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Leaching of Organic Molecules from Composite Silica/ Surfactant Films into Water

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Silica−surfactant composite films have been formed by dip-coating in gels made of aqueous surfactant micelles and tetraethoxysilane. Both ionic and non-ionic surfactants have been used. Each gel contained a hydrophobic or a hydrophilic dye that was subsequently incorporated in the film. The films were then immersed in water, and dye leaching was monitored by absorption spectrophotometry. Surfactant leaching was monitored by either absorption spectrophotometry or, in the case of ionic surfactants, by conductimetry. Hydrophobic probes were relatively rapidly leached following surfactant leaching rate, since they reside in the surfactant subphase. Hydrophilic probes were more slowly leached since they are supported by the silica network. The remaining material in the film after leaching of the organic content has been characterized by atomic force microscopy and transmission electron microscopy.

Introduction

Silica−surfactant composite materials were recently studied with a lot of interest since surfactant self-assemblies can be used as templates to engineer ordered mesoporous materials with tailor-made pore sizes and shapes.[1−10] The greatest volume of the work published so far deals with bulk materials, even though mesoporous thin films are technologically highly desirable.[11−17] The usual procedure for the formation of mesoporous materials is the sol−gel transformation of a solution containing a metal alkoxide and a surfactant, followed by calcination. However, common surfactants can be extracted also when these materials come in contact with water, particularly, when the composite is deposited in the form of a thin film. This work concentrates on this last issue.

Composite thin films have been made by dip-coating a glass slide into a silica−surfactant gel. The films were eventually dipped into water, and the leaching of the organics was followed by absorption spectrophotometry or conductimetry. The remaining film was structurally characterized by TEM and AFM. Surfactant leaching is not immediate. Surfactant goes into water by obeying slow rates, which depend on controllable parameters. Transfer of surfactant into the aqueous phase is accompanied by simultaneous leaching of other organic material, which is present in the film, both hydrophilic and hydrophobic. These data are tempting to examine organic−inorganic films as potential carriers for controlled release of active dopants, whether they are drugs, pesticides, dyes, or other related technologically important substances.

Materials and Methods

Cetyltrimethylammonium bromide (CTAB, Fluka), sodium dodecyl sulfate (SDS, Fluka), Triton X-100 (TXT, Aldrich), tetraethoxysilane (TEOS, Aldrich), pyrene (Fluka), coumarin-153 (C-153, Aldrich), and rhodamine 6G (RH6G, Lambda Physik) were used as received. Millipore water was used in all experiments.

Composite silica−surfactant thin films were deposited by dip-coating on glass slides, previously cleaned in sulfochromic solution. The precursor solution and gel were prepared in the following manner:[15] TEOS was first partially hydrolyzed by mixing with water containing HCl (pH 3.0). The molar ratio was TEOS:water 1:2. The mixture was continuously stirred for 3 h. At the beginning it was turbid but in the course of proceeding hydrolysis it became clear. Then, to 1 mL of this sol, we added 5 mL of 0.1 M aqueous surfactant solution. Dipping was performed immediately after preparation of the final mixture. The slide was withdrawn at a speed of 44 mm/min. The film was left to dry in air. The whole procedure was carried out at ambient conditions. The thickness of the

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films was estimated gravimetrically and with the help of a scanning electron microscope (side view of the film). It was approximately 160 nm in the case of films made with CTAB and about 300 nm in the case of films made with TXT or SDS.

The dyes were incorporated in the film by solubilization in the aqueous surfactant solution which contains micelles, at surfactant concentration equal to 0.1 M, and is capable of solubilizing hydrophobic probes. In all cases studied, the dye concentration in the micellar solution was 2 mM.

Absorption measurements were made with a Carry 1E spectrophotometer and conductivity measurements with a metrohm 660 conductometer and a low conductivity cell ($\kappa = 0.074\ \text{cm}^{-1}$). Fluorescence measurements were made with a home-assembled spectrofluorometer using Oriel parts. Transmission electron microscopy (TEM) images were obtained with a Philips 300 microscope and atomic force microscopy (AFM) images with a Nanoscope III Digital Instruments in the tapping mode. Measurements have been carried out at ambient conditions.

