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Dynamics of Micellar Oligomeric and Monomeric
Sodium 10-Undecenoate

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Abstract

Multi-field carbon-13 NMR longitudinal relaxation time measurements were used to probe the dynamics and structure of monomeric and oligomeric sodium 10-undecenoate in micellar solutions. Longitudinal relaxation data were fit to a two-state model for the spectral density function which utilizes as adjustable parameters a fast correlation time and an order parameter for each carbon atom, and an overall slow correlation time for the entire aggregate. This model was needed to explain the relaxation phenomena because of the anisotropic reorientation of the amphiphiles. The monomeric fast correlation profile indicated a motional gradient increasing towards the micellar core. Comparison of the fast correlation time profiles for monomer and oligomer revealed that the motional gradient found in the monomer was not present in the oligomer. Slow correlation times extracted from the two-state model indicate that the radii of the oligomeric micelles, approximated from the Debye-Stokes-Einstein equation, are slightly larger than the monomeric micelles; 10.6 versus 9.4 Å, respectively. Radii calculated using self-diffusion coefficients also suggest a larger radius for the oligomeric micelles; 13.4 Å for oligomeric micelles and 10.6 Å for the monomeric micelles. The values determined for the micellar radii are less than that for the extended monomeric chain, 14.7 Å.

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Introduction

Micellar solutions of oligomerized and polymerized surfactants have a variety of potential applications ranging from drug delivery systems to oil recovery. One surfactant in which oligomers and polymers have been produced in micellar solution and liquid crystalline media is sodium 10-undecenoate (1-4). Paleos *et al.* (3) have concluded that there is essentially no critical micelle concentration (CMC) for polymerized sodium 10-undecenoate. A polymeric surfactant which forms micelles at all concentrations is desirable for applications where dilute micellar solutions are necessary. In addition, the potential exists for greater stability of solubilized species in these micelles because the individual surfactant molecules do not exchange with others in the continuous regions or other micelles.

Segmental motions of ordinary amphiphilic molecules in aqueous micellar solutions are known to be influenced by the ordered structure of spherical micellar aggregates (5). This results in a motional gradient along the hydrocarbon chain of the amphiphile. The motional restriction of methylene groups close to the head group may be attributed to their position close to the micellar surface. Methylene groups towards the hydrophobic tails of the surfactant have increased motional freedom and their segmental motions and microviscosities are similar to those of hydrocarbons. Therefore, typical micelles are said to have a liquid-like core.

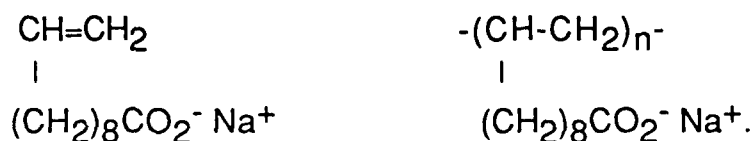
Carbon-13 spin-lattice relaxation times (T_1 's) have been used as a probe for molecular motion for a number of systems ranging from small molecules to polymers. A comparison of surfactant spin-lattice relaxation times in micellar solutions with those of similar molecules in isotropic media reveals that the complex motions of the micelles cannot be described using a simple single-correlation time model. Consequently, a two-step model for molecular motion was developed with two modes described by fast and slow correlation times (6). The fast motions are usually assumed to be short range motions such as local conformational changes. Slow motions are assumed to be due to amphiphile diffusion over the surface of the micelle and aggregate tumbling. This model has provided information about dynamics and order for a broad spectrum of micellar, microemulsion and liquid crystalline systems (6-11).

The system of interest in this study was oligomeric sodium 10-undecenoate and water. This surfactant is different from other surfactants because several surfactant molecules are covalently bonded to one another at the end of their hydrophobic tails. A schematic diagram of the monomeric and oligomeric micelle is shown in Figure 1. Synthetically, it is of interest because it is readily prepared by free radical initiation from sodium 10-undecenoate in organized media despite potential autoinhibition from allylic protons (2,4). Recently, it was found in a carbon-13 spin-lattice relaxation time study that monomeric sodium 10-undecenoate behaves in an analogous fashion to most amphiphiles whereas the opposite is true for an oligomerized micellar solution of sodium 10-undecenoate (4). However, a multi-field relaxation study of micellar monomeric and oligomerized sodium 10-undecenoate was necessary to determine the details of how oligomerization effects the relative short and long range dynamics as well as orientational order. This analysis was accomplished via the two-step spectral density function developed previously to fit multi-field relaxation data and the results used to compare the oligomeric micelle system with its monomeric counterpart.

In this study, the carbon-13 longitudinal relaxation times of monomeric and oligomeric sodium 10-undecenoate micellar solutions were measured at three magnetic field strengths. The two-step model for spectral density was then fit to the experimental T_1 's with fast correlation times, (τ_c^f), order parameters, S , and a slow correlation time, (τ_c^s), as adjustable parameters. Each fast correlation time and order parameter was assigned to a methylene group along the amphiphile chain. The slow correlation times were used to estimate micellar sizes using the Debye-Stokes-Einstein equation and the diffusion equation for the monomeric and oligomeric micelles. Translational self-diffusion coefficients were also used to estimate the micellar sizes for each system. The estimates of micellar radii obtained were then compared to independent measurements by other techniques.

