Solubilization of Aromatic Molecules in Templating Micelles of Mesoporous Silicas Followed by ^{1}H NMR

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Liquid-phase ^{1}H NMR measurements of M41S synthesis gels were performed to characterize the structure of the alkyltrimethylammonium salt micelles swelled with benzene or trisubstituted aromatic compounds. The chemical shift and the line width of the aromatic species allowed the determination of the locus of the aromatic compounds within the templating micelle. Benzene is incorporated and immobilized close to the surface of the micelle, whereas the more hydrophobic trisubstituted aromatic compounds are located in the hydrophobic core of the micelle, where they retain some mobility. The variation of the amount of the aromatic swelling agent further supports this idea. The decreasing mobility of the alkyltrimethylammonium surfactants in the course of the synthesis could be followed from the broadening of the signals in ^{1}H NMR. It showed that the organic−inorganic mesophase is formed within the first 24 h of synthesis.

Introduction

In a parallel study[1] we investigated the effect of aromatic swelling agents on the pore geometry and pore size of mesoporous M41S materials. Benzene and 1,3,5-trisubstituted aromatic compounds were used as swelling agents. The characterization of the final products and SAXS measurements in the course of the synthesis showed that the nature and the amount of swelling agent influenced both the size and the geometry of the templating micelles and pores of the final M41S material. It was observed that the surface curvature of the templating micelle increased together with the hydrophobicity of the aromatic swelling agent. On the basis of NMR[2] and UV[3] results of others, this effect could be rationalized with the locus of incorporation of the aromatic swelling agent in the templating micelle. It was proposed that benzene and substituted aromatic molecules distribute according to their polarity between the highly nonpolar core and the relatively polar interfacial region of the hexadecyltrimethylammonium bromide micelles in water. Calorimetric measurements of an aqueous solution of tetradecyltrimethylammonium bromide showed that benzene decreases the micelle curvature.[4] Simultaneously, a transition of the micelles from a spherical to a rodlike geometry was observed. The transformation of rodlike tetradecyltrimethylammonium bromide micelles to spherical micelles as a consequence of the addition of both aliphatic and aromatic compounds was also described.[5]

Here we report a ^{1}H NMR investigation of the distribution of aromatic molecules in the silica−surfactant micelles of M41S synthesis gels. The goal of the study was to provide direct evidence for the locus of incorporation of the aromatic molecules in the real synthesis mixture.

Experimental Section

Mesoporous pure silica M41S materials were synthesized by thermal treatment of a gel with sodium silicate solution, cationic quaternary ammonium surfactants (C_{16} and C_{12} chains), organic swelling agent, and water for 96 h at 373 K in a sealed Teflon vessel, as described in detail in the first part of this study.[1] The molar composition of the gel was 1 SiO_2/0.262 Na_2O/0.109 HTMA-Cl/0.040 DTMA-Br/31.5 H_2O. The nature and the amount of the aromatic swelling agent SA (benzene, mesitylene, 1,3,5-triisopropylbenzene (TiPB), and 1,3,5-tri-*tert*-butylbenzene (TtBB)) were varied while all the other parameters were kept constant. In the standard recipe a molar ratio of SA/SiO_2 = 0.72 was used.[1,6] For simplicity, this relative molar amount of swelling agent was defined as 100%. Smaller and larger SA/SiO_2 ratios are expressed by the corresponding values in percent (Table 1). Fifteen syntheses of mesoporous materials were performed and monitored in situ with ^{1}H NMR (Table 1). Samples from the synthesis gel were taken at different stages of the synthesis procedure. For all measurements the synthesis gel was cooled to ambient temperature and stirred for at least 15 min before the sample was taken. A Wilmad coaxial insert capillary (1 mm o.d.) was filled with synthesis gel and was introduced into an ordinary 5 mm NMR tube with TMS in deuterated chloroform ($CDCl_3$) as external standard. Proton NMR spectra of the synthesis gels were recorded on a Bruker AVANCE 500 at ambient temperature (^{1}H frequency 500.13 MHz, ^{1}H recycle delay 2.7 s).

TABLE 1: Amounts of Aromatic Swelling Agents Employed

swelling agent	relative molar amount, %	molar ratio SA/SiO_2[a]	swelling agent	relative molar amount, %	molar ratio SA/SiO_2[a]
no swelling	0		TiPB[b]	5	0.04
benzene	5	0.04		20	0.14
mesitylene	5	0.04		30	0.22
	20	0.15		40	0.29
	50	0.36		80	0.58
	100	0.72	TtBB[c]	5	0.04
	200	1.45			

[a] SA = swelling agent. [b] TiPB = 1,3,5-triisopropylbenzene. [c] TtBB = 1,3,5-tri-*tert*-butylbenzene.

