Modification of the Wettability of a Polymeric Substrate by pH Effect. Determination of the Surface Acid Dissociation Constant by Contact Angle Measurements

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The wetting properties of a substrate can be changed by chemical reaction. Here, we studied simple materials with acid−base properties, by preparing poly(vinyl chloride) films containing lauric acid. These substrates constitute simple polymeric surfaces the wettability of which can be easily controlled by the acid−base equilibrium. The roughness of the material was then varied by adding Aerosil (hydrophobic fumed silica). We then studied the wettability of these materials toward aqueous buffer solutions between pH 2 and 12 from contact angle measurements. The variation of the contact angle of a droplet of buffer solution with the pH of the solution was described by a simple thermodynamic model requiring only two parameters. Thus, we could characterize the acid polymer by an effective surface acid dissociation constant the value of which was consistent with those obtained with a similar surface. We showed that the behavior of any substrate could be described even if the surface geometry was not well-known.

Introduction

Controlling the wettability of a substrate is essential in many industrial fields, such as paint, inks, or material protection agents. Many applications require either totally wetting surfaces or totally nonwetting surfaces, such as those obtained through fractal dimensional surfaces. Certain studies[1−3] have sought to control wettability by applying an electrical potential to a droplet of solution placed on a solid surface. However, functionalizing the surface with chemical groups is an efficient method for controlling wettability, as the chemical groups can react with other reagents present in the aqueous solution in contact with the surface. Depending on the nature of the fixed groups[4] or the adsorbed molecules[5] and on the reagents, wetting or nonwetting surfaces can be created.[6]

Although the phenomenon of wettability is well-known, studying its thermodynamics presents certain theoretical problems because most of the usual relationships require a perfect knowledge of the geometry of the support. Thus, most studies define the surfaces as either a plane with a controlled roughness[7] or even as fractal.

We have considered this problem from a different point of view by assuming that usual materials can have changeable wettabilities without having ideally constituted surfaces. Initially, we sought to obtain simple materials having controllable wettabilities. Thus, we deposited on a previously silanized glass slide a PVC film containing a given concentration of lauric acid. We then modulated the roughness of the material by adding variable amounts of Aerosil. We studied the wettability of these materials toward aqueous buffer solutions between pH 2 and 12 using contact angle measurements.

We then considered using classic thermodynamics relationships to describe the behavior of these polymer surfaces of which the geometrical borders are not clearly defined. This expands on a previous study[8] on the possibility of using thermodynamic approaches to describe the behavior of complex media of which the geometrical borders are unknown (bicontinuous, porous, dispersed media).

I. Experimental Section

I-1. Materials and Methods. Polymer films were made from very high molecular weight (1 500 000 g mol^{-1}) poly(vinyl chloride) (PVC) (Janssen Chimica). Lauric acid ($C_{12}H_{24}O_2$, 99%) and NH_4F (40% in water) were from Fluka, and toluene (99.5%), methanol (99.8%), and tetrahydrofuran (THF, 99.9%) were from Acros Organics. Dimethyldichlorosilane (DMDCS, 5% in toluene) was from Supelco. Silanized Aerosil R812, a gift from Degussa, was used as received.

The buffer solutions were prepared from a solution of a mixture of acids (HCl, CH_3COOH, NaH_2PO_4, NH_4Cl) at equal concentrations (10^{-2} mol L^{-1}) in water with KCl (0.1 mol L^{-1}) to fix the ionic strength of the medium. The pH of these buffer solutions was adjusted by adding aqueous sodium hydroxide solution (NaOH, 1 mol L^{-1}). The pH was measured with a millivoltmeter (Radiometer Analytical, PHM 250) using a pH glass-electrode (XG100, Radiometer-Analytical) combined with a KCl-saturated calomel reference electrode.

I-2. Contact Angles Measurement. Contact angles were measured with a DSA10 (Krüss instrument) using a CCD video camera and a horizontal light source to illuminate the liquid droplet. The droplets of solution were placed on the surface under an optical vessel to

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[1] Bateni, A.; Susnar, S. S.; Amirfazli, A.; Neumann, A. W. *Langmuir* **2004**, *20*, 7589.

[2] Bateni, A.; Laughton, S.; Tavana, H.; Susnar, S. S.; Amirfazli, A.; Neumann, A. W. *J. Colloid Interface Sci.* **2005**, *283*, 215.

[3] Lin, J. L.; Lee, G. B.; Chang, Y. H.; Lien, K. Y. *Langmuir* **2006**, *22*, 484.

[4] Holmes-Farley, S. R.; Bain, C. D.; Whitesides, G. M. *Langmuir* **1988**, *4*, 921.

[5] Bain, C. D.; Whitesides, G. M. *Langmuir* **1989**, *5*, 1370.

[6] Jiang, Y.; Wang, Z.; Yu, X.; Shi, F.; Xu, H.; Zhang, X. *Langmuir* **2005**, *21*, 1986.

[7] Jopp, J.; Grüll, H.; Yerushalmi-Rozen, R. *Langmuir* **2004**, *20*, 10015.

[8] Turmine, M.; Mayaffre, A.; Letellier, P. *J. Phys. Chem.* B **2004**, *108*, 18980.

