NMR studies of complex fluids and solids formed
by surfactants

by
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Abstract

NMR methods have been designed and employed in studying of complex liquids and solids formed by surfactants. PGSE NMR experiments are easily biased by convection; this artifact can be avoided by changing the sample holder and by using convection-compensated pulse sequences. The temperature distribution within samples was controlled using the temperature dependent order parameter for CBr₂H₂ dissolved in a thermotropic nematic solvent. Electronic ringing that often spoils accurate NMR experiments for broad lines was removed by the using composite pulses and quadrupole echo sequences with appropriate phase cycles.

Field-dependent ⁸¹Br and ³⁵Cl NMR relaxation studies in micellar solutions of C₁₆TAX surfactants showed that the structure or dynamics of the hydration shell is more influenced by the surfactant cation for bromide than for chloride, in agreement with their position in the Hoffmeister series. The presence of a small but significant frequency-dependent relaxation showed that the lateral self diffusion of the anions may be reduced as compared to its bulk value in diluted solutions but only with a factor of 1.0 - 2.5. The ions are clearly not “bound” to the surface. A field-dependent ²H NMR relaxation study on the CTABr-α-d₂ and benzene-d₆ showed an initial one-dimensional micellar growth followed by the appearance of microemulsion droplets on addition of benzene. The local mobility of the benzene was reduced when solubilized in small amounts, consistent with an initial average location of benzene at the micellar interface. The surfactant diffusion coefficients from convection-compensated PGSE NMR experiments in the C₁₂E₈-D₂O system showed monotonous growth of the micelles upon increasing temperature. Emulsion droplets in the C₁₁E₆-decane-D₂O system where shown to coarsen according to the Ostwald ripening theory after being brought out of equilibrium by a temperature drop. X-ray scattering and ²H NMR line-shape and relaxation experiments suggested that complex solids formed by a partly-sulfated polysaccharide and C₆TAB exhibit regular ordering at both microscopic and mesoscopic length scales.

Keywords: CTAB, CTAC, C₁₂E₉, C₁₂E₅, decane, benzene, CBr₂H₂, polysaccharide, micelle, microemulsion, emulsion, Ostwald ripening, NMR, ⁸¹Br, ³⁵Cl, ²H, field-dependent spin relaxation, PGSE, self diffusion, convection, ringing, thermometer, generalized Bloch equations, EXORCYCLE, quadrupole echo, SAXS, WAXS, cryo-TEM.
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Introduction

The aim has been to improve and use NMR (Nuclear Magnetic Resonance) methods to study aspects of colloidal solutions and mesoscale compounds. Three main projects are included. The molecular dynamics of counterions, surfactants and solubilizate (benzene) were studied with field dependent NMR relaxation on quadrupolar nuclei. NMR self-diffusion measurements, both at high temperatures and under non-equilibrium conditions, provided information about the size of the structural entities in these systems. NMR lineshape and relaxation experiments on mesoscale surfactant-polysaccharide complexes offered complementary information to X-ray scattering experiments on the same complexes. All the studied systems had a common denominator in that the colloidal order was (at least partly) induced by surfactants.

The following chapters introduce the compilation of the papers forming this thesis and consist of three sections. The first section gives a background to NMR and presents the NMR-related findings. In the second section, the different types of self-aggregated structures under study are described. In the final section, I discuss specific aspects of the results and draw conclusions therefrom.
1. List of papers

The following papers are included in this thesis.

1.) N. Hedin, I. Furó; Temperature imaging by $^1$H NMR and suppression of convection in NMR probes, Journal of Magnetic Resonance; 1998; 131; 126-130.

2.) N. Hedin, O. Regev, I Furó; Mesomorphic solid-like structures of sulfated extra-cellular polysaccharide-$C_n$TAB compounds, Progress in Colloid and Polymer Science; 1999; 112; 140-145.

3.) N. Hedin, R. Sitnikov, I. Furó, U. Henriksson, and O. Regev; Shape changes of $C_{16}$TABr micelles on benzene solubilization, The Journal of Physical Chemistry B; 1999; 103; 9631-9639.


5.) N. Hedin, I. Furó; Accurate intensities of broad NMR lines from composite pulse experiments, Journal of Magnetic Resonance; 2000; 142; 32-36.


7.) N. Hedin, T. Y. Yu, and I. Furó; Growth of $C_{12}E_8$ micelles with increasing temperature. A convection-compensated PGSE NMR study, Langmuir; 2000; 16; 7548-7550.

8.) N. Hedin, I. Furó; Ostwald ripening of an emulsion monitored by PGSE NMR, manuscript/ submitted

9) I. Furó, N. Hedin; Noise reduction in quadrupolar echo spectra at short echo times, manuscript/ submitted.
2. Basic NMR and NMR-related results

NMR means Nuclear Magnetic Resonance. The following description is mainly using classical physics, but intuitive quantum mechanics are included, as well. The spin angular momentum, \( j \), for a nucleus is characterized by its length, \( |j| = \hbar \sqrt{(I(I + 1))} \), and its projection along an arbitrary axis \( j_z \in h(I, I - 1, ..., -I) \). (\( I \) is an integer or half-integer number depending on the nucleus.) To these states nuclear magnetic moments are associated, \( \mu_z = \gamma j_z \) where \( \gamma \), called the magnetogyric ratio, is constant. These magnetic moments interact with magnetic field applied and the states with different \( \mu_z \) have different energies and populations.

In a macroscopic sample, a nuclear magnetism that is a collective property is induced. The small energy difference between nuclear magnetic moments parallel and anti-parallel to the applied field gives rise to this equilibrium magnetization. For the \( 7 \times 10^{22} \) protons in a 1 ml sample of room-temperate water placed in a homogenous field of 11.7 T, approximately \( 3 \times 10^{18} \) more protons will align with the field than against the field. This small fraction ultimately means that the sensitivity of the NMR method is often low. The huge absolute number of spins with a preferable orientation along the field assures that there is no uncertainty and the collective magnetic moment (dipoles or multipoles) can be measured and manipulated coherently. Compare this with a single spin for which the value of magnetic moment is subject to quantum uncertainty.

2.1 The Bloch equations

The time evolution of the macroscopic nuclear magnetization in a strong magnetic field can be described by the phenomenological Bloch equations. (Most of the magnetization induced in a sample placed in a strong magnetic field is associated with the angular moments for the electrons even for diamagnetic substances. Nevertheless, the small nuclear contribution can be separated by resonance techniques.) In thermal equilibrium, the induced nuclear magnetization (\( \mathbf{M} \)) is collinear with the applied field with the energy, \( U = -\mathbf{M} \cdot \mathbf{B} \). The time evolution of the magnetization becomes, \( \dot{\mathbf{M}} = \gamma \mathbf{M} \times \mathbf{B} = -\gamma \mathbf{B} \times \mathbf{M} \) or in a rotating coordinate system, \( \dot{\mathbf{M}}' = -\gamma (\mathbf{B} + \omega) \times \mathbf{M} \). The resonance frequency is, \( \omega_0 = |\omega_0| = -\gamma |\mathbf{B}| \). In a simple NMR experiment the
applied field $\mathbf{B}$ consists of a large static field along the $z$-axis $B_0 \mathbf{e}_z$ and during the radiofrequent (rf) pulses (linearly polarized) oscillating field in the transverse plane within the coil placed in the magnet, $\mathbf{B}(t) = 2B_1 \cos(\omega_{rf}t + \phi) \mathbf{e}_x$. If this oscillating field ($\omega_1 = -\gamma B_1$) is on resonance, $\omega_{rf} = \omega_0$, the effect is a rotation of the magnetization in the rotating coordinate system, $\mathbf{M} = \mathbf{M}_1 \mathbf{e}_z$. The flip angle of the rf-pulse is the angle by which the magnetization rotates on applying the time dependent field for a time $\tau_p$, $\beta = \omega_1 \tau_p$. The magnetization can be moved in various ways by choosing the length and the phase ($\phi$) of the pulse. The phase angle of the linearly polarized field $B(t)$ is a sum of different phase contributions, from the various electronical components of the spectrometer as well as from a controllable part $\phi_{RF}$ and is measured from the coil axis. The magnetization of $\gamma > 0$ and $\gamma < 0$ nuclei rotate clockwise and counterclockwise (for positive $B_1$) around the direction of $\mathbf{e}_1$ under a pulse. (In Paper 2 we used an old convention in the line of reference$^{2-4}$, which means that an X-pulse ($\phi = 0$) transforms to –X ($\phi = 180^\circ$), and visa versa. This procedure has no impact on the results and is noted here for clarity.) Off-resonance effects are represented as another rotation, $\mathbf{M} = (0 \ 0 \ (\omega_0 - \omega_{RF}))$.