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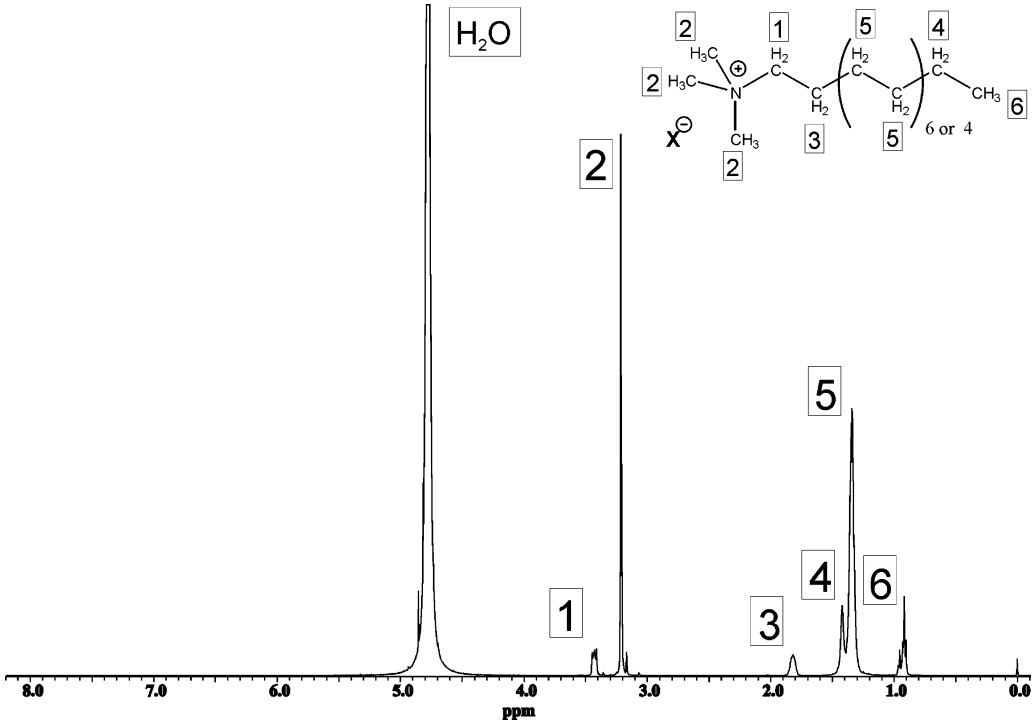

Figure 1. ^{1}H NMR spectrum of an aqueous solution of cationic quaternary ammonium salts used as templates for the synthesis. The large peak at 4.8 ppm is due to water.

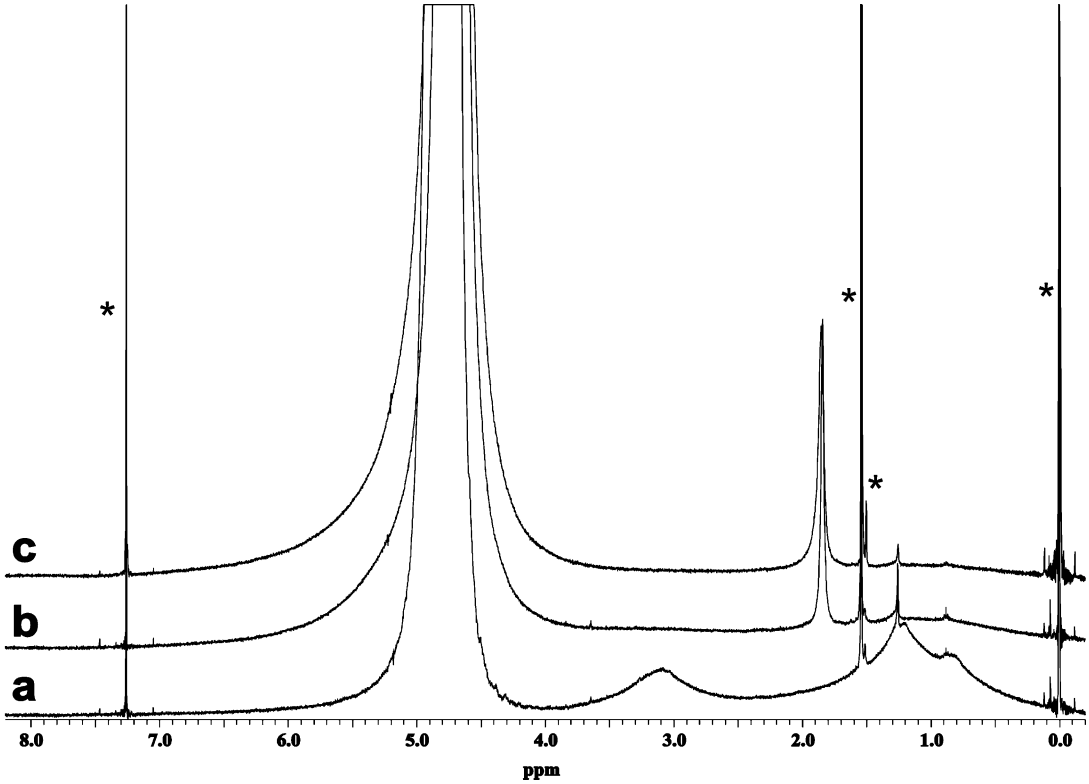

Figure 2. ^{1}H NMR spectra of the synthesis gel without aromatic swelling agent (a) after mixing the gel for 60 min, (b) after 24 h of thermal treatment at 373 K, and (c) after 96 h of thermal treatment at 373 K. The sharp peaks caused by the external reference are marked with asterisks (7.26 ppm for $CHCl_3$ in $CDCl_3$, 1.54 ppm for HDO in $CDCl_3$, 1.50 ppm for H_2O in $CDCl_3$, 0.00 ppm for TMS).

