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Surface Free Energy, Adsorption and Zeta Potential in Leacril/Tannic Acid System

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Surface free energy components, apolar Lifshitz–van der Waals, γ_s^{LW} , and polar electron acceptor, γ_s^+ , and electron donor, γ_s^- , were determined for leacril (a copolymer of 90% acrylonitrile and 9% vinyl acetate) fibers with preadsorbed tannic acid solutions (10^{-5} – 10^{-2} M). A thin layer wicking method was applied for this purpose. The components were calculated considering van Oss et al.'s (*J. Chem. Rev.* **1988**, *88*, 927) polar components of surface tension of probe liquids (formamide and water, $\gamma_w^- = \gamma_w^+ = 25.5$ mJ/m² for water) as well as those suggested very recently by Lee (*Langmuir* **1996**, *12*, 1681), who considered for water $\gamma_w^- = 19$ mJ/m² and $\gamma_w^+ = 34.2$ mJ/m². The trend of changes of the calculated components is the same, except for the surface treated with 10^{-2} M tannic acid. However, the electron donor components of the leacril calculated with Lee's data are somewhat lower. From the calculated work of spreading of water, results indicate that the bare leacril surface is slightly hydrophobic, the surface treated with 10^{-5} M tannic acid becomes low hydrophilic, and in the range of concentrations 10^{-4} – 10^{-3} M becomes increasingly hydrophobic. When equilibrated with 10^{-2} M it is again hydrophilic. The changes can be explained by reorientation of the tannic acid molecules on the leacril surface and micelle formation above cmc, which was determined to be at ca. 3×10^{-4} M. Adsorption measurements show that the process is very fast and physical in nature. The rate constants and empirical diffusion coefficients were evaluated at 275, 283, 293, and 303 K. Also thermodynamic functions for the adsorption process were calculated from the adsorption isotherms. It was concluded that hydrogen bonding and Lifshitz–van der Waals interactions are responsible for the adsorption, while electrostatic interactions play a rather second-order role. The leacril shows small negative zeta potentials which drop almost to zero at concentrations higher than 10^{-4} M.

1. Introduction

Although interfacial free energy interactions play an essential role in practically all phenomena occurring at interfaces, solid/liquid, solid/gas, liquid/liquid, or even liquid/gas, an effort is taking place over 3 decades¹ to describe them properly, not only quantitatively but also qualitatively. There was many approaches to express the interactions in terms of various intermolecular and interfacial forces.^{2–10} At present, it may be said that since Fowkes' pioneer paper,¹ many doubts still exist as to expressing the nondispersion interactions across an interface. Despite the fact that the apolar London dispersion interaction can be relatively easily determined, considering the van Oss, Chaudhury, and Good^{5,6,11,12} approach as the most appropriate by now is doubtful

because they included the dispersion, dipole–dipole, and dipole–induced dipole interactions into one component termed the “apolar Lifshitz–van der Waals”, γ_i^{LW} . In the authors' approach these polar interactions are of second order (2–3% for water) because in the condensed phase they mutually saturate. The essential advantage of this approach is quantitative formulation of Lewis acid–base interaction as the electron donor γ_i^- (basic) and electron acceptor γ_i^+ (acidic) parameters. However, it should be stressed that numerical values of these parameters are relative ones as they result from an arbitrary assumption^{5,6} that for water $\gamma_i^- = \gamma_i^+ = 25.5$ mJ/m², which was taken as a reference liquid. In other words, electron donor ability of water molecules is equal to the electron acceptor ability. Moreover, it has appeared very soon that for almost all real surfaces the acidic parameter is low,^{11–15} and many times the square root of γ_i^+ , which results from simultaneous solution of two equations with the two unknowns (γ_i^- and γ_i^+), has negative value. This negative value is often too big to be a result of possible experimental error, for example, in measured contact angle. Obviously, it rather makes no physical sense and the negative root was interpreted as the zero value of the γ_i^+ parameter.^{11–15} One may conclude that these problems, at least partially, may result from above-mentioned assumption about equality of γ_i^- and γ_i^+ parameters for water. Despite these problems, using van Oss et al.'s approach it was possible to explain, to a large extent, many phenomena occurring

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(1) Fowkes, F. M. *J. Phys. Chem.* **1962**, *66*, 382.

(2) Good, R. J.; Girifalco, L. A. *J. Phys. Chem.* **1960**, *64*, 561.

(3) Owens, D. K.; Wend, R. C. *J. Appl. Polym. Sci.* **1969**, *13*, 1741.

(4) Ward, C. A.; Neumann, A. W. *J. Colloid Interface Sci.* **1974**, *49*, 186.

(5) van Oss, C. J.; Chaudhury, M. K.; Good, R. J. *J. Chem. Rev.* **1988**, *88*, 927.

(6) Good, R. J.; Chaudhury, M. K.; van Oss, C. J. In *Fundamentals of Adhesion*; Lee, L. H. Ed.; Plenum Press: New York, 1991; p 153.

(7) Lee, L. H. *J. Adhes. Sci. Technol.* **1993**, *7*, 583.

(8) Xu, Z.; Liu, Q.; Ling, J. *Langmuir* **1995**, *11*, 1044.

(9) Schneider, R. P. *J. Adhes. Sci. Technol.* **1997**, *11*, 65.

(10) Janczuk, B.; Zdziennicka, A.; Wojcik, W. *Przem. Chem.* **1995**, *45*, 429.

(11) van Oss, C. J.; Chaudhury, M. K.; Good, R. J. *J. Adv. Colloid Interface Sci.* **1987**, *28*, 35.

(12) van Oss, C. J. *Interfacial Forces in Aqueous Media*; Marcel Dekker: New York, 1994.

(13) Chibowski, E.; Holysz, L. *Langmuir* **1992**, *8*, 710.

(14) Chibowski, E.; González-Caballero, F. *J. Adhes. Sci. Technol.* **1993**, *7*, 1195.

(15) Jacobasch, H.-J.; Grundke, K.; Schneider, S.; Simon, F. *J. Adhes.* **1995**, *18*, 57.

at the interfaces, e.g., solid/liquid, involving adsorption of surfactants,^{16–20} in which interfacial free energy interactions play an essential role.

