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Two-dimensional NMR study of surface water dynamics in hydrated silica spheres

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Partially hydrated LUDOX silica spheres (LUDOX colloidal silica HS-40, E.I. DuPont de Nemours & Co.) of 15 nm diameter represent a system where the wetting layer of water is quite well defined in the sense that the study of the structure and dynamics of this layered water is not obscured by the much stronger signal of bulk water. When placed in a homogeneous magnetic field, the magnetic susceptibility differences of the silica and water create a distribution of local magnetic fields at the solid-liquid boundary. These fields encode the NMR frequency of the resonant nuclei and label water molecules in the surface layer. The distribution of local fields was determined by the deuteron two-dimensional (2D) separation of interactions NMR technique. The characteristic autocorrelation time τ_c for the motion of water molecules in the surface layer was studied by measuring the deuteron quadrupolar spin-lattice and spin-spin relaxation times, and taking their ratio. The τ_c characterizing the fluctuations of the electric-field gradient tensor at the deuteron site was determined at room temperature for a set of hydrations corresponding to an estimated thickness of surface water from 2 to 22 water monolayers. The magnitude of τ_c, which is on the order of 10^{-8} s, demonstrates that the quadrupolar relaxation mechanism is the intramolecular rotational diffusion. This dynamic process slows down only insignificantly with a decreasing thickness of the wetting layer. A search for slower motions was made by the 2D exchange NMR of deuterons in a 6% hydrated LUDOX. No slow molecular motions were detected within the observation window of the experiment, demonstrating that the motional frequencies are faster than $2\pi \times 10^5$ s^{-1}. [S0163-1829(98)03536-X]

The structure and dynamics of a liquid layer next to the solid surface in hydrated porous media has been investigated extensively. When the liquid is confined to a region that approaches molecular dimensions, its dynamic and thermodynamic properties differ from those of the bulk liquid. Examples include anomalous[1] and lamellar diffusions,[2] an increase of the correlation times,[3] and shifts of melting and freezing temperatures.[4,5] The surface interaction may also induce orientational ordering at the liquid-solid boundary. This has been reported for liquid-crystal molecules confined to submicrometer cavities[6,7] where the deuteron NMR quadrupolar splitting was observed even in the isotropic phase. Such surface-induced ordering of water is particularly interesting for the physics of porous media and membranes. A spectroscopic study of the wetting layer is, however, difficult due to the high mobility of water molecules and because the surface molecules undergo a fast exchange with the bulk. In such a case the lifetime of the surface-bound molecular state is shorter than the time-observation window of most spectroscopic techniques. Fast dynamics also averages the spatially anisotropic intra- and intermolecular interactions to their time-averaged values. In the bulk, the motion is isotropic and all the interactions are averaged to their isotropic values. Traceless interactions relevant in the high-field NMR, like the secular part of the magnetic dipole-dipole interaction, the electric quadrupole interaction, and the anisotropic part of the chemical shift interaction are all averaged to zero. Inside the surface layer, however, the water motion is anisotropic due to the molecular confinement and the above interactions are averaged only partially, even in the fast motion limit. The fast exchange between the surface layer and the bulk, however, makes it difficult, if not impossible, to resolve spectroscopically these two types of water. The standard one-dimensional (1D) NMR spectra show motionally averaged lines from which the surface-bound water cannot be discriminated from the bulk.

Recently, a new method has been proposed[8] to obtain information on the structure and rotational dynamics of simple polar liquids at the surface of nanopores. The method is based on the separation of surface ($1/T_{1s}$) and bulk ($1/T_{1b}$) contributions to the overall deuteron spin-lattice relaxation rate of a deuterated polar liquid confined to a nanoporous silica glass. Polar molecules interact strongly with the pore surface by hydrogen bonding and this slows down the deuteron rotations to such an extent that the electric quadrupole-induced relaxation rate of surface molecule deuterons is strongly enhanced. In the reported experiment, the polar liquid was a selectively deuterated pyridine and it was shown that the enhancement (in the range between 30 and 150) with respect to the bulk-relaxation rate depended on the deuteration site. In the above study it was essential that the glass material used contained no paramagnetic impurities. The presence of paramagnetic centers on the surface would provide another source of surface relaxation and make the analysis ambiguous.

In a hydrated porous glass, fast exchange between the surface layer and the bulk water makes the analysis difficult because of the very short time the molecules spend on the surface before they exchange with a bulklike molecule. During the NMR observation, the molecules are located in the surface layer for a small part of the time only, so that the measured physical quantities represent a not-too-well-understood time average of the surface and bulk observables. The study of this surface layer dynamics would be better in a system where the bulk water is absent, since in such a case there is no exchange between the surface and the bulk. In addition, the model system should contain no paramagnetic impurities. A system that satisfies both these conditions is LUDOX silica glass[9] (SiO_2) spheres of 15 nm diameter hydrated with water. The solid spheres are efficiently cleaned of paramagnetic impurities by a repeated washing cycle of immersion in HCl or a 1-mM ethylenediamine tetra-acetic acid (EDTA) solution[10] and a subsequent rinsing with pure water. The touching LUDOX spheres form a giant irregular surface to which the H_2O molecules bind by hydrogen bonding. It was estimated that, on average, the silica has five Si-O-H sylane groups per square nanometer surface. Water has been chosen as the wetting medium because of the interest in the surface water ''structure'' and dynamics. Upon hydration of LUDOX spheres, a surface layer is formed. Its average thickness depends on hydration and can be estimated as follows. The hydration h is defined as the ratio of the total masses of water and LUDOX,

