Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

The Effect of Micellularization on Octylglucoside Spinlattice Relaxation

Thomas H. Fischer [a]
[a] The Center for Thrombosis and Hemostasis, The University of North Carolina at Chapel Hill, Chapel Hill, NC, 27514
Version of record first published: 28 Mar 2007.

To cite this article: Thomas H. Fischer (1983): The Effect of Micellularization on Octylglucoside Spinlattice Relaxation, Molecular Crystals and Liquid Crystals, 92:1, 7-13

To link to this article: http://dx.doi.org/10.1080/01406568308083781

Mol. Cryst. Liq. Cryst. Vol. 92 (Letters), pp. 7-13
0140-6566/83/9201-0007$18.50/0

Printed in the United States of America

THE EFFECT OF MICELLULARIZATION ON OCTYLGLUCOSIDE SPIN-LATTICE RELAXATION

(Received for Publication November 17, 1982)

THOMAS H. FISCHER
The Center for Thrombosis and Hemostasis, The University of North Carolina at Chapel Hill, Chapel Hill, NC 27514
Submitted for publication on November 15, 1982.

ABSTRACT: ^{13}C-spin-lattice relaxation measurements are used to examine the effect of the monomer-to-micelle transition on the molecular motion of octylglucoside molecules. The octylglucoside concentration dependence of the spin-lattice relaxation rate is used to determine spin-lattice relaxation rates for the detergent in the monomer and micelle states. Two observations are made. First, a motional gradient exists along the octylglucoside alkyl chain, which is approximately as pronounced in the micelle as in the monomer state. Second, motional restriction is observed for all examined carbon atoms upon passing from the monomer to the micelle state.

INTRODUCTION

Carbon-13 NMR is a useful tool for examining the physical state of detergent systems. This is largely because ^{13}C spin-lattice (T_1) relaxation is principally driven by ^{1}H-^{13}C dipole interactions with directly bonded protons.[1,2] Thus, spin-lattice relaxation rates ($1/T_1$) are sensitive indicators of segmental motions of the alkyl chains of detergents. Spin-lattice relaxation studies involving a variety of surfactants, including n-alkyl compounds containing sulfate,[3] carboxyl,[4,5] primary amine,[6] and quaternary amine[7] headgroups are reported. These studies generally show that, in the micelle state, segmental motion increases as a function of distance from the headgroup region. This is similar to the pattern observed with lecithins.[8] Several of the above-mentioned studies also examine the effect of the micelle-to-monomer transition on $^{13}C—T_1$ values.[4,5,7] Increases in overall molecular motion are observed as the amphiphile concentration is lowered below the critical micelle concentration (cmc).

To date, $^{13}C-T_1$ studies involving straight alkyl chain, nonionic detergents are not reported. The results of experiments involving the concentration dependence of octylglucoside $^{13}C-T_1$ values are presented in this communication. Two questions are addressed. First, in the micelle state, is a motional gradient observed which is similar to that of ionic amphiphiles? Second, what is the effect of the micelle-to-monomer transition on spin-lattice relaxation?

EXPERIMENTAL

Samples were prepared by dispersing the desired amount of octylglucoside (1-octyl-β-glycopyranoside, Calbiochem) in D_2O (Sigma, 99.996% D_2O). The D_2O was degassed with three freeze-thaw cycles before being used to prepare the detergent solutions. $^{13}C-T_1$ measurements were carried out on a Bruker HX-270 pulse Fourier transform spectrometer at 270 MHz. A $(180^0 - \tau - 90^0\text{-FID-5sec})_n$ IRFT pulse sequence was used. The value of n ranged from 20 at 150 mM octylglucoside to 500 at 20 mM octylglucoside. A Bruker variable temperature unit was used to regulate the probe temperature at 24 ± 1° C. Peak assignments were based on a comparison with the assignments for the compounds dioctyl ether and 1-methyl-α-glycopyranoside.

RESULTS

The principal finding of this study was that spin-lattice relaxation times (T_1) were larger at octylglucoside concentrations below the cmc than above the cmc. This effect was demonstrated in Figure 2 for the number three carbon of the alkyl chain (see Figure 1 for numbering scheme). Similar effects were observed for the other carbons in the alkyl chain and the headgroup regions of the octylglucoside molecule. Because of the direct proportionality between $1/T_1$ and the $^1H-^{13}C$ dipole-dipole reorientation correlation time constant, these results showed that molecular motion was less restricted in the monomer than the micelle state. Because the exchange rate of detergents between micelle and aqueous phases has generally been found to be fast on the NMR timescale,[9] the following equation was used to analyze data obtained at octylglucoside concentrations above the cmc.

$$\frac{1}{T_1} = \frac{[d]t - [d]cmc}{[d]t} \frac{1}{T_{1\text{-mic}}} + \frac{[d]cmc}{[d]t} \frac{1}{T_{1\text{-mon}}} \qquad \text{(Eq. 1)}$$

