A New Type of Surfactant. The Annelides. Characterization of Organized Metal Ion Assemblies Obtained by Cationic Complexation at the Micelle Subsurface

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The first members of a new class of amphiphiles, the annelides, consisting of a macrocyclic polar head able to include spherical or quasi-spherical cations and a long paraffinic tail, have been synthesized and characterized. They are shown to behave successively as nonionic or ionic surfactants depending on the presence of a complexable cation. The geometric parameters of the metal ion assemblies obtained by micellization are thoroughly determined by various physical methods including light scattering. The intersite degree of organization and the cooperative effect at the micellar interface are evaluated. The cationic complexation at the micellar subsurface is characterized. A convenient method for determining the local electrostatic properties of the interfacial region is exposed.

Introduction

In the last 10 years a new type of ligands, the crown ethers, has been under intense investigation.^{1,2} They are characterized by their macrocyclic nature leading to the presence of a central cavity lined with coordinating heteroatoms. The cation which best "fits" this cavity will selectively enter it to form usually very stable complexes. In the case of the nonpolarizable alkali and alkaline earth ions, the criteria of selection are mainly based upon the size and the charge of the complexed ion.^{3,4} This can be considered as a particularly simple illustration of the "lock and key" principle applied to spherical species (Figure 1a). The crown ethers are thus an elegant way, first, to choose a convenient cation and, second, to maintain it at a precise place in an organic moiety. If one now designs a ligand possessing an amphiphilic character and thus susceptible of forming ordered aggregates, metallic supermolecular structures will be obtained (Figure 1b). The addition of a long paraffinic chain to the macrocyclic ligands is a straightforward way to produce such assemblies. A few molecules of this type have been previously described^{5,6} but their aggregation properties in water have not been studied.⁷ The combination of their macrocyclic nature and their wormlike shape led us to propose "annelides" as the generic name for this new class of molecules.⁸ It is clear that the polar head will entirely determine the type of cation included. We are here mainly concerned with alkali and alkaline earth cations. The two ligands synthesized thus possess the same macrocyclic polar head (see Figure 2) which is most suitable for the inclusion of 2.6-3-Å diameter species, namely, potassium and strontium ions.^{3,9} For obvious reasons of simplicity, the supermolecular structure first studied was derived from micellar systems.

A preliminary report concerning the synthesis of an annelide and its dynamic properties of complexation has been already published.¹⁰

Results and Discussion

Cmc Measurements. There is a clear dichotomy between ionic and nonionic surfactant behaviors in solution.¹¹ Critical micellar concentrations (cmc), micellar sizes and shapes, and stability domains are very dependent on the state of ionization of the polar head. It was thus tempting to study the aggregation properties of annelides by varying the charge of the polar head (from neutral to doubly charged in the case of alkaline earth cation complexation). The fluorescence probe technique has recently been con-

TABLE I:	Effects of Complexation and Protonation or	ı
Cmc Values	of Annelides 1 and 2	

	cn	*****	
surfactant	fluorescence	surface tension or other	ref
C12-E6		8.7×10^{-5}	15
C12+ NMe ₃ Cl ⁻		$2.03 imes 10^{-2a}$	16
C18+NMe_Cl		$3.4 imes10^{-4a}$	16
C12-SO, Na ⁺		8.3×10^{-3}	16
1	$3.7 imes10^{-5}$		this work
$1 + Li^+$	3.4×10^{-5b}	6×10^{-5c}	
$1 + Ba^{2+}$	9.2×10^{-5b}	4.5×10^{-4c}	
$1 + H^+$ (excess)	<10 ⁻⁵ d	6×10^{-3d}	
$1 + Pb^{2+}$	<10-50	$>\!2 imes$ 10 ⁻⁴ e	
$\frac{2}{2}$ + Li ⁺		4.0×10^{-sc}	

^{*a*} Determined by specific conductance. ^{*b*} 0.01 M in LiNO₃ or Ba(NO₃)₂, pH adjusted to 10.5 with NEt₄OH. ^{*c*} 0.001 M in LiOH. ^{*d*} pH 2.7 (HNO₃). ^{*e*} A 1:1 metalligand ratio had to be used to avoid precipitation. The abbreviations used were as follows C12-E6, dodecylhexaethylene glycol; C12+NMe₃Cl⁻ and C18+NMe₃Cl⁻, dodecyl- and octadecyltrimethylammonium chlorides; C12-SO₃⁻Na⁺, sodium dodecyl sulfate.

firmed as a quite sensitive method for determination of low cmc values. $^{12\text{-}14}\,$ However, it has been shown 12 that it is not applicable in the case of charged surfactants because of ion pair formation between the amphiphile and the fluorescent probe well below the expected cmc. Surface tension measurements must thus be carried out to check the fluorescence results when necessary. It is worth noting that a precise physical definition of a cmc is not obvious.⁴ We will take it as the concentration at which there is a detectable amount of micelles by the technique used. It is thus not surprising that different values of the cmc can be obtained if the technique employed is changed (see ref 20, p 412). Table I gathers the different results obtained for annelides 1 and 2 in the presence or absence of a complexable cation. The cmc values of various well-known surfactants are added for comparison. Annelide 1 has been the most thoroughly studied since 2 only forms complexes of low stability (vide supra).

From an examination of Table I it can be seen that the macrocyclic nature of the polar head does not influence the cmc very much when compared to the open chain analog (C12-E6). The addition of a cation too small to be complexed by annelide 1 does not affect the cmc. On the contrary, formation of the stable barium complex signif-



Figure 1. (A) Spherical recognition of alkali cations by a macrocyclic ligand. (B) Formation of a supermolecular polymetallic assembly by aggregation of an annelide-cation complex.