$$h = \frac{m_{H_2O}}{m_{\mathrm{LUD}}}. \tag{1}$$

The masses are determined by weighting. The volume of a single water molecule is taken to be 30 Å.^{3} Since five water molecules are attached to a 1-nm^2 surface, the effective thickness of a water monolayer becomes $\lambda = 5V_{H_2O}/S = 0.15$ nm. The mass of the LUDOX spheres is calculated as $m_{\mathrm{LUD}} = N(4\pi r^3/3)\rho_{\mathrm{LUD}}$, where N is the number of spheres, $r = 7.5$ nm, and $\rho_{\mathrm{LUD}} = 2.1$ g/cm^3. Similarly, the water mass is $m_{H_2O} = \rho_{H_2O} S_{\mathrm{LUD}} d = \rho_{H_2O} N 4\pi r^2 d$, where d is the average thickness of the surface layer. It is convenient to write d as a multiple of a water monolayer thickness λ; $d = n\lambda$. Using Eq. (1), we find the number of monolayers n in the wetting surface water as a function of hydration as

$$n = \frac{1}{3}\frac{r}{\lambda}\frac{\rho_{\mathrm{LUD}}}{\rho_{H_2O}} h. \tag{2}$$

At 6% hydration the surface is coated, on average, with two water monolayers, whereas at 64% hydration the wetting layer consists of 22 monolayers. In a typical hydration experiment the bulk phase starts to appear at hydrations above 64%, whereas for smaller hydrations the bulk phase is absent and only the surface layer exists. The proof will be shown later by comparing the NMR spin-lattice relaxation rates of bulk water with the rates of water in LUDOX at various hydrations. In contrast, in a dehydration experiment—where the water is evaporated from the fully hydrated LUDOX—the pendular water trapped between the silica spheres is not easily removed so that some bulk component persists down to the lowest hydrations. The surface layer is thus well defined only in a hydration experiment, which starts with a dry sample and is allowed to proceed until a few monolayers are deposited. Here, it should be noted that in the derivation of Eq. (2) the touching between spheres was neglected. Because of that the total wetting layer thickness should be somewhat larger than the above geometrical prediction.

The existence of the surface layer is manifested in the NMR absorption spectra of hydrated LUDOX, which show an inhomogeneous broadening due to the susceptibility effect. This effect is the consequence of a small difference in magnetic susceptibilities of the solid SiO_2 matrix and the surface water. When the sample is placed in a homogeneous external magnetic field, the field slightly changes its direction each time the solid-liquid boundary is crossed. This creates a distribution of spatially random local magnetic fields, which inhomogeneously broaden the NMR spectrum. The relevant nuclear spin interaction in the high field NMR is the Zeeman interaction of the spins with the local magnetic fields. This is a traceless interaction that can be averaged to zero by the fast isotropic translational and rotational diffusion of water molecules. The inhomogeneous broadening should thus be absent whenever the water can move over the whole space isotropically. In the surface layer, however, the motion is anisotropic due to molecular confinement to the geometry of the surface so that the Zeeman interaction is only partially averaged even in the fast motion limit. The resulting inhomogeneous broadening identifies the surface water.

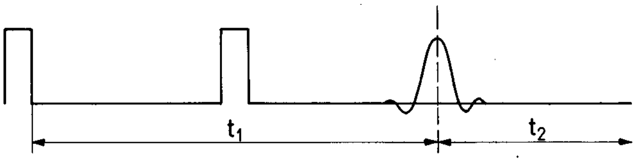

FIG. 1. The spin-echo pulse sequence used for the 2D NMR separation of inhomogeneous and homogeneous line shapes.

A convenient method to determine the inhomogeneous broadening and the distribution of static local magnetic fields is the two-dimensional (2D) NMR separation of an inhomogeneous and homogeneous line-shape technique.[11] The method uses the fact that nuclear spin precession in static local magnetic fields H_i can be refocused within a well-defined time interval called the evolution period (t_1) of the spin-echo pulse sequence (Fig. 1). This sequence is designed to refocus the spin precession under the Hamiltonian terms linear in the I_z-spin variable ($90_x - 180_x$). Refocusing eliminates the effect of the local fields on the spin precession during t_1 and the system effectively evolves under the influence of the interactions, which are not refocused due to their different spin symmetry. For spin $I = 1/2$ nuclei (e.g., protons), this is the magnetic dipole-dipole interaction, whereas for $I = 1$ nuclei (e.g., deuterons), there is in addition, the time-dependent electric quadrupole interaction with randomly fluctuating elements of the electric-field gradient tensor. The quadrupole interaction affects also the inhomogeneous spectrum when the random electric fields are static on the NMR line-shape scale. It will be shown later that the electric fields in LUDOX hydrated with heavy water are predominantly of the intra-D_2O origin and fluctuate so fast that they provide a very efficient spin-lattice relaxation mechanism. The fluctuation frequencies are, however, too high to produce an inhomogeneous broadening.

