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^{1}H NMR relaxation of water: A probe for surfactant adsorption on kaolin

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ABSTRACT

In this study, ^{1}H NMR is used to investigate properties of sodium dodecyl sulfate (SDS), tetradecyl trimethyl ammonium bromide (TTAB), and dodecyl trimethyl ammonium bromide (DTAB) adsorbed on kaolin by NMR T_1 and T_2 measurements of the water proton resonance. The results show that adsorbed surfactants form a barrier between sample water and the paramagnetic species present on the clay surface, thus significantly increasing the proton T_1 values of water. This effect is attributed to the amount of adsorbed surfactants and the arrangement of the surfactant aggregates. The total surface area covered by the cationic (DTAB and TTAB) and anionic (SDS) surfactants could be estimated from the water T_1 data and found to correspond to the fractions of negatively and positively charged surface area, respectively. For selected samples, the amount of paramagnetic species on the clay surface was reduced by treatment with hydrofluoric (HF) acid. For these samples, T_1 and T_2 measurements were taken in the temperature range 278–338 K, revealing detailed information on molecular mobility and nuclear exchange for the sample water that is related to surfactant behavior both on the surface and in the aqueous phase.

1. Introduction

Liquid–solid interfacial properties of surfactants and water in the vicinity of a mineral surface are important in many different technological processes and can be determinant in the field of enhanced oil recovery (EOR) [1]. During chemical flooding for EOR, surfactants are used to lower the interfacial tension or capillary pressure in order to increase oil production. However, application of these methods is usually limited due to the adsorption of surfactants onto the rock of the oil containing formation, thus increasing the cost of such injections. The use of mixtures of different surfactants [2,3] and addition of co-surfactants [4–6] such as alcohols has received some attention due to lower surfactant depletion in these systems. In order to improve methods for EOR, a better understanding of the molecular mechanisms involved in adsorption of surfactants on mineral surfaces is desirable.

The main concern in the previous studies on surfactant adsorption has been bulk properties such as the adsorption isotherm and/or ζ potential [2–12]. In general, the adsorption isotherm is found to level off to a plateau value as the concentration of dissolved surfactant reaches the critical micelle concentration (CMC). At this adsorption plateau, the surface is saturated with surfactant. Several experimental techniques have been employed to study the adsorption mechanisms and structure of adsorbed surfactants in more detail. Studies employing electron spin resonance (ESR) [13,14], UV spectroscopy and fluorescence probe studies [15,16], and Raman spectroscopy [17] have revealed molecular properties such as aggregation numbers, internal micropolarity, and microviscosity, as well as some structural information on adsorbed surfactants.

Further details about surfactant adsorption on a silica surface were obtained by ^{2}H NMR on deuterium labeled (in the moiety of the charged head group) dodecyl trimethyl ammonium (DTAB) and hexadecyl trimethyl ammonium bromide (CTAB) [18]. Here, surfactant aggregation was found to occur already at about 20% coverage of the surface, and at surface coverage, higher than this bilayer organization is indicated. Similarly, molecular details of SDS adsorption at the later stages of the adsorption plateau studied by ^{2}H NMR on SDS (deuterium labeled at the α-position of the alkyl chain) suggest bilayer organization of the SDS aggregates [19]. From such investigations employing ^{2}H NMR, the order parameter, $\boldsymbol{S}$, for surfactant motions is used to describe the state of the surfactants in the surface aggregates, and dynamical information can be deduced from molecular correlation times describing both fast and slow motions [18–20]. ^{13}C NMR has been employed on sodium octanoate micelles in solution [21], and the ^{13}C T_1 relaxation measurements show that the interior of the micelles is liquid-like and that the slow micellar motion contributes to the spin–lattice relaxation.

Despite the information available, there is still uncertainty about the molecular organization in the surface aggregates. At the adsorption plateau, bilayer surfactant coverage has been

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suggested [19]. However, monolayer coverage [5], surface micelles [22], and formation of small surface aggregates [23] have also been proposed. Results from different analytical techniques often give rise to different interpretations. ESR and luminescence spectroscopy data have revealed a higher microviscosity in the surface aggregates compared to in micelles, and this was interpreted as being the result of a higher degree of order in the surface aggregates compared to in micelles [13,14,24]. ^{2}H NMR measurements, on the other hand, contradict this due to a reduced order parameter for the surface aggregates, where the increased microviscosity is explained by reduced lateral diffusion and internal motions [19].

In this study, we employ ^{1}H NMR on the water resonance as a probe for surfactant adsorption on kaolin. ^{1}H NMR experiments are more time efficient than ^{2}H and ^{13}C NMR experiments due to the high ^{1}H NMR sensitivity. Furthermore, the cost of ^{2}H and ^{13}C labeled surfactants can be high. A consequence of employing ^{1}H NMR to systems containing a large amount of water is that the water ^{1}H resonance will dominate the spectra making it difficult to do measurements on the surfactant itself. However, due to the paramagnetic nature of natural rock surfaces, it is possible to correlate the water relaxation behavior with the adsorption of surfactants. It has previously been demonstrated that adsorbed hydrocarbons will create a barrier between the paramagnetic surface and water, increasing the observed T_1 relaxation value of water in the sample [25]. In this way, the T_1 relaxation of water can be used to monitor adsorption of the surfactant, as well as provide structural information on the surface aggregates. To the best of our knowledge, this is the first report of the use of ^{1}H NMR relaxation of water to study surfactants in this type of system.

