CONTACT ANGLE AND SURFACE FREE ENERGY OF SELECTED PEAT-MOORSH SOILS

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A b s t r a c t. Surface free energy and contact angle for peat-moorsh soils were determined on soil samples consisted of two kinds of moorsh formations, i.e., peaty moorsh (Z_1) and proper moorsh (Z_3). The samples represented peat soil mass in different state of its secondary transformation, so they essentially differed in values of W_1 index. In study a thin-layer (TLW) technique based on Washburns equation was used. For this purpose the penetration rate of n-alkanes and diodomethane were measured. If the content of humous compounds in the soil exceeds 40%, wetting rate measurements can only be performed using apolar liquids, such as diiodomethane and alkanes. Polar liquids, on the other hand, such as water or formamide, do not penetrate porous soil layers. This shows that the tested material displays only dispersion-type surface interactions. Therefore, for "mor" and peat soils, the technique of thin-layer wicking with n-octane could only be used to determine the dispersive component . The investigated peat soil no exhibit a polar interactions because the water does not penetrate into γ_i^{LW} the sample. For the peaty-moorsh soils only dispersive surface free energy components can be determined by the technique of thin-column wicking (TCW). Contact angles can be calculated from the determined dispersive surface free energy components and water surface tension by Young equation. Ranges of water contact angles for peat-moorsh soils are $97.5^o < \theta < 102.0^o$.

K e y w o r d s: surface free energy, contact angle, wettability, peat-moorsh soils.

INTRODUCTION

The phenomena and processes occurring at the solid-gas and solid-liquid interfaces of the soil system differ from phenomena taking place in the bulk phases in that they are subjected to the effect of surface forces. Without an analysis of the essence of the surface phenomena, it is virtually impossible to comprehend and control, on a macro scale, the physicochemical processes taking place in the soil. For example the processes of soil water transport, observed at the field scale, reflect the hydrophilicity of the particles of the soil solid phase, water vapour adsorption, swelling

of clay minerals and organic matter, hydration of surface cations, value of the surface free energy, micro-porosity, etc.

Non-wettability of soils, and especially peats, has been a known fact for a hundred years. Probably one of the first attempts at a scientific explanation of the phenomenon was the analysis by Stelwaag [14]. Later, Ramann [12], and Stadnikov [13] included it in their books, and a number of authors wrote dedicated papers [6,15]. Wladyschenskij [17], Dragunov [5] and Tschapek [16] showed that humous substances are hydrophobic.

In 1972, Busetti and Tschapek [1] arrived at the conclusion that on the surface of humus water was less "organised" than on the surface of montmorillonite. According to those authors, the total entropy ÄS of water adsorption is negative, while in the case of humus it is positive. In the first case entropy increases with increasing adsorption, while in the second case entropy decreases with increasing adsorption.

The literature referenced above permits the conclusion that the principal causes of the weak wettability of soils are as follows:
a) hydrophobic organic substances of plant and animal origin (waxes, chitin, etc.),
b) hydrophobic organic substances formed *in situ* in the course of soil formation (derivatives of aliphatic and aromatic compounds),
c) hydrophobic inorganic substances formed *in situ* in the course of soil formation (sulfides).

One of the more significant components of soil organic substance is humic acid containing phenol groups. Groups -CH, -CH$_2$, -CH$_3$ occurring in the acid, are hydrophobic, causing soil hydrophobicity and flotability, while the polar groups OH and COOH are hydrophilic, increasing soil hydrophilicity.

THEORY

On the surface of a solid, a liquid can spread more or less easily, which is related to the intermolecular forces of the solid and the liquid. If the interactions of the liquid molecules with the solid are stronger than within the liquid, the liquid will spread on the solid surface. In such a case we say that the liquid wets the solid surface, and the process is called spreading. If, on the other hand, liquid molecules are less attracted by the solid molecules (i.e., there is a strong interaction among the liquid molecules), the liquid will not wet the solid surface and its drop will not spread on the solid surface.

Then, a measure of the solid surface wetting can be angle θ (Fig. 1), formed by the tangent to the liquid surface (*j*) and the solid surface (*i*) at the point of contact

between the phases (at the interface). The angle, called the contact angle or the wetting angle, characterises the interaction between the liquid and the solid surface. The value of the adhesion energy (a phenomenon consisting in the joining of the surfaces of two different bodies) of a liquid to a solid can be determined on the basis of measurement of the wetting angle θ and the value of the surface tension of the wetting liquid (γ_j). The balance of the surface forces (wettability) at the solid-liquid interface is described by a Young equation:

$$\gamma_i = \gamma_{ij} + \gamma_j \cos\theta \qquad (1)$$

where: γ_i- is the surface free energy of the solid, γ_j- is the surface tension (surface free energy) of the liquid, and γ_{ij} - is the interface free energy.