10.1021/la061324p CCC: $33.50

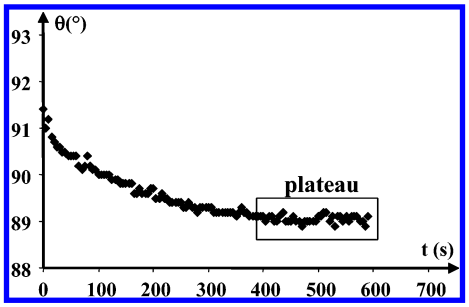

Figure 1. Variation of contact angle vs time of a droplet of buffer solution at pH 10.74 on a smooth PVC layer.

Table 1. Variation of Surface Tensions of Different Buffer Solutions with pH

pH	3.015	4.518	5.785	7.765	9.069	10.389
γ (mN m^{-1})	72.18	72.36	72.58	72.355	72.19	71.36

minimize evaporation. The entire system was located in a thermostated chamber at 25.0 ± 0.5 °C. The moisture in the environment around the sample was kept constant by filling the wells in the sample chamber with distilled water. Four different surfaces were prepared in the same way at the same time and were used to acquire contact angle data. We verified the reproducibility of the measurement by placing small droplets of solution (1.5 μL) at a given pH on four different samples. We also checked the uniformity of the surface by placing droplets of solution at the same pH at different points on the surface. We measured the contact angles over at least several minutes and took the value corresponding to the most stable value of the angle. Each point represents an average of at least four measurements. For contact angles greater than 60°, most of the measurements were within ±1° of the reported value. For contact angle of less than 60°, the errors were ±3° (contact angles less 10° did not give accurate measurements). Figure 1 shows the variation of the contact angle over time of sessile droplet of buffer solution at pH 10.74 on a pure PVC surface. Equilibrium was not obtained until after 5−7 min. We recorded the average of the angle on the right and left sides for the four drops.

Some studies[9] have claimed that the size of the droplet influences the measure contact angle. Thus, on all the studied substrates, we checked that the contact angle did not vary significantly as the volume of the drop varied between 0.5 and 4 μL.

I-3. Interfacial Tensions. The same equipment for measuring the contact angle also allows the liquid−vapor surface tension, γ^{LV}, of the buffer solution to be measured using the pendant drop method (Table 1). The drop is formed inside a small optical vessel covered by a layer of Parafilm to avoid evaporation as much as possible. The measurements were recorded for 15 min and gave a value of 72.2 ± 0.4 mN m^{-1}, which was in good agreement with the literature value of 72.8 mN m^{-1} at 25 °C.

I-4. Preparation of PVC Films. All polymer films were prepared on silanized glass. The glass samples were commercial microscope slides (22 × 32 mm^2, Menzel France). The glass was silanized to make it hydrophobic to aid adhesion of the PVC layer. All the glass surfaces were immersed in 40% aqueous NH_4F solution for 3 min and then washed with water before being silanized by immersion in a DMDCS solution for 5 min. The slides were then immersed in a toluene solution to eliminate excess DMDCS, washed with methanol, and left to dry under cover at ambient conditions.

I-5. Smooth Polymers. Silanized glass slides were covered with 400 μL of a solution containing 0.1 g of PVC and differing amounts of lauric acid in 20 mL of THF and were left to dry for 2 h. The obtained films were perfectly fixed on the glass surface and are referred to as smooth polymers in this paper.

I-6. Rough Polymers. We obtained rough surfaces by adding varying amounts of Aerosil (small spheres of silanized silica) to the previous preparation. The Aerosil creates and amplifies any irregularities on the smooth polymers. The concentrations of lauric acid and Aerosil are expressed as a ratio of grams/grams of PVC. The regular spreading of the mixture was obtained in a way similar to the previous one.

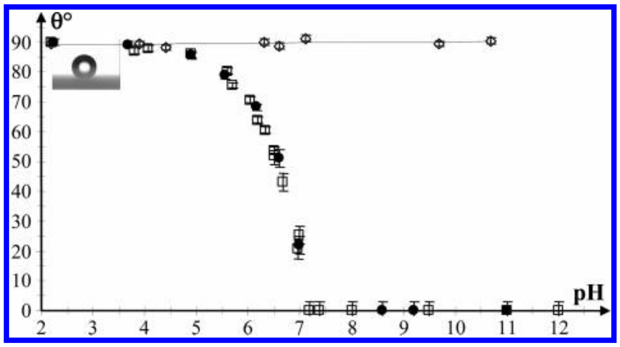

Figure 2. Variation of contact angle of buffer aqueous solutions vs pH for pure, smooth PVC films (open diamonds) and for smooth PVC films containing lauric acid at 0.20 g/g PVC (open squares) and at 0.27 g/g PVC (black circles).

II. Results

The preparation of the substrates gave, in almost all the cases, uniform surfaces the reproducibility of which was checked by the contact angle measurements. Reproducibility only became a problem for rough surfaces with an Aerosil concentration of 1 g/g PVC. However, we will present these results to demonstrate the limit of the technique used and also to show that the results from reproducible surfaces are consistent with the behavior observed with the other supports.