If the magnetization is put out of equilibrium, irreversible processes restore its equilibrium value, $\mathbf{M}_\parallel = M_0 \mathbf{e}_z$ and $\mathbf{M}_\perp = 0$. The time-scale for these are often given by the transverse relaxation time, $T_2 = 1/ R_2$, that describes the disappearance of the magnetization in the transverse plane and the longitudinal relaxation time $T_1 = 1/ R_1$, by which the magnetization restores its equilibrium polarization. Collecting all these effects into one formula provides the Bloch equation,

$$\mathbf{M}' = (\mathbf{M} + \mathbf{e}_1) \mathbf{e}_1 \mathbf{M}' - R_1 (M_z - M(0)) \mathbf{e}_z - R_2 (\mathbf{e}_x M_1' + \mathbf{e}_y M_2') \quad \text{(2.1)}$$

Most textbooks discuss the solution to this equation for the case when the pulse length is negligible compared to the relaxation times$^5$ but it is solvable for more general cases, by either analytical$^{2-4}$ (used in Paper 5), or numerical$^6$ means. In Paper 5 we used the analytical solution for the case when the magnetization relaxes during the pulse$^{2-4}$. A solution to eq. (2.1) contains three transient and one steady state term.
The steady state term is \( \mathbf{M}' = \frac{M_0}{1 + \alpha^{-1} \beta^{-1}} [0, -\beta^{-1}, 1] \) (\( \phi = 0 \)), \( \alpha \) is \( R_1 / \omega_1 \) and \( \beta \) is \( R_2 / \omega_1 \). This corresponds to a residual magnetization of approximately \([0, -\alpha, \alpha \beta] \) if the relaxation rates \( R << \omega_1 \). The magnetization reaches this point by a spiral. Still, most of the physical insight of the transient behavior is hidden by the complexity of the solution.

The general solution of the Bloch equation for \( \omega_i \) with phase \( x \) can be described as \( \mathbf{M} = G_x(M_i) \), where \( M_i \) and \( \mathbf{M} \) are the initial and final magnetization. This solution can be transformed to create the solution to excitation with another phase by a transformation procedure, \( \mathbf{M} = \exp(-i\phi)G_x(\exp(i\phi)M_i) \), where \( \phi \) is the phase difference between the \( x \)-pulse and the new pulse and the transformations are rotations around the \( z \)-axis. Note, that the result of non-negligible relaxation during the pulses means that the effect of pulse combinations as \( 90_x90_x90_x \) and \( 90_x90_x90_x \) are not the same, see the Figure below.

![Figure 1. Trajectories for the magnetization are shown for the composite pulses, 90_x90_x90_x (a) and 90_x90_x90_x (b) under relaxation. The relaxation rates \( R_1 = R_2 = 0.2 \omega_1 \). A black arrowhead marks the end-point for the first pulse, a gray the second and white the last. (Compare with the non-relaxed case, for which the magnetization is brought to the \( y' \)-axis.)](image)

This simple classical vector representation of the magnetization is incomplete for many systems. For example, it can not describe one \(^{13}\text{C} \) nucleus in a molecule J-
coupled to a $^1$H nucleus. For this and other systems NMR spectroscopy is not a “dipolar” but a “multipolar” spectroscopy. In such cases, the nuclear magnetization (corresponding to a spin density matrix) should be represented by product operators or by irreducible tensor operators.$^5$

### 2.2 Some NMR experiments

Here I introduce some of the applied NMR experiments. For a full description, I refer readers to textbooks and articles.

**Spin echo and inversion recovery**

A spin-echo is a remarkable phenomenon. Two pulses separated by a delay $\tau$ refocus the magnetization lost by field inhomogeneities (reversible) after another time $\tau$. Varying $\tau$ and measuring the echo intensity determines the time constant $T_2$. This is important when the field inhomogeneity is large part of the spectral line-width.$^1$

![Figure 2](image)

**Figure 2.** After a $90^\circ$-pulse the magnetization is aligned (a) along the $x'$-axis of the rotating frame. After a delay $\tau$, the magnetization spreads out because of field inhomogeneities (b). A $180^\circ$-pulse inverts the magnetization (c) and after a time $\tau$ after the $180^\circ$ pulse the spins are aligned again (d) creating an echo.

The J-spectroscopy method$^7$ used in Paper 1 is a 2D spin-echo by which the chemical shift or frequency offset can be separated from J-coupling in isotropic liquids and from dipolar couplings (or other rank-2 interactions) in anisotropic systems. In Paper 2 a quadrupolar echo ($90^\circ-\tau-90^\circ$) is used to detect a very broad solid spectrum. The $90^\circ$ pulse (on resonance) rotates the magnetization to the $x'$-axis in the rotating frame. Because of the bilinear quadrupole interaction $\sim I_z^2$, the spin coherence
oscillates between its measurable (in-phase) and undetectable (anti-phase) states during $\tau$. If the second 90° pulse has a phase that is orthogonal to the first (i.e. 90°) there is no effect on the in-phase coherence but the undetectable anti-phase coherence is inverted. This inverted anti-phase magnetization will then refocus into measurable in-phase coherence after another time $\tau$. The purpose of this sequence is partly to refocus the inhomogeneous spread of bilinear interactions ($I_z^2$) and partly to avoid electronic or electro-acoustic ringing (see Paper 9 and next sub-chapter). If the phase cycle is chosen with care, it is also possible to refocus dephasing by inhomogeneous fields ($\sim I_z^2$).

The inversion recovery experiment measures the time-constant $T_1$. It consists of two pulses with a variable delay $\tau$ in-between. The signal-to-noise ratio is highest if the first pulse turns the magnetization by 180° and the second by 90°. The first pulse brings the magnetization out of equilibrium and the second measures how much of the equilibrium longitudinal magnetization that has been restored during $\tau$. Recording the restored level of magnetization as a function of the delay time, $\tau$, estimates the time-constant, $T_1$.

**Anti-ringing pulse-sequences**

Measuring broad NMR lines requires short rf-pulses, a short ring-down delay, and a fast digitizer. Fast digitizers (> MHz bandwidth) are available. A solenoid coil is preferable if short rf-pulses are a requirement. At an equal amount of input power, $B_1(t)$ is higher in a solenoid coil than in a saddle coil, because of more turns of wire. In addition, larger power can be fed into solenoid coils before arcing occurs. On the other hand, solenoids are not optimal for studying complex fluids because of the horizontal position of the sample in a normal cryomagnet. A high-resolution probe equipped with saddle coils enables a vertical sample position and is preferred for such studies. Last, for a short ring-down delay, the electro-acoustic or purely electronic ringing has to be suppressed. A careful design of the probe and the electronics is not always sufficient, and in such cases one must rely on composite pulses or echo experiments.

The ringing pattern is to a first approximation independent of other pulses, but the NMR signal is strongly dependent on the pulses already applied and this fact
can be used to cancel ringing. A $90\phi_1 90\phi_2 90\phi_3$ sequence does this when the phases are cycled such as $\phi_i = (-y, -y, y, y), \phi_2 = (y, y, y, y), \phi_3 = (x, -x, -x, x)$ and $\phi_w = (x, -x, x, -x)$. The ringing signal is dependent on the phase difference between the receiver and the pulse as $A_{ring} \sim f(t)e^{i(\phi + \phi_{rec})}$. (The sign convention for the receiver phase is equivalent to that used by the quadrature detector of Bruker spectrometers.) The induced signal is not complex valued but is split into two signals and mixed with reference signals shifted $90^\circ$ with respect to each other. Therefore, it becomes convenient to describe the signals in the two channels as components of one complex number. More explicitly, the ringing from the first pulse in the composite will be $f(t)(2e^{i\pi/2} + 2e^{3i\pi/2}) = 0$, from the second pulse $f(t)(2e^{i\pi/2} + 2e^{i3\pi/2}) = 0$ and from the last pulse $f(t)(2e^{i\pi/2} + 2e^{i-\pi}) = 0$. The NMR signal behaves differently. The first and third elements in the phase cycle rotate the magnetization from $+M_z$ to $-M_y$, the other two elements rotates it in an anti-parallel direction, from $M_z$ to $M_y$. By alternating the receiver phase $180^\circ$ the signal accumulates.

For the quadrupole echo, two different phase sequences are popular, with the first, $\phi_1 = 2*(x), \phi_2 = (y, -y), \phi_w = 2*(x)$, the ringing from the second pulse cancels as $f(t)(e^{i\pi/2} + e^{3i\pi/2}) = 0$, but it accumulates from the first pulse as $f(t)(2e^0)$. The first pulse distorts the spectrum if the echo time $\tau$ is shorter than the characteristic decay time for the ringing signal. If the phase of the second pulse is cycled with four steps the ideal signal-to-noise will be a factor $2^{1/2}$ lower because the $(90_{\phi} - \tau - 90_{\phi} - \tau)$ combination does not give any echo signal, but this scheme has two big advantages. It refocuses inhomogeneous $I_z$ and $I_z^2$ contributions (in contrast to the first sequence that refocuses inhomogeneous fields $I_z$ only partly) and ringing from the first pulse cancels. With the second, $\phi_1 = 4*(x), \phi_2 = (y, -x, -y, x), \phi_w = 2*(x, -x)$, the ringing for the second pulse cancels as $f(t)(e^{i\pi/2} + e^{i0} + e^{i\pi/2} + e^{3i\pi/2}) = 0$, but it does also cancel the ringing for the first pulse as $f(t)(2e^{i\pi/2} + 2e^0) = 0$. All together, the longer phase cycle is recommended if the $T_2$ is short.

