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Pulsed field gradient spin-echo NMR experiments in micellar solutions of the water/cetyltrimethylammonium bromide system

L. Coppola, R. Muzzalupo, G. A. Ranieri and M. Terenzi

Chemistry Department, University of Calabria, 87036 Arcavacata di Rende, Italy

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Abstract. — Pulsed Field Gradient NMR experiments, in their original time domain, have been carried out to separate both water and surfactant self-diffusion coefficients in the micellar solution of the system cetyltrimethylammonium bromide/water. These results have been supported by those obtained by NMR experiments performed with a Fourier Transform spectrometer. The water self-diffusion coefficients were used to calculate the obstruction effect of the micellar aggregates in accordance with a stoichiometric model already used for lyotropic mesophases. It was found that the micellar aggregates change shape with the concentration and are characterized by an average hydration number of approximately 9 +/- 3.

Introduction.

Water and surfactant self-diffusion studies in micellar surfactant solutions have recently provided useful information at the molecular level, regarding motion, aggregate shape and structure. The water self-diffusion coefficients in surfactant systems at concentrations higher than the critical micellar concentration, are generally found to be smaller than in pure water, the reduction being mainly related to the hydration of surfactant molecules as well as to obstruction effect, decreasing the mean free path of water molecules. Such reduction can be accounted for by a geometrical parameter (obstruction factor, $f$) depending on the particular structure and on excluded volume to molecular motion. In the liquid crystal regions the obstruction factor has been found for lamellar ($f = 0.66$), capillary ($f = 0.33$) and hexagonal structure ($f = 0.76$) [1].

The self-diffusion coefficient can be experimentally measured by the spin-echo NMR experiments in the presence of magnetic pulsed field gradients (PGSE) [2]. In the original form the PGSE experiments are performed in the time domain ; applied to multi-component systems they cannot distinguish between individual contributions to multi-exponential echo decay unless rather restrictive criteria are fulfilled with regard to relations between individual diffusion rates and transverse spin relaxation rates. In this regard, there is the important study of Boss et al. [3] who used the PGSE method for the determination of the diffusion coefficient of the benzene in the benzene/polyisobutylene system. Von Meerwall et al. [4] have used
similar PGSE experiments to measure the self-diffusion coefficients of all three components of the solution containing polystyrene, hexafluorobenzene and tetrahydrofuran as a solvent.

Recently the determination of self-diffusion coefficients has been performed on a variety of commercial spectrometers by means of Fourier Transform experiments (FT-PGSE). In a single frequency resolved spin-echo experiment, often requiring less than 20 min measurement and evaluation time, one can simultaneously determine self-diffusion coefficients of several constituents in a solution. The typical procedure has been described in detail in a 1987 review [5]. FT-PGSE experiments are of difficult application in organized solutions, anisotropic phases and in viscous systems. With the exception of problems due to short relaxation times, these systems are characterized by molecules or aggregates with low mobilities. In particular aqueous surfactant solutions, the viscosity is strongly dependent on the surfactant amount. High viscosities are observed in solution close to the liquid crystal boundaries or in biphasic region. In consequence the molecular mobility is strongly reduced and the self-diffusion experiments by PGSE sequences must be conveniently performed in the time domain by using strong gradients. Also, strong gradients can be used like a selective procedure to separate the contributions to the echo signal due to species with appropriate different rates.

Here we report studies employing the PGSE method for the determination of the self-diffusion coefficients of both components in the system cetyltrimethylammonium bromide (CTABr)/water. We are interested in analysing the microstructure in the solution micellar phase and the change of the aggregate shape in solution mixtures close to the hexagonal liquid crystal phase, present at high surfactant concentrations.

The paper also focus on accuracy and applicability of time domain PGSE experiments to monitor the molecular mobilities in surfactant aqueous systems. The aim is to demonstrate that this procedure may be viewed as a useful tool for the measurement of the self-diffusion of one component in the presence of a second.

Finally the water self-diffusion coefficients have been used to calculate the obstruction factor of the CTABr/water micellar solution and deduce some information about the aggregate shape and size.

Experimental section.