II-1. Smooth, Pure PVC. We first characterized the behavior of smooth, pure PVC toward droplets of solution at different pH. The contact angles were distributed randomly around a constant average value (89.6 ± 1°) indicating that the wettability of PVC is not affected by the acidity of the aqueous droplets in the studied pH range between 2 and 12. The obtained value is close to those published elsewhere.[10]

II-2. Smooth, Acidified PVC. We studied how the wettability of smooth PVC films varied for lauric acid concentrations of 0.2 and 0.27 g/g PVC. At concentrations of less than 0.17 g/g PVC, we could not obtain reproducible contact angles for a droplet of solution at neutral and high pH. It may be that the concentration of lauric acid in the polymer was not high enough and is not uniformly distributed at the surface. Thus, both wetting behavior and nonwetting behavior may occur at the surface depending on the position of the droplet. For concentrations higher than 0.30 g/g PVC, the lauric acid crystallized on the polymer surface. The variation of contact angle (θ) with pH is shown in Figure 2. Considering the precision in measurements, the superimposition of the two curves shows that once the concentration of lauric acid is sufficient to give a uniform surface the relationship between contact angle and droplet pH becomes independent of lauric acid concentration. For the most acidic droplets, the contact angle is very close to that of pure PVC ($\theta = 88.4 \pm 1°$). Thus, the presence of lauric acid molecules on the surface does not markedly change the wettability of the substrate. However, for basic droplets, we observed a strong variation in the wettability of the surface. This transition occurs at a pH of between 2 and 3 and has been observed on other substrates.[4,5,11−17]

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(9) Drelich, J.; Miller, J. D.; Hupka, J. *J. Colloid Interface Sci.* **1993**, *155*, 379.

(10) Della Volpe, C.; Siboni, S. *J. Colloid Interface Sci.* **1997**, *195*, 121.

(11) Wamser, C. C.; Gilbert, M. I. *Langmuir* **1992**, *8*, 1608.

(12) Creager, S. E.; Clarke, J. *Langmuir* **1994**, *10*, 3675.

(13) Holmes-Farley, S. R.; Reamey, R. H.; McCarthy, T. J.; Deutch, J.; Whitesides, G. M. *Langmuir* **1985**, *1*, 725.

(14) Lee, T. R.; Carrey, R. I.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 741.

(15) Cheng, S. S.; Scherson, D. A.; Sukenik, C. N. *Langmuir* **1995**, *11*, 1190.

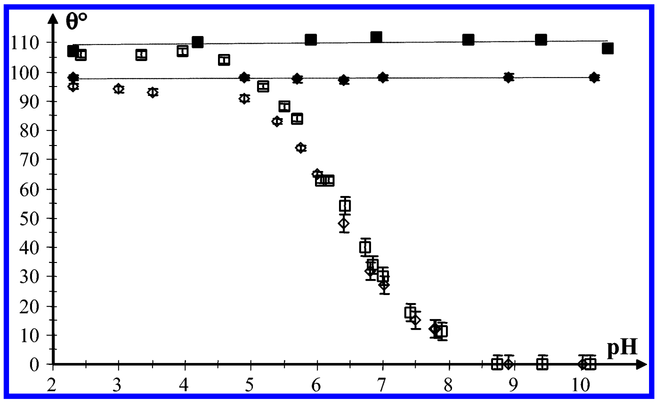

Figure 3. Variation of contact angle of buffer aqueous solutions vs pH for pure, rough PVC films containing 0.50 g Aerosil/g PVC (black diamond) or 0.64 g Aerosil/g PVC (black square) and for rough PVC films containing lauric acid at 0.27 g/g PVC and 0.50 g Aerosil/g PVC (open diamond) or 0.64 g Aerosil/g PVC (open square).

II-3. Rough PVC. As observed for the smooth PVC surface, the contact angle θ was independent of the pH of the droplet (see Figure 3), although the presence of Aerosil increased the nonwettability of the PVC film. The contact angle was 110 ± 1° for an Aerosil concentration of 0.64 g/g PVC and was 97.8 ± 1° for an Aerosil concentration of 0.50 g/g PVC. The origin of this wettability change must be discussed like the relevance of its attribution to the only roughness effect. In fact, this is a two-component system (PVC−Aerosil) whose chemical properties can be different than that of pure PVC. To answer this, Aerosil was first deposited on the silanized glass slides and covered with the PVC. In this configuration, one can suppose that the small glass spheres were perfectly covered with the polymer. The contact angle measured under this condition was similar to the previous one. Then, we will consider that the contact angle variations were mostly due to the roughness of the substrate.

II-4. Rough, Acidified PVC. We measured the contact angle of buffered aqueous solution droplets at different pH on rough PVC containing two concentrations of Aerosil and the same concentration of lauric acid (0.27 g/g PVC) (Figure 3). The curves were similar to those obtained with the smooth polymer. The incorporation of lauric acid slightly modifies the wettability of the rough PVC for acidic droplets. The contact angle decreased by 3° for the two lauric acid-containing PVC layers versus rough PVC without lauric acid. At basic pH, the surface is totally wetted.

III. Interpretation

The variation in the wettability of the support with the acidity of the sessile droplet can be linked to the ionization state of the carboxylic acid groups (AH) on the surface, σ, of the PVC. We presume that for acidic droplets the AH_σ groups are hydrophobic and confer a nonwetting character to the substrate, whereas for basic droplets the A_σ^- carboxylate groups are hydrophilic. Thus, for basic droplets, the surface density of carboxylate groups is sufficient for totally wetting surface. However, this is not the only phenomenon we need to consider, as the ionization state of carboxylic acid groups at the polymer surface and the surface geometry determine the value of the contact angle. Thus, we will first consider the behavior of a model, ideally smooth, composite surface made of polymer and acid.