At the end of the syntheses, the gels were filtered. The as-synthesized material was dried, calcined, and characterized with nitrogen sorption. All materials showed pore characteristics comparable to those prepared without the removal of small amounts of gel for ^{1}H NMR measurements in the course of the synthesis.[1] The formation of silica−surfactant micelles in these synthesis systems is rather slow since sodium silicate is used as the silica source.[7] The ^{1}H NMR measurements lasted 10 min, which is fast compared to the 96 h total synthesis time. In addition, the ^{1}H NMR spectra were recorded at ambient temperature, whereas the temperature of the thermal treatment was 373 K. Therefore, it can be safely assumed that the synthesis mixtures change only to a very small extent during the NMR measurements. This was verified by repeating some of the

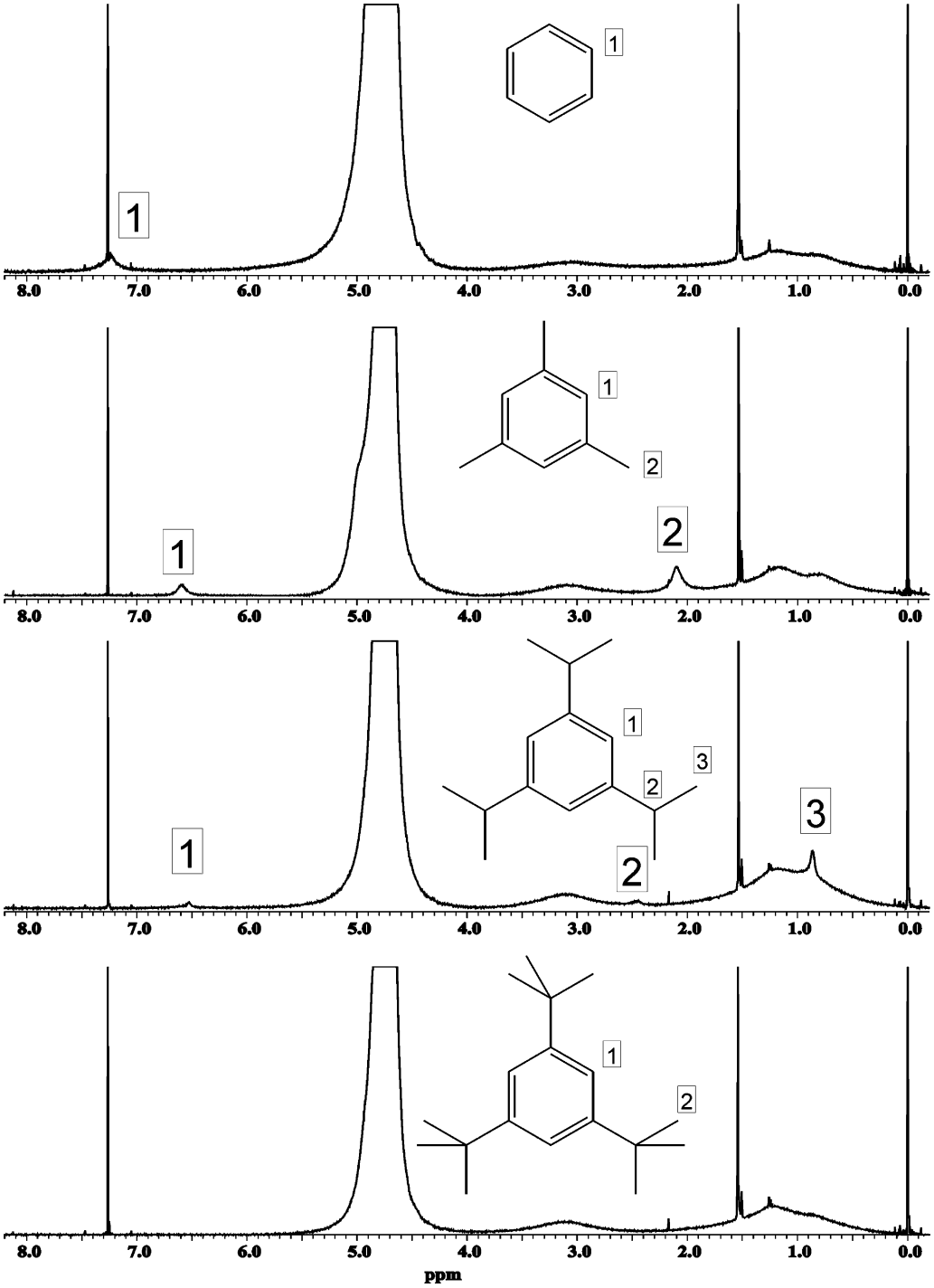

Figure 3. ^{1}H NMR spectra of the synthesis mixture with a 5% relative molar amount of varying aromatic swelling agent after 60 min of stirring (before the thermal treatment): benzene (BEN 5), mesitylene (MES 5), TiPB (TiPB 5), TtBB (TtBB 5).

measurements; no differences could be observed. The sedimentation of the silica particles during the measurements was very slow and did not interfere.

Results

No Aromatic Swelling Agents. For the peak assignment an aqueous solution of the two quaternary ammonium salts with the same concentration as used in the syntheses was measured (Figure 1). The two surfactants differ only in the length of the hydrophobic chain. Without any swelling agent or silicate present one obtains a clear solution with sharp ^{1}H NMR signals. The chemical shifts of the peaks were very close to those of a similar solution measured in D_2O.[8]

When the template and the silicate were mixed to obtain the synthesis mixture, a white precipitate formed immediately. From that point the synthesis mixture was a homogeneous white gel throughout the synthesis. The effect of the gel formation on the ^{1}H NMR spectrum of the quaternary ammonium template can be seen in the spectrum of a synthesis mixture recorded after the gel was stirred for 60 min (Figure 2a). Because all ^{1}H NMR spectra of the synthesis gels were recorded with an external reference of TMS in $CDCl_3$, they all showed the following sharp signals coming from the external reference: $CHCl_3$ impurity at 7.26 ppm, water impurity at 1.50 ppm, HDO at 1.54 ppm, and TMS at 0.00 ppm. Directly after the synthesis gel was mixed, the quaternary ammonium species could be

