Colloid Polym Sci (2006) 285:359–363
DOI 10.1007/s00396-006-1565-9

SHORT COMMUNICATION

^{13}C NMR study of the influence of the Aerosil surface charge on the short-chain surfactant adsorption

M. V. Popova · Y. S. Tchernyshev · D. Michel

Received: 27 January 2006 / Accepted: 22 August 2006 / Published online: 12 October 2006

Abstract ^{13}C NMR chemical shift measurements have been used to study the adsorption of short-chain ionic surfactants on the Aerosil surface from aqueous solutions. The investigations were carried out in a wide concentration range above and below the critical micelle concentration value. The values and the character of the chemical shift changes of $\Delta\delta$ are mainly determined by the surface charge, which is generally assumed to change with the initial pH value of the silica aqueous dispersion. Most sensitive to changes of the surface charge are the ^{13}C NMR parameters of the first and second carbon atoms in the hydrophobic chain of the surfactant molecules. This allows investigating the influence of the Aerosil surface charge on the structure of the adsorbed aggregates.

Keywords Short-chain surfactants · Surfactant adsorption · Surfactants self-association · ^{13}C chemical shifts

Introduction

The adsorption of surfactants at solid/liquid interface is widely used in many industrial processes such as mineral flotation, emulsion polymerization, dewatering and many others. The structure of adsorption sites, adsorption kinetics and dynamics were studied in detail by various NMR techniques [1–16], infrared spectroscopy [17–20], calorimetric measurements [21–24], fluorescence [25–27], and electronic spin resonance [28]. On the basis of experimental and theoretical investigations, it is shown that the adsorption process results from energetically favorable interactions between the solid adsorbate and the solute species. It is often a very complex process because of the influence of all components of the systems (solid, solvent, and solute). Previous experimental results (see for example reviews [29–31]) have demonstrated that the adsorption process depends on surface charge density, pH, surfactant structure and concentration, electrolyte concentration, and the type of the adsorbent surface (hydrophobic or hydrophilic). It is shown that several interactions can contribute to the adsorption process, such as electrostatic attraction, covalent and hydrogen bonding, hydrophobic interaction between the adsorbed molecules and these molecules with adsorbent surface, as well as the lateral interaction between the adsorbed species and their desolvatation.

Our recent work [32] has shown that the adsorption of short-chain surfactant (potassium nonanoate) from aqueous solution strongly depends on the Aerosil surface charge. On the basis of ^{13}C chemical shifts, we investigated structural changes of the adsorbed layers at various surfactant concentration and/or surface charges. Measurements of the ^{13}C spin-lattice relaxation time T_1 for separate segments of the hydrophobic chain allowed conclusion of the molecular dynamics in the adsorbed state. Thus, we confirmed the results already derived from the chemical shifts. In this article, we show that the diamagnetic shielding of the carbon atoms is very sensitive to the bonding between the active sites on the Aerosil surface and the adsorbed surfactant molecule. The changes are especially essential for the first and second carbon atoms of the amphyphilic

M. V. Popova (✉) · Y. S. Tchernyshev
Department of Quantum-Magnetic Phenomena,
Physical Institute, St. Petersburg State University,
Ulyanovskaya 1,
St. Petersburg 198504, Russia
e-mail: masha@esr.phys.spbu.ru

D. Michel
Faculty of Physics and Geosciences,
University of Leipzig,
04103 Leipzig, Germany

molecules. In ternary systems with a nearly neutral Aerosil surface, we observed a maximum downfield change of the chemical shifts of about 1 ppm. For a relatively strongly charged Aerosil surface, the upfield shift of 3 to 4 ppm was observed for these atoms.

We have carried out similar measurements for four different short-chain ionic surfactants with different chain hydrophobic length. The aim of this study is to investigate the influence of the hydrophobic chain length and Aerosil surface charge on the adsorption of the short-chain amphyphilic molecules and to confirm our previous conclusions [32].

