Nuclear Spin Relaxation and Dynamical Behaviour of Short-chain Surfactants in Micellar and Liquid-crystalline Aggregates

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The dynamical behaviour and conformations of the octylphosphate anion in micellar solution and liquid-crystalline hexagonal (H_I) and lamellar (L_α) phases formed from pyridinium octylphosphate (OCTP) have been investigated by ^{13}C relaxation at several frequencies. In the H_I and L_α phases the conformer populations, the rate of conformational changes and the reorientation correlation times were derived from the fits of the $^{13}C-^1H$ dipolar splittings and of the longitudinal relaxation rates. In isotropic micellar solution the same information was only available from the frequency dependence of these rates. The experimental data were interpreted by means of a rotational jump model corresponding to *trans* ⇌ *gauche* isomerizations about one bond at a time. In these phases, the aggregation results in a strong enhancement of the probabilities of the *trans* rotamer, generally found in the 0.8–0.95 range. The surfactant therefore behaves as a quite rigid entity undergoing a very anisotropic and quasi-axial reorientation, a behaviour expected from the computation of the inertial tensor averaged over all accessible conformers. Similar conclusions have been drawn from the deuteron splittings and longitudinal relaxation rates of an octanoate probe diluted in the OCTP–H_2O mesophases. The deuteron longitudinal relaxation of this probe being the same at 13.4 and 46 MHz, the contribution of collective motions (ODF) appears to be negligible under our experimental conditions.

The aggregation of surfactants to form a micelle or a lyotropic liquid crystal is mainly a problem of hydrocarbon chain packing due to confinement, which has been treated in a number of theoretical studies and computer simulations (see for instance ref. 1–9). In spite of some limitations, nuclear resonance methods provide the main experimental support to these studies, since they give conformational and dynamical information on each part of the molecule as well as its average orientation within the aggregate. In liquid crystals, such information is generally provided by the deuteron quadrupolar splittings and relaxation rates, whereas in micellar solutions it is only available from multifrequency relaxation experiments on carbon 13.

The methods adopted for the interpretations of nuclear resonance and relaxation data in our recent studies of surfactants[10,11] are well illustrated by the example of the octylhydrogenphosphate anion $C_8H_{17}PO_4H^-$, denoted hereafter as octylphosphate, in micellar solutions and in mesophases formed from pyridinium octylphosphate (OCTP, Fig. 1). This compound has been chosen in preference to the corresponding alkaline salts because it forms mesophases of low melting point that are easy to orient in magnetic fields and give well resolved spectra. At increasing water concentrations, OCTP successively gives rise to lamellar and hexagonal mesophases[11] and micellar solutions.[12] For non-stoichiometric pyridine/octylphosphoric acid ratios between 0.2 and 0.8, a thermotropic ionic lamellar phase is also obtained.[13] We thus have the possibility of examining the dynamical behaviour of a surfactant in several kinds of aggregates.
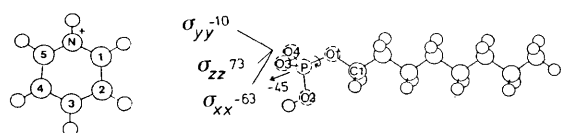
Because an OCTP sample deuterated on the chain was not available, we have extended the frequency range of our experiments by using a perdeuteriated octanoic acid probe (weight fraction 0.05) in OCTP–H_2O lamellar and hexagonal phases. It has been verified that at such a dilution, the OCTP–H_2O phase diagram is not appreciably modified. The experiments reported here have been performed on ^2H, ^{13}C and ^{31}P at magnetic field strengths of 2.15, 7.05 and 11.75 T. The preparation of the samples as well as the details of experimental procedures have been reported previously.[10–13]

Theoretical Background

Isotropic micellar solutions

In nuclear relaxation studies on micellar solutions, the most commonly used model is the two-step model proposed by Wennerström et al.[14] For this model, the spectral densities are of the form

$$J(\omega) = \frac{2}{5}\left(\frac{\tau}{1 + \omega^2\tau_s^2} S^2 + \frac{\tau_f}{1 + \omega^2\tau_f^2}(1 - S^2)\right) \quad (1)$$

The parameters of this equation are generally interpreted as follows: S is the order parameter of a C—H bond expressed as $\frac{1}{2}\langle 3\cos^2\beta - 1\rangle$, β being the time-dependent angle between the C—H bond and a local director, perpendicular to the interface of the micelle with water at the surfactant position. $\tau_s = (\tau_R^{-1} + 6D_L R^{-2})^{-1}$ is the slow-motion correlation time, τ_R being the reorientation correlation time of a micelle of radius R, and D_L is the lateral diffusion coefficient of the micellized surfactant. τ_f is an effective fast-motion correlation time associated with the internal motions of the surfactant and depending, like S, on the position of the C—H group in the hydrocarbon chain.

If the relaxation experiments are performed in a wide frequency range, the two-step model generally yields very good

Fig. 1 Pyridinium octylphosphate: σ_{xx}, σ_{yy} and σ_{zz} are the principal values of the ^{31}P chemical shielding tensor taken from ref. 30

fits of the ^{13}C or ^{2}H relaxation rates, and the order parameters are often very close to those measured on the same surfactant in lyotropic mesophases. There are, however, significant exceptions for which the S parameters derived from the best fits of relaxation data cannot be considered as an actual order parameter as defined above. This has been recently observed in the case of surfactants whose internal motions are partially inhibited.[10] Lipari and Szabo[15,16] have shown that eqn. (1) holds for any kind of restricted motion, S being considered as a 'generalized order parameter' related to its amplitude. Furthermore, they have extended their 'model-free approach' to the case of an overall anisotropic motion, generally not considered in NMR studies on micelles. Using expressions given by these authors, it can be shown that it is virtually impossible to determine the anisotropy of the surfactant motion from the ^{13}C longitudinal relaxation at usual field strengths[10] (2–11 T). These difficulties in the applications of the two-step model or the model-free approach to the dynamics of micellized surfactants led us to analyse the relaxation data by means of a rotational jump model related to the $trans \rightleftharpoons gauche$ isomerizations of aliphatic chains.

