Nitroxide-Labeled Ruthenium(II)--Polypyridyl Complexes as EPR Probes To Study Organized Systems. 1. Micellar Solutions and Micellization of Sulfon Alkyl Sulfates

M. Francesca Ottaviani,1 Naresh D. Ghatli,1 and Nicholas J. Turro*2

Department of Chemistry, Columbia University, New York, New York 10027, and Department of Chemistry, University of Florence, 50121, Firenze, Italy (Received: January 28, 1992; In Final Form: April 3, 1992)

EPR probes that structurally resemble ruthenium(II) trisphenanthroline complexes have been utilized to monitor the binding and dynamics of these complexes with different anionic detergents in aqueous solutions. The results and interpretation of these EPR experiments are compared with the results and interpretations of photophysical studies involving interactions of ruthenium(II)--trisphenanthroline complexes and micelles. The EPR spectra have been evaluated in terms of both the hyperfine splitting (a polarity-sensitive parameter) and the rotational correlation time (a dynamics parameter). All experimentally recorded spectra could be successfully simulated as a single component or as the superposition of two components. Stronger binding of these probes is observed as the chain length of the detergent increases. For the same chain length, stronger interactions are observed for micelles containing a sulfate head group compared to a carboxylate group. The rotational diffusion coefficients obtained are found to correlate extremely well with the translational diffusion coefficients obtained in photophysical studies. Previously reported observations of the formation of premicellar aggregates at concentrations below the critical micelle concentration (cmc) have also been corroborated in this study.

Introduction

Ruthenium--polypyridyl complexes have been extensively used for investigations of polyamionic microheterogeneous structures such as alkyl sulfate micelles,1 polymer solutions,2 DNA,3 and starburst dendrimers (SBD).4 The most commonly used polypyridyl ligands are 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen). Previous studies have primarily involved photochemical measurements exploiting the well-understood luminescence properties of the Ru(II) complexes;5 both steady-state and time-resolved photoluminescence measurements using these complexes with different cationic quenchers have provided an insight into the cooperative phenomena occurring in these microheterogeneous systems, such as micellization6 or changes in surface morphology for the dendrimer systems.4

In experiments employing a probe to report on its environment it must always be considered that the probe may perturb its surroundings and therefore result in erroneous conclusions regarding the properties of the regions it is probing. The size of these probe molecules (about 18 Å diameter for Ru(phen)3+) is comparable with the size of some of the systems that have been studied (such as sodium alkyl sulfate micelles with seven or eight carbon atoms in the chain of the detergent or starburst dendrimers of generations 1 and 2). The oppositely charged nature of the carbon atoms in the chain of the detergent or starburst dendrimers studied (such as sodium alkyl sulfate micelles with seven or eight

This expression is essentially the same as \( r = 1.5w \).

(23) Rex, G. C.; Schlick, S. Polymer, in press.
rate constants to the Sano–Tachiya model\textsuperscript{8} for diffusion leads to an evaluation of the diffusion coefficients of these probes on the micelles.\textsuperscript{46} These coefficients are found to decrease progressively as the size of the micelle increases. A comparison of sodium dodecyl sulfate (SDS, C\textsubscript{12}) micelles and sodium laurate micelles (C\textsubscript{12}H\textsubscript{25}COONa, NaL) reveals that for these two micelles of similar size and charge the quenching rate constant is more than twice as large in NaL relative to SDS micelles.\textsuperscript{46}

The accepted paradigm for the interaction of ruthenium-polypyridyl complexes with anionic micelles segregates the regions where the Ru probe may be found in at least three conceptually distinct zones (Figure 1).\textsuperscript{9} (1) The probe may be unbound and “free” in the bulk solution; (2) the probe may be associated with the micelle by electrostatic binding. This may be either territorial binding in the Gouy–Chapman layer where diffusional motion is relatively unrestricted or it may be ionic site binding at the micellar surface in the electrical double layer. (3) Finally, the complex may be surface bound where both electrostatic and hydrophobic attractions between the ligand and the micellar core are responsible for the binding. Associated with each of these binding modes are different binding dynamics: (1) rate of association and dissociation of the complex with a given site; (2) diffusional and rotational motion within the site.

Two photophysical parameters which report on the different binding sites are the quantum yield of emission and the excited-state lifetime. It has been established that as a rule both of these parameters dramatically increase upon going from an aqueous environment to a more nonpolar environment.\textsuperscript{7} Conclusions regarding the mobility of the probe can be drawn from the quenching rate constants (\(k_q\)) which are obtainable from dynamic quenching studies of luminescence intensity or lifetimes.