Materials and methods

As adsorbent, we used Aerosil with a specific surface of 200 m^2/g (Degussa) without further pretreatment. Four different anionic surfactants, potassium butanoate [$CH_3(CH_2)_2COOK$], heptanoate [$CH_3(CH_2)_4COOK$], octanoate [$CH_3(CH_2)_6COOK$], and nonanoate [$CH_3(CH_2)_7COOK$], were synthesized in our laboratory. The purity was better than 99.8%. The experiments were carried out using an aqueous Aerosil dispersion with initial pH values of 2 and 6. To prepare the samples with an adsorbent, an amount of 40 mg Aerosil was introduced into a polyethylene tube, and the required pH value of 2 and 6 was set by adding HCl and water. After addition of the acid, the aqueous Aerosil dispersion was kept for 24 h to ensure equilibrium before the surfactant solution was added. Then, the surfactant solution was added. After stirring, all samples were centrifuged for 30 min at a rate of 15,000 rpm. Then, the supernatant formed after this procedure was removed. At the end, the ratio of weight fractions of solid to liquid phases was 1:10 in all samples. For brevity, in the further text, we will denote systems with a relatively high charge density on the Aerosil surface by "systems with pH=2". Similarly, systems with a nearly neutral Aerosil surface are referred to as "systems with pH=6".

^{13}C NMR measurements were made at DC magnetic fields of 11.7 T (Bruker MSL, 500 NMR spectrometer). To increase the ^{13}C chemical shift resolution, magic angle spinning (MAS) techniques and proton broadband decoupling were applied. The MAS frequency was about 2 kHz. For the MAS measurements, 7-mm ZrO_2 rotors were used. All measurements were carried out at 293 K.

The carbon atoms of the surfactant molecules are numerated beginning with the carbon in the polar group of the amphyphilic molecule. The surfactant concentration was varied between 1.5 and 20 wt.%. This range corresponds to concentrations from 0.08 to 2.0 mol/l depending on the molecular size. The values between 1.5 and 20% cover the range above and below the critical micelle concentration (CMC) values for an aqueous solution of the investigated surfactants. As usual, the ^{13}C chemical shifts were referenced to liquid tetramethylsilane. In the following, only the changes $\Delta\delta^1=\delta^1-\delta_0{}^1$ of the chemical shifts relative to the sample with the maximum concentration (20%, chemical shift $\delta_0{}^1$) are given for various concentrations.

Results

In the following, we discuss for the Aerosil dispersion only the chemical shifts of the first carbon because for this atom the changes are maximum. The concentration dependencies of the ^{13}C chemical shift change $\Delta\delta^1$ for all investigated systems with pH=2 are shown in Fig. 1 and for systems with pH=6 in Fig. 2.

As we may see from Figs. 1 and 2, the largest changes $\Delta\delta^1$ occur at small concentrations of the surfactant molecules in our systems, corresponding to a range that is much smaller than the CMC value (for octanoate and nonanoate, these values are 0.39 and 0.34 mol/l [33]). The changes $\Delta\delta^1$ are much larger for the system with pH=2 (for instance, 3.5 ppm for nonanoate) than in the system with pH=6 (1.5 ppm for nonanoate). The distinct changes $\Delta\delta^1$ in the ^{13}C shifts of the carboxylic carbons for systems with pH=2 may be due to the influence of strong adsorption interactions with active surface sites, as well as to the reduction of the carbonic acids in the solution. Since we observe only one line in the NMR spectra, we should consider the simple case of the surfactant system with a fast exchange between the dissociated form of the surfactant molecules (fraction p_{diss}) and the non-dissociated (reduced) form of the carbonic acid (fraction $p_{non\text{-}diss}$) in the solution,

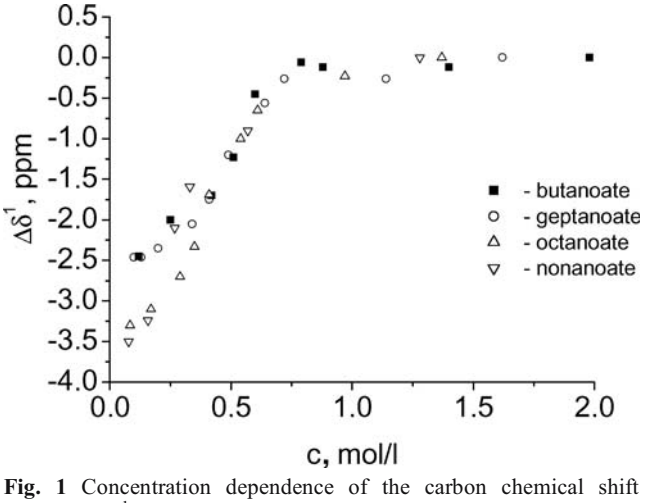

Fig. 1 Concentration dependence of the carbon chemical shift changes $\Delta\delta^1$ for some short-chain ionic surfactants in Aerosil dispersion with pH=2 at 293 K