Figure 2. Synthesized ligands and nomenclature.

icantly increases the cmc. Under the conditions used more than 75% of the available macrocyclic sites are occupied by a barium ion (vide supra). Although there is reasonable agreement between fluorescence and surface tension measurements for the neutral ligand or its barium complex, there exists a clear discrepancy between them in the cases of fully protonated annelide 1 and for the lead adduct. This can be rationalized by assuming a stronger affinity of the anionic dye used, the tetraethylammonium salt of 2,6-toluidinosulfonic acid (TNS), for the two last cationic species than for the less polarizable barium complex. The barium complex of 1, although showing cmc values far from those observed for the charged dodecyl homologue, no longer behaves as a neutral surfactant. There is no clear relationship between the nature of the polar head and the cmc of ionic surfactants.¹⁸ The large difference observed between the barium complex of 1 and its charged homologue is thus hardly explainable in a simple way.

More characteristic is the cmc dependence on temperature. It is well known¹¹ that ionic and nonionic amphiphiles have quite different temperature dependences, the cmc of the former increases with temperature while the cmc of the latter exhibits the opposite pattern. Figure 3 shows the results obtained for 1 with or without barium ion present in the solution. Clearly, the complexation makes the ligand behave as an ionic surfactant. Confirming this observation, the "cloud point", the temperature above which a solution of a neutral amphiphile separates into two phases, increases with the amount of barium added: $T_{\rm CP} = 40-50$ °C for pure 1, $T_{\rm CP} = 58$ °C for Ba²⁺/L = 0.25, and $T_{\rm CP} > 60$ °C for Ba²⁺/L = 1. One thus obtains a quasi-classical ionic surfactant by cationic complexation into the macrocyclic polar head of the annelide. The largely developed theoretical basis used for conventional amphiphiles^{11,17} can therefore be employed to rationalize their behavior.

The influence of methanol addition on the cmc has also been examined (see Table II) since use of binary solvents permits an increase in the solubility domains and in the temperature ranges usable for physical determinations (in particular for NMR studies, see ref 10). As expected,¹⁹ the



Figure 3. Cmc of the annelide 1 as a function of temperature in presence (O) or absence (+) of barium (0.01 M). The pH was adjusted to 10.2 with NEt₄QH.

 TABLE II: Cmc Values of the Annelide 1-Barium

 Complex as a Function of Methanol Concentration

% MeOH ^a	cmc, M	temp, °C
0	9.2×10^{-5}	25
	$1.34 imes 10^{-4}$	36
5	1.0×10^{-4}	25
	1.15×10^{-4}	40
33	$>5 imes \ 10^{-4} b$	25
	1×10^{-4}	6
	8×10^{-5}	-11
50	$>5 imes 10^{-4b}$	25
	•	

^a Methanol-water proportion (v:v). ^b Precipitation occurred for C < cmc. Ba(NO₃)₂, 0.01 M; cmc determined by the fluorescence method (TNS⁻⁺NEt₄, 5 × 10⁻⁶ M).

cmc rapidly increases when significant amounts of alcohol are added, this has been explained by the strong influence of MeOH on the structure of water.

Light Scattering Experiments. At this stage, it is possible to envisage a more detailed characterization of the micellar state. In order to use metallic ion assemblies and to see to what extent the organization might bring new properties (i.e., two-dimensional catalysis, cooperative effects between metal centers, cationic "hopping" rate between macrocyclic subunits, ...) it is of utmost importance to get some information about the geometry and the degree of order of the system. In homogeneous solutions, no structural parameter is easily accessible. On the contrary, it is fairly straightforward to entirely characterize a micellar state by almost routine methods and to derive a fairly precise description of the geometry of the system. Moreover, ionic and nonionic surfactants have been extensively studied by light scattering which is the most suitable technique for obtaining such information. The properties of annelide 1 have been more particularly determined by this method. The classical Debye equation

$$\frac{K^*(C - \text{cmc})}{R_0 - R_{\text{cmc}}} = \frac{1}{\bar{M}_w} + 2A_2(C - \text{cmc}) + \dots$$
(1)

where K^* is the optical constant, \overline{M}_w the weight average molecular weight of the micelle, and R_0 the Rayleigh ratio for observations near angle zero, has been used throughout this paper.²¹ Since the dissymmetry of scattered light ($Z = R_{45}/R_{135}$) was found to be close to unity, R_{90} vs. the monomer concentration can be plotted to check if the second virial coefficient A_2 is negligible. Since this was the case, we will further use the approximate equation

$$\frac{K^*(C-\operatorname{cmc})}{R_0 - R_{\operatorname{cmc}}} = \frac{1}{(\bar{M}_{\mathrm{w}})_{\mathrm{app}}} \simeq \frac{1}{\bar{M}_{\mathrm{w}}}$$
(2)

 $(\bar{M}_{w})_{app}$ is the apparent weight average molecular weight.

TABLE III: Concentration Dependence on Aggregation Number of Annelide 1^a

conen, M	$(\overline{M}_{\mathrm{W}})$	$\overline{N}_{\mathbf{A}}$	Ζ	ρ	
$\begin{array}{c} 5.6\times10^{-3}\\ 1.05\times10^{-2}\\ 1.56\times10^{-2}\\ 1.98\times10^{-2} \end{array}$	$\begin{array}{c} 31 \ 000 \\ 49 \ 000 \\ 49 \ 000 \\ 43 \ 000 \end{array}$	70 110 110 100	$1.11 \\ 1.01 \\ 1.02 \\ 1.01$	$\begin{array}{c} <5\times 10^{-3} \\ <5\times 10^{-3} \\ <5\times 10^{-3} \\ <5\times 10^{-3} \\ <5\times 10^{-3} \end{array}$	-

^a T = 25 °C. pH 10.5 in D₂O. $\overline{N}_{\rm W}$ is the weight average molecular weight, $\overline{N}_{\rm A}$ is the corresponding aggregation number. Z is the dissymetry of the scattered light. ρ is the depolarization factor.