**Pulse gradient spin echo NMR**

Pulse-field-gradient spin-echo NMR (PGSE NMR) is a good tool for investigating diffusive processes directly on a time scale of ms – s. This time corresponds to a close
to macroscopic length scale \( \sim \mu m \). The self-diffusion coefficient relates to the slope of the average spatial displacement as \( 6D_t = \langle r(t) - r(0) \rangle^2 \). The NMR spectrum is molecular and by that the self-diffusion coefficient measured by NMR, consequently not only the hydrodynamics of a colloidal particle can be studied but also the degree of association.

Self-diffusion measurements with NMR may employ either static or pulsed magnetic field gradients. If the molecules move while the gradient is applied during the delay time of a spin-echo, there is an extra irreversible loss of magnetization not described by the \( T_2 \)-processes and this is related to the inhomogeneity of the magnetic field and the self diffusion. In a PGSE experiment, the inhomogeneity is controlled and varied by using strong pulsed magnetic gradient fields, which results in an attenuation of the detected signal.

\[
E(g) \propto e^{\left(-\gamma \delta^2 g^2 D_0 (\Delta - \delta/3)\right)}.
\]

(2.2)

Here \( D \) is the self-diffusion coefficient and \( \delta, \Delta, g, \) and \( \gamma \) are the duration of the gradient pulse, the diffusion time, the applied gradient strength and the magnetogyric ratio. Molecules may change positions both coherently and randomly. PGSE NMR may differentiate between different types of motions. For freely diffusing molecules in a plug flow with velocity \( v \), the flow will be visible as a phase twist of the echo attenuation decay curve \( E(g) \propto e^{-\gamma \delta^2 g^2 D_0 (\Delta - \delta/3) \times i \gamma g \Delta} \). In the case where there is a balanced internal flow both up and down (i.e. with no net flow), the phase twist disappears and convection becomes difficult to distinguish from diffusion (Chapter 4.3 and Paper 7). However, the PGSE NMR experiment can be modified to cancel constant velocity contributions by a double echo experiment where both the spatial position and the velocity are “labeled”, making it possible to distinguish one from the other. (Higher order contributions such as acceleration could, in principle, also be cancelled.)

In cases where the spectral lines are broad and the \( T_1 \) is reasonably long \((T_1^* < < T_1)\) one should use the stimulated echo version of the PGSE NMR experiment. The 180° pulse is exchanged with a 90° - \( \tau \) - 90° sequence and the magnetization is stored along the z-axis during \( \tau \), where it relaxes more slowly. Such a sequence gives a
multitude of echoes but the echo of interest comes as if the 90° - τ - 90° sequence was a 180° pulse. Alternating the relative phases of the three pulses and the receiver according a specific pattern filters out the other echoes.

**Reducing and compensating for convection artifacts**

Convection artifacts easily bias a self-diffusion experiment on a low-viscosity sample\(^\text{21}\) in most NMR-probes. When a sample is heated from below, the hotter liquid in the bottom expands and ultimately convection occurs. For a given liquid, the convection starts when the temperature gradient exceeds a critical number called the critical Rayleigh number, \(R_a\). The Rayleigh number itself, \(R_a\), is the dimensionless temperature gradient defined by the temperature gradient, the dimensions of the sample and material properties, while \(R_a\) is defined by the boundary conditions of the sample. The convection onset can be delayed by reducing the tube diameter or the temperature gradient. A safe way of avoiding this type of convection is to invert the temperature gradient for example by heating the sample from the top, but the commercially available gradient probes seldom have this construction. Constraining the sample liquid by capillaries or glass wool can also reduce the convection\(^\text{22}\).

By changing the surroundings using a bath of fluorinated oil in an outer tube, the temperature distribution can be made more even (Paper 1) and this delays the onset of convection to higher temperatures. A clear sign of strong convection is the deviation of the experimental attenuation curve from that of the Stejskal-Tanner expression\(^\text{12}\). Where there is only weak convection, the attenuation decay fits the traditional expression rather well and the derived diffusion coefficient is biased as

\[ D_{app} = D + \frac{\Delta \nu^2}{2}. \]

As long as the signal-to-noise ratio is reasonably high the straightforward procedure is to use a double echo procedure\(^\text{16,18}\), see Fig. 3 and Paper 7.
Figure 3. The apparent self-diffusion coefficient for the nonionic surfactant C_{12}E_8 (5 w\%) in D_2O at T \sim 319 \text{ K}. Filled symbols represent diffusion coefficients for a stimulated-echo-type PGSE NMR experiment while the open symbols are from double-stimulated-echo-type.

2.3 NMR Relaxation in liquids – in motional narrowing

The nuclear spins experience the static B_0 and the time-dependent B_1 field but they also face internal fields. In isotropic liquids these are averaged to zero by thermal motions and their fingerprints are left in the relaxation times, marking the molecular dynamics and the strength of the spin interactions.

The fluctuating internal fields (\omega_{\text{int}}) may have different physical origins\(^1\). The one relevant for this thesis is the interaction between the nuclear quadrupole moment (for a spin I > 1/2 nucleus) and the surrounding electrical field gradients. This interaction is strong and often dominant for I > 1/2. The effect of these fields can be treated at different levels of sophistication\(^5\): by classical, semi-classical, or fully quantum mechanical means. The semi-classical description, often used in practice\(^23\), treats the spin ensemble quantum mechanically but the nuclear environment by classical variables. There are approximations in this theory and I only state those that are important here. First, it is a perturbation theory truncated after the leading term. The interaction strength should therefore be compared with the correlation time and the theory remains valid if \omega_{\text{int}}\tau, \ll 1. This condition is known as the Redfield or
motional narrowing limit. The relaxation rates become functions of the spectral densities \( J \) that are proportional to the reduced motional spectral densities,

\[
j(\omega) = \tilde{g}(\tau) \cos(\omega \tau) d\tau.
\]  

(2.3)

where \( g(\tau) \) is a correlation function, a measure of the correlation between the interaction at two time points, \( g(\tau) = \langle F(0) F'(\tau) \rangle \). (For most relaxation phenomena these are auto- correlation functions, \( F = F' \). But, interference between different interactions sometimes becomes important\(^{24,25}\).) There are two different conventions for calculating motional spectral densities. One is presented in Eq. 2.3, while the other uses a regular Fourier transform. In Paper 3 we used the regular Fourier transform but here as in Paper 4 and 6 the cosine transform is used. For many processes, the correlation functions can be approximated as (a sum of) exponentials, \( g(\tau) = e^{-\tau/\tau_c} \) where \( \tau_c \) is a correlation time for the processes driving the relaxation. In this case, the spectral density becomes Lorenzian, \( \tilde{g}(\omega) = \frac{\tau}{1 + (\tau \omega)^2} \), for a cosine transform.

**Quadrupolar relaxation rates**

When describing the spin quantum system with a density operator it is convenient to decompose that on some basis formed, for example, by the irreducible spin tensor operators. For a spin \( I = 1 \) nucleus the density operator can be represented by nine operators\(^{26}\). Among these, \( T_{10}, T_{20} \) represents populations called as dipolar order (\( T_{10} \)) and quadrupolar order (\( T_{20} \)). One important property of the multipole polarizations is their parity; \( T_{00} \) is even, \( T_{10} \) odd and \( T_{20} \) even. The other six operators of importance correspond to coherences, in-phase \( T_{1\pm1} \) and anti-phase \( T_{2\pm1} \) single quantum coherences (SQC), and \( T_{2\pm2} \) double quantum coherences (DQC). Spin \( I = 3/2 \) nuclei are represented in a similar way, by 3 populations, \( T_{10}, T_{20} \) and the octupolar order (\( T_{30} \)), 3 SQCs (\( T_{1\pm1}, T_{2\pm1}, \) and \( T_{3\pm1} \)), 2 DQCs (\( T_{2\pm2} \) and \( T_{3\pm2} \)) and one triple quantum coherence, \( T_{3\pm3} \) (TQC).
Most of my relaxation studies concern isotropic fluids, for which the relaxation pathways are rather simple. Because the quadrupolar interaction only couple polarization with the same parity 27 an inversion recovery sequence reports about the level of the longitudinal magnetization \( T_{10} \) which relaxes mono-exponentially for spin \( I = 1 \) system with a

\[
R_1 = \left(2J_1 + 8J_2\right)/5. \tag{2.4}
\]

For spin \( I = 3/2 \), the relaxation behavior becomes slightly more complex 27-29 because the relaxation couples the measurable \( T_{10} \) to the \( T_{30} \), because they are both of odd parity. Hence the longitudinal magnetization recovers double-exponentially,

\[
M_z - M_0 \propto \frac{4}{5} e(-R_{11}t) + \frac{1}{5} e(-R_{12}t). \tag{2.5}
\]

If \( R_{11} \approx R_{12} \), this process can be approximated as a single-exponential relaxation with the rate,

\[
R_1 = \frac{1}{5} R_{11} + \frac{4}{5} R_{12} = \left(2J_1 + 8J_2\right)/5. \tag{2.6}
\]