The Hamiltonian of the spin system can be written as

$$\mathcal{H} = -\gamma\hbar \sum_i H_i I_z^i + \mathcal{H}_{dd} + \mathcal{H}_Q(t). \tag{3}$$

In the 2D separation spectrum the ω_2 domain (conjugated to the detection time t_2 of the pulse sequence) shows the inhomogeneous line $F(\omega_2)$ determined by the full Hamiltonian of Eq. (3), whereas the ω_1 domain shows the homogeneous line $L(\omega_1)$ determined by the dipolar ($\mathcal{H}_{dd}$) and the time-dependent quadrupolar $[\mathcal{H}_Q(t)]$ terms only.

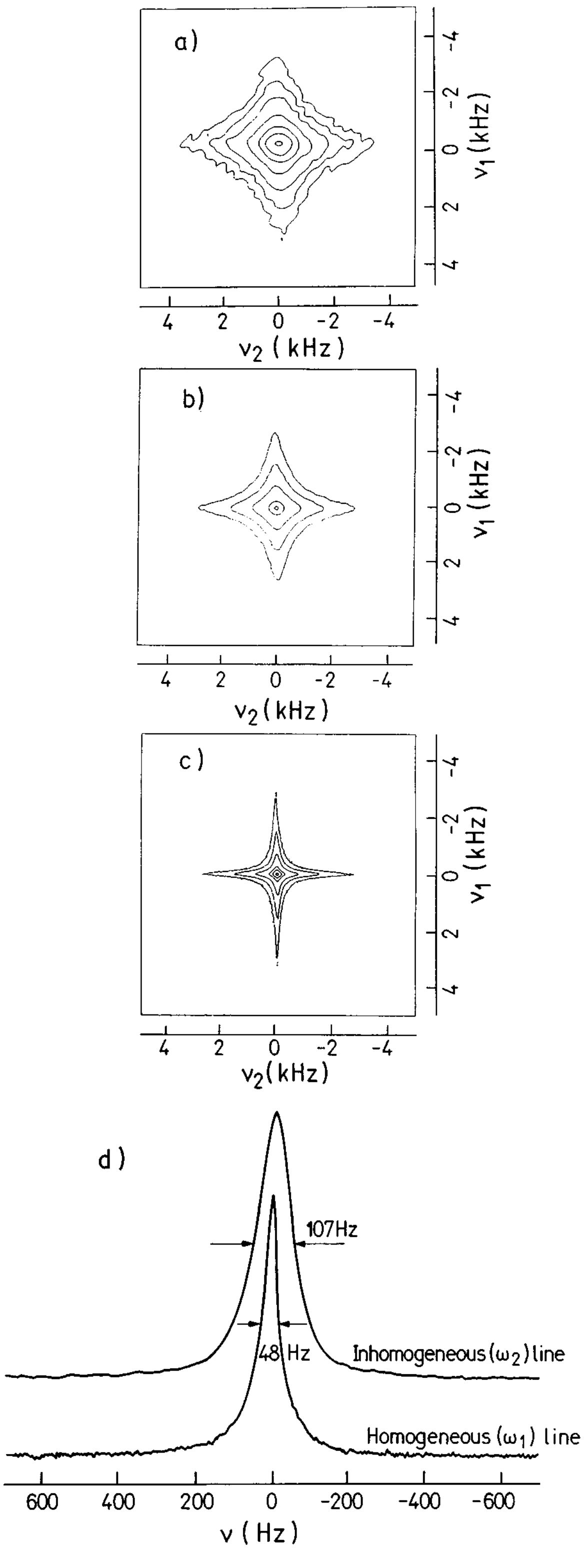

FIG. 2. Deuteron 2D NMR spectra of LUDOX spheres hydrated with D_2O showing separated inhomogeneous (ν_2 domain) and homogeneous (ν_1 domain) lines $[\nu_0(^2H)=30.714$ MHz, room temperature]. The 2D spectra are displayed in the magnitude mode: (a) 6% hydrated sample, (b) 12% hydrated sample, (c) 33% hydrated sample, (d) 64% hydrated sample. Here the pure absorption inhomogeneous and homogeneous line shapes are shown instead of the full 2D spectrum.

