# Hydration-dependent internal dynamics of reverse micelles: A quasielastic neutron scattering study

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We studied the overall atomic mobility of sodium bis-(2-ethylhexyl) sulfosuccinate (AOT) reverse micelles in deuterated cyclohexane ($C_6D_{12}$) as a function of the molar ratio $W=[D_2O]/[AOT]$ with an incoherent quasielastic neutron scattering experiment at high energy resolution. For the almost anhydrous sample, the quasielastic broadening can be entirely attributed to the reverse micelle global motion, by considering explicitly both the rotational and the translational terms. As $W$ increases above a threshold value $W\sim 1$ a wide quasielastic signal appears, which has been interpreted as the onset of a hydration-dependent intrinsic micelle dynamics. Such a contribution, which involves the AOT monomer hydrogen atoms, has a characteristic time of 0.2 ns. This result has been compared with previous dielectric measurements, which detected a relaxation process of the AOT fully hydrated head groups with the same characteristic time. The internal macromolecule mobility evaluated as a function of $W$ numerically correlates with that of the mobile head groups, calculated by dielectric measurements. These findings suggest that both the hydrophobic and hydrophilic moieties dynamics is activated by the progressive hydration of the reverse micelle.

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## I. INTRODUCTION

The possibility of confining water in a controllable way into reverse micelles is a useful tool to study the structural and dynamical properties of hydration water close to hydrophilic or ionic groups. Among the surfactants capable of forming reverse micelles, one of the most studied is the well known AOT or sodium bis-(2-ethylhexyl) sulfosuccinate which forms stable reverse micelles, even with high water content, in a large variety of solvents [1–3]. In the last years we performed a systematic IR and dielectric study [4–8] of AOT-based reverse micelles as a function of their hydration degree $W$, by varying the apolar solvent, the counterion of the surfactant molecule, and by filling the micelle with $D_2O$. The IR spectra of the hydrated micelles were interpreted in terms of an equilibrium between ''bulklike'' water and ''hydration'' or ''bound'' water, assuming the formation of an hydration shell around each surfactant head group made, on the average, by three water molecules. On the other hand, the dielectric spectra of AOT micelles as a function of $W$ in the mesoscopic region of frequency (from tens of MHz up to few GHz) [5–7] showed a relaxation process reflecting complex intrinsic dynamics of the micelle. This process appears to be strongly dependent on the hydration degree and, in absence of interaction, it was interpreted in terms of two coexisting diffusion mechanisms: the reorientation of the micelle in the solvent, described by the Debye-Stokes law, and the reorientation of the completely hydrated AOT head groups [5–7]. The last relaxation mechanism, on the subnanosecond time scale, becomes predominant at hydration degree above a certain threshold $W\sim 1$. The net effect of hydration can be rationalized as a fine balancing of repulsive and attractive electrostatic interactions between surfactant charged groups, with a consequent enhancing of their individual mobilities. Recently, an incoherent elastic neutron scattering experiment was devoted to study the overall mobility of $AOT/D_2O/CCl_4$ reverse micelles as a function of hydration [9]. In this experiment what is detected is the strong incoherent scattering cross section of hydrogen atoms belonging to the aggregate. The hydrogen atoms are, in turn, uniformly and abundantly distributed through the surfactant chains, thus sampling all the relaxation features of the whole system. The collected data indicated that for small water content the average micelle local mobility, represented by the mean square displacements of hydrogen atoms $\langle u^2\rangle$, significantly increases as a function of hydration, again above a threshold $W\sim 1$, as first observed by dielectric measurements.

The overall picture emerging from dielectric and elastic neutron scattering data is that in the subnanosecond time scale not only the charged head groups but the whole surfactant dynamical behavior is affected by progressive hydration, in agreement with past nuclear magnetic resonance (NMR) investigations [10].

In this work we try to better elucidate the dynamical behavior of reverse micelles on the nanosecond time scale, by performing a high resolution incoherent quasielastic neutron scattering study on $AOT/D_2O$ reverse micelles in deuterated cyclohexane ($C_6D_{12}$), at low volume fractions $\phi$ of the dispersed phase ($AOT+D_2O$) and as a function of the hydration degree $W$. The measured spectra have been analyzed by considering explicitly the micelle translational and rotational diffusion. We provided a coherent description of the hydration-dependent dynamics of the aggregate in agreement with the results already obtained by dielectric and IR techniques on the same system.