For an aliphatic chain without intermolecular constraints, the probabilities per unit time of the jumps among the $trans$ (T), $gauche^+$ (G^+) and $gauche^-$ (G^-) rotamers are[17]

$$W_1 = W_{T \rightarrow G^+} = W_{T \rightarrow G^-} = W_0 \exp(-E_{TG}/kT) \qquad (2a)$$

$$W_2 = W_{G^+ \rightarrow T} = W_{G^- \rightarrow T} = W_0 \exp[-(E_{TG} - \Delta E_{TG})/kT] \qquad (2b)$$

$$W_3 = W_{G^+ \rightleftharpoons G^-} = W_0 \exp(-E_{GG}/kT) \qquad (2c)$$

W_0 is a frequency factor of the order of 10^{12} s^{-1}. E_{TG} and E_{GG} are potential barriers and ΔE_{TG} is a potential-energy difference of $ca.$ 10, 40 and 2.5 kJ mol^{-1}, respectively.[18] The populations of the T, G^+ and G^- rotamers, denoted hereafter p_1, p_2 and p_3, are then

$$p_1 = [1 + 2 \exp(-\Delta E_{TG}/kT)]^{-1}$$

$$p_2 = p_3 = p_1 \exp(-\Delta E_{TG}/kT) \qquad (3)$$

At room temperature and in the absence of constraints, the probability of a $trans$ rotamer about the C—C bonds in an alkyl chain should be $p_1 = 0.55$–0.6. The value of p_1 is enhanced by the occurrence of the sterically disallowed $G^\pm G^\mp$ local forms[18] involving an energy increment of 10–12 kJ mol^{-1}. In surfactant aggregates, the rotamer populations are expected to be appreciably modified by intermolecular interactions which have been represented by a potential of mean torque,[19] or by a Lennard-Jones potential between a chain segment and the walls of a volume of confinement.[20]

The probability of a conformer u of potential energy E_u, which is the sum of inter- and intra-molecular contributions, is usually expressed as

$$p_u = \frac{\exp(-E_u/kT)}{\sum\limits_v \exp(-E_v/kT)} \qquad (4)$$

In our calculations of relaxation rates it is more convenient to express p_u as an element of the vector[21]

$$P_v = \prod_{l=1}^{N-2} \{(1 - M_G)(U \otimes P_1) + \tfrac{1}{2}M_G[U \otimes (1 - P_1)]\} \qquad (5)$$

where N is the number of bonds, M_G a binary array of dimensions $3^{N-2} \times N - 2$ giving the occurrences of the $gauche$ rotamers along the surfactant chain and U, the unit vector of dimension $N - 2$. P_1 is the vector of $trans$ probabilities along the chain, introduced as adjustable parameters. The $\prod$ and $\otimes$ symbols denote the product of the column of

the array within brackets and the direct product of two vectors, respectively.

The second set of adjustable parameters is the vector W_2 of probabilities per unit time of the $gauche \rightarrow trans$ transitions. Owing to the high potential barrier E_{GG}, the $G^+ \rightleftharpoons G^-$ probability per unit time, W_3, is much smaller than W_1 and W_2, so that the timescale of internal motions is in practice determined by P_1 and W_2. Assuming for simplicity that the rotational diffusion tensor is axially symmetric about a molecular axis denoted hereafter as Δ_M, the third set of parameters is the eigenvalues $D_\perp$ and $D_\parallel$ of this tensor, or the corresponding relaxation times.

The principles of the calculation of relaxation rates in a chain undergoing $gauche \rightleftharpoons trans$ isomerizations has been reported by Wittebort and Szabo.[22] The spectral densities are of the form

$$J(\omega) = \frac{2}{5} \sum_{k,n} \frac{\tau_{k,n}}{1 + \omega^2 \tau_{kn}^2} \left| \sum_u \mathscr{D}_{k0}^{(2)}(\Omega_u)C_u^{(0)}C_u^{(n)} \right|^2 \qquad (6)$$

with

$$\tau_{kn} = [6D_\perp + k^2(D_\parallel - D_\perp) + \lambda_n]^{-1}; \quad k = 0, \pm 1, \pm 2 \qquad (7)$$

$\mathscr{D}_{k0}^{(2)}(\Omega_u)$ is an element of the second-rank Wigner matrix, Ω_u being the Euler angles defining for a conformer u, the orientation of the principal axes of a magnetic tensor in a molecular frame. Here, one axis of this frame is the Δ_M axis, another one being the perpendicular to the mean plane of the all-$trans$ conformer of the surfactant. λ_n and $C^{(n)}$ are the eigenvalues and eigenvectors of the symmetrized transition matrix

$$M_{ij} = (1 - 2\delta_{ij})(K_{ij}K_{ji})^{1/2} \qquad (8)$$

with $K_{ij} = \sum_{j \neq i} K_{ij}$, K_{ij} being the transition rate from conformer i to conformers j. The transition matrix is constructed from the vectors W_1, W_2 and W_3, the former being related by $W_1 = W_2(1 - P_1)/2P_1$.

Liquid-crystalline Phases

In liquid-crystalline phases the relaxation rates are the sum of non-collective (reorientation and internal motions) and collective [order director fluctuations (ODF)] contributions. For smectic phases, the ODF contribution is proportional to $\bar{P}_2^2 \omega^{-1}$,[23,24] $\bar{P}_2$ being the molecular order parameter of rank 2. It will be shown that, under our experimental conditions, the ODF contribution to the longitudinal relaxation is negligibly small.

For a director oriented parallel to the magnetic field $(\Psi = 0)$, the spectral densities for non-collective motions are[25]

$$J_{km}(\omega, 0) = \sum_n 2\kappa(k, m) \frac{\tau_{km}}{1 + \omega^2 \tau_{km}^2}$$

$$\times \left| \sum_u \mathscr{D}_{k0}^{(2)}(\Omega_u)C_u^{(0)}C_u^{(n)} \right|^2 + 2\delta_{m0} \bar{P}_2^2$$

$$\times \sum_n \frac{\lambda_n}{\lambda_n^2 + \omega^2} \left| \sum_u \mathscr{D}_{00}^{(2)}(\Omega_u)C_u^{(0)}C_u^{(n)} \right|^2 \qquad (9)$$

with

$$\kappa(k, m) = \langle |\mathscr{D}_{km}^{(2)}(\Omega_{MD})|^2 \rangle - |\langle \mathscr{D}_{km}^{(2)}(\Omega_{MD}) \rangle|^2 \delta_{k0} \delta_{m0} \qquad (10)$$

Ω_{MD} being the Euler angles between the molecular and director frames. The matrix elements $\kappa(k, m)$ are taken from ref. 26 for the strong-collision model of diffusion. They depend on the second- and fourth-rank order parameters. $\bar{P}_4$ is derived from $\bar{P}_2$ obtained experimentally, assuming a restoring potential of the form $\exp[-(u/kT)\bar{P}_2]$.