The separate determination of the inhomogeneous and homogeneous line shapes in the 2D experiment enables us to determine the distribution of local magnetic fields along the direction of the external field. Let the local field distribution function be $g(H)$. The number of nuclei that resonate in the frequency interval $[\omega,\omega+d\omega]$ equals the number of nuclei that experience local fields in the interval $[H,H+dH]$; therefore

$$f(\omega)d\omega=g(H)dH. \tag{4}$$

The frequency distribution function $f(\omega)$ can be obtained when the relation $\omega(H)$ is known. For a pure Zeeman interaction between the nuclear spins and the local fields this relation is given by $\omega=\omega_0+\gamma H$. Equation (4) now yields

$$f(\omega)=\frac{1}{\gamma}\,g(H). \tag{5}$$

The frequency distribution function $f(\omega)$ therefore represents a one-to-one mapping of the distribution function of local fields $g(H)$, the proportionality constant being the inverse gyromagnetic ratio γ. The function $f(\omega)$ can be obtained from the measured inhomogeneous and homogeneous line shapes. The inhomogeneous NMR spectrum $F(\omega)$ is a convolution of $f(\omega)$ with the homogeneous line shape $L(\omega)$,

$$F(\omega)=\int f(\omega_c)L(\omega-\omega_c)d\omega_c. \tag{6}$$

In the 2D separation spectrum both $F(\omega)$ (appearing in the ω_2 domain) and $L(\omega)$ (from the ω_1 domain) are known independently. The distribution $f(\omega)$ and, thus, $g(H)$ is obtained by a deconvolution technique.

The sample preparation procedure involved first a thorough cleaning of commercial LUDOX material (SiO_2 spheres of 15 nm diameter suspended in a multi-ion solution). Usually ~25 cc of material was cleaned at one time. In the cleaning procedure water is first evaporated. Next, 10 cc of HCl acid or a 1-mM EDTA solution[10] is added and the solution is stirred. Since in dry LUDOX the intergranular spaces are well connected, both above liquids are very effective in removing the ions. After 10 min, HCl is drained off and 50 cc of deionized water is added. The rinsing as well as the complete cleaning cycle are repeated three times. Finally, the sample is dried in vacuum. The presence of residual water after drying is inspected by measuring the intensity of the proton NMR signal of the dry sample, and the drying is repeated until no measurable signal is detected. The same NMR criterion also shows that in a dehydration run—where the water is gradually evaporated from a fully hydrated sample—some pendular water is trapped inside the voids between the silica spheres and cannot be removed from the sample as easy as the water from the surface layer. In the cleanup process, all the ions that prevented the conglomeration of LUDOX spheres in the original solution, are removed. For this reason the dry material includes clumps of SiO_2 spheres. From electron microscopic pictures it is appar-

TABLE I. Parameters obtained from the 2D NMR separation of inhomogeneous and homogeneous line shapes and the spin-lattice relaxation experiments performed at room temperature in LUDOX hydrated with D_2O.

Hydration	Inhomogeneous linewidth $\Delta\nu_{1/2}^{\mathrm{INH}}$ (Hz)	Homogeneous linewidth $\Delta\nu_{1/2}^{\mathrm{HOM}}$ (Hz)	Inhomogeneous broadening $\Delta\nu_{1/2}^{\mathrm{INH}}-\Delta\nu_{1/2}^{\mathrm{HOM}}$ (Hz)
6%	1270 ± 5	1221 ± 5	49 ± 5
12%	638	593	45
33%	206	156	50
64%	107	48	59

Hydration	T_1 (ms)	T_2 (ms)	T_1/T_2	τ (s)	$(\omega_0\tau_c)^2$
6%	21.7 ± 1.5	0.26 ± 0.01	83.5	$(5.47\pm0.1)\times10^{-8}$	111.3
12%	38	0.54	70.8	5.17×10^{-8}	99.4
33%	109	2.04	53.4	4.37×10^{-8}	71.0
64%	188	6.63	28.4	3.19×10^{-8}	37.8
100%	246				

ent that some voids within the clean LUDOX are as large as 50 nm. This makes the dry LUDOX's porosity larger than the porosity of randomly packed model spheres of 0.38. We estimated from the proton NMR transverse relaxation T_2 study that the full hydration of clean LUDOX is reached at an ~40% H_2O/dry sample weight ratio, which corresponds to a porosity of ~0.43.

The 2D separation experiment has been performed at room temperature on deuterons in LUDOX hydrated with D_2O. An initially dry sample has been hydrated to hydrations $h=6\%$, 12%, 33%, and 64% by exposing the substance to the D_2O vapor for a limited time, typically of the order of a few minutes. The estimated number of water monolayers in the total wetting layer according to Eq. (2) was $n=2$, 4, 11, and 22, respectively. The 2D NMR spectra are displayed in Fig. 2. It is observed that the spectrum is the broadest in both frequency domains at the smallest hydration (6%). There the full width at half height (FWHH) of the inhomogeneous spectrum $F(\omega_2)$ is $\Delta\omega_{1/2}/2\pi=1270$ Hz, whereas the FWHH of the homogeneous spectrum $L(\omega_1)$ is 1221 Hz. The difference, of 49 Hz, is the inhomogeneous broadening. On increasing the hydration, the spectrum narrows in both frequency domains and, for example at 64% hydration, the inhomogeneous FWHH is 107 Hz, whereas the homogeneous width narrows to 48 Hz. At larger hydrations these values do not change considerably. It is quite remarkable that the difference in widths of 50 ± 5 Hz is observed at all hydrations (Table I). The independence of the inhomogeneous broadening on hydration and thus on the wetting layer thickness can be explained by the existence of the susceptibility-induced local magnetic fields. The effect of these fields is strongest for those deuteron nuclei that are next to the solid-liquid boundary, whereas the remote nuclei are affected increasingly less in proportion to their distance from the surface. The susceptibility-induced inhomogeneous broadening thus identifies the surface water molecules.