Results and Discussion

Study of Leaching in Films Containing Triton X-100 (TXT). Silica–TXT composite films were made, as above by starting with an aqueous TXT micellar solution containing 0.1 M surfactant. TXT forms aqueous micelles with critical micellization concentration (cmc) equal to 0.22 mM.[18,19] Films made after mixing with the prehydrolyzed TEOS, contained a dye: either water soluble (e.g., Rh6G) or scarcely soluble in water (e.g., C-153 and pyrene). The dye content of the films was monitored by absorption spectrophotometry. Leaching in water was studied by two procedures. First, slides supporting films were dipped in Millipore pure water for 15 min. After this time, colored water was changed with fresh pure water while the colored aqueous solution containing leached surfactant and dyes was disposed. Absorption of the film was monitored every 15 min, just before dipping in fresh water. The procedure ended when no absorption from the film was detected any more. Figure 1 presents the obtained results, showing absorbance at the wavelength of its maximum. In the second procedure the slide was dipped in pure water and was left there until equilibrium was reached. The results are shown in Figure 2. If water is not changed, not all of the dye content can be leached. Leaching stops when the amount of dye in water is in equilibrium with the amount of dye remaining in the film. In addition to Rh6G, other dyes have been tried and gave similar results. The above data show that the hydrophobic dyes C-153 and pyrene are more easily leached than the hydrophilic dyes. This result may look unexpected, but it is justified by the solubilization site for each dye in the composite film and by taking into account the fact that leaching of dyes is the consequence of leaching of the surfactant itself. Indeed, the quantity of TXT in the film can be also monitored by absorption spectrophotometry. Since TXT absorbs in the UV, its absorption cannot be detected on the film itself, because of the UV absorbing glass support. For this reason, TXT was detected in the water where it was dissolved by leaching from the film. Figure 3 shows this result. It is seen that the surfactant leaches fast at the beginning. In about 1.5 h, most TXT content in the film is leached. Further leaching is extremely slow. The release kinetics of TXT matches with the release of hydrophobic probes. It is concluded that the solubilization site of pyrene and C-153 is within the surfactant assembly and not in the SiO_2 network.

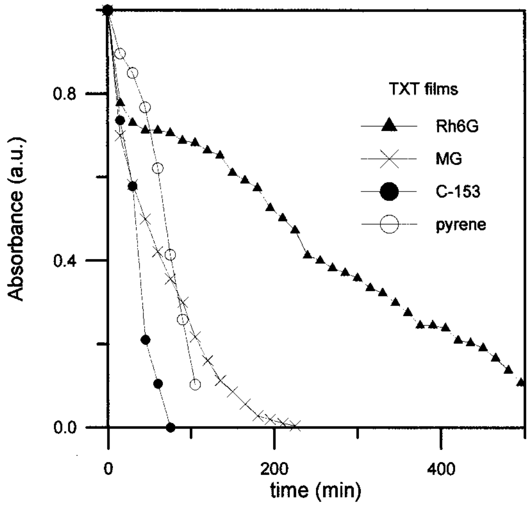

Figure 1. Absorbance of composite silica surfactant films containing various dyes after successive 15 min leaching in pure water.

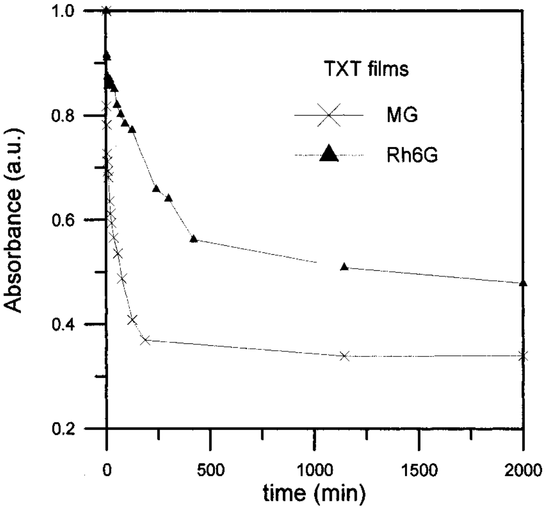

Figure 2. Leaching and equilibrium distribution of Rh6G between film and water.