For oriented hexagonal and lamellar phases, $\Psi = 0$ and $90°$, respectively. In the latter case, the spectral densities become[26]

$$J_{k0}(\omega, 90°) = \tfrac{1}{4}J_{k0}(\omega, 0) + \tfrac{3}{4}J_{k2}(\omega, 0) \qquad (11a)$$

$$J_{k1}(\omega, 90°) = \tfrac{1}{2}[J_{k1}(\omega, 0) + J_{k2}(\omega, 0)] \qquad (11b)$$

$$J_{k2}(\omega, 90°) = \tfrac{3}{8}J_{k0}(\omega, 0) + \tfrac{1}{2}J_{k1}(\omega, 0) + \tfrac{1}{8}J_{k2}(\omega, 0) \qquad (11c)$$

The expressions for the ^{13}C and ^{2}H longitudinal relaxation rates are

$$(T_1^{-1})_{13C} = \tfrac{1}{4}(\gamma_C\gamma_H\hbar)^2 r_{CH}^{-6} \sum_{k=-2}^{2} [J_{k0}(\omega_H - \omega_C)$$
$$+ 3J_{k1}(\omega_C) + 6J_{k2}(\omega_H + \omega_C)] \qquad (12)$$

$$(T_1^{-1})_{2H} = \tfrac{3}{4}\pi^2\chi_q^2 \sum_{k=-2}^{2} [J_{k1}(\omega) + 4J_{k2}(2\omega)] \qquad (13)$$

with $r_{CH} = 1.1$ Å and $\chi_q = 185$ kHz.

In the following, it is assumed that the lifetime of the conformers $\tau_u = (\sum_{j \neq i} K_{ij})^{-1}$ is short compared to the reorientation correlation times of the surfactant. One can therefore consider effective molecular order parameters S_{11}, S_{22} and S_{33} averaged over all the conformations, instead of a particular set for each individual conformer. This problem has been discussed, for instance, in ref. 27. S_{33} is the largest order parameter in absolute value and is associated with the Δ_M axis defined above. In the calculation of relaxation rates or splittings, $\bar{P}_2$ is positive and taken equal to S_{33} (lamellar phase) or $-2S_{33}$ (hexagonal phase) and therefore defined with respect to the normal to the interface of the aggregate with water.

The molecular and local (C—H bonds) order parameters are obtained from the chemical shift anisotropy (CSA) and/or from the quadrupolar or dipolar splittings. For the ^{31}P of octylphosphate, the CSA is given by

$$\overline{\Delta\sigma} = \tfrac{3}{4}\bar{\sigma}_{\parallel}[(3l_{3z}^2 - 1)S_{33} + (l_{1z}^2 - l_{2z}^2)(S_{11} - S_{22})] \qquad (14)$$

$\bar{\sigma}$ being the averaged chemical shielding tensor. A similar expression holds for the quadrupolar or dipolar splittings Δv independent of the surfactant conformation, replacing the factor of eqn. (14) by $K = \tfrac{3}{8}\chi_q(3\cos^2\Psi - 1)$ or $-(\gamma_I\gamma_S\hbar/4\pi)r_{IS}^{-3}(3\cos^2\Psi - 1)$. For the flexible residue of the surfactant, these splittings are given by

$$\Delta v = K[\langle 3l_{3z}^2 - 1\rangle S_{33} + \langle l_{1z}^2 - l_{2z}^2\rangle(S_{11} - S_{22})] \qquad (15)$$

In the two above equations, $l_{1,2,3z}$ denotes a direction cosine of the symmetry or quasi-symmetry axis Z of a magnetic tensor in the $\Delta_{1,2,3}$ frame of the molecular ordering tensor S.

In eqn. (15) the terms within angled brackets are weighted by the conformer populations calculated by means of eqn. (5). In the expressions of spectral densities, these populations correspond to the square of the eigenvector $C^{(0)}$ of the transition matrix [eqn. (8)]. For the calculation of the splittings and relaxation rates one has to define the frame of the effective ordering tensor S. The method that we use is derived from the work of Samulski and Dong.[28] These authors assume that the principal axes of the ordering tensor coincide with those of the inertial tensor, the latter being calculated for each of the conformers. The long axis of the inertial tensor is taken as the symmetry axis of a cylinder in which the mesogen is confined. This rather complicated procedure, which has been successfully applied to the calculation of the ^{2}H splittings in thermotropic[28] and more recently in lyotropic[20] liquid crystals, seems justified if the timescale of internal motions is not much smaller than the reorientation correlation times. In the present study it is more appropriate

to determine the $\Delta_{1,2,3}$ frame by computing the inertial tensor as an average over all the accessible conformers. The validity of this approximation is supported by the fact that the orientation of the long axis Δ_3 coincides within a few degrees with the one of the Δ_M axis, which optimizes the fits between the computed and observed relaxation rates or splittings. The equivalent ellipsoid of the surfactant may be derived from the calculation of the effective inertial tensor. The elongation and asymmetry parameters of the equivalent ellipsoid $\rho = A_3/\tfrac{1}{2}(A_1 + A_2)$ and $\eta = (A_1 - A_2)/A_3$ give at least an indication of the anisotropy and axiality expected for the surfactant reorientation within the aggregate. The asymmetry of the S tensor being very difficult to estimate accurately, we have taken $S_{11} - S_{22} = \eta S_{33}$ in some of our calculations of the dipolar or quadrupolar splittings.

As pointed out above, the conformation and dynamics of the micellized surfactants are obtained only from the frequency dependence of the relaxation rates, the chemical shifts and J-coupling being practically of no help. For liquid crystals, the conformational information is contained in the dipolar or quadrupolar splittings, and the relaxation may be useful in order to make a discrimination between different sets of parameters giving nearly equivalent solutions. Our approach in the interpretation of the experimental data on micelles and liquid crystals may be summarized as follows.