The wetting angle is a very important value characterising the interactions at the solid-liquid interface, and it is still considered by many authors to be one of the fundamental parameters in the determination of the wettability of solids.

Such phenomena as aggregation of particles, adhesion, and wettability of soils by liquids, are directly related to the presence of surface free energy. In the case of soils, the most important issue is their good wettability, and therefore easy penetration of water into the deeper layers. The process is determined by the energy level of interfacial interactions.

The theory of surface thermodynamics can be used to describe interfacial interactions between solids, and thus provide the basis for a quantitative description of hydrophobicity and hydrophilicity by means of the interfacial free energy resulting from the presence of interactions among particles in the water medium. Such a definition may reveal which of the properties of the solid and the liquid medium are responsible for the interfacial interactions. That value, γ_i, equals the energy (work) required to create 1 cm^2 of new surface, and therefore is expressed in J m^{-2}.

The value of the surface free energy γ_i depends on the kind of forces acting on the surface of the solid, i.e., on the chemical character of the solid. On the surface of a solid there are always dispersion forces of the London type (*d*), and, depending on the chemical character of the surface, there may be dipole-dipole polar-type forces (*p*), dipole-induced dipole induction-type forces (*i*), hydrogen bond forces (*h*), π type bond forces, acceptor-donor forces (*ad*), and electrostatic forces (*e*).

According to Fowkes [7,8], the surface energy can be expressed as a sum of surface tensions originating from the effect of the particular forces:

$$\gamma = \gamma^d + \gamma^p + \gamma^i + \gamma^h + \gamma^\pi + \gamma^e + \gamma^{ad} \qquad (2)$$

In 1987-1991, van Oss *et al.* [acc. 10] presented a quantitative consideration of hydrogen bond in the interfacial interactions. The model constitutes a modern concept of presentation of surface tension and surface free energy as a sum of two components: γ^{LW} (Lifshitz-van der Waals) and γ^{AB} (Lewis acidic-basic).

$$\gamma_i = \gamma_i^{LW} + \gamma_i^{AB}. \tag{3}$$

This model correctly describes primarily those systems where a solid borders on a water medium, where significant adhesive interactions, apart from the dispersive interactions, are hydrogen bond interactions and, more generally, electron-donor and electron-acceptor interactions.

All solids show LW type interactions (γ_i^{LW} 0). The AB component of surface free energy, on the other hand, determines the acidic-basic activity of a material. Two parameters of interactions are distinguished here: the electron-acceptor (Lewis acid) γ_i^+ - and the electron-donor (Lewis base) - γ_i^- .

The LW interfacial free energy results from the individual surface free energies of the solid and the liquid:

$$\gamma_{ij}^{LW} = \left(\sqrt{\gamma_i^{LW}} - \sqrt{\gamma_j^{LW}} \right)^2. \tag{4}$$

On the other hand, the AB acidic-basic component is related to the components of the surface free energy by the equation:

$$\gamma_{ij}^{AB} = 2\left(\sqrt{\gamma_i^+ \gamma_i^-} + \sqrt{\gamma_j^+ \gamma_j^-} - \sqrt{\gamma_i^+ \gamma_j^-} - \sqrt{\gamma_j^+ \gamma_i^-} \right). \tag{5}$$

Substituting Eqs(4,5) to Eq.(3) we get:

$$\gamma_{ij} = \left(\sqrt{\gamma_i^{LW} \gamma_j^{LW}} \right)^2 + 2\left(\sqrt{\gamma_i^+ \gamma_i^-} + \sqrt{\gamma_j^+ \gamma_j^-} - \sqrt{\gamma_i^+ \gamma_j^-} - \sqrt{\gamma_j^+ \gamma_i^-} \right). \tag{6}$$

By introducing the Eq.(6) into the Young Eq.(1), describing the balance of the surface and interfacial free energy in the solid-liquid-gas system, where γ_j is the liquid surface tension, γ_{ij} is the interfacial free energy at the solid-liquid interface, γ_t - is the surface free energy of the solid, π is the pressure of liquid film outside of a drop set on a solid surface, we get the relation:

$$(1 + \cos\theta)\gamma_j + \pi = 2\left(\sqrt{\gamma_i^{LW} \gamma_j^{LW}} + \sqrt{\gamma_i^+ \gamma_j^-} + \sqrt{\gamma_i^- \gamma_j^+} \right) \tag{7}$$

Assuming that $\pi = 0$, and that the surface and interfacial tension is numerically equal to the surface free energy, and basing on measurements of the wetting angle of three different liquids on a solid surface, we can use Eq.(7) to determine the Lifshitz-van der Waals component, as well as the electron-donor and electron-acceptor parameters of the surface free energy.