## II. THEORETICAL BACKGROUND: QUASIELASTIC NEUTRON SCATTERING

In an inelastic neutron scattering experiment on an isotropic sample, the measured quantity, providing physical infor-

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mation about the studied system, is the dynamical structure factor $S(Q,\omega)$; here, $Q$ is the modulus of the momentum transfer and $\omega$ is the energy transfer, both in units of reduced Planck constant $\hbar$. We performed measurements of the dynamical structure factor on AOT micelle samples in $C_6D_{12}$ as a function of $W$. The measured signal is the superposition of coherent and incoherent contributions. In analyzing the spectra one should consider that the scattering intensity from the AOT reverse micelles is dominated by the strong incoherent cross section of hydrogen atoms uniformly distributed over the double-branched chain of AOT. It is well known that the neutron-hydrogen cross section (81.7 b) is mainly incoherent ($\sim$98%) and is more than one order of magnitude larger than the neutron cross sections of other atoms of AOT molecule (C, S, O, etc.). This disproportion holds, in particular, for the neutron-deuterium cross section (7.6 b). Therefore, the large majority of the detected signal is due to the hydrogen atoms of the AOT chains. To single out the intensity of the sole micelle we have removed the deuterated solvent contribution, which is prevalently coherent in nature, from the signal of the whole sample. To perform this subtraction the spectrum of a pure $C_6D_{12}$ sample was separately measured and successively subtracted from the total intensity of $AOT/D_2O/C_6D_{12}$ solution. Thus, the final scattering function for the $AOT/D_2O$ system was obtained by the following relation:

$$S_{mic}(Q,\omega)=S_{sample}(Q,\omega)-(1-\phi)S_{solvent}(Q,\omega), \quad (1)$$

where $\phi$ is the volume fraction of the dispersed phase ($AOT+D_2O$) in the solvent. Then, the term containing $\phi$ accounts for the excluded volume effects. In dealing with solutions of reverse micelles, one must consider explicitly the Brownian motion of the whole aggregate. In general, if we take into account the different global and internal motions contributing to the micelle dynamics, the relevant scattering law can be written in the form [11]

$$S_{mic}(Q,\omega)=S_{in}(Q,\omega)\otimes S_{trans}(Q,\omega)\otimes S_{rot}(Q,\omega)\otimes R(Q,\omega), \quad (2)$$

where $S_{in}(Q,\omega)$ accounts for any internal relaxation motion in the micelle, $S_{trans}(Q,\omega)$ and $S_{rot}(Q,\omega)$ describe, respectively, the translational and the rotational contributions, $R(Q,\omega)$ is the experimental resolution function. From Eq. (2) it is clear that, to extract some information on the micelle internal dynamics and its behavior as a function of the hydration degree, a deconvolution must be performed of the measured scattering function $S_{mic}(Q,\omega)$ from the contributions arising from global motions and the experimental resolution function. To represent the terms constituting Eq. (2), we have applied some approximations. As described in the Appendix, the rotational and translational global motions have been calculated accounting for the location of the scatterers, i.e., the hydrogen atoms, in the reverse micelle. As already found for a similar system [12], we have shown that the convolution of rotational and translational motions is properly described by a Fick-like law, i.e., through a Lorentzian function with half width at half maximum (HWHM) given by $\Gamma_{eff}$:

$$S_{trans}(Q,\omega)\otimes S_{rot}(Q,\omega)=L_{eff}(Q,\omega)=\frac{1}{\pi}\frac{\Gamma_{eff}}{\omega^2+\Gamma_{eff}^2}, \quad (3)$$

where $\Gamma_{eff}$ is an effective half width that describes on the average the motion of the micelle as a whole through the solvent. The main feature of the internal motions in a structured system is the confinement of the scatterers within a certain volume of space. Due to this confinement, the relative scattering law includes both an elastic and a quasielastic term, namely,

$$S_{in}(Q,\omega)=e^{-\langle u^2\rangle Q^2}\{A_0(Q)\,\delta(\omega)+[1-A_0(Q)]L_{in}(Q,\omega)\}, \quad (4)$$