The most critical set of parameters is the probability distribution of trans conformers along the chain. Three models have been considered to fit the experimental data. (I) The conformational changes of the surfactant occur by rotation about one bond at a time. The probabilities p_1 are adjusted for the successive C—C bonds, starting from the polar head. (II) These changes involve one, two or three bonds at a time. A model illustrating this, proposed by Wittebort and Szabo,[22] has recently been applied by Dong[29] to the relaxation in liquid crystals. (III) The molecule is confined in a cylinder whose symmetry axis is the long axis of the inertial tensor. The trans probabilities are all initially fixed to the standard 0.55–0.6 value and the single adjustable parameter that governs the conformer populations is the radius of the cylinder. These probabilities are modified by removing the conformers extending out of this volume.

For models I and III, the conformers containing at least one $G^+ G^-$ form are also eliminated. This reduces appreciably the number of accessible conformers. If necessary, a further reduction is operated by removing the conformers whose probabilities are less than a threshold, generally fixed at 10^{-4}. The trans probabilities being fixed, the timescale of conformational changes is determined by the probabilities per unit time of the gauche → trans transitions (W_2), which are kept constant or nearly constant along the chain. Lastly, the reorientation correlations times $\tau_\perp$ and $\tau_\parallel$ are obtained from the frequency dependence of the relaxation rates.

Results and Discussion

OCTP Micellar Solutions

The micellar aqueous solutions of OCTP have been investigated by ^{1}H and ^{13}C relaxation at different magnetic field strengths. The ^{1}H longitudinal relaxation experiments have been performed at eight frequencies in the 6–500 MHz range to determine the slow correlation time τ_s by means of the two-step model, and have an estimate of the concentration dependence of the micellar size.[12] Here we report the results obtained with a 0.5 mol dm^{-3} solution of OCTP, which have been reinterpreted using the rotational jump model. Knowing $\tau_s = \tau_\perp$ from proton relaxation experiments, the parameters P_1, W_2 and $\tau_\parallel$ are adjusted to fit the ^{13}C relaxation rates at 22.6, 75 and 125 MHz. The best agreement (Fig. 2) is

achieved, assuming that the conformational changes involve one bond at a time (model I of the previous section), with p_1 between 0.8 and 0.9 (Table 1). There is more reorientational freedom about the O—C_1 bond ($p_1 = 0.35$) which is probably related to the large area per polar head, which is 80 Å^2, as against 34 and 37 Å^2 in the lamellar and hexagonal phases of the same surfactant.

The order parameters of the C—H bonds have been calculated with respect to a molecular axis Δ_M, making an angle $\theta = 35°$ with the O—C_1 bond and which nearly coincides with the mean axis of the fully extended conformer of the surfactant. The order parameters obtained for the jump model are in quite unexpected agreement with those derived from the two-step models. Eqn. (1) indeed holds for isotropic motion, whereas the reorientation of the OCTP is highly anisotropic with $\tau_\perp/\tau_\parallel = 18$. Fig. 3, giving the dependence of the elongation parameter p upon p_1, shows that the high probabilities found for the *trans* rotamer along the oxyalkyl chain are consistent with the anisotropy of the surfactant motion, evidenced by relaxation experiments at several fre-
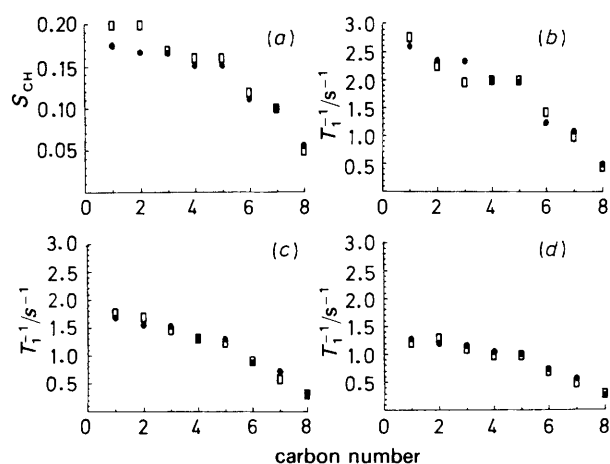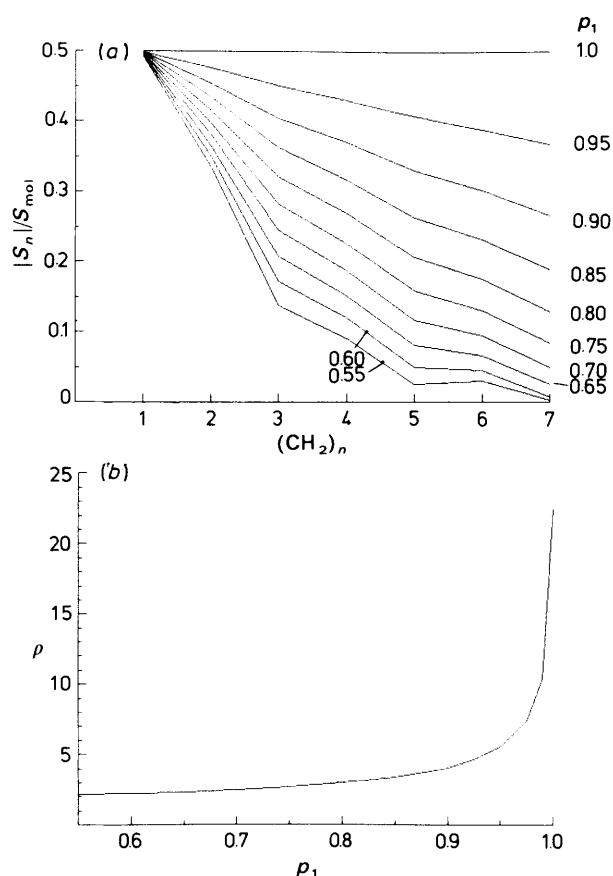

Fig.3 (a) Computed dependence of the order parameters of CH bonds with respect to the Δ_M molecular axis, on the *trans* probabilities about C—C bonds in an octyl phosphate chain, assuming that P—O—C_1—C_2 is *trans*. S_{mol} denotes the order parameter of Δ_M with respect to the local director of the aggregate. (b) Elongation parameter of the equivalent ellipsoid of the surfactant whose long axis is Δ_M

Fig. 2 (a) Order parameters of C—H bonds in 0.5 mol dm^{-3} micellar solutions of OCTP, calculated from the frequency dependence of the ^{13}C relaxation rates: □, two-step model; ●, rotational jump model. (b)–(d) Frequency dependence of the ^{13}C relaxation rates: □, experimental and ●, computed values (Table 1) ν/MHz: (b) 22.6, (c) 75.5, (d) 125.5

quencies. According to recent molecular dynamics simulations on micelles[6-9] the probabilities p_1 would only increase from 0.55–0.6 to *ca.* 0.7 upon aggregation. Comparing the order parameter profiles of Fig. 2 and 3, it is clear that in this case, the decrease of $|S_{CH}|$ along the chain would be much steeper than actually observed.

