The Surface Free Energy of Soil Colloids

M. D. Zabidi[†], M. M. Saffan[†] and A. M. Elprince[†]
[†]Department of Soils and Agricultural Chemistry, Alexandria University, Alexandria, Egypt, and [†]Department of Soils and Water, Kafr El-Shaikh University, Egypt.
Corresponding author: A. M. Elprince, e-mail: aelprince@gmail.com

ABSTRACT: Water repellency, floatability, hydrophobicity, swelling, wetting processes, water adsorption, and structure of adsorbed water are examples of interactions at interfaces. A property of solids involved in these interactions is the surface free energy (tension). Because surface free energies measurements for soil colloids are scarce it was the purpose of this paper to report values of the surface free energy for soil clay fraction (<2 μm) of Torrifluvents. X-ray diffraction patterns indicated that the clay fractions of the P5 and P9 soil samples (Nile delta, Egypt) were mainly formed of smectite, followed by kaolinite and illites. Chlorite, vermiculite, and mixed layers appeared only in traces. The spreading surface pressures of soil clays were determined using water vapor adsorption isotherms at 28° C and a nonlinear least squares fitting the BET equation to the experimental data. The values: 36.93 and 38.37 mJ. m^{-2} were computed for the spreading pressures of the two soil-clay samples P5 and P9, respectively. Then, the surface free energies for the soil clays were computed following a recently developed procedure that utilized a formula obtained by combining the Young equation with the general equation of pair interaction. This procedure gave the values 183.76 and 191.45 mJ m^{-2} for the surface free energies of the soil clays P5 and P9, respectively. These values seemed comparable but little less than values of the surface free energy of clay minerals; and soil clays seemed less hydrophilic than pure clay minerals. The Helmy's method used in this study for determining the surface free energy is independent of the extra-thermodynamics assumed by the other methods and seems useful for other soils.
Keywords: Adsorption isotherms, Young equation, BET equation, Spreading pressure,

INTRODUCTION

The interaction of water with soil colloids plays a critical role in all areas of soil science. Water repellency (Bauters et al., 2000), floatability (Chibowski and Holysz, 1986), hydrophobicity (Zettlemoyer, 1969; van Oss and Giese, 1995), swelling (Low, 1987), wetting (Dekany et al., 1986), water adsorption (Dontsova et al., 2004), and structure of adsorbed water (Jurinak, 1961; Low, 1982; Sposito and Prost, 1982; Elprince, 1986) are examples of interactions at interfaces. A property of solids involved in these interactions is the surface free energy (tension).

Despite the fact that surface free energy has been measured for many of the clay minerals (Schultz et al., 1977ab; Janczuk and Bialopiotrowicz, 1988; Christenson, 1993; Helmy et. al., 2003, 2004, 2006), measurements for soil colloids are scarce (Goebel et al., 2004). Several approaches can be used (Zettlemoyer, 1969; Wu, 1980) but no direct method for the determination of the surface free energy exists. One method relies on the determination of the adsorption isotherm of a liquid vapor. From this isotherm the spreading pressure, Π, can be calculated. Based on the Π value, the surface free energy of the solid can be estimated (Zettlemoyer, 1969; Staszczuk, 1984; Helmy et. al., 2003, 2004, 2006). This method employs the Fockes type formula (Fockes, 1964 and 1968), the Lifshitz-VDW-acid/base approach (Giese and van Oss, 2002), or the Helmy's procedure (Helmy et al., 2006). The advantage of the Helmy's procedure is that it is independent of the extra-thermodynamics assumed by the other approaches.

In the present study, the surface free energy of soil clay fraction (< 2 μm) of Torrifluvents have been determined by means of water vapor adsorption isotherm measurements and computed using the Helmy's procedure.