III-1. Behavior of a Model, Ideally Smooth, Composite Surface. The species AH and A^- are confined within the polymer matrix, with some of these groups being located at the surface. Let us consider an ideally smooth PVC surface occupied by a total number, n_T^σ, of AH groups that are likely to be ionized into A^- groups according to the following interfacial equilibrium reaction:

$$AH_\sigma = A_\sigma^- + H_{aq}^+$$

This equilibrium is characterized by a surface acid dissociation constant, K_a^σ. The PVC is solid and is below its glass transition temperature ($T_g = 70$ °C), and thus, the lauric acid introduced into the film can be considered as being immobilized in both the polymer matrix and at the polymer surface. By convention, the presence of acidic or basic groups on the surface is characterized by the "surface excess", defined by

$$\frac{n_T^\sigma}{A} = \Gamma_T = \frac{n_{AH}^\sigma + n_{A^-}^\sigma}{A} = \Gamma_{AH} + \Gamma_{A^-} \qquad (1)$$

where n_i^σ is the number of moles of the species i at the polymer surface and A is the area of the polymer surface. The ionization state of the acid group at surface is characterized by its ionization rate:

$$\tau = \frac{\Gamma_{A^-}}{\Gamma_{AH}} \qquad (2)$$

For a smooth acidic surface, $\Gamma_T = \Gamma_{AH}$, and the contact angle $\theta = \theta_{a,S}$. Therefore, for a smooth basic surface, $\Gamma_T = \Gamma_{A^-}$ and $\theta = \theta_{b,S}$.

Young's relationship allows the different states of the surface to be formalized. As ionization of the substrate only occurs on the surface, A^{SL}, the solid−vapor interfacial tension can be considered as being independent of the ionization state of A^{SL}. Thus, this interfacial tension will be γ^{SV} for all droplet acidities. As shown in Table 1, all the aqueous solutions have the same surface tension, γ^{LV}. Then,

$$\gamma^{LV} \cos \theta_{a,S} = \gamma^{SV} - \gamma_a^{SL} \qquad (3)$$

$$\gamma^{LV} \cos \theta_{b,S} = \gamma^{SV} - \gamma_b^{SL} \qquad (3')$$

γ_a^{SL} and γ_b^{SL} are the solid−liquid interfacial tensions for the acidic and basic substrates, respectively. If we now consider an intermediate ionization state for which the contact angle is $\theta_{\tau,S}$, Young's relationship is now written as

$$\gamma^{LV} \cos \theta_{\tau,S} = \gamma^{SV} - \gamma_\tau^{SL} \qquad (4)$$

Thus, variations in the contact angle are linked to changes in the surface tension, γ_τ^{SL}. If we suppose that γ_τ^{SL} varies according to a simple composition rule with a surface fraction, x, being occupied by A_σ^-, then

$$\gamma_\tau^{SL} = (1 - x)\gamma_a^{SL} + x\gamma_b^{SL} \qquad (5)$$

Consistency between eqs 3−5 leads to the Cassie−Baxter relationship[18] that is classically used to describe the behavior of composite surfaces:

$$\cos \theta_{\tau,S} = (1 - x)\cos \theta_{a,S} + x \cos \theta_{b,S} \qquad (6)$$

The fraction, x, can be related to ionization rate, τ, as

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(16) Liu, Y. J.; Navasero, N. M.; Yu, H. Z. *Langmuir* **2004**, *20*, 4039.

(17) Barlett, P. N.; Grossel, M. C.; Barrios, E. M. *J. Electroanal. Chem.* **2000**, *487*, 142.

(18) Cassie, A. B. D.; Baxter, S. *Trans. Faraday Soc.* **1944**, *40*, 546.

$$x = \frac{\Gamma_{\mathrm{A}^-}}{\Gamma_{\mathrm{T}}} = \frac{\tau}{1-\tau} \tag{7}$$

Relations 6 and 7 allow the ionization rate to be expressed according to the contact angles

$$\tau = \frac{\cos\theta_{\mathrm{a,S}} - \cos\theta_{\tau,\mathrm{S}}}{\cos\theta_{\tau,\mathrm{S}} - \cos\theta_{\mathrm{b,S}}} \tag{8}$$

The relationship between the surface ionization rate of lauric acid and the drop in pH is obtained from the ionization equilibrium condition involving the electrochemical potentials of the various species involved in the reaction

$$\tilde{\mu}_{\mathrm{H}^+}{}^{\mathrm{aq}} + \tilde{\mu}_{\mathrm{A}^-}{}^{\sigma} - \mu_{\mathrm{AH}}{}^{\sigma} = 0 \tag{9}$$

Previously, we have shown[19] that at a constant temperature and pressure, the contribution of the charged species, i, of charge z_i, participating in the surface equilibrium may be written as

$$\tilde{\mu}_i = \mu_i{}^{\sigma} + \gamma^{\mathrm{SL}}A_i' + z_i F\phi^{\sigma} \tag{10}$$

where $\mu_i{}^{\sigma}$ is the chemical potential of i at the surface, ϕ^{σ} is the electric potential of the substrate, F the Faraday constant and A_i' is the partial surface area of i at the surface. This last term becomes significant for systems having interfaces with large areas or with strong curvatures, such as in dispersed media. On smooth supports, this contribution is negligible and thus will not be taken into account. The equilibrium condition is then written as

$$\mu_{\mathrm{H}^+}{}^{\mathrm{aq}} + \mu_{\mathrm{A}^-}{}^{\sigma} - \mu_{\mathrm{AH}}{}^{\sigma} + F(\phi^{\mathrm{aq}} - \phi^{\sigma}) = 0 \tag{11}$$

where ϕ^{aq} is the electric potential of the aqueous solution. The surface chemical potential can be written using an approach proposed by Defay[20] that takes into account the presence of the species at the surface by the surface excess variable. Thus, for species i, we can write