MATERIALS. — Cetyltrimethylammonium bromide, Fluka, was purified by recrystallization from ether/ethanol [6]. The critical micellar concentration at room temperature was found by conductimeter analysis to be about 0.02 % CTABr weight percent, in agreement with previous findings. Water was bidistilled, deionized and degased; when required it was partly replaced by D$_2$O, Merck, with a 99 % isotopic enrichment.

The samples were prepared by mixing the components in a 5 mm NMR test tube. The tube was sealed under nitrogen and the mixture was homogenized by alternate centrifuging and heating of the samples.

METHODS. — PGSE experiments were performed on a home-made NMR spectrometer working at 16 MHz on $^1$H [7] using a spin-echo sequence. Two magnetic gradient pulses of magnitude $g$, duration $\delta$ and separation $\Delta$ were applied during the dephasing and rephasing period, respectively [2]. A pulsed current supply, giving a dc current up to 20 A, feeds the coils to obtain a field gradient up to 170 G/cm. The gradient strength was calibrated to values of the self-diffusion coefficient $D_0$ in pure water for different values of temperature and current.

The temperature was measured with a calibrated copper-constantan thermocouple, which was placed near the sample. The temperature was measured immediately before and after the spin-echo experiments; we have obtained an accuracy of about $+/-$ 0.2 °C.
The self-diffusion measurements using a pulsed field gradient experiment in Fourier Transform mode (FT-PGSE) were performed on a Bruker WM 300 NMR spectrometer. All measurements were made at room temperature (about 25 °C). The implementation of the FT-PGSE method, for measuring self-diffusion coefficients, was described by Stilbs [5]. In the present study the interval (Δ) between the magnetic field gradient pulse is kept constant and equal to interval (τ) between the 90°-180° rf pulses. The proton diffusion measurements were monitored by using Δ equal to 400 ms while δ was varied in the range of 5 to 90 ms. The magnetic field gradient (about 1.5 G/cm) was calibrated to 1% accuracy through parallel measurements on trace amounts of protons in D₂O, using established values from the literature [8].

Results and discussion.

The isotropic micellar solutions and liquid crystal phases have been studied by preparing solutions in the range of concentration 5-40 wt% of surfactant (CTABr). In table I are reported the mixtures analyzed in this work. Microscopy and D-NMR experiment were used to define the phase equilibria and the phase transitions observed by varying the temperature [9].

For unrestricted isotropic self-diffusion and for vanishing steady field gradient, the echo amplitude due to self-diffusion can be expressed as follows [2]

\[ A(2\tau, g) = A^0(2\tau) \exp(-KD) \]  

(1)

where \( K = (\gamma g)^2 \left( \frac{\Delta - \delta}{3} \right) \), \( A(2\tau, g) \) and \( A^0(2\tau) \) are the echo amplitude at time \( 2\tau \) with and without pulsed magnetic gradient, respectively, and \( \gamma \) is the gyromagnetic ratio of the observed nuclei.

Table I. — L1 and E are the isotropic micellar solution and hexagonal liquid crystal phase, respectively.

<table>
<thead>
<tr>
<th>Mixtures</th>
<th>wt% CTABr</th>
<th>Phase at 50 °C</th>
<th>( 10^{-5} D_w ) (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>4.75</td>
<td>L1</td>
<td>3.55</td>
</tr>
<tr>
<td>b</td>
<td>10.07</td>
<td>L1</td>
<td>3.40</td>
</tr>
<tr>
<td>c</td>
<td>15.03</td>
<td>L1</td>
<td>3.16</td>
</tr>
<tr>
<td>d</td>
<td>19.92</td>
<td>L1</td>
<td>3.10</td>
</tr>
<tr>
<td>e</td>
<td>25.07</td>
<td>E</td>
<td>2.43</td>
</tr>
<tr>
<td>f</td>
<td>29.05</td>
<td>E</td>
<td>2.07</td>
</tr>
<tr>
<td>g</td>
<td>40.05</td>
<td>E</td>
<td>1.90</td>
</tr>
</tbody>
</table>