where $\langle u^2\rangle$ is the mean square displacement of the average hydrogen atom. The first term $A_0(Q)\,\delta(\omega)$ represents the elastic response of the system, i.e., the contribution from motions slower than the longest observable time which is settled by the experimental energy resolution. The $Q$ dependence is provided by the elastic incoherent scattering factor $A_0(Q)$, which represents the space-Fourier transform of the scatterers distribution, taken at infinite time and averaged over all the possible initial positions. The second term, appearing in the spectra as a broadening of the elastic peak, accounts for the relaxational motions sampled by the hydrogen atoms. In particular, in the present simple representation the internal motions are described through a Lorentzian function $L_{in}(Q,\omega)$, whose linewidth provides an indication of the characteristic correlation time of the associated relaxation. This phenomenological approach will be completely justified in the ''Results and discussion'' section. From Eqs. (2)–(4) it results a simple expression for the measured intensity,

$$S_{mic}(Q,\omega)=e^{-\langle u^2\rangle Q^2}\{A_0(Q)L_{eff}(Q,\omega)+[1-A_0(Q)]\tilde{S}_{in}(Q,\omega)\}\otimes R(Q,\omega) \quad (5)$$

with

$$\tilde{S}_{in}(Q,\omega)=L_{in}(Q,\omega)\otimes L_{eff}(Q,\omega). \quad (6)$$

It should be remarked that the intensity $A_{in}$ of the quasielastic contribution $\tilde{S}_{in}(Q,\omega)$ is proportional to the number of scatterers that participate in internal motions. In addition, the $A_{in}$ value can grow up also if the amplitude of these motions increases. On these grounds, we can provide a quantitative measure of the macromolecule internal mobility represented by Eq. (6) through the ratio

$$r(W)=A_{in}/(A_{in}+A_{eff}), \quad (7)$$

where $A_{eff}$ is the intensity of $L_{eff}(Q,\omega)$.

## III. EXPERIMENTAL DETAILS

### A. Sample preparation

AOT 99% (Alfa product) purified by recrystallization from methanol and dried in vacuum, was stored in vacuum over $P_2O_5$. $C_6D_{12}$ and $D_2O$ were obtained from Aldrich and used without further purification. All samples were prepared starting from a stock solution, consisting of [AOT] $=0.22$ M in $C_6D_{12}$. In the following, with the addition of appropriate amounts of $D_2O$, eight different values of W were settled: 0.3 (stock solution), 1.4, 1.9, 2.4, 3.5, 5.8, 7.7, and 12.0.

### B. Neutron scattering measurements

To measure the quasielastic spectra of micelle samples in the $\mu$eV range, the backscattering spectrometer IN10 at the Institut Laue-Langevin (ILL) in Grenoble (France) was employed. An incoming neutron wavelength of 6.27 Å was used, achieving an elastic $Q$-range from 0.5 $Å^{-1}$ to 1.96 $Å^{-1}$, an exchanged energy range from $-12$ $\mu$eV to 12 $\mu$eV, and an elastic energy resolution with HWHM of about 0.5 $\mu$eV. The energy range and resolution allow observing motions with characteristic times between about 100 ps and few ns. The samples were placed in a cylindrical aluminum can, with internal spacing of 0.5 mm. All quasielastic spectra were measured at 300 K. The spectra of an empty can, pure $C_6D_{12}$, and vanadium standard were also measured to take into account sample environment scattering, pure solvent in empty can scattering, and different detector efficiencies, as well as to measure the resolution function. Standard ILL programs were then used to correct the collected data for incident flux, solvent and cell environment scattering, detector efficiency, and cell and sample absorption. Since the lowest measured transmission is of the order of 84%, no corrections for multiple scattering are considered. The scans were performed for at least 10 to 12 h for each sample.

## IV. RESULTS AND DISCUSSION

Figure 1 shows the experimental dynamical structure factor $S_{mic}(Q,\omega)$ of the AOT micelle in $C_6D_{12}$ at $W=12$ for $Q=0.5$ and 0.9 $Å^{-1}$; the instrumental resolution, as measured by the vanadium sample, is also reported in the figure for comparison. The measured intensity clearly shows a quasielastic broadening distinguishable from the resolution for both the $Q$ values. We have interpreted this signal in terms of the convolution between the global rototranslational motion and the internal motions of the micelle, as described in the ''Theoretical Background'' section. The intensity of the dynamical structure factor abruptly decreases and remarkably broadens on passing from $Q=0.5$ $Å^{-1}$ to $Q=0.9$ $Å^{-1}$, due to the global rototranslational motion.