Table 1 Conformational and dynamical parameters of OCTP in mesophases and micellar solution (W_2 in 10^{10} s^{-1})

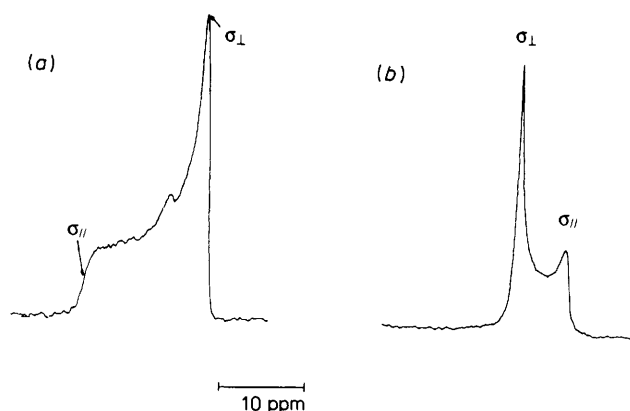|		lyotropic lamellar ($X_w = 0.85$)						
	P----O$_1$----C$_1$----C$_2$----C$_3$----C$_4$----C$_5$----C$_6$----C$_7$----C$_8$							
P_T	1.0	0.90	0.90	0.90	0.90	0.90	0.80	
$W_2(G \rightarrow T)$	—	3	3	3	3	3	3	
	$\bar{P}_2 = 0.345$, $\tau_\perp = 3.5 \times 10^{-10}$, $\tau_\parallel = 2.2 \times 10^{-11}$ s							
		thermotropic lammellar[13]						
	P----O$_1$----C$_1$----C$_2$----C$_3$----C$_4$----C$_5$----C$_6$----C$_7$----C$_8$							
P_T	1.0	0.80	0.80	0.80	0.90	0.85	0.80	
$W_2(G \rightarrow T)$	—	3	3	3	3	3	3	
	$\bar{P}_2 = 0.330$, $\tau_\perp = 3.0 \times 10^{-10}$ s, 2.0×10^{-11} s							
		lyotropic hexagonal ($X_w = 0.6$)						
	P----O$_1$----C$_1$----C$_2$----C$_3$----C$_4$----C$_5$----C$_6$----C$_7$----C$_8$							
P_T	1.0	0.87	0.90	0.90	0.85	0.85	0.75	
$W_2(G \rightarrow T)$	—	3	3	3	3	3	4	
	$\bar{P}_2 = -2S_{33} = 0.390$, $\tau_\perp = 2.0 \times 10^{-10}$ s, $\tau_\parallel = 1.2 \times 10^{-11}$ s							
		0.5 mol dm^{-3} micellar solution[12]						
	P----O$_1$----C$_1$----C$_2$----C$_3$----C$_4$----C$_5$----C$_6$----C$_7$----C$_8$							
P_T	0.35	0.90	0.90	0.90	0.90	0.90	0.80	
$W_2(G \rightarrow T)$	—	3	3	4	4	4	4	
	$\tau_\perp = 1.5 \times 10^{-9}$ s, $\tau_\parallel = 8.3 \times 10^{-11}$ s							

Fig. 4 ^{31}P spectra (121.6 MHz) of the OCTP–H_2O mesophases. The shape of the hexagonal phase signal is due to a planar orientation distribution of the director: (a) lamellar phase, (b) hexagonal phase

Fig. 6 Experimental (□) and computed (●) ^{13}C dipolar splittings and relaxation rates in the OCTP–H_2O lamellar phase (Table 1). v/MHz: (b) 22.6, (c) 75.5, (d) 125.5

OCTP Lamellar and Hexagonal Phases

The molecular order parameter $\bar{P}_2$ or S_{33} of the octylphosphate anion has been derived from the ^{31}P chemical shift anisotropy (CSA) and the ^{31}P–^{13}C dipolar splitting (Fig. 4 and 5), taking $\sigma_{xx} = -63$ ppm, $\sigma_{yy} = -10$ ppm and $\sigma_{zz} = 73$ ppm for the ^{31}P chemical shielding tensor[30] and 2.58 Å for the distance of the phosphorus atom from C_1. The σ tensor being averaged by the rotation of the phosphate group about the O—C_1 bond and the proton exchange about the oxygens, the CSA becomes -67.5 ppm for $\bar{P}_2 = 1$. Assuming that the molecular ordering tensor is axially symmetric about the Δ_M axis, one obtains $\theta = 32°$, $\bar{P}_2 = S_{33} = 0.345$ and $\theta = 31°$, $\bar{P}_2 = -2S_{33} = 0.366$ for the lamellar ($X_w = 0.85$) and hexagonal ($X_w = 0.60$) phases, respectively, X_w being the OCTP weight fraction and θ the angle between Δ_M and O—C_1. The order parameters of CH bonds have been obtained from the ^{13}C–^1H dipolar splittings determined by heteronuclear J-resolved two-dimensional NMR.[11,13]

