



Full paper/Mémoire

Brownian dynamics of water confined in AOT reverse micelles: A field-cycling deuteron NMR relaxometry study

Ghazi Kassab^{a,*}, Dominique Petit^b, Jean-Pierre Korb^b, Tahar Tajouri^a, Pierre Levitz^{b,*}

^a Unité de recherche 01UR13-04, université de Tunis, Tunis, Tunisia

^b UMR 7643, laboratoire de physique de la matière condensée, CNRS-école polytechnique, 91128 Palaiseau, France

ARTICLE INFO

Article history:

Received 4 May 2009

Accepted after revision 7 September 2009

Available online 2 December 2009

Keywords:

Reverse micelles

AOT

Nuclear magnetic relaxation dispersion

Intermittent Brownian motion

Mots clés :

Micelles inverses

AOT

Dispersion RMN

Mouvement brownien intermittent

ABSTRACT

Reversed micelles and water in oil micro-emulsions can be used to solubilize biopolymers and genetic materials allowing analyzing their properties in a confined geometry. Nuclear Magnetic Resonance Dispersion (NMRD) provides a powerful and a noninvasive experimental technique to probe the long-term dynamics of these confined systems. However, the first step is to analyze and understand the slow dynamics of water inside these micro-reactors without any guest molecule. This is the aim of this presentation. Experimental results have been obtained for deuteron ²H NMRD of water confined in reverse micelles of bis (2-ethylhexyl) sodium sulfosuccinate (AOT) dispersed in isooctane C₈H₁₈. The water content is expressed as the molar ratio $W_0 = [\text{Water}]/[\text{AOT}]$. The radius of the spherical reversed micelles, R_m , increases almost linearly with W_0 . In our case, W_0 is chosen in the range $20 \leq W_0 \leq 50$ ($35 \leq R_m \leq 80 \text{ \AA}$). The frequency dependence for the spin-lattice relaxation rate $R_1(\omega)$ exhibits two regimes, for all W_0 values: a plateau at low frequency, proportional to $1/R_m$, followed by the beginning of an algebraic decay. These experimental observations are discussed and compared to a numerical simulation of the intermittent Brownian diffusion of a water molecule inside a rotating reverse micelle. The possibility to probe some properties of the confinement, such as the localisation time on the sulfonated palisade and/or the water self-diffusion inside the water pool is emphasised.

© 2009 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

R É S U M É

Les micelles inverses sont des nano-gouttelettes d'eau thermodynamiquement stables qui peuvent être utilisées pour solubiliser des systèmes biologiques et d'étudier leurs propriétés physicochimique en confinement. La dispersion RMN est une technique non invasive, permettant l'étude de la dynamique lente de ces systèmes confinés. Cependant, dans un premier temps nous cherchons à comprendre la dynamique lente de l'eau confinée dans ces micelles inverses. Nous présentons les variations avec le champ magnétique des vitesses de relaxation spin-réseau R_1 des deutérons de l'eau confinée dans des micelles inverses formées par le mélange d'un tensioactif bis (2-éthylhexyl) sodium sulfosuccinate (AOT), de l'isooctane et de l'eau. La quantité d'eau solubilisée est exprimée par le rapport des concentrations molaires $W_0 = [\text{Water}]/[\text{AOT}]$. Le rayon aqueux R_m de ces micelles sphériques varie linéairement avec W_0 . Dans notre cas, W_0 est compris entre 20 et 50 ($35 \leq R_m \leq 80 \text{ \AA}$). Les profils de dispersion RMN $R_1(\omega)$ passent par deux régimes pour toutes les valeurs de W_0 : un plateau à basse fréquence, proportionnel

* Corresponding authors.

E-mail addresses: kassabi2001@yahoo.fr (G. Kassab), pierre.levitz@polytechnique.edu (P. Levitz).