It is of interest to compare the paradigm and conclusions obtained from the photophysical experiments with a totally independent form of spectroscopy and to determine if the conclusions derived from different methods were mutually supportive. Electron paramagnetic resonance (EPR) spectroscopy using stable nitroxides seemed excellent for these purposes, since the EPR probes cannot report not only on the polarity of their environment (reflected in changes in the hyperfine coupling constant \(a_N\) of the odd electron with the N atom) but also on the strength of the interaction of the probes with the microheterogeneous environment (reflected by a change in the correlation time parameter \(\tau\)).

To compare the photophysical results obtained using Ru-polypyridyl complexes, with those of EPR studies, it is necessary to synthesize probes that are structurally similar to the photophysical probes. This objective was achieved by synthesizing a 1,10-phenanthroline derivative (1, Chart I) to which a nitroxide moiety was covalently attached\textsuperscript{10} and which could be employed to synthesize the appropriate complexes. We refer to this ligand the phen-T which was utilized to synthesize the complexes Ru(bpy)\textsubscript{2}phen-T\textsuperscript{2+} (2, RuBT) and Ru(phen)\textsubscript{2}phen-T\textsuperscript{2+} (3, RuPT).

The interactions between the dichloride salts of the complexes 2 and 3 and alkyl sulfates were studied by means of EPR spectroscopy (Chart I).

Nitroxides are known to be good probes to study the properties of micellar surfaces.\textsuperscript{11} For instance, the positively charged nitroxide TempTMA\textsuperscript{+} [(4-trimethylamino)-2,2,6,6-tetramethylpipеридин-N-оксилю, 4] has been used to obtain direct information on the negatively charged micellar surface of sodium alkyl sulfates.\textsuperscript{12a}

The Ru(II)-polypyridyl complexes are believed to interact with the micellar surface by localizing in the hydrophobic core of the micelles.\textsuperscript{7} Furthermore, these complexes have been found to monitor the formation of small premicellar aggregates at concentrations below the critical micellar concentration (cmc)\textsuperscript{9} and to serve as a basis for measuring aggregation numbers.

The present paper presents an EPR analysis of the interactions of the complexes 2 and 3 with sodium alkyl sulfate micelles formed from detergent molecules possessing chain lengths from 7 to 14 carbons (indicated as C\textsubscript{7}–C\textsubscript{14}). For C\textsubscript{12} micelles the results obtained with both 2 and 3 are analyzed and compared with results obtained with the complexes interacting with sodium laurate micelles.

The EPR probes 2 and 3, which structurally (both sterically and electronically) resemble the corresponding photophysical probes Ru(bpy)\textsubscript{2}phen-T\textsuperscript{2+} and Ru(phen)\textsubscript{2}phen-T\textsuperscript{2+}, allow (1) a check of the reliability of the Ru complexes as photophysical probes for alkyl sulfate micelles; (2) an analysis of their interaction with the micellar surface; (3) a comparison of the information reported by the probes on the nature of the surfaces of differently sized micelles; (4) an elaboration of the mechanism of micellization.

The diffusional coefficients obtained by the analysis of the EPR spectra are related to the correlation time for reorientational motion (\(\tau\)) of the nitroxide radical at the micellar surface. The \(\tau\) parameters determined in this report are compared with the diffusion coefficients for translational motion which have been evaluated using the Sano–Tachiya model for diffusion\textsuperscript{13} from the photophysical measurements of the quenching rate constants of the ruthenium complexes.

**Analysis of the EPR Spectra**

As mentioned above, two main parameters were evaluated from the EPR spectra: (1) the isotropic hyperfine coupling constant (hfc = \(a_N\)); (2) the correlation time for the reorientation motion (\(\tau\)). The value of \(a_N\) is expected to decrease (lower polarity) and the value of \(\tau\) is expected to increase (slower rotational motion) when the probe binds to micellar aggregates and therefore provides

![Chart I](image-url)
an experimental parameter which monitors the formation of micelles or premicellar aggregates.

The evaluation of the correlation time for motion was performed by three different methods, as described in the literature for EPR spectra of nitroxides.11

**Method 1:** On the basis of the dependence of the line width on the nitrogen magnetic quantum number ($m_N$):

$$\Delta H(m_N) = A + Bm_N + Cm_N^2$$  \hspace{0.5cm} (1)

Two values of the correlation time for motion can be calculated from the $B$ and $C$ coefficients:

$$B = 0.103\omega_2[\Delta g\Delta A_N + 3(\delta g)(\delta A_N)]\tau_B[1 + \frac{1}{2}(1 + \omega_2^2\tau_B)]$$  \hspace{0.5cm} (2a)

$$C = 1.81 \times 10^4[(\Delta A_N)^2 + 3(\delta A_N)^2]\tau_C[1 - \frac{1}{2}(1 + \omega_N^2\tau_C^2) - \frac{1}{2}(1 + \omega_2^2\tau_C^2)]$$  \hspace{0.5cm} (2b)

Where

$$\Delta A_N = A_{N,zr} - \frac{1}{2}(A_{N,xx} + A_{N,yy})$$

$$\delta A_N = \frac{1}{2}(A_{N,xx} - A_{N,yy})$$

$$\Delta g = g_x - \frac{1}{2}(g_{xx} + g_{yy})$$

$$\delta g = \frac{1}{2}(g_{xx} - g_{yy})$$

$$\omega_N = (8.8 \times 10^9)A_N$$

$$\omega_2 = 5.97 \times 10^{10} \text{Hz}$$  \hspace{0.5cm} (3c)

$A_{N,zr}$, $A_{N,xx}$, and $A_{N,yy}$ are the principal components of the hyperfine coupling tensor $A_N$, and $g_{xx}$, $g_{yy}$ and $g_{zz}$ are the components of the $g$ tensor.