MATERIALS AND METHODS

The Soil Samples: The soils used in this study were Torrifluvents located in Kafer El-Shaikh governorate in the Nile delta, Egypt. The P5 soil sample composite (depth 0 – 30 cm; five random cores) was located at latitude 31° 15' 57" N. and longitude 30° 58' 56" E. On the other hand, the P9 soil sample composite was located at latitude 31° 14' 23" N. and longitude 30° 55' 47" E (Fig. 1). Site locations were determined using Garmin receiver GPS (GARMIN, 2005).
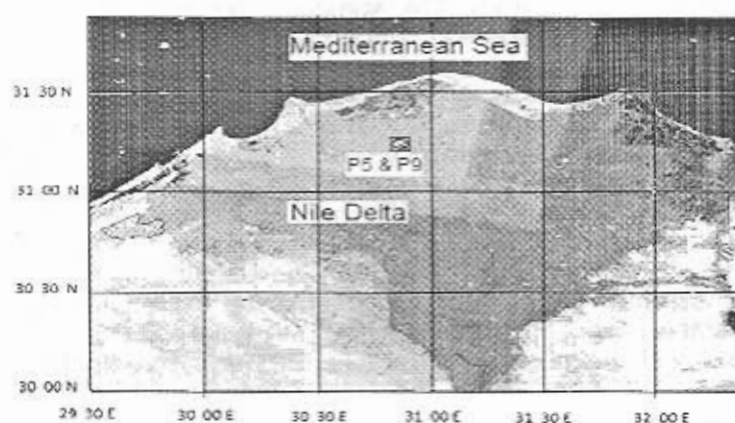

Figure 1. Locations of the soil samples P5 and P9

Soil analyses included the hydrometer method for particle size distribution, the Walkley-Black method for organic carbon content, and the gas-volumetric method for calcium carbonate content. Composition of the saturation soil paste using flame photometer for Na^+ and K^+; AAS for Ca and Mg^{+2}; electrometric titration with $AgNO_3$ for Cl^-; precipitation with $Pd(NO_3)_2$ and then determination of excess of Pb^{2+} with AAS for SO_4^{2-}; and titration with H_2SO_4 for HCO_3^- and CO_3^{2-} (Black, 1965; Jackson, 1965). Exchangeable cations were determined by the Mehlich's method (Mehlich, 1948). Table (1) shows the results of soil analysis.

Soil Clay Preparation: The clay fraction was obtained by allowing the less than 2 mm fraction air-dried soil to settle out of a suspension and then decanting the suspension as of Stock's law. Na-clay was prepared by saturating the < 2μm fraction with 0.5 mol/L NaCl solution. This treatment was repeated five times. Then, the clay was washed with distilled water in high-speed centrifuge until the supernatant solution was free of chloride (tested negative with $AgNO_3$).

Table 1 Properties of soil samples P5 and P9
(0-30 cm depth, < 2mm fraction), Kafer El-Shaikh

Property	P5	P9
Clay %	77	55.4
Silt %	19.6	25.9
Sand %	3.4	8.7
Organic matter, g kg^{-1}	5.7	15.8
Calcium carbonate g kg^{-1}	14.2	29.4
Exchangeable cations, cmol$_c$ kg^{-1}		
Ca	33.9	27.1
Mg	14.8	17.1
Na	17	1.8
K	1	0.9
Saturation extract, mmol$_c$ L^{-1}		
Ca	79.9	9.5
Mg	140.9	7.8
Na	404.6	19.1
K	3.8	0.3
Cl	943.7	21.2
HCO$_3$	0.9	3.2
SO$_4$	4.7	0.1

‡ Saffan (1984).

Soil Clay Mineralogy: X-ray diffraction was measured using Muller Mikro 111 mit Goniometer (Germany). The soil-clay fraction (<2µm) for both P5 and P9 soil samples was mainly formed of smectite, followed by Kaolinite and Illites. Chlorite, vermiculite, and mixed layers appear only in traces (Fig. 2). Although the P5 soil was extremely saline-sodic relative to the P9 soil (Table 1), the mineralogy of clay fractions P5 and P9 seemed identical. This result was expected due to the solute leaching and the cation exchange process during the separation and preparation of the < 2µm fraction for the X-ray analysis. As seen in Fig. 2 the X-ray diffraction patterns indicated that the soil clay P5 had lower content of smectite and was poorly crystalline relative to the soil clay P9. A semi quantitative analysis (determined using impulses per second) indicated that the clay fraction of the P5 and P9 samples contained approximately (66 - 87%) smectite, (10 – 14%) kaolinite and (9 – 22%) Illite (with trace vermiculite and chlorite) (Saffan, 1984).These results are in agreement with recent data by Abou-Khatita (2011) who quantitatively determined clay mineralogy of the Nile Delta soil as 84% montmorillonite, 8.4% kaolinite, 4.8% illite, 1.2% chlorite, and 1.6% mixed-layers illite/vermiculite and illite/chlorite.