TABLE IV:Effects of Complexation and Protonationon the Aggregation Number of Annelide 1

cond	itions	$(\overline{M}_{W})_{app}$	$(\overline{N}_{A})_{app}$	Ζ	ρ
1		4.9×10^{4}	110	1.02	0.005
$1 + HNO_{2}$	(1:1)	$2.3 imes 10^4$	50		
1 + LiNO	(10^{-2} M)	$1.6 imes 10^{\circ}$	370	1.08	0.006
1 + Ba(NO)	(4:1)	$3.4 imes 10^{4a}$	70^{a}	1.14	0.008
1 + Ba(NC)	$(1:1)^{3}$	3.6×10^{4a}	60^{a}	2.3	0.009

 a Estimated value not taking into account the dissymmetry of the light scattered.

By extrapolation of R_{90} to 0 it is possible to determine a new cmc value for annelide 1. The value obtained $(1.8 \times$ 10^{-3} M) is approximately 50 times higher than those previously determined. Similar findings have been already published by many authors, particularly in the C12-E6 case.²² This discrepancy can arise from (i) approximations made in the Debye equation, 20 and/or (ii) a real concentration dependence on the degree of association at low concentration. Since this difficulty is not encountered with conventional ionic detergents where the aggregation properties are generally far more defined, the latter hypothesis seems most likely. Cmc values from surface tension measurements were thus used to calculate the different average molecular weights of the annelide 1 micelle pictured in Table III. As expected,²² a plateau value in \overline{M}_{w} is obtained only when some kind of "critical" concentration is reached ($\sim 10^{-2}$ M). That nonionic amphiphiles form various aggregates of different weights but of comparable stabilities is not unexpected since the repulsions between the polar heads are predominant in defining the size and geometry of the micelles (see ref 24, for example). The van der Waals forces which are the only interactions present for neutral surfactants do not ensure a sufficiently defined repulsive potential.

The depolarization factor (ρ) is found to be very close to zero, indicating a fairly high symmetry for the aggregates. Since no more than 55 dodecyl alkyl chains in their fully extended conformation can be accommodated into a spherical particle, a disklike shape (oblate spheroid) can be very reasonably postulated.²³ A more precise definition would be hazardous owing to the highly fluctuating geometry of the micelles.^{23,24}

The effect of ligand protonation (HNO₃) and the addition of a complexable (Ba²⁺) or noncomplexable (Li⁺) cation have also been examined (Table IV). The previous method for $\bar{M}_{\rm w}$ calculation was used as long as the dissymmetry of the light scattered was low enough (Z < 1.1). Due to the appearance of electrostatic intersite repulsions, protonation of the amines expectedly leads to a significant decrease in $\bar{M}_{\rm w}$. More surprising is the fairly large increase in aggregation number observed when the lithium salt is added, even though no cmc change had been noticed. The small size of the lithium cation did not permit an inclusion complexation under the conditions used³ and thus only the well-known effect of this cation on water structure can explain this observation.



Figure 4. Plot of the inverse of the particle scattering factor $P^{-1}(\theta)$ against $\sin^2(\theta/2)$ (θ is the scattering angle): (a, b) theoretical curves for a spherical or a rod model, respectively; (c) experimental curve.



Figure 5. Zimm plot for the system annelide 1-barium complex (1:0.25).

TABLE V: Characteristic Values of the Low Mass Particles Formed by the Addition of $Ba(NO_3)_2$ to Annelide 1

surfactant and conditions	$M_{\rm W}$,	$N_{\mathbf{A}_1}$	
$ \begin{array}{l} 1 \\ 1 + Ba(NO_3)_2 (4:1) \\ 1 + Ba(NO_3)_2 (1:1) \end{array} $	$4.9 imes 10^4 \\ 4.9 imes 10^4 \\ 3.2 imes 10^4$	$\begin{array}{c}110\\100\\55\end{array}$	

On the other hand, addition of barium nitrate to a solution of annelide 1 leads to the formation of large particles (L > 270 Å) as indicated by the dissymmetry of the light scattered (Table IV). In the plot of

$$P^{-1}(\theta) = \frac{K^*(C - \operatorname{cmc})/R_{\theta}}{K^*(C - \operatorname{cmc})/R_{\theta}} \quad (C - \operatorname{cmc}) \to 0$$

vs. $\sin^2(\theta/2)$ (Figure 4), a very pronounced curvature is found, typical of the presence of a small amount of very large particles mixed with a majority of small ones.^{20,25} Interpretation of such results is difficult²⁰ without making some additional assumptions. Fortunately, previous studies on polyoxyethylene showed a striking similarity.²⁷ In particular, the classical Zimm plots of C/I vs. $\sin^2(\theta/2)$ + kC show the same distortion at low angles (Figure 5). It is thus possible, using hypotheses and formalism used in the polyoxyethylene studies,^{26,27} to interpret our light scattering results. However, we have to assume, in addition the presence of two and only two species in solution, this excludes in particular the presence of intermediate aggregates. Within these limitations, the weight average molecular weight of the smaller aggregates can be first calculated (i) from R_{90} neglecting the dissymmetry effects (Table IV), and (ii) by extrapolating to $\theta = 0$ the high angle linear part of C/I in Figure 5 (Table V). The difference