$$\mu_i{}^{\sigma} = \mu_i{}^{\sigma,\infty} + RT\ln\Gamma_i \tag{12}$$

where $\mu_i{}^{\sigma,\infty}$ is the standard chemical potential at a "null surface excess" for the species i and is thus a hypothetical state. The equilibrium condition is then expressed as

$$\mu_{\mathrm{H}^+}{}^{\mathrm{aq},\infty} + \mu_{\mathrm{A}^-}{}^{\sigma,\infty} - \mu_{\mathrm{AH}}{}^{\sigma,\infty} + \mathrm{RT}\ln(\tau a_{\mathrm{H}^+}) + \mathrm{F}(\phi^{\mathrm{aq}} - \phi^{\sigma}) = 0 \tag{13}$$

where a_{H^+} is the proton activity within the drop at an infinite molar dilution.

If the standard chemical potentials are constant

$$\Delta_{\mathrm{r}}G^{\infty} = \mu_{\mathrm{H}^+}{}^{\mathrm{aq},\infty} + \mu_{\mathrm{A}^-}{}^{\sigma,\infty} - \mu_{\mathrm{AH}}{}^{\sigma,\infty} = -2.3RT\log(K_{\mathrm{a}}{}^{\sigma}) = 2.3RT\,\mathrm{p}K_{\mathrm{a}}{}^{\sigma} \tag{14}$$

When the aqueous solutions are strongly ionic but independent of pH, the potential difference between the substrate and the solution is assumed to be weak and constant. Thus, the electrical term can be neglected or integrated into a constant term, K^{eff}, such that

$$\mathrm{p}K^{\mathrm{eff}} = \mathrm{p}K_{\mathrm{a}}{}^{\sigma} + \frac{F(\phi^{\mathrm{aq}} - \phi^{\sigma})}{2.3RT} \tag{15}$$

The ionization rate, τ, can then be linked to the pH of the solution by

$$\mathrm{pH} = \mathrm{p}K^{\mathrm{eff}} + \log\tau \tag{16}$$

Combining eqs 8 and 16, we obtain a relationship between the variation of $\cos\theta_{\tau,\mathrm{S}}$ and the pH of the solution:

$$\cos\theta_{\tau,\mathrm{S}} = \frac{10^{-\mathrm{pH}}\cos\theta_{\mathrm{a,S}} + 10^{-\mathrm{p}K^{\mathrm{eff}}}\cos\theta_{\mathrm{b,S}}}{10^{-\mathrm{pH}} + 10^{-\mathrm{p}K^{\mathrm{eff}}}} \tag{17}$$

III-2. Behavior of Real, Nonideally Smooth Surfaces. The previous discussion implies an "ideally smooth" behavior of the polymeric surface. We have adopted an approach similar to that proposed by Wenzel[21] to explain the deviation from this model behavior. Thus, we have introduced a deviation coefficient, r, for the polymer, such that

$$\cos\theta_{\mathrm{polymer}} = r\cos\theta_{\tau,\mathrm{S}} \tag{18}$$

where $\theta_{\mathrm{polymer}}$ is the measured angle. In Wenzel's approach, r is a roughness coefficient representing the ratio between the area of the real surface of the support and the area of an "ideally smooth" surface having the same geometrical borders. Thus, r is always greater than 1.

For polymers having very irregular surfaces, this notion of roughness has no sense, and also eq 18 cannot be determined because the only known parameter is the angle measured on the real polymer. This explains why we consider r to be a deviation coefficient to the hypothetical "ideally smooth" behavior of the polymer without considering a particular geometrical model of the surface. From this point of view, the measured angle is considered to be the angle on a model polymer corrected by the factor r.

If the irregularities on the surface are voluntarily increased, we must also consider the existence of a grid effect, in which the droplet of solution can be partially in contact with the air. The surface is then described as a statistical distribution of polymeric domains, sensitive to both the pH of the drop and to the air. We apply the Cassie−Baxter relationship to this new composite surface

$$\cos\theta = N\cos\theta_{\mathrm{polymer}} + (1-N)\cos\theta_{\mathrm{air}} \tag{19}$$

where N is the fraction of the surface occupied by the polymer. The domain relative to the air corresponds to complete non-wettability, that is, $\cos\theta_{\mathrm{air}} = -1$, leading to

$$\cos\theta = N(\cos\theta_{\mathrm{polymer}} + 1) - 1 \tag{20}$$

Equations 17, 18, and 20 lead to a very general relationship that takes into consideration both the grid effect and the deviation of the behavior of an ideally smooth polymer:

$$\cos\theta = N\left(r\frac{10^{-\mathrm{pH}}\cos\theta_{\mathrm{a,S}} + 10^{-\mathrm{p}K^{\mathrm{eff}}}\cos\theta_{\mathrm{b,S}}}{10^{-\mathrm{pH}} + 10^{-\mathrm{p}K^{\mathrm{eff}}}} + 1\right) - 1 \tag{21}$$

We tested the validity of this relationship that allows the behavior of a possibly very irregular, composite surface to be described

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[19] Lair, V.; Turmine, M.; Peyre, V.; Letellier, P. *Langmuir* **2003**, *19*, 10157.

[20] Sanfeld, A. *Entropie* **1990**, *153*, 73.

[21] Wenzel, R. A. *Ind. Eng. Chem.* **1936**, *28*, 988.