Actually, as is shown in Fig. 2, the peak intensity of the calculated $L_{eff}(Q,\omega)$ diminishes for a factor of about 3 when the $Q$ value changes from 0.5 $Å^{-1}$ to 0.9 $Å^{-1}$, the same as the experimental spectra. This suggests that the estimated convolution between rotational and translational

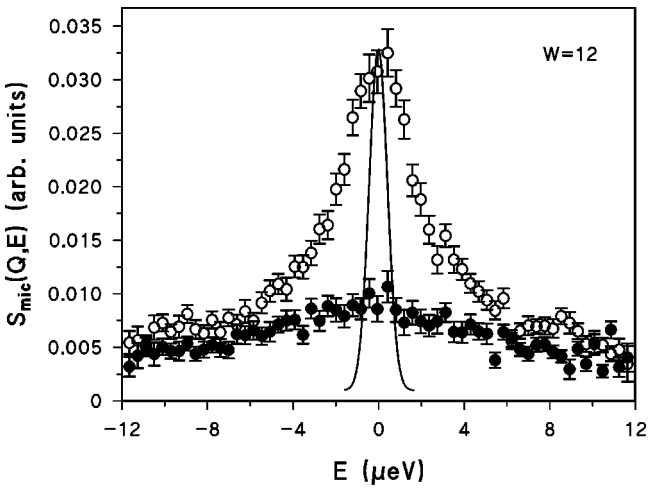


FIG. 1. Experimental dynamical structure factor $S_{mic}(Q,E)$ as a function of energy $E$. (○) $Q=0.5$ $Å^{-1}$, (●) $Q=0.9$ $Å^{-1}$, (—) instrumental resolution (vanadium sample).

terms can account quite well for such a decrease. Since the signal-to-noise ratio is very low at high $Q$ values for all the investigated hydration levels, the analysis of the experimental data was performed by considering only the spectrum at $Q=0.5$ $Å^{-1}$, which has a suitable statistics to be processed and interpreted via the model developed in the preceding section. In agreement with the scenario predicted by Eqs. (5) and (6), where two distinct bands $L_{eff}(Q,\omega)$ and $\tilde{S}_{in}(Q,\omega)$ represent the micelle global and global-convoluted internal motions, two terms having sensibly different widths are needed to properly fit the experimental dynamical structure factor, as shown in Fig. 3 for the sample at $W=12$. Therefore, we will use this phenomenological approach to attribute a physical meaning to the fit results. The narrow Lorentzian has a width of $3.5\pm0.3$ $\mu$eV, and it likely represents the Lorentzian $L_{eff}$ of the rototranslational micelle global motion, whose calculated width was found to be 3.4 $\mu$eV (for details see the Appendix). It should be noted that the width

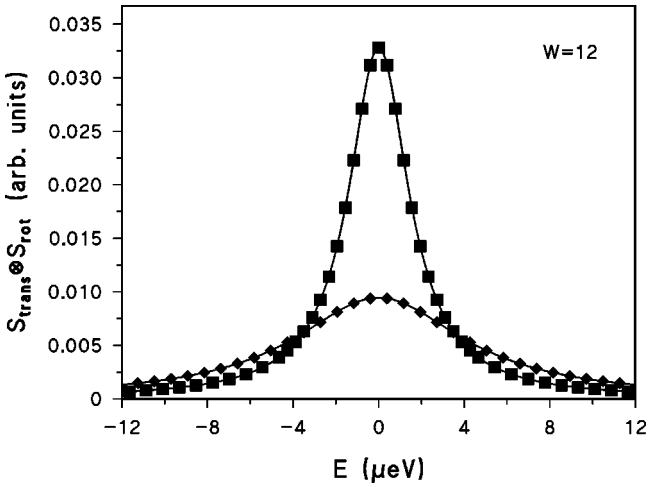


FIG. 2. Calculated convolution product $S_{trans}\otimes S_{rot}$. (■) $Q=0.5$ $Å^{-1}$, (◆) $Q=0.9$ $Å^{-1}$, (—) fit with a Lorentzian curve, $L_{eff}$ (see the text).