Experimental

10-Undecenoic acid (Aldrich Chemical Co., Milwaukee WI) was purified by vacuum distillation. The acid was neutralized with NaOH. The sodium alkylcarboxylates were then dried under vacuum at 60-70 °C. The oligomers were prepared by a method similar to that described earlier (4). The oligomerized sodium 10-undecenoate was prepared by heating 5.1 g of sodium 10-undecenoate, 0.5 g of potassium persulfate, and 20.1 g of distilled water in a nitrogen purged three neck flask at 75 °C for 20 hours. Oligomeric material was precipitated and washed with cold ethanol and dried under vacuum. The product yield was found to be 2.1 g (40 wt %). Subsequent FTIR, ¹H NMR and ¹³C NMR analysis confirmed oligomerization. The absence of vinyl proton resonances in the proton spectra confirmed the product was predominantly oligomerized surfactant. The structure of the monomeric and oligomeric surfactant are shown below:



Oligomeric sodium 10-undecenoate was analyzed using plasma desorption time-of-flight mass spectrometry (PDMS) (12,13). A 30 µl sample, 2 mg / ml oligomer in methanol, was added to 10 µl of 1 mM NaCl solution and applied to a nitrocellulose coated aluminized mylar foil. The sample was then spin dried. An accelerating voltage of 18 kV was used. Viscosity measurements were made using a Cannon-Ubbelohde semi-micro viscometer.

Relaxation time (T_1) studies were performed on 17.1 and 17.4 wt % solutions of monomeric and oligomeric surfactant, respectively, in deuterium oxide which was used as the lock solvent. Concentrated solutions were used in the T_1 measurements to maximize signal to noise in the carbon-13 spectra and minimize the contribution of unassociated surfactant to the T_1 . The variable field ¹³C spin-lattice relaxation measurements were performed at 25.0, 50.4 and 75.0 MHz. The instruments used were a JEOL FX-100, a Varian VXR-200, and a Varian XL-300. Spin-lattice relaxation data were collected using an inversion-recovery sequence with at least 8 different τ

values and fit by a simplex method to a single exponential function. All measurements were made at 25 °C.

Multi-field experimental spin-lattice relaxation times for ^{13}C nuclei were fit to the two-step model by minimizing the difference between experimental and calculated T_1 values using (τ_c^s) , (τ_c^f) and S as adjustable parameters. An overall slow correlation time was used for each system. The fast correlation times and order parameter variables were calculated for resolved ^{13}C resonances for each system. The minimization was done using a FORTRAN program utilizing the IMSL subroutine NEQNF (14).

Self-diffusion coefficients were measured with a JEOL FX-100 using the pulsed field gradient spin-echo (PGSE) technique (15,16). The gradient used was $5.40 \text{ G}\cdot\text{cm}^{-1}$. The time between the initial and refocusing pulses, τ , was about 77 ms. Based on typical diffusion coefficients, D , the typical distance probed, $(2D\tau)^{1/2}$, is about $1 \mu\text{m}$ which is much larger than the size of the micelles. Typically, the accuracy of these measurements in this range is better than 10%.

Background

The primary mode of ^{13}C longitudinal relaxation of protonated carbons for the sodium carboxylates under study is through magnetic dipole-dipole interactions of the observe nucleus with the directly bonded protons. The spin-lattice relaxation time for the i th carbon can be expressed as follows:

$$(T_{1i})^{-1} = \left(\frac{N_i}{20}\right) \left[\frac{\mu_0 \gamma_H \gamma_C h}{8\pi^2 r_{C-H}^3} \right]^2 (J(\omega_H - \omega_C) + 3J(\omega_C) + 6J(\omega_H + \omega_C)) \quad [1]$$

where N_i is the number of directly bonded protons on carbon i , μ_0 is the permeability of a vacuum, γ_H and γ_C are the magnetogyric ratios of ^{13}C and ^1H nuclei, h is Planck's constant, ω_C and ω_H are the Larmor frequencies for carbons and protons and J represents the spectral density function (17). The distance between ^{13}C and ^1H nuclei, r_{C-H} is assumed to be 1.09 Å.

The complexity of motions in micellar solutions such as those under study here, require a relaxation model more complicated than a single exponential one. Wennerstrom *et al.* (6) defined a two-step spectral density function consisting of slow (long range) and fast (short range) motions as:

$$J(\omega) = (1 - S^2) 2\tau_c^f + S^2 \left(\frac{2\tau_c^s}{1 + (\omega\tau_c^s)^2} \right) \quad [2]$$

where τ_c^f is the fast correlation time, τ_c^s is the slow correlation time, S is the order parameter, and the product of τ_c^f and ω is assumed to be much less than unity. Lipari and Szabo have arrived at a similar functional form of the two-step model for macromolecular solutions (18). The fast correlation time is usually associated with molecular motions in the 10^{-11} s range characteristic of small segmental jumps. The slow correlation time is normally found be in the 10^{-9} s range and is attributed to longer range motions such as aggregate tumbling and surfactant diffusion over the curved micellar surface. The order parameter is a measure of the local order of the methylene group. It also serves as a weighting factor of the spectral density function between the fast and slow motion terms. A value of zero for the order parameter would reduce the two-step model to

that used for simple isotropic motion with a single correlation time. The order parameter may be defined as follows:

$$S \equiv \left(\frac{1}{2} \right) \left\langle 3 \cos^2 \theta_{LD} - 1 \right\rangle_f \quad [3]$$

where θ_{LD} denotes the angle between the C-H bond vector and the local director axis which is assumed to be normal to the micellar surface. The order parameter is a measure of the ensemble averaged conformations of the hydrocarbon chain. The residual anisotropy in ordinary micellar systems is a result of the head group of the surfactant being restricted near the surface of the micelle. This restriction of the head group inhibits the C-H bond vector from experiencing all of the different orientations with respect to the external magnetic field over the time scale of the experiment. If all possible orientations were experienced, the anisotropy would be averaged out. In the expression for the order parameter, $\langle \rangle_f$ represents the averaging over the fast local motions. It has been found by others in micellar systems that the order parameter for ^{13}C nuclei decreases down the hydrocarbon chain away from the head group due to fast motional averaging (8).

Results

Experimental T_1 data at three magnetic field strengths for oligomeric and monomeric sodium 10-undecenoate micelles is listed in Table I and shown in Figure 2 as a function of the carbon position. The carbonyl carbon in the head group is assigned as C-1. In both the oligomer and monomer cases, the overlap of resonances from carbons 5-7 made it necessary to treat these as a composite resonance. The field dependence of the longitudinal relaxation times for both monomeric and oligomeric surfactants demonstrates that a fast isotropic motional model is not appropriate to describe the dynamics in these systems. The NT_1 values for all of the carbon positions in the monomeric species are greater than the oligomeric species. The average error based on the precision of the T_1 measurements is about 3 %.