The result $\tau_B \neq \tau_C$ is assumed to be indicative of motional anisotropy of the probe. In the so-called fast motion conditions ($\tau < 10^8$ s), the $B$ and $C$ coefficients become proportional to $\tau_B$ and $\tau_C$, respectively, the values of which can be easily calculated, assuming the line widths of the three $m_N$ manifolds are known.12 A mean value of the correlation time has been also defined as

$$\tau = (\tau_B\tau_C)^{1/2}$$

**Method 2:** Instead of eqs 1–3, the following simplified formulas are often used for the evaluation of $\tau_B$ and $\tau_C$ in fast motion conditions:

$$\tau_B = B*\Delta H_0[\left(h_0/h_2\right)^{1/2} - \left(h_0/h_{-2}\right)^{1/2}]$$  \hspace{0.5cm} (4a)

$$\tau_C = C*\Delta H_0[\left(h_0/h_2\right)^{1/2} + \left(h_0/h_{-2}\right)^{1/2} - 2]$$  \hspace{0.5cm} (4b)

$$\tau = K*\Delta H_0[\left(h_0/h_2\right)^{1/2} - 1]$$  \hspace{0.5cm} (4c)

Where $h_i$ are the peak heights. The coefficients $B$, $C$, and $K$ depend on the nitroxide structure and, on the basis of eqs 3, are obviously correlated with the components of the $g$ and $A$ tensors. For nitroxides such as 2,2,6,6-tetramethylpiperidin-1-oxyl (Tempo) or 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (Tempol) it is usually assumed that $B = C = K = 6.5 \times 10^{-10}$.

**Method 3:** For a more accurate analysis of the line shape, the spectra have been fully simulated with the program developed by Schneider and Freed.13 The key parameters that were checked to improve the fitting between the experimental and calculated spectra were the $g$ and $A$ tensor components (evaluated by computing the spectra in frozen solution); the model assumed for the rotational diffusion motion (Brownian, free or jump); the principal components of the diffusion tensor (including the diffusion tilt angle with respect to the magnetic frame and taking due consideration of both the mean rate of diffusion and the anisotropy of motion); parameters related to an ordering potential; the intrinsic line width and the Heisenberg spin-exchange frequency.

When there are two signals contributing to the overall EPR spectrum (arising from probes in different mobility conditions which do not exchange with each other on the EPR time scale), each signal has been computed separately and then added to the other one at the correct relative intensity ratio to reproduce the experimental spectrum. A subtraction-addition procedure was performed on the spectrometer computer to define the spectrum line shapes more clearly.

**Experimental Section**

All the reported EPR spectra were recorded on a Bruker ESP300 interfaced to a computer with the ESP1600 software system. Temperature control was achieved with a Bruker ER 4111T unit. The line widths of the resonances were obtained from the spectrometer computer system.

Electrophoresis grade sodium dodecyl sulfate was obtained from Bio-Rad and used as received. Sodium laurate (Aldrich) was used as received. All other detergents were obtained from Lancaster Synthesis and recrystallized from ethanol/ether mixtures prior to use. All detergent solutions were prepared in deionized (Millipore) water. The values for the cmc's and aggregation numbers for all the surfactant solutions were obtained from ref 14, and those for the laurate micelles were obtained from ref 4b.

The synthesis of the ligands phen-T and the complexes RuPT and RuBT will be described elsewhere. The concentrations of the complexes were estimated spectrophotometrically; for RuBT it was assumed that its extinction coefficient at 449 nm was the same as Ru(bpy)$_2$phen$^+$, and for RuPT it was assumed that its extinction coefficient at 452 nm was the same as Ru(phen)$_2$.$^{24,36}$

The concentrations of the probes used were 0.1 mM in all of the experiments. Concentrated solutions of the detergent were prepared and diluted to volume to obtain the desired concentration of surfactant. The concentrations of the micelles [M] were evaluated according to the formula $[M] = (1\text{surf} - [\text{cmc}])/N$, where [surf] is the total surfactant concentration and $N$ is the aggregation number.

The spectra were computed using the program kindly provided by Schneider and Freed in ref 13.