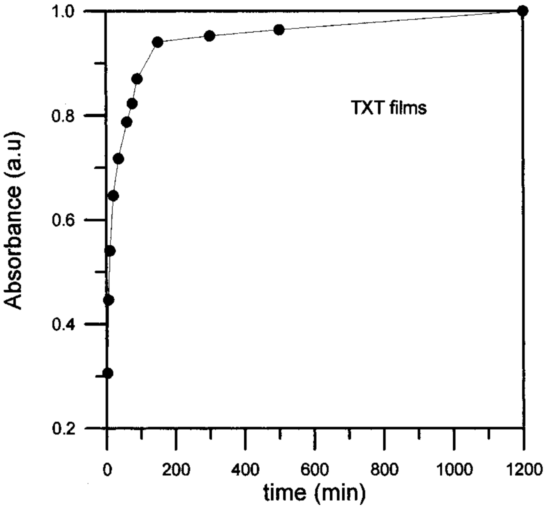

Figure 3. Absorbance of leached TXT (●) and conductivity of leached CTAB (■), and SDS (▲) in water as a function of time.

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Table 1. Absorbance Maximum for C-153 and I_1/I_3 Value for Pyrene in Different Environments

solvent or microenvironment	C-153[a] abs. max (nm)	pyrene[a,b] I_1/I_3
cyclohexane	395	0.59
methanol	422	1.31
dimethyl sulfoxide	426	
TXT micelles	427	1.17
TXT films	425	1.25
CTAB micelles	435	1.24
CTAB films	434	1.34

[a] Probe concentration in pure solvents and in micelles was 10 μM. In films it is expressed as ratio over surfactant concentration and it was 1/50 for C-153 and pyrene monomer. [b] Non-corrected fluorescence spectra.

Such a conclusion is supported by the photophysical behavior of pyrene and C-153 in all the stages of the formation of the film, from the original aqueous micelles till the final product, as seen in the following paragraph.

C-153 and Pyrene Photophysics in Different Environments. Both substances possess photophysical properties that are sensitive to the nature of their environment. The absorbance and the fluorescence spectral maximum of C-153 is sensitive to solvent polarity, and it is red-shifted in polar solvents.[17,20] Table 1 shows the position of absorbance maxima of C-153 in some model solvents, in the original micellar solution and in the final film. The red shift in polar solvents is seen by the variation from 395 nm in cyclohexane to 422 nm in dimethyl sulfoxide. In TXT micelles, the absorbance maximum indicates that C-153 lies in a very polar environment. Since C-153 is insoluble in water, especially at the concentration used to prepare films (cf. footnote of Table 1), we conclude that the solubilization site is at the interface between the polar surface and the nonpolar interior of the TXT micelles. Upon film formation, C-153 microenvironment became slightly more micellar, i.e., hydrophobic. As already suggested in the previous paragraph, C-153 remains in the surfactant phase both before and after film formation and is leached from the film together with the surfactant. Pyrene microenvironment can be characterized by studying the I_1/I_3 ratio of its fluorescence spectra vibronic structure.[21-23] The I_1/I_3 value increases in going from nonpolar to polar solvents or microenvironments. As seen in Table 1, it is 0.59 in cyclohexane and 1.31 in methanol. The I_1/I_3 value was 1.17 for pyrene in TXT aqueous micelles and it increased to 1.25 in TXT films. This small increase in microenvironment polarity does not mean that pyrene has exited the surfactant subphase. Pyrene solubilized in pure-silica films in the presence of alcohol and without surfactant does not even preserve its monomeric form (and its vibronic structure), but it is in an aggregate form with complete loss of its spectral structure. Increase of I_1/I_3 value from 1.17 to 1.25 simply means rearrangement of the residual site of pyrene at the polar/hydrocarbon interface.

