

ADHESION OF HUMIC ACIDS TO NONREACTIVE SURFACES: EFFECT ON SURFACE FREE ENERGY AND WETTABILITY OF GLASS

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A b s t r a c t. Contact angles of glycerol and diiodo-methane were measured on glass surface covered by different amounts of humic acids, extracted from a sandy forest soil. The surface coverages with humic acids, surface free energy components and wettabilities of the obtained mixed surfaces were calculated from contact angle values. The dispersion component of the surface free energy increased and the nondispersion one decreased tending to the values for pure humic acids, what was connected with surface coverage increase. The wettability coefficient decreased with humic acids content increase showing hydrophobic action of humic acids.

K e y w o r d s: humic acids, surface free energy, contact angle

INTRODUCTION

Organo-mineral interactions are recently under an increasing interest of many workers. One of the way for investigation of such systems is the surface free energy approach, which has been successfully applied for a qualitative description of some surface and interfacial properties: wettability, floatability, adhesion, interparticle attraction, aggregate stability etc. of polymers, minerals, soils or soil organic matter [1,2,7,10,13,16]. However, most of reports concern organo-mineral systems involve well defined organic compounds and their interactions with the reactive surfaces of soils or minerals [8,9,11,12]. And so we wanted to study the surface free energy (SFE) of the systems containing naturally occurring organic materials on nonreactive surfaces.

THEORY

In the case of composite surfaces, a contact angle of liquid on such a surface, θ_L , is a function of the relative inputs of the surfaces of different natures to the total (composite) surface [12];

$$\cos \theta_L = \sigma_1 \cos \theta_{L,1} + \sigma_2 \cos \theta_{L,2}, \quad (1)$$

where:

$$\sigma_1 + \sigma_2 = 1 \quad (2)$$

and σ_1 and σ_2 are the parts of the surfaces of nature 1 and 2 and $\theta_{L,1}$ and $\theta_{L,2}$ are the liquid contact angles on surfaces 1 and 2, respectively.

The contact angle θ_L , between a surface of solid (S) and a drop of a liquid (L) is a result of the equilibrium of the respective surface free energies (surface tensions), γ :

$$\gamma_S - \Pi_L = \gamma_L \cos \theta_L + \gamma_{SL}, \quad (3)$$

where Π_L is a two-dimensional pressure of an eventually present liquid film, diminishing the SFE of the solid.

According to the Young-Girifalco-Good-Kaelble-Fowkes approach [8,10], the solid-liquid SFE, γ_{SL} , may be expressed by geometric means of dispersive, γ^d , and non-dispersive, γ^n , components of solid and liquid surface

free energies:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\left(\gamma_S^d \gamma_L^d\right) - 2\left(\gamma_S^n \gamma_L^n\right). \quad (4)$$

Combining Eqs (1) and (2) one obtains:

$$\gamma_L (\cos \theta_L + 1) = 2\left(\gamma_S^d \gamma_L^d\right)^{1/2} + 2\left(\gamma_S^n \gamma_L^n\right)^{1/2} - \Pi_L \quad (5)$$

The work of adhesion of water to a solid surface, W_A , is [5]:

$$W_A = \gamma_S + \gamma_L - \gamma_{SL}, \quad (7)$$

and it can be expressed as a function of dispersion and nondispersion components of surface free energy of solid and water as [8]:

$$W_A = 2\left(\gamma_S^d \gamma_W^d\right)^{1/2} + 2\left(\gamma_S^n \gamma_W^n\right)^{1/2} \quad (8)$$

The wettability of the solid surface by water can be predicted using the wetting coefficient, S_S , [5]:

$$S_S = W_A - W_C, \quad (9)$$

where $W_C = 2\gamma_W$ is the work of cohesion.

