Hydrophobization of Glass Surface by Adsorption of Poly(dimethylsiloxane)

Krastanka G. Marinova, Diana Christova, Slavka Tcholakova,
Evtim Efremov, and Nikolai D. Denkov*

*Laboratory of Chemical Physics & Engineering, Faculty of Chemistry, Sofia University,
1164 Sofia, Bulgaria*

Silica or glass particles are introduced in a poly(dimethylsiloxane) (PDMS) matrix for various applications. A particular feature of these systems is that PDMS adsorbs on the surface of the dispersed particles, thus rendering them more hydrophobic with time. The mechanism of this process of in situ hydrophobization is still poorly understood. The major aims of the present study are (1) to quantify the rate of surface hydrophobization by PDMS and, on this basis, to discuss the mechanism of the process; (2) to compare the contact angles of surfaces that are hydrophobized by different procedures and are placed in contact with different fluid interfaces−PDMS−water, hexadecane−water, and air−water; and (3) to check how the type of surfactant affects the contact angles, viz., the effective hydrophobicity of the surface. We present experimental results for the kinetics of hydrophobization of glass surfaces, which are characterized by measuring the three-phase contact angle of glass−surfactant solution−PDMS. The data reveal two consecutive stages in the hydrophobization process: The first stage is relatively fast and the contact angle increases from 0° to about 90° within several minutes. This stage is explained with the physical adsorption of the PDMS chains, as a result of hydrogen-bond formation with the surface silanol groups. The second stage is much slower and hours or days are required at room temperature to reach the final contact angle (typically, 150−160°). This stage is explained as grafting of the PDMS molecules on the surface by chemical reaction with the surface silanol groups. If the glass surface had been pretreated by hexamethyldisilazane (HMDS), so that CH$_3$ groups had blocked most of the surface silanol groups, the first stage in the hydrophobization process is almost missing−the contact angle slowly changes at room temperature from about 90° up to 120°. The experiments aimed to compare several hydrophobization procedures showed that PDMS ensures larger contact angle (more hydrophobic surface) than grafted alkyl chains. The contact angles at the PDMS−water and hexadecane−water interfaces were found to be very similar to each other, and much larger than that at the air−water interface. Interestingly, we found that the ionic surfactants practically do not affect the contact angle of PDMS-hydrophobized surface, whereas the nonionic surfactants reduce this angle. Similar trends are expected with silica surfaces, as well.

1. Introduction

Solid particles are used in various oil-based products as fillers (for improving the rheological and mechanical properties), emulsion stabilizers, pigments, and promoters of antifoam action.[1−10] The successful application of such particulate components strongly depends on their hydrophobicity.[1−18] The mixtures of silica or glass particles with poly(dimethylsiloxane) (PDMS) oils form an important class of such oil−particle systems. A particular feature of these mixtures is that the PDMS molecules may adsorb on the surface of the dispersed particles, rendering them more hydrophobic with time. This in situ hydrophobization of the particles by PDMS is used in several technologies to improve the product performance.[11,19,20]

Various explanations were proposed in the literature for the forces governing the PDMS adsorption on silicate surfaces. Cohen-Addad et al.[13] described this process as

* Corresponding author. Phone: (+359−2) 962 5310, Fax: (+359−2) 962 5643, E-mail: nd@lcpe.uni−sofia.bg.

(1) Garrett, P. R., Ed. *Defoaming: Theory and Industrial Applications*; Marcel Dekker: New York, 1993.

(2) Kralchevsky, P. A.; Nagayama, K. *Particles at Fluid Interfaces and Membranes*; Elsevier: Amsterdam, 2001.

(3) Exerowa, D.; Kruglyakov, P. M. *Foams and Foam Films: Theory, Experiment, Application*; Elsevier: Amsterdam, 1998.

(4) Denkov, N. D. Mechanisms of foam destruction by oil-based antifoams. *Langmuir* **2004**, *20*, 9463.

(5) Binks, B. P.; Lumsdon, S. O. Influence of particle wettability on the type and stability of surfactant-free emulsions. *Langmuir* **2000**, *16*, 8622.

(6) Aveyard, R.; Binks, B. P.; Clint, J. H. Emulsions stabilised solely by colloidal particles. *Adv. Colloid Interface Sci.* **2003**, *100−102*, 503−546.

(7) Horozov, T. S.; Aveyard, R.; Clint, J. H.; Neumann, B. Particle zips: Vertical emulsion films with particle monolayers at their surfaces. *Langmuir* **2005**, *21*, 2330−2341.

(8) Horozov, T. S.; Aveyard, R.; Clint, J. H.; Binks, B. P. Order−disorder transition in monolayers of modified monodisperse silica particles at the octane-water interface. *Langmuir* **2003**, *19*, 2822.

(9) Levine, S.; Sanford, E. Stabilization of emulsion droplets by fine powders. *Can. J. Chem. Eng.* **1985**, *63*, 258.

(10) Binks, B. P. Particles as surfactants similarities and differences. *Curr. Opin. Colloid Interface Sci.* **2002**, 7, 21.

(11) Marinova, K. G.; Denkov, N. D.; Branlard, P.; Girauld, Y.; Deruelle, M. Optimal hydrophobicity of silica in mixed oil−silica antifoams. *Langmuir* **2002**, *18*, 3999.

(12) Marinova, K. G.; Denkov, N. D.; Tcholakova, S.; Deruelle, M. Model studies of the effect of silica hydrophobicity on the efficiency of mixed oil-silica antifoams. *Langmuir* **2002**, *18*, 8761.

(13) Cohen-Addad, J.-P.; Huchot, P.; Jost, P.; Pouchelon, A. Hydroxyl or methyl terminated poly(dimethylsiloxane) chains: Kinetics of adsorption on silica in mechanical mixtures. *Polymer* **1989**, *30*, 143.

(14) Aranguren, M. I. Morphology and rheology of silica reinforced silicone rubbers, Ph.D. Thesis, 1990, University of Minnesota.

(15) Aranguren, M. I.; Mora, E.; DeGroot, J. V.; Macosco, C. W. Effect of reinforcing fillers on the rheology of polymer melts. *J. Rheol.* **1992**, *36*, 1165.

(16) Aranguren, M. I.; Mora, E.; Macosco, C. W. Compounding fumed silicas into polydimethylsiloxane: Bound rubber and final aggregate size. *J. Colloid Interface Sci.* **1997**, *195*, 329.

(17) DeGroot, J. V., Jr.; Macosko, C. W. Aging phenomena in silica-filled polydimethylsiloxane. *J. Colloid Interface Sci.* **1999**, *217*, 86.

(18) Leger, L.; Hervet, H.; Deruelle, M. Adsorption of polydimethylsiloxane chains on plane silica surface. In *Adsorption on Silica Surfaces*, Papirer, A., Ed., Marcel Dekker: New York, 2000; Chapter 18.

(19) Ross, S.; Nishioka, G. Monolayer studies of silica/polydimethylsiloxane dispersions. *J. Colloid Interface Sci.* **1978**, *65*, 216.

physical adsorption with diffusion-controlled kinetics. DeGroot and Macosco[17] also considered the PDMS adsorption at room temperature as physical adsorption and concluded that the saturation of the adsorption layer is controlled by a slow process of rearrangement of the adsorbed molecules.