Water Vapor Adsorption Isotherm: Samples of ≈ 2.6 g of soil clays <2µm in suspension (0.1587 and 0.1549 g L^{-1} for P5 and P9, respectively) were placed in Pyrex bettry dishes (diammeter = 55 mm, height = 15 mm) and were placed in oven at 50°C overnight to evaporate most of the water and then in vacuum desiccators with aqueous concentrations of H$_2$SO$_4$ of different p/p° values (0.005 to 0.500) and were maintained at 28°C. When equilibrium adsorption was reached (constant weight) the quantities of water adsorbed were determined by weighing and expressed in mg H$_2$O per g soil clay in equilibrium with water vapor of p/p° value of 0.005. The experiments were carried out in duplicates.
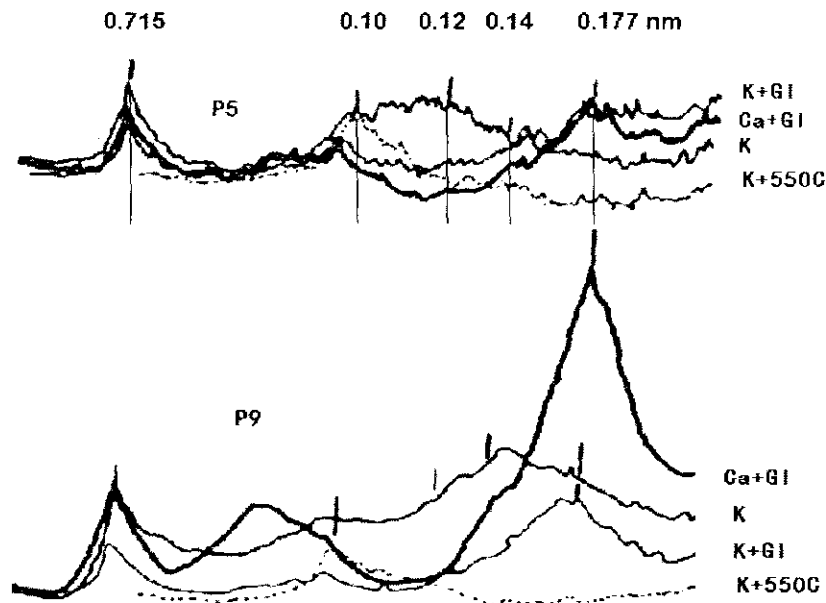
Figure 2. X-ray diffraction patterns for the clay fraction (<2 μm) of soil samples P5 and P9 (Saffan, 1984)

Computing Spreading Pressure: Brunaur, Emmett, and Teller (Brunaur et al., 1938) extended the Langmuir's monolayer equation to multilayer adsorption, and their equation had been come to be known as the BET equation:

$$v \, / \, v_m = \{ \, c \, x \, / \, [\, (1\text{-} \, x) \, (1 + (c\text{-}1) \, x) \,] \, \}\qquad(1)$$

where, $x = p/p^o$, p^o = saturation or condensation pressure = 3167.20 Pa, v = amount of adsorbed water in $mg_{H2O} \ g^{-1} \text{ soil clay}$, the constant v_m = the amount of H_2O adsorbed at the monolayer point, and the constant $c = exp(Q_1 - Q_n) \, / \, RT$, where Q_1 is energy of adsorption for surface covered by single layer and Q_n is energy of adsorption for surface covered by n layers. Keren and Shainberg (1975) considered Q_n = the heat of liquefaction of the gas (= 43.848 kJ mol^{-1} for water at 25°C). We had used a nonlinear least squares method to find the v_m and c parameters that minimized the weighted residual sum of squares.

The specific surface area (sa in $m^2.g^{-1}$) of the soil clay was computed from the value of v_m ($mg_{H2O} \ g^{-1} \text{ soil clay}$) using the equation:

$$sa = 4.182 \ v_m\qquad(2)$$

where, 4.182 ($m^2 \ mg_{H2O}^{-1}$) was the cross sectional area of H_2O.

The spreading (surface) pressure Π, was obtained by numerical integration (using the trapezoidal rule) according to the Gibbs equation:

$$\Pi = (RT \,/\, sa) \int_{\ln p=0}^{\ln pm} v \; d(\ln[p]) \qquad (3)]$$

where R = the gas constant (8.314×10^3 mJ mol^{-1} K^{-1}) , T = temperature in Kelven = $273.16 + t°$ C, sa = specific surface area (m^2 g^{-1}), and p_m is the p value corresponding to the v_m value at the monolayer point. A value for p_m was obtained by substituting v_m in place of v in Eq. (1) and by solving the resulted quadratic equation to yield the positive-real-root equation:

$$p_m = p_o\, [\, (c^{1/2} - 1) \,/\, (c - 1) \,] \qquad (4)$$

Furthermore, the v function in Eq. (3) was made a function of (ln p) by replacing x in Eq. (1) by exp [ln p – lnp_o]. Upon using a value of v_m expressed in mmol$_{H2O}$ g^{-1} $_{soil\ clay}$, the integral (area) in Eq. (3) became in mmol$_{H2O}$ g^{-1} $_{soil\ clay}$ and the desired value of Π would be in mJ m^{-2}.