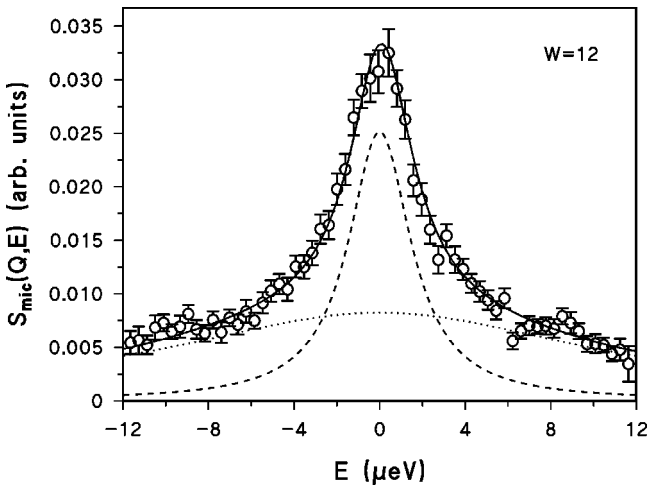


FIG. 3. (○) Experimental dynamical structure factor $S_{mic}(Q,E)$ as a function of the energy $E$ for the sample at $W=12$. (—) Fit of $S_{mic}(Q,E)$ with the sum of two curves. (- - -) $L_{eff}$, ( . . . ) $\tilde{S}_{in}$ (see the text).

of the purely translational Lorentzian function at this $W$ value results to be 2.7 $\mu$eV. This means that the effect of convoluting the rotational term with the translational one causes an extra broadening of the translational term of about 25%. This increment is quite important here and cannot be considered negligible, due to the very narrow energy resolution. On the other hand, the second band is a much wider spectral contribution, which can be identified with the term $\tilde{S}_{in}(Q,\omega)$ accounting for the convolution of global rototranslational and micelle internal motions. The deconvoluted Lorentzian function $L_{in}(Q,\omega)$, which is characterized by a width of $21\pm5$ $\mu$eV, indicates the presence of relaxation motions on the time scale of 0.2 ns, distinguishable from the slower rototranslation of the aggregate in the solvent. Quite strikingly, this characteristic time is practically the same as that of the relaxations of the completely hydrated AOT head groups evaluated through dielectric measurements [5,6]. This agreement, together with the coincidence of the narrow spectral component with the effective rototranslational contribution, supports the reliability of the model represented by Eq. (5). Then, the same data analysis has been performed for the other high hydration samples at $W=5.8$ and 7.7. The results are shown in detail in Table I, where the values $2\Gamma_{eff}$ have been reported as obtained from the fitting procedure (column 4) and from the numerical estimation (column 3). The numerical coincidence is evident, within the fitting errors, between the calculated and the fitted width of the $L_{eff}(Q,\omega)$ curve, together with the widening of the rototranslational Lorentzian for the 20–25 % with respect to the pure translational term (column 2). This result confirms the necessity of using both translational and rotational models to account for the global motions of reverse micelles. From Table I it should also be noted that $L_{in}(Q,\omega)$ shows the same width as the sample at $W=12$. On the other hand, a single Lorentzian curve with width $7.7\pm0.4$ $\mu$eV is able to fit the dynamical structure factor of the stock solution ($W=0.3$). Again, this contribution can be reasonably interpreted as the signal of

TABLE I. Effective widths of the Lorentzian curves accounting for the translational ($Q=0.5$ Å$^{-1}$) and the roto-translational contributions calculated theoretically (see Appendix and text) and extracted from the fitting procedure of the experimental spectra.

| $W$ | $2D_sQ^2$ ($\mu$eV) | $2\Gamma_{\text{eff}}$ (theor.) ($\mu$eV) | $2\Gamma_{\text{eff}}$ (fit) ($\mu$eV) | $2\Gamma_{\text{in}}$ (fit) ($\mu$eV) |
|---|---|---|---|---|
| 0.3 | 6.6 | 8.1 | $7.7\pm0.4$ | |
| 1.4 | 5.7 | 6.9 | 6.9 | $21\pm5$ |
| 1.9 | 5.4 | 6.5 | 6.5 | $21\pm5$ |
| 2.4 | 5.1 | 6.2 | 6.2 | $21\pm5$ |
| 3.5 | 4.6 | 5.6 | 5.6 | $21\pm5$ |
| 5.8 | 3.9 | 4.7 | $4.6\pm0.4$ | $21\pm5$ |
| 7.7 | 3.4 | 4.2 | $4.4\pm0.3$ | $21\pm5$ |
| 12.0 | 2.7 | 3.4 | $3.5\pm0.3$ | $21\pm5$ |

the micelle global motion whose width has been estimated to be 8.1 $\mu$eV. This result suggests that in extremely anhydrous conditions the internal relaxational motions do not take place, i.e., the appearance of fast diffusive motions is proper of largely hydrated reverse micelles. In the intermediate region $1.4\leqslant W\leqslant3.5$, the intensity of the second wide Lorentzian band, always necessary to well reproduce the experimental data, progressively rises. However, since in this hydration region such a signal is rather weak, we have fixed the $\Gamma_{eff}$ parameter to the numerically estimated values to keep stable the fitting procedure.