To study the possible chemical reaction between HO groups in the PDMS molecules and the silanol groups on the solid surface, Leger et al.[18] used hydroxyl-terminated PDMS molecules in their studies. These authors assumed that at 20 °C the PDMS adsorption is physical and is due exclusively to hydrogen-bond formation, whereas at sufficiently high temperature (120 °C), they showed that covalent bonds were formed.[18] The effect of temperature on the kinetics of PDMS adsorption was studied also by Ross and Nishioka,[19] who concluded that the observed kinetics is characteristic for chemical reaction. In more recent studies,[21] formation of chemical bonds between terminal HO groups in the PDMS molecules and the surface silanol groups was detected by NMR methods, after mild thermal treatment of a silica−PDMS mixture at 50 °C for 2 h. An indirect indication that chemical reaction of that type is possible even at room temperature is provided by the results of Leger et al.,[18] who found that, despite the higher rate of PDMS adsorption at elevated temperature, the saturation level of PDMS was temperature independent in the range between 20 and 120 °C.

Several groups[17,18,22,23] showed that the amount of bound PDMS, at the end of the adsorption process, is much lower when the silica surface was pretreated by grafting CH_3 groups. These results were explained with the decreased number of free surface silanol groups, which are available for chemical interaction with the PDMS molecules.[22,23]

The amount of adsorbed PDMS on the solid surface is known to affect its hydrophobicity. However, only few studies have been published in which the changes in surface hydrophobicity as a result of PDMS adsorption were quantified.[12,24] In contrast, the variations of the wettability of solid surfaces by grafting CH_3 or longer alkyl groups were widely studied in the literature.[5−8,25−27] Therefore, comparison of the changes in surface hydrophobicity as a result of PDMS adsorption and alkyl-group grafting is of definite interest from both scientific and application viewpoints.

The hydrophobicity of the solid surface is usually characterized by the three-phase contact angle, α (Figure 1), which is related to the interfacial tensions of the contacting phases through the Young equation. The value of α does not depend on the geometry of the contacting phases (at negligible line tension effects[2]) and should be
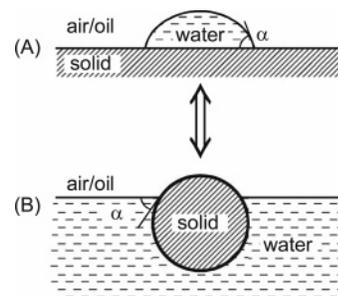

Figure 1. The three-phase contact angle, α, characterizing the hydrophobicity of a solid surface, could be measured by observing a sessile drop on the surface (A) or by observing a solid bead attached to a fluid interface (B).

one and the same for phases arranged in different configurations (cf. Figure 1A,B). This allows the researchers to choose the most convenient configuration for experimental measurement of the contact angle and to transfer the results to other configurations of interest.[1,2,4−8,24−30]

The major aims of the present paper are (1) to study the kinetics of surface hydrophobization by adsorption of PDMS molecules and, on this basis, to discuss the mechanism of surface hydrophobization; (2) to compare the contact angles of surfaces (viz. their effective hydrophobicity) that were treated by different procedures and were placed in contact with PDMS−water, hexadecane−water, or air−water interface; and (3) to check how the type of surfactant dissolved in the aqueous phase affects the contact angles.

As model substrate we use the surface of submillimeter glass spheres that were precleaned and, in several series of experiments, pretreated by grafting methyl groups. We characterized the changes in the surface hydrophobicity by measuring the three-phase contact angle of the glass beads in the configuration shown in Figure 1B. Since both silica and glass surfaces exhibit silanol groups, we expect that the conclusions drawn with glass surfaces would be relevant to silica, as well.

2. Experimental Section

2.1. Materials. Several silicone oils, commercial products of Rhodia Silicones (Saint Fons, France), were studied: 47V1000, 48V750, 48V14000, and 621V600. 47V oil is predominantly methyl-terminated, 48V oils are hydroxyl-terminated, and 621V oil is vinyl-terminated. The numbers after the letter in the oil name correspond to the oil viscosity in mPa s.

The spherical glass beads were a product of Sigma Co. (catalog number G-9268) and had diameter between 425 and 600 μm. Hexamethyldisilazane (HMDS, product of Sigma) was used as hydrophobizing agent for grafting H_3C groups onto the glass surface. In another series of experiments, octadecyltrichlorosilane (ODS) and trimethylchlorosilane (TMS), dissolved in toluene (all products of Merck), were used in a hydrophobization procedure, aimed to graft octadecyl chains onto the glass surface.

The following surfactants were used: anionic sodium dioctyl sulfosuccinate, called AOT ($C_{20}H_{37}O_7SNa$, product of Sigma Co., catalog No D-0885); anionic sodium dodecyl sulfate (SDS, product of Sidobre Sinnova); amphoteric cocoamidopropylbetaine (Betaine, product of Goldschmidt Chemical Co.); nonionic Triton X-100 (octylphenol decaethylene glycol ether, product of Merck); and nonionic polyoxyethylene-8 tridecyl ether ($C_{13}E_8$, product of Rhodia). As polymer surfactant we used poly(vinyl alcohol) (PVA) with the commercial name Rhodoviol 25/140 ($M_n \approx 12\,600$, $M_w \approx 63\,000$, degree of hydrolysis 88%, product of Rhodia). The surfactant solutions were prepared with deionized water from Milli-Q purification system (Millipore).

Hexadecane was used as oil phase in one series of contact-angle measurements. Hexane was used to wash the glass beads from the excess of PDMS, after they had been immersed in silicone

(20) Patterson, R. E. Influence of silica properties on performance of antifoams in pulp and paper applications 2. In-situ hydrophobing. *Colloids Surf. A* **1993**, *74*, 115.

(21) Litvinov, V. M.; Barthel, H.; Weis, J. Structure of a PDMS layer grafted onto a silica surface studied by means of DSC and solid-state NMR. *Macromolecules* **2002**, *35*, 4356.

(22) Zeghal, M.; Deloche, B.; Albouy, P.-A.; Auroy, P. Chain-segment order and dynamics in a grafted polymer melt: A deuterium NMR study. *Phys. Rev. E* **1997**, *56*, 5603.

(23) Brebner, K. L.; Chahal R. S.; St.-Pierre, L. E. Adsorption of poly(dimethyl siloxanes) from solution on silica. *Polymer* **1980**, *21*, 533.

(24) Lichtman, I. A.; Sinka, J. V.; Evans, D. W. *Assoc. Mex. Tec. Ind. Celul. Pap. (Bol.)* **1975**, *15*, 2632.

(25) Laibins, P. E.; Whitesides, G. M.; Allara, D. L.; Tao Y.-T.; Parikh, A. N.; Nuzzo, R. G. Comparison of the structure and wetting properties of self-assembled monolayers of *n*-alkanethiols on the coinage metal surfaces, Cu, Ag, Au. *J. Am. Chem. Soc.* **1991**, *113*, 7152.

(26) Aveyard, R.; Binks, B. P.; Fletcher, P. D. I.; Rutherford, C. E. Measurement of contact angles of spherical monodisperse particles with surfactant solutions. *Colloid Surf. A* **1994**, *83*, 89.

(27) Horvolgyi, Z.; Mate, M.; Daniel, A.; Szalma, J. Wetting behaviour of silanized glass microspheres at water−air interfaces: A Wilhelmy film balance study. *Colloids Surf. A* **1999**, *156*, 501.

oil. Hexadecane and hexane were purchased by Sigma Co. and used without further purification.