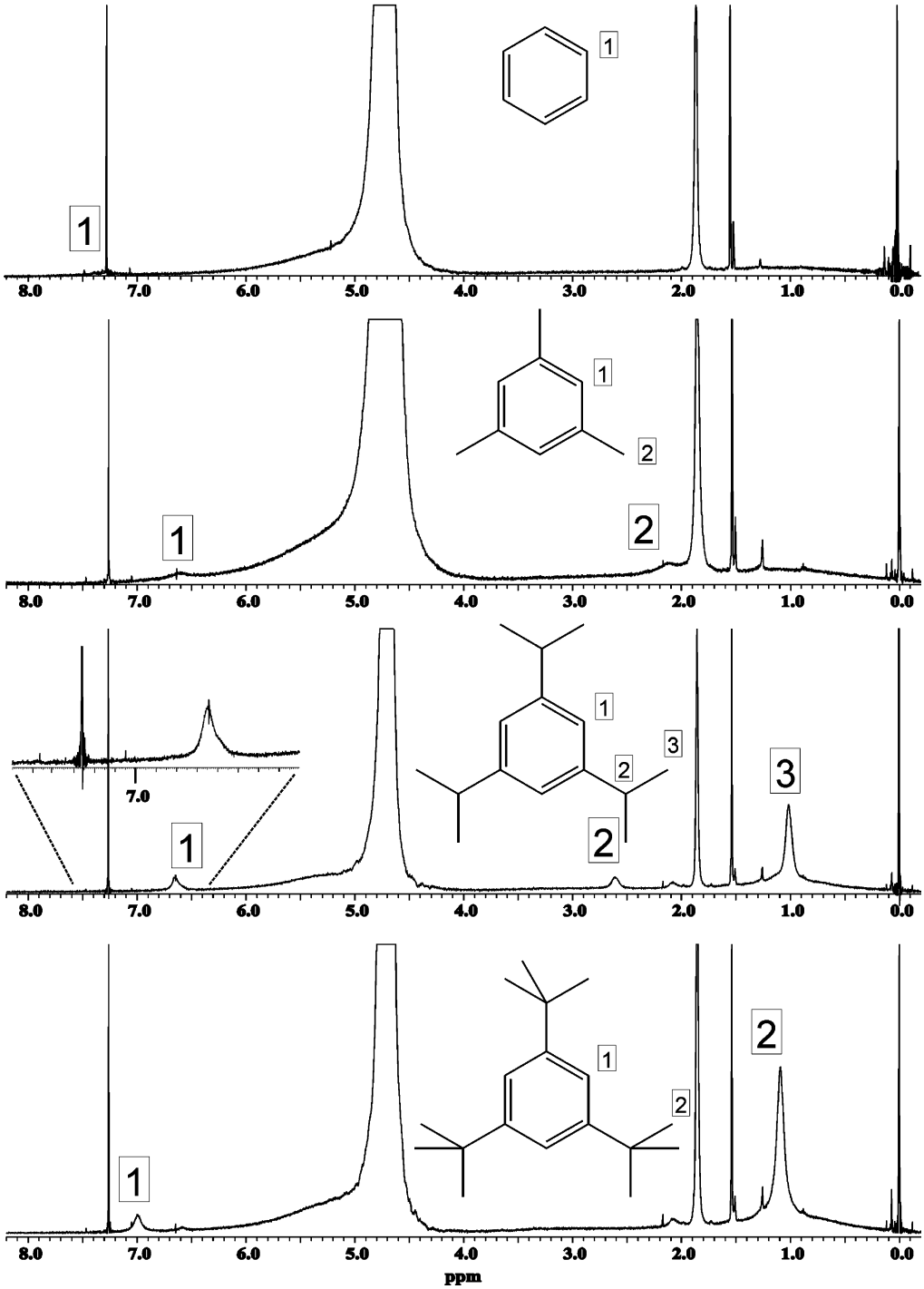

Figure 4. [1]H NMR spectra of the synthesis mixture with a 5% relative molar amount of varying aromatic swelling agent after 96 h of thermal treatment at 373 K: benzene (BEN 5), mesitylene (MES 5), TiPB (TiPB 5), TtBB (TtBB 5).

identified by three very broad peaks in the [1]H NMR spectrum (Figure 2a). One peak with a maximum at 3.09 ppm can be assigned to the protons bound to the carbon atoms next to the nitrogen atom. The signal at 1.21 ppm comes from the protons in the middle of the hydrophobic chain of the surfactant molecule. The signal with a maximum at 0.85 ppm can be assigned to the CH_3 groups at the end of the hydrophobic chain. In addition to these three very broad peaks, two very weak but sharp signals were observed at 1.26 and 0.88 ppm. They are most probably caused by a small fraction of the quaternary ammonium salt that is still dissolved in the aqueous phase of the synthesis gel. The chemical shift of these two signals was slightly lower than those in the aqueous solution (Figure 1), because the synthesis gel has a higher ionic strength. The reason for the broadening of the peaks of the cationic quaternary ammonium species in the synthesis gel is the binding of negatively charged silicate oligomers and polymers to the quaternary ammonium cations. The large S^+I^- units have a low mobility and are partly insoluble.[9] After 24 h of synthesis (Figure 2b), the proton peaks of the quaternary ammonium species were broadened into the baseline. This is due to the condensation between adjacent silicate species and the actual formation of the solid organic−inorganic mesophase during the first 24 h of synthesis. No more peak maxima could be identified in the spectra. On the other hand, a new and relatively sharp signal at 1.85 ppm appeared in the spectrum recorded after 24 h of