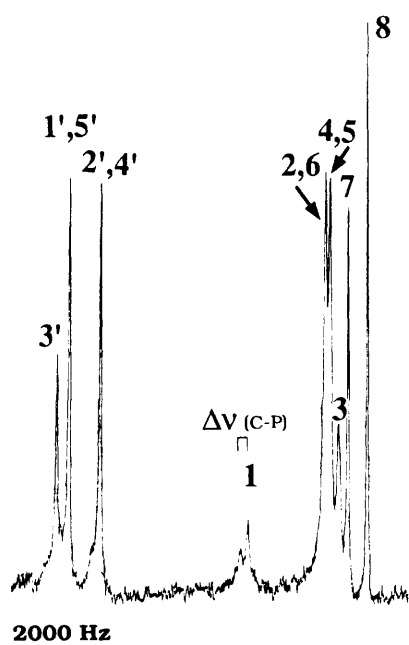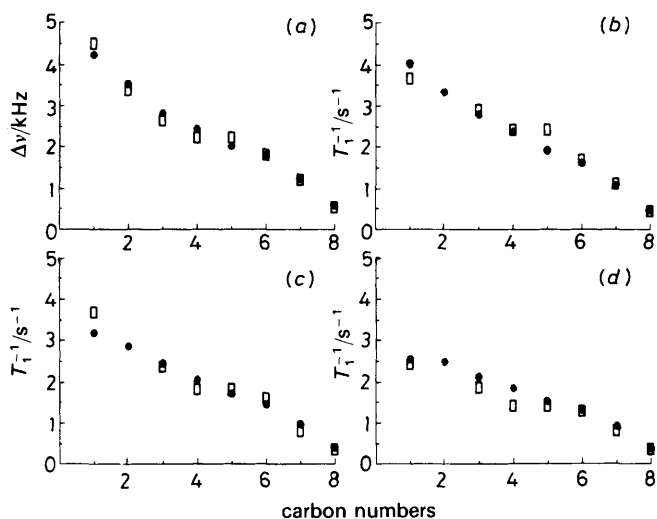The three models quoted in the preceding section have been tested on the OCTP lyotropic and thermotropic lamellar phases. All the attempts to fit the dipolar splittings or relaxation rates, assuming that the conformational changes involve several bonds at a time (model II) were unsuccessful. The model of confinement of OCTP in a cylinder whose axis is Δ_M or Δ_3 (model (III) has also been tentatively applied to the thermotropic and lyotropic mesophases of OCTP (Tables 2 and 3). An approximate fit of the splittings in the OCTP–H_2O lamellar phase has been achieved for a cylinder radius of 4.2 Å. The same model gave better agreement with experiment for the thermotropic lamellar phase of OCTP,[13] but the computed density across the hydrocarbon bilayer was far from being uniform as required. Furthermore, in all cases the variation of the computed relaxation rates upon the carbon position is too small, and their frequency dependences are not correctly reproduced. For this model indeed, the large-amplitude motions responsible of the decrease of the relaxation rates along the chain are virtually precluded.

Assuming, on the other hand, that the conformational changes occur about one bond at a time (model I), both the splittings and relaxation rates can be fitted with the same set of conformer probabilities as shown in Fig. 6–8 and Table 1. This model, which also gives a smoother density profile than model III,[13] has therefore been adopted in our recent studies on flexible molecules.[10,11]

The conformational and dynamical parameters of octylphosphate in different phases are compared in Table 1. The

Fig. 5 ^{13}C spectrum (75.5 MHz) of the octylphosphate anion in the oriented OCTP–H_2O hexagonal phase

Table 2 ^{13}C–^1H dipolar splittings (in kHz) for octylphosphate, thermotropic OCTP lamellar phase[13]

atom	experimental	calculated[a] model 1 (Table 1)	calculated[a] model III ($R = 3.2$ Å)
C1	3.850	3.742	3.742
C2	2.970	3.063	3.027
C3	2.400	2.413	2.459
C4	2.100	2.173	2.499
C5	2.100	1.965	2.192
C6	1.800	1.776	1.758
C7	1.150	1.278	1.320
C8	0.300	0.291	—

[a] Model I: The probabilities p_1 of the *trans* rotamer are taken as adjustable parameters. Model III: p_1 is initially fixed to 0.6 for all the C—C bonds and the surfactant is confined in a cylinder of adjustable radius R whose axis is the long axis of the equivalent ellipsoid.

Table 3 $^{13}C-^{1}H$ dipolar splittings (in kHz) for octylphosphate, lyotropic OCTP–H_2O lamellar phase
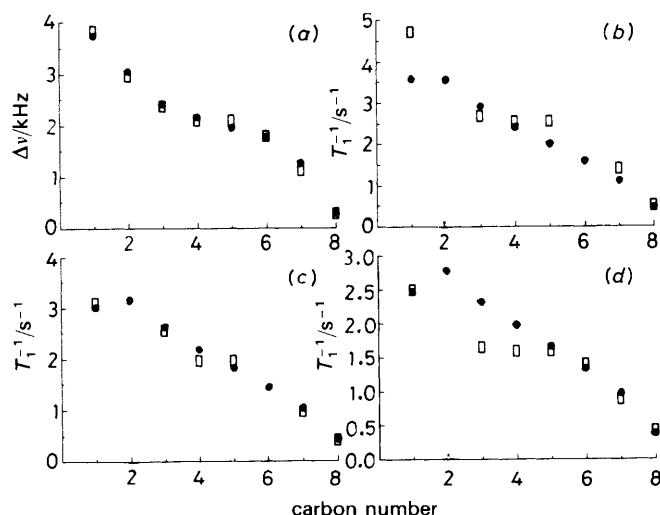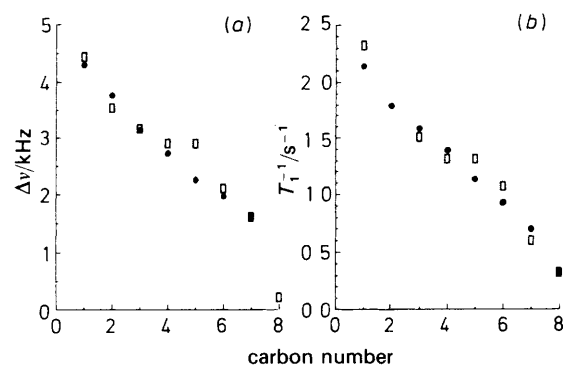
atom	experimental	calculated[a]	
		model I (Table 1)	model III ($R = 4.25$ Å)
C1	4.532	4.229	4.240
C2	3.418	3.535	3.776
C3	2.656	2.826	3.258
C4	2.246	2.463	3.013
C5	2.246	2.030	2.209
C6	1.856	1.800	1.684
C7	1.230	1.221	0.853
C8	0.572	0.592	—

[a] See Table 2.

