

Influence of Micellization on Complexing Properties of Amphiphilic Ligands toward Metal Ions

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Abstract: The NMR and ESR study of the complexing properties of an amphiphilic ligand toward paramagnetic divalent cations shows a drastic difference upon micellization. The present study deals with the complexation of Mn^{2+} , Ni^{2+} , and VO^{2+} ions by sodium mono-octyl phosphate below and above its critical micellar concentration (cmc). The ESR experiments show that the divalent cations are entirely bound to the micelles. The ^{31}P nuclear magnetic relaxation measurements indicate the formation of mono- and bicoordinated complexes below and above the cmc, respectively. The residence time of the amphiphilic ligand in the first coordination sphere of the metal is considerably shortened upon micellization. All these measurements can be understood from some characteristic properties of micelles.

The complexation of metal ions in aqueous solvents is of great interest in such different applications as extraction, water deionizing, or softening. Moreover, many biological processes involve complexation of ions in heterogeneous media. In homogeneous aqueous solutions the ligand and water molecules are in competition for binding to the ion. With micelles, this reaction may occur in bulk water but also at the water-hydrocarbon interface.¹

The present study deals with the complexation of divalent ions by micelles from anionic amphiphilic ligands. The hydrocarbon-water interface of micelles has interesting properties for complexation. It is indeed constituted with an important density of polar complexing heads and thus a high charge density.^{1,2} In order to screen the electrostatic repulsions between these polar heads, a fraction of the counterions is condensed around the micelle.³ As divalent ions provide a larger screening effect than monovalent ones, they are preferentially condensed at the micellar surface.⁴ Such an effect is only electrostatic in origin and creates an important local concentration of ions surrounding a large concentration of polar heads. It makes the solution quite nonideal and prohibits the use of the same equilibrium constants for complexation along the whole concentration range.

One of the main goals of this work is to compare the complexation of divalent ions by an amphiphilic molecule below and above the cmc and to explain the observed changes. For that purpose, the chosen amphiphilic molecule was the sodium mono-octyl hydrogen phosphate.^{5,6} The phosphate head group has indeed complexing properties toward divalent and trivalent metal ions which justify the use of organophosphates such as tributyl phosphate of diethylhexyl phosphate in solvent extraction. The Mn^{2+} , Ni^{2+} , and VO^{2+} ions were used because of their paramagnetic properties which are particularly convenient for NMR relaxation and ESR experiments.

Materials and Methods

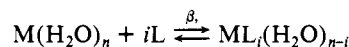
Materials. The octyl phosphate was used as its sodium mono-octyl-hydrogen phosphate ionic form ($C_8H_{17}OPO_3H^-$, Na^+) which has the same molecular charge as most of the common anionic surfactants. It is obtained by neutralization of mono-octylphosphoric acid by sodium hydroxide up to pH 4.5. The mono-octylphosphoric acid was purchased from IRCHA (France); its purity is more than 98% as checked by 1H and ^{31}P NMR. $MnCl_2$, $NiCl_2$, and $VOSO_4$ were purchased from Merck; deuterated water was from CEA (France). Some general physico-chemical properties of sodium mono-octyl phosphate are reported in ref 6. It gives rise to micelles above a cmc = 0.14 M at 30 °C without any added salt. The aggregation number of a 0.5 M solution is 43 ± 5 . The spherical micelles grow and become cylindrical for concentrations above 0.6 M.

Methods. The methods used were ^{31}P NMR and ESR. ^{31}P NMR experiments were performed with Bruker WH 90 and WM 500 spectrometers operating at 36.446 and 202.49 MHz, respectively. The

spin-lattice relaxation rates were measured by using an inversion-recovery pulse sequence (180° , τ , 90°) under broad-band proton decoupling. The spin-spin relaxation rates T_2^{-1} were measured from line widths. As the T_2^{-1} of interest are obtained from differences between two line widths, the contribution of the field inhomogeneity is removed. ESR measurements were carried out with a Varian E9 X band spectrometer. It is interfaced to a Hewlett-Packard 9835A microcomputer for spectrum accumulation. In all NMR and ESR experiments, the temperature was regulated at 30 ± 1 °C.

Theoretical Background

Complexation. The complexation of a metal ion M by a ligand L in water is represented by the following equilibria:



with

$$\beta_i = \frac{[ML_i(H_2O)_{n-i}]}{[M(H_2O)_n][L]^i} \quad (1)$$

n is 6 for Mn^{2+} and Ni^{2+} and 5 for VO^{2+} . $\beta_i = \prod_{j=1}^i k_j$ denotes the overall stability constants, k_j being stepwise stability constants.

The metal-to-ligand ratio p being less than 10^{-4} in our experiments, the concentration of free ligand $[L]$ is practically equal to the overall ligand concentration C . The mole fraction of complexed ligand is then

$$x_{\text{bound}} = p\bar{q} = \frac{p \sum_{i=1}^n i\beta_i C}{1 + \sum_{i=1}^n i\beta_i C} \quad (2)$$

where \bar{q} is an effective coordination number.