However, very recently Lee²¹ has presented an interesting approach to the problem of the reference γ_i^- and γ_i^+ parameters for water. Considering Taft and Kamlet's²² solvatochromic parameters of "linear free energy relationship", or as they call it "linear solvation energy relationship" (LSER), which deals with a solvation process, they have found that for water a more appropriate ratio of γ_i^+/γ_i^- is 1.8 instead of 1, as assumed by van Oss et al.^{6–9} This leads to new values of these parameters not only for water but also for all probe liquids used for contact angle measurements or the thin-layer wicking technique.^{13,23–26} Thus, the new values for water are $\gamma_i^+ = 34.2$ and $\gamma_i^- = 19$ mJ/m². Lee has recalculated literature data for many polymers, proteins, and others.²¹ He found that the new acidic and basic parameters for probe liquids (usually water, formamide, glycerol, and ethylene glycol) in general lead to a decreased value of the basic parameter γ_i^- and a bit increased γ_i^+ parameter. As the author²¹ stated, this finding does not solve the problem of interfacial free energy components determination but moves a step ahead in our knowledge about these parameters. Moreover, Lee's considerations also prove validity of the concept of the surface free energy components at all. The concept was questioned by the authors equation of state approach.^{4,27,28}

In our previous papers^{16–19} we have used van Oss et al.'s approach to describe changes in the surface free energy components for several fabrics (mainly polymeric), which were due to adsorption of surfactants and/or dyes. The purpose of this paper is to conduct a similar study for leacril fabric treated with tannic acid. However, this time we would like to compare results using the two sets of surface tension components of the probe liquids (water and formamide). It seemed to us interesting to learn whether in both case the obtained results would lead to the same conclusions. To get better insight into the energetic changes taking place in the system, kinetic of adsorption and adsorption isotherms were also determined for tannic acid at different temperatures. Finally, the zeta potentials were determined for these systems by the streaming potential method.

2. Experimental Section

The leacril fabric and fibers used in these experiments were from Montefiber S.A., Barcelona, and they consist of 90% acrylonitrile and ca. 9% vinyl acetate.²⁹ During the copolymerization process a large number of sulfonate and sulfate end

groups originate from.^{29,30} Before being used for the experiments, the fabric and fibers were repeatedly rinsed with deionized water until a constant conductivity (several μ S) was obtained. Then they were dried in an oven at 313 K and kept in a desiccator.

Tannic acid, C₇₆H₅₂O₄₆, was A.R. grade from Merck, and it was used without further purification. It is a derivative of glucose in which five hydroxyl groups are substituted for digallic acid. The result is a large number of phenolic hydroxyl groups in the tannic acid molecule.³¹

For determination of the surface free energy components by the thin-layer wicking method,^{13,23–26} *n*-decane and formamide (anal. grade, from Merck) and water (from Mili-Q System) were used. The details of the thin-layer wicking method were described elsewhere.^{16–19,23–26} Strips of the fabric, 25 cm long and 2.5 cm wide, were first equilibrated in tannic acid solutions (10^{–5}–10^{–2} M) for 24 h at 293 K, then dried in an oven at 313 K, and kept in a desiccator. To determine the surface free energy components of leacril, one set of the strips were equilibrated with vapors of the probe liquids, and then the liquids wicked the strips in a closed vessel (so-called precontacted strips). In other series, the strips were used for wicking without any contact with the liquid vapors (bare strips). Having these two series of the experiments done, it was possible to calculate the surface free energy components, Lifshitz–van der Waals γ_s^{LW} , electron acceptor γ_s^+ , and electron donor γ_s^- .^{23–26}

The adsorption measurements of tannic acid on leacril were conducted using 1 g of the fibers that was contacted with 100 mL of the solution in the concentration range from 10^{–6} to 10^{–2} M in conical Pyrex flasks fitted with ground glass stoppers. The flask were kept in a water bath at a desired temperature. Both the adsorption kinetic (from 5 × 10^{–5} M solution) and adsorption isotherms were determined at 275, 283, 293, and 303 K. The adsorbed amounts were established from the difference between the initial and final (or at the moment of the measurements) concentrations. The concentrations were determined using spectrophotometer model U-2000 (Hitachi).^{32,33} The maximum absorbance was at $\lambda = 271$ nm. The adsorption equilibrium has been attained within 2–3 h. However, the adsorption measurements were conducted up to 24 h. To determine kinetics of the adsorption, first it was measured every second minute, up to the 32nd minute of the process duration, then every 4–5 min, and later for longer periods of time.

Zeta potentials of leacril versus tannic acid concentration were determined by the streaming potential method, which was also used in our previous papers dealing with fabrics.^{17,32,33} The plugs of leacril were packed between two movable perforated platinum electrodes at various pressure, thus giving densities of the plug 75.7, 86.6, 101, 121.2, 151.5, and 202 kg/m³. The streaming potentials were measured with a Keithley digital electrometer (model 616) and the conductivity was measured with a Crison conductivity bridge (model CM 2202) at 3300 Hz. To calculate zeta potential from the streaming potential three different models of the capillary bundles were applied:^{34–36}

$$(i) \text{ Goring and Mason, } (\Delta\Phi_s)_{P=0}/\Delta P = [\epsilon\zeta R/(2\eta C)](1 - \alpha_\zeta C_F) \quad (1)$$

$$(ii) \text{ Bieffer and Mason, } (\Delta\Phi_s)_{P=0}/\Delta P = [\epsilon\zeta R/(\eta C)](1 - \alpha'_\zeta C_F)^{5/2} \quad (2)$$

$$(iii) \text{ Chang and Robertson, } (\Delta\Phi_s)_{P=0}/\Delta P = [\epsilon\zeta R/(\eta C)]e^{-BC_F} \quad (3)$$

where $\Delta\Phi_s$ is the streaming potential generated between the electrodes at the applied pressure ΔP , ϵ and η are dielectric constant and viscosity of the permeant, respectively, R is the

(16) Espinosa-Jiménez, M.; Ontiveros-Ortega, A.; Giménez-Martín, A. *J. Colloid Interface Sci.* **1997**, *185*, 390.

(17) Espinosa-Jiménez, M.; Ontiveros-Ortega, A.; Giménez-Martín, A. *J. Colloid Interface Sci.* **1997**, *193*.

(18) Ontiveros-Ortega, A.; Espinosa-Jiménez, M.; Chibowski, E.; González-Caballero, F. *J. Colloid Interface Sci.* **1998**, *199*, 99.

(19) Espinosa-Jiménez, M.; Ontiveros-Ortega, A.; Chibowski, E.; González-Caballero, F. *J. Colloid Interface Sci.*, in press.