In Fig. 4 we show the ratio $r(W)$ introduced in Eq. (7) of the ''Theoretical Background'' section. As we already said, $r(W)$ gives a quantitative measure of the mobility of AOT hydrogen atoms that are involved in internal relaxational motions, beside the global roto-translation. Such term increases as a function of the hydration degree up to high $W$ values where it seems to attain an asymptotic behavior. In the same figure the fraction $X(W)$ of mobile, fully hydrated AOT head

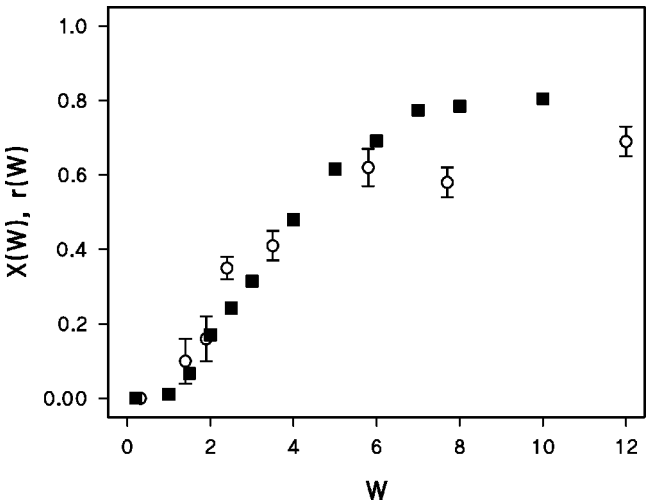


FIG. 4. (○) Plot of $r(W)=A_{in}/(A_{in}+A_{eff})$ calculated from the fit of $S_{mic}(Q,E)$. (■) Fraction $X(W)$ of mobile AOT head groups, calculated from dielectric measurements [5].

groups, calculated from high frequency dielectric measurements [5] is shown for comparison. It is clear that $r(W)$ and $X(W)$ show a quite similar trend as a function of the hydration degree. In fact, both quantities are negligible for $W=0$, with a marked rise above a threshold value located at $W\sim 1$. This result shows that both the motion of the AOT head group and the average motion of the hydrogen atoms belonging to its tails are strongly correlated. Within this picture, the progressive hydration of the surfactant causes at the same time the free reorientation of the head groups as well as an additional mobility of hydrogen atoms belonging to the AOT monomer. This additional mobility may be ascribed to the confined relaxation of the AOT chains and/or to the lateral diffusion of AOT monomers on the shell of the reverse micelle. With this respect, it is worth noting that previous quasielastic neutron scattering studies on AOT micelle in $C_6D_{12}$, performed with an energy resolution lower than our experiment, already revealed an additional broadening of the elastic line [13]. This contribution to the quasielastic signal, attributed to the lateral diffusion of AOT molecules along the curved micelle water/oil interface, was found to have a width of the order of 100–200 $\mu$eV, which is significantly broader than the width we revealed. Actually, the lateral free diffusion of AOT monomers as estimated in Ref. [13] could give rise to a quasielastic signal with a full width of 20–30 $\mu$eV at $Q=0.5$ Å$^{-1}$, well comparable to the width we measured for the $\tilde{S}_{in}(Q,\omega)$ component. The present data do not allow to single out the physical origin of the quasielastic component $\tilde{S}_{in}(Q,\omega)$. Despite the difficulties of a microscopical analysis of the micelle internal dynamics, they confirm and complete the experimental results already obtained on the same system with other experimental techniques (dielectric measurements, IR absorption measurements) [4–6]. The data are also in agreement with previous NMR investigations [10] on the same samples in the nanosecond time scale, which indicated a progressive flattening of the water/oil micelle interface and a consequent increased mobility of the surfactant chains as a function of the hydration degree. Our analysis of the intrinsic micelle motion provides the first direct experimental comparison between the motions of the hydrogen atoms belonging to the AOT chains, revealed by the neutron scattering, and the head group relaxation, accessible by means of high frequency dielectric spectroscopy. Finally, we remark that the increase of the internal dynamics above a threshold value of the hydration is a phenomenon observed also in other complex macromolecules, such as proteins where the subnanosecond thermal fluctuations give them the flexibility necessary to perform their biological activity [14–16]. We may speculate that in this kind of systems water performs its plasticizing action in a similar way.