MATERIALS AND METHODS

Humic acids (HA) were extracted with water from an acidic sandy forest soil (<1 % clay content, 1.37 % organic carbon). Prior to the extraction the soil was adjusted to pH 3 with HCl (1 week) and changed into homoionic sodium form by triple equilibration with N NaCl. HA extracts were filtered by G4 glass bed, coagulated with HCl and washed with distilled water by centrifuging until a brownish color appeared in the supernatant. Next the HA were peptized in the excess of water with ultrasounds and after a final G4 filtering the stock suspension of HA concentration $c_0 = 8 \text{ gdm}^{-3}$ was obtained.

Microscopic glass slides of 2.5x4cm were cleaned with methanol-NaOH solution, rinsed with water and dried, and next they were

covered with humic acids attempting to prepare as uniform HA layer as possible. The best way we found was as following: One drop ($1/40 \text{ cm}^3$) of the HA suspension of a given concentration was placed upon a slide and spreaded on its surface with a glass rod in a water vapor saturated chamber. When taking a slide out of the chamber, water has evaporated instantaneously from its surface leaving a HA layer. For $c = 2c_0$ coverage, an additional slide was coated twice with $c = c_0$ HA suspension.

Wetting (advancing) contact angles of glycerol and diiodometane were measured on minerals-HA pellets and glass slides by the sessile drop method [14] at $20 \pm 0.1^\circ\text{C}$, using telescope goniometer system, in at least 30 replicates. Before contact angles measurements the glass slides were dried for 24 h over a mixture of 4A and 5A molecular sieves (1Pa).

We additionally tested whether the glass surface adsorbs humic acids. The glass plates were milled and from the resulting powder the $< 2\mu\text{m}$ fraction was separated. The suspensions of HA of different concentration of humic acids was measured colorimetrically in the supernatants. Zero adsorption of HA was detected.

It is important to note that the HA adhesion to glass surface was so strong, that after drying, the HA present on glass slides did not peptize after a few weeks immersion in water.

RESULTS AND DISCUSSION

The average values of contact angles for glycerol (θ_G), and diiodometane (θ_D) on glass surface in relation to HA content are presented in Table 1.

Following the HA content increase, the values of contact angles for polar glycerol increase and for nonpolar diiodometane decrease, indicating the increase of surface hydrophobicity with the increase of HA content, tending to reach the respective (limiting) values for pure HA. The evident changes of the contact angle values start from the initial $c = 1/512 c_0$ (at least for glycerol) and finish at $c = 1/2 c_0$. In the case of diiodomethane, the contact angles

for HA covered slides are higher than for pure glass up to $c=1/16 c_0$, indicating the higher polarity of the mixed surface. Glycerol, however, indicates the drop of the mixed surface polarity just from the beginning of HA additions.

Introducing either glycerol or diiodomethane contact angle values to the set of Eqs (1) and (2) and taking: $\theta_{G1}=44.3^\circ$ and $\theta_{D1}=32.1^\circ$ for pure HA; $\theta_{G2}=26.5$ and $\theta_{D2}=43.4$ for glass we calculated the HA coverage (σ_1) for the studied surfaces. The obtained values are presented in Table 2.

It can be seen that the surface coverage increases slowly to about $1/16c_0$ and more rapidly between $1/16$ to $1/2c_0$, where it reaches the constant value.

Knowing the values of the surface coverage we calculated the apparent quantities of monomolecular HA layers present in surface coating in the way presented below.

We assumed the bulk density of HA, d_{HA} , equal to 1.3 g cm^{-3} and its molecular weight, MW, equal to 1500 g mol^{-1} then assuming the cubic shape of HA molecule we calculated the

apparent thickness of the single HA molecule equal to $1.24 \cdot 10^{-7} \text{ cm}$. Then we calculated the apparent thickness of HA surface coating, t_{HA} :

$$t_{HA} = \nu c / (d_{HA} S \sigma_1), \quad (10)$$

where ν is the volume of HA suspension added to the sample (1/40 ml); c is the concentration of the suspension; S is the surface area of the sample (10 cm^2); and σ_1 is the HA surface coverage at concentration c .

Now when t_{HA} is divided by the apparent thickness of HA molecule, the apparent quantity of monomolecular HA layers present in HA coating is obtained. These values are presented in Table 3.