TABLE VI: Characteristic Values and Proportion (x) of the High Mass Particles Formed by the Addition of Ba(NO₃), to Annelide 1

conditions	$\rho_{\mathbf{R}_2},^a$ Å	$M_{\rm W_2}$	N_{A_2}	x, %
$\frac{1 + Ba^{2+} (4:1)}{1 + Ba^{2+} (1:1)}$	$\begin{array}{c}1000\\950\end{array}$	3.3×10^{7} 3.5×10^{7}	$\begin{array}{c} 6.7 imes \ 10^4 \ 6.0 imes \ 10^4 \end{array}$	0.2 3

^{*a*} $\rho_{\mathbf{R}_{a}}$ is the radius of gyration of the large particles.

between these two values emphasizes the contribution of the high molecular weight particles for $\theta = 90^{\circ}$ and thus the magnitude of the correction due to the dissymmetry of the light scattered. Upon addition of barium ion, a slight decrease in $\overline{M}_{\rm w}$ of the smaller aggregates is found. This again illustrates the increase of the repulsion between the polar heads by complexation.

Calculation of the radius of gyration of high molecular weight particles is straightforward, using the previously stated formalism.^{26,27} The general law of scattering light gives

$$R(\theta) = KCM_1P_1(\theta) + KCxM_2P_2(\theta)$$
(3)

where R is the Rayleigh ratio of the mixture of aggregates; $P_1(\theta)$, $P_2(\theta)$ are the respective contributions of the small and large aggregates; C is the small particles concentration in g cm⁻³; x is the proportion of large particles. If $x \ll 1$, it can be demonstrated²⁷ that

$$R_2(\theta) = R(\theta) - R_1(\theta) = KCxM_2P_2(\theta)$$
(4)

where $R_2(\theta)$ and $R_1(\theta)$ are, respectively, the Rayleigh ratios of the large and small micelles, M_2 being the molecular weight of the former. The Guinier representation $(\log R_2(\theta)$ vs. $\sin^2(\theta/2))$ directly gives the radius of gyration of the large particles (Table VI). In both cases a comparable value is found ($\rho_R \sim 1000$ Å). This result indirectly strengthens the previous nondistribution hypothesis.

It is then necessary to postulate a shape for these large aggregates. It is generally accepted that the very large aggregates have a rodlike shape^{31,32} with a fairly high flexibility.^{33,34} However, an alternative model has been proposed $^{23,28-30}$ in which nonionic surfactants form associations of spherical micelles by overlapping of the nonpolar head regions while retaining distinct hydrophobic cores. It is, of course, not possible to determine which is most appropriate in our case. The calculations are made here by postulating the first model but the second one should give results very similar for the molecular weight of the large particles. By plotting log $(KC/R_2(\theta))$ against $\sin^2(\theta/2)$, one can readily obtain the aggregation number, the corresponding molecular weight, and the proportion of larger particles²⁷ (Table VI). Flexibility of the rods was taken from previous viscosity measurements.³⁴ Its value indicates a very flexible structure quite in agreement with the small depolarization factors obtained in all cases. In spite of the uncertainties concerning the model used, clear conclusions can be drawn from the examination of Tables IV-VI. On addition of the complexable barium cation, the neutral annelide disklike micelles are transformed into slightly smaller aggregates of the same shape. A small amount of very large rod-shaped particles are formed, which are responsible of the dissymmetry of the light scattered. The concentration of these enormous aggregates is related to the quantity of barium added. The formation of high molecular weight particles is not observed when the noncomplexable lithium ion is used. In that case only an overall increase of the average molecular weight is obtained. Changes in micellar weight and shape upon addition of an electrolyte are not by themselves surprising^{35,36} but they had been observed only for far higher salt con-



Figure 6. Schematic picture of the micelle formed from annelide 1.

centrations. Owing to the complexity of the system, no straightforward explanation can entirely rationalize such a behavior.

Ultracentrifugation studies^{37,38} have been carried out in a few cases and the results were found to be in reasonable agreement with the light scattering values. However, the two different types of aggregates were not observed.

Geometric Parameters of the Micellar State. At this stage, all the elements are gathered to derive a precise picture of the micellar phase geometry. We will limit ourselves to a detailed study of pure annelide 1. The specific area per polar head can be readily obtained from knowledge of the partial specific volume of the micelle and the hydration number of the polar head. The former was experimentally determined ($V_p = 1.008 \pm 0.003 \text{ cm}^3/\text{g}$) by density measurements (see Experimental Section). The latter can confidently be taken as being 18 ± 4 from pre-vious studies on the C12-E6 surfactant.^{37,39} The dodecyl side chain was considered either fully extended or not^{23,25} giving similar results within error limits. The same calculations have been carried out by using the prolate spheroid model; the intersite distances differ by less than 1 Å. The geometrical parameters so determined are gathered in Figure 6. It can be seen that the surface offered to each macrocycle polar head is not sufficient to allow a full free rotation of the rings at the micelle subsurface, therefore, there is necessarily some intersite organization. This degree of order is still low, but any increase in \overline{M}_{w} will contribute, at the same time, to higher organization by decreasing the surface available for each polar group.^{23,24} As a matter of fact, substitution in annelide 1 of the dodecyl chain by an octadecyl paraffinic tail gives far higher aggregation numbers.¹⁰ The corresponding changes in specific areas per polar head are under study. This contact might have been expected since repulsive forces between head groups can only be provided by steric constraints in contrast to ionic surfactants, where electrostatic interactions are predominant.¹⁸ This has been further investigated by determining the surface pressure-area isotherms for 1 in the presence and absence of barium nitrate. In both cases, no sharp transition between randomly oriented and organized polar heads is observed. Only a very faint discontinuity corresponding to a specific area of 90 Å² for a pressure of about 10 dyn/cm could be detected. This indicates the beginning of a long range structuring. An almost infinite number of intermediates between the random and ordered arrangement of the macrocyclic rings is possible, however.