All glassware was carefully cleaned by detergent solutions, followed by 5 h of soaking in 10 wt % KOH solution in ethanol and abundant rinsing with distilled water prior to each experiment. The glass beads were cleaned by another procedure, explained in section 2.2.1.

2.2. Methods. *2.2.1. Surface Treatment.* The glass beads were carefully cleaned before hydrophobization by using the following procedure: (1) soaking in sulfochromic acid for 5−6 h; (2) abundant rinsing in multiple steps with deionized water for 4−5 h; (3) soaking in 0.01 M NaOH for 10−12 h; (4) abundant rinsing with deionized water for 8−10 h, and a neutral pH for the rinsing water was measured at the end of this washing cycle; and (5) drying at 80 °C for 8 h. This cleaning procedure includes prolonged contact of the glass surface with basic NaOH solution, which ensures the formation of reactive silanol groups before the final drying of the beads.[31,32]

Several procedures for surface hydrophobization were used.

(1) Cleaned glass beads were put in silicone oil at room temperature for different periods of time. Adsorption of PDMS molecules on the bead surface takes place during this period. As a result, the initially hydrophilic beads become more and more hydrophobic with time. The kinetics of surface hydrophobization was studied in this way.

(2) A second portion of cleaned glass beads was first heated in silicone oil for 4 h at 150 ± 2 °C. Chemical reaction of the silanol groups from the glass surface with the HO groups in the PDMS molecules leads to grafting of PDMS chains on the glass.[16,21] After this thermal treatment, the beads were stored immersed in the same PDMS oil at room temperature for different periods of time before making the contact angle measurements.

(3) A third portion of clean glass beads was pretreated by grafting H₃C groups on their surface. Similar treatment is used by silica manufacturers to produce hydrophobic silica, which is easily dispersed in silicone oils.[19,28] In our experiments, this treatment was accomplished by storing the glass beads for 4 h, at room temperature, in a closed vessel saturated with HMDS vapors. Some of these beads were used in the measurement of the contact angle at water−air and water−hexadecane interfaces. Another portion of the HMDS-pretreated beads was immersed in PDMS and stored for different periods of time at room temperature, before making the contact angle measurements.

(4) A fourth portion of clean glass beads was hydrophobized by grafting of octadecyl chains (C18). The beads were first heated at 150 °C for 24 h under vacuum. Then they were dipped in toluene containing 5 vol % ODS and heated at 100 °C for 8 h. Next, the ODS-treated beads were dipped in dried toluene containing 1 vol % TMS, at room temperature, for 2 h. Finally, the beads were rinsed with toluene. The second step (treatment with TMS) is used to cover with methyl groups those silanol groups that did not react with ODS during the first step of the hydrophobization procedure. Therefore, after this procedure we obtain a glass surface that is densely covered with chemically grafted octadecyl and methyl groups.[31]

Therefore, by these hydrophobization procedures we prepared the following types of glass surfaces: (1) treated by PDMS at room temperature, (2) heated in PDMS, (3) treated by HMDS, (4) pretreated by HMDS and then treated by PDMS at room temperature, and (5) grafted with octadecyl chains.

The contact angles of the obtained beads were measured at various interfaces, as a function of the duration of contact of the glass beads with the PDMS (viz., as a function of the time for PDMS adsorption on bead surface). When contact angle mea-
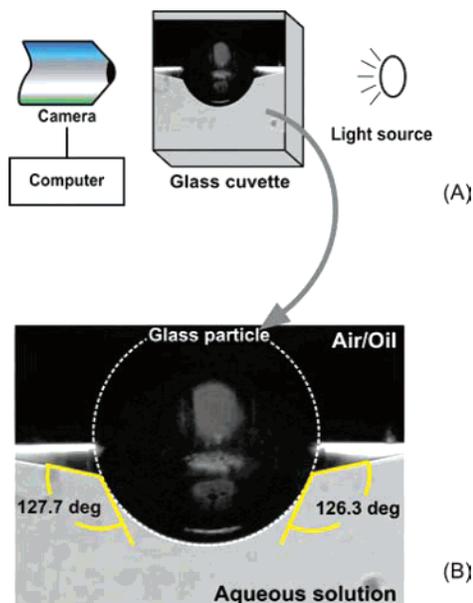
(28) *Degussa Technical Bulletin No 42 (Synthetic Silicas for Defoamers),* 3rd ed.; Degussa AG: Frankfurt, Germany, 1988.

(29) Pouchelon, A.; Araud, C. Silicone defoamers: The performance, but how do they act. *J. Disp. Sci. Technol.* **1993**, *14*, 447.

(30) Bergeron, V.; Cooper, P.; Fischer, C.; Giermanska-Kahn, J.; Langevin, D.; Pouchelon, A. Polydimethylsiloxane (PDMS)-based antifoams. *Colloids Surf. A* **1997**, *122*, 103.

(31) Vansant, E. F.; van der Voort, P.; Vrancken, K. C. *Characterization and chemical modification of the silica surface;* Elsevier: Amsterdam, 1995.

(32) Wang, M.; Liechti, K. M.; Wang, Q.; White, J. M. Self-Assembled silane monolayers: Fabrication with nanoscale uniformity. *Langmuir* **2005**, *21*, 1848.

Figure 2. (A) Schematic presentation of the setup used to observe spherical solid particles at the water−oil (or water−air) interface. The observed image is digitized by means of a CCD camera connected to a PC equipped with an image analysis system. (B) The image is further processed to obtain the three-phase contact angle through the water phase.

surements at the PDMS−water interface were made, one and the same PDMS was used for both bead hydrophobization and as oil phase in the contact angle measurements.

In the measurements of the contact angle at air−AOT and hexadecane−AOT interfaces, the glass beads were first treated with PDMS (following procedures 1−3 as described above), washed in multiple steps with abundant volumes of hexane, and dried for 3 h at room temperature. To verify that no PDMS was released from the surface of the washed beads upon their placement on the air−water or hexadecane−water interface, we measured the surface tension of 10 mM AOT solution by the Wilhelmy-plate method in the absence and in the presence of PDMS-treated and hexane-washed beads; the surface tension was measured to remain the same after bead placement on the interface.