**Results and Discussion**

**Analysis of Spectra Recorded above the Cmc.** In this series of experiments the concentration of the probe was kept fixed at 0.1 mM and the concentration of the micelles was kept fixed at 1 mM. This was done to minimize a distribution of probes which resulted in the occupancy of more than one radical in a given micelle, since multiple occupancy of micelles by probes would complicate the analysis of the EPR line shapes due to the effect of spin exchange.

Figure 2 shows the EPR spectra of RuPT in C12 (SDS) micelles at 283, 298, and 313 K. The main characteristic of these spectra is the line-width trend $\Delta H(1) < \Delta H(0) < \Delta H(-1)$ which is usually found for radicals associated with partially ordered systems such as liquid crystals or membranes.$^{11a,15}$ The integrated intensity for each of the three nitroxide lines was almost the same for all cases when the spectra were recorded at detergent concentrations larger than the cmc and above the Krafft point. (The
Krafft point is defined as the temperature at which the solubility of the detergent equals its cmc. At temperatures below this value, micellization is not achieved.) This result allows the use of either the peak line widths (eqs 1–3) or the peak heights (eqs 4a–c) to evaluate the correlation times of motion.

Radicals at the micellar surface can localize in a microscopically ordered environment, but we expect a micellar solution to be a macroscopically disordered system. Therefore the spectra were tentatively analyzed by considering the ordering potential (with a preexponential λ value ranging from 0.5 to 3.5) in the program by Schneider and Freed and then averaged over all the orientations as described in the literature. However such a procedure did not lead to an acceptable reproduction of the experimental line shape; on the contrary, the satisfactory fitting shown in Figure 2 (dashed line superimposed on the 298 and 313 K spectra) was obtained by including in the calculation a diffusion tilt angle (ranging from 70° to 90°) between the main directions of the diffusion and the magnetic tensor. The parameters used for the computation were

\[
\begin{align*}
S_{xx} &= 2.0097 \\
S_{yy} &= 2.0063 \\
S_{zz} &= 2.0035 \\
A_{xx} &= 6.2 \text{ G} \\
A_{yy} &= 6.8 \text{ G} \\
A_{zz} &= 36.8 \text{ G} \\
D_+ &= 1.0 \times 10^8 \text{ s}^{-1} \\
N &= 10 \text{ at 298 K} \\
D_- &= 1.7 \times 10^8 \text{ s}^{-1} \\
N &= 10 \text{ at 313 K} \quad \text{(where } N = D_1/D_\perp \text{)}
\end{align*}
\]

The Brownian model for the diffusional motion gave the best theoretical fit to the experimentally recorded spectra. A lower anisotropy of motion (\(N < 10\)) decreased the goodness of the fit as did values of \(N\) larger than 20 (a value of \(N = 4\) is required to simulate the spectrum of 3 in homogeneous aqueous solutions).

The line-shape modifications found at temperatures close to the Krafft point (282 K for C12 micelles) were indicative of the precipitation of the surfactant from the solution as evidenced by the precipitation of the surfactant from the solution as evidenced by the Krafft point.

The mean \(\tau_B\) value obtained from eqs 4 was 30% lower than the value obtained from eqs 3. However, by using a value of 8.5 \(\times 10^{-10}\) instead of 6.5 \(\times 10^{-10}\) (as the value of the constants \(B, C,\) and \(K\) in eqs 4), the calculations of the correlation time of motion from eqs 3 and 4 gave almost identical results for the spectra in different experimental conditions. Therefore, either eq 3 or 4 may be used in our case to monitor the trends in the variation of \(\tau_B\) and \(\tau_C\) for different experimental conditions. Similarly the \(\tau_B/\tau_C\) ratios for the different conditions were independent of the method of their evaluation. The \(\tau_B/\tau_C\) ratio, on the other hand, was always lower (7–8 times) than the \(N\) ratio used for computation. Thus the discrepancy between \(\tau_B\) and \(\tau_C\) has been considered a reliable, but not quantitative, appraisal of the anisotropy of motion.

Figure 3a shows the logarithmic plots of \(\tau_B\) as a function of the reciprocal of temperature for RuPT in solutions of different sized alkyl sulfate micelles and for an aqueous solution of the probe. In all cases log \(\tau_B\) increases linearly with a decrease of temperature. These Arrhenius plots allowed us to evaluate the activation energy for the reorientational diffusion motion. The \(E_a\) value for RuPT in water solution (5.7 kcal/mol) was higher than that found for the smaller nitroxides (like Tempol and TempTMA*: 5.0 kcal/mol). In the presence of micelles the value decreased slightly to 4.8–5 kcal/mol. A similar decrease in the activation energy for motion has already been found for nitroxides interacting with surfaces. Almost identical \(E_a\) values as well as the same anisotropy of motion, evaluated from the \(\tau_B/\tau_C\) ratio (\(=1.3\)), were found for the different sized micelles.