à $1/R_m$, suivi du début d'une décroissance en loi de puissance. Une simulation numérique de dynamique brownienne de molécules d'eau confinées dans des micelles inverses sphériques en rotation dans l'isooctane est proposée et comparée aux résultats expérimentaux. Cette simulation offre la possibilité d'étudier l'effet de confinement sur la diffusion interne de l'eau et/ou sur le temps de localisation des molécules d'eau sur la palissade sulfonotée.

© 2009 Académie des sciences. Publié par Elsevier Masson SAS. Tous droits réservés.

1. Introduction

Water in oil micro-emulsions are thermodynamically stable systems which, under certain conditions, consist of discrete aqueous droplets dispersed in a continuous oil medium. One of the most well characterized droplet-type micro-emulsions is the one that formed in the ternary system sodium bis(2-ethylhexyl) sulfosuccinate AOT/water/oil. These systems have been studied by a great number of physicochemical methods [1,2]. It is now well established that AOT reverse micelle in isooctane consists of an approximately spherical water core surrounded by closed AOT palisade. An important and potential property of AOT reverse micelles is to confine various amounts of solubilized water. There is an apparent linear relationship between the molar ratio $W_0 = [\text{H}_2\text{O}]/[\text{AOT}]$ and the radius R_m of the water core. Reverse micelles and water in oil micro-emulsions can be used in order to solubilize biopolymers such as proteins, enzymes and genetic material in apolar solvents and to study their physicochemical properties in the presence of a limited amount of water [3]. The guest molecules are either dissolved in the water core or oriented to the AOT-water interface. They may acquire properties and reactivities that are different from those measured in the bulk aqueous phase.

It is known that by using a variety of physical techniques, the part of the water present in the water core of reverse micelles is bound to the AOT polar group as well as to the sodium counter-ions. Spectroscopic techniques, such as NMR, IR and Raman spectroscopies [4–8], have shown that the physicochemical properties of AOT reverse micelles change at low water content up to a molar ratio $W_0 = 10$. In this regime, water is structured by its interaction with Na^+ counter-ions and the strong dipole of the polar AOT. Above this threshold, the properties of the solubilized water approach progressively those of the bulk water. The water dynamics in reverse [9] or direct micelles [10] was investigated using molecular dynamics simulations. These works point out the existence of a slow orientational water dynamics near the surfactant interface. Similar trends, related to the water residence time, were found in various NMR studies of water molecules bonded to biological molecules such as DNA [11,12] or proteins [13,14].

Only few experimental tools are actually able to probe, on a very large extent, the liquid dynamics in confinement. A promising way is to measure the Nuclear Magnetic Resonance Dispersion (NMRD) of the proton or deuteron spin-lattice relaxation rate (R_1) on a large range of Larmor frequency [15]. The dynamical information is thus drawn

out from these NMRD data according to a dynamical model. Several basic models and experiments have been proposed either for reorientational [16–18] and/or translational [19] molecular diffusion in interfacial confined media.

In an earlier work [20], we have studied the water dynamics in AOT reverse micelles for a single value of W_0 ($W_0 = 50$). An experimental NMRD study was conducted for the proton and/or the deuterium belonging either to the water, the surfactant or the isooctane molecule. A preliminary simulation of the NMRD dispersion curve was presented taking into account the intermittent Brownian dynamics of water inside reverse micelle [17,18]. At this stage, the Brownian rotational diffusion of the entire reverse micelle immersed in isooctane was not considered. This simulation was found to be qualitatively in agreement with the experiments but no serious attempt to fit the experimental data was conducted.

In the present work, ^2H NMRD measurements are obtained by varying W_0 in the range $20 \leq W_0 \leq 50$. In parallel to the experimental investigation, we present a numerical simulation of the intermittent Brownian [16,17,19] dynamics of the water molecule inside a rotating reverse micelle, taking into account the internal intermittent Brownian motion of the water molecule and the overall Brownian motion of the reverse micelle. These simulations allow the computation of the NMRD dispersion curves, which are compared to the experimental data.