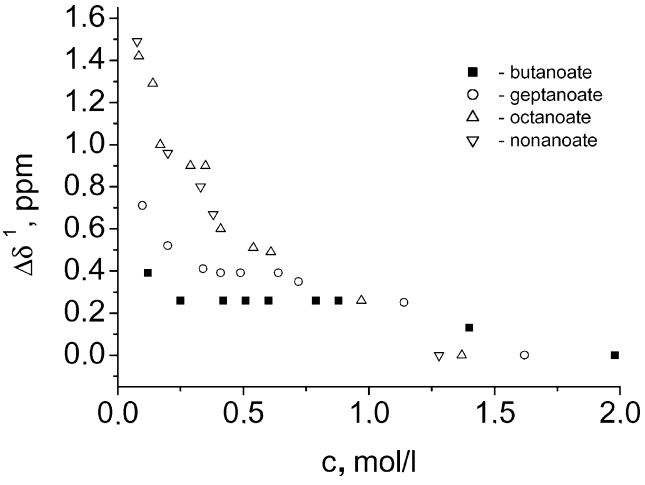

Fig. 2 Concentration dependence of the carbon chemical shift changes $\Delta\delta^1$ for some short-chain ionic surfactants in Aerosil dispersion with pH=6 at 293 K

as well as with molecules on the surface (fraction p_{ads}). Then, the measured chemical shift can be written as

$$\delta = p_{diss}\delta_{diss} + p_{non-diss}\delta_{non-diss} + p_{ads}\delta_{ads}, \quad (1)$$

where δ_{diss}, $\delta_{non\text{-}diss}$, and δ_{ads} are the chemical shifts of the dissociated surfactant molecules, the non-dissociated ones, and the adsorbed species, respectively.

Since the concentration of the HCl acid in the aqueous Aerosil dispersion is small (≤0.01 mol/l), we may assume that the concentration of reduced molecules is still lower than the total surfactant concentration in the whole concentration range (0.1–1 mol/l). If we neglect, for a first inspection, the influence of the surface, we may take into account (see, e.g., [34]) that the formation of the carbonic acid molecules leads to an upfield shift of 8 ppm for the

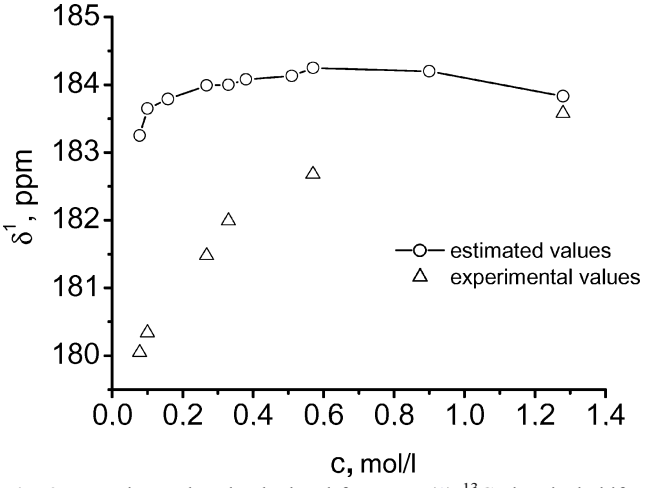

Fig. 3 Experimental and calculated from Eq. (1) ^{13}C chemical shifts $\Delta\delta^1$ for potassium nonanoate in Aerosil dispersion with pH=2 at 293 K. The *lines* drawn are only a guide for the eyes

difference in the chemical shifts for dissociated and non-dissociated molecules. We, then, may calculate the contribution $p_{diss}\delta_{diss}+p_{non\text{-}diss}\delta_{non\text{-}diss}$ in Eq. 1, assuming that the concentration of $c_{non\text{-}diss}$ is equal to the maximum possible value c_{HCl}. The results of the calculations are shown on Fig. 3 for potassium nonanoate and are compared with the experimental values δ^1. As can be seen (Fig. 3), the calculated difference in the chemical shifts for the maximum and minimum concentrations does not exceed a value of 1 ppm and is clearly less than the experimental difference of 3.5 ppm. Moreover, in ternary systems, the fraction $p_{non\text{-}diss}$ may be still reduced on account of p_{ads}, i.e., as compared with the case where the Aerosil is absent. Therefore, the value for the chemical shift contribution $p_{diss}\delta_{diss}+p_{non-diss}\delta_{non-diss}$, as discussed here, may be considered as a maximum estimation, and the difference between these values in Fig. 3 may indicate a lower limit for the influence of surface interactions.