Using the above model, one can determine the width of the distribution function of local magnetic fields. To a good approximation, both the inhomogeneous and the homogeneous line shapes of the spectra displayed in Fig. 2 can be represented by Lorentzians. In this case, the deconvolution of Eq. (6) to obtain $f(\omega)$ is particularly simple, as it yields another Lorentzian with the FWHH equal to the difference between the widths of $F(\omega)$ and $L(\omega)$. The FWHH of $f(\omega)$ in the case of hydrated LUDOX is 50 ± 5 Hz and the resulting FWHH of $g(H)$ obtained from Eq. (5) is $(7.6\pm0.7)\times10^{-2}$ G. The susceptibility broadening effect is thus small but can be measured accurately.

To demonstrate the local magnetic field origin of the inhomogeneous broadening we repeated the 2D separation experiment on protons in LUDOX hydrated with H_2O instead of D_2O (Fig. 3). The initially fully hydrated sample was dehydrated to 80%. Due to the 6.5 times larger magnetic moment of protons, the inhomogeneous broadening is expected to increase by that factor. The proton inhomogeneous FWHH was found to be 965 Hz, whereas the homogeneous width amounted to 715 Hz. The proton's inhomogeneous broadening is thus 250 Hz, which is five times larger than the deuteron's broadening. This value is comparable to the theoretical value of 6.5 expected for the pure Zeeman character of the inhomogeneous broadening. The above result confirms that the susceptibility-induced local magnetic fields are created at the solid-liquid surface in a hydrated LUDOX when the sample is placed in an otherwise homogeneous external magnetic field. The same situation should exist also in other porous media with a large irregular surface, e.g., the controlled pore size glasses and hardened cements. However, the susceptibility effect can be easily masked by the much stronger local fields of the paramagnetic impurities in contaminated samples, such as ordinary Portland cement.

An important information on the dynamics of D_2O molecules in the wetting layer can be obtained from the deuteron homogeneous linewidth. This width is inversely proportional to the deuteron spin-spin relaxation time; $\Delta\nu_{\mathrm{HOM}}=1/\pi T_2$. The T_2 of deuterons is governed predominantly by the electric fields, which fluctuate with the autocorrelation time τ_c and couple to the deuteron nuclear electric quadrupole moment. In the slow motion limit $\omega_0\tau_c\gg1$ (ω_0 is the deuteron Larmor frequency), the quadrupole T_2 can be written as[12]

$$\frac{1}{T_2}=\frac{1}{160}\left(\frac{eQ}{\hbar}\frac{\partial^2 V}{\partial z^2}\right)^2\left(1+\frac{\eta^2}{3}\right)18\tau_c . \qquad (7)$$

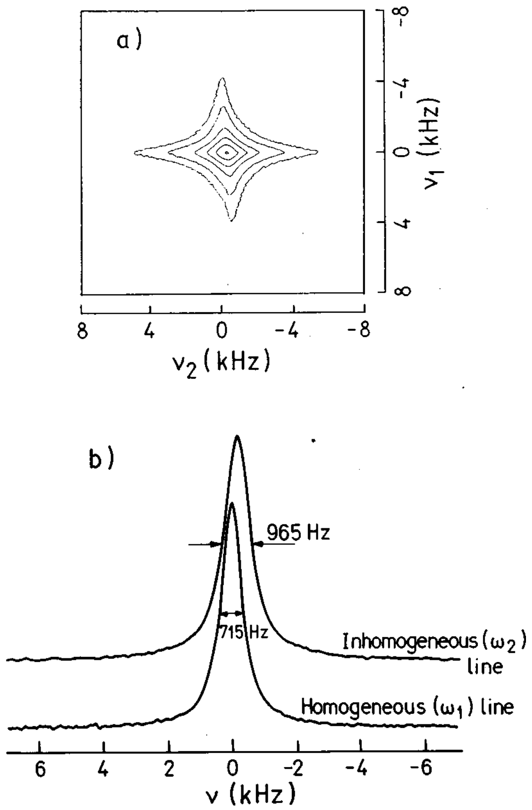

FIG. 3. A similar 2D separation experiment as in Fig. 2 performed on water protons at $\nu_0(^1H)=200$ MHz and room temperature in a LUDOX sample hydrated with H_2O (80% dehydration). (a) Full 2D separation spectrum (magnitude representation) with the inhomogeneous (ν_2) and homogeneous (ν_1) domains. (b) Pure absorption inhomogeneous and homogeneous line shapes.