A graphic representation of the equilibrium of forces at the solid-liquid interface is given in Fig. 1.
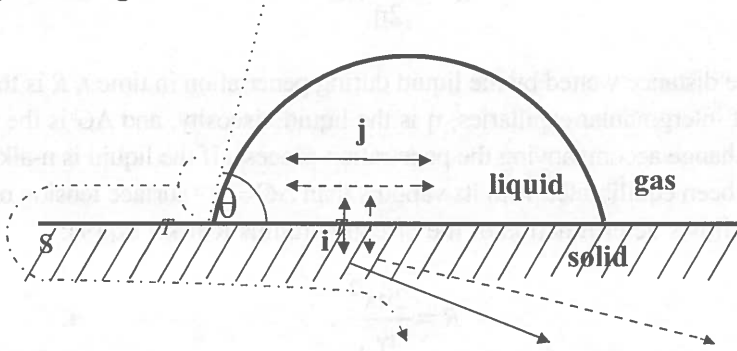
$$(1 + \cos\theta)\gamma_j^{ToT} = -\Delta G_{ij}^{ToT} = -\Delta G_{ij}^{LW} - \Delta G_{ij}^{AB}$$

$$(1 + \cos\theta)\gamma_j^{ToT} = 2\left(\sqrt{\gamma_i^{LW}\gamma_j^{LW}} + \sqrt{\gamma_i^+\gamma_j^-} + \sqrt{\gamma_i^-\gamma_j^+}\right)$$

Fig. 1. Wetting angle (θ) as equilibrium of forces. Cosine of θ is a measure of balance between the energies of liquid particles cohesion (*j*) (horizontal arrows, left side of the equation) and the forces of liquid-solid adhesion (*i*) (vertical arrows, right side of the equation) TOT is total. Apolar energies are shown by means of solid vertical or horizontal arrows, while polar energies are indicated as broken line arrows, vertical or horizontal (adapted from [12]).

The "thin-layer wicking" or "thin-column" wicking method for the determination of the surface free energy and its components

For low-energy solids the method most frequently used for the determination of the components of the surface energy is a method based on the Young Eq.(1) and on wetting angle measurements.

For some solids, the measurement of the wetting angle is difficult. This is due to the necessity of obtaining a smooth surface of the solid. These difficulties led to the introduction of the thin-layer wicking method (TLW) [2,4], proposed by van Oss [17] for determination of the surface free energy components. A modification of the TLW method is the liquid penetration in a column of powder placed in a

glass tube (thin-column wicking (TCW)). The latter method proved especially suitable for the study of soils [11].

For the calculation of the surface free energy components the Washburn equation is used, as it relates the liquid penetration rate with changes in the free energy, accompanying the process of penetration [2]:

$$x^2 = \frac{Rt}{2\eta}\Delta G \qquad (8)$$

where x is the distance wetted by the liquid during penetration in time t, R is the effective radius of intergranular capillaries, η is the liquid viscosity, and ΔG is the specific free energy change accompanying the penetration process. If the liquid is n-alkane and the solid has been equilibrated with its vapours than $\Delta G = \gamma_j$ - surface tension of the alkane which allows determination of the effective radius R from Eq.(9):

$$R = \frac{2\eta x^2}{t\gamma_j} . \qquad (9)$$

Having determined the value of R, we can use Eq.(8) to determine the dispersive component of the surface free energy (Lifshitz-van der Waals γ_i^{LW}):

$$\gamma_i^{LW} = \frac{\eta^2 x^4}{R^2 t^2 \gamma_j} + \frac{2\eta x^2}{Rt} + \gamma_j . \qquad (10)$$

The method consists in measuring the rate of liquid penetration within a thin layer of a solid granulometric fraction (mineral or soil), placed on a glass plate or in a glass tube. For the measurements, one should use a number of liquids of well-known parameters, such as viscosity, surface tension and its components (for details see [3]).

MATERIAL AND METHOD

The investigated four soil materials (T10, T12, T5, T13) represent two kinds of moorsh formations: the peaty moorsh and the proper moorsh. They are also characterizing by the secondary transformation index W_1 [9]. The soil samples were taken from the Polesie Lubelskie and from the Biebrza River Valley.

The tests were conducted in horizontal thin-layer liquid chromatography teflon chambers, adapted for plates or tubes.

The measurements were conducted in two stages. First, n-alkanes were used to wet a series of plates previously saturated with their vapours. The liquid penetration

rate ($\Delta x^2 = f(\Delta t)$) was the base to calculating the effective radius of pores (R), using Eq.(9). In all the cases, the mean time from ten measurements was taken into consideration in all calculations. Next, having determined the R values, Eq.(10) can be used to calculate the dispersive component (γ_i^{LW}), using the results of the function $x^2 = f(t)$ for plates dried at 105 $^{\circ}$C (which had no contact with n-alkane vapour) and for plates wetted with n-alcanes. An example of the relation of x^2 to t for peat sample No. T10 wetted with n-dodecane is presented in Fig. 2.