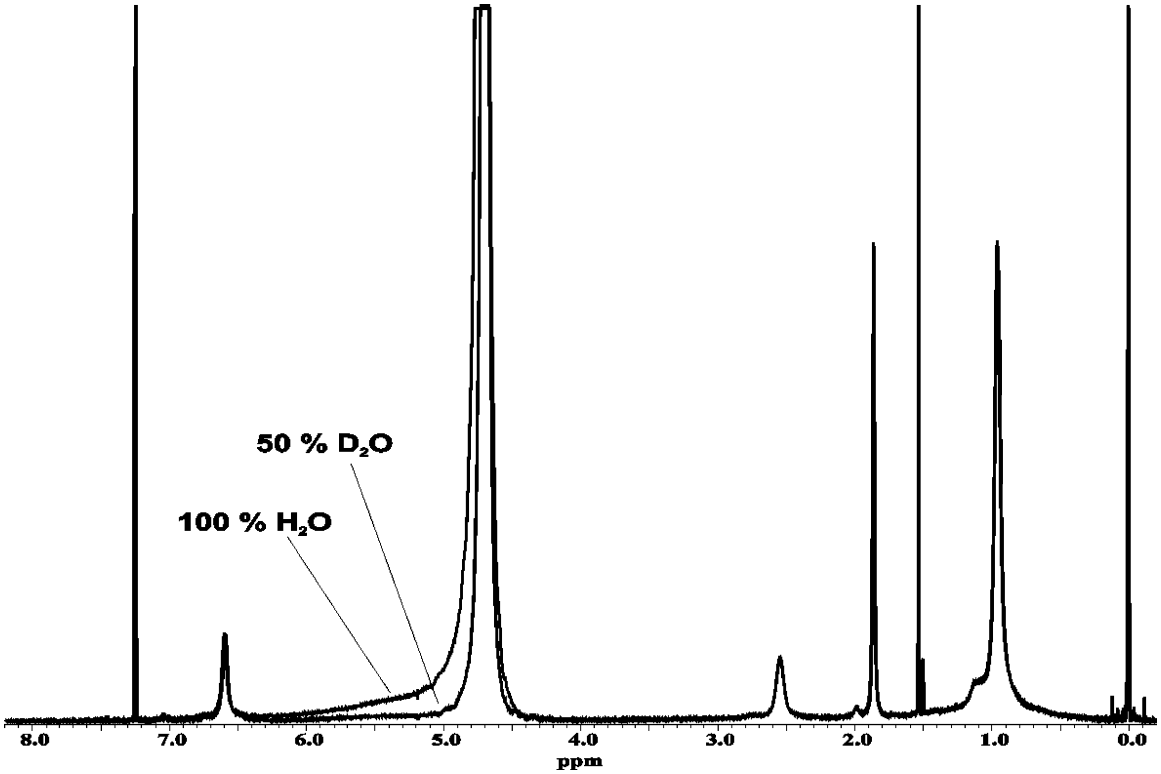

Figure 5. ^{1}H NMR spectra of the synthesis mixture with a 20% relative molar amount of TiPB as swelling agent after 96 h of thermal treatment in H_2O and with 50% of the H_2O replaced by D_2O.

synthesis and also in the subsequent ^{1}H NMR spectra recorded in the course of the synthesis. This signal comes from the methyl group of the acetic acid which is added to the synthesis mixture after 24 h. The addition of acid was shown to improve the stability of this kind of mesoporous material.[6,7] The acid proton of the acetic acid was not visible because it exchanges rapidly with the water in the synthesis mixtures. Until the end of the synthesis (Figure 2c) the ^{1}H NMR spectrum of this synthesis gel did not change significantly anymore.

Identical Amounts of Benzene, Mesitylene, TiPB, and TtBB as Swelling Agents. The same peaks of the quaternary ammonium salts and the acetic acid as described above were also observed in all the syntheses performed with aromatic swelling agents. In the following, only the evolution of the peaks ascribed to the aromatic swelling agents are discussed. In general, the signals of the aromatic swelling agents were sharper than those of the surfactant molecules. This is a consequence of the fact that the swelling agents are more mobile than the surfactant molecules, which are bound to the silicate by ionic bonds. The differences between the chemical environments of the four aromatic swelling agents could be best seen in materials with very small SA/SiO_2 ratios, i.e., a 5% relative molar amount of each swelling agent. Figures 3 and 4 show the ^{1}H NMR spectra of the respective gels before and after 96 h of thermal treatment at 373 K, respectively. In the case of benzene, the aromatic protons were clearly visible in the gel before the thermal treatment. After 96 h at 373 K, no signal for the aromatic protons could be identified anymore. This indicates that the benzene was immobilized in the templating micelle, causing a broadening of its NMR signal. The broad signal disappeared in the baseline. In the case of mesitylene, the peak of the aromatic protons was strongly diminished after 96 h of thermal treatment, but could still be identified. Ninety percent of its intensity was lost in the baseline, as in the case of benzene. The same effect was observed for the aliphatic protons of the mesitylene molecule. At the end of the synthesis all spectra showed a broad shoulder at the low-field side of the water signal. The intensity of the shoulder strongly decreased when D_2O was used as a solvent instead of H_2O (Figure 5). Therefore, the shoulder is ascribed to water incorporated into the cationic palisade layer of the silica−surfactant micelles.