NMR Relaxation.⁷ The NMR spin-lattice or spin-spin relaxation rate T_1^{-1} or T_2^{-1} , respectively, of a ligand nucleus in the presence of a paramagnetic ion and in fast exchange is a weighted average of the relaxation rates of the free and bound ligands:

$$T_{1,2\text{obsd}}^{-1} = x_{\text{free}} T_{1,2\text{dia}}^{-1} + p\bar{q} T_{1,2M}^{-1} \quad (3)$$

with $x_{\text{free}} = 1 - p\bar{q} \approx 1$. The subscript M refers to the coordinated ligand. If the exchange rate has to be considered, and taking into account the condition $p \ll 1$ ($p < 10^{-4}$), we have to introduce an effective relaxation rate as

$$T_{1,2\text{para}}^{-1} = \frac{T_{1,2\text{obsd}}^{-1} - T_{1,2\text{dia}}^{-1}}{p} \quad (4)$$

The general expressions of $T_{1,2\text{para}}^{-1}$ are⁸

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$$T_{1\text{para}}^{-1} = \frac{\bar{q}}{T_{1M} + \tau_h} \quad (5)$$

and

$$T_{2\text{para}}^{-1} = \bar{q}\tau_h^{-1} \frac{T_{2M}^{-1}(T_{2M}^{-1} + \tau_h^{-1}) + \Delta\omega_M^2}{(T_{2M}^{-1} + \tau_h^{-1})^2 + \Delta\omega_M^2} \quad (6)$$

τ_h is the mean residence time of the ligand in the first coordination sphere of the metal ion. T_{1M}^{-1} , T_{2M}^{-1} , and $\Delta\omega_M$ are the spin-lattice, spin-spin relaxation rates, and paramagnetic shift of a nucleus in the metal coordination sphere. They are related to the geometry and electronic delocalization onto the atoms of the ligand, and to the rates of isotropic molecular motion τ_R^{-1} , chemical exchange τ_h^{-1} , and electronic relaxation T_{1e}^{-1} and T_{2e}^{-1} by the Solomon, Bloembergen, and Morgan equations^{9,10}

$$T_{1M}^{-1} = \frac{2}{15}S(S+1)\gamma_1^2\gamma_S^2\hbar^2r_{IS}^{-6} \left[\frac{3\tau_1}{1 + \omega_1^2\tau_1^2} + \frac{6\tau_2}{1 + (\omega_S - \omega_1)^2\tau_2^2} + \frac{\tau_2}{1 + (\omega_S + \omega_1)^2\tau_2^2} \right] + \frac{2}{3}S(S+1)\frac{A_1^2}{\hbar^2} \frac{\tau_{e2}}{1 + \omega_S^2\tau_{e2}^2} \quad (7)$$

$$T_{2M}^{-1} = \frac{1}{15}S(S+1)\gamma_1^2\gamma_S^2\hbar^2r_{IS}^{-6} \left[4\tau_1 + \frac{3\tau_1}{1 + \omega_1^2\tau_1^2} + \frac{13\tau_2}{1 + \omega_S^2\tau_2^2} \right] + \frac{1}{3}S(S+1)\frac{A_1^2}{\hbar^2} \left[\tau_{e1} + \frac{\tau_{e2}}{1 + \omega_S^2\tau_{e2}^2} \right] \quad (8)$$

where $\tau_{1,2}^{-1} = \tau_R^{-1} + \tau_{e1,2}^{-1}$ and $\tau_{e1,2}^{-1} = \tau_h^{-1} + T_{1,2e}^{-1}$. A_1 is the hyperfine coupling constant, S the electron spin, γ_1 and γ_S the nuclear and electronic magnetogyric ratios, and ω_1 and ω_S the relevant Larmor frequencies. The hyperfine coupling constant and the paramagnetic shift are related by

$$\Delta\omega_M = \frac{\omega_1 A_1 \gamma_e S(S+1)}{3\gamma_1 kT} \quad (9)$$

Since most of our experiments were performed with Mn^{2+} as a relaxation reagent, we can introduce some usual simplifications. The largest expected τ_R value is given by the Stokes-Einstein relation $\tau_R = 4\pi\eta R^3/3kT$ for the rotation of the micelle. The gyration radius being 18 Å⁶ and the viscosity 10⁻³ kg/ms; this largest τ_R value is 5 × 10⁻⁹ s. The rate of rotational motion is thus always faster than the expected τ_h^{-1} value (between 10⁶ and 10⁷ s⁻¹)¹¹ and $T_{1,2e}^{-1}$,¹² τ_1 and τ_2 reduce then to τ_R . The value of A ($A/\hbar = 3.3$ MHz¹³) is such that $\Delta\omega_M \ll \tau_h^{-1}$ and T_{2M}^{-1} , its contribution to $T_{2\text{para}}^{-1}$ (eq 6) is then negligible. Moreover, this A value together with the T_{1e} magnitude allows us to neglect the scalar term in the expression of T_{1M}^{-1} (eq 7) and the dipolar term in that of T_{2M}^{-1} (eq 8). Owing to the magnitude of ω_S , all the terms including it may also be removed. The simplified expressions for Mn^{2+} are then^{14,15}

$$T_{1,2\text{para}}^{-1} = \frac{\bar{q}}{T_{1,2M} + \tau_h} \quad (10)$$

$$T_{1M}^{-1} = \frac{2}{5}S(S+1)\gamma_1^2\gamma_S^2\hbar^2r_{IS}^{-6} \frac{\tau_R}{1 + \omega_1^2\tau_R^2} \quad (11)$$

$$T_{2M}^{-1} = \frac{1}{3}S(S+1)\frac{A^2}{\hbar^2}(\tau_h^{-1} + T_{1e}^{-1})^{-1} \quad (12)$$