2. Experimental set-up

Sodium bis (2-ethylhexyl) sulfosuccinate, *i.e.* AOT of 99% purity and trimethyl-2,2,4 pentane (isooctane C_8H_{18}) have been purchased from Sigma Aldrich. Both compounds have been used without further purification. H_2O water has been double distilled and de-ionized (resistivity of 18 $\text{M}\Omega$) and was used at $\text{pH} = 6$. D_2O water (99.9%) has been provided by CEA (Saclay). The appropriate amounts of D_2O have been injected into AOT solutions in isooctane by means of a Hamilton syringe. The amount of water incorporated into AOT reverse micelles corresponds to $W_0 = 20, 30, 40$ and 50 with a micelle volume fraction ranging from 0.08 to 0.12. Table 1 gives the spherical reverse micelles radius R_m versus W_0 [1,2]. The hydrodynamics radius R_h was measured by Dynamics Light Spectroscopy (DLS) using a nano sizer Malvern. R_h values are in good agreement with the data published by Zulauf and Eicke [1]. NMRD measurements have been performed, at a stabilized temperature of 298 K, on a fast-field-cycling spectrometer from Stelar Company.

Table 1
Variation of the spherical reverse micelles R_m versus the molar ratio W_0 [1–2].

W_0	R_m (nm)
20	3.5
30	5.1
40	6.5
50	7.9

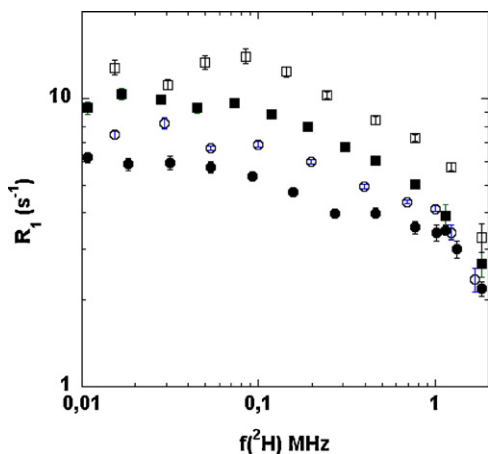


Fig. 1. ^2H water spin-lattice relaxation rates recorded as a function of the magnetic-field strength plotted as the Larmor frequency for water confined in spherical reverse micelles (AOT/ $\text{C}_8\text{H}_{18}/\text{D}_2\text{O}$) of molar ratio $W_0 = 20$ (open squares), 30 (full squares), 40 (open circles) and 50 (close circles) at $T = 298\text{ K}$.

3. Experimental results

Four deuteron NMRD profiles have been performed for (AOT/ $\text{C}_8\text{H}_{18}/\text{D}_2\text{O}$) reverse micelles ($W_0 = 20, 30, 40$ and 50). In these experiments, the longitudinal magnetizations exhibit a mono-exponential decay in all the Larmor frequency range studied (10 kHz–3 MHz). All profiles present a similar behavior for dispersion curves $R_1(\omega)$: a plateau up to a cut-off frequency followed the beginning of an algebraic decay (Fig. 1). The cut-off frequency and the spin-lattice relaxation rate of the plateau $R_{1,\text{plateau}}$ decrease as W_0 increases. As shown in Fig. 2, the spin-lattice relaxation rate of the plateau $R_{1,\text{plateau}}$ is inversely proportional to the micelle radius R_m (or to the molar ratio W_0). This result is due to the rapid exchange between bound water in interaction with the sulfonated polar surface and water in the internal micellar pool. Interesting enough, the interpolation to infinite radius R_m gives a relaxation rate very close to the spin-lattice relaxation rate of bulk water R_1 (0.33 s^{-1}).