Computing Surface Free Energy: The Helmy's method (Helmy et al., 2006) was based on a formula obtained by combining the equation of pair interactions:

$$\gamma_S + \gamma_L - k\,\gamma_{SL} = 0 \qquad (5)$$

with the Young equation (Young, 1805):

$$\gamma_S - \gamma_{SL} = \gamma_L \cos\alpha + \Pi \qquad (6)$$

where γ_S was the surface tension of the solid, γ_L was the surface tension of the liquid (72.8 mJ m^{-2}), γ_{SL} was the solid/liquid interfacial tension, k was a constant, and α was the solid/liquid contact angle. From combining Eq.(5) and Eq.(6) one got :

$$k = [\, \gamma_S + \gamma_L \,] \,/\, [\gamma_S - \gamma_L \cos\alpha - \Pi\,] \qquad (7)$$

Eq.(7) was rewritten as:

$$k = (1 + x) \,/\, (1 - m\,x) \qquad (8)$$

where x = (γ_L / γ_S) and m = ($\gamma_L \cos\alpha + \Pi$) / γ_L.

An important feature of this procedure for obtaining γ_S was the use of Young equation to determine the range in which the value of γ_S lies and to be used in Eq. (7). This range of values for γ_S was obtained from Young equation subject to the conditions: $\gamma_L < \gamma_{SL} < \gamma_S$ and $\gamma_{SL} \le (\gamma_S\, \gamma_L)^{1/2}$, so that the lower (Lγ_S) and upper (Uγ_S) limits of γ_S were estimated using Eq.(9) and Eq.(10), respectively:

$$L\gamma_S = \gamma_L + \gamma_L \cos\alpha + \Pi \qquad (9)$$

$$U\gamma_S - (\gamma_L)^{1/2}\, (U\gamma_S)^{1/2} - (\gamma_L \cos\alpha + \Pi) = 0 \qquad (10)$$

Knowing the range where γ_S lies the mean value of x, i.e. $<x> = \gamma_L / <\gamma_S>$, can be calculated from the formula:

$$<x> = [1 / [k(x_1) - k(x_2)]) \int_{x_2}^{x_1} x \left(\frac{dk}{dx}\right) dx \qquad (11)$$

where x_1 and x_2 are the limit values of x in the range where the surface energy lies. Integration of Eq. (11) gives:

$$<x> = \frac{\left[\frac{(1 + m)}{m^2} \left(\ln(1 - mx) + \frac{1}{(1 - mx)}\right)\right]_{x_2}^{x_1}}{k(x_1) - k(x_2)} \qquad (12)$$

RESULTS AND DISCUSSION

1. The Spreading Pressure

The water vapor adsorption isotherms at 28°C for the soil fraction (< 2 µm) of soils P5 and P9 are presented in Fig. 3. The points are the experimental data and the solid curves resulted from fitting the BET equation to data. The v_m parameter is found equal to 46.00 and 47.25 mg_{H2O} g^{-1} $_{soil-caly}$ for the soil clays P5 and P9, respectively. The c parameter is found equal to 4.158 and 4.725 for the soil clays P5 and P9, respectively.

Following our procedure described above the sa for the soil-clays P5 and P9 are computed equal to 192.4 and 197.6 m^2 g^{-1}, respectively. In a study by Likos and Lu (2002) the specific surface area value (sa) for smectite-kaolinite mixtures varied from 21 to 212 m^2 g^{-1} for the end members kaolinite and smectite, respectively, while specific surface area of a mixture (sa_{mix}) could be predicted from the equation:

$$sa_{mix} = (1- m_K) sa_S + m_K sa_K \qquad (13)$$

where, sa_S and sa_K are specific surface area for smectite and kaolinite, respectively and m_K was mass fraction of kaolinite. Extension of Eq.(13) to a mixture of smectite, kaolinite, and illite has predicted a mineral composition for the soil clay P5 equal to 87% smectite, 7% kaolinite, and 6% illite; and a mineral composition for the soil clays P9 equal to 90% smectite, 6% kaolinite and 7% illite. These approximate compositions are in agreement with the results of X-ray analysis with the assumption that the sa of illite equal to 100 m^2 g^{-1}. The value 100 m^2 g^{-1} for sa of illite (with trace vermiculite and chlorite) seems reasonable.
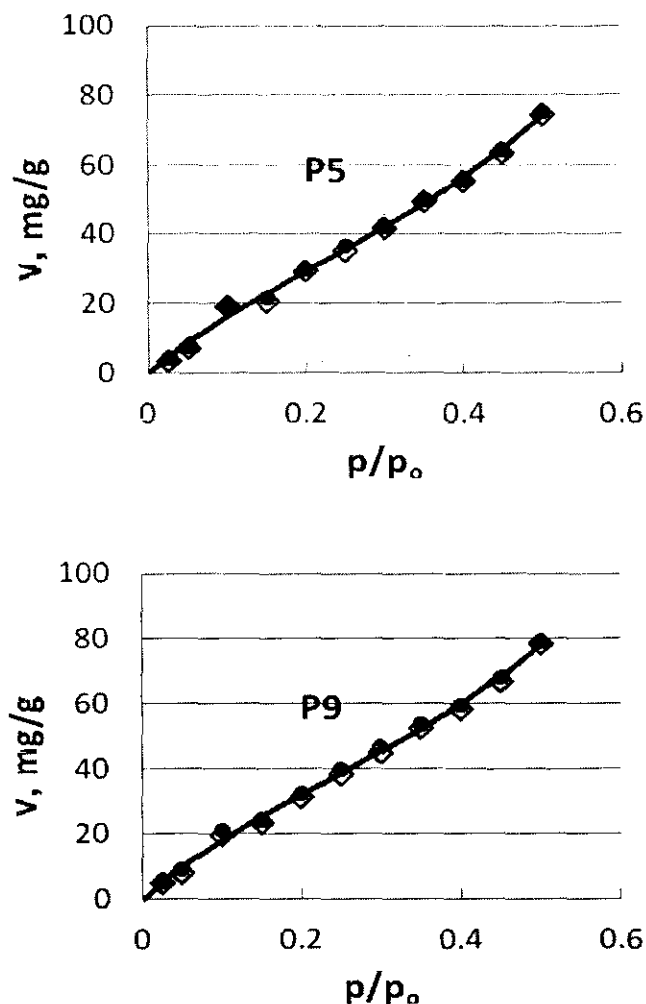
Figure 3. Water vapor adsorption isotherms (28°C) for soil clays P5 and P9

Using the measured c values, the energy (heat) of adsorption for surface covered by single layer (Q_1 - Q_L) are computed equal to 4.05 and 4.15 kJ mol^{-1} for the soil clays P5 and P9, respectively. These values are lower than the 7.366 and 6.159 kJ mol^{-1} values reported by Likos and Lu (2002) for kaolinite and smectite, respectively; and higher than the 1.42 kJ mol^{-1} reported by Keren and Shainberg (1975) for Na-smectite.

The ln P_m (Eq. 3) values for the soil-clays P5 and P9 are computed equal to 6.949, and 6.907 (with p_m in Pa), respectively. The values of the integral in Eq.(3) (area under the isotherms in Fig. 4) are numerically computed equal to 2.8373 and 3.0275 mmol$_{H2O}$ g^{-1} for the soil clays P5 and P9, respectively. Subsequently, the Π values for the soil clays P5 and P9 are computed equal to 36.932; and 38.365 mJ m^{-2}, respectively. These estimated parameter values are summarized in Table 2. The values of the estimated spreading pressures, Π, for both the soil clays P5 and P9 (Table 2) are less than those reported for kaolinite (97.8 mJ m^{-2}) (Helmy et al., 2004) and smectite (60 mJ m^{-2}) (Helmy et