On the other hand, previous calculations have shown that one micelle contains almost as much water $(6 \times 10^4$ Å³) as amphiphilic ligand $(8 \times 10^4$ Å³). Some of the properties of this interfacial water have been determined (vide supra), but one can already wonder what this water contains. In the light scattering experiments, any "charge effect" due to inclusion of cations has been implicitly neglected.²⁰ This is justified since more than 50% of the counterions accompany the cations in the Stern layer of the micelle which corresponds roughly to the hydrated head group size. The remaining ions are distributed outside the shear surface in a Gouy-Chapman type diffuse atmosphere (see, for example, ref 40). Thus, the interfacial water must also ensure the solvation of a large part of the corresponding anions when the macrocyclic sites are occupied. One can therefore expect a drastic change in the hydration number per polar head during the complexation process. The number of factors to be considered makes a calculation of the previous type to determine the geometric parameters of the complexed annelides difficult. However, one does not expect very large differences if the aggregation number is comparable. Figure 6 can thus also represent the smallest aggregates in the annelide 1-barium system, when a small amount of cation is added to the solution.

Characterization of the Cationic Complexation at the Micelle Subsurface. A classical method^{41,42} based upon the competition at the nitrogen sites between complexation and protonation has been used to determine the various cation-ligand association constants. It can be summarized by the equation

$$LH^{+} + M^{n+} \rightleftharpoons M^{n+} \subset L + H^{+}$$
(5)

when L is the ligand, M^{n+} the metal, and $M^{n+} \subset L$ the inclusion complex of the metal. This technique has been widely used for characterizing cryptate and crown ether complexation.³⁴⁹ In the case of dibasic annelides the three following equations have to be considered:⁴³

$$L + H^+ \leftrightarrows LH^+ \tag{6}$$

$$K_{1} = [LH^{+}]/[L][H^{+}]$$
$$LH^{+} + H^{+} \rightleftharpoons LH_{2}^{2+}$$
(7)

$$K_{2} = [LH_{2}^{2+}] / [LH^{+}] [H^{+}]$$
$$L + M \rightleftharpoons M \subset L$$
(8)

$$K = [M \subset L] / [L] [M]$$

However, complications stem from the presence of micellar phases. A micelle should be considered as an unique supermolecule possessing $2N_A$ nitrogen atoms and N_A complexation sites all made different by the repulsive (or attractive) internal interactions between the various subunits. Previous related studies⁴⁴ ignore this difficulty and a general treatment⁴⁵ is hardly feasible. We prefer a method first proposed for weak polymeric acid titrations,^{46,47} which has more recently been applied to micelles.⁴⁸ Assuming a purely electrostatic intersite repulsion, it can be demonstrated that, for a single ionic monomer

$$\mathbf{pH} = \mathbf{p}K_0 - \log \frac{\beta}{1-\beta} - \frac{0.43}{kT} \left(\frac{\partial F_e}{\partial \nu}\right) \tag{9}$$

where β is the degree of ionization and in which pK_0 is the "intrinsic basicity constant", i.e., the constant in absence of any electrostatic intersite repulsion. F_e represents the electrostatic free energy of the micelle carrying ν charged groups. pK_0 can be readily obtained by plotting

$$pH + \log \frac{\beta}{1-\beta}$$

against β and by extrapolating to $\beta = 0$ where $(\partial F_e / \partial \nu) =$

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 TABLE VII:
 Protonation Constants of Ligands 1 and 3

	ligand			intrin-	
	solvent	3	1	sic pK	
$egin{array}{c} \mathbf{p}K_1 \ \mathbf{p}K_2 \ \mathbf{p}K_1 \ \mathbf{p}K_2 \ \mathbf{p}K_1 \ \mathbf{p}K_2 \end{array}$	$\begin{array}{c} H_2O\\ H_2O\\ MeOH/H_2O^a\\ MeOH/H_2O^a \end{array}$	9.7 7.6 9.6 7.2	8.5 7.1 9.6 7.3	8.9 7.5	

^{*a*} 90% methanol-10% H₂O (v:v). The intrinsic pK's of 1 are calculated from ref 47 and 50 (see text).

TABLE VIII: Stability Constants $(\log K)$ for the Complexation of the Alkaline Earth Cations with Ligands 1, 2, and 3

			log K	
$\mathbf{solvent}$	cation	3	1	2
H ₂ O MeOH/H ₂ O ^a	$\begin{array}{c} Ca^{2+} \\ Sr^{2+} \\ Ba^{2+} \\ Ca^{2+} \\ Sr^{2+} \\ Ba^{2+} \end{array}$	$2.4 \\ 4.2 \\ 4.0 \\ 4.7 \\ 7.0 \\ 6.9$	<2 2.2 2.2 3.9 6.4 6.6	b 2.5 4.1 4.2

^a 90:10 (v:v). ^b No complexation.

0. In our case a somewhat different expression has to be used for taking into account the previous two equilibria of protonation:⁴⁹

$$pH = \frac{pK_{0.1} + pK_{0.2}}{2} + \log\left[\frac{2(2-\bar{n})}{[D^2(1-\bar{n})^2 + 4\bar{n}(2-\bar{n})]^{1/2} - D(1-\bar{n})}\right] - \frac{0.43}{kT} \left(\frac{\partial F_e}{\partial \nu}\right) (10)$$
$$\bar{n} = ([H_0] - [H]) / [L_0]$$

$$\log \mathbf{D} = (\mathbf{p}K_{0.1} - \mathbf{p}K_{0.2})/2$$

 $[H_0]$ and $[L_0]$ are the proton and ligand initial concentrations, respectively.