## V. CONCLUSIONS

We performed neutron quasielastic scans at high energy resolution on AOT/$D_2O$/$C_6D_{12}$ reverse micelle as a function of the water content *W*. The analysis we carried out on quasielastic spectra puts in evidence in a coherent way the global rototranslational motion of the micelle in the solvent, well detectable owing to the high spectral resolution, and the presence of some internal micelle motion proper of the AOT monomer whose intensity increases as a function of the hydration degree *W*. The whole data are treated by considering explicitly both the rotational and the translational motion of the aggregate, showing that the presence of the rotational term is not negligible, since its convolution with the translational contribution can be treated as a single effective Lorentzian much wider than that of the sole translation. With increasing *W* the single Lorentzian of the global rototranslational dynamics cannot adequately fit the $S_{mic}(Q,\omega)$. The fast dynamics appearing with *W* is characterized by times of the order of 0.2 ns, the same as the reorientational time proper of the fully hydrated AOT head groups calculated from dielectric measurements. Furthermore, the internal mobility of the system numerically correlates with the fraction of AOT mobile head groups. Thus, we have observed a strong correlation between the hydrophobic and hydrophilic moieties dynamics that progressively increases with the reverse micelles hydration.

## ACKNOWLEDGMENTS

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## APPENDIX

As already done in Ref. [12] for globular proteins in aqueous solutions, we will schematize the motion of reverse micelle as a whole as the superposition of global translation and rotation. In fact, the system investigated here is morphologically very similar to a solution of proteins, since in both cases we are dealing with a dispersion of almost spherical, nanometer sized macromolecules. The incoherent scattering function of the translational contribution is described by the Fick's law, i.e., through a Lorentzian function with a half width at half maximum (HWHM) given by $D_sQ^2$, where $D_s$ is the self-diffusion coefficient:

$$S_{trans}(Q,\omega)=\frac{1}{\pi}\frac{\Gamma}{\omega^2+\Gamma^2} \tag{A1}$$

with $\Gamma=D_sQ^2$ and $D_s=K_BT/6\pi R\eta$. In the Einstein's formula of $D_s$ reported above, *R* is the hydrodynamic radius of the diffusing particle and $\eta$ is the solvent viscosity. The scattering function contains in this case the macroscopic parameter $D_s$, because all scatterers within the sphere translate at the same time in the same way. The diffusion coefficient of the almost anhydrous reverse micelle is of the order of $2.0\times10^{-10}$ m$^2$ s$^{-1}$ [13], which corresponds to a width of 6.6 $\mu$eV at $Q=0.5$ Å$^{-1}$. More in general, the values of the translational half width as a function of *W* range from 6.6 to about 2.7 $\mu$eV at $Q=0.5$ Å$^{-1}$. Since these values are rather larger than the instrumental resolution (width of about 1 $\mu$eV at $Q=0.5$ Å$^{-1}$), it is crucial to account for the translational contribution in the data analyzis even at the lowest *Q*. On the other hand, the rotational motion of the micelle, as

we verified experimentally with dielectric measurements on AOT micelles in various solvents [5], is characterized by a rotational $\tau$, calculated by the Stoke-Einstein formula, and a rotational diffusion coefficient $D_{rot}$ given by

$$\tau=\frac{4\pi\eta R^3}{K_B T}, \quad D_{rot}=\frac{3}{4}\frac{D_s}{R^2}. \tag{A2}$$