The T_1 results were fit to the two-state model and the values of τ_c^f and S were calculated for each carbon position along with an overall τ_c^s . The fast correlation times as a function of carbon position are shown in Figure 3 for both monomer and oligomer. The magnitudes of the fast correlation times for oligomer methylenes are at least twice that of the monomeric methylenes. The fast correlation times for carbons 8-11 for the oligomer were not determined because the carbon-13 resonances were too broad to resolve and/or the intensity was too low to determine accurate enough T_1 's for model fits. However, the trend of these T_1 's seems to indicate longer fast correlation times for these carbons.

The order parameter profiles produced from the two-state model are shown in Figure 4. The order parameters decrease towards the micellar core for the monomer. The order parameters for the methylenes with T_1 's used in the model fit for the oligomer generally increase towards the micellar core.

The slow correlation times for the monomer and oligomer were 3.2 ± 0.3 and 4.1 ± 0.4 ns, respectively. Error in the slow correlation time is based on the error estimate of 3% in the T_1 data. The normalized spectral density functions based on the monomeric and oligomeric C-2 model parameters, are shown in Figure 5. This figure demonstrates how the spectral density is sampled at different magnetic field strengths. If these are the true spectral densities, higher magnetic field strengths will not improve the fit of the data because the slow motional contribution to the spectral density function will no longer be sampled, efficiently. Therefore, improved sensitivity and

resolution through higher field strengths is probably not appropriate for the systems studied.

The viscosity of solutions of monomeric and oligomeric solutions were determined to be 4.72×10^{-3} and $3.43 \times 10^{-3} \text{ kg m}^{-1}\text{s}^{-1}$, respectively. The translational diffusion coefficients for monomeric and oligomeric sodium 10-undecenoate were measured to be $4.38 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ and $4.76 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ using the PGSE technique.

Plasma desorption time-of-flight mass spectral analysis of the oligomerized sample revealed a distribution of molecular weights. The highest detected molecular weight corresponded to a 14-mer. Each oligomer can be documented from the mass spectrum, however, fragmentation precludes a detailed assignment of an average molecular weight.

Discussion

Fast Correlation Times. The location of the head group in the monomer at the micellar surface has an effect on molecular motions of methylenes close to it. Without association, a fast correlation time profile similar to that in hydrocarbons with groups in the middle of the molecule moving slower than at the ends would be expected. Since the surfactant is associated in the micelle and has the hydrophobic and hydrophilic groups on opposite ends of the molecule, the observed profile is expected. Therefore, the fast correlation times for methylenes generally decrease as the distance from the head group is increased for single-head/single-tail surfactants. The fast correlation time trend for single head/single-tail surfactants in micellar solutions has also been found to be independent of the type of head group.

The fast correlation times for monomer and oligomer differ in magnitude and trend as shown in Figure 3. The generally higher value in the oligomer case indicates that the short range motions in the oligomerized chains are slower than those in the monomeric counterparts. The effect of oligomerization at the tails of the surfactant significantly affect the head group methylene motions at the opposite end of the chain. Experimental T_1 data of the oligomeric carbon segments close to the oligomer backbone indicate longer fast correlation times relative to the rest of the chain. However, a reasonable fit could not be obtained using these resonances due to their broadness and low intensity. Consequently, it is concluded that the general trend the monomeric surfactant micelles follow of increased motional freedom down the hydrocarbon chain is not present in the oligomerized surfactant micelles. The short range motional freedom of the oligomerized micelle decreases inward towards the center of the micelle and is diminished overall relative to the monomer. The covalent bonding and steric hindrance at the oligomer backbone significantly affects short range motions.

Order Parameters. The magnitude of the order parameter weights the contribution of the slow motion term to the spectral density - the larger the order parameter the more significant the slow motional term (eqn. 2). The order trend of the parameter for the monomeric micelle is typical of single-head and single-tail surfactant micelles. The trend for the order parameter of the

oligomeric micelle is different than those of normal monomeric micelles. Figure 4 demonstrates how the monomeric and oligomeric micelle methylenes have similar order parameter values close to the head group. However, in the case of the oligomerized micelle, the closer to the center of the micelle a C-H group is, the greater its order parameter is. This phenomena is due to the covalent bonding at the surfactant tails in the oligomer. The covalent bonding in the oligomer prevents the angle the C-H bond vector makes with the local director axis from being averaged by molecular motions.

Although the fast correlation time and order parameter profiles for single-tail (and single-head) surfactants follow the same trend, other systems do have the potential to differ in profile. Spin-lattice and nuclear Overhauser enhancement measurements on micellar solutions of a double-headed surfactant, N, N'-1, 20-eicosanediybis(triethylammonium bromide), revealed the order parameter and fast correlation time profiles that were relatively flat (9). These results are relevant to this work because that system can be considered an intermediate case between the monomeric and oligomerized micelles investigated here. The oligomerized sodium 10-undecenoate surfactant has multiple head groups connected through alkyl chains. Thus, it is possible to create systems with different structures and dynamics.

Slow Correlation Times. Below the CMC of the monomeric surfactant, it could be expected that slow motions would still affect the relaxation behavior of the oligomerized material. Oligomerization not only increases the overall slow motional contribution to spin-lattice relaxation but it also guarantees this dependence below the monomer CMC. Relaxation in normal monomeric micellar solutions have slow motional dependence only when associated in micellar aggregates. Consequently, these materials no longer have this dependence below the CMC.

One of the interesting aspects of the two-step model is that it can provide information about the micellar size through the slow correlation time. The influence of micellar size in nuclear magnetic relaxation was investigated by applying the same two-step model to relaxation data of alkylammonium chloride micellar solutions with alkyl groups of varying lengths (8). It was found in that study that as micellar size was increased, the slow correlation time also increased, as expected based on the Debye-Stokes-Einstein equation. Hence, if oligomerization perturbs the size

and shape of the micelle, the slow correlation time magnitude could be sensitive to these changes.