2.2.2. Contact Angle Measurement. The experimental setup used to measure the three-phase contact angle of glass beads is schematically shown in Figure 2A. When the contact angle at the water−air interface was measured, a bead was gently placed on the surface of the aqueous surfactant solution by using stainless steel tweezers. When the contact angle at the oil−water interface was measured, the glass bead was gently dropped into the oil phase and allowed to sediment toward the fluid interface. It took between several seconds and several minutes (depending on the used oil) before the bead entered the oil−water interface. Direct experimental checks showed that the beads acquired a stable contact angle within several minutes after entering the interface. Therefore, all reported contact angles are measured 10 min after the beads entered the fluid interface. When PDMS was used to hydrophobize the beads and as an oil phase in the contact angle measurements, the angles did not change for days after placing the bead at the oil−water interface, which shows that the PDMS hydrophobic coat is very stable upon contact with water. (No such long-term checks were made for the H₃C-grafted surfaces, which are known to lose gradually their hydrophobicity after exposure to an aqueous phase, due to formation of a surface siliceous gel.[33])

The bead positioned at the fluid interface was observed in transmitted light by means of horizontal microscope, equipped with a long-focus objective ×5 (Figure 2A). Images of the beads were digitized by means of a CCD camera connected to a PC,

(33) Blake, T. D.; Kitchener, J. A. Stability of aqueous films on hydrophobic methylated silica, *J. Chem. Soc. Faraday Trans. 1* **2000**, *68*, 1435.
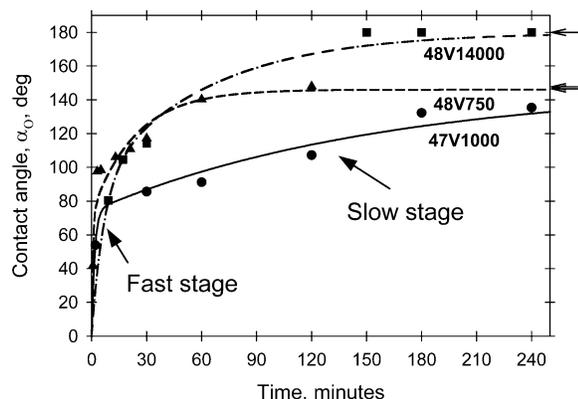
Figure 3. Kinetics of the three-phase contact angle of glass beads at the interface PDMS−10 mM AOT solution, as a function of the contact time of the beads with the silicone oil, t (viz, the PDMS adsorption time). The experimental data for three different silicone oils are shown: 47V1000 (circles), 48V750 (triangles up), and 48V14000 (squares). The curves represent the best fits to all experimental points (including those that were measured after 240 min and are not shown in the figure), plotted according to eq 1. The horizontal arrows indicate the final angles, α_{FIN} (see Table 1).

which was equipped with a Targa+ image analysis system. The images were further processed to determine goniometrically the three-phase contact angle of the beads (Figure 2B). The contact angles measured on the left-hand side and on the right-hand side of the bead contour were averaged. For each system studied, two or three independent series of measurements with beads hydrophobized in different batches were performed (each series including at least three beads), and the results were averaged. The reproducibility of the results obtained with beads hydrophobized together in a given batch was typically ±3°. The repeatability in independent experimental runs was about ±5°.

The following convention is used in the paper: the contact angles of glass−water−air (α_A) and glass−water−oil (α_O) are both measured through the aqueous phase, thus larger values of α_O and α_A mean more hydrophobic beads. Note that the used procedure for beads placement on the fluid interface leads to formation of advancing contact angles. The used procedure does not allow us to evaluate the hysteresis of the contact angle.

2.2.3. Interfacial Tension. The interfacial tension of the studied solutions was measured by using the drop-shape analysis method on a DSA10 instrument (Kruss GmbH). The measurements were performed at 24 ± 0.5 °C.

3. Experimental Results

Two different types of experiments were performed: The first measured the contact angle of glass beads that were stored at room temperature in contact with PDMS for different periods of time. The aim of this type of experiment was to study the kinetics of bead hydrophobization by the adsorbing PDMS molecules. These contact angle measurements were performed only with beads placed at the PDMS−water interface. The second measured the final contact angles (after heating or after prolonged storage in PDMS) at various fluid interfaces with the aim to compare the effect of the fluid phases on the contact angle. These measurements were made at the PDMS−water, air−water, and hexadecane−water interfaces, where water means either pure water or surfactant solution. The results from these different series of experiments are separately presented and discussed below.

3.1. Kinetics of Hydrophobization of Glass Beads by PDMS Adsorption. *3.1.1. Beads Hydrophobized by Procedure 1.* The dependence of the three-phase contact angle, α_O, of initially hydrophilic glass beads versus the time allowed for PDMS adsorption on bead surface at room temperature, t, is shown in Figure 3. The results for three
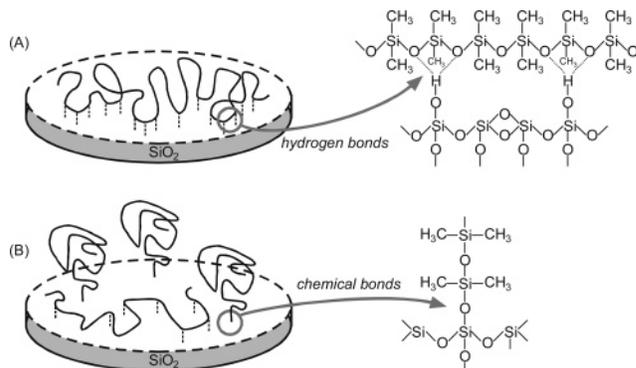

Figure 4. Schematic presentation of the two stages of the process of PDMS adsorption onto a glass (silica) surface: (A) fast stage, physical adsorption of PDMS molecules in "side-on" configuration due to hydrogen bonds; (B) slow stage, formation of a layer of chemically grafted PDMS molecules ("end-on" configuration), as a result of a chemical reaction between the silanol groups on the solid surface and the terminal HO groups of the polymer molecules.

PDMS oils, which differ in their molecular mass and type of terminal groups, −OH or −CH$_3$, are shown. The points represent the contact angles of glass beads placed at the interface between 10 mM AOT solution and the same PDMS oil that was used for hydrophobization. The initial contact angle, $\alpha_O(t=0) = 0$, is taken to be equal to zero, because the AOT solution spontaneously displaces PDMS from hydrophilic glass surface. Only the values measured during the first 4 h of bead−PDMS contact are shown in Figure 3, because the most significant changes in the contact angles were measured during this initial period (α_O remained practically constant at adsorption times longer than ca. 1 day).

One can see from Figure 3 that the bead hydrophobization occurs in two different stages: Very rapid initial increase of the contact angle during the first several minutes, followed by much slower increase during the next several hours. Since the bead hydrophobization is due to PDMS adsorption on the glass surface, the observed distinct regions in the kinetic curves should reflect two consecutive stages in the formation of the PDMS adsorption layer. As discussed in section 4 below, on the basis of the results of other authors[13−18,20−23] and our own experimental results, we suppose that the first stage consists of physical adsorption of PDMS molecules on the glass surface, whereas the second stage is explained by chemical reaction of the terminal HO groups in the PDMS molecules with the silanol groups on the glass surface (see Figure 4). This molecular explanation of the hydrophobization process is used throughout the paper to discuss the observed trends and is explained in more detail in section 4.

To characterize quantitatively the kinetics of the two stages of the hydrophobization process, we used the following empirical formula to fit the data (see the curves plotted in Figure 3):

$$\alpha_O(t) = \alpha_{FIN}\left[1 - \frac{1}{2}\exp\left(-\frac{t}{\tau_{FS}}\right) - \frac{1}{2}\exp\left(-\frac{t}{\tau_{SL}}\right)\right] \quad (1)$$

Here $\alpha_O(t)$ is the instant value of the contact angle, α_{FIN} is the final value reached at saturation of the PDMS adsorption layer on the glass surface, and τ_{FS} and τ_{SL} are the characteristic times of the fast and the slow stages, respectively. The experiments showed that α_O remains almost constant after the first day of glass−PDMS contact. That is why, when fitting the experimental data with eq

Table 1. Characteristic Times for the Fast, τ_{FS}, and the Slow, τ_{SL}, Processes of Surface Hydrophobization, As Obtained from the Best Fits by eq 1 to the Experimental Data Shown in Figure 3

fit parameters	47V1000	48V750	48V14000
α_{FIN},[a] deg	148 ± 4	146 ± 3	180
τ_{FS}, min	1.6 ± 0.3	0.8 ± 0.3	6.6 ± 1.0
τ_{SL}, min	158 ± 22	24 ± 5	62 ± 11

[a] The value of α_{FIN} is average of the measured values of α_O in the period between the 1st and 6th days of PDMS adsorption.

