyfikujących powierzchnię składników glebowych na wielkości składowych despersyjnej i niedyspersyjnej energii powierzchniowej, właściwości agregacyjne oraz wodne. Przedstawiono również aspekty metodyczne pomiarów swobodnej energii powierzchniowej oraz dane liczbowe dla różnych minerałów i gleb.