On the other hand, one can more simply calculate averaged pK_1 and pK_2 by merely ignoring intersite repulsions. It can be seen from Table VII that, within experimental errors, the values found by both methods are almost identical. This indicates that the basicity constants do not depend to a large extent on the degree of ionicity of the micelle. The pK can thus be considered as constant throughout the titration. A very good agreement is generally found^{47,50} between the intrinsic pK_0 and the basicity constants of the isolated homologous subunit. Table VII shows that this is far from being the case for the micellar form of 1, as compared to ligand 3, whose structure does not permit micelle formation. That this difference really resulted from the micellar state has been checked by determining the pK's in a methanol-water (90:10, v:v) mixture where, whatever the ligand, no micellization occurs.^{19,51} Under these conditions both ligands give identical results (Table VII). Therefore, although only a small cationic filling effect can be detected, a fairly large micellar effect on basicity constants is observed.

The same phenomenon occurs in the case of alkaline earth cation complexation (Table VIII). The reference compound 3 behaves quite normally and leads to the usual stability constants and selectivities.^{3,4} On the contrary, there is a dramatic decrease in binding constants for the micellar form of 1. As previously, identical results are obtained in the methanol-water mixture (Table VIII).

	ligands			
solvent	ref^a	1	3	
H,O	17	45	22	
$MeOH/H_2O$	22	21	20	
^a From $(pK_2)_1 - (pK_2)_2$,),.			

By use of ¹³C NMR, it has been possible to demonstrate a one-to-one stoichiometry of complexation for all the cations studied (Ba²⁺, Sr²⁺, Ag⁺, Pb²⁺).⁵² Moreover, the barium cation-annelide 1 stability constant could be determined (log $K = 2.6 \pm 0.2$), confirming the potentiometric determination. In this case also, an unique constant can be assumed to fit the whole experimental curve.

Therefore, some peculiarity of the medium around the polar heads has to be the cause of such differences. The local properties of the micellar subsurface can be determined by using simple electrostatic calculations employed 60 years ago to study the ionization of dicarboxylic acids.^{53,54} The ratio of the first to the second association constant of a symmetrical dibasic molecule was shown to be

$$\log (K_1/K_2) = \Delta p K = \log \sigma + \frac{N}{RT} \Delta \omega$$
 (11)

The statistical factor σ stems from the entropy variation associated with the symmetry changes during the protonation of the molecule; $\Delta \omega$ is a purely electrostatic term, namely, the electrical work $e^2/(DR')$ required to bring two charges from infinity to the distance of separation R' in a medium of dielectric constant D. However, problems come from the nature, by essence macroscopic, of D when employed to obtain local properties. To solve them an "effective" dielectric constant D_e was used^{53,54} and was interpreted as being the dielectric constant inside an hypothetical cavity formed around the solute molecules.⁵⁴ We will indifferently call it the local or effective dielectric constant and we will merely consider it as a measure of the local electrostatic properties of the medium. The nitrogen-nitrogen distance in the annelide polar heads can be accurately estimated from X-ray measurements of similar compounds,⁵⁵ taking into account the principal conformational isomerism (endo-endo/exo-exo) due to nitrogen inversion.⁵⁶ Annelide 2, bearing a cationic quaternary ammonium side chain at a precisely known distance from the complexation and protonation sites, is most suitable to check the validity of this approach. The local dielectric constant is first calculated from

$$\Delta pK = (pK_2)_{\text{annelide } 1} - (pK_2)_{\text{annelide } 2}$$

in water and in the methanol-water mixture (Table IX). Remarkably close values are obtained in both solvents, emphasizing the very weak bulk solvent effect on local electrostatic properties. If the model used is correct, comparable D_e 's should be found for annelide 1 and ligand **3** by taking $\Delta pK = pK_2 - pK_1$. A very good agreement indeed exists between the D_e values of all isolated monomeric species. On the contrary, the micellar form of 1 leads to a local dielectric constant more than twice as large (Table IX). The local electrostatic properties of the interfacial region of micelles are thus most peculiar. The same conclusion has been reached independently in the studies of alkyl pyridinium iodides.^{57,58} It has been advanced⁵⁸ that those peculiarities arise partly from the self-potential of ionic groups coming from electrostatic image forces. On the contrary, the presence of high local

concentrations of ions seems not to influence the interfacial properties.⁵⁸ Whatever the cause may be, utilization of difunctional molecules appears to be a quite sensitive and reliable method to demonstrate local anomalies in micromediums. The rather unexpected electrostatic properties of the micelle subsurface must largely influence the chemical reactivities of the molecules present and thus might be of importance in rationalizing some micellar effects.^{59,60}

Conclusion

The properties of a new class of amphiphiles, the annelides, have been determined by most of the classical physical methods available. A few new features related to their particular nature could be demonstrated, especially their successive ionic and nonionic behavior depending on the cation present in solution. More importantly, the annelides have been shown to be a very efficient way to produce ordered metal ions assemblies while maintaining all the characteristics of a homogeneous solution. The main geometrical parameters of these assemblies could be readily determined. No intersite cooperativity has been noticed toward protonation or cationic complexation even though some degree of organization between the polar heads was demonstrated. The determination of local dielectric constants enabled us to evaluate local electrostatic properties of the micellar subsurface. These properties were found to be of a great importance toward cationic inclusion by the macrocyclic polar heads of the annelides.

We have been concerned in this publication only with alkaline earth complexations which were the most suitable cations for the easy determination of the geometric parameters of metal ion assemblies. Owing to their inertness and their nonpolarizable character only a limited number of applications are possible. Two-dimensional catalysis by ion pair formation has been envisaged in addition to the previously described dynamical properties of complexation of the annelides, namely, the favored hopping rate of the cation from one macrocycle to another.¹⁰ However, an immense field might be opened by studying transition metal assemblies. Work is in progress toward this direction.