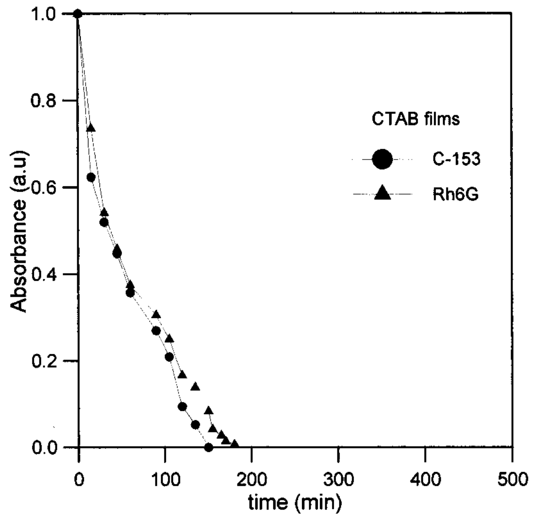

Figure 4. Absorbance of composite silica−CTAB films containing various dyes after successive 15 min leaching in pure water.

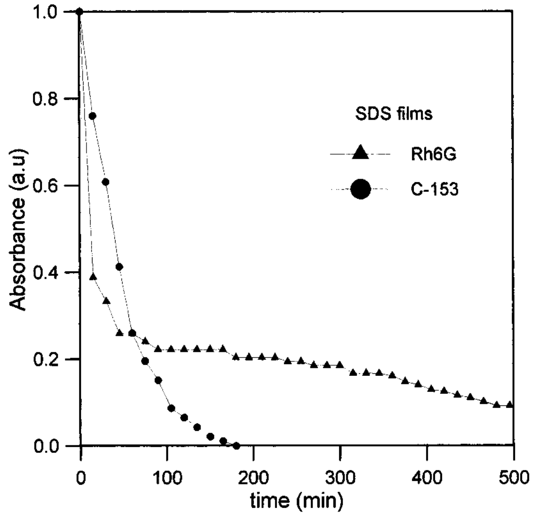

Figure 5. Absorbance of composite silica−SDS films containing various dyes after successive 15 min leaching in pure water.

Study of Leaching of Dyes from Films Containing CTAB or SDS. Aqueous solutions of CTAB at 0.1 M form micelles, since the cmc of CTAB is 0.9 mM.[24] The films made after mixing prehydrolyzed TEOS with the aqueous CTAB micellar solution gave leaching rates different from those at TXT. Figure 4 shows results obtained with a hydrophilic (Rh6G) and a hydrophobic probe (C-153). Both probes were leached with practically similar rates, while similar results were also obtained with other hydrophilic and hydrophobic probes. On the basis of the data of Table 1 and the arguments of the previous paragraph, we believe that C-153 exits the film together with surfactant in the subphase of which it is solubilized. Leaching of CTAB can be monitored by conductivity measurements on the ensuing aqueous solutions, since the amounts of leached surfactant from such thin films is small and the surfactant concentration is then below cmc. Indeed, the conductivity values we have recorded are of the center of 10 μS cm^{-1}, which corresponds to an ionic content well below cmc. As seen in Figure 3, the conductivity of the water we used before leaching was practically zero. Conductivity increased fast, after dipping a slide covered with the SiO$_2$/CTAB film, and it arrived at