4. Discussion and numerical simulations

One of the main interests to look at deuteron NMRD is the knowledge of the magnetic interaction inducing the relaxation, mainly the quadrupolar interaction [21]. In the Larmor frequency range studied (10 kHz–3 MHz for deuteron), the spin-lattice relaxation rate is mainly due to two mechanisms: (i) the reorientation modulation

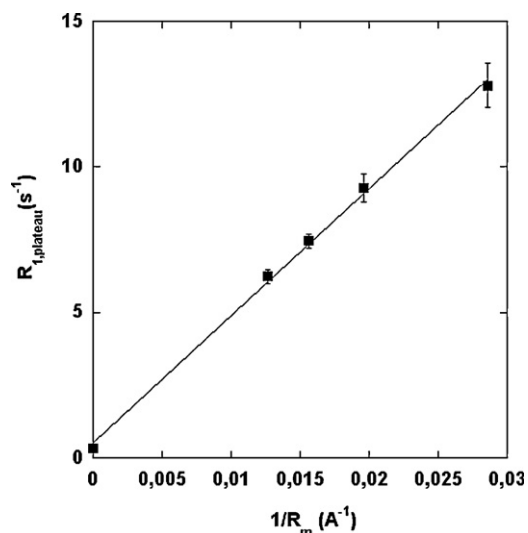


Fig. 2. Variation of the spin-lattice relaxation rate of the plateau $R_{1,\text{plateau}}$ versus the reverse micelle radius ($1/R_m$). The linearity between $R_{1,\text{plateau}}$ and ($1/R_m$) proves the rapid exchange between water in interaction with the sulfonated polar surface and water molecule inside the micellar pool.

coupled with translational diffusion of a quadrupolar interaction for ^2H [16]; and (ii) the Brownian rotational diffusion of the entire reverse micelle in isoctane [7]. Concerning the first mechanism, as shown elsewhere [17,18], a two-step model can be considered to describe the magnetic relaxation of the aqueous fluid nearby the interface. This model involves the superposition of fast motions (local rotations. . .) and slow dynamics depending on the time correlation of the spherical surface director probed by the molecule during its self-diffusion near the interface. We consider that fast and slow motions, in this two-step model, occur on different time-scales and are statistically independent [22]. At low frequencies, the spin lattice relaxation rate can be decomposed into a fast and a slow contribution such as $R_1(\omega) = R_1^{\text{slow}}(\omega) + R_1^{\text{fast}}$. The fast contribution is related to local molecular dynamics and is almost constant at low frequency. For the slow contribution, the fluid trajectories are modelled as an alternate successions of adsorption steps (A) where the magnetic interaction $I(t)$ is acting and Brownian bridge (B) in the confined bulk media where $I(t) = 0$. The slow motion contribution can be written as:

$$R_1^{\text{slow}}(\omega) \propto J(\omega) + 4J(2\omega) \quad (1)$$

where $J(\omega)$ is the time Fourier transform of the correlation function $G(\tau) = \langle I(0)I(\tau) \rangle$.

Following [17,18], for a flat surface in the strong adsorption limit, $J(\omega)$ can be written as:

$$J(\omega) \propto 1 / \left[(\omega/\omega_0)^{1/2} + (\omega/\omega_0) + 1/2(\omega/\omega_0)^{3/2} \right] \quad (2)$$

where ω_0 is a characteristic frequency evolving as:

$$\omega_0 = \frac{\delta^2}{2D\tau_A^2} \quad (3)$$

δ is about the size of a water molecule, D is the self-diffusion of the water molecule nearby the interface (during the Brownian bridge) and τ_A is the average residence time on the interface. At low frequencies ($\omega \ll \omega_0$), $J(\omega)$ evolves as $1/\sqrt{\omega}$. Around ω_0 , we have a $(1/\omega)$ regime. Finally, for ($\omega \gg \omega_0$), $J(\omega)$ is dominated by the term $(1/\omega)^{3/2}$. Such a regime should be observed in reverse micelle at relatively high frequencies where, in the corresponding time scale, the water molecule probes an intermittent interaction with the sulfonate heads on a locally flat internal surface. At a longer time-scale, a cut-off should appear, linked to the finite size of the reverse micelle and the appearance of an upper terminal time for the bridge statistics. In parallel, the Brownian rotation of the entire reverse micelle in iso-octane could impose its own orientation relaxation. A Lorentzian profile of $J(\omega)$ (or $R_I(\omega)$) corresponds to this mechanism.