For the transverse magnetization, the description is similar. For isotropic spin \( I = 1 \) nuclei the transverse magnetization \( T_{1\pm 1} \) relaxes mono-exponentially with a transverse rate constant of

\[
R_2 = \left(3J_0 + 5J_1 + 2J_2\right)/5. \tag{2.7}
\]

For spin \( I = 3/2 \), the SQCs \( T_{1\pm 1} \) and \( T_{3\pm 1} \) couple together and the transverse magnetization will decay as \( M_t \propto 2e(-R_{22}t)/5 + 3e(-R_{21}t)/5 \), which again can be approximated as a mono-exponential relaxation if \( R_{22} \approx R_{21} \) with an average rate of

\[
R_2 = \frac{2}{5} (J_1 + J_2) + \frac{3}{5} (J_0 + J_1) = \left(3J_0 + 5J_1 + 2J_2\right)/5. \tag{2.8}
\]
The experimental spectral density, \( J \), relates to the reduced motional spectral density via the strength of the coupling constant. For axially symmetric quadrupole interaction, their relation is,

\[
J(\omega) = \frac{3\pi^2 \chi^2}{4} j(\omega),
\]

for \( I = 1 \) nuclei and,

\[
J(\omega) = \frac{\pi^2 \chi^2}{5} j(\omega),
\]

for \( I = 3/2 \) nuclei (rank 1). Here \( \chi \) is the quadrupole-coupling constant, measures (in units of Hz) the strength of the quadrupole interaction.

**Field-dependent relaxation**

NMR relaxation techniques are complementary to PGSE NMR techniques; the relaxation method is sensitive to the time scale of angular correlation. This is in the ranges of picoseconds for small (Å) molecules and nanoseconds for larger molecules or micellar aggregates\(^3\). \( J(\omega) \) is frequency dependent and thereby the molecular dynamics can be studied in detail if the time scale of molecular motion overlaps with the region of the inverse of the Larmor frequency \( \sim 1/\omega_0 \) (1 \( \mu \)s – 0.1 ns). For small molecules, the NMR relaxation is usually field independent but for colloidal objects, such as micelles and proteins, the field dependency of the NMR relaxation carries detailed information about molecular dynamics.

There are at least two different ways of analyzing the molecular dynamic information inherent in the relaxation rates. One is to describe the frequency dependence of the spectral densities within a model. The other is to use a modified Fourier transform method enabling direct information about the time domain. The small frequency domain available by NMR spectroscopy and the low density of measured relaxation rates makes this latter method less attractive to use. A more
explicit description of the dynamical models for the motional spectral density for molecules in or around micelles is given in Chapter 4.1.

2.4 Lineshape analysis of quadrupole powder NMR spectra

The lineshapes of NMR spectra from solid and liquid crystalline materials provide information about the supramolecular structure or dynamics. In general, these materials can be described as “powder” consisting of randomly oriented domains or single crystals. Each crystal contributes with a spectrum that depends on its orientation with respect to the applied magnetic field. If $\omega_0 >>> \omega_Q^0$, where $\omega_Q^0$ is the quadrupolar splitting, the angular dependence for the resonance frequency ($s^{-1}$) becomes

$$\omega = \omega_Q^0 \left[ \left( 3 \cos^2 \nu - 1 \right) + \eta \sin^2 \nu \cos 2\phi \right]/2,$$

(2.11)

for a spin $I = \frac{1}{2}$ nucleus, where $\nu$ and $\phi$ are spherical polar coordinates and $\eta$ the asymmetry parameter of the electrical field gradient tensor. The quadrupole splitting relates to the quadrupole coupling constant (in angular units, $s^{-1}$) as $\omega_Q^0 = \frac{3}{4} \chi_c$. (In Paper 2 there are misprints in Table 1 and Figure 5, where the quadrupole constant should be changed to quadrupole splitting, $\omega_Q^0$.)

The observed NMR spectrum is a superposition of the spectra from the different oriented domains that can be calculated by spatially integrating Eq. 10 and involving the natural line-width by a convolution. Fitting the experimental spectrum to the calculated powder lineshapes can then provide information about the local properties.

2.5 Temperature sensors and settings

In our investigations, the absolute temperature needed to be set within ± 2 K and this was easy to accomplish. For the field-dependent relaxation measurements the temperature had to be reproduced at several spectrometers with a much higher
relative accuracy. This is often difficult and ultimately we had to rely on an external calibration performed by NMR on temperature sensitive samples.

In NMR probes the temperature is regulated with an air-flow, a heater, a sensor and a PID-regulator. The sensor usually measures the temperature under the sample and therefore its signal should not be used directly if temperature accuracy is important. Instead one should measure directly within the sample space. We avoided electronic sensors for two major reasons. First, temperature sensors and sometimes their can be effected by the magnetic field. This is usually not a problem when the sensor is chosen with care. Nevertheless, we avoided using non-electronic external thermometers. The other advantage with a NMR parameter as a temperature sensor is that they measure the temperature gradient within the sample space (Paper 1).

Different NMR parameters can be used as thermometers: chemical shifts, dipolar and quadrupolar couplings. The well known chemical shift of the Co(III)(CN)$_6^{3-}$ complex in water solution$^{33,34}$ is an excellent thermometer when calibrated to the temperature independent shift of another nucleus for example $^{23}$Na$^+$. The precision of this sensor is very high except at low fields. This sensor was used to set the temperatures in Paper 3.

Another excellent temperature sensor, is the quadrupolar splitting for benzene-$d_6$ in a thermotropic liquid crystal. Benzene is preferably used instead of chloroform$^{35}$ or methylene chloride, because of its higher boiling point. It is the molecular order parameter that strongly varies with temperature$^{36}$ leading to a temperature dependent quadrupolar or dipolar splitting. To test an eventual field-dependence of this order parameter, the observed line splitting was cross calibrated to the $^{59}$Co shift method at two different fields (4.7 and 7.0 T) and no field dependency (within ± 0.05 K) was found.

Such splitting can provide an image of the temperature distribution in the sample, see Paper 1. In that paper the $^1$H homonuclear dipolar coupling for CH$_2$Br$_2$ oriented in a nematic solvent was used to monitor the temperature distribution. This molecule has advantages over $^1$H NMR of benzene$^{36}$. First, there are only two narrow $^1$H lines (instead of the > 60 lines$^{37}$ for benzene) and, second, the two coupled protons form an $I = 1$ spin system, where the spin dynamics are known. The image is produced by spatially labeling the spins by a constant z-gradient and refocusing this spread of frequencies in the echo-time domain using a 2D spin echo (J-spectroscopy)
sequence. The spectrum provided by a 2D Fourier transformation maps the frequency (the z-position) to the dipolar splitting and, hence, the temperature at that location. This experiment is direct, but with the (eventual) drawback of long experimental time.

When a rf-field is applied, the sample is heated by the electric field components. Ideally, there should not be any electrical field components under near-field conditions valid inside the coil, but in reality there are. This electrical field oscillates and heats the sample by forcing the molecules to translate (ions) or rotate (dipoles) back and forth. The absorbed energy (heat) varies as $\sim \omega_0^2$ and is problematic for ionic samples at high fields. The cobalt temperature sensor offers a way to detect overall heating via its chemical shift and the $^{59}$Co line width gives a qualitative measure of the temperature distribution. In our preliminary studies of the $^{81}$Br relaxation in micellar solutions we used a short recycling time at an applied magnetic field of 11.7 T, with the resulting heating of 1 K. Later, a cobalt sensor was used to select a repetition time that prevents heating.

3. Complex fluids – colloidal solutions and mesoscale complexes

We all interact with colloidal and mesoscale systems in our everyday life. The book in front of you consists of at least three different types of mesoscale systems: the paper, the ink and the glue. In your household you interact with colloidal solutions of which milk, soaps and paints are just a few examples.

Colloidal means glue-like in Greek and Thomas Graham introduced the modern meaning of the word. He divided all substances into: crystalloids and colloids with respect to their diffusion behavior. Crystalloids diffused readily through a membrane but the colloids do not. In those early days, a colloidal solution meant a solution with small solid particles moved around by thermal fluctuations. Such particles are of a mesoscale with sizes of 1 - 1000 nm. In contrast the microscale connected to small and medium-sized molecules structures over 0.1-1 nm and the macroscale is loosely defined as > 1 µm. Consequentially, phenomena occurring on the macroscale can be studied in many ways, by for example optical means.

Today the term “colloidal solution” does not denote just a suspension of solid particles but other systems as well, such as large polymer and protein molecules in
solution, assemblies of amphiphilic molecules or solid particles, with at least one mesoscaled dimension. They may have very different local dynamics (molecular) ranging from solid, over polymer, to various self-aggregated objects with liquid-like internal dynamics. Despite this large difference in “local degree of freedom”, there are strong similarities in the mesoscale dynamics when dispersed in solutions. Such solutions not only diffuse slowly but also have special optical and rheological properties and are, therefore, sometimes refereed to as complex fluids\(^{39}\). Those systems studied here all have at least one mesoscale introduced by amphiphilic molecules. All but one were complex fluids (or if you rather want, colloidal solutions). The exception is a solid-like mesoscale polysaccharide – surfactant association presented in Paper 2.