With TiPB as swelling agent no loss of ^{1}H NMR signal intensity was observed after 96 h of thermal treatment; i.e., no intensity was lost in a broadened peak. Each of the three resonances at 6.65 ppm (aromatic protons), 2.62 ppm (C−H of the isopropyl group), and 1.01 ppm (CH_3 of the isopropyl group) could be deconvoluted into a narrow signal at a higher chemical shift and a broader signal at a lower chemical shift. The broader signal had a relative intensity of about 40%. A similar situation was found in the spectrum of TtBB after 96 h of thermal treatment: Each peak consisted of two overlapping signals. The separation of the two signals was larger than in the case of TiPB. The one at lower chemical shifts was also broader and accounted for 10% of the intensity. The signal intensities of TiPB and TtBB increased from the spectrum measured after the synthesis gel was mixed to the spectrum measured after 96 h of thermal treatment (compare Figures 3 and 4). This is ascribed to the low solubility of these compounds. TtBB is a solid at ambient temperature and was still undissolved after 60 min of stirring the synthesis gel.

Varying Amounts of Mesitylene and TiPB as Swelling Agent. ^{1}H NMR spectra of synthesis gels with varying amounts of mesitylene (Figure 6) and TiPB (Figure 7) as swelling agent were recorded after 96 h of thermal treatment at 373 K. When the relative molar amount of mesitylene increased, the peaks were shifted to higher field (Table 2). In all the spectra only one signal of the aromatic protons could be identified. On the other hand, all materials prepared with TiPB as swelling agent showed a splitting of all three proton resonances into two or more distinct signals, as already mentioned above. The chemical shift of the most intense TiPB resonance was not changed by the variation of the amount of TiPB.

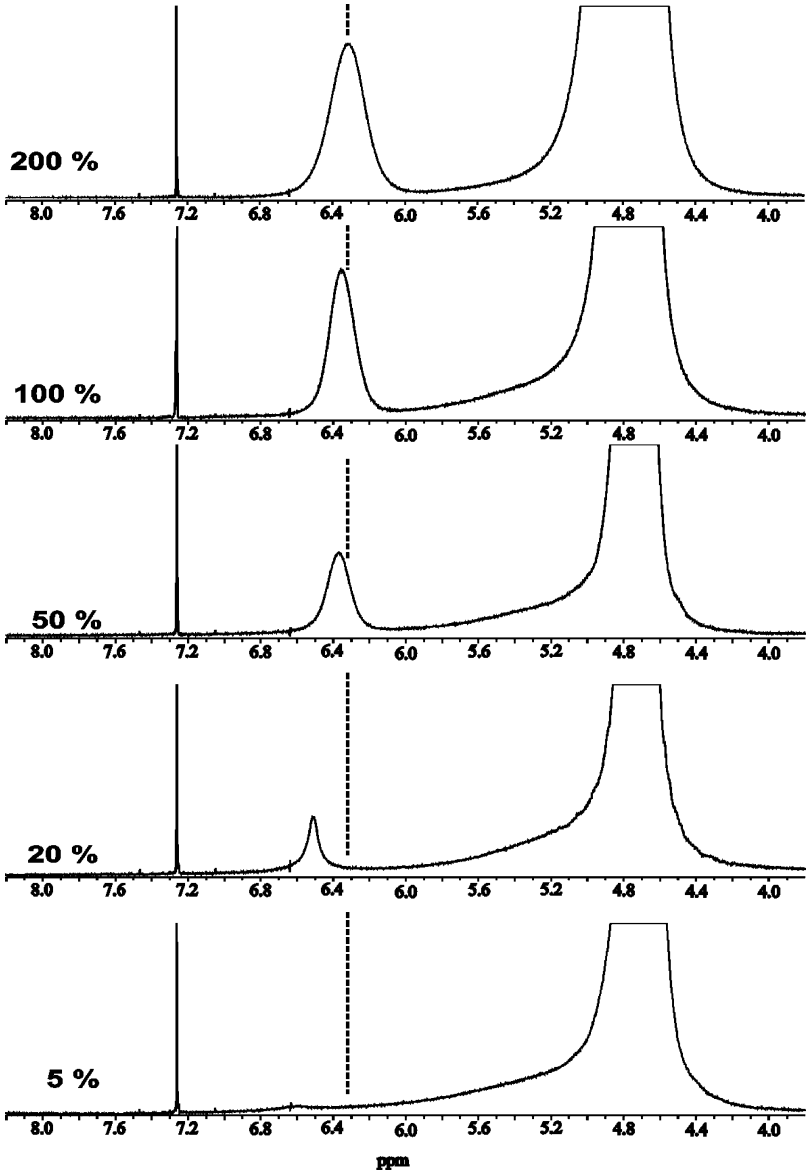

Figure 6. ^{1}H NMR spectra of the aromatic and water regions of synthesis mixtures with varying relative molar amounts of mesitylene after 96 h of thermal treatment at 373 K (MES 200, MES 100, MES 50, MES 20, and MES 5).

It was mentioned above that with a 5% relative molar amount of mesitylene only a very small peak could be observed. Most of the mesitylene in this material was incorporated and immobilized between the aliphatic surfactant chains, causing a severe broadening of the ^{1}H NMR signal, so that it could not be identified anymore. If the amount of mesitylene was increased, a larger fraction of the original amount could be detected at the end of the synthesis. Also a decrease of the chemical shift of the aromatic protons was observed. Both effects are due to an increasing amount of mesitylene molecules that have an aromatic environment. The reason for the smaller chemical shifts of the species in such an aromatic environment is the change in magnetic susceptibility compared to that of the environment with aliphatic surfactant chains. At a 50% relative molar amount of mesitylene the chemical shift remains almost constant, indicating that with larger amounts of swelling agent the average chemical environment of the mesitylene did not change anymore. The chemical shifts of all the peaks of the TiPB in the templating micelles were very similar for all investigated amounts of TiPB as swelling agent. This clearly indicates that the change from a less aromatic environment to one with more aromatic character did not occur if TiPB was used as swelling agent. Already very small amounts of TiPB are incorporated into the core of the micelle, where it forms nests with aromatic character. Although TiPB has an aromatic environment in the core of the micelle, the chemical shift is smaller than in a pure TiPB solution (Table 2). The resonance of mesitylene in materials with large amounts of swelling agent showed the same shift to higher fields with respect to that of the pure compound. The reason for this effect must be the magnetic susceptibility of our synthesis gels, which are more diamagnetic than the pure aromatic solutions. The signal around 7 ppm that appeared when larger amounts of TiPB swelling agent were used is assigned to TiPB species between the aliphatic chains of the surfactant molecules.