(20) Chibowski, E.; Holysz, L. *Prog. Colloid Polym. Sci.* **1992**, *89*, 173.

(21) Lee, L. H. *Langmuir* **1996**, *12*, 1681.

(22) Taft, R. W.; Kamlet, M. J. *J. Org. Chem.* **1983**, *48*, 2877.

(23) Giese, R. F.; Costanzo, P. M.; van Oss, C. J. *J. Phys. Chem. Miner.* **1991**, *17*, 611.

(24) Holysz, L.; Chibowski, E. *Langmuir* **1992**, *8*, 717.

(25) Chibowski, E. *J. Adhes. Sci. Technol.* **1992**, *6*, 1069.

(26) Chibowski, E.; González-Caballero, F. *Langmuir* **1993**, *9*, 330.

(27) Neumann, A. W.; Good, R. J.; Hope, C. J.; Seipel, M. J. *J. Colloid Interface Sci.* **1974**, *49*, 291.

(28) Kwok, D. Y.; Li, D.; Neumann, A. W. *Langmuir* **1994**, *10*, 1323.

(29) Frushour, B. G.; Knorr, R. S. In *Acrilic Fibers. Handbook of Fiber Science and Technology*; Lewin, M., Pearce, E. M., Eds.; Marcel Dekker: New York, 1985; Vol. VI.

(30) Cegarra, J.; Puente, P.; Valdeperas, J. *Tintura de Fibras Textiles*; Universidad Politécnica de Cataluña; Tarrasa: Barcelona, 1984.

(31) Blücher, R. In *Enciclopedia de Química Industrial*; Editorial Tecnos S.A.: Madrid, 1958.

(32) Espinosa-Jiménez, M.; González-Caballero, F.; González-Fernández, F.; Pardo, G. *Acta Polym.* **1987**, *38*, 96.

(33) Espinosa-Jiménez, M.; Giménez-Martín, A. *Acta Polym.* **1996**, *47*, 181.

electric resistance of the plug, C is the streaming cell constant evaluated for each packing C_F using 10^{-1} M KCl solution, the parameters α_ξ and α'_ξ are electrokinetic specific volumes in each model, and B is Chang's constant. The experimental data of $[(\Delta\Phi_s)_{j=0}/\Delta P](C/R)$, $[(\Delta\Phi_s)_{j=0}/\Delta P](C/R)^{0.4}$, and $\ln[(\Delta\Phi_s)_{j=0}/\Delta P - (C/R)]$ versus C_F were fitted by the linear least-squares method in the tested concentration range of tannic acid. The correlation coefficient was always higher than 0.97. The zeta potentials were calculated from intercept of the straight line of the above linear regressions. Although the significant levels were always higher than 95%, the best fit was obtained with the linear model of Goring and Mason.

Finally, to determine critical micelle concentration (cmc) in tannic acid solutions, the surface tension of the solutions was measured with a Rame-Hart goniometer.

3. Results and Discussion

Although leacril possesses many sulfonate and sulfate end groups on its surfaces, it was considered a hydrophobic material.^{37–40} However, hydrophobicity is sometimes understood in several different ways. The simplest one seems to be that which considers that a surface is hydrophobic if water droplets form contact angle bigger than 90° . One may also consider that a hydrophobic surface is that which does not expose any polar (dipole–dipole, acid–base, etc.) interactions with water. In our opinion a good measure for a surface hydrophobicity is the magnitude of the work of spreading, W_s , of water, which is the difference between its work of adhesion, W_a , to the surface and the work of water cohesion, W_c , which is equal to double value of surface tension of water. Applying van Oss et al.'s^{5,6,11,12} approach to the interfacial free energy, the relationship reads

$$W_a - W_c = W_s = 2[(\gamma_s^{LW} \gamma_l^{LW})^{1/2} + (\gamma_s^+ \gamma_l^-)^{1/2} + (\gamma_s^- \gamma_l^+)^{1/2}] - 2\gamma_l \quad (4)$$

where subscripts s and l deal with the solid and water, respectively. The more negative the work of spreading, the more hydrophobic the surface is. Thus, to learn about hydrophobicity in a quantitative way, one has to determine the surface free energy components and then calculate the work of adhesion and the work of spreading.

3.1. Surface Free Energy and the Work of Spreading of Water. The surface free energy components were determined from the thin-layer wicking method,^{13,14,18,19} which is based on Washburn's equation,⁴² a general form of which reads^{13,14}

$$x^2 = \frac{Rt}{2\eta} \Delta G \quad (5)$$

where x is the penetrated distance by the liquid during time t , R is effective diameter of the interparticle capillaries, η is the liquid viscosity, and ΔG is the specific free energy changes accompanying the process (in this notation the positive values of the energy changes mean the process is spontaneous). The changes depend on the solid and

the liquid surface free energy as well as whether a duplex film is present on the solid surface (bare and precontacted with the liquid vapors the strips). From eq 5 results show that the relationship $x^2 = f(t)$ should be linear at constant temperature.

Depending on the liquid tested and the experimental conditions chosen, four cases can be distinguished in the thin-layer wicking experiments.^{13,14}

(i) A low-energy liquid, for example n -decane, which completely wets the surface of the solid thin porous layer (e.g., deposited on a glass plate), or in this case the material strip. When the surface is exposed to saturated vapor of the liquid an equilibrium state is achieved on the surface (duplex film). Then in eq 5 $\Delta G = \gamma_l$ (γ_l is the surface tension of the liquid) and thus the effective radius, R , can be determined. In such a case, eq 5 assumes the original form of Washburn's equation.

(ii) When the same liquid (n -decane) is used as above, but the strip has not been exposed to the saturated vapor (bare strip), then the specific free energy change accompanying the penetration process in eq 5, $\Delta G = \Delta G_b$, equals $W_a - W_c$ (work of adhesion minus work of cohesion). This allows determination of γ_s^{LW} from eq 4, because no acid–base interactions are present at the interface.

(iii) The penetrating liquid (water or formamide) does not completely spread onto the solid surface. A duplex film of the liquid is formed on the surface (for example by adsorption of the vapor) before the liquid penetration. Now the free energy change in eq 5, $\Delta G = \Delta G_p$, is not equal to $W_a - W_c = W_s$.

(iv) The same liquid as in case iii, but the thin layer of the investigated solid (the strip) was not equilibrated with the saturated vapor of the liquid. Then in eq 5 $\Delta G = \Delta G_b$.