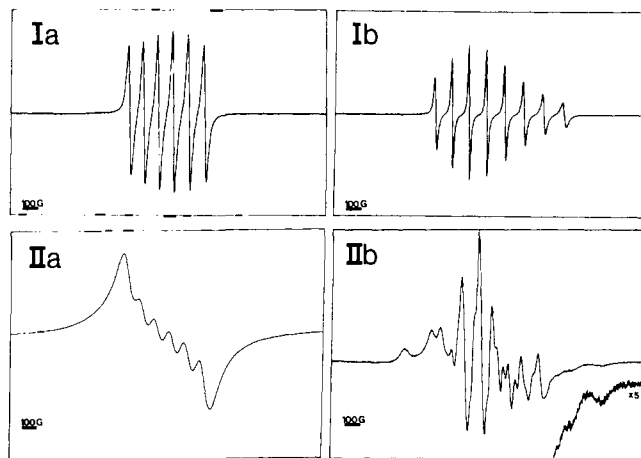


Figure 1. ESR spectra of Mn^{2+} (Ia) and VO^{2+} (Ib) ions in aqueous solution and of 5×10^{-3} M Mn^{2+} (IIa) and 5×10^{-3} M VO^{2+} (IIb) in a 1.5 M micellar octyl phosphate solution.

The parameters τ_R , \bar{q} , r_{IS} , and τ_h were first obtained from the simplified expressions (eq 10–12) and then introduced in eq 5–9 to check the validity of our approximations.

Experimental Results

A direct estimate of the extent of complexation is provided by the ESR spectra of the Mn^{2+} and VO^{2+} ions in the presence of monoctyl phosphate. The electronic relaxation times of these ions are long enough ($T_{2e} > 10^{-10}$ s) to be observed under our experimental conditions. This is not the case for Ni^{2+} , since its relaxation times are smaller than 5×10^{-11} s under similar conditions.²²

The Mn^{2+} spectrum consists of six resolved lines separated by 96 G owing to the coupling of the electronic spin with the $5/2$ nuclear spin of ^{55}Mn . The fine structure due to the $5/2$ electronic spin is unresolved and contributes only to the line width.¹⁶ This line width is mainly dependent on the frequency of collisions with the solvent which modulates the zero-field splitting tensor.¹⁷

The VO^{2+} spectrum corresponds to eight allowed transitions due to the coupling of the $1/2$ electronic spin with the $7/2$ spin of the ^{51}V nucleus. The line width results from the modulation of the anisotropic g and A tensors by molecular motions.¹⁸ The VO^{2+} ion is therefore widely used to probe the mobility or microviscosity. When the motions are slow, the anisotropies of the magnetic tensors are not completely averaged out, the spectrum spreads over a large spectral width of 1200–1400 G against 820 G under fast motion.¹⁹

Owing to the high electron Larmor frequency (9.1 GHz) the exchange of the paramagnetic ions between the fully hydrated and micellar sites is expected to be slow in the ESR time scale.^{20,21} The average Mn^{2+} line widths, expressed in frequency units increases indeed from $(1.5\text{--}3.0) \times 10^7$ to $(5.5\text{--}6) \times 10^9$ Hz upon exchange between these sites. Likewise, the total spectrum widths of VO^{2+} changes from 2.3×10^9 to 3.5×10^9 Hz in the same conditions. The coexistence of two sites, above the cmc, should be evidenced by the superposition of the relevant ESR spectra. Figure 1 shows clearly that this is not the case and that we are dealing only with the spectra of Mn^{2+} or VO^{2+} bound to a micellar site. On the other hand, below the cmc, the ESR spectra are virtually the same as those of the fully hydrated ions. Such a sudden change between the monomeric and micellar solutions is also evidenced by the ^{31}P NMR relaxation data. The ESR spectra

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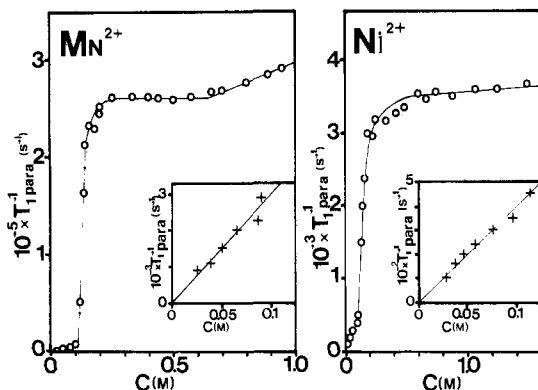


Figure 2. $T_{1\text{para}}^{-1}$ of the ^{31}P nucleus induced by Mn^{2+} and Ni^{2+} ions. In the insets are the extended regions below the cmc showing the linearity of the plot.