1, we fixed the value of α_{FIN} to be equal to the experimentally determined angle, taken as an average from all measurements between the first and the sixth days. Therefore, the only adjustable parameters in the numerical procedure were the characteristic times, τ_{SL} and τ_{FS}. Note that the fit was performed over all measured contact angles (including those at $t > 4$ h, not shown in Figure 3), which means over 10−15 experimental points for each sample. The obtained values for τ_{SL}, τ_{FS}, and α_{FIN} are summarized in Table 1.

A significant effect on the rate of bead hydrophobization is found for both the oil molecular mass (viz., oil viscosity) and the density of terminal HO groups. This effect is particularly pronounced during the second stage, characterized by τ_{SL}. The hydroxyl-terminated oils exhibit shorter characteristic times, $\tau_{SL} \approx 24$ min for the less viscous oil 48V750, and $\tau_{SL} \approx 62$ min for the more viscous oil 48V14000, whereas $\tau_{SL} \approx 158$ min for the methyl-terminated oil 47V1000. From the molecular mass[34] of the 48V oils (22 400 g/mol for 48V750 and 75 600 g/mol for 48V14000), one can calculate the concentration of the terminal HO groups: 8.9×10^{-2} M for 48V750 and 2.6×10^{-2} M for 48V14000. Assuming that the second stage of hydrophobization is governed by the chemical reaction of the terminal HO groups of the PDMS molecules with the silanol groups on the glass surface, one can speculate that the estimated 3-fold difference in the concentration of the HO groups for the studied 48V oils is reflected by the 3 times difference in the respective values of τ_{SL}. Following the same reasoning, one can speculate that the used 47V1000 oil contained about 10^{-2} M terminal HO groups (this is approximately one out of 10 terminal groups), which is a realistic estimate. Indeed, as discussed by Leger et al.,[18] the procedure for production of methyl-terminated PDMS, like the oils of 47V type, does not exclude the possibility for formation of some fraction of hydroxyl-terminal groups.

The characteristic times of the first stage, τ_{FS}, seem to be more affected by the oil viscosity, rather than by the concentration of HO groups: $\tau_{FS} \approx 0.8$ min for 48V750, ≈ 6.6 min for 48V14000, and ≈ 1.6 min for 47V1000. These results could be explained by assuming that the first stage is governed by rearrangement of the segments of the physically adsorbed PDMS molecules, a process that is expected to be slower for more viscous oils.

The final contact angles of the glass spheres treated with 47V1000 and 48V750 oils, which have similar molecular mass, are practically the same, $\alpha_O = 148 \pm 4°$ for 47V1000 and $146 \pm 3°$ for 48V750, despite the large difference in the kinetics of hydrophobization. Interestingly, the hydrophobization by 48V14000 oil resulted in final contact angle $\alpha_O \approx 180°$, which means that the bead remained entirely immersed inside the oil phase; no bead entry at the oil−water interface was observed even after

(34) O'Lenick, A. J., Jr. Silicones−Basic chemistry and selected applications. *J. Surfactants Detergents* **2000**, *3*, 229.
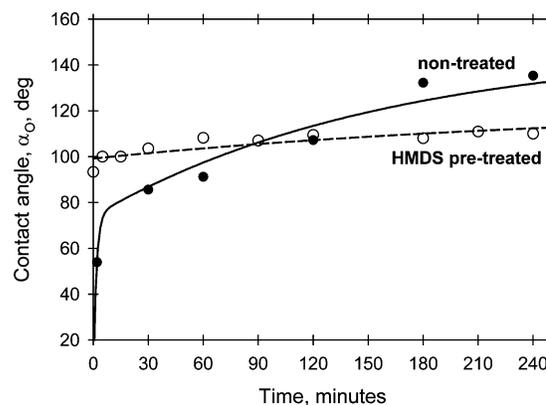

Figure 5. Kinetics of the three-phase contact angle of glass beads at the interface PDMS−10 mM AOT solution, as a function of the contact time of the beads with PDMS 47V1000. The full circles represent angles measured with nontreated beads (data from Figure 3), while the empty circles correspond to HMDS-pretreated beads. The curves represent the best fits, plotted according to eq 1 for the nontreated (solid line) and to eq 2 for the pretreated beads (dashed line).

days of observation. We cannot exclude the possibility that the oil film, which was formed between the glass beads treated by 48V14000 and the oil−water interface, was stabilized by strong steric forces due to the adsorbed PDMS on the glass surface, which suppressed the bead emergence at the oil−water interface.

3.1.2. Beads Hydrophobized by Procedure 3. The results for the kinetics of hydrophobization of beads that were pretreated by HMDS and afterward stored in 47V1000 oil at room temperature (procedure 3 from section 2.2.1) are shown in Figure 5. For comparison, the data for the initially hydrophilic beads (not treated with HMDS) are also shown. There is an obvious difference between the kinetic curves for these two types of surfaces: the α_O for the HMDS-treated beads changes in a relatively narrow range, from $93 \pm 5°$ to $110 \pm 4°$ for 4 h. On the same time scale, the nontreated beads change their contact angle from 0 to 140°. The final contact angle, α_O, established after ca. 1 day of glass−PDMS contact is also very different for the nontreated ($148 \pm 4°$) and HMDS-treated beads ($122 \pm 4°$).

These observations indicate that the PDMS adsorption occurs in a different manner for bare glass surface and for H_3C-covered surface. The initial angle (at zero time) of the H_3C-covered surface is well above zero and the first (rapid) stage of hydrophobization is missing in this system. Since the data shown in Figure 5 indicate only one (slow) stage of hydrophobization for H_3C-covered surface, the following equation with one characteristic time was used to fit the measured dependence $\alpha_O(t)$:

$$\alpha_O(t) = \alpha_{INI} + (\alpha_{FIN} - \alpha_{INI}) \left[1 - \exp\left(-\frac{t}{\tau_{SL}}\right) \right] \quad (2)$$

Here α_{INI} is the initial value and α_{FIN} is the final value of the contact angle; τ_{SL} is the characteristic time of hydrophobization. The experimental data were interpolated with eq 2, by fixing the value of $\alpha_{FIN} = 122°$, the average from the values measured between the first and the sixth days of observation. Thus, the fit of the data was performed by varying two parameters that were determined by the least-squares method, $\alpha_{INI} = 99°$ (which is close to the experimentally measured angle at short times, in the frame of the experimental reproducibility) and $\tau_{SL} = 278 \pm 80$ min. The value of τ_{SL} shows that the kinetics of adsorption is about twice slower for the HMDS-treated

Table 2. Mean Contact Angle, α_O, of Glass Beads at the Interface PDMS−10 mM AOT Solution, after 1 day of PDMS−Glass Contact for Different Particle Treatments

silicone oil	PDMS adsorption at rt	heated in PDMS	pretreated with HMDS
47V1000	148 ± 4	154 ± 4	122 ± 5
48V750	146 ± 3	158 ± 3	119 ± 5
48V14000	→180	→180	→180

surface when using the same PDMS oil for hydrophobization (278 ± 80 min for HMDS-treated surface vs 158 ± 22 min for bare glass surface).