Discussion

It is known that benzene is incorporated into the palisade layer of micelles of quaternary ammonium surfactants,[3−5] whereas aromatic compounds with more hydrophobic substitutents tend to reside in the hydrophobic core of the micelle.[2−4,10,11] Our NMR data show that this is also valid for silica−surfactant S^+I^- micelles: A comparison of Figures 3

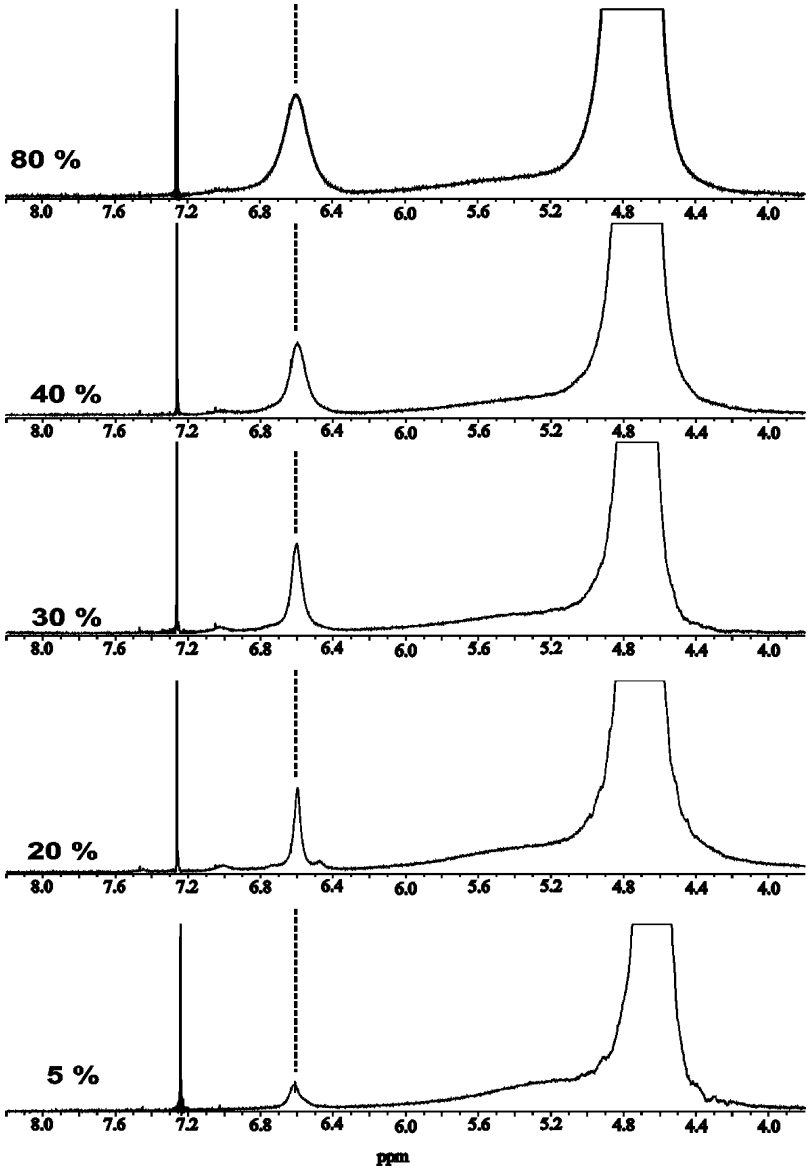

Figure 7. ^{1}H NMR spectra of the aromatic and water regions of synthesis mixtures with varying relative molar amounts of TiPB after 96 h of thermal treatment at 373 K (TiPB 80, TiPB 40, TiPB 30, TiPB 20, and TiPB 5).

TABLE 2: Chemical Shifts (ppm) of the Predominant Peaks in the ^{1}H NMR Spectra after Synthesis with Varying Amounts of Mesitylene and TiPB as Swelling Agents

rel molar amount of swelling agent (%)	aromatic H	aliphatic H(2)[a]	aliphatic H(3)[a]
MES 200	6.32	1.85	*b*
MES 100	6.36	1.88	
MES 50	6.37	1.89	
MES 20	6.51	2.03	
MES 5	6.59	2.11	
pure mesitylene[c]	6.63	2.16	
TiPB 80	6.61	2.54	0.94
TiPB 40	6.60	2.53	0.94
TiPB 30	6.60	2.54	0.95
TiPB 20	6.60	2.54	0.95
TiPB 5	6.65	2.62	1.01
pure TiPB[c]	6.85	2.78	1.19

[a] Labeled as in Figure 3. [b] No second aliphatic proton. [c] As a reference.