$1/T_1$ was the measured spin-lattice relaxation rate. $1/T_{1\text{-mic}}$

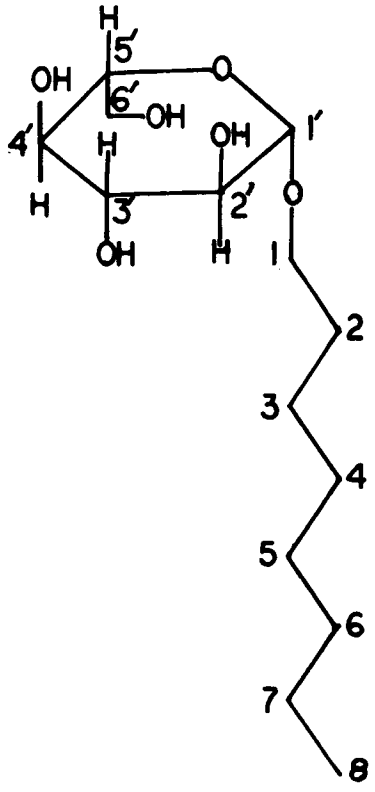

FIGURE 1 Structure and number scheme for 1-octyl-β-glycopyranoside

TABLE I Effect of the Monomer-to-Micelle Transition on Spin-Lattice Relaxation

Carbon Number	$\frac{1}{T_{1\text{-mon}}}$ (sec^{-1})	$\frac{1}{T_{1\text{-mic}}}$ (sec^{-1})	$\frac{T_{1\text{-mon}}}{T_{1\text{-mic}}}$
1	2.30 ± 0.23	6.47 ± 0.51	2.81
3	1.00 ± 0.10	2.55 ± 0.10	2.55
4	0.86 ± 0.15	2.30 ± 0.23	2.67
6	0.46 ± 0.07	1.27 ± 0.13	2.76
1′	1.20 ± 0.04	3.76 ± 0.03	3.13
3′	1.18 ± 0.04	3.76 ± 0.03	3.18
4′	1.54 ± 0.25	4.39 ± 0.08	2.85
5′	1.25 ± 0.15	3.41 ± 0.07	2.73
6′	1.05 ± 0.35	3.85 ± 0.12	3.67

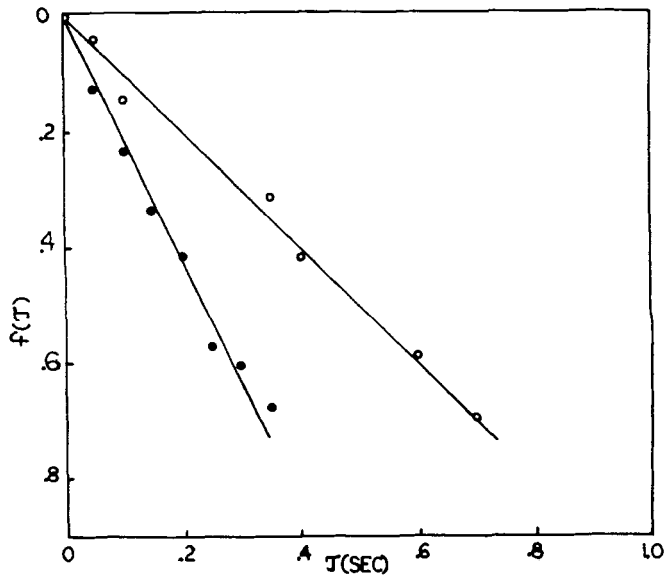

FIGURE 2 Spin-lattice relaxation curves of carbon-3 for samples containing 100 mM (●) and 20 mM (o) octyl-glucoside.

$$f(\tau) = \ln \frac{h_\infty - h(\tau)}{h_\infty - h_0}$$

where h_∞ is the peak height at long τ values, and h_0 is the peak height at $\tau = 0$.