At the end of this section, we note that the beads that were hydrophobized by using procedure 2 in section 2.2.1 (first the beads were heated for 4 h in PDMS and then stored in the same PDMS at room temperature) did not show any variations of the contact angle during the period of storage in PDMS. This observation means that the final angle, α_{FIN}, was reached during the heating in PDMS. For this reason, the results obtained with these beads are presented in the following section, where the final angles obtained after all used hydrophobization procedures are discussed.

3.2. Comparison of the Contact Angles after Various Hydrophobization Procedures and in the Presence of Surfactants. *3.2.1. Effect of the Hydrophobization Procedure and Used PDMS Oil.* Here we compare the final contact angles, α_{FIN}, obtained after different hydrophobization procedures (see section 2.2.1) and by using different PDMS oils. For the beads hydrophobized by PDMS adsorption at room temperature (procedures 1 and 3), α_{FIN} is determined as the average from the contact angles measured between the first and the sixth day of storage in PDMS. For the beads hydrophobized by heating in PDMS (procedure 2), α_{FIN} is determined as an average of all measurements, because no trend in the contact angle was observed with these samples after the thermal treatment. All measurements were made at the interface between the PDMS oil, used for bead hydrophobization, and 10 mM AOT solution.

The comparison of the data for the various systems, summarized in Table 2, shows that most hydrophobic are the beads that had been heated in PDMS, where $\alpha_{FIN} \approx$ 156° for the oils 47V1000 and 48V750 and $\alpha_{FIN} \approx$ 180° for 48V14000. This result is anticipated, because chemical reaction is known to occur between the PDMS molecules and the silicate surfaces at high temperature.[16,18,21] Thus, thicker and denser layers of chemically adsorbed PDMS molecules are formed upon heating. Note that the final contact angles are practically the same for the beads, which were treated with 47V1000 and 48V750 oils having similar molecular mass and different main terminal groups. This result suggests that final adsorption layers similar in density and structure are formed in these two systems, despite the different adsorption kinetics illustrated in Figure 3 (as explained in ref 18 and section 3.1, some fraction of the 47V1000 molecules are expected to be terminated by reactive HO groups).

As mentioned in the previous section, the contact angles of HMDS-pretreated glass surfaces are smaller than those of bare glass surfaces, when the PDMS adsorption occurs at room temperature. The grafted H_3C groups are known to block the surface silanol groups, thus decreasing the number of reactive sites for chemical interaction with the PDMS molecules.[22,23] As a result, less PDMS adsorbs on the surface at the end of the procedure and the surface remains less hydrophobic. This negative effect of the pregrafted H_3C groups on the final surface hydrophobicity

Table 3. Contact Angles, α_O, of Glass Beads at PDMS−Water Interface in the Presence of Different Surfactants in the Aqueous Phase[a]

aqueous phase	α_O, deg	σ_{OW}, mN/m
pure H_2O	162 ± 5	41.0 ± 0.5
10 mM AOT	152 ± 5	4.8 ± 0.2
9 wt % SDS	164 ± 5	7.0 ± 0.5
1 wt % CTAC	165 ± 5	−
5 wt % Betaine	155 ± 5	7.0 ± 0.5
1 wt % PVA	160 ± 5	20.9 ± 0.5
1 mM Triton X-100	145 ± 5	4.7 ± 0.2
10 wt % $C_{13}E_8$	130 ± 5	2.5 ± 0.2

[a] The glass beads are hydrophobized by heating in 621V600 silicone oil. The interfacial tension, σ_{OW}, in the presence of different surfactants is also given.

could be explained, if one assumes that the PDMS molecules form a thicker adsorption layer (in comparison with the grafted H_3C groups), which plays the role of a very efficient hydrophobic coat of the solid surface; see Figure 4B. The viscous 48V14000 oil always led to very hydrophobic surfaces—the hydrophobized beads remained entirely immersed in the oil phase and did not enter the PDMS−AOT interface for days.

3.2.2. Effect of Surfactant Type. Table 3 summarizes the contact angles, measured with several surfactants of different type, for glass beads that were hydrophobized by heating for 4 h in 621V600 silicone oil (no significant difference between the final angles obtained with hydroxyl-terminated 48V750, predominantly methyl-terminated 47V1000, and predominantly vinyl-terminated 621V600 oils was found in comparative experiments). The surfactant concentration was always well above the critical micelle concentration to ensure dense adsorption surfactant layers at the oil−water and solid−water interfaces.

As one can see, the measured values of the contact angles for all surfactants (except for the nonionic surfactants) are very similar to the contact angle measured with pure water, $\alpha_O \approx 162 \pm 5°$. To explain this interesting result, we make use of the Young equation:

$$\cos \alpha_O = \frac{\sigma_{SO} - \sigma_{SW}}{\sigma_{OW}} \quad (3)$$

Combining the Gibbs adsorption isotherms for the various interfaces with the Young equation, Lucassen-Reynders[35] obtained the following relation between the surfactant adsorption at the various interfaces, Γ_{XY}, and the contact angle:

$$\cos \alpha_O + \frac{d \cos \alpha_O}{d(\ln \sigma_{OW})} = \frac{\Gamma_{SO} - \Gamma_{SW}}{\Gamma_{OW}} \quad (4)$$

The experimental fact that the contact angles in the presence of surfactant are very close to that of pure water indicates that the second term in the left-hand side of eq 4 is very small and can be neglected in comparison with the first term. Furthermore, for most of the surfactants (e.g., SDS and PVA) we can assume that $\Gamma_{SO} \approx 0$, because these surfactants are insoluble in the oil phase. With these assumptions, eq 4 simplifies to[36]

$$\cos \alpha_O = -\frac{\Gamma_{SW}}{\Gamma_{OW}} \quad (4')$$

From the experimentally measured value of $\alpha_O \approx 162°$,

(35) Lucassen-Reynders, E. H. Contact angles and adsorption on solids. *J. Phys. Chem.* **1962**, *67*, 969.

we can estimate that the ratio $\Gamma_{SW}/\Gamma_{OW} = 0.95 \approx 1$ for all surfactants showing contact angle close to that of water. This estimate shows that the adsorption on the oil–water and solid–water interfaces is very similar for these surfactants. This interesting observation can be explained with the fact that the glass surface is covered by a dense layer of PDMS molecules, which makes the chemical structure of the oil–water and solid–water interfaces very similar. As a result, the interaction of the surfactant molecules with these surfaces and the surfactant adsorption are also similar.

The measured values of α_O with solutions of $C_{13}E_8$ (129 ± 3°) and Triton X-100 (145 ± 5°) are significantly lower than the contact angle with pure water. Two possible explanations can be suggested for this result. First, eq 3 can be represented in the following form:

$$\cos \alpha_O = \frac{\sigma_{SO}}{\sigma_{OW}} - \frac{\sigma_{SW}}{\sigma_{OW}} \qquad (3')$$

The facts that, in the presence of ionic surfactants, the contact angles are relatively large and are not affected by the surfactant suggest that (1) the first term in eq 3′ is small, $\sigma_{SO} \ll \sigma_{OW}$, and (2) the interfacial tensions of the solid–water and oil–water interfaces are similar, $\sigma_{SW} \approx \sigma_{OW}$. Assumptions 1 and 2 explain why $\cos\alpha_O \approx -1$ for the ionic surfactants. However, if the interfacial tension of the oil–water interface is lower (which is the case with the studied nonionic surfactants), then the first term in eq 3′ could become significant and the contact angle would decrease, as observed experimentally.