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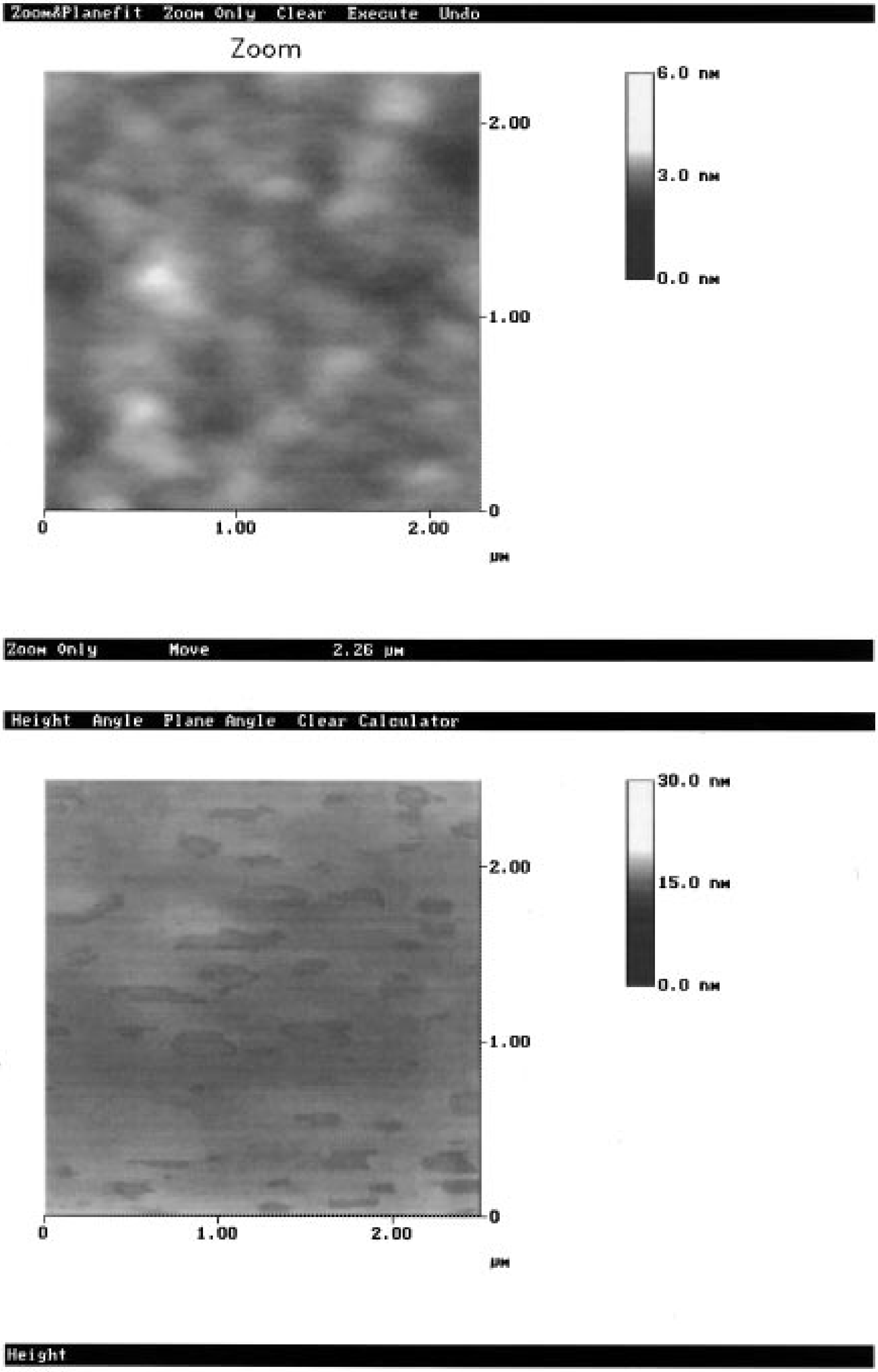

Figure 6. AFM image of a silica–CTAB film, as prepared (upper image) and after extensive leaching (lower image).

equilibrium after about an hour. The fast initial increase of conductivity and the rapid reach of equilibrium are indicative of a fast release of this ionic surfactant. The equally fast release rates observed with Rh6G could be associated with the particular features of the silica–CTAB films. From gravimetric and scanning electron microscopy measurements, we have found that TXT-containing films are twice as thick as CTAB-containing