Figure 3b shows the variation of both \(\tau_B\) and \(\tau_C\) for C8/RuPT and C12/RuPT systems as a function of \(1/T\). In all cases \(\tau_B > \tau_C\), as is expected for the line-height trend \(h_{\parallel} > h_{\perp} > h_{\text{di}}\). The observation that \(\tau_B > \tau_C\) is typical of situations for which the main diffusion rotational axis \(Z_a\) is coincident with \(X_m\), the magnetic axis (corresponding to the N–O direction). Such a situation corresponds to introducing a diffusion tilt angle in the computation of the spectra (vide infra). Furthermore, the constant ratio between \(\tau_B\) and \(\tau_C\) allowed us to choose a constant \(N\) ratio between the parallel and perpendicular components of the rotational diffusion tensor (\(N = 10\) ) in the simulation of the spectra.

From the plots in Figure 3 it is evident that at each temperature the correlation time for motion increases consistently with an increase of the micellar size. This result is completely consistent with the photophysical result that the "unimolecular" quenching rate constant decreases as micelle size increases. The observed increase in correlation time, however, was not linear with the chain length. Figure 4 shows the variation of \(\tau_B\) as a function of the chain length at 298 and 303 K. There is an almost linear increase found for the C7–C10 micelles, whereas C11–C14 micelles present a marked positive deviation, indicating a stronger interaction of the ruthenium complex with the micellar surface for the larger micelles. This result is qualitatively similar but not identical to that from the photophysical measurements, for the unlabeled...
Dynamic quenching experiments of photoexcited Ru(phen)$^{2+}$, with cationically charged quencher molecules, which are attracted to the micellar surface, has allowed the evaluation of the quenching rate constant of these probes on the micellar surface. Modeling this quenching behavior using the Sano-Tachiya model for diffusion allows for the evaluation of the coefficients for translational diffusion on the surface of the different sized micelles. The results are presented as open circles in Figure 5. The same graph also presents, as filled triangles, the variation of the rotational diffusion coefficient, of RuPT, obtained from the analysis of the EPR spectra, which have been normalized by a constant coefficient in order to have coincident numerical values of $D$(trans) and $D$(rot.) for C8 micelles (the selection of C8 as the normalizing point was determined by its position as the first member of the series). This coincidence is nearly true also for C9 and C10 micelles, whereas the rotational motion becomes slightly faster (as opposed to SDS micelles). This result is also consistent with the photophysical quenching experiments wherein a larger quenching rate constant (indicative of faster motion and hence weaker binding) was found for NaL relative to SDS micelles.

Furthermore, the RuBT complex shows both a lower activation energy for motion (smaller slope) and a lower correlation time for motion (as determined by EPR measurements) when compared with the RuPT complex. This may be rationalized by recognizing the higher hydrophobicity of the phenanthroline ligand as compared to the bipyridine ligand which leads to a stronger interaction with the hydrophobic micellar core.

The isotropic hyperfine coupling constant ($a_N$) of the probe, where the quenching behavior changes from "bimolecular" (indicating rapid exchange of the probe with the bulk solvent) to unimolecular (indicating that all the quenching occurs on the micellar surface) upon going from C8 to C9 micelles. This suggests that the addition of the temp moiety makes the complex more hydrophilic.

Figure 6 shows the variation of $\tau_R$ as a function of 1/$T$ for both the RuPT and RuBT complexes in C12 and NaL micelles. The higher correlation time for motion seen in the RuPT/C12 system as opposed to the RuPT/NaL system is clear evidence for a stronger interaction between the probes and the sulfate head groups as opposed to the carboxylate head groups in the laurate micelles. This result is also consistent with the photophysical quenching experiments wherein a larger quenching rate constant (indicative of faster motion and hence weaker binding) was found for NaL relative to SDS micelles.

The isotropic hyperfine coupling constant ($a_N$) of the probe is also affected by the variation of the micellar size. This parameter is a measure of the environmental polarity and is larger in more polar environments. Figure 7 shows the decrease of the hfc of RuPT in micellar solutions with an increase of the surfactant chain length at 303 and 313 K. The most interesting feature is the very small variation of the environmental polarity from the C10-C12/RuPT systems as opposed to the variation found from C7-C10/RuPT systems and from C12-C14/RuPT systems. This should mean that the radical moiety probes almost the same (less polar) environment when the ruthenium complex is interacting with the C10-C12 micelles. The environmental polarity of the RuPT complex at the C7 surface undergoes a small change (16.95...
With an increase in concentration of surfactant, both the line width of spectrum A decreases and the contribution of spectrum A to the total spectrum increases. This occurs till concentrations above the cmc are reached when the pattern found for the micellar solutions is obtained (only spectrum A). Furthermore, the variations of both the line shape of spectrum A and the relative intensities of spectra A and B are different for the various surfactants. For instance, at the same intensity ratio between the two components, spectrum A is narrower for the shorter surfactant chains. This makes it more and more difficult to discern the presence of this signal (both visually and by subtraction) with a decrease of the chain length; thus, for C7 surfactant it is almost impossible to establish if spectrum A is present at concentrations far below the cmc, due to the very large preponderance of spectrum B. On the other hand, close to the cmc spectrum A becomes as narrow as spectrum B.