Another possible explanation could be that $C_{13}E_8$ and Triton X-100 adsorb more strongly on the solid–water interface, as compared to the oil–water interface. Indeed, from eq 3 one can deduce that, if the values of σ_{SO} or σ_{OW} decrease as a result of surfactant adsorption, this would lead to smaller (more negative) values of $\cos \alpha_O$, which is the opposite to the observed experimental trend. On the other hand, a stronger decrease of σ_{SW} (as compared to σ_{OW}) would lead to a smaller contact angle, as observed with the nonionic surfactants. However, we cannot suggest any molecular explanation at the moment why these surfactants would preferentially adsorb on the solid–water interface. The reasons for the qualitatively different behavior of the studied nonionic surfactants deserve further investigation, because it might be important for practical applications.

3.2.3. Comparison with Results of Other Authors. Pouchelon and Araud[29] measured the three-phase contact angles formed when droplets of 12 mM AOT solution were placed on glass substrate covered by an adsorption layer of PDMS (configuration shown in Figure 1A, where the external fluid phase was either air or silicone oil with viscosity 1000 mPa s). In an independent series of experiments, Bergeron et al.[30] measured the three-phase contact angle of droplets of $\approx$10 mM (3 × cmc) AOT solution on solid PDMS elastomer. As fluid oil phase they used silicone oil with viscosity 100 mPa s. In Table 4 we compare our results with the values of the three-phase contact angles air–water–solid and PDMS–water–solid, measured in refs 29 and 30. The agreement between the three sets of results is very good, despite the fact that the experiments were made on different substrates and with different silicones. This comparison indicates that the contact angles of the PDMS-covered surfaces are determined mainly by the polymer backbone, whereas the

(36) Fletcher, P. D. I.; Nicholls, R. J. Contact angles in oil solvents on low energy solid surfaces. *Phys. Chem. Chem. Phys.* **2000**, *2*, 361.

Table 4. Comparison of the Three-Phase Contact Angles (deg) Measured by Different Research Groups[29,30]

system	Pouchelon and Araud[29] [a]	Bergeron et al.[30] [b]	current study[c]
solid/AOT/PDMS	~160	155	154 ± 4
solid/AOT/air	45	48	46 ± 2

[a] On glass covered by adsorbed PDMS. [b] On PDMS elastomer. [c] On glass heated in 47V1000.

Table 5. Contact Angle (deg) of Glass Beads After Different Surface Treatments, Placed at the Interface between 10 mM AOT Solution and Air, Hexadecane, or PDMS

hydrophobic phase	non-treated	heated in 47V1000	heated in 48V750	treated with HMDS	treated with ODS + TMS
PDMS	→0	154 ± 4	158 ± 3	93 ± 5	130 ± 4
hexadecane	→0	150 ± 2	159 ± 3	96 ± 3	126 ± 3
air	→0	44 ± 2	–	28 ± 2	28 ± 2

terminal groups and the exact procedure for substrate preparation have much smaller effect.

3.3. Hydrophobized Glass Beads at Hexadecane–Water and Air–Water Interfaces. We compared the contact angles of glass beads, hydrophobized by several procedures, including heating in PDMS and treatment by HMDS or ODS + TMS (without subsequent immersion in PDMS), at PDMS–water, hexadecane–water, and air–water interfaces (see Table 5). The aqueous phase in the contact angle measurements was 10 mM AOT solution.

Several interesting conclusions can be drawn from the data shown in Table 5. First, the contact angles of glass beads placed at the air–water interface show that the glass surface treated by heating in PDMS is significantly more hydrophobic ($\alpha_A \approx 44°$) as compared to the surfaces treated with HMDS or ODS + TMS ($\alpha_A \approx 28°$). Second, the contact angles at PDMS–water and hexadecane–water interfaces are very similar to each other, after an equivalent hydrophobization procedure. Third, the treatment by silicone oil leads to larger contact angles ($\sim$155°) than the treatment by HMDS ($\sim$95°) even for hexadecane–water interface. One can conclude from all these results that the hydrophobization by PDMS is much more efficient than grafting of alkyl chains, even when hydrocarbon–water fluid interfaces are considered.

To analyze the difference between the contact angles α_O and α_W, we can subtract the Young equation for the oil–water interface (see eq 3) from the respective equation for the air–water interface

$$\cos \alpha_A = \frac{\sigma_{SA} - \sigma_{SW}}{\sigma_{AW}} \qquad (5)$$

to derive

$$\sigma_{AW} \cos \alpha_A - \sigma_{OW} \cos \alpha_O = \sigma_{SA} - \sigma_{SO} \qquad (6)$$

By using the experimental values of $\sigma_{AW} = 27.9$ mN/m, $\sigma_{OW} = 4.8$ mN/m, α_O, and α_W shown in Table 5 and eq 6, we found for all studied systems that $\sigma_{SA} - \sigma_{SO} \approx 25 \pm 3$ mN/m. On the other hand, by using the approach from Chapter 11 of ref 37, one can estimate $\sigma_{SA} - \sigma_{OW}$ from the relation[37]

$$\sigma_{SA} - \sigma_{SO} = -\sigma_{OA} + \frac{A_H}{12\pi h_0^2} \qquad (7)$$

where A_H is the Hamaker constant for the van der Waals

interaction of the solid and oil phases across vacuum and $h_0 \approx 0.165$ nm is the minimal distance between two condensed phases upon contact.[37] Equation 7 can be derived by considering the energy of van der Waals interaction in an imaginary process of placing in contact (at a small distance, h_0, set by the molecule dimensions) an oil−air and a solid−air interface that were initially separated at an infinite distance from each other. Taking $\sigma_{OA} \approx 20.6$ mN/m (the surface tension of PDMS) and $\sigma_{SA} - \sigma_{SO} \approx 25$ mN/m, one can estimate from eq 7 the Hamaker constant $A_H \approx 4.7 \times 10^{-20}$ J, which is a reasonable value.[37] One can conclude from this consideration that the main reason for the smaller contact angles at the air−water interface (in comparison with the oil−water interfaces) is the important contribution of the van der Waals interaction between the bulk oil and solid phases.

4. Discussion−Mechanism of Surface Hydrophobization

It is often assumed in the literature that, at room temperature, the PDMS molecules interact with the glass−silica surface only by physical forces (such as hydrogen bonds and van der Waals forces).[13−18] However, our results and the results of Leger et al.[18] show that a similar adsorption layer of PDMS is obtained after heating at 150 °C (when chemical reaction is known to occur) and after long time of adsorption at room temperature. These results indicate that chemical reaction between the terminal HO groups of the PDMS molecules and the silanol groups on the solid surface probably occurs at room temperature, though at a lower rate. Therefore, taking into account the results of other authors and our own results, we suppose that the observed kinetics of glass hydrophobization (section 3.1) is explained by the adsorption processes illustrated in Figure 4.