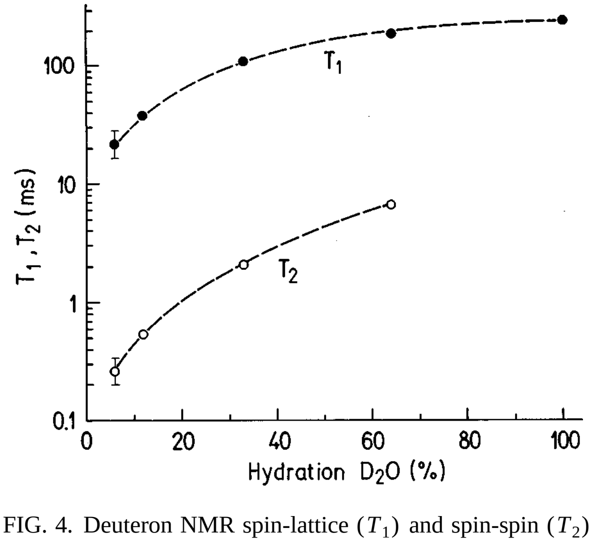

FIG. 4. Deuteron NMR spin-lattice (T_1) and spin-spin (T_2) relaxation times at room temperature as a function of hydration in LUDOX hydrated with D_2O [$\nu_0(^2H)=30.714$ MHz]. The dashed lines are guides for the eye.

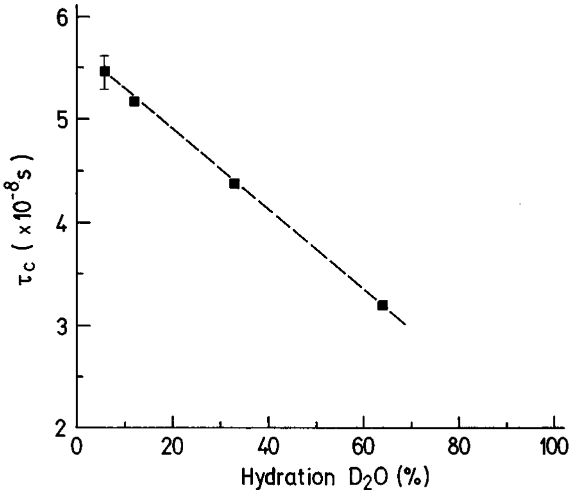

FIG. 5. Deuteron autocorrelation time τ_c at room temperature as a function of hydration in LUDOX hydrated with D_2O.

Here $(eQ/\hbar)(\partial^2V/\partial z^2)$ is the quadrupole coupling constant and η the asymmetry parameter. In the same $\omega_0\tau_c \gg 1$ limit, the quadrupole-induced deuteron spin-lattice relaxation time T_1 equals

$$\frac{1}{T_1}=\frac{3}{80}\left(\frac{eQ}{\hbar}\frac{\partial^2V}{\partial z^2}\right)^2\left(1+\frac{\eta^2}{3}\right)\frac{4}{\omega_0^2\tau_c}. \tag{8}$$

The square root of the ratio of the two relaxation times gives the autocorrelation time

$$\tau_c=\frac{1}{\omega_0}\sqrt{\frac{4}{3}\frac{T_1}{T_2}}. \tag{9}$$

By measuring T_1 and T_2, the τ_c is obtained. In LUDOX this autocorrelation time is a measure of the surface water dynamics.

The deuteron relaxation times T_1 and T_2 of hydrated LUDOX at room temperature are shown in Fig. 4 as functions of hydration. In Table I, both are listed together with parameters obtained from the analysis. In progressively dryer samples both T_1 and T_2 become shorter, whereas their ratio increases; e.g., at the 64% hydration $T_1=188$ ms and $T_2=6.63$ ms, their ratio is $T_1/T_2=28.4$. This value of T_1 is considerably shorter from that of the bulk water deuterons ($T_1=246$ ms) in the 100% hydrated sample. The correlation time obtained from Eq. (9) and using the experimental Larmor frequency $\omega_0=2\pi\times30.714$ MHz is $\tau_c=(3.2\pm0.1)\times10^{-8}$ s. In the 6% hydrated sample, the T_1 is shortened to 21.7 ms and T_2 to 260 μs, but their ratio is larger, $T_1/T_2=83.5$, indicating an increase of τ_c (Fig. 5). As the hydration is reduced from 64% to 6%, the correlation time increases by a factor of 2. This demonstrates that the deuteron dynamics in D_2O molecules is slowed down because of water-surface interactions. In Table I, the values of $(\omega_0\tau_c)^2$ are also listed to justify the use of the slow motion limit $\omega_0\tau_c \gg 1$ for T_1 and T_2 in Eqs. (7) and (8). Since the $(\omega_0\tau_c)^2$ values are much larger than 1, the slow motion approximation is well justified.