Slow correlation times for monomeric and oligomeric micelles of sodium 10-undecenoate have a slight but notable difference in value (3.2 ± 0.3 and 4.1 ± 0.4 ns, respectively). However, large changes in aggregate motions do not appear to be evident due to oligomerization. The slow correlation time can be expressed by:

$$(\tau_c^s)^{-1} = (\tau_c^s)_{\text{diff}}^{-1} + (\tau_c^s)_{\text{rot}}^{-1} \quad [4]$$

which includes terms for micellar rotation and monomer diffusion over the curved micellar surface. These two terms may be expressed in terms of the Debye-Stokes-Einstein equation and the diffusion equation as shown below.

$$(\tau_c^s)_{\text{rot}} = 4\pi R^3 \eta / 3k_B T \quad [5]$$

$$(\tau_c^s)_{\text{diff}} = R^2 / 6 D_L \quad [6]$$

where η represents the viscosity of the medium, k_B is Boltzmann's constant, R is the radius of the micelle, T is temperature and D_L represents the lateral diffusion coefficient of the surfactant. The lateral diffusion coefficient for the monomeric surfactant is assumed to be on the order of $1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ based on comparison to the results of Eriksson *et al.* (19) in liquid crystals. The micellar radius R can be calculated by combining equations 4, 5 and 6 using a packaged software iterative procedure (20). The calculated value of R obtained for monomeric sodium 10-undecenoate micelles is a conservative estimate of $9.4 \pm 0.4 \text{ \AA}$. The error is based upon the average error estimated from the T_1 values. If the lateral diffusion coefficient was larger than the assumed $1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ the calculated micellar radius would be larger.

The oligomeric micellar radius can be estimated in a similar manner from the measured slow correlation time. However, it is safe to assume $(\tau_c^s)_{\text{diff}}^{-1} \ll (\tau_c^s)^{-1} \cong (\tau_c^s)_{\text{rot}}^{-1}$ because the lateral diffusion of the oligomer is much slower than that of the monomer species. The calculated micellar radius in this case is $10.6 \pm 0.5 \text{ \AA}$.

The micellar radii, R , may also be estimated by using the translational self-diffusion coefficients and the Stokes-Einstein equation:

$$D_T = k_B T / 6\pi\eta R \quad [7]$$

where D_T is the translational diffusion coefficient, η is the viscosity of the medium and k_B is Boltzman's constant. The radii were calculated from the Stokes-Einstein equation, [7], based on the measured diffusion coefficients and the solution viscosity, used as a first order correction for concentration effects, the values obtained from this calculation are 10.6 ± 1.1 and 13.4 ± 1.3 Å for monomer and oligomer, respectively. The difference in viscosities of the solutions are responsible for much of the differences in micellar radii as the diffusion coefficients are similar.

Size Comparisons. Table II contains the radii calculated from relaxation and diffusion data from this work, ESR (21) and X-ray diffraction (2) data from the literature. The combined results of these various measurements indicate the size of the oligomerized micelles is slightly larger than the monomeric micelles. Sprague *et al.*(21) used spin-labeled compounds suitable for electron spin resonance (ESR) study to probe how amphiphilic and hydrophobic substrates interacted with monomeric and oligomeric micelles of sodium 10-undecenoate. Rotational correlation times calculated for the amphiphile, sodium 5-doxytstearate, led to calculated micellar radii of 12.1 and 11.8 Å for monomer and oligomer, respectively. Although the spin-labeled testosterone, used as a hydrophobic probe, has a high potential to perturb the micelles due to its bulky nature; results are comparable to those in this work.

Hexagonal liquid crystals are typically considered to have cylindrical morphology. Consequently, radii calculated from this phase should be similar to that in micellar media, although the different chain packing may force further extension. Thundathil *et al.* (2) calculated a hexagonal cylinder radius in this phase of 14.1 Å for relatively high molecular weight sodium 10-undecenoate, $MW \cong 50,000$, using low-angle X-ray diffraction measurements.

Results in each of the above mentioned experiments indicate the micellar radii for both oligomerized and monomeric sodium 10-undecenoate are close to the theoretical value of a fully extended monomer chain which is 14.7 Å. Collectively, the data suggest that oligomeric micelles may be slightly larger than their monomeric counterparts. The size similarities between monomeric and oligomeric micelles would also suggest the molecular weight of the oligomerized material is on the order of the aggregation number for the monomeric micelles. High molecular weight material in the oligomerized case would significantly perturb the micelle. Consequently, the size of the

micelle would increase dramatically. The aggregation number of surfactants in a micelle of monomeric sodium 10-undecenoate at 37 °C was determined to be 12 ± 5 by vapor pressure osmometry (22). A degree of polymerization of about 10 was found for material polymerized in the micellar phase by photoinitiation (1). PDMS revealed the molecular weight of the surfactant oligomers prepared in this study corresponded to a maximum of 14 monomer units. These results indicate the number of units in the oligomeric surfactant is on the order of the normal aggregation number for monomeric micelles or less. Therefore, the oligomeric micelles are probably comprised of one or more oligomerized surfactants depending upon the molecular weights of the individual oligomeric surfactants. Consequently, the size of the oligomeric micelles should be on the order of the monomeric micelles.