(A) Immediately after placing the surface in contact with PDMS, the polymer molecules physically adsorb due to van der Waals attraction and hydrogen-bond formation between the oxygen atoms in the polymer backbone and the silanol groups on the solid surface (see Figure 4A). This process has a characteristic time of one to several minutes and consists mainly of rearrangement of the adsorbed polymer chains, so that a dense physisorbed monolayer of PDMS molecules is eventually formed. The characteristic time of this process is governed mainly by the length of the PDMS chains and the PDMS viscosity.

The thickness of the adsorption layer at the end of this stage is expected to be about the diameter of the silicone molecule, independent of the polymer chain length. The respective contact angle for such surface, covered by a thin monolayer of "side-on" placed PDMS molecules, is about 90° (see the contact angle at the end of the first stage in the hydrophobization process, Figure 3). Since the hydrogen bonds are continuously broken and reestablished by the thermal motion of the molecules, the adsorption layer at this stage is dynamic−a perpetual detachment of some fragments from the PDMS molecules and their replacement by other fragments takes place.

For beads pretreated by HMDS, a similar process of physical adsorption may occur, but the density of the physisorbed layer is probably much lower, because most of the silanol groups on the solid surface are occupied by methyl groups.[22,23] No significant increase of the contact angle at the end of the first stage is observed with pretreated beads.

(B) The second stage of the hydrophobization process consists of formation of chemical bonds between the PDMS molecules having terminal HO groups and the silanol groups on the solid surface (Figure 4B). This stage is relatively slow at room temperature, because it involves the overcoming of the activation energy barrier, typical for chemical reactions. The rate of this chemical reaction depends on the temperature and on the concentration of reactive HO groups in the oil and on the solid surface.

The chemisorbed PDMS molecules are oriented mainly in the "end-on" configuration, because more silanol groups are available for reaction in this arrangement.[21] However, when the PDMS-covered solid surface is placed in contact with poor solvents (including air and aqueous solutions) the PDMS layer is "squeezed" between the solid−PDMS and PDMS−solvent interfaces, so that a compact PDMS adsorption layer is formed, in which the motion of the PDMS chains is strongly hindered.[21] The final thickness of the layer, formed during this second stage of chemical reaction, depends on the molecular mass of the polymer— the longer the polymer chains, the thicker the final layer.

Similar processes are expected to take place on the surface of fractal silica particles, used in antifoam compounds and for stabilization of Pickering emulsions. However, several important differences should be noticed between the smooth glass surface used in the current study as model substrate and the fractal silica particles used in various formulations: (i) the fractal shape of the silica agglomerates might decelerate the approach of the PDMS molecules toward the reactive sites on the particle surface, because some of these sites are "hidden" in the agglomerate interior; (ii) the specific surface area of the silica particles is much larger than that of the spherical glass beads, so that more PDMS molecules should react with the same amount of particles for reaching similar density of the chemisorbed polymer layer. These factors should lead to slower hydrophobization of fractal silica as compared to smooth glass surfaces, which is indeed observed experimentally: the characteristic time scale of glass hydrophobization at room temperature in the present study was on the order of several hours, whereas the observed characteristic time for hydrophobization of fractal silica in antifoam compounds was on the order of days and weeks.[11,12] Despite the different kinetics of particle hydrophobization in these two systems, the main trends observed in the present study are expected to be relevant to silica particles as well, because the main processes and phenomena are governed by the same types of interaction.

5. Main Results and Conclusions

The kinetics of hydrophobization of glass surface as a result of PDMS adsorption was studied. For this purpose, glass beads (clean or pretreated by HMDS) were immersed in bulk PDMS at room temperature for different periods of time (i.e. time for adsorption, t_{ADS}) and then the contact angle, α_O, of the beads was measured at the PDMS−water interface to characterize the surface hydrophobicity. The main results can be summarized as follows:

The kinetic curves α_O vs t_{ADS} for beads with initially hydrophilic surface consist of two distinct regions. The first region is very steep and the contact angle increases up to $\approx$90° for several minutes, when measured on the surface of AOT solutions. The second region describes much slower process, with a characteristic time of several hours, for reaching the final contact angle $\approx$150−160°.

The increase of the number concentration of HO-terminal groups of the oil leads to significant acceleration of the second (slow) process of reaching the final contact angle.

(37) Israelachvili, J. N. *Intermolecular and Surface Forces*, 2nd ed., Academic Press: London, 1992.

For beads that are pretreated by HMDS, the kinetic curves start from a contact angle of about 95° and show only slow process of reaching the final contact angle ≈125°.

The heating of the system leads to strong acceleration of the hydrophobization process.

All these experimental results, combined with the results of other authors,[13−18,21−23] can be explained by assuming a two-stage mechanism of surface hydrophobization by PDMS:

(A) Immediately after placing the surface in contact with PDMS, the polymer molecules physically adsorb by forming hydrogen bonds between the oxygen atoms in the polymer backbone and the silanol groups on the solid surface. This fast stage consists mainly of rearrangement of the adsorbed polymer chains, so that a dense physisorbed monolayer of PDMS molecules is formed.

(B) In the second stage, the PDMS molecules having terminal HO groups form chemical bonds with the silanol groups on the solid surface. This process is relatively slow at room temperature, because it presents a chemical reaction with an activation barrier. The final thickness of the layer formed during this second stage depends on the molecular mass of the polymer—longer polymer molecules lead to a thicker adsorption layer.

We compared the contact angles for beads hydrophobized by different procedures, at various fluid interfaces and in the presence of various surfactants. The main conclusions from these measurements can be summarized as follows:

The contact angles for all surfactants (except for the nonionic surfactants) are very similar to the angle measured with pure water for PDMS-treated surfaces, $\alpha_O \approx 162 \pm 5°$. This result can be explained by the fact that the glass surface is covered by a dense layer of PDMS molecules, which make the chemical structure of the oil−water and solid−water interfaces very similar. Hence, the interaction of the surfactant molecules with these surfaces and the resulting surfactant adsorption are very similar.

The measured values of α_O for $C_{13}E_8$ ($129 \pm 3°$) and for Triton X-100 ($135 \pm 5°$) are significantly lower; possible explanations of this result are proposed.

The contact angles at the PDMS−water and hexadecane−water interfaces are very similar, for equivalent hydrophobization procedures. The treatment by silicone oil produces a significantly more hydrophobic surface than the treatment by HMDS or ODS + TMS (the contact angle is about 60° larger) at both the PDMS−water and hexadecane−water interfaces.

The contact angles of glass beads placed on the air−water interface show that a significantly more hydrophobic ($\alpha_A \approx 44°$) surface is obtained after heating in PDMS, as compared to surface treatment with HMDS or ODS + TMS ($\alpha_A \approx 28°$). Thus, the hydrophobization by PDMS adsorption was most efficient for all studied systems (viz., for various surfactants and fluid interfaces).

Comparison of our results with the results by other authors[29,30] show that a glass surface, once covered by an adsorption layer of PDMS, is energetically equivalent to the surface of the solid PDMS elastomer.

The surfaces hydrophobized by reaction with PDMS do not change their contact angle even after days in contact with an aqueous phase, which is in contrast to the surfaces treated with methylsilanes (whose contact angle decreases gradually after placing them in contact with water, due to formation of surface siliceous gels[33]).

The observed trends are expected to apply for hydrophobized silica particles, which are widely used in antifoam compounds, for stabilization of Pickering emulsions, and as fillers in various elastomers.