It can be seen that the thickness of HA coatings is very high (more than few molecules) in the whole range of HA content what together with the low surface coverages at low HA additions certifies that HA do not react with the glass surface.

On the basis of measured contact angle values and the Eq. 5 (the set of two equations for the liquids $L=G$ (glycerol) or $L=D$

Table 1. Values of diiodomethane (θ_D) and glycerol (θ_G) contact angles at different HA additions (c/c_0) $G = \text{pure glass}$

c/c_0	G	$\frac{1}{512}$	$\frac{1}{256}$	$\frac{1}{128}$	$\frac{1}{64}$	$\frac{1}{32}$	$\frac{1}{16}$	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{1}{2}$	1	2
θ_D	43.4	45.9	43.9	45.0	42.7	43.0	44.1	38.8	36.2	33.8	33.9	33.2
θ_G	26.5	27.4	28.0	28.9	30.0	31.3	32.2	34.4	40.3	42.8	43.2	43.5

Table 2. Values of surface coverages calculated from θ_D (σ_{1D}) and θ_G (σ_{1G}) at different HA additions (c/c_0)

c/c_0	$\frac{1}{512}$	$\frac{1}{256}$	$\frac{1}{128}$	$\frac{1}{64}$	$\frac{1}{32}$	$\frac{1}{16}$	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{1}{2}$	1	2
θ_D	-	-	-	-	-	-	0.44	0.67	0.87	0.86	0.91
θ_G	0.04	0.07	0.11	0.16	0.23	0.27	0.39	0.74	0.90	0.93	0.95

Table 3. Values of the apparent quantities of HA layers in HA surface coating (M_{HA}) at different HA additions (c/c_0). Average from diiodomethane and glycerol data

c/c_0	$\frac{1}{512}$	$\frac{1}{256}$	$\frac{1}{128}$	$\frac{1}{64}$	$\frac{1}{32}$	$\frac{1}{16}$	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{1}{2}$	1	2
M_{HA}	6	7	9	12	17	29	37	44	70	138	267

(diiodometane), we calculated the dispersion, γ_S^d , and the nondispersion, γ_S^n , components of the surface free energy of glass surface at different HA contents. Following the theoretical analysis of Jańczuk *et al.* [8] we assumed $\Pi_G = \Pi_D = 0$. The values of dispersion and nondispersion components of the liquids used, γ_L^d , and γ_L^n (L=G or D) were taken from Good and Elbing [4] and Jańczuk and Białopiotrowicz [6].

The dependencies of the dispersion and

CONCLUSIONS

Humic acids adhere to glass surface non uniformly - possibly as islands of a high thicknesses, what was indicated by high values of HA coatings thicknesses at very low surface coverages.

The hydrophobic action of humic acids begins significant at rather high surface coverages (more than 0.4) and it is due in a greater extent to the lowering of the nondispersive component of the mixed surface than to the rise of its dispersive component.

Table 4. Dispersive (γ^d) and nondispersive (γ^n) components of surface free energy at different HA contents (c/c_0)

c/c_0	G	$\frac{1}{512}$	$\frac{1}{256}$	$\frac{1}{128}$	$\frac{1}{64}$	$\frac{1}{32}$	$\frac{1}{16}$	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{1}{2}$	1	2
γ^d (mJ m^{-2})	32.8	31.5	32.6	32.0	33.3	33.2	32.6	35.5	37.0	38.3	38.3	38.7
γ^n (mJ m^{-2})	272.	27.7	26.7	26.7	25.5	25.0	24.9	22.3	18.7	17.0	16.8	16.5

Table 5. Wetting coefficients (S_s) vs. HA addition (c/c_0)

c/c_0	G	$\frac{1}{512}$	$\frac{1}{256}$	$\frac{1}{128}$	$\frac{1}{64}$	$\frac{1}{32}$	$\frac{1}{16}$	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{1}{2}$	1	2
$-S_s$ (mJ m^{-2})	17.6	18.0	18.5	19.0	19.6	20.4	21.0	22.5	27.0	28.9	29.3	29.5

nondispersion components of surface free energy for the investigated systems are shown in Table 4. It be seen that the dispersion component increases and the nondispersion decreases reaching, at surface coverage equal to about 70 molecules, the values calculated for HA. So this coating thickness one can take as necessary to screen the surface.