As has already been shown, the isotropic rotational diffusion of a scatterer moving at the surface of a sphere of radius $R$ is determined by the rotational diffusion coefficient $D_{rot}$ [12]. In this case the scattering unit is a hydrogen atom since, as shown in the ''Theoretical Background'' section, its incoherent cross section largely dominates the scattering function. The rotational contribution of this single scatterer is given by [11]

$$S_{rot,single}(Q,\omega)=\sum_{l=0}^{\infty} A_l(Q)\frac{1}{\pi}\frac{\tau_l}{1+\omega^2\tau_l^2} \tag{A3}$$

with

$$A_l(Q)=(2l+1)j_l^2(QR), \quad \tau_l=\frac{1}{l(l+1)D_{rot}}. \tag{A4}$$

In the preceding equation, $j_l$ is the spherical Bessel function of the order $l$. At a fixed value of $Q$, the rotational contribution $S_{rot,single}(Q,\omega)$ of Eq. (A3) is an infinite sum of normalized Lorentzian curves with increasing width, each weighted by a factor $A_l(Q)$, whose half width is given by

$$\Gamma_{rot}=\frac{1}{\tau_l}=l(l+1)D_{rot}. \tag{A5}$$

Note that $\tau_l$ in the Eq. (A5) depends only on $D_{rot}$, and $A_l(Q)$ depends only on the radius of rotation. In the reverse micelle, the hydrogen atoms of the surfactant chains, responsible for the incoherent scattering, are distributed over a spherical crown whose internal radius is $R_w$, the radius of the aqueous core, and the external radius is given by $R_w+R_p$, where $R_p$ is the length of the AOT hydrocarbon chains. Thus, we calculated the total $S_{rot}(Q,\omega)$, by considering that each infinitesimal volume occupied by hydrogen atoms at a distance $r$ from the center of the micelle produces a scattering function given by Eq. (A3), where $R$ has to be replaced by $r$. To obtain the total rotational scattering function, these contribution must be integrated over the spherical crown with radius $R_w$ and $R_w+R_p$,

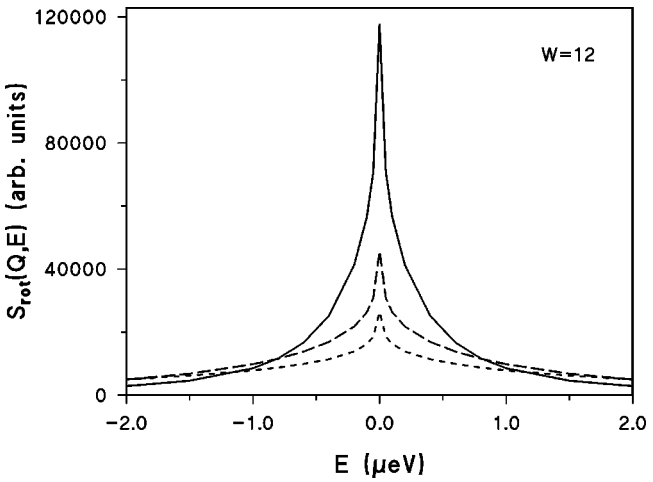


FIG. 5. Calculated rotational contribution $S_{rot}(Q,E)$ of the dynamical structure factor at $W=12$. (—) $Q=0.5$ Å$^{-1}$, (- - -) $Q=0.9$ Å$^{-1}$, $(\cdots)$ $Q=1.2$ Å$^{-1}$.

$$S_{rot}(Q,\omega)=\sum_{l=0}^{\infty} B_l(Q)\frac{1}{\pi}\frac{\tau_l}{1+\omega^2\tau_l^2}, \tag{A6}$$

with

$$B_l(Q)=\int_{R_w}^{R_w+R_p} A_{l,r}(Q)4\pi r^2 dr \tag{A7}$$

and

$$A_{l,r}(Q)=(2l+1)j_l^2(Qr). \tag{A8}$$

As an example, Fig. 5 shows the contribution $S_{rot}(Q,\omega)$ for the sample at $W=12$ and for the first three available values of $Q$, i.e., 0.5, 0.9, and 1.2 Å$^{-1}$. These curves are obtained by using Eqs. (A6)–(A8). The integration limiting values $R_w$ and $R_w+R_p$ are calculated considering a linear dependence of the aqueous core radius $R_w$ on $W$, and $R_p$ as the AOT length [17,18]. When convoluted with the translational Lorentzian contribution (see Fig. 2 in the ''Results and Discussion'' section) $S_{rot}(Q,\omega)$ gives rise for all investigated samples to a single effective Lorentzian whose width is consistently larger than that of the sole translational contribution (see Table I). This agrees with the results obtained by Perez and co-workers [12] for aqueous solution of lysozyme.

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