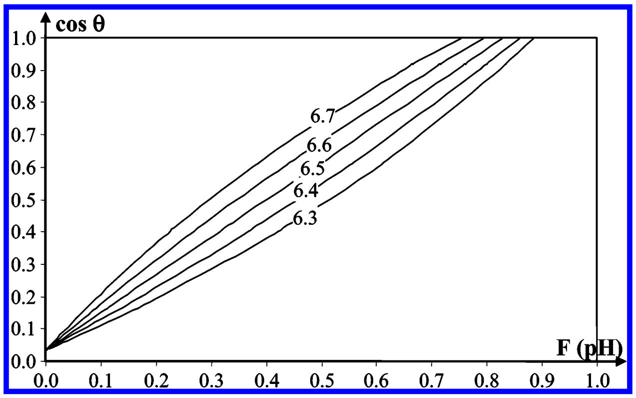

Figure 4. Plots of cos θ against F(pH) according to eq 22 for different pK^{eff} (the values are given on the curves).

by the parameters N and r, while referring to an ideally smooth model behavior.

IV. Discussion

First, we used the results obtained from the real smooth supports. For these supports, we assumed a negligible grid effect; thus, $N = 1$. Equation 21 can be written as

$$\cos\theta = r\cos\theta_{\mathrm{a,S}} + r(\cos\theta_{\mathrm{b,S}} - \cos\theta_{\mathrm{a,S}})\frac{10^{-\mathrm{p}K^{\mathrm{eff}}}}{10^{-\mathrm{pH}} + 10^{-\mathrm{p}K^{\mathrm{eff}}}} \tag{22}$$

If the proposed description is correct, cos θ must vary linearly with the function $10^{-\mathrm{p}K^{\mathrm{eff}}}/(10^{-\mathrm{pH}} + 10^{-\mathrm{p}K^{\mathrm{eff}}})$, which we will call F(pH). The data analysis consists of determining the value of pK^{eff}, if it exists, for which the correlation between cos θ and F(pH) gives the best linear relation. The maximum value of F(pH) obviously corresponds to a pH for which the surface becomes totally wetting. The values of the slope and the intercept of this straight line allow us to determine $r\cos\theta_{\mathrm{a,S}}$ and $r\cos\theta_{\mathrm{b,S}}$. The plots of cos θ against F(pH) for different pK^{eff} values are shown in Figure 4 and clearly show that pK^{eff} must be between 6.4 and 6.6.

From this, we determined that the best value of pK^{eff} was 6.50 ± 0.05, giving an excellent linear correlation with maximum standard deviation of ±2° on the experimental contact angle values. For the smooth polymer, we obtained $r\cos\theta_{\mathrm{a,S}} = 0.035$ and $r\cos\theta_{\mathrm{b,S}} = 1.196$. From this, we were unable to determine the values of $\theta_{\mathrm{a,S}}$ and $\theta_{\mathrm{b,S}}$. However, the minimum value of $\theta_{\mathrm{b,S}}$ was 0°, giving a minimum value of 1.196 for the coefficient r. For a value of r greater than 1, a $\theta_{\mathrm{a,S}}$ value greater than 90° would involve an increase in the contact angle measured with the acid solution. Thus, the angle $\theta_{\mathrm{a,S}}$ should lie between $88.32° \leq \theta_{\mathrm{a,S}} < 90°$ ($\theta_{\mathrm{a,S}}$ does not depend on r and thus an increase of $\theta_{\mathrm{a,S}}$ of 1° leads to $r = 2.949$ and $\theta_{\mathrm{b,S}} = 66.1°$, which does not appear very realistic). The "ideally smooth" model behavior of the acidified polymer is more conveniently defined if we assume $\theta_{\mathrm{b,S}} = 0°$, which gives a deviation coefficient of 1.196 and $\theta_{\mathrm{a,S}}$ of 88.32°.

The good fit between the experimental contact angles and the angles calculated from eq 22 using the above parameters vs pH is shown in Figure 5. We also show the ideal smooth polymer behavior ($r = 1$, $\theta_{\mathrm{b,S}} = 0°$, $\theta_{\mathrm{a,S}} = 88.3°$, p$K^{\mathrm{eff}} = 6.50$), which clearly shows that the wettability of the real surface is greater than the ideally smooth surface.

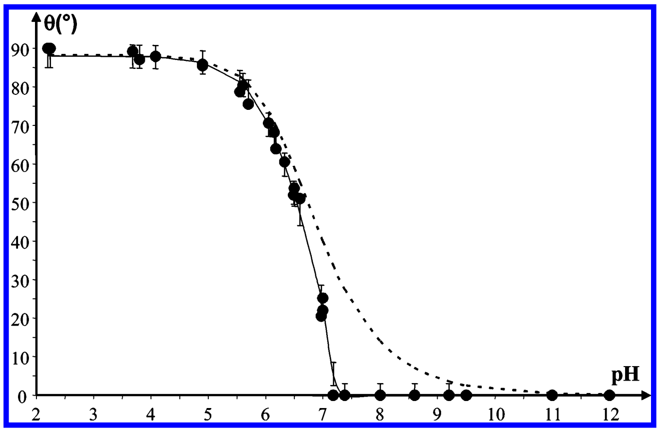

Figure 5. Experimental contact angle on smooth PVC vs pH. The solid line is the calculated contact angle from eq 22 with $r = 1.196$, $\theta_{\mathrm{a,S}} = 88.32°$, and $\theta_{\mathrm{b,S}} = 0°$; the dotted line is the calculated contact angle from the same equation with $r = 1$, $\theta_{\mathrm{a,S}} = 88.32°$, and $\theta_{\mathrm{b,S}} = 0°$.