allow an easy distinction between an electrostatic "condensation" and a chemical binding to the polar heads. A condensed ion remains fully hydrated whereas a complexed ion loses some water molecules for direct binding to the ligand. The ESR spectrum of Mn^{2+} is only broadened by a factor of ca. 1.5 upon addition of sodium dodecyl sulfate above the cmc²³ in contrast with the broadening by a factor of 300 observed when this ion is tightly bound to micellar octyl phosphate. The behavior of the VO^{2+} spectrum provides an even clearer distinction. The VO^{2+} spectrum is again slightly broadened upon addition of sodium octyl sulfate or decyl sulfate above the cmc²⁴ but the main point is that the isotropic-like line shape remains unchanged. On the other hand, the binding to the polar head at a micellar surface drastically changes the line shape as observed with sodium octyl phosphate, dibutyl phosphate,²⁵ and octanoate.²⁶ Another way to monitor the condensation or complexation type of binding is the shift or broadening of the NMR lines of the surfactant nuclei induced by the paramagnetic ion.²⁷⁻²⁹

It appears therefore that the complexation is quite different depending on whether the octyl phosphate is in the micellar or monomeric state. The octyl phosphate molecule behaves therefore as a different ligand below or above its cmc. The following ^{31}P NMR study will contain two parts. The first one deals with the complexation of micelles and the second one with that of monomers obtained below the cmc. A third part will be a comparison between the results of the two previous ones.

Complexation of Micellar Monoctyl Phosphate. A striking feature is the concentration dependence of the ^{31}P NMR spin-lattice relaxation rate $T_{1\text{para}}^{-1}$ induced by the paramagnetic ion. In an aqueous solution, the octyl phosphate and water are in competition for binding to the ion, depending on the concentration of the amphiphile. The ^{31}P $T_{1\text{para}}^{-1}$ is a measurement of the fraction of ion bound to the phosphate head group (see eq 2 and 5). In a classical homogeneous aqueous solution of ligand, this relaxation rate should increase monotonically with the ligand concentration. Experimental results shown in Figure 2 follow this classical behavior for ligand concentrations below the cmc. A sharp increase of $T_{1\text{para}}^{-1}$ and thus of the phosphate complexation occurs at the cmc, followed by a plateau. This plateau indicates that the competition between phosphate and water for binding no longer occurs. The paramagnetic ions are thus entirely bound to the phosphate micelles as shown by ESR. A further increase

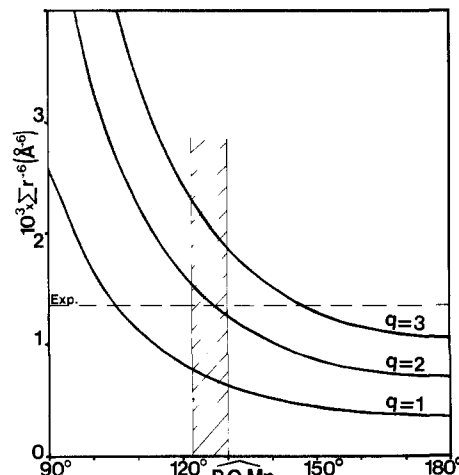


Figure 3. Dependence of Σr^{-6} upon the P-O-Mn angle and coordination number q . To the angular domain expected from the crystal structure of LiMnPO_4 ³⁰ and the experimental value correspond the hatched area and the dotted line, respectively.

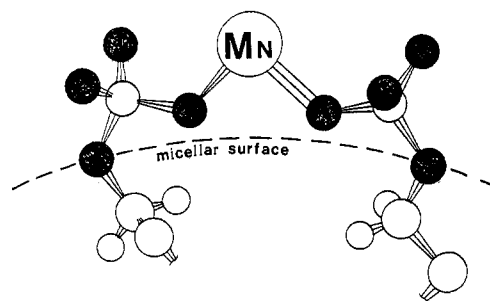


Figure 4. Coordination site of Mn^{2+} at the micellar surface.

of $T_{1\text{para}}^{-1}$ induced by Mn^{2+} occurs when the concentration exceeds 0.6 M. This effect, not observed with Ni^{2+} , suggests a slowing down of the motion due to a growth of the micelle. The relaxation induced by Mn^{2+} depends indeed mainly on the rotational correlation time τ_R , while that induced by Ni^{2+} is governed by the short electronic relaxation time ($\tau_{1,2} = T_{1,2e}$).²² Such a growth of the micelles has previously been reported from ^{31}P spin-lattice relaxation measurements in the diamagnetic solution⁶ and was interpreted as a sphere-to-rod transition. The Ni^{2+} -induced relaxation rate remains constant upon this transition, and the coordination of the divalent ion is likely insensitive to the micellar shape or size.