Conclusions

The cores of sodium 10-undecenoate micelles have molecular motions similar to hydrocarbons. Oligomerized sodium 10-undecenoate micellar solutions contain cores which are substantially more rigid. Spin-lattice relaxation time profiles of oligomer and monomer carbons support this conclusion and the details of molecular motions were extracted through the two-step model for molecular motion. Fast correlation times determined by the two-step model are longer in the oligomeric micelles implying that short range motions are slower due to the terminal linkages. The fast correlation time profile shows that these short range motions are slower towards the center of the micelle in the oligomerized micelles. This result is the opposite of the monomeric case where the fast correlation profile indicates faster short range motions in the methylene groups farther away from the anchored head group. The order parameter of the methylene carbons next to the carbonyls for the monomer and oligomer are similar, indicating similar structural ordering near the head group. However, the order parameter profiles diverge from head to tail carbons. Experimental data suggest that the radii of both monomeric and oligomeric micelles are similar to, but smaller than, their theoretical value of 14.7 Å. NMR relaxation and diffusion data suggest radii for the oligomeric micelles are slightly larger than the monomers.

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Table I
T₁ Data (seconds)

Carbon Number	Monomer			Oligomer		
	25 MHz	50 MHz	75 MHz	25 MHz	50 MHz	75 MHz
1	3.418	5.223	7.414	-	-	-
2	0.291	0.472	0.613	0.219	0.31	0.39
3	0.338	0.529	0.679	0.168	0.253	0.323
4	0.425	0.623	0.682	0.129	0.212	0.266
5-7	0.415	0.519	0.664	0.111	0.185	0.256
8	0.556	0.741	0.766	0.111	0.185	0.256
9	0.83	1.059	1.33	-	-	-
10	2.674	3.203	4.031	0.048	0.127	0.217
11	0.856	1.198	1.455	0.05	0.117	0.247

Table II
Comparison of Micellar Radii

Method	Micellar Radius (Å)	
	<u>Monomer</u>	<u>Oligomer</u>
NMR Relaxation ^a	9.4 ± 0.4	10.6 ± 0.5
Diffusion (PGSE) ^a	10.6 ± 1.1	13.4 ± 1.3
ESR (Sodium 5-Doxylstearate) ^b	12.1 ± 0.3	11.8 ± 0.7
ESR (Labeled testosterone) ^b	8.9 ± 0.2	12.1 ± 0.3
Low-Angle X-ray ^c		14.1
Extended Chain ^d	14.7	

a. This work.

b. ref 21.

c. ref 2, (this value is from the surfactant in liquid crystalline media.)

d. the distance from the acid oxygen to the proton at the end of the chain for the all trans conformation.

Figure Captions

Figure 1. Schematic diagram of monomeric and oligomeric sodium 10-undecenoate micelles.

Figure 2. ^{13}C - T_1 values for monomeric sodium 10-undecenoate at 25 (\square), 50 (\triangle) and 75 (\diamond) MHz and for oligomeric sodium 10-undecenoate at 25 (\blacksquare), 50 (\blacktriangle), and 75 (\blacklozenge) MHz.

Figure 3. Fast correlation time values for micellar monomeric (\square) and oligomeric (\blacksquare) sodium 10-undecenoate as a function of position on the chain.

Figure 4. Order parameters for micellar monomeric (\square) and oligomeric (\blacksquare) sodium 10-undecenoate as a function of position on the chain.

Figure 5. The normalized spectral density functions based on the monomeric (-----) and oligomeric (——) C-2 position model parameters. Monomer C-2 position model parameters are $S = 0.226$, $\tau_c^s = 3.19 \times 10^{-9}$ s, and $\tau_c^f = 22.1 \times 10^{-12}$ s. Oligomer C-2 position parameters are $S = 0.231$, $\tau_c^s = 4.13 \times 10^{-9}$ s, and $\tau_c^f = 47.7 \times 10^{-12}$ s. The vertical lines are at the experimental carbon Larmor frequencies.