Table 2. Variations of Contact Angles Calculated from Eq 22 for Different Roughness Factors, *r*

θ_{S} (deg)[a]	88	80	70	60	50	40	35	33.56
θ_{calc} (deg) r =1.23	87.5	77.7	65.1	52.0	37.8	19.6	0	0
θ_{calc} (deg) r =1.20	87.6	78.0	65.8	53.1	39.5	23.2	10.6	1.8
θ_{calc} (deg) r =1.17	87.7	78.3	66.4	54.2	41.2	26.3	16.6	13.0

[a] θ_{S} is the contact angle on an "ideally smooth" surface ($r = 1$).

The determined pK^{eff} is two units higher that the corresponding pK_{a} for carboxylic monoacids in aqueous solution. Certain authors[13,15,17] have suggested superficial stabilization of the acid form at the expense of the conjugated base. This can be explained by the greater difficulty of generating negative charges at the solid–liquid interface than in water.[4] The dielectric constant of the medium, which is lower than that of water, has also been suggested to disfavor the dissociation. Hydrogen-bond formation between carboxylic acid groups and carboxylate groups has also been suggested.[5] However, K^{eff} does not only depend on the acid nature but also on its environment. When the solvent is changed, the surface composition may change, leading to a change in the surface acid dissociation constant.

The analysis of the smooth polymer behavior showed that the Cassie–Baxter relationship is useful for describing the wettability of supports made of interpenetrated domains, such as those having acid–base couples present on the surface. Experimentally, being able to condition reproducibly the surface properties of slides prepared following a well-defined protocol, but without grafting, appears remarkable considering the simplicity of the technique.

We then characterized the obtained support using a reduced number of parameters: a surface pK_{a} and the deviation coefficient r. Although, this coefficient has no particular geometrical significance in our approach, it describes the imperfections of the prepared surface and its value probably depends on how the substrate was prepared. The observed distribution of contact angles of ±1°–3° about the average value for each series of droplets of solution of a given pH no doubt arises from r not being constant for different slides prepared in the same way. This variability will be less for contact angles close to 90°, whereas it becomes noticeable for angles corresponding to wetting substrates. This is consistent with the smaller distribution of about ±1° for angles greater than 50°.

This point is illustrated in Table 2, which shows how the calculated contact angles vary as r varies around the determined value ($r = 1.23$).

Table 2 shows that if r changes slightly between two substrates, there can be a large variation in the observed angle for angle values less than 50°.

We can now analyze the results of voluntarily "undulating" polymeric substrates using the behavior of the "ideally smooth"

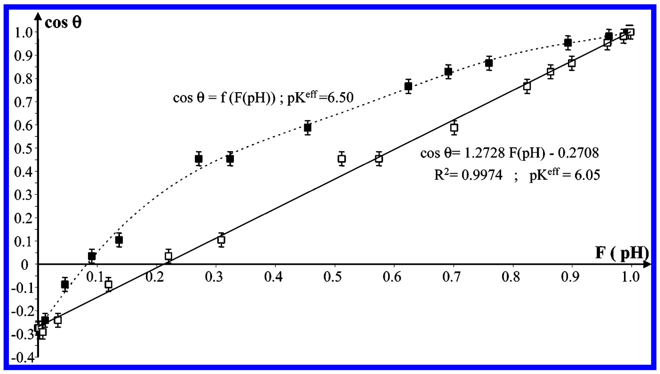

Figure 6. Contact angle variation with $F(\mathrm{pH}) = (10^{-\mathrm{p}K^{\mathrm{eff}}}/10^{-\mathrm{pH}} + 10^{-\mathrm{p}K^{\mathrm{eff}}})$ calculated with $\mathrm{p}K^{\mathrm{eff}} = 6.5$ (black squares and dashed line) and $\mathrm{p}K^{\mathrm{eff}} = 6.05$ (open squares and solid line).

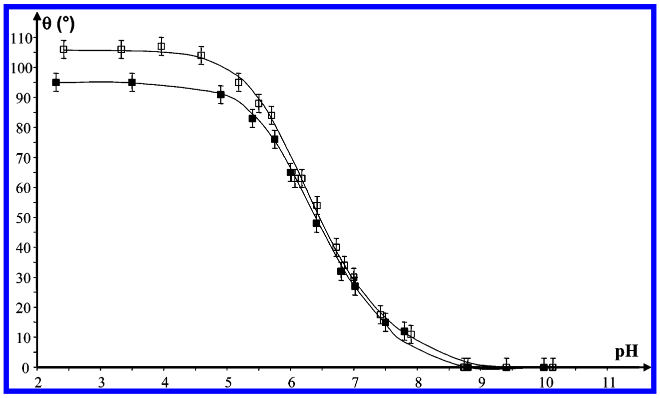

Figure 7. Variation of contact angle (θ) with the pH of the buffer aqueous solutions on a rough surface containing Aerosil at 0.5 g/g PVC (black squares) and 0.64 g/g PVC (open squares). Solid lines correspond to the calculated contact angles from eq 23 and parameters given in Table 3.

substrate as a reference and by considering a possible grid effect. Equation 22 can be written as

$$\cos\theta = [N(r\cos\theta_{\mathrm{a,S}} + 1) - 1] + Nr(\cos\theta_{\mathrm{b,S}} - \cos\theta_{\mathrm{a,S}})F(\mathrm{pH}) \quad (23)$$

As previously, this description of the wettability by this relationship assumes a linear correlation between cos θ and F(pH) for a given value of pK^{eff}. Values of the intercept and the slope then allow us to determine the values of N and of r.