The coordination number of Mn^{2+} may be deduced from the geometrical factor of $T_{1\text{M}}^{-1}$, i.e., Σr^{-6} . The distances Mn-O and ^{31}P -O are, respectively, 2.2 and 1.55 Å from the crystal structure of LiMnPO_4 .³⁰ The same ^{31}P -O distance is found in sodium ethanolate hydrogen phosphate.³¹ The angle ^{31}P -O-Mn is found between 122° and 130°.^{30,31} The resonance frequency and the hyperfine coupling constant of the ESR spectrum remain unchanged upon complexation, thus preserving the symmetry of the Mn^{2+} complex, the angle O-Mn-O of a possible multicoordinated complex being 90°. From these geometrical considerations, the possibility of a bidentate complex is ruled out as distorting the octahedron (the angle O-Mn-O should be 70°). In order to obtain the two unknown parameters Σr^{-6} and τ_R from eq 11, $T_{1\text{para}}^{-1}$ has been measured at two different Larmor frequencies. The $T_{1\text{para}}^{-1}$ value of the plateau at 36.446 and 202.49 MHz are respectively 2.5×10^5 and $6.3 \times 10^4 \text{ s}^{-1}$, yielding $\tau_R = 1.5 \times 10^{-9} \text{ s}$ and $\Sigma r^{-6} = 1.35 \times 10^{-3} \text{ Å}^{-6}$. A calculation of Σr^{-6} for different ^{31}P -O-Mn angles and coordination numbers q is shown in Figure 3. The experimental value falls in the expected angular domain for $q = 2$, the ^{31}P -O-Mn angle being 127°, with

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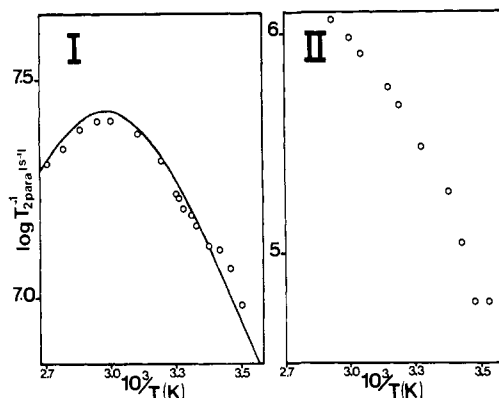


Figure 5. Temperature dependence of $T_{2\text{para}}^{-1}$: (I) in a micellar solution, the solid line is calculated with $\tau_h = 8 \times 10^{-8}$ s at 30 °C and $\Delta H^* = 6.4$ kcal/mol; (II) experimental values for a monomeric solution.

a ^{31}P -Mn distance of 3.37 Å. In these calculations, we have neglected the contribution of the paramagnetic relaxation of the ^{31}P nuclei which are not in the first coordination sphere of Mn^{2+} . In a micelle, all the ^{31}P nuclei are rather close to the Mn^{2+} ion, their contribution is estimated by assuming a distribution of the phosphate head groups on an hexagonal lattice at the spherical surface of the micelle. The outer sphere contribution is then found to be about 1% of the total ^{31}P relaxation rate and is thus negligible. A representation of the binding site at the micellar surface is shown in Figure 4. $T_{1\text{para}}^{-1}$ decreases with the temperature, its dependence thus follows that of $T_{1\text{M}}^{-1}$ ($T_{1\text{M}} \gg \tau_h$), and the exchange is fast and justifies the previous interpretation. From this temperature dependence and the geometry previously calculated, the temperature dependence of τ_R may be deduced. τ_R follows well an Arrhenius law from 17 to 95 °C with $\Delta H^* = 6.6$ kcal/mol. Similar ^{31}P relaxation experiments have been performed with VO^{2+} . At the two Larmor frequencies, the values of $T_{1\text{para}}^{-1}$ differ from that obtained with Mn^{2+} only by the value of the $S(S+1)$ factor. In the absence of any crystallographic data about this complex, we can conclude that the geometry and τ_R are the same.

A study of the exchange has been carried out on a 0.5 M solution using spin-spin relaxation rates $T_{2\text{para}}^{-1}$. $T_{2\text{para}}^{-1}$ is an increasing function of the temperature (Figure 5I) and is thus dependent on the exchange rate τ_h^{-1} . Using eq 10 and 12 with $T_{1e} = 4.6 \times 10^{-8}$ s at 36.446 MHz¹² and $A/\hbar = 3.3 \times 10^6$ Hz,¹³ we find two solutions at a given temperature. We can lift this ambiguity by using a measurement performed at 202.49 MHz taking $T_{1e} = 1.2 \times 10^{-6}$ s¹² for the calculation. Another way of carrying out this discrimination is to examine the temperature dependence of $T_{2\text{para}}^{-1}$ (Figure 5I). τ_h is then found to be 8×10^{-8} s at 30 °C. The τ_h dependence on temperature follows an Arrhenius law with an activation energy of 6.4 kcal/mol. From these results we can calculate the terms neglected in eq 7, they are 5% of the total relaxation rate and fully justifies the use of eq 11.