To verify the data obtained by means of n-alkanes, wetting experiments were also conducted using diiodomethane as the penetrating liquid, on dry plates and on the plates saturated with its vapour.
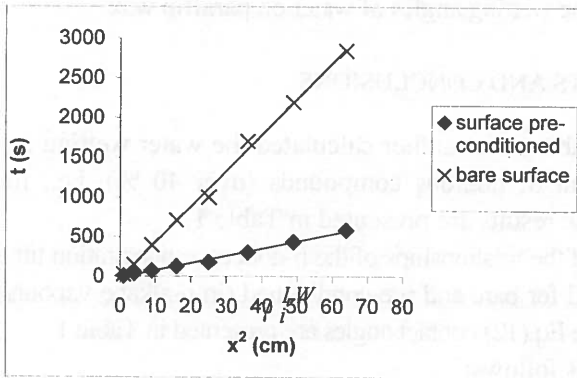
To determine the polar components of a solid water and formamide were used, as liquids with high polarity, whose surface free energy components are known. Using Eq.(7), is possible to calculate the polar components γ_i^+ and γ_i^-. All the measurements were conducted at a temperature of 20 $^{\circ}$C.

Fig. 2. Penetration time of the peat-moorsh soil (T12) by n-dodecane against distance obtained by TCW method for the bare and pre-conditioned surfaces.

If the content of humous compounds in the soil exceeds 40 %, wetting rate measurements can only be performed using apolar liquids, such as diiodomethane and alkanes. Polar liquids, on the other hand, such as water or formamide, do not penetrate porous soil layers. This shows that the tested material displays only dispersion-type surface interactions. Therefore, for "mor" and peat soils, the technique of thin-layer wicking with n-octane could only be used to determine the dispersive component γ_i^{LW}.

On the basis of numerous data concerning wetting angle measurements, Fowkes [7] arrived at the conclusion that for solid-liquid systems with practically only dispersive interactions, the parameter γ_{ij} occurring in Young equation can be determined by means of the geometric mean of dispersive components of the surface free energy of the liquid and the solid, which, as a consequence, leads to the relation:

$$\gamma_j \cos\theta = -\gamma_j + 2\sqrt{\gamma_i^{LW}\gamma_j^{LW}} - \pi . \tag{11}$$

Assuming that for $\gamma_j \geq \gamma_i$, $\pi \approx 0$ we get:

$$\cos\theta = -1 + 2\sqrt{\gamma_i^{LW}}\left(\frac{\sqrt{\gamma_j^{LW}}}{\gamma_j}\right). \qquad (12)$$

If we substitute in Eq.(12) the value of the dispersive component for the solid, γ_i^{LW} determined from the rate of wetting with n-alkane, and the value of surface tension of water γ_j and its dispersive component γ_i^{LW}, we can calculate the expected wetting angle for water. That exactly was the manner in which Fowkes [8], using the Zisman method [18], determined the wetting angles of water on paraffin wax.

RESULTS AND CONCLUSIONS

Using the method described above, the author calculated the water wetting angles for soils with a high content of humous compounds (over 40 %), i.e., for "mor" type soils and for peats. The results are presented in Table 1.

Figure 2 presents an example of the relationships of the n-dodecane penetration time against distance of wetting obtained for bare and pre-conditioned (in n-alkane vapours) moorsh surface. Calculated from the Eq.(12) contact angles are presented in Table 1.

In conclusions one can state as follows:

1. The investigated peat-moorsh soils no exhibit polar interactions because the water does not penetrate into the sample. For these soils only dispersive surface free energy components can be determined by the technique of TCW (thin layer technique).

2. Contact angles can be calculated from the determined dispersive surface free energy components and water surface tension by Young equation.

3. Ranges of water contact angles for peat-moorsh soils are $97.5^o < \theta < 102.0^o$

T a b l e 1. Physico-chemical properties of the surface of soils studied

Sample No.	Kind of moorsh	R (cm)	γ_i^{LW} (mJm^{-2})	(mJm^{-2})	(mJ m^{-2})	θ_y (^{o})	W_l	S_{H2O} (m^{2}g^{-1})
T10	proper moorsh	1.780E-04	38.13	-	-	102.00	0.60	294.7
T12	peaty moorsh	1.570E-04	42.90	-	-	99.21	0.44	248.4
T5	proper moorsh	1.300E-04	38.30	-	-	101.92	0.82	192.7
T13	peaty moorsh	6.150E-05	45.95	-	-	97.53	0.61	345.4

Explanations: R-effective radius of intergranular capillaries; γ_i^{LW} - dispersive component of the solid surface free energy; θ_y wetting angle calculated from the Young equation; W_l index of peat secondary transformation acc. to Gawlik [9]; S_{H2O} - specific surface area determined from water vapour adsorption.

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