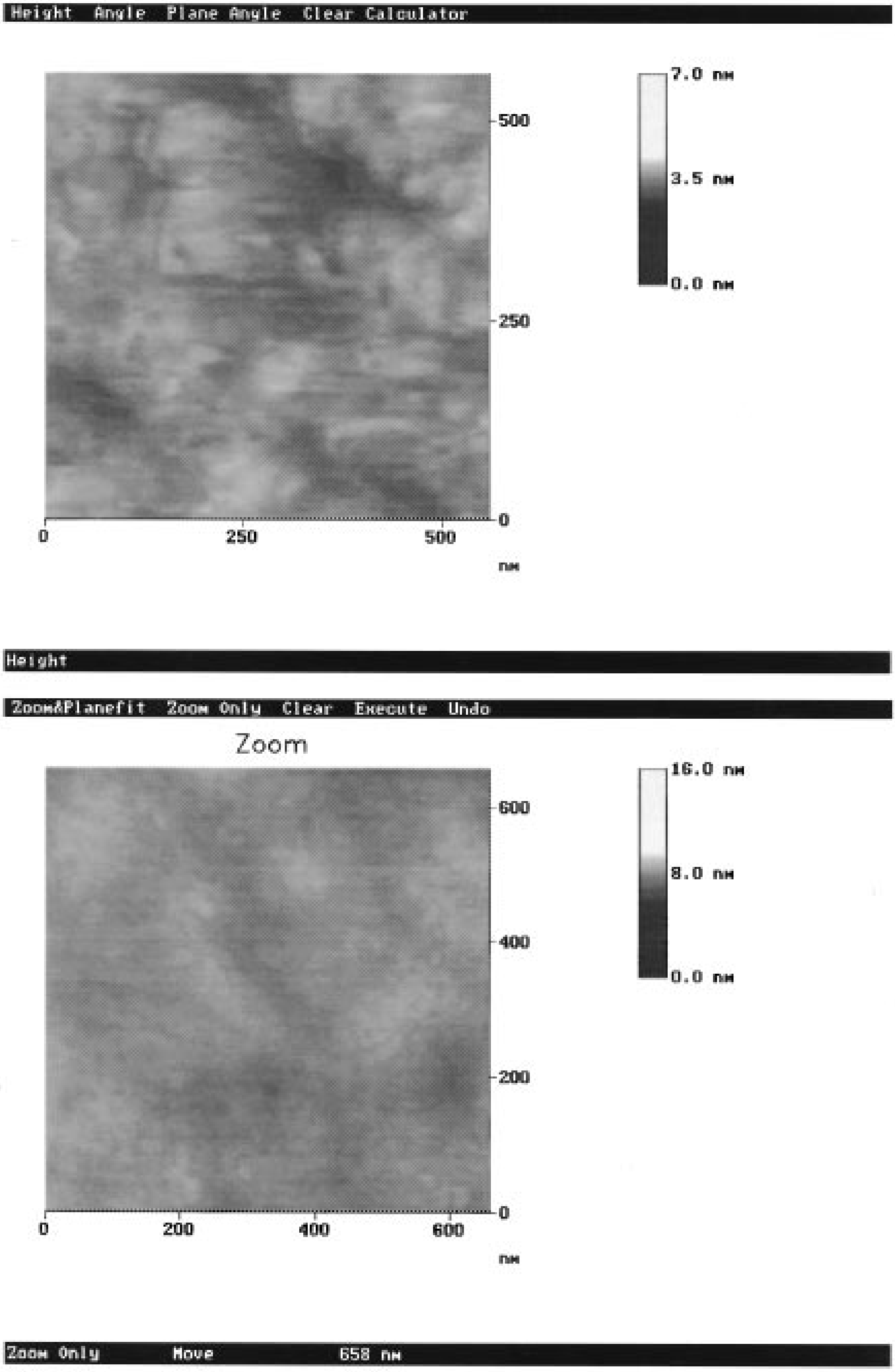

Figure 7. AFM image of a silica−TXT film, as prepared (upper image) and after extensive leaching (lower image).