Complexation of the Monomeric Octyl Phosphate. Below the cmc, the concentration dependence of the ^{31}P $T_{1\text{para}}^{-1}$ is roughly linear for both Mn^{2+} and Ni^{2+} (Figure 2). Such a concentration dependence does not allow us to determine the equilibrium constants unless $T_{1\text{M}}^{-1}$ is known, since the slope of the plot of $T_{1\text{para}}^{-1}$ against the ligand concentration C is $\bar{q}T_{1\text{M}}^{-1} = [k_1C/(1 + k_1C)]T_{1\text{M}}^{-1}$ (eq 2). In order to extract \bar{q} thereof, the value of $T_{1\text{M}}^{-1}$ is required. Experiments at two different Larmor frequencies do not allow its estimate since for Larmor frequencies considered $T_{1\text{para}}^{-1}$ is the same. The molecular motion is then fast enough to satisfy the extreme narrowing condition ($\omega_1\tau_R \ll 1$). In order to obtain an estimate of these complexation constants, $T_{1\text{M}}^{-1}$ was calculated by using the ^{31}P -Mn $^{2+}$ distance of the micellar complex and an isotropic rate of motion deduced from that of a free monomer. This value, $\tau_R = 6.5 \times 10^{-11}$ s at 30 °C, calculated from the frequency dependence of the diamagnetic relaxation rate of the ^{31}P nucleus⁶ due to the chemical shift anisotropy contribution

Table I. Comparison between the Complexing Properties of Monomeric and Micellar Ligands

	coordn no.	equil constants, M^{-1}	mean residence time, s	activation energy of the exchange, kcal/mol
monomers	1	$k_1 = 3.2$	$\tau_h = 5 \times 10^{-7}$	
micelles	2	very large k_2	$\tau_h = 8 \times 10^{-8}$	6.4

is multiplied by the ratio of the molar volume of the manganese complex with five water molecules and the free monomer. τ_R is about 10^{-10} s leading to $T_{1\text{M}}^{-1} = 9.6 \times 10^3 \text{ s}^{-1}$. The initial slope ($d\bar{q}/dC$) is $k_1 = 3.2 \text{ M}^{-1}$ close to that of nucleotides.^{32,33} This rather low value of k_1 explains why no change are observed between the ESR spectra of fully hydrated ions and those recorded with a low octyl phosphate concentration ($C < 0.1 \text{ M}$). A study of the temperature dependence of a 0.06 M solution shows that $T_{1\text{para}}^{-1}$ is under fast exchange and that $T_{2\text{para}}^{-1}$ is dependent on τ_h . The k_1 value calculated above allows us to obtain \bar{q} and thus τ_h . The exchange is slow ($T_{2\text{M}} \ll \tau_h$) (Figure 5II) with $\tau_h \approx 5 \times 10^{-7}$ s at 30 °C. The activation energy cannot be deduced from the temperature dependence of $T_{2\text{para}}^{-1}$ only since it depends on both τ_h and k_1 .

Discussion

Some properties of the Mn^{2+} octyl phosphate complex below and above the cmc are compared in Table I. The enhancement of the complexing properties of amphiphilic molecules upon micellization seems to be scarcely studied up to now. Such an effect has been suggested to account for the increase of solubility of Ca^{2+} ions in sodium dodecyl sulfate above the cmc.³⁴ This explanation holds likely for the solubility of Mn^{2+} in micellar octyl phosphate solutions. The complexation of Mn^{2+} is likely to occur in two steps: a first condensation on the micellar surface forming a second sphere complex with the phosphate group and then a removal of a water molecule for direct binding. Several papers are dealing with the counterion condensation at a micellar surface or on polyelectrolytes which are, from an electrostatic point of view, similar to micelles.^{35,36} The related theoretical descriptions have been proposed from Poisson-Boltzmann cell models or Monte Carlo calculations.³⁷⁻⁴² An experimental evidence of the enhanced complexation in polyelectrolytes is shown in ref 43-45. The work of Walters et al.⁴⁶ and of Leroy and Guéron⁴⁴ on the complexation of Mn^{2+} by tRNA provide a satisfactory quantitative explanation of the observed enhanced complexation. For a monomeric ligand, the free energy of dissociation ΔG_{mono} is the energy required to replace the ligand by water, or in other words to get the metal remote from the ligand into the bulk water. This latter description applied to a polyelectrolyte ligand is separable into two contributions. The dissociation requires ΔG_{mono} to replace the ligand by water and an additional electrostatic free energy to remove

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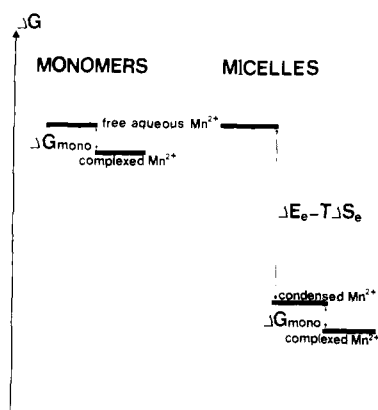


Figure 6. Free energy diagram for the complexation of Mn^{2+} by monomeric and micellar ligands.

the metal ion from the polyelectrolyte ionic atmosphere into bulk water (Figure 6). This approach holds in the high-dilution regime which is not the case of micellar solutions and it arbitrarily separates the counterions between two states as condensed or free, the difference in their normal chemical potential being the electrostatic energy at the micellar (or polyion) surface. Because of the long-range character of electrostatic interactions, the concept of counterion condensation should be discarded but it is often used as an easy qualitative way for explaining the counterions behavior. Here again, this concept, although not quantitatively, shows the role of Coulombic interactions in the complexation. A more accurate calculation is possible using the Poisson-Boltzmann cell model. In all our experiments the ligand concentration $[L]$ is much larger than the Mn^{2+} concentration ($p < 10^{-4}$), and $[L]$ does not therefore vary with complexation and can be removed from the mass action law giving

$$k = [Mn_b] / [Mn_f] \quad (13)$$

where $[Mn_b]$ and $[Mn_f]$ denote the complexed and hexahydrated Mn concentration. $[Mn_f]$ is the probability of having a free Mn^{2+} ion at the complexing site; for a monomer solution, this probability is just the overall concentration of free Mn^{2+} , so that k is the classical equilibrium constant for a given concentration of ligand. In micelles this probability is the local concentration of Mn^{2+} at the micellar surface giving

$$k = [Mn_b] / [Mn_f(R)] \quad (14)$$

R being the micellar radius.