Furthermore, most previous studies investigating details of surfactant adsorption mechanisms have been conducted with silica or alumina as adsorbent. In this study, kaolin is used as adsorbent providing a more complex mineralogical composition and surface properties compared to alumina or silica. Kaolin consists primarily of the mineral kaolinite, which is also one of the common petroleum reservoir minerals. The surface of kaolin is primarily negatively charged, but with positively charged edge surfaces consisting of protonated aluminol sites.

In order to obtain dynamical information about the system, some samples were prepared with hydrofluoric acid (HF) washed kaolin in order to remove some of the paramagnetic species from the rock surface. The most abundant paramagnetic species present in clays will be Fe (III) in the form of iron oxides. In samples containing paramagnetic species, the T_1 relaxation rate will be determined by both the electron relaxation time of the paramagnetic species and the correlation time of molecular motion, τ_c, of the adsorbed water molecules. By reducing the amount of paramagnetic sites on the surface, the relaxation of the water protons will depend more on molecular motion, rather than being totally dominated by the residence lifetime and access to paramagnetic sites on the kaolin surface. In this way, the HF washed kaolin samples can give further information about water dynamics in the various samples. It has become generally accepted that one of the main factors governing the formation of surfactant aggregates is the water structure [26]. Conversely, specific interactions between the solid surface and surfactants may, to some extent, dictate the local water structure in the vicinity of the surfactant aggregate [27]. Thus, information obtained about water dynamics can give further information on the arrangement of surfactants.

The water T_1 relaxation at several temperatures gives information about water dynamics due to the temperature dependent relation of the correlation time for molecular motion, τ_c. In case of water molecules adsorbed on clay, or alternatively onto a surfactant aggregate, the exact expression of the T_1 relaxation rate ($1/T_1$) in terms of τ_c can be difficult to evaluate. However, it is possible to relate $1/T_1$ to the proportionality given in Eq. (1) [28]:

$$1/T_1 \sim \tau_c/(1+\omega_0^2\tau_c^2), \tag{1}$$

where ω_0 is the proton nuclear resonance frequency expressed in angular units. By assuming an Arrhenius relationship for T_1, an activation energy for molecular motion can be deduced. Furthermore, the relaxation rate approaches its maximum value when $\omega_0\,\tau_c$ approaches unity. Assuming a hypothetical, isotropic, spherical-molecular condensed phase, rotational, and translational motions gives rise to a T_1 minimum at which [29,30]

$$\omega\tau_c \cong 0.6158 \tag{2}$$

Thus, it is possible to estimate a value for τ_c if the relaxation rate ($1/T_1$) passes through a maximum value. For water adsorbed on various clays, this maximum value has been found to occur at approximately −40 °C [28].

In this study, the investigation of water dynamics in relation to surfactant adsorption concerns SDS and TTAB adsorbed on kaolin to the plateau adsorption level, attempting to obtain further insight on the equilibrium adsorbate structure.

2. Materials and methods

The powdered kaolin used in this study was obtained from KEBO Lab AB (Stockholm, Sweden). Scanning Electron Microscopy (SEM) was used to approximate the particle sizes (Fig. 1) and found to be in the range 1–25 μm. The surface area of the unwashed kaolin used is 10.6 m^2/g. The surfactants studied were sodium dodecyl sulfate (SDS) ($C_{12}H_{25}SO_4Na$), tetradecyl trimethyl ammonium bromide (TTAB) ($C_{14}H_{29}N(CH_3)_3Br$), and dodecyl trimethyl ammonium bromide (DTAB) ($C_{12}H_{25}N(CH_3)_3Br$) (See Scheme 1).

2.1. Sample preparation

Two sets of samples were prepared, one set with untreated kaolin and other set with hydrofluoric acid (HF) washed kaolin prior to adsorption. Treatment with HF is shown to be an effective method for removing paramagnetic species on rock surfaces [31].

About 10 g kaolin and 100 ml 10% HF were placed in a 500 mL polyethylene beaker and stirred for three hours. The suspension was allowed to settle for about 24 h, after which the supernatant was removed with a plastic syringe. This procedure was repeated three times. The remaining sediment was washed with distilled water and dried at 50 °C overnight. To check the effectiveness of the procedure, subsamples of both untreated and HF washed kaolin were stirred with 1 M HCl at 60 °C for 1 h. After filtration of the solution, the amount of Fe in the extracts was determined by atomic absorption spectrometry. The HCl treatment releases only small amounts of iron. However, due to the highly corrosive nature of hydrofluoric acid, the supernatant of the HF treatment was not injected into the atomic absorption spectrometer. The results revealed that the amount of Fe in kaolin was reduced by 51% after treatment with HF.

Samples for NMR were prepared by mixing about 5 ml surfactant solution and 0.5 g kaolin in a sample tube. The sample was then tumbled for 24 h at room temperature. Excess liquid was removed by centrifugation at 18,000 rpm, giving a kaolin/liquid ratio of 1.7 ± 0.1 for samples containing unwashed kaolin. In samples containing washed kaolin, the resulting kaolin/liquid ratio is 1.0 ± 0.1, probably due to the increased surface area as a result of the acid treatment. The acid washing of clays is often referred to as ‘acid activation’ due to the resulting increase in surface area. Finally, the samples were packed into 4 mm ZrO_2 Magic Angle Spinning (MAS) rotors and sealed with Kel-F rotor caps.

^{1}H NMR spectra of the supernatant were recorded and compared with spectra of the original surfactant solutions. In pure liquid samples, the water resonance is narrow allowing investigation of the