It was found^{13,14} that the energy difference between (iii) and (iv) equals the difference between the work of adhesion and the work of cohesion; $\Delta G_b - \Delta G_p = W_a - W_c = W_s$.

Having determined ΔG_b and ΔG_p for water and formamide, it is possible to solve simultaneously two equations (4) and thus determine the polar components of the solid surface free energy.

As an example in Figures 1–3 are presented the $x^2 = f(t)$ relationships for the leacril strips with preadsorbed tannic acid from 10^{-3} M solutions for both bare and precontacted with vapors of n -decane, water, and formamide. In some cases they are shifted a bit from the origin of the axes, which is due to the moment of the liquid contact with the strip. This, however, does not influence the calculated results, as the difference of Δx^2 and Δt is used for the calculations. As mentioned in the Introduction, still some doubts exist as to the formulation and determination of the free energy components. The used values of surface tension components of probe liquids suggested by van Oss et al.⁴¹ usually lead to high values of the electron donor component γ^- and low values of electron acceptor component γ^+ . As suggested by Lee²¹ values of γ^- and γ^+ for water should give at least a decreased values for the electron donor interactions. To examine this problem, we have calculated the surface free energy components for leacril surface applying both sets of the surface tension components of probe liquids. The surface tension components of the probe liquids are listed in Tables 1 and 2, respectively, and the surface free energy components of leacril bare and treated with tannic acid are shown in Table 3. It can be seen that the apolar Lifshitz–van der Waals interaction, γ_s^{LW} , increases slightly after the surface treatment with 10^{-5} – 10^{-3} M solutions, from 43.4 (untreated surface) to 51.2 mJ/m², but the component does not change after treatment in this concentration range. When the surface was equilibrated with 10^{-2} M solution,

(34) Goring, D. A. I.; Mason, S. G. *Can. J. Res.* **1950**, 28 (B), 307.

(35) Biefer, G. J.; Mason, S. G. *Trans. Faraday Soc.* **1959**, 55, 1239.

(36) Chang, M. Y.; Robertson, A. A. *Can. J. Chem. Eng.* **1967**, 45, 66.

(37) Teli, M. D.; Prasad, N. M.; Vyas, U. V. *J. Appl. Polym. Sci.* **1993**, 50, 449.

(38) Lokhande, H. T.; Androsov, V. F.; Golovanov, E. N. *Indian J. Technol.* **1970**, 8, 89.

(39) Lokhande, H. T. *Colourage* **1970**, 11, 11.

(40) Madan, G. L.; Shrivastava, S. K. *Colloid Polym. Sci.* **1977**, 255, 269.

(41) van Oss, C. J.; Good, R. J. *J. Macromol. Sci. Chem.* **1989**, A26, 1183.

(42) Adamson, A. W. *Physical Chemistry of Surfaces*, 4th ed.; Wiley: New York, 1982.

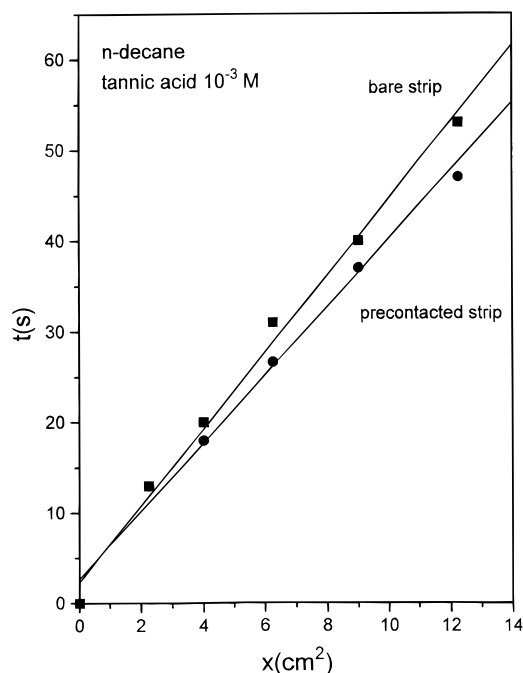


Figure 1. Penetration times of *n*-decane into the strips of untreated leacril (bare) and equilibrated with decane vapor (precontacted strip) versus squared the penetrated distances.

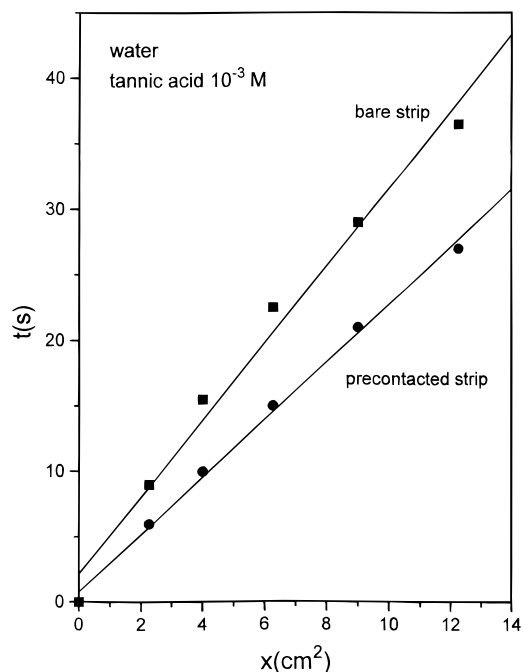


Figure 2. Penetration times of water into the strips of untreated leacril (bare) and equilibrated with water vapor (precontacted strip) versus squared penetrated distances.

the component increases up to 66.9 mJ/m². Now, on analysis of the electron acceptor component, γ_s^+ (Table 3), its values are practically zero from van Oss' data both for bare surface and with adsorbed tannic acid solutions from 10⁻⁵ to 10⁻³ M. However, it becomes significant (28.5 mJ/m²) if the surface was contacted with 10⁻² M solution. The changes of the electron donor component, γ_s^- (Table 3), are more complicated. At the lowest concentration of tannic acid (10⁻⁵ M) the component is practically the same as for the untreated surface (Table 3), but the surface treated with higher tannic acid concentrations becomes less electron-donating. As for the γ_s^- component obtained