As the contact angle begins to fall at a pH close to that of smooth surfaces, the determined value of pK^{eff} of 6.5 would seem appropriate. As seen for the substrate containing Aerosil at a concentration of 0.64 g/g PVC, the correlation obtained with this value (dashed line in Figure 6) is not linear. However, we obtained an excellent fit with a pK^{eff} value of 6.05 (Figure 6). This validates the analysis for "undulating" surfaces and show that the Aerosil slightly increases the surface acidity of lauric acid.

The excellent description of the wettability of these rough substrates depending on the pH of the sessile droplet solution was confirmed by comparing the calculated contact angles and experimental contact angles (Figure 7). The parameters used to calculate the curves are given in Table 3. Although the value of pK^{eff} was different from that for the substrate without Aerosil, its value is similar for the two lowest Aerosil concentrations. For rough polymers, we cannot neglect the surface energy term in the chemical potential as was done for the smooth polymers. In this case, the roughness directly influences the surface reactivity and may be responsible for the increase in the observed acidity.

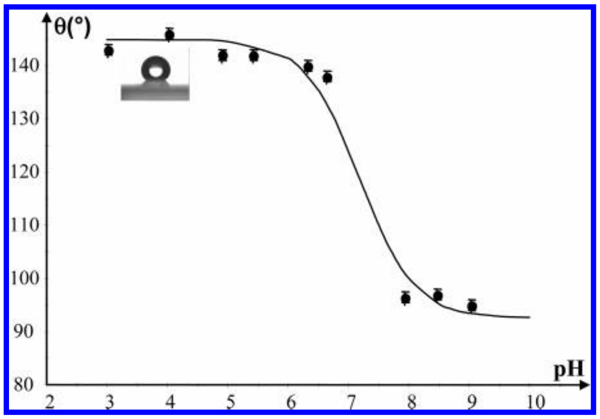

Figure 8. Variation of contact angle (θ) with the pH of the droplet on a rough surface containing Aerosil at 1 g/g PVC. The solid line corresponds to the calculated contact angle from eq 23 and the parameters given in Table 3.

Table 3. Values of the Parameters *N*, *r*, and p*K*$^{\mathrm{eff}}$ for Rough PVC Surfaces Containing Different Concentrations of Aerosil

Aerosil (g/g PVC)	$\theta_{\mathrm{a,S}}$°	$\theta_{\mathrm{b,S}}$°	N	r	pK^{eff}
0.5	88.3	0	0.88	1.28	6.10
0.64	88.3	0	0.69	1.90	6.05
1.0	88.3	0	0.16	5.0	7.3

The parameters for rough PVC surfaces containing Aerosil at 1 g/g PVC are given in Table 3 as an indication only because, unlike the other cases, the surface obtained under these conditions did not seem to be uniform. This surface behaved as either a totally wetting surface or a totally nonwetting surface toward a basic droplet of solution at different places on the same substrate. The limiting conditions for reproducible and uniform preparations of composite surfaces are near to this point for our conditioning technique. For example, the θ vs pH plot shown in Figure 8 and the curve calculated from the parameters given in Table 3 for this rough polymer surface show that the grid effect is starting to dominate.

In the other cases, the addition of Aerosil leads to reproducible and uniform rough surfaces that could be characterized by an acid dissociation constant and in which the behavior could be described from the parameters N and r. Variations in the Aerosil concentration modify both the surface fraction of polymer, N, in contact with the aqueous sessile droplet (this fraction decreases by about 14.5% when the Aerosil concentration increases by 0.1 g/g PVC) and the deviation coefficient, r, which increases with this concentration.

Conclusion

For applications, the "functionalized" surface preparation technique we propose allows materials to be simply prepared reproducibly and the wettability to be controlled by pH of the droplet. From different acid−base couples, we can prepare substrates for which the wettability varies from nonwetting to ultrawetting over a narrow range of pH (a range of about 1.5) around a value that can be fixed by the choice of the couple.

Adding Aerosil to the polymer can increase the hydrophobicity of the polymer substrate due to the "grid effect" without greatly affecting the acid dissociation constant.

During this work, we have shown that contact angle variations can be described from a very simple thermodynamic model and

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(22) Della Volpe, C.; Maniglio, D.; Morra, M.; Siboni, S. *Colloids Surf. A* **2002**, *206*, 47.

(23) Marmur, A. *Soft Matter* **2006**, *2*, 12.

that a nonideally smooth surface can also be described. We have also shown that an interfacial equilibrium between reactants and products confined in the PVC and other species in the aqueous solution in contact can be characterized by a thermodynamic constant. However, it should be noticed that the experimental conditions in which we operated do not guarantee that thermodynamic equilibrium is really achieved. In fact, as pointed out by one of the referees, simply expecting a certain time will not enable the meniscus to arrive by itself at an equilibrium state; the meniscus remains generally entrapped in a metastable minimum, which is one of the infinite advancing states.[22,23] Correctly describing the behavior of the system from the suggested model is facilitated by the very large variations of angles. In this framework, parameters *r* and *N* must be regarded as adjustable parameters.

This work is currently being continued with the aim of characterizing systems having a roughness as perfectly controlled as possible and of establishing a relationship between the parameters *r*, *N*, and the surface geometry.

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