al., 2003). These differences in the Π values seem due to the predominance of smectite, different crystallinity, and contamination with organic matter in the soil clay samples.
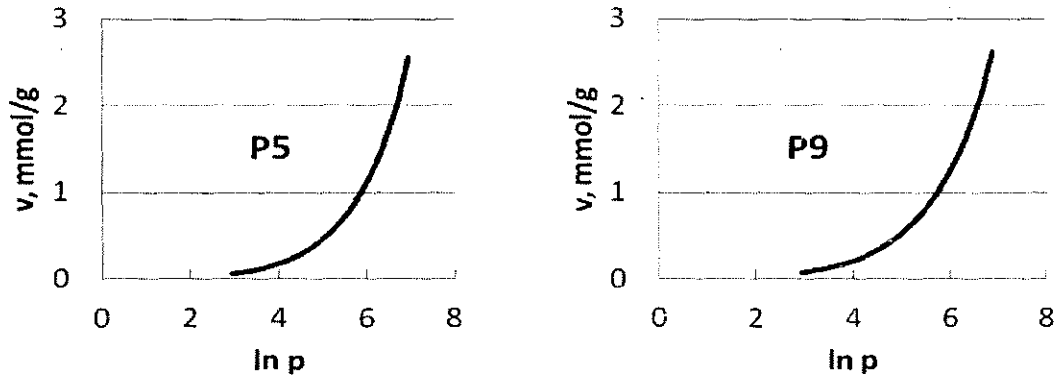

Figure 4. Water vapor adsorption on soil clays P5 and P9 vs. ln p (p is in Pa)

Table 2. Parameter values of water vapor adsorption isotherms (28 C) for soil clays (< µm) of soils P5 and P6

Soil	Vm mmol/g	c unitless	sa m2/g	ln pm (pm in Pa)	Integral Eq(3) mmol/g	Π mJ/m2
P5	2.5554	4.1583	192.4	6.949	2.8373	36.932
P9	2.6248	4.7247	197.6	6.907	3.0275	38.365

2. The surface free energy

In computing the surface free energy (γ_S) we used literature data for γ_L = 72.8 mJ m^{-2} and α = 0° (Helmy et. al., 2003). Following Helmy's procedure described above [(Eq.(9) and Eq. (10)], the ranges of γ_S values are computed equal to [182.6 : 242.8] and [184.02 : 244.7] mJ m^{-2} for the soil clays P5 and P9, respectively. Subsequently, the employment of Eq.(12) gives <x> equal to 0.4559 and 0.4462 for soil clays P5 and P9, respectively; hence the mean surface energy of soil clays P5 and P9 (< γ_S >) are equal to 158.62 and 163.15 mJ m^{-2}, respectively.

With the value of γ_S known, γ_{SL} is computed equal to 74.03 and 80.29 mJ m^{-2} for soil clays P5 and P9, respectively, using Young equation (6). Using the Gibbs equation:

$$\Pi = \gamma_S - \gamma_{SV}, \qquad (14)$$

the solid/vapor interfacial tension (γ_{SV}) is computed equal to 146.83 and 153.09 mJ m^{-2} for the soil clays P5 and P9, respectively. These estimated parameter values are summarized in Table 3.

Table 3. Surface free energies for soil clays P5 and P9

Soil	m	Lγ_S	Uγ_S	γ_S	γ_{SL}	γ_{SV}
				mj/m2		
P5	4.2610	177.25	235.3	183.76	74.03	146.83
P9	4.2624	178.68	237.3	191.45	80.29	153.09

The estimated surface free energy γ_S values (183.76 and 191.45 mJ m^{-2} for both the soil clays P5 and P9, respectively) (Table 3) are less than those reported for kaolinite (231.4 mJ m^{-2}) and montmorillonite (223.3 mJ m^{-2}) (Helmy et al., 2006) but greater than the values (130-170 mJ m^{-2}) for mica (Christenson, 1993). This comparison suggests that the soil clay surfaces are less hydrophilic than the clay minerals; apparently due to contamination with organic matter.

The work of water adhesion (W_A) to the surface of soil clay can be calculated using the equation (Chibowski and Staszczuk, 1988):
$$W_A = 2 (\gamma_S \gamma_L)^{1/2} \qquad (15)$$
the values of which are found equal to 231.32 and 236.12 mJ m^{-2} for the soil clays P5 and P9, respectively. These values suggest that in the present experiments water wet the surface of the soil clays, because the work of water adhesion is higher than the work of water cohesion $W_C = 2 \gamma_L = 145.6$ mJ m^{-2}.

In summary, the surface free energy values of soil clays are comparable but little less than values of the surface free energy of clay minerals. Thus soil clays seem less hydrophilic than the clay minerals. The Helmy's method used in this study for determining the surface free energy of soil colloids is independent of the extra-thermodynamics assumed by the other methods and seems useful for other soils.

REFERENCES

Abou-Khatita, A. M. 2011. Assessment of soil and sediment contamination in the Middle Nile Delta area (Egypt) – Geo-Environmental study using combined sedimentology, geophysical and geochemical methods. Friedrich-Alexanar University, Germany. Ph.D Thesis.