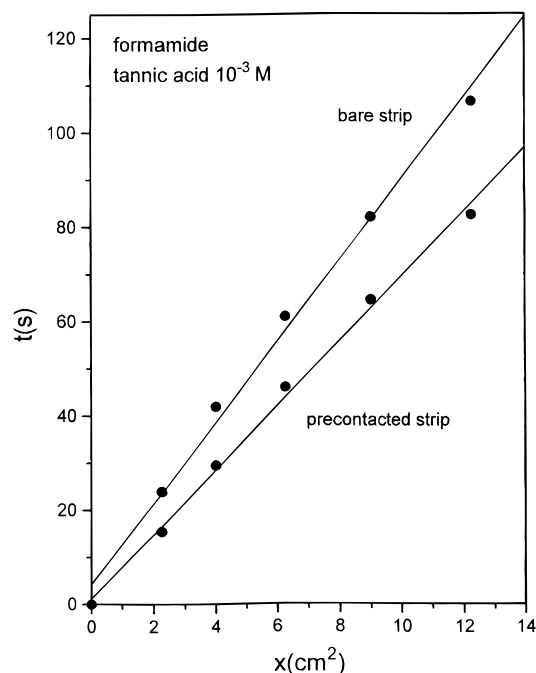


Figure 3. Penetration times of formamide into the strips of untreated leacril (bare) and equilibrated with formamide vapor (precontacted strip) versus squared penetrated distances.

Table 1. Surface Tensions, γ_1 , of the Probe Liquids and Their Components, Apolar Lifshitz–van der Waals, γ^{LW} , Electron Acceptor, γ^+ , and Electron Donor, γ^- , in mJ/m², According to van Oss et al.⁴¹

liquid	γ_1	γ^{LW}	γ^+	γ^-
<i>n</i> -decanane	23.9	23.9	0.0	0.0
water	72.8	21.8	25.5	25.5
formamide	58	39.0	2.28	39.6

Table 2. Surface Tensions, γ_1 , of the Probe Liquids and Their Components, Apolar Lifshitz–van der Waals, γ^{LW} , Electron Acceptor, γ^+ , and Electron Donor, γ^- , in mJ/m², According to Lee²¹

liquid	γ_1	γ^{LW}	γ^+	γ^-
<i>n</i> -dodecane	23.9	23.9	0.0	0.0
water	72.8	21.8	34.2	19.0
formamide	58	39.0	3.1	29.1

with Lee's²¹ data (Table 3), the values are lower, as predicted, but here an increase in this component is observed at the highest concentration of tannic acid (10⁻² M). By use of the data of Lee, the calculated electron acceptor components, γ_s^+ , have increased a bit, but still they are low and actually within standard error of the experiment. Using Lee's data the calculated electron acceptor component is still low and electron donor high. So, it is difficult to state undoubtedly which values are the more real ones.

To learn about hydrophobicity of the surface, the work of spreading for water was calculated using both sets of the components (Table 3). Theoretically the values should be the same, regardless of which set of the surface tension components of the probe liquids was taken for the calculations. This is because the values of surface tension components are based on the same value of water acid–base interaction $\gamma_1^{AB} = 51$ mJ/m². The minor differences in the work of spreading that appeared (Table 3) show that the surface tension components of formamide and water given by van Oss and those recalculated by Lee are not fully compatible. Then, they produce some differences in the leacril surface free energy components and, in

Table 3. Surface Free Energy Components of Leacril Surface, Untreated and Tannic Acid Treated, Calculated Using the Surface Tension Components of the Probe Liquids According to van Oss et al. (Table 1) and Lee (Table 2), and Respective Values of the Work of Spreading of Water on the Leacril Surface, in mJ/m²

concentration of tannic acid, M	γ_s^{LW}	γ_s^{+a} (van Oss ⁴¹)	γ_s^{-a} (van Oss ⁴¹)	γ_s^{+b} (Lee ²¹)	γ_s^{-b} (Lee ²¹)	W_s (van Oss ⁴¹)	W_s (Lee ²¹)
0 (ref 19)	43.3	0.00	60.5	0.20	45.5	-5.6	-1.4
10 ⁻⁵	51.2	0.66	62.2	0.87	46.6	9.1	9.2
10 ⁻⁴	51.2	0.00	48.5	0.19	35.4	-8.5	-5.4
10 ⁻³	51.2	0.00	12.0	0.04	9.3	-43.8	-41.4
10 ⁻²	66.9	28.5	10.8	0.50	45.6	17.9	15.9

^a The values of surface tension components of probe liquids from Table 1. ^b The values of surface tension components of probe liquids from Table 2.

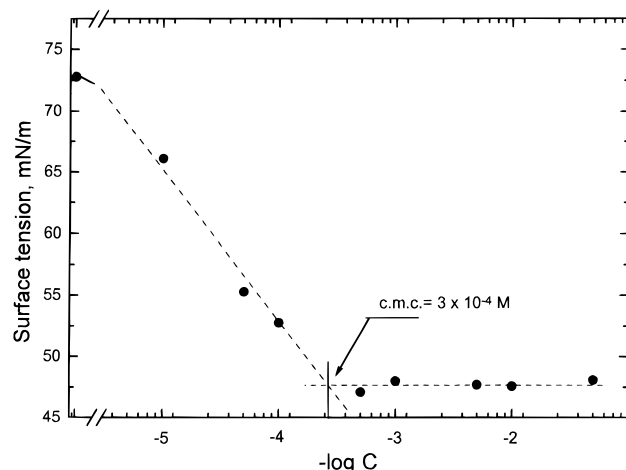


Figure 4. Surface tension of the tannic acid solutions against its concentrations.

consequence, in the calculated work of spreading. Some interesting conclusions can be drawn from the work of spreading values. The work for the bare surface of leacril is a small negative. This means, that a water droplet will not fully spread on its surface. Thus, the surface is slightly hydrophobic. After equilibration with 10⁻⁵ M tannic acid, it becomes low hydrophilic (Table 3, positive work of spreading). With increasing concentration of tannic acid (10⁻⁴ and 10⁻³ M) it becomes increasingly hydrophobic, and finally when equilibrated with 10⁻² M tannic acid, the surface converts to hydrophilic. To explain such behavior, determination of cmc for tannic acid could be helpful. The cmc was determined from surface tension measurements of its solutions. The results are shown in Figure 4, from which results show that cmc of tannic acid lies at ca. 3×10^{-4} M solution. Taking this into account, the changes in the hydrophobicity of tannic acid treated leacril can be explained as follows. At low concentration (10⁻⁵ M) only a few molecules of tannic acid are adsorbed on the leacril surface (see Figure 6), probably by hydrogen bonding between phenolic hydroxy groups of the acid and sulfonate and sulfate end groups of leacril, as well electrostatic interaction. The molecules may lie flat. With this, more polar hydrogen bonding interactions appear on the surface, and the surface becomes slightly hydrophilic. When the concentration of tannic acid increases, there is less and less room for the adsorbed molecules and they have to pack, probably, with polar groups directed toward the leacril surface. This leads to increasing hydrophobization of the surface (10⁻⁴ and 10⁻³ M). However, at concentrations above 3×10^{-4} M micellization takes place, and on the surface premicelles and then micelles adsorb. It is possible to imagine that in the case of, say two-molecule premicelles, they have mutually saturated polar interactions thus giving rise to hydrophobicity of the leacril surface (Table 3, 10⁻³ M concen-