In surfactant/water solutions above the CMC concentration, the measured signals are mainly due to protons in two different environments: the solvent and the surfactant in the aggregate state. In this case, as for general binary solutions in which the two components diffuse at different rates, the expression for the echo amplitude becomes:

\[ A(2\tau, g) = A^0(2\tau) \exp(-KD_w) + B^0(2\tau) \exp(-KD_m) \]  

(2)

where \( D_w \) and \( D_m \) are the self-diffusion coefficients of two components, \( A^0(2\tau) \) and \( B^0(2\tau) \) are the respective contributions to the total echo signal in the absence of magnetic field gradients, they do not contain any effects of diffusion but include terms of relaxation and spin population.
Liquid crystal mesophases present different anisotropic properties not displayed in simple solutions. When we measure the self-diffusion in liquid crystalline mesophases (e.g. hexagonal, lamellar, cubic, gel) the protons of the surfactant molecule do not contribute to the echo signal, because of the short transverse relaxation times. Consequently, the analysis of the PGSE experiments is simplified and can be carried out using equation (1) which, if applied in the condition $KD \ll 1$, gives the apparent self-diffusion coefficients [10, 11].

In the CTABr/water system the micellar proton transverse relaxation times were studied using mixtures prepared with heavy water. For the sample c, at 50 °C, we found a relaxation time for the surfactant micellar aggregates ($T_{2m}$) of about 120 ms. We also measured, for the same sample, the micellar aggregates and water self-diffusion coefficients using FT-PGSE experiments. Figure 1a, b shows the NMR spectra and the echo attenuation behavior at room temperature as a function of different gradient durations ($\delta$). The micellar and water diffusion coefficients were $D_m = 2.8 \times 10^{-7}$ and $D_w = 1.7 \times 10^{-5}$ cm$^2$/s, respectively, obtained by fitting the echo amplitude in accordance with equation (1).

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**Fig. 1.** — a) A proton FT-PGSE experiment in a CTABr/D$_2$O solution performed at 300 MHz using $\Delta = \tau = 400$ ms, $g = 1.41$ G/cm; b) the logarithm of the normalized echo amplitudes vs. the experimental parameter $K$ in sample c at room temperature.
Considering the preliminary results we decided to carry out two different types of self-diffusion experiments in the time domain. A first set of PGSE experiments is carried out with fixed values of \( r, g \) and \( \Delta \) (20 ms, 63.5 G/cm and 20 ms, respectively), while \( \delta \) is varied in the range 0.2-2 ms and the repetition time of sequences is 7 s. In such a situation, while the term \( KD_w \) is close to one, the exponential factor \( \exp(-KD_m) \) varies in the interval 1.05-0.99 corresponding to a variation of about 1% of the second term in equation (2), less than the experimental accuracy. Neglecting this small variation, it is possible to analyze these experiments by the expression

\[
A(2\tau, g) = A^0(2\tau) \exp(-KD_w) + C \tag{3}
\]

where \( C \) is a constant term.

In a second set of PGSE experiments, monitored with other fixed values of \( r, g \) and \( \Delta \) (40 ms, 110.2 G/cm and 40 ms, respectively), \( \delta \) is varied in the range 0.75-4 ms, and the repetition time of sequences is 2 s. The exponential term \( \exp(-KD_m) \) is very close to zero, while \( KD_m \) is always close to one. Equation (2) can then be reduced to:

\[
A(2\tau, g) = B^0(2\tau) \exp(-KD_m) \tag{4}
\]

with a trend very similar to equation (1).

Using the methods described by equations (3) and (4) it is possible to obtain separately self-diffusion coefficients for surfactant and water protons. This procedure can be applied to similar binary micellar solutions when the respective diffusion coefficients differ by at least one order of magnitude.