### 3.1 Micelles

Normal micelles are perhaps the simplest self-aggregated colloidal entities. A typical micelle is a dispersed and closed aggregate of surfactants (surface-active agents). The name comes from the fact that these molecules often accumulate at interfaces and change the properties of the boundary. Surfactants are molecules with a Janus face and consists of one hydrophilic (water loving) part that is chemically linked with a hydrophobic (water fearing) part. It is this duality that gives these molecules the ability to form complex liquids. The surfactants used in this work have single hydrocarbon tails (12-16 carbons) and ionic or non-ionic head groups. Three examples are shown in Figure 4.

\[
\text{Figure 4. The chemical structure of two typical ionic and one nonionic surfactants. The uppermost is CTABr (hexadecyltrimethyl ammonium bromide) the middle one is SDS (sodium dodecyl sulfate) and the last is C}_{1_2}\text{E}_5, \text{a member in the oligooxyethylene alkyl ether family with 12 carbons in the alkyl change and five oxyethylene groups constituting the head group.)}
\]
The typical micelle is a sac-like aggregate, often spherical, with surfactants arranged in a way that the water-soluble head groups shields the oily parts from the water. Micelles form when the free energy gain shielding the hydrophobic tails from the water overcomes the entropic penalty of aggregating the surfactants together.

Surfactants first dissolve as molecules in water, but at a certain concentration the energy gain forming aggregates starts to overcome the entropic penalty. At this point, called the cmc (critical micellar concentration), the concentration dependence of the physical characteristics such as turbidity, surface tension, conductivity of the solution change. The cmc reflects the micellar free energy of formation\(^{40}\). This free energy can be divided into a term that promotes micelle formation, the “the hydrophobic free energy contribution” and into, electrostatic, conformational and water contact terms\(^{40,41}\) terms that fights micelle formation. Such a division might help to explain the changes in cmc upon different actions. For example it becomes clear that adding a screening salt will reduce the energetic penalty from electrostatic repulsion among the headgroups for ionic surfactants and the cmc drops\(^{40}\).

To describe the concept of one-dimensional micellar growth, first let the free energy of micelle formation be a sum of the energy (enthalpy) and the ideal gas entropy contributions for each \(N\)-aggregate, where \(N\) is the aggregation number. The number fraction of surfactant molecules incorporated in micelles with aggregation number \(N\) becomes\(^{42}\) \(P_N = N e^{\nu(\mu - \varepsilon_N)}\), \(\varepsilon_N\) is the energy (dimensionless) per surfactant in an aggregate and \(\mu\) is the chemical potential (also dimensionless). When \(\mu < \varepsilon_N\), the surfactant is most probable to be in solution as a monomer, on the other hand if the quantity \((\mu - \text{min}(\varepsilon_N))\) is small aggregation becomes more probable. Further development of the distribution will depend on the \(N\)-dependency of \(\varepsilon_N\). For micelles that prefer a spherical shape \(\varepsilon_N\) has a deeper minimum at \(N \sim M\) than for those that prefer a cylindrical shape. In a cylindrical micelle there is no energetic penalty for adding another molecule, except that from the end caps\(^{43,44}\). Hence, the energy term may be written as \(\varepsilon_N = \varepsilon_i + \alpha / N\). A large promotes long micelles and in a dilute solution, only the entropy penalty for forming very long aggregates stops such growth. The distribution of the aggregation numbers in cylindrical micelles becomes
\[ P_N \approx N e^{-N/(\lambda)} \]. Note that in this model it is the intricate energy balance within the \( N \)-aggregate that determines micellar growth.

### 3.2 Swollen micelles, microemulsions and emulsions

If hydrophobic molecules (solubilizates) are incorporated in a micelle, the micelle may swell. These molecules disturb the delicate energy balance within the micelle, which leads to changes in the micellar shape. In Paper 3, this phenomenon is studied for a particular case\(^{45-47} \) where the micelles first start to grow uni-dimensionally upon addition of small molecules. On further addition of solubilizates the micellar growth process changes character and becomes three-dimensional. The final aggregates formed at maximum solubilization are almost spherical microemulsion droplets.

An oil-droplet in water\(^{48} \) with a monolayer of surfactants covering the oil molecules is a particular type of microemulsion droplet, that is nothing more than a large swollen micelle. A microemulsion droplet is often bigger than a swollen micelle and can be described with molecular or macroscopic approaches\(^{49} \). However, the term microemulsion is rather general and is used for thermodynamically stable dispersion of oil, surfactant and solvent and may consist of oil drops in water, water drops in oil or of intermediate bicontinuos structures.

In contrast to microemulsions, an emulsion is a non-equilibrium structure. A traditional emulsion consists of oil droplets in water\(^{50} \), often produced by mechanical agitation. The surfactants form a stressed monolayer around each droplet with a lower curvature than the optimal. The tensions in the monolayer can be relaxed by nucleation of holes and this leads us to the topic of emulsion stability. Flocculation and creaming enhance the effects of the nucleation of holes because they move the droplets closer together. Even if the film is reasonably stable, the emulsions are destabilized by diffusion of oil from small to large droplets and this is called Ostwald ripening\(^{51} \) (see Paper 9).

### 3.3 Polyelectrolyte-surfactant mesoscale complexes

When ionic surfactants are mixed with water-soluble and oppositely charged polyelectrolytes, the surfactants self aggregate (critical aggregate concentration, CAC) at a bulk concentration often far below the critical micelle concentration. The
surfactants are concentrated in the vicinity of the charged polymer and the local concentration is large enough for surfactant aggregation to occur.

Above CAC there is often an associative phase separation where one phase is enriched in small ions and the other in PE-surfactant aggregates. This second phase precipitates when the molecular weights involved are sufficiently high. The properties of the precipitate can be tuned by changing the polymer or the surfactant. This phase can, by further treatment, be processed into mesoscale films.

4. Results for complex liquids and solids

In this section the more system-oriented aspects of my work are discussed. A short description/discussion of the dynamics models used for interpreting relaxation data is included as well.

4.1 Molecular dynamics in and around ionic micelles

A common denominator of this sub-chapter is that all work was performed on complex liquids all having hexadecyltrimethyl ammonium halide surfactants with Br and Cl counterions as a component. These surfactants are model cationic surfactants. Our experimental method was field-dependent NMR spin relaxation on quadrupolar nuclei such as $^2$H, $^{35}$Cl and $^{81}$Br.

Dynamic models for the motional spectral densities in dilute micellar solutions

Micellar aggregates have at least two characteristic length scales. One that corresponds to the size of the counterion, the water molecule, a segment or a couple of segments (a few Å) of the surfactant molecule, and the other corresponding to the characteristic lengths of the aggregate itself (a few nm). The angular correlation times strongly scale with spatial extension, $\tau \sim R^\alpha$, with $\alpha \sim 2 - 3$, this means that there is an effective time-scale separation even if there is no strong length scale separation. The motions connected to the shorter of these two length scales are fast on the $< 0.1$ ns and do therefore not contribute to the frequency dependence of the observed relaxation rates.
If these fast motions would average the quadrupolar coupling to zero the relaxation rates would be frequency independent.

Nevertheless, the NMR relaxation rates are frequency dependent in micellar solutions, surfactants, solubilizates, counterions and sometimes even water. This means that the fast motions are not averaging the quadrupole coupling to zero, but only to a residual value of the coupling, $\chi_R$. The direction of this coupling is defined by the normal of the water-hydrocarbon interface. The effective time-scale separation leads to the experimental spectral density,

$$J(\omega) = J_f + \pi^2 \chi_R^2 c j$$

(4.1)

where $j$ is the reduced spectral density that contains the effect of the slower motion. The $c$ is a spin (and also rank) dependent constant with the value 1/5 for a $I = 3/2$ nucleus (Eq. 2.10) and 3/4 for a $I = 1$ nucleus (Eq. 2.9). In isotropic micellar systems, the residual coupling is averaged to zero by the random translational motion of the molecules, in and around the micelles and by the rotational tumbling of the micelles. Counterions, solubilizates, water molecules or surfactants are confined to the surface to such a large extent that the exchange of molecules in and out from the surface will not modulate the residual interaction. This means that the random motions, both translational and the rotational could be modeled with Gaussian propagators. The residual coupling is often described by the use of a generalized order parameter, $S$, and the fast motion by a single effective correlation time such as $\chi_R^2 = S^2 \chi^2$ and $J_f = (1 - S^2) \pi^2 \chi_R^2 c \tau_f$. The fast correlation time, $\tau_f$ should be interpreted with care for a surfactant, because there are strong indications that the fast local motions for the methylene segments proceeds on more than one time-scale. For a small and more rigid molecule such as benzene the $\tau_f$ can be interpreted as the joint correlation time for the anisotropic reorientation of the benzene molecule.