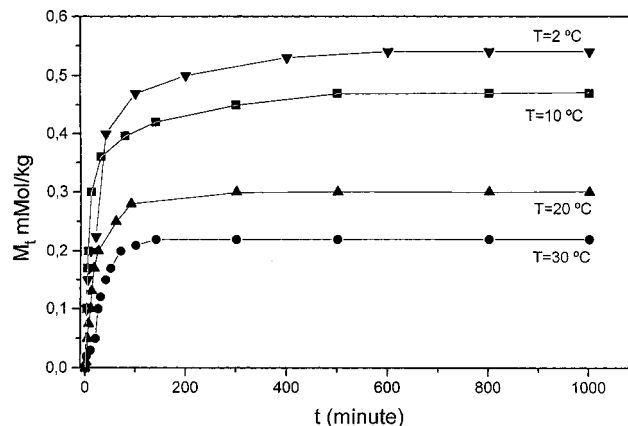


Figure 5. Adsorption kinetics of tannic acid on the leacril surface at different temperatures.

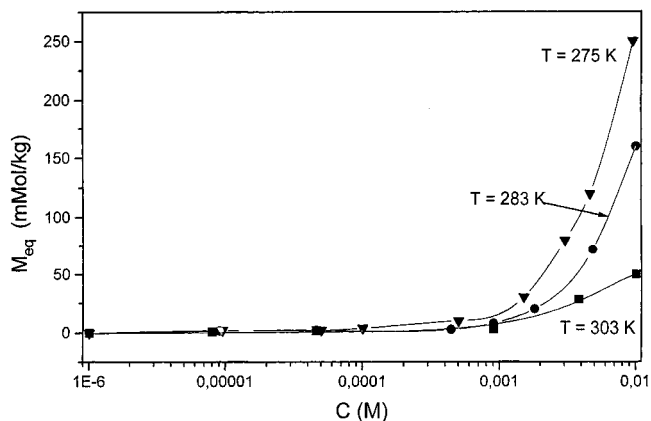


Figure 6. Adsorption isotherms of tannic acid on the leacril surface at 275, 283, and 303 K.

tration). However, when micelles are already formed and adsorbed on the surface, their polar phenolic -OH groups will interact with the leacril surface, as well as directed toward liquid phase (water), thus causing hydrophilization of the surface, which results from Table 3.

Thus, it seems that the changes of surface free energy components of leacril caused by the adsorbed tannic acid molecules can be explained with a help of cmc of tannic acid solutions. However, it is hardly possible to decide which set of the values are more real, those obtained from van Oss et al.'s⁴¹ or Lee's²¹ data. Actually, it is not so much important for considerations about hydrophobicity of the surface based on the work of spreading. More information can be obtained from the adsorption data.

3.2. Kinetic of Adsorption of Tannic Acid. First the adsorption kinetic of tannic acid on leacril surface from 5×10^{-5} M solution was studied at four temperatures, 275, 283, 293, and 303 K. The results of the measurements are presented in Figure 5. It is seen that even at the

Table 4. Equilibrium Adsorbed Amounts of Tannic Acid on Leacril M_{eq} (mmol/kg), Adsorption Rate Constant k (min^{-1}), Half-Time of the Adsorption τ (min), and Diffusion Coefficient D (cm^2/s)

T , K	k , min^{-1}	$\tau_{1/2} \times 10^{-3}$, min	M_{eq} , mmol/kg	$D \times 10^{-10}$, cm^2/s
275	50.39	13.75	0.54	5.39
283	44.92	15.43	0.47	4.34
293	31.73	21.84	0.30	2.64
303	30.60	22.65	0.22	1.14

highest temperature (30 °C) the adsorption process lasts no more than 100 min and is very fast. The adsorbed amounts of tannic acid decrease with increasing temperature (Figure 5), which points out that the adsorption is physical in nature. To better visualize the adsorption kinetics, the parameters describing the process are listed in Table 4. Because the shape of the curves of adsorption kinetic suggests a first-order process,⁴³ the rate constant can be determined from the following equation⁴⁴

$$M_t = M_{eq} (1 - e^{-kt}) \quad (6)$$

where M_t is the adsorbed amount of tannic acid on the leacril surface at time t , M_{eq} is equilibrium adsorbed amount, and k is the empirical rate constant. This equation has been solved numerically and thus obtained values of the rate constant are listed in Table 4 together with equilibrium amounts adsorbed, M_{eq} . Then, the half-adsorption times were calculated for particular temperatures, which for first-order processes are expressed as follows

$$\tau_{1/2} = \ln 2/k \quad (7)$$

which is independent of initial concentration of the adsorbate. These values are also placed in Table 4. Having determined the rate constant k , it is possible to calculate the activation energy of the adsorption process from an Arrhenius type equation⁴⁵

$$k = Ae^{-(E/RT)} \quad (8)$$

whose logarithmic form should be a linear dependence against $1/T$, and this appeared to be the case in the studied system. As can be seen from Table 4, the rate constant k decreases with the adsorption process temperature increase. From the slope, the activation energy can be estimated. It was found to be 13.63 kJ/mol.