**WATER SELF-DIFFUSION.** — In figure 2a, b is reported the echo amplitude of a PGSE experiment made with the first set of parameters for the mixture c at two different temperatures; the data are both fitted by equation (1) and equation (3) using non-linear least-square programs. In all mixtures the spin-echo data are well fitted by equation (3), confirming
Fig. 2. — The plots show the normalized echo amplitudes vs. the experimental parameter $K$ in a PGSE experiment in sample c with $g = 63.5$ G/cm. $A = \tau = 20$ ms. The solid line indicates the best fits to equation (3). a) at 35 °C $D_v = 2.69 \times 10^{-5}$ cm$^2$/s. b) at 55 °C $D_v = 3.23 \times 10^{-5}$ cm$^2$/s.
that this numerical procedure can be utilized to obtain selectively and directly the water self-diffusion. Water self-diffusion trends, as an Arrhenius plot, are reported in figure 3a, b for two different mixtures. The self-diffusion coefficients obtained by equation (3) are physically correct and with slopes similar to pure water, while the coefficients calculated by equation (1) decrease inexplicably when the temperature increases. A similar improper behavior can be observed in the study of Blinc et al. [12] on the water self-diffusion for the water/potassium palmitate system when the liquid crystalline phase changes in the micellar solution.

The water self-diffusion in a surfactant solution system is influenced by micelle hydration and by obstruction effect due to the micelle. It has been demonstrated that the latter effect can be structurally interpreted and it is then possible to deduce the structural configuration or structural defectiveness. In accordance with the above considerations the measured water self-diffusion coefficient, $D_w$, can be interpreted using the following equation (13, 1)

$$D_w = f(1 - P_b)D_0 + P_b D_b$$

where $P_b$ is the fraction of bound water, $D_b$ and $D_0$ are the bounded and free water self-diffusion coefficients, respectively.

Physically the obstruction factor $f$ accounts for the constraints to water self-diffusion due to micellar aggregates and therefore its value ranges between zero (no diffusion) and 1 (free water diffusion). Singular considerations supported by experimental results have permitted us to obtain the obstruction factor for different lyotropic mesophases. As demonstrated in reference [14], the obstruction factor can be obtained by applying equation (5) to two mixtures $i$ and $j$ of the same solution having a different composition, with the same structure. The following relation holds

$$f = \frac{D_{w,i} - K_{ij} D_{w,j}}{(1 - K_{ij}) D_0}$$

where $K_{ij}$ is the ratio $P_{b,i}/P_{b,j}$ between the fraction of bound water in the sample $i$ and $j$, respectively. Under reasonable hypotheses, as in reference [14], the term $K_{ij}$ can be obtained from the water weight fraction for the mixture $i$ and $j$

$$K_{ij} = \frac{W_j(100 - W_i)}{W_i(100 - W_j)}$$

The composition dependence of the obstruction factors for the present system are shown in figure 4. Each value has been obtained by combining the experimental data by two different mixtures, almost similar in composition. In a temperature range of 30-55 °C, we did not observe any particular effect on the composition behavior of the obstruction factor. This indication is supported by the observation that the water self-diffusion as a function of the temperature shows an Arrhenius plot. Within the experimental errors, the translational activation energy found is very close to the value of the pure water.

Figure 4 clearly shows that the obstruction factor remains constant in mixtures with 5-20 wt% surfactant. This interval can be considered to be the region in which the micellar shape is approximately globular with little dependence on the composition. A considerable decrease in obstruction factor can be observed at concentrations higher than 20 wt%. Here the micellar aggregate probably changes from globular to rod-like shape. In addition it can be observed that near the liquid crystal boundaries the micellar aggregates progressively increase in size as supported by the continuous change of the obstruction factor which influence the hexagonal liquid crystal phase limit becomes close to 0.77 (Fig. 4). This value is the same as that found in the
Fig. 3. — The plots a) and b) show the logarithm of the water self-diffusion vs. the inverse absolute temperature for the sample c and d, respectively. The symbols (■) and (○) refer to self-diffusion coefficients obtained by the fits to equation (1) and equation (3) respectively. The solid lines indicate the pure water self-diffusion trend.
hexagonal liquid crystal phase of the system water/potassium palmitate by means of water self-diffusion data [14].

The results analyzed above are in satisfactory agreement with the studies by Ekwahl et al. [15] where the viscosity measurements were used to calculate the activation energy for viscous flow. The increase in viscosity and activation energy in CTABr solution above 15 wt% were ascribed to hydration of the micelles and to resulting deformation to more or less rod-shaped micelles. Above this concentration an exceptionally rapid increase in viscosity and activation energy for viscous flow was observed suggesting a fairly rapid increase in the size of rod-shaped micelles.