The spectral densities resolved in the frequency dependent relaxation rates are modeled as the combination of tumbling of the micelle and diffusion over the micellar surface. Such models have been derived for different geometries: spheres, spherocylinders, ellipsoids. The prolatic model was used in modeling the micellar dynamics (Paper 3-5). Both prolate ellipsoids and spherocylinders are reasonable
model\textsuperscript{67} for CTAX aggregates. The prolate ellipsoidal model was chosen instead of the spherocylinder model (which connects more directly to the thermodynamics models for micellar growth) mainly because of prior neutron scattering experiments that were evaluated in such models\textsuperscript{69-71}. Another attractive feature is that the curvatures over spheroid surfaces are continuous. For very long micelles (axial ratio perhaps > 4) and for more concentrated solutions there are difficulties modeling the spectral densities. The micellar tumbling becomes geometrically (or electrostatically) restricted and for the shapes of long flexible aggregates neither prolates nor cylinders are good approximations for the type of works discussed here. Therefore, it becomes important to exclude the existence of very long micelles with other methods before evaluating spin relaxation data in this model.

The modeled spectral densities involves the rotational correlation times $\tau_{m}^{rot}$ for the different tumbling modes of the aggregate as well as a characteristic diffusion time $\tau_{diff} = r_{diff}^{2} / D_{lat}$\textsuperscript{68}. $D_{lat}$ is the surface diffusion coefficient and $r_{diff}$ defines the surface over which the diffusion is force free. (There is a minor complication for surfactant molecules, the $r_{diff}$ is $\sim 2$ Å shorter than the corresponding hydrodynamic radius, see Paper 3.) The function $b$ in Eq. 4.2,

$$j_s = \frac{1}{5} \left( S_{AM}^2 \frac{\tau_0}{1 + (\omega \tau_0)^2} + h(\omega; \tau_{diff}, \tau_{m}^{rot}) \right)$$

(4.2)

denotes the combined numerical solution of the diffusion problem and parts of the rotational contributions. The model spectral density becomes sensitive to small deviations from a spherical shape because the tumbling mode of the rotational diffusion partly separates together with the geometrical aggregation order-parameter $S_{AM}$ into a distinctive step\textsuperscript{68}. This order parameter informs about the shape of the aggregate and it is zero for a sphere. The motional spectral density given in Eq. 4.2 is plotted in Figure 5 for a sphere and a prolate with an axial ratio of three, the slow step corresponds to the $\tau_0$. 
Figure 5. Calculated motional spectral densities including rotational tumbling and spinning and surface diffusion for a sphere of 1 nm and a prolate with a small axis of 1 nm and large axis of 3 nm. For the rotational part the parameters are those of water at a temperature of 303 K and $\tau_{\text{eff}} = 1\,\text{ns}$ (corresponding to $1/6\,\text{ns}$ if another defining equation is used $\tau = r^2/6D$).

Solubilization of benzene in CTABr micelles

As early as 1966 there were indications that micelles formed by the cationic surfactant, hexadecyltrimethyl ammonium bromide (CTABr) grow upon solubilization of benzene$^{46}$ and others have continued to study this phenomenon$^{72-77}$. The original indications were from viscosity measurements and $^1$H NMR chemical shifts. We chose to study the micellar structure upon solubilization using field-dependent $^2$H NMR spin relaxation and cryogenic transmission electron microscopy$^{78}$ (cryo-TEM). The $^2$H NMR relaxation experiments were performed on both the surfactant-$\alpha$-$d_2$ and the
benzene-$d_6$, which lent internal consistency interpreting the data. The time-scale separation between the dynamics of the aggregate and that for the solubilized benzene allowed information through its local dynamics about average location of benzene.

For a 0.10 $m$ solution of CTABr we determined the axial ratio to $\sim 1.6 - 1.7$, which coincides with recent neutron scattering$^{69}$ and previous NMR findings$^{67}$ but clearly incompatible with the value 2.2 obtained by a later neutron scattering experiment$^{70}$. See Figures 6 as an illustration of the quality of the model fits to the experimental data. Prolonged micelles are polydisperse and when this was included in our model, the average axial ratio became shorter, approximately around 1.4.

![Figure 6](image-url)

**Figure 6.** The frequency dependent $^2$H relaxation rates of CTABr-α-$d_2$ (0.10 $m$) is plotted in (a) where empty and full symbols corresponds to longitudinal ($R_1$) and transverse ($R_2$) relaxation rates and the fitted line is a dynamic model for prolate micelles with an axial ratio = 1.6. In (b) the reduced merit function, $\chi^2$ is presented for a set of 3-parameter fits to the experimental data in (a) changing the axial ratio. This merit function is the sum of the squares of the residual divided by the estimated error estimates squares and reduced by the degree of freedom in the model fit.

In these fittings the $\tau_{\text{diff}}$, the frequency independent contribution to the experimental spectral density $J_f$ and the residual coupling constant $\chi_R$ was varied and the axial ratio $\rho$ was successively changed to test conclusions from SANS. The small axis was held constant using estimates of the hydrodynamic small axis for the prolate$^{67,79}$, these were supported by small angle neutron scattering (SANS)
data\textsuperscript{69,71}. This might seem to be very non-robust but the general approach has been shown to be sound for interpreting relaxation data\textsuperscript{66,80}. Before evaluating the \textsuperscript{2}H NMR relaxation data for CTABr-\(\alpha\)-d\textsubscript{2} and benzene-d\textsubscript{6} the coexistence of very long micelles was excluded by the use of cryo-TEM (Figure 7).

![Figure 7](image.png)

**Figure 7.** The cryo-TEM picture of a (0.10 m CTABr)/ (0.10 m benzene) micellar solution. Note that there are no long micellar structures present. The bar in the picture represents 100 nm.

When evaluating the \textsuperscript{2}H NMR relaxation data obtained upon addition of benzene, four parameters was varied, \(\tau_{\text{diff}}\), \(J_r\), \(\chi\), and \(\rho\). Because of the strong covariance via \(\tau_{\text{diff}} = r_{\text{diff}}^2 / D_{\text{lat}}\)\textsuperscript{68} either the value of the small axis or the self-diffusion coefficient was fixed. For the surfactant relaxation, we proceeded in two ways. First, the surface-diffusion constant was fixed to the value obtained by the model fit of the spin relaxation data from the pure CTABr and \(r_{\text{diff}}\) was set free. In the other, the short axis length was fixed to the all-trans length value the pure CTABr solution and \(D_{\text{lat}}\) varied. Both procedures showed a one-dimensional growth of the micelles. This finding was supported by the benzene relaxation.

When a large amount of benzene was added (\(X_o = 2\), number fraction oil-to-surfactant) it was not possible to fit the NMR relaxation data for the surfactant with a value for the short-axis length fixed to that of a pure CTABr aggregate. Hence, we continued under the assumption that the surface layer was saturated with benzene.
where lower amounts were added ($X_{os} = 1.3$). Using the $D_{aw}$ value obtained, the results suggest a swollen micelle, a small micro-emulsion droplet.

The relaxation of benzene-$d_6$, when added in a small amount, showed a slower fast dynamics ($\tau_f \sim 6$ ns) than that in bulk$^{81}$. When added in large amount, the dynamics were faster ($\tau_f \sim 2$ ns). Taken all together this supports that benzene is solubilized in the surface layer in the beginning of the solubilization process and later solubilizes in the middle of the micelle.

The micelles grow because of the reduction of the electrostatic penalty in the surface region, which favors a more elongated form. Above a certain benzene concentration the surface layer is saturated and the benzene becomes increasingly solubilized in the micellar core. This sequence could qualitatively be explained with help of the membrane theory$^{42,49,82}$. The estimates of the spontaneous curvature ($H_0$) in micelles with different benzene content are presented in Table 1.

<table>
<thead>
<tr>
<th>$X_{os}$</th>
<th>$r$ (nm)</th>
<th>$\rho$</th>
<th>$H_0$ (nm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.6 (fix)</td>
<td>1.4</td>
<td>0.66</td>
</tr>
<tr>
<td>0.8</td>
<td>2.6 (fix)</td>
<td>2.4</td>
<td>0.55</td>
</tr>
<tr>
<td>1.3</td>
<td>2.6 (fix)</td>
<td>2.7</td>
<td>0.53</td>
</tr>
<tr>
<td>2.0</td>
<td>3.3</td>
<td>1.3</td>
<td>0.54</td>
</tr>
</tbody>
</table>

Table 1. The mean curvature ($H_0$) is presented for the CTABr-$\alpha$-$d_2$ micelles with different addition of benzene. The axial ratios are determined by the model fits of the $^2$H-NMR spin relaxation data. The micelles without benzene have a higher curvature than the one with benzene.

The data in Table 1 show that the $H_0$ remains approximately constant after an initial decrease. That fact that a transition from cylindrical to spherical geometry happens (at a constant $H_0$) on increasing the volume fraction of oil-to-surfactant $\phi_{os}$ is explained by the membrane theory$^{49}$. Close to the “emulsion failure” there is an equilibrium in-between spherical microemulsion droplets and free oil.