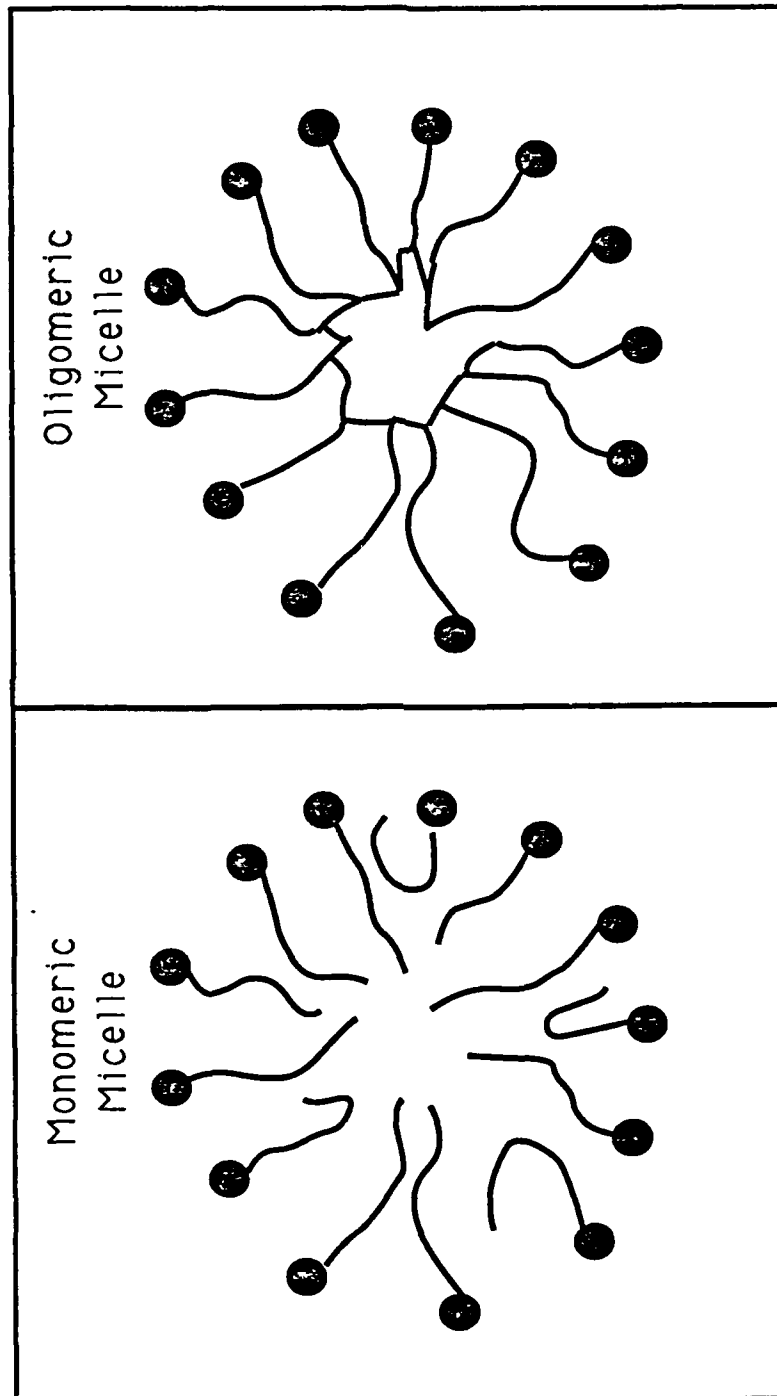


Figure 1. Schematic diagram of monomeric and oligomeric sodium 10-undecenoate micelles.

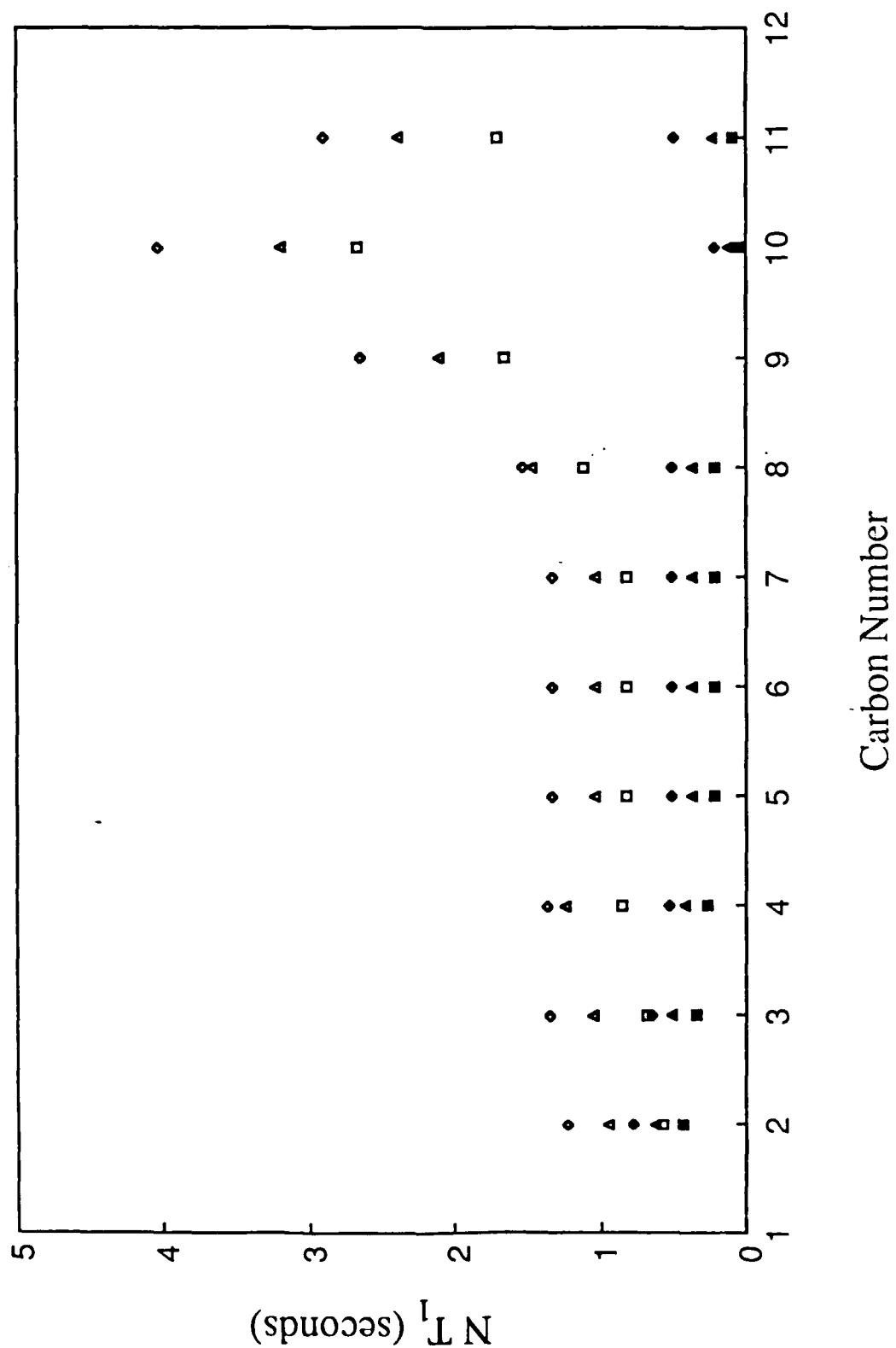


Figure 2. ^{13}C -T₁ values for monomeric sodium 10-undecenoate at 25 (□), 50 (△) and 75 (◇) MHz and for oligomeric sodium 10-undecenoate at 25 (■), 50 (▲), and 75 (◆) MHz.