and 4 shows that the initially rather sharp ^{1}H NMR resonance of benzene disappeared in the course of the synthesis. In the first part of this study it was found that benzene as swelling agent leads to the formation of a lamellar organic−inorganic mesophase.[1] A lamellar phase can only be advantageous for this system if the surface curvature of the organic template is decreased by the incorporation of the benzene between the cationic headgroups of the surfactant molecules. The reasons for the observed decrease of surface curvature as a consequence of the incorporation of the benzene might be the reduction of the electrostatic repulsion between the cationic headgroups of the micelles or a change in charge matching between the cationic micelle and the anionic silicate species.[11] The incorporation of the benzene molecules between the surfactant molecules bound to the growing silica polymers leads to a strong reduction of their mobility. This would cause a severe broadening of the benzene signal similar to the broadening of the signals of the surfactant species. This is in agreement with the experimental observation. We conclude that with increasing synthesis time an increasing fraction of the benzene was immobilized in the organic−inorganic mesophase, near the cationic headgroups. At the end of the synthesis, the incorporation into the surfactant layer was complete, since the NMR peak of the mobile benzene had completely disappeared.

The same was observed if mesitylene was used as swelling agent, but to a smaller extent: The ^{1}H NMR peaks of mobile

mesitylene did not disappear completely at the end of the synthesis (Figure 4). The residual peaks are attributed to mesitylene molecules that still possess some mobility. Their chemical shift is relatively large because these molecules feel the aliphatic chains and the polarizing environment of the cationic headgroups of the surfactant molecules. Both effects lead to a shift of the signals to lower field. The shift of mesitylene in cyclohexane, for example, is 0.4 ppm larger than in pure mesitylene. The majority of the mesitylene molecules, however, did not give rise to a detectable NMR resonance because they are trapped between the aliphatic chains of the surfactant. The driving force for incorporation of mesitylene into the surfactant layer was smaller than in the case of benzene.

In the case of TiPB the intensity of the relatively sharp peaks originating from the mobile species was retained. No broadening of the signals which could be attributed to molecules immobilized in the surfactant layer was observed. With TtBB relatively sharp signals could only be identified at the end of the synthesis. Two components could be identified in the spectra of TiPB and TtBB. This indicates that two different environments, which both allow some mobility, are populated. The predominant signal is attributed to swelling molecules in the core of the micelle. The other signal, which is broader and occurs at smaller shifts, could not be unequivocally assigned. The following two hypotheses could explain this signal: (1) TiPB/TtBB molecules are located between the aliphatic chains of the surfactant molecules. The reason for the smaller chemical shift of TiPB/TtBB molecules in this position is the polarizing effect of the water that is occluded in the palisade layer of the micelle if such small amounts of swelling agent are used. (2) There is formation of ordered domains (e.g., π-stacking) of the aromatic compounds in the core of the micelle.

The discussion above referred to the spectra measured in synthesis mixtures containing 5% swelling agent. If the amount of the swelling agent mesitylene was increased, a decrease in the chemical shifts of the one species could be observed. This is due to an increasing amount of mesitylene in the aromatic environment in the core of the micelle. The chemical shifts of the main species of the TiPB in the templating micelles were very similar for all investigated amounts of TiPB as swelling agent (Table 2).

By combining these findings, the following conclusion can be drawn: The TiPB is under no conditions immobilized in the surfactant shell in a way that severe line broadening would occur. The fact that the chemical shifts of the main TiPB signal did not change as a function of the amount of this swelling agent indicates that these molecules are exclusively incorporated into the core of the micelle or into positions where an exchange of the molecules is still possible. Mesitylene is incorporated into both the surfactant shell and the core of the micelle. At low amounts of swelling agent most of the mesitylene is immobilized in the surfactant shell, but at high concentrations a fast exchange between the molecules in the core and in the shell of the micelle takes place.

The ^{1}H NMR spectra of the synthesis gel without aromatic swelling agent (Figure 2) show that the signals of the surfactant molecules are severely broadened during the first 24 h of synthesis. This is due to the formation of an organic−inorganic mesophase where the surfactant molecules are ionically bound to the solid silicate. The broadening does not change anymore during further synthesis. This shows that all surfactant molecules are incorporated into the solid organic−inorganic mesophase after 24 h of synthesis. The broadening of the signals of small amounts of benzene and mesitylene as swelling agent followed exactly the same pattern (Figure 4). This is in good agreement with the results of the SAXS measurements in the first part of this study, where it was shown that mesophases do not change much after the first 24 h of synthesis.[1] This supports the mechanistic model that the mesophase is formed within the first 24 h of synthesis and that the last 72 h of synthesis is necessary to strengthen the silicate network by further condensation between adjacent silicate units.

Conclusions

The ^{1}H NMR data show that benzene is located preferentially near or between the headgroups of the surfactant molecules. Mesitylene is distributed between the core and the shell of the micelle, whereas 1,3,5-triisopropylbenzene and 1,3,5-tri-*tert*-butylbenzene reside exclusively in the core of the micelle. The preferred locus of these swelling agents in the templating micelles for the M41S synthesis follows the same trend as in purely aqueous surfactant solutions. This different location of the swelling agent within the micelle explains the change in geometry of the silica−surfactant micelles described in the first part of this study.[1] By incorporating benzene close to the headgroups of surfactant molecules, it reduces the surface curvature, which leads to a lamellar structure. Mesitylene has a lower tendency to adsorb near the headgroups. The curvature of the micelle surface is therefore larger, and cylindrical pores are obtained. Yet the ability of mesitylene to exchange between the core and the shell of the micelles allows the stabilization of the micelles with very low curvature and large internal volume. Large pore volumes and pore sizes can be obtained. 1,3,5-Triisopropylbenzene resides exclusively in the core of the micelle. As a result, the curvature of the micelle has to increase and a transition to a spherical micelle is observed.

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