The analysis of spectrum A is complicated by the presence of spectrum B which masks the features of spectrum A. To obtain "pure" spectrum A it was necessary to subtract out the signal corresponding to spectrum B. It was not possible to subtract the experimentally recorded spectra for RuPT in aqueous solution or dilute surfactant solutions, since those spectra display a larger hyperfine splitting relative to spectrum B for the surfactant solutions. For this reason the three-line signals with the same hyperfine splittings and the same line widths as spectrum B were computed using the Schneider–Freed program,15 for all the surfactants at the different concentrations, and these computed spectra were subtracted from the experimentally recorded signals.

Spectrum B, for different detergent concentrations, was computed by using the Schneider–Freed program15 assuming the same mean correlation time for motion (2 × 10⁻¹¹ s) and the same N ratio (N = 4) for all different concentrations and only changing the mean A₄ value to fit the three line splitting of the experimental spectra. Figure 9 shows some examples of the spectrum A signals obtained by subtraction from C12 (3 and 7 mM), C10 (15 and 25 mM), and C8 (110 mM) solutions. The resultant spectra were also computed by using the Schneider–Freed program15 simply starting from the spectra of the micellar solutions and increasing the line widths. Attempts to reproduce the line broadening by increasing the Heisenberg spin-exchange contribution did not result in a good fit since experimentally, the splitting between the lines did not change with the increase of line widths. This lets us conclude that spin exchange is not experimentally significant.

For the C12 surfactant at concentrations of 2–4 mM the appearance of broad lateral flags were indicative of a slowing of motion. In such a case an increase in the mean correlation time for motion was also considered for the spectral computation. For instance, the two computed spectra reported in Figure 9 for [C12] = 7 and 3 mM were obtained by using (τ) = 5.0 × 10⁻¹⁰ s, ΔH = 3 G, and (τ) = 1.0 × 10⁻⁸ s, ΔH = 5 G respectively (to be compared with the C12 micellar spectrum computed with (τ) = 5.0 × 10⁻¹⁰ s, ΔH = 0.75 G).

The broadening of the lines and the increase in the correlation time for motion of spectrum A can be ascribed to dipole–dipole interaction among the probes which are localized at the surface of surfactant aggregates. The formation of surfactant premicellar aggregates on which ruthenium–polypyridyl complexes aggregate has already been deduced from photophysical measurements.6 In fact, clusters containing as many as 13 Ru(bpy)₃²⁺ moieties at 3 mM SDS concentrations have been estimated.60 However, the concentration of these clusters is dependent on the amount of Ru added and hence would seem to indicate that cluster formation is a resultant of the presence of Ru species. The higher probability to find more than one probe molecule into these aggregates leads to the occurrence of spin–spin dipolar interaction.

In the present investigation the dimensions of the surfactant and the probe are comparable especially for the lower chain surfactants, and this is a further factor for the perturbing effect of the probe. However the perturbing effect seems to be the same for all the differently sized surfactants. For instance spectrum A is almost the same for C9–C12 surfactants at concentrations equal to half the cmc which corresponds to a ratio between the
Figure 9. Experimental (obtained after subtraction) and computed EPR spectra of component A of Ru(phen)_2phen-T at various different concentrations of C8, C10, and C12 surfactant.

surfactant, and the total probe molecules of about 40 for C12 and about 300 for C9. However, this ratio is not an accurate reflection of exact ratio between interacting probe molecules and the surfactant since it neglects the fact that the probe is partitioned between two different environments.

The subtraction procedure allowed us to obtain the intensity ratios between the two components at each concentration. The reliability of those ratios was also tested by adding the two computed A and B spectra to reproduce the experimental line shape.

Figure 10 shows the variation of the percent intensity of spectrum A as a function of the concentration of C9, C10, C11, and C12 surfactants. At half the cmc, spectrum A contributes 25% of the total intensity for C9, whereas the contribution increases up to 58% for C12 surfactant. Since it is only this reduced percentage of the probe molecules (25% for C12 and 58% for C9) that is responsible for component A, the ratio between surfactant and "interacting" probe (defined as those probe molecules which result in a signal different from that in homogeneous solution) increases from 40 (vide supra) to 70 for C12 and from 300 (vide supra) to 1200 for C9. It is useful to bear in mind that this analysis considers the ratios between the clustered Ru and all the detergent molecules and not only those detergent molecules which are involved in the cluster formation.