Experimental Section

Syntheses of the Ligands. N-Undecanoyl-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (4). The starting macrocyclic diamine (Merck Kryptofix 22, No. 10953) was purified by chromatography on alumina (Woelm basic) and recrystallized (benzene-heptane) before use. A solution of 15.2 mmol of dodecanoyl chloride (Fluka) in 400 mL of anhydrous benzene was added dropwise to 15.2 mmol of Kryptofix 22 and 80 mmol of triethylamine in 250 mL of anhydrous benzene. After the addition was complete, the unreacted macrocyclic diamine was removed by extraction with three 100-mL portions of a solution of sodium hydroxide (5%). The organic phase was then vigorously stirred with 100 mL of hydrochloric acid (20%) for 10 min. The whole solution was extracted with three 500-mL portions of water containing 20% ethanol to avoid emulsification. The combined aqueous extracts are made basic with sodium hydroxide (20%), partially evaporated to discard most of the ethanol and extracted with three 200-mL portions of benzene. The organic phase dried on sodium sulfate was evaporated to give compound 4 sufficiently pure to be used for the further steps (yield, 22%). Chromatography on alumina (toluene-chloroform eluent, 60:40 v:v) and recrystallization from hexane gave analytically pure 4 (overall yield 19%).

Calcd for $C_{24}H_{48}O_5N_2$ (444.64): C, 64.82; H, 10.88; N, 6.30. Found: C, 64.63; H, 10.89; N, 6.32.

N-Dodecyl-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (5). 4 (4 mmol) was dissolved in 100 mL of THF freshly distilled over LiAlH₄. LiAlH₄ (30 mmol) was then added and the mixture heated under reflux for 15 h. Calcium chloride drying tubes must be used to maintain a dry atmosphere. The excess of hydride was destroyed with a mixture of THF/water (80:20 v/v). The alumina formed was filtered off and the filtrate was evaporated to dryness to give crude 5 which was purified by chromatography on alumina (toluene-chloroform eluent, 50:50 v/v). A colorless oil was obtained which crystallizes slowly at room temperature (yield, 83%; mp 33.5 °C).

Calcd for $C_{24}H_{50}O_4N_2$ (430.65): C, 66.93; H, 11.70; N, 6.50. Found: C, 66.73; H, 11.78; N, 6.41.

N-Methyl-N'-dodecyl-1,10-diaza-4,7,13,16-tetraoxacy-clooctadecane (1). The *N*-methylation of **5** was carried out by the Eschweiler–Clarke method.⁶⁷ **5** (10 mmol) in 100 mL of formic acid and 40 mL formaldehyde was heated at 100 °C for 20 h. The solution was cooled and 45 mL of concentrated hydrochloric acid was added. The mixture was heated at 80 °C for 4 h. The mixture was evaporated to dryness and 200 mL of 10% lithium hydroxide was added. After complete solubilization, the solution was extracted with three 200-mL portions of chloroform. The combined extracts were dried (MgSO₄) and evaporated to dryness. The slightly yellow oil obtained was purified by chromatography on alumina (chloroform–toluene eluent, 50:50 v/v) and recrystallized in pentane at -30 °C (yield 91%, colorless oil at room temperature).

Calcd for $C_{25}H_{52}O_4N_2$ (444.68): C, 67.52; H, 11.79; N, 6.30. Found: C, 67.58; H, 11.90; N, 6.47.

N-Heptadecanoyl-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (6) is obtained by a method similar to that for 4 in 13% yield (mp 52 °C).

Calcd for $C_{30}H_{60}O_5N_2$ (528.79): C, 68.14; H, 11.43; N, 5.30. Found: C, 68.02; H, 11.26; N, 5.32.

The (carboxymethyl)trimethylammonium bromide methyl ester which had been synthesized⁶⁸ was converted into the corresponding acid by hydrolysis in hydrobromic acid (10%) under reflux (24 h). The solution was evaporated to dryness and the residue obtained was recrystallized from methanol-water (70% yield; mp 248 °C). This acid (5 mmol) was dissolved in 10 mL of ethanol and 5 mL of water; 5 mmol of picric acid in 10 mL of EtOH was then added at 50–60 °C. After allowing the solution to cool to -5 °C, an abundant precipitate was formed corresponding to the picrate derivative (quantitative yield; mp 182 °C). The activation of this acid is achieved by transformation into its *p*-nitrophenolic ester derivative. The previous compound (1.44 mmol) was treated with 1.1 mmol of bis(*p*-nitrophenyl)sulfite in 20 mL of anhydrous pyridine at room temperature for 20 h. The ester derivative (7) crystallized in the reaction mixture (quantitative yield; mp 219 °C).

Calcd for $C_{17}H_{17}O_{11}N_5$ (467.34): C, 43.69; H, 3.67; N, 14.98. Found: C, 44.06; H, 3.31; N, 14.80.

N-(Carboxymethyl)-N-(trimethylammonio)-N'-heptadecanoyl-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane Chloride (8). 6 (22.7 mmol) in 50 mL of anhydrous pyridine was treated with 22.7 mmol of 7 for 1 h at 50 °C, 1 h at 80 °C, and 1 h at 100 °C. The mixture was evaporated to dryness and passed through an ionic exchange resin (Dowex 1X8) in its Cl⁻ form. The aqueous fractions were evaporated to dryness and the residue recrystallized from acetonitrile furnished the chloride salt of 8 in 84% yield. Calcd for $C_{35}H_{70}O_6N_3Cl\cdot 1.5H_2O$ (690.38): C, 60.80; H, 10.64; N, 6.08. Found: C, 61.03; H, 10.41; N, 5.98.