Combining the Eqs (8) and (9) and introducing to the resulting equation the γ_S^d and γ_S^n values for HA covered glass and $\gamma_W = 72.8$, $\gamma_W^d = 21.8$ and $\gamma_W^n = 51$ mN/m [3], the wettability coefficient values (for water) for all studied systems were calculated. They are presented in Table 5.

It is seen that wettabilities of all samples decrease with HA content increase showing the hydrophobic action of humic acids it was postulated by Robinson and Page [15].

REFERENCES

1. Chassin P., Jouany C., Quiquampoix H.: Measurement of the surface free energy of calcium montmorillonite, *Clay Minerals*, 21, 899-907, 1986.
2. Chibowski E., Staszczuk P., Stawiński J.: Correlation between surface free energy and water adsorption capacity for some minerals and other solids. *Polish J. Soil Sci.*, XXII, 1, 67-72, 1989.
3. Fowkes F.M.: Attractive forces at interface. *Ind. Eng. Chem.* 56(12), 40-52, 1964.
4. Good R.J., Elbing E.: Generalization of theory for estimation of interfacial energies. *Ind. Chem. Eng.* 62(3), 54-57, 1970.
5. IUPAC: Pure and Applied Chemistry. *Off. J.*, 31, 985-986, 1972.
6. Jańczuk B., Białopiotrowicz T.: Surface free energy components of liquids and low energy solids and contact angles. *J. Colloid Interface Sci.*, 127, 189-203, 1989.
7. Jańczuk B., Hołysz L., Białopiotrowicz T., Chibowski E.: Studies of dispersion and nondispersion components of the surface free energy of soil minerals in a presence of water film. *Polish J. Soil Sci.*, XXII/1, 39-43, 1989.

8. **Jańczuk B., Hajnos M., Białopiotrowicz T., Kliszcz A., Biliński B.:** Hydrophobization of the soil by dodecylammonium hydrochloride and changes of the components of its surface free energy. *Soil Sci.*, 150, 753-762, 1990.
9. **Jańczuk B., Białopiotrowicz T., Kliszcz A., Biliński B., Stawiński J.:** Influence of polyacrylamide on the surface free energy and wettability of a chemozem soil. *Geoderma*, 50, 173-184, 1991.
10. **Jańczuk B., Białopiotrowicz T., Zdziennicka A., Hajnos M., Józefaciuk G.:** The influence of soil clay constituents on surface free energy of clay fractions. *J. Soil Sci.*, 43, 27-35, 1992.
11. **Jouany C.:** Surface free energy components of clay-synthetic humic acid complexes from contact-angle measurements. *Clays Clay Miner.*, 39, 1, 43-49, 1991.
12. **Jouany C., Chassin P.:** Determination of the surface energy of clay-organic complexes by contact angle measurements. *Colloids and Surfaces*, 27, 289-303, 1987.
13. **Kaelble D.H., Cirlin F.H.:** Dispersion and polar contributions to surface tension of poly (methylene oxide) and Na-treated polytetrafluoroethylene. *J. Polymer. Sci. Sec., A-2*, 9, 363-368, 1971.
14. **Neumann A.W., Good R.J.:** Techniques of measuring contact angles. In: *Surface and Colloid Science*, Vol. 11, R. J. Good and R.R. Stromberg, Eds., Plenum Press, New York, 31-91, 1979.
15. **Robinson D.O., Page J.B.:** Soil aggregate stability. *Soil Sci. Soc. Am. Proc.*, 15, 25-29, 1950.
16. **Tschapek M., Pozzo Ardizi G., de Bussetti S.G.:** Wettability of humic acids and its salts. *Z. Pfl. Bodenk.*, 135, 1, 16-31, 1973.