Then, a perturbing effect of the radical cannot be ascribed to too high a concentration of the radical in the surfactant solution, but it can still be related to the large size of the RuPT complex.

Anyway, the equivalence of spectrum A at the same dilution of the surfactant with respect to the cmc is indicative of the formation of aggregates which differ from one surfactant to another in the same way as do the corresponding micelles. The smaller percent of spectrum A for the shorter surfactants is expected, since this signal is obviously absent when no surfactant is present in solution; thus all the patterns in Figure 10 can be extrapolated to 0 at [surf] = 0.

The above finding is also supported by the plots in Figure 11 which show the variation of the experimental line splitting distances (Figure 11a) and of the $r_B$ values from eqs 4 (Figure 11b) as a function of the surfactant concentration for all the surfactants from C7 to C12. For C8, C10, and C12 surfactants both $r_B$ and $r_C$ plots are shown in Figure 11c. Below the cmc both the distances between the sharp peaks (and not the computed hyperfine coupling constants) on the experimentally recorded spectrum and the peak heights are mostly determined by the spectrum B features, whereas above the cmc, spectrum A has the main contribution to the overall EPR signal, and the parameters evaluated from the spectra are mainly related to probes localized at the micellar surface. The decrease of the hyperfine splitting and the increase of $r_B$ in correspondence with the usual cmc of the surfactants are strongly indicative of the formation of micelles whose physical properties are negligibly perturbed by the RuPT complex.

Furthermore, the variations of splitting and correlation time became larger and sharper with the increase of the surfactant chain. This has already been found for C8 and C12 surfactants with smaller nitroxide probes.\textsuperscript{11b} The variation of both the coupling constant and the correlation time for motion of RuPT are intermediate to the variations found for Tempol and TempTMA$^+$ nitroxides. For instance the ratio between the correlation times in micelles and in bulk solution of C12 surfactant is about 18 for TempTMA$^+$, 15 for RuPT, and 13 for Tempol. This indicates that the nitroxide moiety localizes in an intermediate region at the micellar surface (probably at the border between the Stern and the Gouy–Chapman layers). The positively charged Ru–(II)–phen complex is expected to interact with the negatively charged sulfate groups; on the other hand, the phenanthroline ligands easily insert into the hydrophobic region of the micelles close to the surface polar groups.\textsuperscript{7}

The picture of the interacting Ru probe with the micelle that emerges then is one where one or both of the nonderivatized ligand phen ligands is/are partially inserted into the hydrophobic core of the micelle and the piperidine-N–O moiety, separated by the five-bond structure from the ligand, resides in the hydration layer at the micellar–water interface. However, it is the link with the ruthenium complex which is responsible for the motional anisotropy that is almost absent below the cmc and becomes evident at and above the cmc (Figure 11c).

Conclusions

We have utilized new EPR probes that mimic Ru(phen)$_2^{2+}$ and Ru(bpy)$_3^{2+}$ both structurally and electronically, to monitor their interactions with detergent solutions.

EPR spectra of these probes were recorded, at different temperatures, in the presence of alkyl sulfate micelles of varying lengths (from C7 through C14) at concentrations greater than the cmc and at ratios of [micelle]/[probe] of 10. The results and conclusions from these experiments were mutually supportive of the conclusions that have been obtained by exploiting the photophysical properties of Ru(phen)$_2^{2+}$ and Ru(bpy)$_3^{2+}$ as probes. Scheme I represents these results and comparisons in a pictorial format.

There is a monotonic increase in the rotational correlation time for motion of the complex bound to the micelle as the chain length of the detergent increases. This result is consistent with stronger...
translational diffusional coefficients obtained from the quenching measurements using the Sano–Tachiya model for diffusion. There is a good correlation observed between these two sets of diffusional coefficients.

The suggestion, from photophysical experiments, that the interaction of these Ru complexes may be stronger with micelles containing a sulfate head group as opposed to a carboxylate head group has been verified in our experiments for both the RuPT and the RuBT probes as judged by the different rotational correlation times and hfc in C12 and NaL micelles.

Only very modest changes in the hfc constant were observed upon going from an aqueous solution to a micellar solution (max Δhfc ≈ 0.4). This is indicative of the fact that the nitroxide moiety itself is not in the hydrophobic core of the micelle but is probably localized in the Gouy–Chapman layer surrounding the micelle while the other ligands are partially solubilized in the hydrocarbon core of the micelle.

Spectra recorded as a function of changing surfactant concentration revealed the presence of a broader EPR signal, at concentrations well below the cmc, that could be ascribed to probe molecules involved in the formation of premicellar aggregates; the broadness of the signal could be ascribed to dipole–dipole interactions. These premicellar aggregates have also been detected by photophysical and other techniques.