N-(Carboxymethyl)-N-(trimethylammonio)-N'-octadecyl-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane Nitrate (2). Ligand 2 was prepared in its diprotonated form (nitric salt), the free ligand being obtained by adjusting the pH of an aqueous solution with lithium hydroxide. 8 (1.45 mmol) was treated with 30 mL of diborane in THF (1 M) under nitrogen at 60 °C for 2 h. Excess diborane was destroyed with water, and 20 mL of hydrochloric acid (50%) was added. The solution was stirred for 2 h at room temperature, and then evaporated to dryness. The white residue was passed through an ion exchange resin column in its hydroxide form. The basic fractions were combined, treated with concentrated nitric acid up to pH 1, and evaporated to dryness. It was then recrystallized from ethanol (65% yield, mp 164 °C).

Calcd for $C_{35}H_{76}O_{13}N_6\cdot 1H_2O$ (807): C, 52.09; H, 9.74; N, 10.41. Found: C, 51.83; H, 8.86; N, 10.44.

The synthesis of 3 has been previously described.⁴

Cmc Measurements. A Fica 55 spectrofluorometer with an excitating wavelength of 365 nm was used throughout the fluorescence experiments. The tetraethylammonium *p*-toluidinonaphthalenesulfonate probe was prepared from the corresponding acid (Sigma) and was recrystallized twice from methanol-acetone before use. All determinations were carried out under nitrogen by using triply distilled water. The temperature could be varied from -15 to 50 \pm 0.5 °C. A solution of Ba(NO₃)₂ (1.5 mL, 10⁻² M, pH adjusted to 10.5 by adding 20% NEt₄OH in water) was added to a solution of TNS⁻NEt₄⁺ (1.5 mL, 10⁻³ M). Increasing amounts of ligand (0.01 M, pH adjusted to 10.5 with NEt₄OH) were added and the intensity of fluorescence at $\lambda_{max} = 425$ nm was recorded. Every cmc was determined three times; the reproducibility was within 10%.

A M.G.W. Lauda tensiometer was employed with the Du Noüy ring method. The temperature was 25 ± 1 °C. Calibration of the apparatus was checked by measuring the interfacial tension of triply distilled water (72 dyn/cm at 25 °C) taking into account the Harkins–Jordan correction. The error limit was 2%. Standard solutions were prepared from LiOH (0.2 mL, 0.1 M) and ligand (x mL, 0.01 M) made to 25 mL volume with Ba(NO₃)₂ (0.01 M). The pH of this solution was determined before and after the surface tension determination and was always found to be higher than 10.4. The cmc's were determined by plotting log C vs. the surface pressure in dyn/cm.

Surface Pressure-Area Isotherms. The Langmuir method was utilized (MGW Lauda apparatus). The solution was prepared as previously (pH 11 adjusted with LiOH under nitrogen, $T = 25 \pm 1$ °C). The sweeping rate was kept constant at 2.8 cm/cm (14.5 Å/min⁻¹ molecule⁻¹). The higher film pressure obtained (39 dyn/cm) for the system annelide 1-barium agreed well with the value determined by the Du Nouy method (31.5 dyn/cm).

Light Scattering and Related Experiments. A Fica 50 light scattering spectrophotometer equipped with a mercury lamp was used (green ray, 546.1 nm). A benzene reference was employed for the calibration.

The cloud points were determined by observing I_{90} as a function of temperature (20-65 °C).

Molecular weights were determined in freshly distilled D_2O (CEA France 99.8%). Dust was discarded by centrifugation (2 h) at 50 000 g. The conditions and various concentrations used are presented in Table I.

The various refractive indices were measured on a Brice Phoenix differential refractometer in D_2O at room temperature (precision 2-5%). The differential refractive indices $(d\eta/dc)$ for annelide 1, 4:1 1 + Ba(NO₃)₂, 1:1 1 + $Ba(NO_3)_2$, and $10^{-2} M 1 + LiNO_3$ were 0.165, 0.165, 0.153, and $0.159 \text{ cm}^3 \text{ g}^{-1}$, respectively.

Calculations of the various $\bar{M}_{\rm w}$ took into account the proportion of complex formed and assumed complete binding of the counterion. These two factors introduced only minor corrections.

The density measurements were made on a modified Kratky type apparatus.^{61,62} A partial specific volume additivity law was postulated.

Potentiometric measurements have been made on an automatic titration apparatus (Mettler DK 14, 15, and DV 10) with an Orion 701 pH meter equipped with a high alcalinity electrode (Metrohm EA 109 H) vs. a standard calomel electrode (Tacussel) filled with 0.1 M NMe₄Cl. This electrode was isolated from the solution by an ionic bridge (NMe₄NO₃, 0.1 M). Commercially available salts (Merck Analysis) were used without further purification. All measurements were made at 20 °C under argon. When the methanol-water mixture was used, Tacussel MeOH B10 and MeOH C10 electrodes were employed, the latter being equipped with an ionic bridge (0.1 M NMe₄Br in MeOH, 90:10 v/v). The calibration was made by using the De Ligny procedure^{63,65} by preparing two buffer solutions in the methanol-water mixture (oxalate buffer, pH 3.59; succinate buffer, pH 6.56). $pK_w = [H^+][OH^-]$ was taken equal to 15.56 ± 0.03 ^{4,9} The ionic strength was maintained constant with 0.1 M NMe_4NO_3 in water and 0.1 M NMe₄Br in the methanol-water mixture. The concentration of the ligand was ~ 0.005 M.

Calculation of the various equilibrium constants was made by using a Fortran program previously described.⁶⁶ The standard deviations were found to be less than 1% in all cases.

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