A final complication is that no initial prolongation for the CTACl micelle on solubilization of benzene$^{76}$ was visible. This reflects the delicate free-energy balance in the head-group region of the micelles. Merely the change of the counterion
determines if the micelles starts two grow in one or three dimensional with the addition of benzene to CTAX solutions.

Counterion relaxation in CTAX aggregates

The state of counterions near oppositely charged surfaces has been studied for a long time, using various methods. By NMR relaxation of counterions with quadrupolar nuclei some consensus has been reached. The micellar surface causes a slight average deformation of the hydration shell compared to that in dilution. This leads to a non-zero $\chi_R$ that is averaged to zero by slower motions, by self diffusion at the surface and rotational tumbling of the aggregate.

$^{79}$Br, $^{81}$Br and $^{35}$Cl NMR experiments have been used for many years to characterize the anionic counterions in micellar solutions. From these studies it is clear that the dynamics of the counterion changes when micelles form and that the counterion is hydrated. Nevertheless, it remained an open question if there is a field-dependency for the spin-relaxation for theses anionic counterions. In such cases this phenomenon would reflect the level of fast and the slow modes. If the dispersion step that belongs to slower motions is large it will carry detailed information about the lateral diffusion of the counterion in the vicinity of a micellar surface. The field-dependent studies presented in Paper 4 and 6 separate the fast and slow contributions to the relaxation rates and provide some answers to these questions.

Measuring the broad NMR lines for $^{81}$Br is difficult because of ringing artifacts. These were avoided by special means, see Chapter 2.2 and Paper 5. Moreover, an accurate reproduction of the actual temperature at the different spectrometers (Chapter 2.5) was necessary for measuring the relaxation rates at different fields. To my knowledge, the $^{81}$Br relaxation study is the first showing field-dependence for this nucleus. For $^{35}$Cl there are previous reports of field-dependent relaxation studies on chloride binding to proteins in red blood cells and solid state properties of pyrazole derivatives. The initial intensity for the quickly decaying $^{81}$Br free induction decay signal was estimated by using the generalized Bloch equations to calculate the effect of the applied ringing suppressive composite pulse sequence. The initial intensity from CTA $^{81}$Br was 93-97% of that for $^{81}$Br at equal molar concentration of NaBr in water. Hence there is no undetected broad component in
the $^{81}\text{Br}$ signal. An undetected broad and lost component would imply an initial intensity estimate of $\sim 40\%$ for the CTABr compared with the NaBr solution.

The experimental relaxation rates were modeled in much the same way as in the $^2\text{H}$ NMR study of benzene solubilization. Hence, the axial ratios were fixed to values from SANS experiments$^{69,71}$. Three parameters were fitted to the $^{81}\text{Br}$ spin relaxation data: $\tau_{\text{diff}}$, $\chi_{\text{red}}$ and $J$. For the $^{35}\text{Cl}$ NMR relaxation, the frequency dependence was weak, because the magnetic moment is smaller for $^{35}\text{Cl}$ than that for $^{81}\text{Br}$. In fact, we had to use a field of 18.79 T to achieve the 78.4 MHz resonance frequency where we could detect $R_1 \neq R_2$ as shown in Figure 8. Hence, it was not possible to fit three parameters as in the $^{81}\text{Br}$ study. Fortunately, independent information about the $\chi_{\text{red}}$ is available in the form of the quadrupole splitting measured as a function of concentration in the hexagonal phase of the same system$^{92}$.

![Figure 8](image_url)

**Figure 8.** NMR relaxation rates for (a) $^{81}\text{Br}$ in 0.10 M CTABr and (b) $^{35}\text{Cl}$ in 0.10 M CTACl in aqueous solutions. Filled symbols denote longitudinal ($R_1$) and non-filled ones transverse ($R_2$) relaxation rates.

The ion diffusion over the micellar surface proved to be quick for both ions, more than 10 times as quick as for the surfactant cation. In fact, the ion diffusion is only slightly reduced by a factor of 1.0 - 2.5 compared to the one of the corresponding ion in diluted aqueous solutions. Compared with behavior of the Na$^+$ ion in micellar solutions with micelles having sulfonate$^{64}$ or sulfate$^{93}$ headgroups, these reductions of the diffusion is smaller.
The frequency-independent contribution to the relaxation was dominant for both Cl\(^-\) and Br\(^-\). This tells us that the fast ps-scale dynamics is effective in averaging out the quadrupolar coupling, which results in an order parameter of \(\sim 2-3\%\). It is worth noting that for a non-methylated ammonium head-group this order parameter was found higher\(^94\).

When interpreting the fast contribution to the spectral density it is not possible to differentiate which changes in the hydration shell structure or the dynamics that causes a particular correlation time. However, the observed difference of about 1.5 – 2 between the reduced and normalized chloride and bromide contributions still indicates that the hydration shell is more disturbed for bromide than for chloride upon micelle formation. This agrees well with the positions of these ions in the Hoffmeister series.

### 4.2 Changes of aggregate size in micelles and emulsions

The long-time self-diffusion coefficient is a macroscopic quantity and represents \(\sim \mu\text{m}\) displacements over long (ms – s) time periods.

**Growth of C\(_{12}\)E\(_8\) micelles with increasing temperature**

There has been early evidence for micellar growth with increasing temperature in the C\(_{12}\)E\(_8\) system\(^{95-98}\). However the PGSE NMR measurements\(^{95,96}\) indicated slower growth than a Quasi-Elastic Light Scattering (QELS) study\(^{97}\). Convection tends to spoil PGSE NMR experiments\(^{15,21}\). We applied special techniques that minimized the effect of convection on the experimental self-diffusion coefficients, which enabled a study of the growth of micelles when the temperature was increased.

By using a double-stimulated-echo-type experiment, a somewhat different picture was established. No initial micellar shrinkage was found in the region \(< 310\text{ K}\) and the detected fourfold decrease in the parameter \(D\eta^*/T\) showed a stronger micellar growth than earlier obtained. See in Figure 9 how the parameter \(D\eta^*/T\) changes with temperature.
Figure 9. The parameter $D\eta/T$ describes the changes of in $C_{12}E_8$ micelles as a function of temperature; note the monotonic decay with increasing temperature. This corresponds to an equally monotonic growth of the micelles.

Ostwald ripening of $C_{12}E_8$-decane-$D_2O$ emulsions

Ostwald ripening belongs to a general class of aging processes for binary systems \(99,100\) where the precipitate, here the expelled oil in large droplets, evolves solely by minimizing the surface energy through decreasing the surface-to-volume ratio. In our non-equilibrium microemulsion created by the temperature drop, the local concentration of oil in the vicinity of small droplets becomes higher than that close to large droplets. Consequently, oil flows from the small to the large droplets with a rate that is diffusion limited. As a result, the total number of droplets is reduced and the volume of the increasing droplets grows linearly with time. Hence, their radius varies as

$$\langle R(t) \rangle = \langle R(0) \rangle + C\sqrt{t}, \quad (4.3)$$

where $\langle R(0) \rangle$ is the initial average droplet size in the microemulsion phase and $t$ measures the time after the temperature drop. For emulsion droplets, $C$ is expressed in terms of the properties of the oil as
where \( D \), \( c \), and \( V_M \) are the self-diffusion coefficient, the solubility, and the molar volume of the oil, respectively, while \( \gamma_{surf} \) is the oil-water surface tension.

The scaling relation between the average size and time holds for emulsions when the Ostwald ripening is dominant\(^ {101-105} \), but the physical interpretation of \( C \) is complex. Many emulsion systems coarse with a rate that is higher than the one predicted by theory. In nonionic emulsions, there are experimental findings that place \( C \) both close to the predicted value\(^ {101} \) and far from that with a factor of \( \sim 20 \)\(^ {106-108} \). A time resolved PGSE NMR study is complementary to the scattering techniques, because it senses both big and small droplets and can easily be performed over days/weeks in contrast to SANS experiments. The emulsions in our study were prepared by a temperature drop following the procedure of Egelhaaf et. al.\(^ {101} \). The initial microemulsions were from the well-studied decane-C\(_{12}\)E\(_5\)-D\(_2\)O system\(^ {109} \) and traces of SDS were added to suppress other destabilization mechanisms. Small amount of HMS was added as a reporter molecule.

The echo attenuation spectra recorded for the microemulsions decayed with a single diffusion coefficient for all molecules but after the temperature drop, the oil spectrum decayed with two distinct diffusion coefficients at all tested time scales. The echo attenuation spectra decay according,

\[
I(g) = I_0 \sum_{i=1}^{N} A_i e^{-D_i \gamma^2 g^2 (\Delta-\delta)^2},
\]

with \( N (= 1 \text{ or } 2) \) diffusing components to the observed signal attenuation on increasing gradient strength \( g \). In Eq.(4.5), \( A_i \) is the relative weight of the different diffusing components, \( \gamma \) is the magnetogyric ratio of \(^1\)H, \( \delta \) is the length of the gradient pulse, \( \Delta \) is the diffusion time, and \( I_0 \) is the signal intensity at zero attenuation. From Figure 10 below it is evident that one component alone can not describe the experimental attenuation decay.
Figure 10. Typical attenuation of the oil molecule signals in a PGSE NMR experiment on increasing gradient strength measured in a C\textsubscript{12}E\textsubscript{5}-decane-D\textsubscript{2}O emulsion with an oil-to-surfactant volume ratio of \(\sim 2.2\) and a total volume fraction of dispersed material \(\sim 0.17\). This experimental points were recorded for 13 hours after the temperature drop from 305 K to 291 K and the lines represent fits to Eq.(1), with one (dotted) and two (dashed) components.