Consequently, the assumption that the large values for the chemical shifts are connected to non-dissociated forms of the carbonic acid seems not to be true. Our estimation of similar values δ^1 for other investigated surfactants has shown that this fact does not depend on the length of the hydrophobic chain. Hence, we suppose that in systems with pH=2, the adsorption of surfactant molecules occurs due to hydrogen bonding between COO^- and free hydroxyl groups on the surface. Taking into account a specific surface area of 200 m^2/g for the Aerosil, the concentration range of 0.11–0.14 mol/l corresponds to a completely formed monolayer on the surface. Here, we assumed that the adsorbed molecules are oriented normal to the surface occupying a mean cross-section area of 22 $Å^2$. Because these values are about the same for all surfactants investigated, one may expect that formation and change of the surface structures take place approximately in the same concentration range.

Above this concentration range, the observable growth of the $\Delta\delta^k$ is caused basically by a continuous adsorption. From this point of view, the concentration dependences of the chemical shift of the first atom (and second atom as shown in [32]) can be considered as a measure for an adsorption isotherm. In this case, the continuous growth of downfield change of the chemical shift in the concentration range of 0.14–0.30 mol/l can be related to the formation of a second layer of adsorbed molecules. This layer is formed due to hydrophobic interactions with the alkyl chains of the molecules. At still higher surfactant concentration, the difference in the $\Delta\delta^1$ values decreases, and for the maximum concentration (about 2.0 mol/l), the difference is practically zero, i.e., the same as for the surfactant molecules in bulk solution.

From Fig. 1, it is visible that the formation of a surface bilayer occurs in the concentration range of 0.3–0.7 mol/l for

all surfactants investigated here, and the concentration at which an adsorption plateau is achieved does not depend on the length of the hydrophobic chain of the molecules.

The difference between the chemical shifts values at low concentration in dependence on the hydrophobic chain length is explained by the formation of the various conformers. To a larger extent, this property is peculiar to still longer molecules.

From the data of concentration dependences of the ^{13}C chemical shifts, we estimated the relative fraction of adsorbed molecules in the systems at pH=2 and the absolute surfactant concentrations in the adsorbed state. The maximum fraction estimated for the adsorbed substance in case of systems at pH=2 does not depend on the length of a hydrophobic chain and corresponds to a completely formed bilayer on the surface.

As seen in Fig. 2, for systems with pH=6, a downfield shift $\Delta\delta^1$ occurs at all surfactant concentrations. But the effect is less pronounced than the (upfield) shifts for systems with pH=2. The character of the chemical shift changes and quantity $\Delta\delta^1$ for systems at pH=6 are different as observed for aqueous surfactant solutions.

We suppose that the surfactant adsorption on the neutral surface is the result of the hydrophobic interaction of the molecular alkyl chains and/or active (non-polar) surface centers. This assumption is established by the dependences of the chemical shift values on the hydrophobic chain length. For the shortest investigated molecule (potassium butanoate), the change of the chemical shift is relatively small. Moreover, this change is observed only at small concentration (0.12–0.25 mol/l). For the longer molecule (potassium geptanoate), the change of the chemical shift is larger and observed for a broader concentration range. Hence, the quantity of the adsorbed molecules increases with the increasing of the hydrophobic chain length. For example, only monolayer formed for potassium nonanoate, for the potassium octanoate and nonanoate the formation of the hemimicelles or addmicelles is possible.

Further insights are possible if we consider the ^{13}C NMR relaxation data. We have carried out measurements of the spin-lattice relaxation time in combination with ^{13}C chemical shifts for potassium nonanoate at various concentrations [32]. The relaxation data confirm that in nonanoate ternary systems an adsorption process takes place. From the comparison of the concentration dependences of the chemical shifts of the potassium nonanoate with the similar dependences for other shorter surfactant, we conclude that the adsorption process occurs in all cases, and this result did not depend on the hydrophobic chain length. In order to confirm this conclusion, as well as to fully quantify the motional processes, the spin relaxation behavior needs to be studied in detail for all systems as a function of the surfactant concentration and/or the Aerosil surface charge. Further investigations in this area are currently in progress.