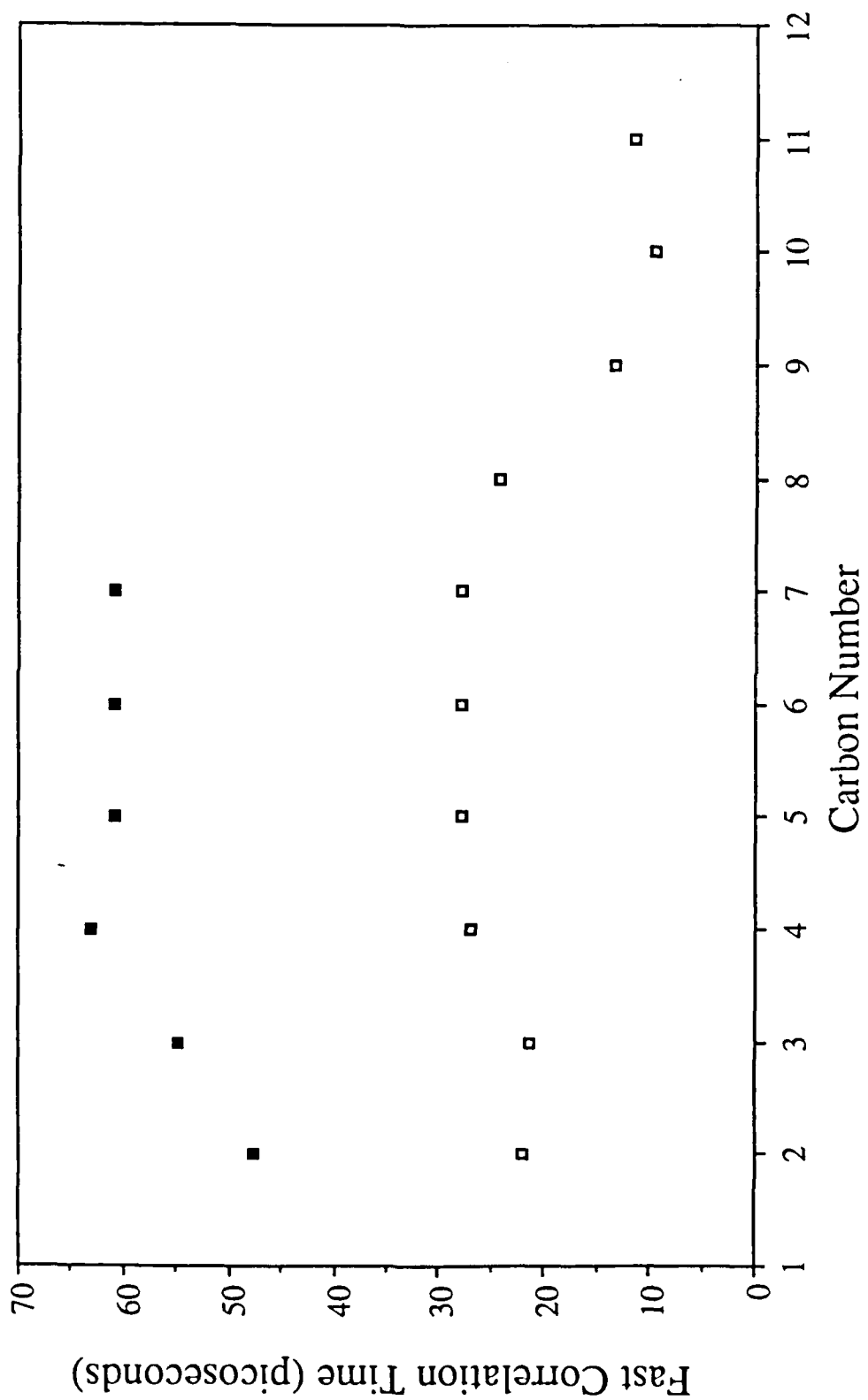


Figure 3. Fast correlation time values for micellar monomeric (\square) and oligomeric (\blacksquare) sodium 10-undecenoate as a function of position on the chain.