We can nevertheless define a "macroscopic equilibrium constant" K as

$$K = [Mn_b] / [Mn_f]_{\text{overall}} \quad (15)$$

the enhancement of complexation induced by the presence of micelles is then

$$K/k = [Mn_f(R)] / [Mn_f]_{\text{overall}} \quad (16)$$

The definition of K is just given in analogy with the classical mass action law and does not have its usual meaning since the complexation occurs on a surface. It should be noted for example that K is not a constant and depends on the amphiphile concentration, ionic strength, etc., which are able to induce changes of micellar properties. This equilibrium constant is only used for the sake of comparison with the complexation of a non-micellar ligand at the same concentration. The local concentration of free Mn^{2+} is obtained from the Boltzmann statistics

$$[Mn_f(r)] = A e^{-E_e(r)/kT} \quad (17)$$

The electrostatic energy $E_e(r)$ is calculated from the Poisson's equation

$$\Delta\psi(r) = -\rho(r)/\epsilon_0\epsilon \quad (18)$$

where ψ is the electrostatic potential ($E_e = -2e\psi$) and $\rho(r)$ the charge density at a distance r from the micellar center. The

resolution of this equation is carried numerically in a spherical cell containing one micelle, all the mean concentrations in this cell being the overall concentrations. More details about the Poisson-Boltzmann cell model can be found in the related papers.^{37-42,47} The calculations were carried out for a 0.5 M solution of octylphosphate, the concentration of micelles being $(0.5 M - \text{cmc})/N_{\text{aggr}}$.

The free octyl phosphate, the concentration of which being nearly equal to the cmc (0.14 M), is considered as an added electrolyte. The influence of Mn^{2+} is neglected in this electrostatic calculation because of its low concentration ($p < 10^{-4}$). The result is then

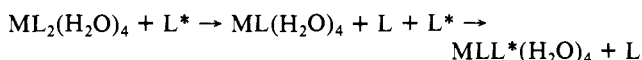
$$\frac{K}{k} = \frac{V_{\text{cell}} e^{-2e\psi(R)/kT}}{\int_0^{R_{\text{cell}}} e^{-2e\psi(r)/kT} 4\pi r^2 dr} = 130 \quad (19)$$

V_{cell} and R_{cell} being the volume and radius of the cell. This rather high value of K/k accounts well for the complete complexation of divalent cations by octyl phosphate micelles.

The coordination number of 1 for the monomeric octyl phosphate is simply a consequence of the low ligand concentration; a further increase of the concentration without micelle formation would give rise stepwise to higher coordination numbers. The coordination of 2 in micelles may be explained by steric effects. From an arrangement of the phosphorus atoms on a hexagonal lattice on a smooth sphere⁴⁸ the phosphorus-phosphorus distance $d(\text{P-P})$ is 8.6 Å. For our bicoordinated complex, the largest value of $d(\text{P-P})$ is 6.2 Å (Figure 4) against 5.2 Å for a hypothetical tricoordinated one. A bicoordination fits well the complexing site, bringing the ligands together, the axis of the fully extended chain being tilted by only 20° from the normal to the micelle surface. When the sphere to rod transition occurs, the micelles grow monotonously from spheres to infinite cylinders in the hexagonal mesophase. The radius of the cylinders remains that of the initial spheres, the surface per polar head and thus $d(\text{P-P})$ decreases from 8.6 to 6.9 Å. These values are quite consistent with a bicoordinated complex, and the insensitivity of the Ni^{2+} -induced relaxation to the micellar shape or size may be explained by an invariant coordination number.

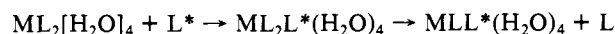
The exchange rate $\tau_h^{-1} = 2 \times 10^6 \text{ s}^{-1}$ at 30 °C of the monomer is close to that of water in the $Mn(\text{H}_2\text{O})_6^{2+}$ complex.¹¹ It increases to $1.25 \times 10^7 \text{ s}^{-1}$ upon micellization. This behavior cannot result from the Mn^{2+} condensation around the micelle. Studies on ligands adsorbed on micelles^{49,50} have indeed shown that the so called catalysis occurs for the rate of formation k^+ of the complex but not for that of dissociation $k^- = \tau_h^{-1}$. In such experiments, the stability constant k^+/k^- is therefore enhanced as in our present work. Three possible explanations can be proposed:

(i) The donor character of the anionic hydrogen phosphate ($-\text{OPO}_3\text{H}^-$) head group exceeds that of water. The metal-to-ligand bond is then tighter in a monocoordinated complex than in a bicoordinated one ($k_1 > k_2$). For a dissociative exchange mechanism



the rate of exchange follows the stability of the complex, increasing with the coordination number of the stronger donor.⁵¹ The observed increase of the exchange rate upon micellization could be only a consequence of the higher coordination in micelles.