Conclusions

In this work, the basic attention is focused on the concentration dependence of ^{13}C chemical shifts for the short-chain ionic surfactants adsorbed on a Aerosil surface. It is shown that the adsorption of the short-chain anionic surfactant from an aqueous solution essentially depends on Aerosil surface charge. For a relatively strongly charged Aerosil surface (systems with pH=2), the amphyphilic molecules are preferentially oriented normal to the surface. The changes in the chemical shifts for certain carbon atoms with increasing concentration allow a similar conclusion as may be derived from the adsorption isotherms. In the ternary systems with a nearly neutral Aerosil surface (systems with pH=6), the adsorption interactions are primarily related to the hydrophobic parts of the molecules, and this process is observed only at rather low concentration. At higher concentrations (from 15 to 20%), observable values of chemical shifts are mainly caused by structural changes of surfactant molecules in micellar aggregates in the solution state and are typical for a fast molecular exchange between these phases.

In a case of an insignificantly charged Aerosil surface, the adsorption process depends on the hydrophobic chain length of a molecule. Hence, for the shortest of the investigated molecules (potassium butanoate), the adsorption is limited to the formation of a monolayer. We estimated the quantity of the adsorbed surfactant molecules as a function of the total surfactant concentration.

Acknowledgments The authors greatly acknowledge the support of the PD05-1.2-284, the DAAD for supporting the scientific stay in Leipzig of one of us (M. Popova), and the Russian Funds for Fundamental Research under the contract no. 04-03-32639a.

References

1. Söderlind E, Björlind M, Stilbs P (1994) Langmuir 10:890
2. Söderlind E, Stilbs P (1993) Langmuir 9:2024
3. Schönhoff M, Söderman O, Li ZX, Thomas RK (1999) Bull Magn Reson 20:25
4. Schönhoff M, Söderman O, Li ZX, Thomas RK (2000) Langmuir 16:3971
5. Zwetsloot JP, Leyte JC (1996) J Colloid Interface Sci 181:351
6. Nagashima K, Blum FD, Coll J (1999) Int Sci 214:8
7. Macdonald PM, Yue Y, Rydall JR (1992) Langmuir 8:164
8. Yue Y, Rydall JR, Macdonald PM (1992) Langmuir 8:390
9. Kuebler SC, Macdonald PM (1992) Langmuir 8:397
10. Macdonald PM, Yue Y (1993) Langmuir 9:1206
11. Söderlind E, Blum FD (1993) J Colloid Interface Sci 157:172
12. Söderlind E, Stilbs P (1991) J Colloid Interface Sci 143:586
13. Söderlind E, Stilbs P (1993) Langmuir 9:1678
14. Colombié D, Landfester K, Sudol ED, El-Aasser MS (1998) J Colloid Interface Sci 202:554
15. Schönhoff M, Söderman O (1997) J Phys Chem B 101:8237
16. Schönhoff M, Söderman O (1998) Magn Res Imaging 16:683

17. Campbell RA, Bain CD (2004) Vibr Spectrosc 35:205
18. Walsh B, Wen Xinyun, Franses EI (2001) J Colloid Interface Sci 233:295
19. Lu Y, Miller JD (2002) J Colloid Interface Sci 256:41
20. Wen X, Franses EI (2001) J Colloid Interface Sci 233:295
21. Benalla H, Zajac J, Partyka S, Rozière J (2002) Colloids Surf, A Physicochem Eng Asp 203:259
22. Burya R, Desmazièresb B, Treiner C (1997) Colloids Surf, A Physicochem Eng Asp 127:113
23. Sivakumar A, Somasundaran P, Thach S (1993) J Colloid Interface Sci 159:481
24. Lindheimer M, Keh E, Zaini S, Partyka S (1990) J Colloid Interface Sci 138:83
25. Misra PK, Mishra BK, Somasundaran P (2003) J Colloid Interface Sci 265:1
26. Tahani A, Karroua M, Damme HV, Levitz P, Bergaya F (1999) J Colloid Interface Sci 216:242
27. Chandar P, Somasundaran P, Turro NJ (1987) J Colloid Interface Sci 117:31
28. Esumi K, Otsuka H, Meguro K (1990) J Colloid Interface Sci 136:224
29. Atkin R, Craig VSJ, Wanless EJ, Biggs S (2003) Adv In Coll And Int Sci 103:219
30. Clint JH (1991) Surfactant aggregation. Chapman and Hall, New York
31. Rosen MJ (1980) Surfactants and interfacial phenomena. Wiley, New York
32. Popova MV, Tchernyshev YS, Michel D (2004) Colloids Surf, A Physicochem Eng Asp 243:139
33. Jönsson B, Lindman B, Holmberg K, Kronberg B (1998) Surfactants and polymers in aqueous solution. Wiley, London
34. Ershov BA (1995) NMR spectroscopy in organic chemistry. Publishing House of St. Petersburg State University, St. Petersburg (in Russian)