**Micellar Self-Diffusion.** — In figure 5 are reported the echo amplitude of PGSE experiments using the second set of parameters for the mixture c at two different temperatures. Both sets of data are satisfactorily fitted by equation (4), which gives the micellar self-diffusion, $D_m$.

Assuming that the bound water molecules have the same mobility as the surfactant ($D_b = D_m$), it is possible to obtain $P_b$ by means of equation (5). From $P_b$, the average hydration number ($n$) of bound water molecules per surfactant molecules can easily be calculated by [1]:

$$n = P_b \frac{C_{\text{water}}}{C_{\text{surf}}}$$

(8)

where $C_{\text{water}}$ and $C_{\text{surf}}$ are the water and surfactant molar concentration in the system, respectively. The $n$-values found in different micellar mixtures was equal to 9 +/- 3 and no clear trend was observed as a function of composition because of too large an uncertainty.
Fig. 5. — The plot shows the normalized echo amplitude vs. the experimental parameter $K$ in a PGSE experiment in sample c with $g = 110.2$ G/cm $\Delta = \tau = 40$ ms. The dashed lines indicate the best fits to equation (4). The symbols (▲) and (■) refer to measurements obtained at 35 °C ($D_m = 2.89 \times 10^{-7}$ cm$^2$/s) and 55 °C ($D_m = 6.54 \times 10^{-7}$ cm$^2$/s), respectively.

**Micellar relaxation times.** — Proton micellar relaxation times, $T_{2m}$ and $T_{1m}$, can be obtained by performing a PGSE experiment in the condition where equation (4) holds.

The experiment was performed keeping constant $\delta$ and $g$, but varying the rf pulses distance ($\tau$) or the sequence repetition time ($t_r$); within these conditions the term $B^0$, in equation (4), changes in accordance to the relation

$$B^0(2\tau) \approx \left[ 1 - \exp\left(-\frac{t_r}{T_{1m}}\right) \right] \exp\left(-\frac{2\tau}{T_{2m}}\right)$$

from which it is possible to calculate the $T_{2m}$ or $T_{1m}$ using an appropriate non-linear fit. The values of $T_{2m}$ obtained were 62 ms and 120 ms at 40 °C and 50 °C, respectively, for the mixture c. The data are in accordance with that measured in a deuterated water micellar solution obtained using the Carr-Purcell spin-echo experiment.

Concentration dependence of the longitudinal relaxation times are shown in figure 6 at a temperature of 50 °C. The micellar solution at the hexagonal liquid crystal transition is sketched by a strong increase of the $T_{1m}$'s values. In the solution region the relaxation times are constant at low concentrations while they begin to increase in mixtures above 20 wt%. This result agrees with the obstruction factor behavior obtained in the above water self-diffusion section and supports the idea of a change of the micellar shape from spherical to cylindrical.

**Conclusions.**

PGSE experiments in the time domain were performed to measure the mobility of two different components in the micellar solution of the system CTABr/water. Micellar relaxation times, both transverse and longitudinal, have been measured accurately.
Fig. 6. — Variation of the longitudinal relaxation time $T_{1m}$ with the surfactant concentration. The frequency is 16 MHz and the temperature 50 °C.

Equations (3), (4) allowed the separation of water and surfactant self-diffusion contributions in the solution, under the condition that these differ by at least one order of magnitude. The method used here is very close to a biexponential analysis that is applied to a set of echo amplitudes collected in a wide range of the experimental parameter $K$. Both mathematical treatments present similar applicability limits [16], but the proposed methodology is more efficient because each measurement set is aimed at a single self-diffusion coefficient.

Transverse and longitudinal relaxation micellar times have been carried out using equation (9) varying the rf pulses distances and the sequence repetition time, respectively.

Water self-diffusion measurements have been used to calculate the obstruction factor as a function of the surfactant composition. The calculation of hydration number has been performed in different mixtures by the surfactant self-diffusion. The obstruction factor and the longitudinal relaxation time provided evidence of the change of the micellar shape, in agreement with the viscosity results obtained by Ekwall et al. [15].

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