The order of magnitude of τ_c in the range 10^{-8} s indicates that the detected motion is the intramolecular rotational diffusion of a single D_2O molecule; i.e., each water molecule rotates around its twofold symmetry axis. The EFG tensor at a deuteron site is predominantly determined by the electric charges of the other deuteron within the molecule and by its oxygen atom. This intramolecular quadrupole relaxation mechanism is by far stronger than any intermolecular mechanism. In the study of the wetting layer dynamics it would be important to understand the influence of the intermolecular interactions as well. These interactions depend on the relative positions and mobility of the nearby water molecules and should be therefore molecular-cluster specific. It could be that each D_2O molecule bonded to a given surface-bound Si-O-D sylane group is a root of a treelike configuration that extends into bulklike water. Such chains of bonded water molecules would exist for a short time during which their dynamics would be considerably slower than that of individual bulklike water molecules due to the much heavier mass of such clusters. The fact that no slow dynamics is observed in the deuteron NMR does not prove that such water chains do not exist, since such cluster-specific intermolecular interactions are obscured in a spectroscopic study by the much stronger intramolecular quadrupolar interaction.

The high D_2O rotational mobility averages the traceless static part of the electric quadrupole interaction to zero. The width of the static deuteron powder spectrum, which is of the order of $\Delta\omega\approx 2\pi\times 110$ kHz (observed in D_2O ice), is motionally averaged out and this excludes the presence of dynamic processes with the correlation times longer than the inverse static linewidth; $\tau_c > 10^{-6}$ s. For τ_c's longer than that value, the deuteron absorption spectrum should exhibit quadrupole-induced inhomogeneous broadening. This was not observed in the reported experiments (see Fig. 2). Indeed, the inhomogeneous broadening was demonstrated to be Zeeman-like.

To search for a slow exchange motion of water molecules in the surface layer of a hydrated LUDOX system, we performed a 2D exchange NMR experiment[13] on the 6% hydrated sample. With this method one monitors slow exchange processes within a well-defined time interval, called the mixing interval (t_m), of the 2D exchange pulse sequence. The low-frequency limit of the frequency observation window is determined by the inverse mixing time t_m^{-1}. In the deuteron exchange experiment t_m was chosen as 5 ms so that the motions with frequencies down to 200 Hz could be detected. The necessary condition for the detection of chemical exchange (or in general any spatial motion of water molecules) is the requirement that the resonant nucleus travels during t_m to a position where its resonance frequency differs from its value at the initial spatial position. Spatial encoding of the resonance frequency in a single line spectrum of hydrated LUDOX is provided by the inhomogeneous broadening of the line. The 2D exchange spectrum shows a typical diagonal shape in the (ω_1,ω_2) plane. In the case of no exchange this diagonal spectrum is narrow, whereas in the presence of exchange an off-diagonal intensity appears. The resolution of the single line inhomogeneously broadened 2D spectrum is limited by the width of the homogeneous spectrum, which broadens the diagonal intensity. We have shown that in the 6% D_2O hydrated LUDOX, the inhomogeneous broadening originates from the susceptibility-induced local magnetic fields and that this broadening is 50 Hz. The conditions for observing exchange are thus rather unfavorable due to the large homogeneous width of 1221 Hz, which differs only insignificantly from the inhomogeneous width of 1270 Hz. We nevertheless performed the 2D exchange experiment (Fig. 6) with the aim of finding the difference in widths of the 2D spectrum along the two orthogonal diagonals in the (ω_1,ω_2) plane. In the case of no exchange, the spectrum width along the positive diagonal (running from the upper-right to the lower-left corner) should be larger by the amount of inhomogeneous broadening than the width measured along the negative (upper-left to lower-right corner) diagonal.[14] In the case of exchange during t_m, this difference should become smaller and should vanish for exchange frequencies considerably higher than the frequency observation window, provided that the nuclei can move over all regions of the sample with different local fields. We measured the difference in widths of the spectrum in Fig. 6 on contours 2, 3, and 4 from the center (contours 5 and 6 are already too noisy). We found that the positive diagonal width of contour 2 was 53± 7 Hz larger than its negative diagonal width, whereas on contours 3 and 4 this difference was 46 ±7 and 59± 7 Hz, respectively. The average of these three values (53 Hz) is within the experimental accuracy equal to the inhomogeneous broadening determined by the 2D separation experiment. This demonstrates that the exchange effects are not observed in the 2D exchange experiment. One explanation of this no-exchange result could be that the water molecules are statically bound to the surface where they reorient around their twofold symmetry axes, but this is not very likely. Instead, we propose that the molecular exchange is fast but the individual molecules are confined to a rather small space of the LUDOX surface. It is proposed that the water molecules move rapidly inside a small confined space and ''see'' an average local magnetic field characterizing that particular region. The fast rotational diffusion also averages out the static electric quadrupole interaction. The motion is thus too fast to make the off-diagonal exchange intensity observable for this dynamics. However, the molecules cannot easily diffuse from one confined region to the next, which is characterized by a different average local magnetic field so that the small susceptibility-induced inhomogeneous broadening is preserved. The situation is somewhat similar to a liquid confined to pores. The inhomogeneous broadening would be averaged out were the molecules able to move over the whole wetting layer with a high average speed. In such a