At this point, there is no trivial and obvious separation between these sources of orientation fluctuations.

In order to classify these relaxation processes mentioned, a Brownian dynamics simulation is performed by taking into account the two mechanisms: the Brownian intermittent dynamics of water inside the reverse micelle core and the Brownian rotational diffusion of the entire reverse micelle. Using the measured hydrodynamic radius R_h of the reverse micelle, a rotation diffusion coefficient is estimated using the Perrin's relationship, allowing one to simulate the rotational Brownian motion of the reverse micelle. The $Y^{m_2}(\Omega(t))$ autocorrelation functions are computed in the laboratory framework. More numerical details can be found elsewhere [16].

In Fig. 3, we present our numerical results for the case $W_0 = 40$. The self-diffusion of water is taken as $D = 10^{-9} \text{ m}^2/\text{s}$. This value, of the same order that the bulk water diffusion, is in the same range that the molecular dynamics simulation

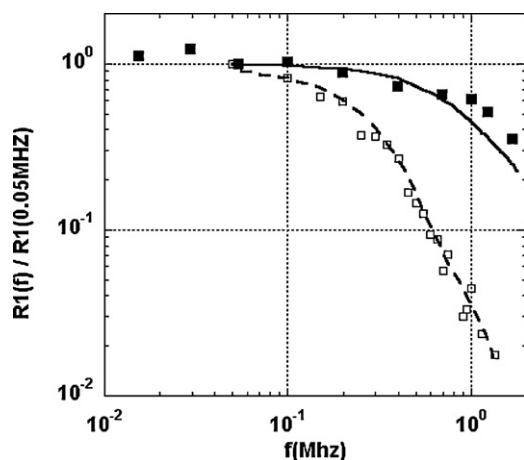


Fig. 3. Numerical simulations of the frequency dependence of normalised deuteron spin-lattice relaxation rate of water molecules (D_2O) inside a reverse micelle that presents a Brownian rotational diffusion in iso-octane. ($W_0 = 40$, $R_m = 6.4 \text{ nm}$, $R_h = 9 \text{ nm}$, $D = 10^{-9} \text{ m}^2/\text{s}$, iso-octane viscosity 0.5 cp).

Continuous line: simulation using an average adsorption time $\tau_A = 5 \text{ ns}$. Opened squares and dotted line: simulation using an average adsorption time $\tau_A = 1 \text{ ms}$. Full squares: re-normalised experimental data for $W = 40$.

proposed in [9]. An increase of D will shift the NMRD dispersion curve towards high frequencies. In a first computation, we have set the adsorption time of the water molecule to a very large value (1 ms). In such a situation, we suppress the intermittent Brownian motion. The only origin of the NMR dispersion is due to the rotation of the reverse micelle. As shown in Fig. 3, the dispersion curve exhibits a Lorentzian shape with a $1/\omega^2$ evolution in the experimental frequency window (0.01–2 MHz). This evolution is far off the experimental trend. In a second computation, we take $\tau_A = 5 \text{ ns}$, an order of magnitude also found in some other hydrophilic surfaces [16,17,23]. An extended plateau is observed at low frequencies followed by the beginning of a decay (which finally evolves as $1/\omega^{3/2}$ (in a range which was not experimentally probed in this present work)). This last part is related to the intermittent Brownian dynamics. Interesting enough, the renormalized experimental data exhibit a similar trend.

Our simulation shows that the rotation of the reverse micelle, almost for $W_0 = 40$, is not the main origin of the deuteron spin-lattice relaxation. The high frequency part of the NMRD dispersion curves reveals the internal dynamics of the water molecule inside reverse micelle.

In a next future, we plan to analyse the NMRD in an extended frequency range from 5 MHz to 50 MHz.