Fig. 8 Experimental (□) and computed (●) ^{13}C dipolar splittings (a) and relaxation rates (b) at 75.5 MHz in the OCTP–H_2O hexagonal phase (Table 1)

most striking features are the high probabilities of the *trans* rotamer along the chain of OCTP in these organized systems ($0.8 < p_1 < 1$). It is also seen that the probabilities per unit time, W_2, are nearly constant along the chain and in the (3–4) $\times 10^{10}$ s^{-1} range. The lifetimes of the conformers are of the order of 10 ps or less, with the exception of the all-*trans* form, and therefore shorter than the reorientation correlation times of the surfactant. It is therefore justified to consider an average inertial tensor and the corresponding equivalent ellipsoid of the surfactant. The values of the relevant asymmetry and elongation parameters found in the $0.05 \leqslant \eta \leqslant 0.12$ and $4 \leqslant \rho \leqslant 6$ ranges account for the quasi-

axiality as well as for the strong anisotropy of the rotational diffusion tensor ($\tau_\perp/\tau_\parallel \approx 15$). The long axis Δ_3 of the equivalent ellipsoid makes an angle of 30–40° with the O—C_1 bond in the plane of the OCTP all-*trans* conformer and coincides within a few degrees with the Δ_M molecular axis.

From the frequency dependence of the ^{13}C relaxation rates, one finds $\tau_\perp$ in the 0.3–0.4 ns range for the OCTP–H_2O thermotropic and lyotropic lamellar phases. For the hexagonal phase, $\tau_\perp$ is shorter (*ca.* 0.2 ns). This larger reorientational freedom is possibly related to a larger area per polar head (37 Å^2 against 30–34 Å^2 for the lamellar phases). Table 1 shows that there is no important influence of the nature of the phase on the rotamer populations in the oxyalkyl residue. In particular, the dynamics and conformer populations of octylphosphate are nearly the same in the thermotropic and lyotropic lamellar phases. The differences between the OCTP/H_2O mesophases are more apparent for the relative order parameters of C—H bonds derived from the $^{13}C-^{1}H$ splittings (Fig. 9). The octylphosphate appears to be slightly more flexible in the lamellar than in the hexagonal phase; for the latter, the volume available for a conformational changes decreases from the polar head to the terminal methyl group.

Table 4 Deuteron quadrupolar splittings (in kHz) for octanoate, lyotropic OCTP–H_2O lamellar phase

atom	experimental	calculated[a]	
		model I (Table 5)	model III ($R = 3.5$ Å)
C1	16.624	17.000	14.660
C2	10.994	11.440	12.520
C3	10.826	10.900	10.980
C4	8.827	8.703	10.340
C5	7.484	7.505	8.100
C6	5.096	5.153	5.178
C7	1.472	1.114	—

[a] See Table 2.

Deuteriated Octanoic Acid Probe in OCTP–H_2O Mesophases

To estimate the ODF contribution to our longitudinal relaxation experiments, it has been necessary to extend the measurements to lower frequencies. We have therefore performed deuteron T_1 measurements at 13.4 MHz on an octanoic acid probe diluted in the OCTP–H_2O mesophases. Within experi-
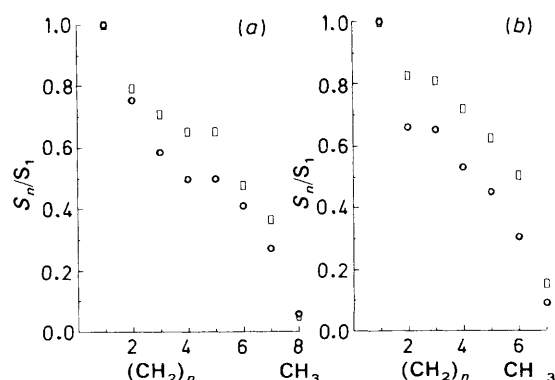

Fig. 7 Experimental (□) and computed (●) ^{13}C dipolar splittings and relaxation rates in the OCTP thermotropic ionic lamellar phase (Table 1). ν/MHz: (b) 25.2, (c) 75.5, (d) 125

Fig. 9 Relative order parameters of C—H bonds of octylphosphate (a) and octanoate (b) in OCTP–H_2O lamellar (○) and hexagonal (□) phases
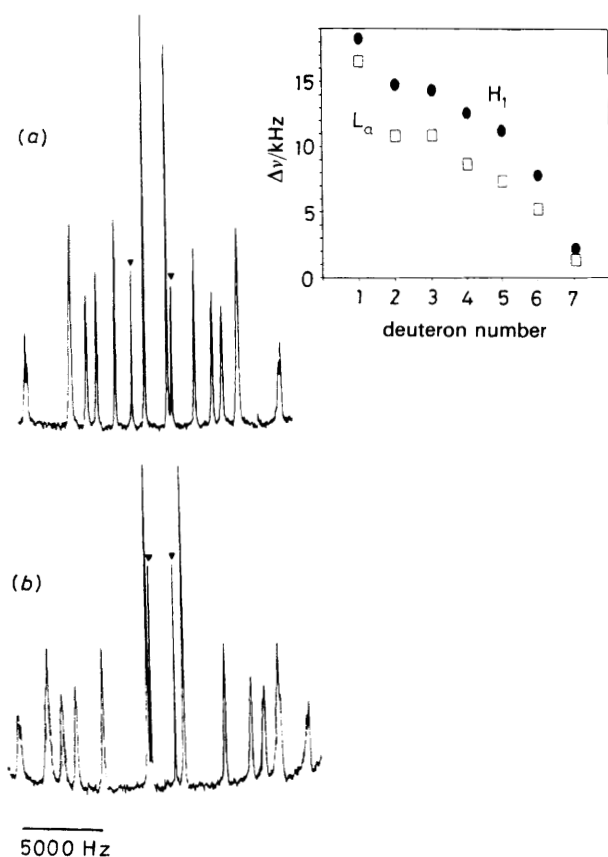
Fig. 10 Deuteron spectra of octanoate in oriented OCTP–H$_2$O lamellar (L$_\alpha$) (a) and hexagonal (H$_1$) (b) phases. The lines corresponding to the exchangeable deuteron from the carboxyl group of the octanoic acid probe are marked by ▼. The total widths of spectra (a) and (b) are similar owing to the orientation of the director which is perpendicular and parallel to the magnetic field in oriented lamellar and hexagonal phases, respectively

Fig. 11 Experimental (□) and computed (○) octanoate deuteron splittings and relaxation rates in OCTP–H$_2$O lamellar [(c), (d)] and hexagonal [(a), (b)] phases (Table 5)

and two C—H bonds but not that of the chain, remaining on average the same as for the all-*trans* conformer. On the other hand, taking the probabilities of the *trans* conformer as adjustable parameters without explicitly introducing the constraints due to confinement yields relaxation rates and quadrupolar splittings in good agreement with experiment (Fig. 11). The fit of the splittings has been substantially improved by taking $S_{11} - S_{22} = \eta S_{33}$, η being the asymmetry parameter of the equivalent molecular ellipsoid. There are some similarities between the behaviour of octanoate in the OCTP–H$_2$O mesophases and of the host surfactant molecules (Tables 1 and 5). The timescales of internal and overall motions are about the same as for the octylphosphate, the reorientation also being very anisotropic and faster in the hexagonal phase than in the lamellar one. On the other hand, the molecular order parameter is smaller for octanoate than for octylphosphate, and the former appears to be more flexible. The difference between the flexibilities of octanoate evidenced by the order parameters of C—H bonds in the lamellar and hexagonal phases is more significant than for octylphosphate (Fig. 9).