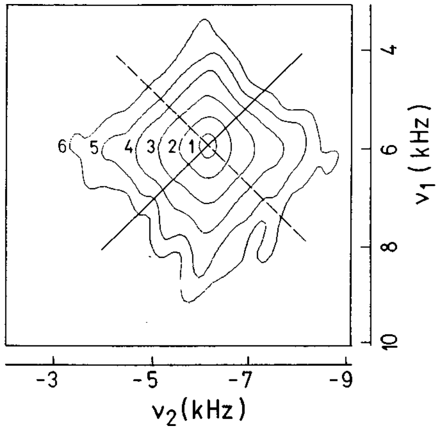

FIG. 6. Deuteron 2D exchange NMR spectrum of the 64% D_2O hydrated LUDOX at room temperature. A standard three-pulse (stimulated echo) sequence was used with the mixing time $t_m = 5$ ms. The spectrum widths along the positive (solid line) and negative (dashed line) diagonals differ slightly by the amount of the inhomogeneous broadening.

quasi-isotropic motion the inhomogeneous broadening would be averaged to zero as soon as the motional frequencies would exceed the inhomogeneous broadening. This is in stark contrast to the reported experiment where the inhomogeneous broadening is observed at all hydrations. The above model explains why the 2D exchange did not uncover any slow dynamics in the hydrated LUDOX. It should be noted, however, that due to the smallness of the inhomogeneous broadening as compared to the homogeneous spectrum width the present results should be taken as qualitative only.

We have demonstrated that in hydrated LUDOX the wetting layer of water is well defined and that the vicinal water dynamics is not obscured by the much stronger signal of bulk water. When the sample is placed in an external homogeneous magnetic field, as in an NMR experiment, the magnetic susceptibility differences at the surface between the solid silica spheres and the water induce a distribution of local magnetic fields, which inhomogeneously broaden the NMR absorption spectrum. These local fields encode the water molecules close to the surface. The dynamics of the surface layer has been studied by measuring the deuteron quadrupolar spin-lattice and spin-spin relaxation times. The autocorrelation time τ_c was determined for a set of hydrations corresponding to an estimated thickness of the wetting layer from 2 to 22 water monolayers. The magnitude of τ_c demonstrates that individual water molecules undergo at room temperature rotational diffusion motion with the characteristic time constant in the range 10^{-8} s. This process appears to slow down with the decreasing thickness of the wetting layer due to the surface-induced hindering of water molecules' reorientations. The strong intramolecular relaxation mechanism screens all the intermolecular relaxation mechanisms, which carry information about the correlation between different water molecules and thus on the structure of the wetting layer. The slow water dynamics in the kHz- and sub-kHz range was searched for by the deuteron 2D exchange NMR experiment. No slow motion was detected at room temperature. The above experiments demonstrate that water molecules hydrating LUDOX spheres are confined to small regions of the silica surface. Within these regions the water molecules move fast enough to motionally narrow their quadrupole NMR spectrum. In addition, the diffusion between neighboring confining regions is so slow that the susceptibility-induced inhomogeneous broadening of 50 Hz is preserved.

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[1] R. Kimmich *et al.*, Appl. Magn. Reson. **4**, 425 (1993).

[2] J.-P. Korb, Shu Xu, and J. Jonas, J. Chem. Phys. **98**, 2411 (1993).

[3] S. Stapf, R. Kimmich, and R. O. Seitter, Phys. Rev. Lett. **75**, 2855 (1995).

[4] R. Mu and V. M. Malhotra, Phys. Rev. B **46**, 532 (1992).

[5] J. H. Strange, M. Rahman, and E. G. Smith, Phys. Rev. Lett. **71**, 3589 (1993).

[6] S. Žumer, S. Kralj, and M. Vilfan, J. Chem. Phys. **98**, 3540 (1993).

[7] G. P. Crawford, D. K. Yang, S. Žumer, D. Finotello, and J. W. Doane, Phys. Rev. Lett. **66**, 723 (1991).

[8] J.-P. Korb, L. Malier, F. Cros, Shu Xu, and J. Jonas, Phys. Rev. Lett. **77**, 2312 (1996).

[9] LUDOX colloidal silica HS-40, E. I. Du Pont de Nemours & Co., Wilmington, DE.

[10] C. Choi, H. Haranczyk, K. G. Soga, R. J. Rumm, and M. M. Pintar, J. Appl. Phys. **80**, 5861 (1996).

[11] J. Dolinšek, J. Magn. Reson. **92**, 312 (1991).

[12] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University, London, 1960), p. 313.

[13] See, e.g., R. R. Ernst, G. Bodenhausen, and A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions* (Clarendon, Oxford, 1987), p. 490.

[14] J. Dolinšek and G. Papavassiliou, Phys. Rev. B **55**, 8755 (1997).