Our EPR probes therefore nicely serve to corroborate the results obtained from photophysical experiments; the virtue in this corroboration lies in the fact that this has been achieved with a nonoptical spectroscopy with probes that are very similar, both sterically and electronically, with the photophysical probes. Using these probes, we do not detect any perturbing effect of the probes themselves on the micelle formation although they do seem to induce the formation of premicellar aggregates. We are extending the range of these studies to look at other systems (starburst dendrimers, DNA) which have been the subject of photophysical scrutiny and to see if the parallelism that holds in the case of micelles is retained for the other systems too.

Acknowledgment. We thank the Air Force Office of Scientific Research, the National Science Foundation, and the Department of Energy for their generous financial support of this research.

Registry No. 2, 141848-65-9; 3, 18981-98-1; SDS, 151-21-3; C7, 141848-66-0; C8, 143-31-4; C9, 1072-15-7; C10, 142-87-0; C11, 1072-24-8; C14, 1191-50-0; NaL, 629-25-4; Ru(phen)_3^2+; Ru(phen)_2^2+.

Figure 11. (a, top) Experimental line splittings for Ru(phen)_3^2+ as a function of varying concentrations of different surfactants (markings on the x axis indicate, in descending order of chain length, cmc values for the different surfactants). (b, middle) τ_B for Ru(phen)_3^2+ as a function of varying concentrations of different surfactants (markings on the x axis indicate, in descending order of chain length, cmc values for the different surfactants). (c, bottom) τ_B and τ_C for Ru(phen)_3^2+ as a function of varying concentrations of C8, C10, and C12 surfactants (markings on the x axis indicate, in descending order of chain length, cmc values for the different surfactants).

The rotational diffusional coefficients obtained from the EPR studies, on different micelles, have been compared with the
References and Notes


(10) Details of the synthesis and characterization will be published elsewhere.


Remarks on the Association of Rodlike Macromolecules in Dilute Solution

Paul van der Schoot

Department of Polymer Technology, Faculty of Chemical Engineering and Materials Science, Delft University of Technology, P.O. Box 5045, 2600 GA Delft, The Netherlands (Received: February 3, 1992; In Final Form: March 31, 1992)

It is argued that van der Waals attraction can induce the parallel association of rodlike macromolecules in solution. Theories describing micellization and condensation are applied to analyze the stability of these aggregates. We conclude that aggregates consisting of only a small number of rods can be stable, at least in principle.

I. Introduction

Association of polymers in solution is often discussed in terms related to the chemical details of the molecules, focusing on mechanisms that involve intermolecular hydrogen bonding, interactions between charged moieties, structural transitions, and so forth. A perhaps less specific mechanism may on the other hand be given by bare van der Waals interactions. Initially one expects these to be too weak to provide the physical bonds that keep the macromolecules in the aggregate together—for, if they were not weak the solution would most likely phase separate. But when the polymers are rigid, rodlike,2 and of large aspect ratio the situation is slightly more delicate. As was pointed out in ref 2, dispersion forces between such long rodlike macromolecules are essentially short-ranged and, as a result of that, highly anisotropic. So, even when the attraction between two (nearly) touching rods is weak, its effect can easily become sizeable in case the rods adopt a parallel configuration.3 The strong anisotropy displayed by the dispersion interaction expresses itself for instance in the second virial coefficient, where nearly parallel configurations of the macromolecules are weighted heavily.2 Note that this is in spite of the tiny angular phase volume that can be attributed to two almost aligned rods. The van der Waals attraction may very well induce the association of rodlike polymers in solution for similar reasons.

In this paper we investigate the aggregation or association of rodlike macromolecules into "bundles" as a result of van der Waals' type of attractive interactions. The relevant thermodynamic quantity determining the size distribution is the chemical potential of the rods, which we calculate approximately by applying notions from the theory of micellization4-6 and the (physical cluster) theory of the condensation of gases.7-9 First the basic expression for the chemical potential is determined without explicitly specifying the contributions from the internal degrees of freedom of the aggregates (section II). In section III this internal free energy is estimated in the continuum limit, i.e. for aggregates consisting of a large number of rods. There we discuss the known result that two-dimensional growth of aggregates is in principle unbound.3 So, if stable or metastable aggregates of finite size are feasible, these can probably only be found in the opposite limit, at relatively small aggregation numbers. The analysis of section IV confirms that aggregation of rods in parallel configurations is possible for values of the model parameters that appear not unreasonable. Some concluding remarks are given in the last section.

II. The Chemical Potential of the Rods

Consider a solution of mutually impenetrable rods that interact via a short-ranged attractive potential. The length L of the rods is much greater than the width D. We follow the route prescribed by physical cluster theory and formulate a plausible criterion whenupon the distinction between free and bound particles is made.8-11 Two rods are defined neighbors of the same cluster or bundle when (1) their center lines have a relative angle smaller

0022-3654/92/2096-6083$03.00/0 © 1992 American Chemical Society