(ii) Another possible explanation is an associative exchange mechanism



(47) We are indebted to Dr. L. Belloni for making available his Poisson-Boltzmann cell computation program.

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This mechanism gives rise to fast exchange rates at high ligand concentrations.⁵² At the binding site, the ligand concentration is indeed locally very high, several phosphate groups being in the second coordination sphere of the Mn^{2+} ion. Such an increase of the exchange rate has, however, not been observed with Co^{2+} . The exchange rates of Co^{2+} complexed by neutral or charged phosphatidylcholine membranes and by their monomeric glycerophosphorylcholine analogue are the same.⁵³

(iii) A third explanation is the possibility of an additional mechanism. The donor properties of the phosphate group and water are of comparable magnitude, k_1 being only $3.2 M^{-1}$. The exchange rate is expected to be nearly independent of the coordination number. The difference $\tau_{h\text{ micelle}}^{-1} - \tau_{h\text{ monomer}}^{-1} = 10^7 s^{-1}$ is close to the exchange rate of an octyl sulfate amphiphilic molecule between a micelle and bulk water at $30^\circ C$.⁵⁴ A reinterpretation of the ultrasonic relaxation experiments⁵⁴ with the theory of Aniansson et al.⁵⁵ leads to $k^-/n = 5 \times 10^6 s^{-1}$ (n = aggregation number). This value is the exchange rate of one labeled amphiphilic molecule among the n indistinguishable others. The coordination number of the complex being 2, the exit rate constant of a complexed ligand is $2k^-/n = 10^7 s^{-1}$. Although this very good agreement could be fortuitous, the explanation seems attractive. The large difference in stability constants of the complex between micellar and monomeric ligands prevents the Mn^{2+} ion from getting away from the micelle while bound to a leaving ligand molecule. Thus it remains preferably bound to its second coordinated ligand, the proximity of other polar heads in the micelle making the restoration of the bicoordination very easy.

Although the third assumption seems the most likely, the discrimination between the three possible interpretations is difficult from our experimental data. The associative mechanism (ii) seems less probable since it does not occur with Co^{2+} .⁵³ The influence of the exchange of an amphiphilic molecule between the micelle and bulk water (iii) could be evidenced from a variation of the surfactant chain length that changes this exchange rate. The first explanation (i) is hard to verify as it is impossible to get a pure bicoordinated complex in an aqueous solution.

Under exchange mechanisms (i) and (ii), the Mn^{2+} diffuses on the micellar surface, jumping from a polar head to another one. Such a motion corresponds to a rotation by an angle $\alpha =$

25° of the vector connecting Mn^{2+} to the sphere center, the correlation time of which is $\tau_R^* = \tau_h/\alpha \approx 2 \times 10^{-7} s$. τ_R^* is 2 orders of magnitude larger than the effective τ_R governing the relaxation⁶ which results from the overall reorientation of the micelle and from the lateral diffusion of the amphiphile- Mn^{2+} complex.^{56,57} Taking $\tau_{trans} = R^2/6D_{trans}$ with $D_{trans} = 2 \times 10^{-10} m^2 s^{-1}$ ⁵⁸ and $\tau_{rot} \approx 5 \times 10^{-9} s$, one finds indeed $\tau_R = (\tau_{trans}^{-1} + \tau_{rot}^{-1})^{-1} = 1.75 \times 10^{-9} s$. From our estimate of τ_h , it can be seen that the diffusion of the metal ion at the micelle surface is not an efficient relaxation process, although contributing to the line broadening.

The decrease of water viscosity with temperature cannot account for the temperature dependence of the motion of the Mn^{2+} - ^{31}P vector. The activation energy $\Delta H^* = 6.6$ kcal/mol corresponds to 800 cal per methylene, close to the hydration energy given by Tanford^{59,60} and to the activation energy obtained from the dependence of k^-/n on the surfactant chain length.⁵⁵ The activation energy of exchange is about the same (6.4 kcal/mol); its value thus can not help for a discrimination between the three possible exchange mechanisms. The variation of τ_R with temperature results likely from the decrease of the aggregation number of micelles^{61,62} the concentration of monomers remaining constant. The relevant activation energy is indeed that required to remove an amphiphilic molecule out from a micelle into water.

Conclusion

The present study of the complexation of amphiphilic ligands by divalent ions shows a drastic change in the complexation properties upon micellization. The rather weak monomeric ligand ($k_1 = 3.2 M^{-1}$) becomes a very strong one above the critical concentration of micellization. This increase of the complexing properties is interpretable from the electrostatic attraction of ions by the highly charged micelle. The coordination number suddenly changes from 1 to 2, owing to the close packing of the complexing polar heads in micelles. Lastly, the mean residence time τ_h of a ligand in the coordination sphere of the ion is drastically shortened. Three possible explanations are given, but the present experimental data do not allow a discrimination between them.

Registry No. $C_8H_{17}OPO_3H^-Na^+$, 30410-34-5; Mn, 7439-96-5; Ni, 7440-02-0; V, 7440-62-2.

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