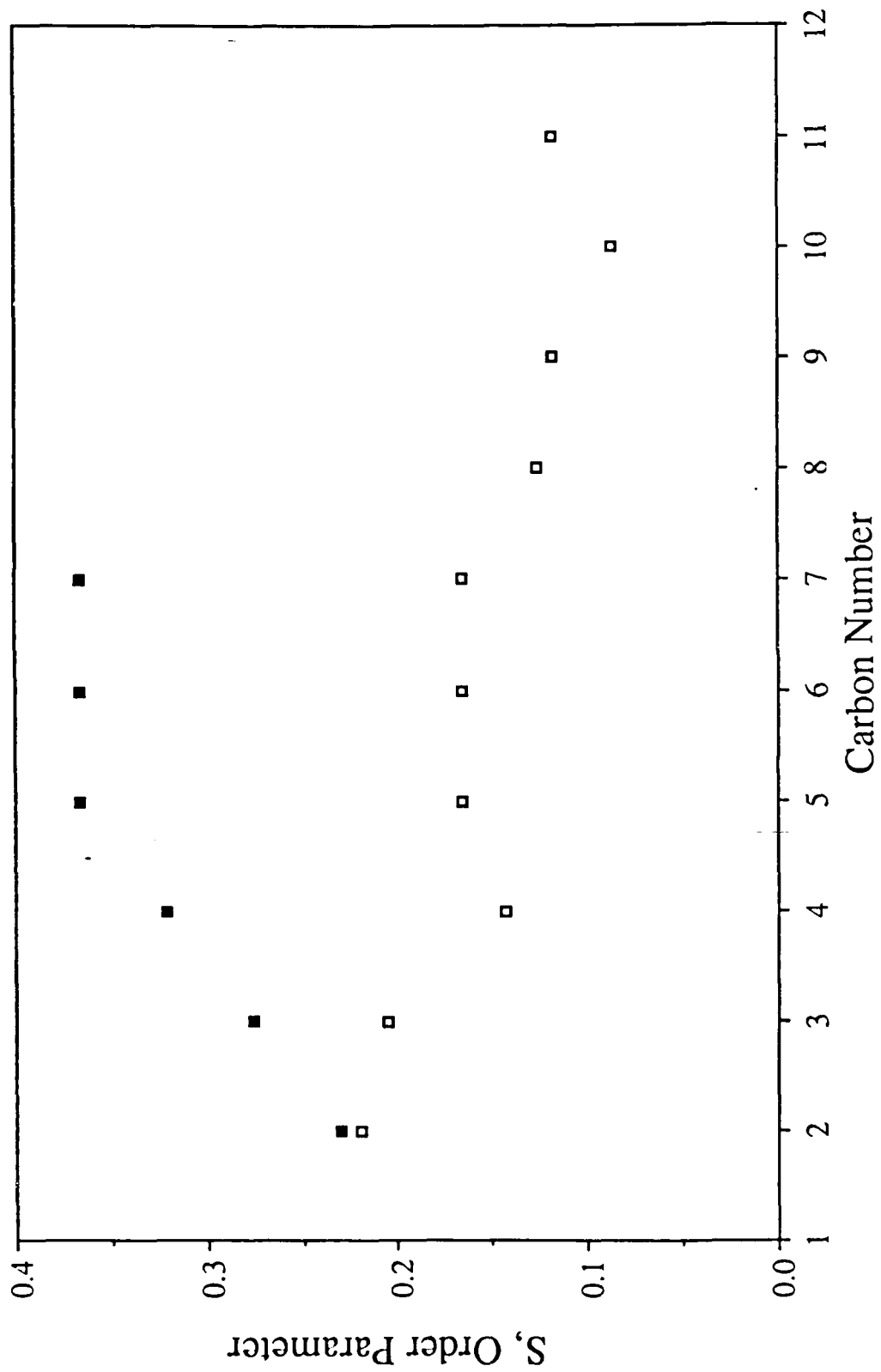


Figure 4. Order parameters for micellar monomeric (\square) and oligomeric (\blacksquare) sodium 10-undecenoate as a function of position on the chain.

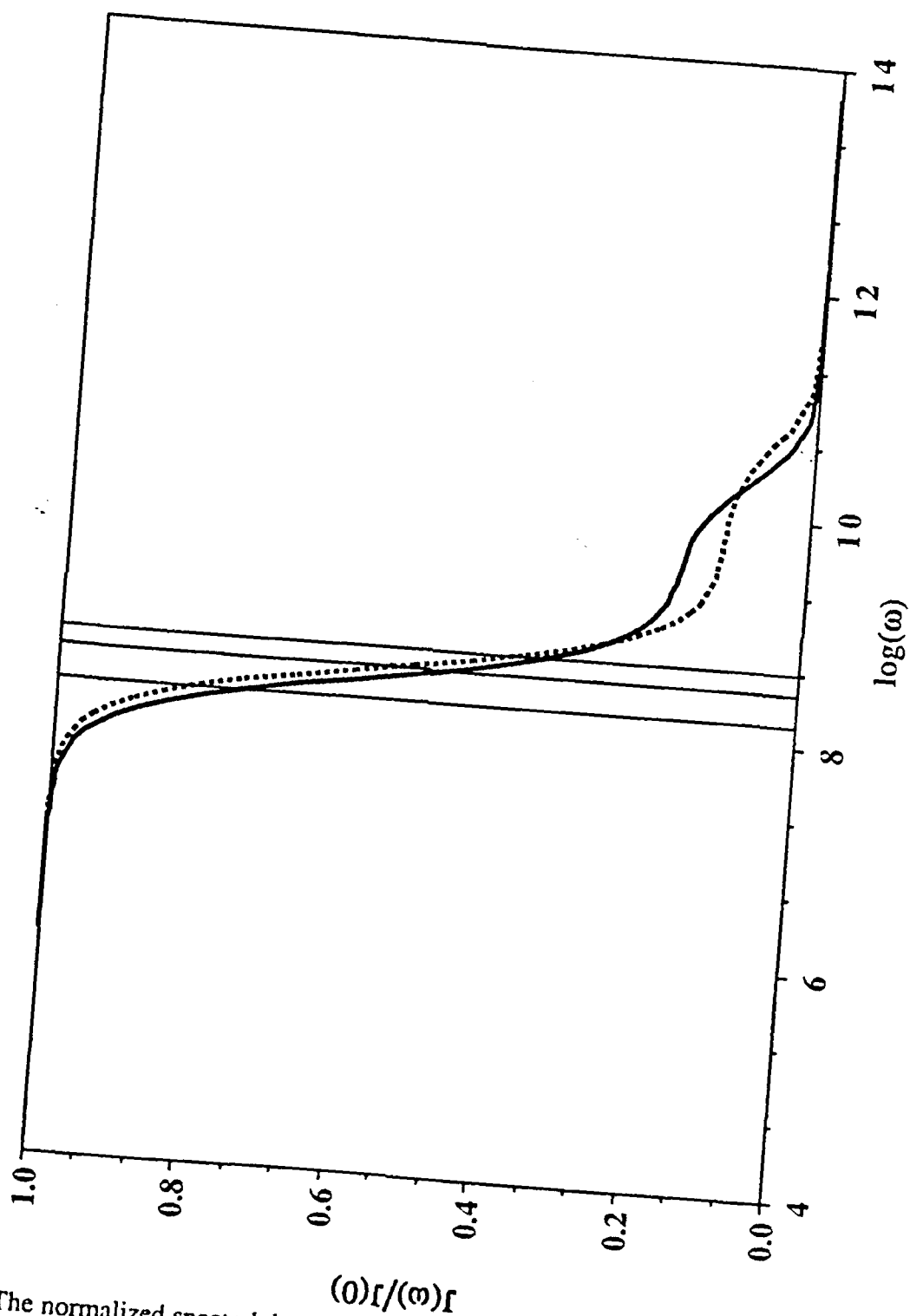


Figure 5. The normalized spectral density functions based on the monomeric (-----) and oligomeric (—) C-2 position model parameters. Monomer C-2 position parameters are $S = 0.226$, $\tau_c^s = 3.19 \times 10^{-9}$ s, and $\tau_c^f = 22.1 \times 10^{-12}$ s. Oligomer C-2 position parameters are $S = 0.231$, $\tau_c^s = 4.13 \times 10^{-9}$ s, and $\tau_c^f = 47.7 \times 10^{-12}$ s. The vertical lines are at the experimental carbon Larmor frequencies.