Bauters, T. W. J., T. S. Steenhuis, D. A. DiCarlo, J. L. Nieber, L. W. Dekker, C. J. Ritsema, J. Y. Parlange and R. Haverkamp. 2000. Physics of water repellent soils. Journal of Hydrology, 231: 333-243.

Black, C. A. (ed). 1965. "Methods of Soil Analysis". ASA and SSSA, Madison, WI.

Brunauer, S., P. H. Emmett, and E. Teller. 1938. Adsorption of gases in multimolecular layers. Journal of the American Chemical Society. 60:309.

Clibowski, E. and L. Holysz. 1986. Correlation of surface free energy changes and flotability of quartz. J. Colloid Interface Sci., 112: 15-23.

Chibowski, E. and P. Staszczuk. 1988. Determination of surface free energy of kaolinite. Clays and Clay Minerals, 36: 455-461.

Christenson, H. K. 1993. Adhesion and surface energy of mica in air and water. J. Phys. Chem modified surface. II. Interlammellar sorption and wetting on organic montmorillonites. J. Colloid Interface Sci. 109: 376-384.

Dekany, I., F. Szanto, and L. G. Nagy. 1986. Sorption of immersional wetting on clay minerals having modified surface. II. Interlammellar sorption and wetting on organic montmorillonites. J. Colloid Interface Sci. 109: 376-384.

Dontsova, K. M., L. D. Norton, C. T. Johnston, and J. M. Bigham. 2004. Influence of exchangeable cations of water adsorption by soil clays. Soil Sci. Soc. Am. J., 68: 1218-1227.

Elprince, A.M. (ed.). 1986. "Chemistry of Soil Solutions". Van Nostrand Reinhold Company, New York, USA.

Fockes, F. M. 1964. Attractive forces at interface. Ind. Eng. Chem., 56: 40-52.

Fockes, F. M. 1968. Calculation of work of adhesion by pair potential summation. J. Colloid Interface Sci., 28: 493-505.

GARMIN 2005. eTrexLegend personal navigator. Owner's manual and reference guide. Garmin International, Inc. KS, USA.

Giese, R. F. and C. J. van Oss. 2002. "Colloid and Surface Properties of Clays and Related Minerals". M. Dekker, New York.

Goebel, Marc-O, J. Bachmann, S. K. Woche, W. R. Fisher and R. Horton. 2004. Water potential and aggregate size effects on contact angle and surface energy. Soil Sci Soc. Am. J., 68: 383-393.

Helmy, A. K., E. A. Ferreiro, and S. G. de Bussetti. 2003. The surface energy of montmorillonite. J. Collid Interface Sci., 268: 263-265.

Helmy, A.K., E.A. Ferreiro, and S.G. de Bussetti. 2004. The surface energy of kaolinite. Colloid Polym Sci. 283: 225-228.

Helmy, A. K., S.G. de Bussetti and E. A. Ferreiro. 2006. The surface energy of palygorskite. Powder Technology, 171: 126-131.

Jackson, M. L. 1965. "Soil chemical analysis. Advanced course", published by the auther. Dept. of soil science , Wisconsin Univ. Madison.

Janczuk, B. and T. Bialopiotrowicz. 1988. Components of surface free energy of some clay minerals. Clays & Clay Minerals, 36: 243-248.

Jurinake, J. J. 1961. The effect of pretreatment on the adsorption and desorption of water by lithium and calcium kaolinite. J. Phys. Chem., 65: 62-65.

Keren, R. and I. Shainberg. 1975. Water vapor isotherms and heat of immersion of the Na/Ca − montmorillonite systems − I. Homoionic clay. Clays and Clay Minerals, 23: 193-200.

Likos, W. J. and N. Lu. 2002. Water vapor sorption behavior of smectite-kaolinite mixture. Clays and Clay Minerals, 50: 553-561.

Low, P.F. 1982. Water in clay-water systems. Agronomie, 5: 909-914.

Low, P.F. 1987. Structural component of the swelling pressure of clays. Langmuir, 3: 18-15.

Mehlich, A.1948. Determination of cation- and anoin − exchange properties of soils, Soil Sci., 66: 429 − 445.

Saffan, M. M. (1984). Zur kenntnis der Böden in der Region Schalma (Nord − Nildelta / Ägypten). Diss. Giessen Uni., Germany.