The expressions of the spectral density for an isotropic solution and a liquid crystal, in the absence of a significant contribution of collective motions [eqn. (6) and (9)] differ by the second term of eqn. (9) and by the factor $\kappa(k, m)$. The former vanishes, whereas the latter tends towards 1/5 when $\bar{P}_2$ approaches zero. Using the parameters obtained for the octanoate in the lamellar phase, we have examined the influence of the molecular order on the longitudinal relaxation. Fig. 12 shows that, at least in extreme narrowing conditions, the effect of the molecular ordering on the relaxation is of the

mental error, the relaxation rates were the same at this frequency and at 46 MHz. It can therefore be considered that there is no significant ODF contribution under our experimental conditions, probably owing to the rather low molecular ordering, $\bar{P}_2$ being of the order of 0.25–0.3 and 0.35–0.40 for the octanoate and octylphosphate, respectively.

In oriented samples, the octanoate probe gives well resolved deuteron spectra (Fig. 10). It has again been observed that the model of confinement in a cylinder provides an approximate fit of the splittings (Table 4) but does not account for the observed relaxation rates. This confinement inhibits the large-amplitude motions, and also results in an important enhancement of the contribution of the $G^+ - T - G^-$ local forms (kinks) which change the orientation of one C—C
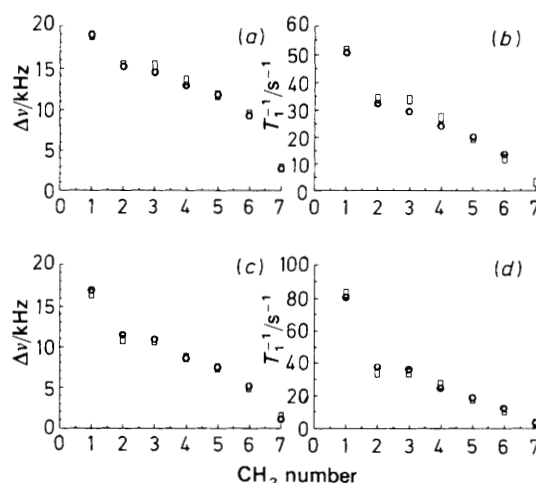
Table 5 Perdeuteriated octanoic acid probe in OCTP–H$_2$O mesophases

<div style="text-align:center">

lamellar phase, 300 K

C$_0$----C$_1$----C$_2$----C$_3$----C$_4$----C$_5$----C$_6$----C$_7$

P_T 0.70   0.95   0.80   0.85   0.68

$W_2(G \to T)$ 3×10^{10} s^{-1}

$\tau_\perp = 5.5 \times 10^{-10}$ s , $\tau_\parallel = 4.0 \times 10^{-11}$ s

$\bar{P}_2 = S_{33} = 0.26,\ S_{11} = -0.115,\ S_{22} = -0.145$

hexagonal phase, 300 K

C$_0$----C$_1$----C$_2$----C$_3$----C$_4$----C$_5$----C$_6$----C$_7$

P_T 0.82   0.95   0.90   0.90   0.80

$W_2(G \to T)$ 4×10^{10} s^{-1}

$\tau_\perp = 4.0 \times 10^{-10}$ s, $\tau_\parallel = 2.7 \times 10^{-11}$ s

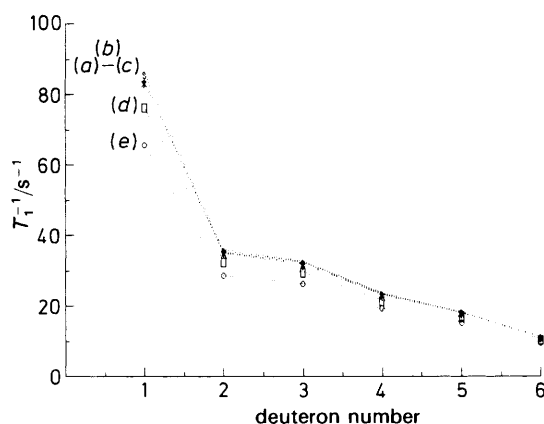$\bar{P}_2 = -2S_{33} = -0.284,\ S_{11} = 0.062,\ S_{22} = 0.080$

</div>

Fig. 12 Computed dependence of the deuteron longitudinal relaxation on the molecular order parameter $\bar{P}_2$, without ODF contribution and in extreme narrowing conditions. The parameters are taken from Table 5. $\bar{P}_2$: (a) 0, (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8

order of experimental uncertainties or smaller for $\bar{P}_2 \leqslant 0.4$ and rapidly attenuated with the distance to the polar head. Eqn. (6) (isotropic solution) and eqn. (9) (liquid crystal) therefore give nearly the same results in this case, an observation which could justify some simplifications in the calculation of relaxation rates.

Conclusion

This study, dealing with comparatively small surfactants in micellar solution and lyotropic liquid crystals, provides some general information on the conformations and dynamical behaviour of flexible molecules in organized aggregates. Most of the results have been shown to be valid for higher homologues.[10]

The aggregated surfactants behave as quite rigid entities, with *trans* rotamer probabilities between 0.80 and 0.95, decreasing slowly from the polar head. As a consequence of their average elongated shape, they undergo a very anisotropic reorientation ($10 \leqslant \tau_\perp/\tau_\parallel \leqslant 20$), a point generally ignored in relaxation studies of micelles. The longitudinal relaxation rates and dipolar or quadrupolar splittings can be accurately fitted, assuming that the conformational changes occur by rotational jumps about one bond at a time, the frequency per unit time of the *gauche → trans* transitions being

typically 3×10^{10} s^{-1} and nearly independent of the C—C bond position.

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