5. Conclusion

In this work we have reported deuteron field-cycling relaxometry for the microemulsion phase in the (AOT/iso-octane/ D_2O) system. This study has allowed us to analyse the slow dynamics of water confined in reverse micelles (of nanometric sizes) and the Brownian rotational diffusion of the spherical micro-emulsion droplet (water and AOT) in iso-octane. The typical relaxation features have been interpreted according to two processes: (i) the molecular reorientation of water molecules coupled with translation diffusion inside a spherical confinement; and (ii) the Brownian rotational diffusion of the entire reverse micelle in iso-octane. A numerical simulation, for $W_0 = 40$, is proposed to analyse the degree of coupling of these mechanisms. In a future work, we aim at extending our study to analyse the influence of the micellar size, the volume fraction and the temperature on the relaxation NMRD profiles in a more extended frequency range.

Acknowledgements

This research was supported by the grant CNRS/DGRSRT N 18518. Grants from ANR project DYOPTRI is also acknowledged.

References

- [1] M. Zulauf, H.F. Eicke, *J. Phys. Chem.* 83 (1979) 480.
- [2] H. Hauser, G. Haering, A. Pande, P.L. Luisi, *J. Phys. Chem.* 93 (1989) 7869.
- [3] Z. Zhi, R.W. Peterson, A.J. Wand, *Langmuir* 21 (2005) 10632.
- [4] A. Maitra, *J. Phys. Chem.* 88 (1984) 5122.
- [5] C. Chachaty, *Progr. NMR Spectrosc.* 19 (1987) 183.
- [6] G. Carlström, B. Halle, *J. Phys. Chem.* 93 (1989) 3287.
- [7] P.H. Kenez, G.C. Strom, I. Furo, B. Halle, *J. Phys. Chem.* 96 (1992) 9524.
- [8] H. MacDonald, B. Bedwell, E. Gulari, *Langmuir* 2 (1986) 704.
- [9] J. Faeder, B.M. Ladanyi, *J. Phys. Chem. B* 104 (2000) 1033.

- [10] S. Balasubramanian, B. Bagchi, *J. Phys. Chem B* 106 (2002) 3668.
- [11] O. Otting, *J. Progr. Nucl. Magn. Reson. Spectrosc* 31 (1997) 259.
- [12] M. Sunnerhagen, V.P. Denisov, K. Venu, A.M.J. Bonvin, J. Carey, B. Halle, *J. Mol. Bio.* 282 (1998) 847.
- [13] V.P. Denisov, K. Venu, J. Peters, H.D. Hörlein, B. Halle, *J. Phys. Chem. B* 101 (1997) 9380.
- [14] V.P. Denisov, J. Peters, H.D. Hörlein, B. Halle, *Biochemistry* 43 (2004) 12020.
- [15] S. Noack, *Progr. NMR Spectrosc* 18 (1986) 171.
- [16] S. Stapf, R. Kimmich, J. Niess, *J. App. Phys* 75 (1994) 529.
- [17] P.E. Levitz, *J. Phys. Condens. Matter* 17 (2005) 4059.
- [18] P. Levitz, M. Zinsmeister, P. Davidson, D. Constantin, O. Poncelet, *Phys. Rev. E* 78 (2008), 030102_R.
- [19] J.-P. Korb, M. Whaley, R.G. Bryant, *Phys. Rev. E* 56 (1997) 1934.
- [20] G. Kassab, D. Petit, J.-P. Korb, T. Tajouri, P.E. Levitz, *C. R. Acad. Sci. Chimie* 9 (2006) 493.
- [21] A. Abragam, *Principles of Nuclear Magnetism*, Oxford Univ. Press, London, 1961.
- [22] B. Halle, H. Wennerstrom, *J. Chem. Phys.* 75 (1981) 1928.
- [23] P.E. Levitz, J.-P. Korb, *EuroPhys. Lett* 70 (2005) 684.