Finally, Fick's equation may be applied to calculate the diffusion coefficient D at the cylindrical walls of the fibers.^{45,46}

$$\frac{M_t}{M_{eq}} = \frac{4}{\pi^{1/2}} \left(\frac{Dt}{a^2} \right)^{1/2} \quad (9)$$

For short periods of time, t , a is the fiber radius, which for this leacril was 1.5×10^{-3} cm. This equation is only exact for a constant concentration of the surfactant on the surface, whose condition is actually never fulfilled exactly. Nevertheless, the calculated values may be informative for the total insight into the adsorption process. From Table 4 results indicate that the apparent diffusion

coefficient decreases from 5.39×10^{-10} to 1.14×10^{-10} cm^2/s , if the temperature of adsorption increases from 275 to 303. This is obviously a consequence of the decreasing adsorption with the temperature increase (Figure 5, Table 4) and may be a result of higher thermal energy of tannic acid molecules in the solution. It is also possible to calculate the activation energy of diffusion, E^* , using again an equation of Arrhenius type.⁴⁵

$$D = D_0 e^{-(E^*/RT)} \quad (10)$$

Here D is the diffusion coefficient and D_0 is a factor that may be interpreted as the diffusion coefficient for the activation energy being zero. The slope of logarithmic form of this equation (which is linear against $1/T$) allows calculation of the energy. For the system studied, the calculated value is 38.13 kJ/mol. This value is about twice that estimated for the activation energy of the diffusion for *n*-cetylpyridinium chloride on leacril⁴⁷ and is much higher than that given above for the activation energy of this adsorption process (13.63 kJ/mol).

3.3. Thermodynamics of the Adsorption of Tannic Acid. The thermodynamic functions of the adsorption process can be calculated from the adsorption isotherms determined at different temperatures. The adsorption isotherms of tannic acid at 275, 283, and 303 K versus its equilibrium concentration in the range of 10^{-6} – 10^{-2} M are presented in Figure 6. Similarly as in the kinetic experiments the adsorption decreases with increasing temperature. The isotherms are concave and the adsorbed amount increases with the increase of equilibrium concentration. Up to 10^{-3} M the adsorption is small and then sharply increases. Contrary to the chemical in nature adsorption of *n*-cetylpyridinium chloride on leacril,⁴⁷ the adsorption of tannic acid, as was already mentioned above, is rather physical. To learn about the energetics of the adsorption process, the thermodynamic functions, ΔG , ΔH , and ΔS have been determined. The changes in standard free energy of adsorption ΔG° were determined assuming the ideal behavior of the solution

$$(\Delta G_a^\circ)_T = -RT \ln[(M_{eq}/V)/C] \quad (11)$$

and that the partition coefficient of the tannic acid between the solution and the fibers in equilibrium describes the equation

$$K = (M_{eq}/V)/C \quad (12)$$

where V is the volume term (here $1 \text{ dm}^3/\text{kg}$)^{45,48} and the standard state for the surfactant on the fibers was assumed as activity of 1 mol/dm^3 . Thus determined changes of the standard free energy against equilibrium concentration of tannic acid are plotted in Figure 7. In all studied temperatures the free energy changes are negative. The lower the temperature of adsorption, the higher the energy is. It is very characteristic that at 303 K the changes reach a maximum for ca. 25 mmol adsorption and then decrease. But at 275 and 283 K the changes reach a plateau at about 50 mmol of adsorbed tannic acid. Because the adsorption is physical, the decrease in the adsorption free energy seen at 303 K may result from increasing thermal energy of the molecules, which compete with physical interactions (dispersion forces, hydrogen bonding and electrostatic interactions) of the molecules with a

(43) Ander, P.; Sonessa, A. P. *Principles of Chemistry*; Macmillan: New York, 1965.

(44) Peters, R. H. *Textile Chemistry*; Elsevier: Amsterdam, 1975; Vol. III.

(45) Alberghina, G.; Longo, M. L.; Torre, M. *Dyes Pigm.* **1983**, 4, 49.

(46) Crank, J. *The Mathematics of Diffusion*; Clarendon Press: Oxford, 1956.

(47) Espinosa-Jiménez, M.; Giménez-Martín, A.; Ontiveros-Ortega, A. *Textile Res.* **1997**, 67.

(48) Dai, M. *J. Colloid Interface Sci.* **1994**, 164, 223.

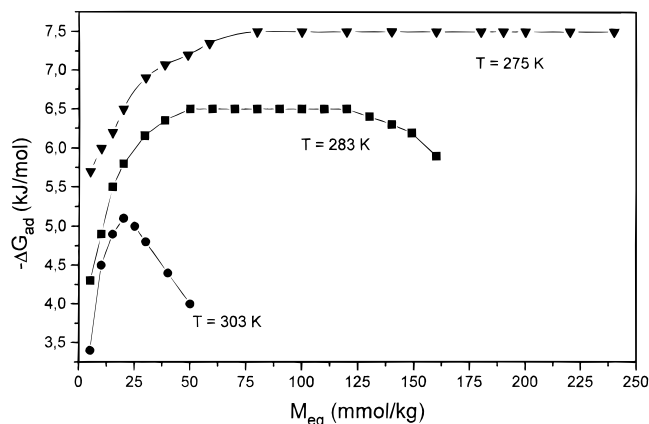


Figure 7. Standard free energy of adsorption of tannic acid on the leacril surface as a function of the equilibrium adsorption at three different temperatures.

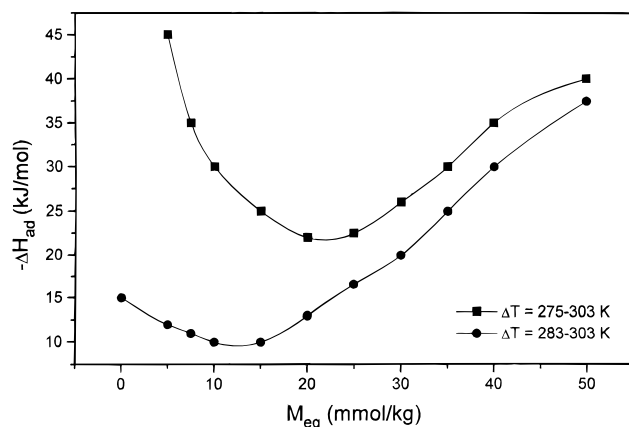


Figure 8. Calculated enthalpy of tannic acid adsorption on the leacril surface as a function of the equilibrium adsorbed amounts in the temperature intervals 275–303 and 283–303 K.

leacril surface. Because at the beginning of adsorption process the free energy increases, it seems that also lateral interactions between the adsorbed molecules play here a role and the observed plateau may result from the adsorption of the micelles, which is not the case at 303 K.