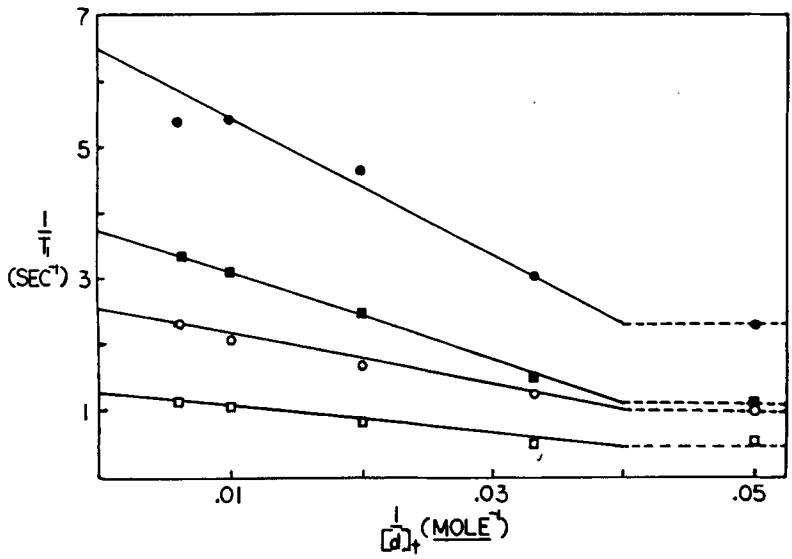

FIGURE 3 Octylglucoside concentration dependence of the spin-lattice relaxation rate ($1/T_1$) for carbon atoms 1 (●), 3 (o), 6 (□), and 3´ (■).

and $1/T_{1\text{-mon}}$ were respectively the relaxation rates in the micellular and monomer states. $[d]_t$ and $[d]_{cmc}$ were respectively the total detergent concentration and the cmc value, equal to 25 mM.[10] Plots of $1/T_1$ vs. $1/[d]_t$ were used to determine $1/T_{1\text{-mic}}$ and $1/T_{1\text{-mon}}$ values. Such plots of data from represent carbon atoms were shown in Figure 3. The results of this type of analysis of the data obtained from each examined carbon atom was presented in Table I. At least five data points were used in the determination of $1/T_{1\text{-mic}}$ and $1/T_{1\text{-mon}}$ values in Table I. The error represented uncertainty in fitting $1/T_1$ vs. $1/[d]_t$ data to a straight line at detergent concentrations above the cmc.

DISCUSSION

A basic finding of this experiment is that the micellularization process is accompanied by a restriction of molecular motion. Similar effects, based on $^{13}C—T_1$ measurements, are reported for the anionic detergents n-octanoate[4] and n-hexanoate,[5] and the cationic detergent n-octyltrimethylammonium bromide.[7] Another point of similarity between the results of this experiment and the results obtained with ionic detergents is the observation of increased segmental motion with distance from the headgroup in both the monomer and micelle phase.[3,4,5,6,7] $^{13}C—T_1$ experiments conducted with n-hexanoate[5] and n-octyltrimethylammonium bromide[7] show that, upon increasing the detergent concentration above the cmc, the carbon atoms near the headgroup are motionally restricted to a larger extent than the carbon atoms near the methyl terminus of the alkyl chain. This contrasts with the result obtained with octylglucoside; the T_1 values of all of the examined alkyl carbons changed by approximately the same factor (about 2.7-fold) upon micellularization. Two phenomena might contribute to this difference. First, the interactions that stabilize the interface region in nonionic octylglucoside might not be as strong as with ionic detergents. Second, the possibility exists that the free detergent that is in equilibrium with micelles is not entirely monomeric, but might be in an oligomeric state. There might thus be differences between nonionic and ionic detergents in this type of "preaggregation" behavior. It should be noted that, with octylglucoside, the ratio $T_{1\text{-mon}}/T_{1\text{-mic}}$ of the headgroup carbons is generally larger than the corresponding ratio for the alkyl carbons, indicating that the motion of the headgroup carbons is affected more by the monomer-to-micelle transition than the motion of the alkyl carbons.

ACKNOWLEDGMENTS

This research was supported by National Institute of Health grant number 1ROEY03501. I am also in debt to Dr. Theodore P. Williams, Mrs. B. Baker, and Mr. R. Rosanski for their assistance while performing this research.

REFERENCES

1. A. Allerhand, D. Doddrell, and R. Komoroski, J. Chem. Phys., 55, 189 (1971).
2. K. F. Kuhlman, D. M. Grant, and R. K. Harris, J. Chem. Phys., 52, 3439 (1970).
3. M. Van Bockstaele, L. Gelan, H. Martens, J. Put, F. De Schryver, and J. Dederen, Chem. Phys. Lett., 70, 605 (1980).
4. H. Wennerström, B. Lindman, O Söderman, T. Drakenberg, and J. Rosenholm, J. Am. Chem. Soc., 101, 6860 (1979).
5. U. Henriksson and L. Odberg, Colloid & Polym. Sci., 254, 35, (1976).
6. G. L. Levy, R. A. Komoroski, and J. A. Halstead, J. Am. Chem. Soc., 96, 5456 (1974).
7. E. Williams, B. Sears, A. Allerhand, and E. Cordes, J. Am. Chem. Soc., 95, 4871 (1973).
8. Y. Levine, N. Birdsall, A. Lee, and J. Metcalfe, Biochemistry II, 1416 (1972).
9. N. Muller, Reaction Kinetics in Micelles (E. Gordes, ed., Plenum Press, New York, N.Y., 1973), Chapter 1.
10. K. Shimoda, T. Yamanaka, and K. Kimoshita, J. Phys. Chem., 63, 648 (1959).