films. Also, as will be seen in the following paragraph, the remaining material, i.e., silica, after surfactant leaching, is very poor, in terms of structure and quantity. By considering the fact that Rh6C is a positively charged molecule, repelled by the also positively charged cationic surfactant, it seems that this probe is washed from the film simply because there is not enough silica to support it. The entrapment of Rh6G in the silica porous network of bulk matrixes has been previously studied and well documented.[25]

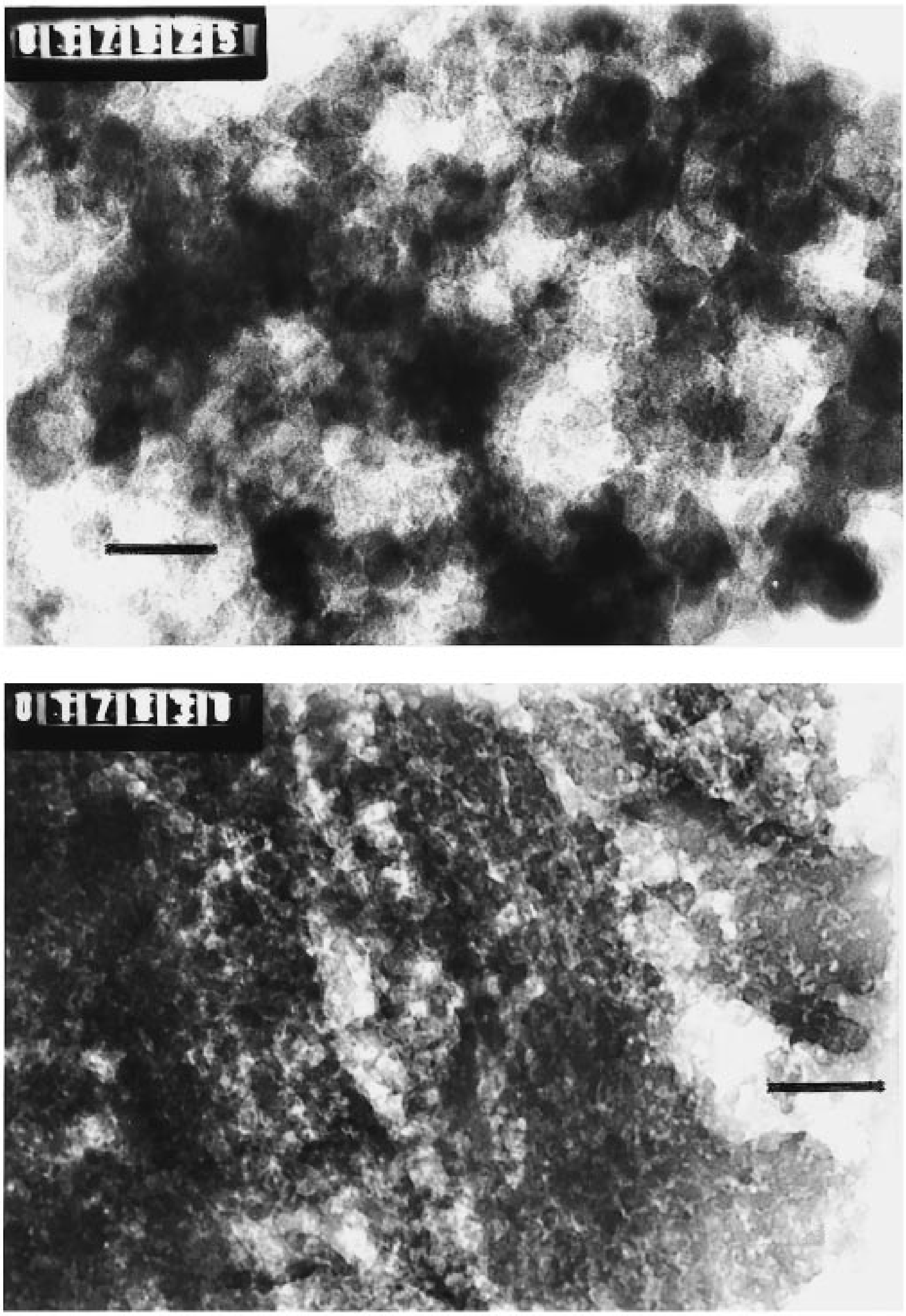

Figure 8. TEM image of a silica−CTAB film after extensive leaching (upper image) or after calcination at 400 °C (lower image). Scale bar = 100 nm.

Aqueous SDS solutions at concentration 0.1 M also contain micelles (cmc = 8.2 mM[24]). Figure 6 shows the leaching rates of Rh6G and C-153 from films made after mixing prehydrolyzed TEOS with aqueous SDS solutions. This time, the hydrophilic probe did not completely leave the film. After a rapid initial release, an important percentage of the dye did stay in the film, steadily bound to the remaining silica network. Gravimetric measurements indicated that the thickness of SDS-containing films were a rough double of the thickness of CTAB-containing films. We thus believe that a large percentage of Rh6G initially rapidly leaves the film with the attractive oppositely charged surfactant while the remaining percentage is held by the polar silica network. This is not possible for the hydrophobic dye C-153 which leaves film with surfactant. Such a conclusion is consistent with the SDS release rates, as can be extracted from the variation of the conductivity values of water containing the leached SDS, shown on Figure 3. Obviously, also in this case, the release of C-153 simply reflects the release of the surfactant.

The differences in the behavior of the three surfactants can also be associated with the gelation rates of the obtained sols. The sols containing TXT or SDS gel in a few hours, while those containing CTAB need a few days to gel, under the same conditions. It is obvious

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that the development of the silica network is very slow in the presence of CTAB, resulting in both thinner films and weaker silica support. Films made with CTAB and with dip-coating performed later and not immediately after mixing of the components are thicker but suffer of lack of uniformity and poor transparency.