Schultz, J., K. Tsutsumi and J.B. Dounet. 1977a. Surface properties of high-energy solids. I. Determination of the dispersive components of the surface

free energy of mica and its energy of adhesion to water and n-alkanes. J. Colloid Interface Sci., 59: 272-276.

Schultz, J., K. Tsutsumi, and J. B. Dounet. 1977b. Surface properties of high-energy solids.I I. Determination of the nondispersive components of the surface free energy of mica and its energy of adhesion to water and n-alkanes. J. Colloid Interface Sci., 59: 277-282.

Sposito, G. and R. Prost. 1982. Structure of water adsorbed on smectites. Chem. Rev., 82: 554-573.

Staszczuk, P. 1984. Applicationof thermal analysis for determination of film pressure and film surface energy on silica gel surface. J. Thermal Analysis, 29: 217-225.

Wu, S. 1980. Interfacial tension of solids: Generalization and reinterpretation of critical surface tension. *In* Lieng-Huang Lee, (ed.), "Adhesion and Adsorption of Polymers". Plenum Press, New York, 53-67 pp.

Zettlemoyer, A.C. 1969. Hydrophobic surfaces. *In* F.M. Fowkes, (ed.), "Hydrophobic Surfaces". Academic Press, New York, 1-27 pp.

Van Oss, C. J. and R. F. Giese. 1995. The hydrophilicity and hydrophobicity of clay minerals. Clays and Clay Minerals, 43: 474-477.

Young, T. 1805. An assay on the cohesion of fluids. Trans. R. Soc. London, 95: 65-87.

الملخص العربى
الطاقة الحرة السطحية لغرويات الأراضى
محمد د. زبيدى[†] – محمد م. صفان[‡] – عادل م. البرنس[†]
[†] قسم الأراضى والكيمياء الزراعية – جامعة الاسكندرية – ج.م.ع.

[‡] قسم الأراضى و المياه – جامعة كفر الشيخ – ج.م.ع.

تعتبر خاصية طرد الماء و الطفو والكراهية و الانتفاخ و الابتلال وادمصاص الماء و والشكل البنائى للماء المدمص هى أمثلة للتفاعلات على السطوح. وتعتبر الطاقة الحرة السطحية (التوتر) أحد خواص السطوح المؤثرة فى هذه التفاعلات. لقد تم قياس الطاقة الحرة السطحية لعديد من معادن الطين ولكن القياسات لغرويات التربة تعتبر نادرة. الهدف من هذا البحث هو تقدير الطاقة الحرة السطحية للجزء الطينى (2> μm) لتوريفليوفنت. لقد أوضحت منحنيات أشعة اكس للجزء الطينى من عينتى التربة P5 و P9 سيادة معدن السميكتيت يليه الكاولينيت وألاليت. بينما الكلوريت والفرموكيوليت و المعادن المختلطة فتتواجد بكميات ضئيلة. تم قياس الضغط السطحى spreading pressure لطين التربة باستخدام منحنى الادمصاص المقدر على درجة حرارة ثابته (C° 28) مع وصف النتائج التجريبية تبعا لمعادلة BET وايجاد قيم الثابتان باستعمال الطريقة غير الخطية لأقل المربعات. فكانت قيم الضغط السطحى هى 36.93 و 38.37 mJ. m^{-2} لعينتى طين التربة P5 و P9 على التوالى. وبناء عليه تم حساب الطاقة الحرة السطحية لطين التربة باتباع طريقه تم تطويرها حديثا و تم استخدامها بنجاح مع عدد من معادن الطين. تستخدم هذه الطريقة معادلة تم الحصول عليها من اشراك معادلة يانج بالمعادلة العامة للتفاعل الزوجى. أنتجت هذه الطريقة القيمتين 183.76 و 191.45 mJ m^{-2} للطاقة الحرة السطحية للجزء الطينى من عينتى التربة P5 و P9 على التوالى. تبدو هذه القيم متشابهة ولكن أقل قليلا من القيم المنشورة للطاقة الحرة السطحية لمعادن الطين مما يعنى أن طين التربة يبدو أكثر كرها للماء بالمقارنة بمعادن الطين النقية. وتمتاز طريقة "حلمى" والمستخدمة فى هذا البحث لتقدير الطاقة الحرة بأنها لاتعتمد على افتراضات الكيمياء الحرارية غير الضرورية extra-thermodynamics والمستخدمة فى الطرق الأخرى وأيضا تمتاز هذه الطريقة بامكانية استعمالها لأراضى أخرى.