We analyze our data under the assumption that the lower of the obtained two oil diffusion coefficients, \(D_{\text{emul}}\) (Figure 11 a), describes the self diffusion of large oil droplets while the higher coefficient, \(D_{\text{micro}}\) (Figure 11 b), belongs to coexisting small microemulsion droplets. The \(D_{\text{micro}}\) is approximately constant in time, but \(D_{\text{emul}}\) decreases with time. The time dependence of \(D_{\text{emul}}\) is supposed to follow Ostwald ripening, and this is supported by the linear dependence of \(1/ D_{\text{emul}}\) with \(t^{1/3}\) (compare with Eq. 4.3).
Figure 11. The time dependence of the self diffusion at the same scale. For the fast component (a) and the slow component (b) in a ripening emulsion of C_{12}E_5-decane-D_2O, brought out of equilibrium by a temperature quench.

The amount oil expelled from the microemulsion phase (from the amplitude factors in Eq. 4.5) agrees qualitatively with the predicted value. The coarsening of the emulsion phase is well described by Ostwald ripening. Growth of the emulsion droplets was similar in form and rate to the prediction. Although the droplets grew in an environment of coexisting microemulsion droplets ripening did not accelerate.

4.3 Solid-like structures in polysaccharide-C_nTABr compounds

This investigation of polysaccharide-C_nTABr associates is unique because it does not concern a complex liquid, but instead a self-associated mesoscale system in solid or solid-like state. Nevertheless, this work relates to previous studies in two important ways. First, the material was prepared by mixing two complex liquids, a surfactant solution and a solution with charged polyelectrolyte molecules. The polyelectrolyte was a natural polysaccharide with a high molar mass 5-7 MDa and approximately every third sugar group carried a negative charge usually a sulfate group. (This polysaccharide is made by a red micro alga and is extracellular. In nature this creates a “jelly”-like coating that protects against sudden environmental changes.) Second, the project also included NMR methodological work that allowed us to accurately measure a broad powder spectrum with a very short $T_2$. 


Mixing the partly sulfated polysaccharide (PS) with alkyltrimethylammonium bromide surfactants (C12-C16 chains) formed a precipitate, which was subsequently washed and dried. The mesoscale (~4 nm) order in the precipitate is clearly shown by the first-order diffraction peak in the small angle X-ray scattering (SAXS) curve contrasted to the broad distribution in the wide angle X-ray scattering (WAXS) domain. Nevertheless, the material was disordered enough to present no higher order peaks in either scattering method, see Figure 12.

**Figure 12.** X-ray scattering curves acquired in small (a) and wide (b) angles for different C$_n$TA-PS compounds. The solid line with a peak at small q (in a) is for n = 16, the dashed is n = 14 and the dotted n = 12. In (b) there is a wide distribution of angles; the dashed-dotted line at the bottom indicates the instrument baseline.

$^2$H NMR provided some insight into the molecular origin of this disorder and revealed a wide variation of the quadrupolar spectral parameters. (Please note that the Figure 3 in Paper 8 has the wrong text. The dotted line is a result of de-convoluting the spectrum into two asymmetric powder NMR spectra.) De-convoluting the NMR spectrum into two spectra generated the dotted lines in Figure 13. To make this more clear I here present three different types of de-convolutions, all having two components, but different symmetries in the interaction between the nuclear quadrupole and its surrounding electrical field-gradient.
Figure 13. The experimental $^2$H NMR spectrum of the polysaccharide-C$_{16}$TABr-$\alpha$-d$_2$ complex (solid line). De-convoluting the spectrum into two NMR spectra under different premises generated the dotted lines. In (a) the spectrum was de-convoluted into two symmetric powder NMR spectra, in (b) into one symmetric and one asymmetric and in (c) into two asymmetric spectra. The dashed line shows the residual.

De-convolution is a typical inverse problem with many solutions and the conclusions derived are usually vague and model dependent. Nevertheless, it is clear that variation of the spectral parameters is large and there is probably an asymmetric component present in the $^2$H NMR spectrum. The measured relaxation rates and coupling constants are consistent with a model where the axial rotation of the surfactant on the 10 - 100 ns time scale reduces the coupling to a residual value. The asymmetric component shows that this reorientation has a low symmetry. The probable explanation is tilted surfactant tails with a large range of tilt angles. This is consistent with the wide distribution of scattering angles in the WAXS curve.

5. Conclusions

There have been NMR studies of complex fluids for some 30 – 40 years and to continue research along such a track has advantages as well as disadvantages. The consensus about how to interpret data and perform NMR experiments is helpful and the very fact that it has been used for such a long time shows that it has given useful information. However, many of the unique questions that the method may answer have already been answered. It would be easy to conclude that NMR today is more suited to study applied aspects of complex fluids and it is indeed used as such. Still, new information can be obtained by applying new, modified, or better controlled
NMR methods to well-studied complex liquid systems. This could perhaps be traced back to the NMR methodology that seems to develop in a rather continuous manner via mutual exchange of experiments among the fields, NMR studies of biomolecules, complex fluids, solids and NMR imaging.

Numerous experimental traps may block the way to proper information. Sometimes it is possible to remove such traps, but at other times new or modified experiments have to be used. For example, it would not have been possible to study the bromide dynamics in detail without the anti-ringing sequence and the backcalculation procedure of the initial intensity. Measuring self diffusion over room temperature would have been biased using the standard PGSE experiment, which typically all heat the sample from below with a stream of hot air – an inappropriate arrangement for many applications.

The dynamic molecular information on the µs-ns time scale from field-dependent nuclear spin relaxation is unique. However, both the temperature and the field have to be well controlled to assure accurate relaxation data and accuracy is important for model fitting. Even if the experimental conditions are under control, other obstacles may appear. Those could be either system or model related. As examples, the time scales for micellar spinning and surface diffusion over the aggregate often coincide. Furthermore, the surface diffusion is measured through a single correlation time, which is a composite of the spatial extension of the aggregate and the surface diffusion coefficient. These facts set limits for the interpretation of the data.

Nevertheless, when the experiment is properly controlled and the data analysis is prudent one finds information about the molecular dynamics. As one example, the largely field independent relaxation of both the $^{35}$Cl and $^{81}$Br ions shows that the fast hydration dynamics of these ions sets their residual quadrupole coupling to almost zero. From the small but significant frequency dependency it was possible to conclude that the ions diffuse fast compared with the surfactant. That the bromide ions diffuse at least 10 times faster than the surfactants at the nanosecond time scale, definitely puts restrictions on the meaning of a statement that the bromides are “bound” to a charged micellar surface.

The self-diffusion coefficients measured by PGSE NMR in complex liquids suffer less from model dependencies, but are averages over a long time from ms to s. They are therefore macroscopic for nm-sized objects. On the other hand, self-
diffusion coefficients are sometimes complicated to measure accurately and to interpret physically. In particular convection artifacts are difficult to suppress. The fact that the self-diffusion coefficients for big particles strongly depend on inter-particle interaction/obstruction even at moderate volume fractions of dispersed material presents a problem for the physical interpretation. As one example, the experimental self-diffusion coefficients provide only the relative size in concentrated emulsions.

What might we have been done differently to improve the experiments with the benefits of hindsight? Some less common relaxation experiments such as $T_{1\rho}$ measurements, field-dependent cross and cross-correlated relaxation could indicate other aspects of the molecular dynamics of the systems (or similar) under study. The first experiment could, when properly controlled, give important information about slow dynamics (~ms) in viscous complex fluids. The second method can in a lucky case measure contact and the last method is very sensitive to anisotropic motion and depends on cross-correlation in the dynamics. A limitation in the field-dependent relaxation is that the method reveals information about dynamics. Structural parameters are hidden within that information, but to extract (too) many parameters from a single curve may easily lead to errors. Especially the study of benzene solubilization in CTABr micelles could have benefited from methods other than $^2$H NMR relaxation and cryo-TEM. A combined SANS-NMR relaxation study would have given quantitative information.

At the risk of seeming pretentious, I am especially proud of the following aspects of this work. The field-dependent NMR study of $^{35}$Cl and $^{81}$Br ions in alkyltrimethyl ammonium halide solutions showed that the breadth of the spectral lines of these ions are mostly connected to fast motional modes. In addition, the frequency-dependent part showed a fast diffusion of these ions, more than 10 times faster for bromide than the lateral diffusion of the surfactant ions. The field-dependent $^{81}$Br study required an acquired skill. It has been known since several years, that convection can bias self-diffusion experiments$^{15}$ and I hope that our efforts show how to deal with theses artifacts. The experimental approach we have developed opens possibilities for temperature dependent studies of self diffusion in complex fluids, without extensive rebuilding of the probes.
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