Structural Characterization of the Films. The structure of the films, with and without surfactant, were studied with AFM and TEM. The AFM images of Figures 6 and 7 show that the surfactant-containing films possess a granular structure with a smoother relief in the presence of surfactant and much deeper empty spaces in its absence. TXT films suffer less dramatic variation than CTAB films, where most of the material making the film seems to be washed out after coming in contact with water. It is then highly probable that part of the silica also leaves the film due to extensive structural rearrangements in the film in the case of CTAB. This could also justify the extensive leaching of hydrophilic probes in the case of this surfactant. The ordered mesoporous structures observed in matrixes with surfactant templates is difficult, if not impossible, to reproduce with films. The TEM image of Figure 8 (upper image) clearly shows the aspect of the CTAB-based film after surfactant release. Clustering of silica and large empty areas compose the main features of the remaining film in agreement with the corresponding AFM images and the data of the previous paragraph. It is, however, also found that CTAB-based films obtained by calcination (Figure 8, lower image) preserve a notion of linear structure, which collapses in contact with water. It should be noted in this respect that structured lamellar phases have been observed[15] in thin surfactant/CTAB films. The above features were detected only with CTAB-containing films while a more compact and more random structure characterized TXT- and SDS-containing films.

Conclusion

Leaching of hydrophobic dyes from composite silica/surfactant films into water lasts about 1.5−2 h. Hydrophilic dyes can stay longer if the film is thick enough and the silica network is extensive enough to support them. SDS and TXT films resist persistent washing and hold an important percentage of incorporated hydrophilic dyes because of their larger thickness and their more developed silica network. On the contrary, in CTAB films, hydrophilic dyes are leached as fast as hydrophobic ones. Release of hydrophobic dyes into water is facilitated by surfactant which is also washed into water. Some order observed in CTAB films could be preserved only by calcination but not by surfactant leaching.

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