From the adsorption isotherms determined in the three temperatures (Figure 6) it is also possible to determine the enthalpy of adsorption (partial molar heat of adsorption) using the Clausius–Clapeyron equation, whose integrated form reads

$$\Delta H_a^\circ = \frac{T_1 T_2}{T_1 - T_2} R(\ln C_2 - \ln C_1) \quad (13)$$

For the calculations an assumption has been made that the heat of dilution can be neglected as small in comparison to the total heat of the process. The results of the calculations are presented in Figure 8 for two ranges of the temperatures, 275–303 and 283–303. The heat of adsorption is negative, so the adsorption process is exothermic. The decrease in the heat of adsorption with increasing coverage of the leacril surface with tannic acid molecules up to 15–20 mmol/kg coverage seems to be obvious. But the increase for the higher adsorbed amounts may be due to the micelles formation on the surface and, thus, increasing lateral interactions. The entropy changes resulting from the tannic acid adsorption were also evaluated from a well-known phenomenological thermodynamic relationship

$$\Delta S_a^\circ = \frac{R(T_1 \ln C_1 - T_2 \ln C_2)}{T_2 - T_1} \quad (14)$$

The resulting changes versus equilibrium adsorbed amounts of tannic acid are presented in Figure 9. In the temperature interval 283–303 K for low the surface coverage the entropy of adsorption is positive, which means that the adsorbed molecules possess a freedom on the leacril surface. When the adsorption increases, the molecules become more ordered and the entropy changes are negative. The changes are in accordance with the above conclusions as to the leacril surface hydrophobicity (changes in surface free energy components) in connection with the molecules ordering on the surface and the micelle formation.

3.4. Zeta Potential. To evaluate possible electrostatic interaction, determinations of the zeta potential were conducted by means of a streaming potential method. As was discussed in the Experimental Section, three models of the capillary bundles^{34–36} were considered, and it seems to us that the most appropriate one is that of Goring and Mason. The zeta potentials as a function of tannic acid concentration applying all three models are plotted in Figure 10. It is seen that the zeta potentials are small negative, but the absolute values drop practically to zero when the concentration is higher than 10^{-4} M. In our previous paper³³ we found that the hydrogen and hydroxyl ions are potential determining for the leacril surface and the isoelectric point occurred at pH = 2.2. The decrease in zeta potentials in tannic acid solutions with its increasing concentration may be explained by adsorption of tannic acid molecules whose polar groups are partially dissociated, thus possessing positive charge. Any way, from the results presented in Figure 10 it can be concluded that the electrostatic interaction plays a minor role in the adsorption process of tannic acid and total interfacial interactions, because the zeta potentials are low. It may be postulated that apolar Lifshitz–van der Waals and polar Lewis acid–base interactions are the dominant ones.

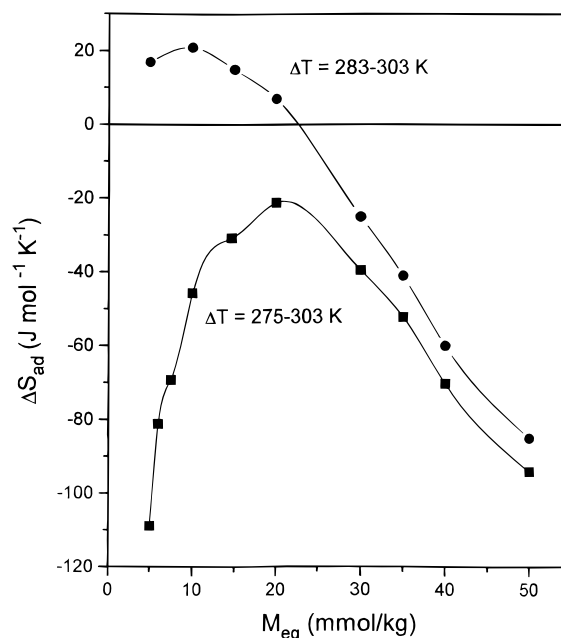


Figure 9. Changes of the entropy in the adsorption process of tannic acid as calculated for the temperatures intervals 283–303 and 275–303 K.

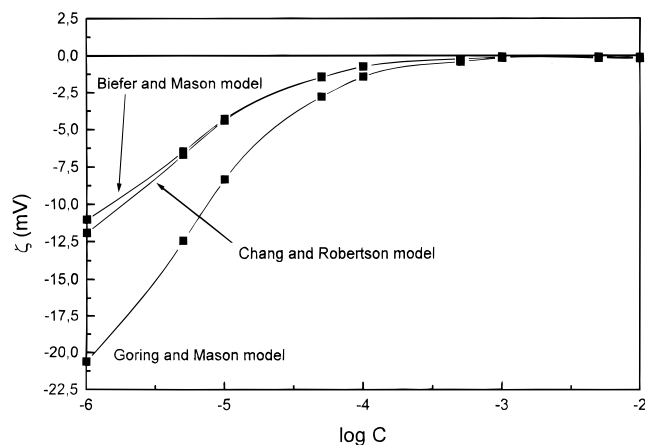


Figure 10. Changes of zeta potential of leacril in tannic acid solutions calculated with a help of three different models of the capillary bundles.

5. Conclusions

On the basis of the results obtained, the following may be concluded:

A bare leacril surface is nearly hydrophobic with relatively strong electron donor interaction and practically no electron acceptor interaction. Adsorption of tannic acid on the surface causes changes of the surface character. At low concentrations it makes the surface slightly hydrophilic, probably because more polar groups originating from tannic acid molecules are present on the surface. However, with increasing concentration of the tannic acid the electron donor character of the surface significantly decreases and, as a consequence, the surface becomes hydrophobic, especially in the range of premicelle formation. When the tannic acid micelles are adsorbed, the

surface converts again to hydrophilic, because the polar heads of the micelles are directed toward water phase.

The adsorption is physical in nature and the process is very fast. The half-time of the adsorption from 5×10^{-5} M solution is within a second and the equilibrium is reached within ca. 100 min. The thermodynamic functions show that the process is exothermic and at low the surface coverage the molecules are probably not strongly bonded. With increasing coverage and decreasing temperature of the adsorption, the adsorbed molecules are more ordered and decrease in the entropy points that the micelles are present on the surface. This reflects in the determined surface free energy components.

Zeta potentials show that electrostatic interaction may play a role only at low concentrations of tannic acid in the solution. With increasing concentration the absolute value of the zeta potential decreases very fast to zero and the adsorption is governed by hydrogen bonding and Lifshitz–van der Waals interactions.

At present it is difficult to decide which approach to the electron donor and electron acceptor components of water (of van Oss or Lee) gives more real results of the surface free energy components of the solid. Obviously, both approaches allow calculation of correct values of the work of spreading of water on bare and tannic acid treated surfaces of leacril.

6. Acknowledgments

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