Geometric characteristics of micellar systems as precursors of lanthanide-containing lyotropic mesophases

N. M. Selivanova,[a]★ V. V. Osipova,[a] M. V. Strelkov,[a] I. R. Manyurov,[a] and Yu. G. Galyametdinov[a,b]

[a]*Kazan State Technological University,*
68 ul K. Marksa, 420015 Kazan, Russian Federation.
Fax: +7 (843 2) 31 4177. E-mail: natsel@mail.ru
[b]*Kazan Physicotechnical Institute,*
Kazan Scientific Center of the Russian Academy of Sciences,
10/7 Sibirskii trakt, 420029 Kazan, Russian Federation.
Fax +7 (843 2) 92 7370

The formation of three-dimensional micellar structures was studied. The structures are precursors of lyotropic mesophases based on the nonionic surfactant, lanthanide nitrates, and water. The geometric parameters and configurations of the micellar structures were determined. Good agreement between experimental data and the results of quantum chemical calculations was obtained.

Key words: lyotropic liquid crystals, metallomesogens, surfactants, micellar structures, self-organization, quantum chemical calculations.

Increased interest in nano-organized materials and the development of basic and applied research in this field are due to the prospects for novel technological applications. A topical avenue of design of highly organized structures is to use self-organization of nanoscale "building blocks" composed of colloidal particles.[1,2] In this connection of particular interest are lyotropic liquid crystals (LLC). Owing to unique properties and relative cheapness of design the LLC have found application in various fields of modern science including molecular electronics,[3,4] nanocatalysis,[5—7] pharmaceutics,[8] and serve models in studies of biological processes.[9]

Lyotropic mesophases can be functionalized in a preset fashion *via* the synthesis of lyotropic metal-containing mesogens in which the metal ion determines the necessary (magnetic, electrical, polarization, and luminescent) properties of the nanomaterial.[10—14] At present, studies on the possibility of using such systems as matrices in the design of nano-organized structures, *e.g.*, nanowires and nanodots are in progress.[15—18] Application of LLC in various devices requires the development of technologies that provide a particular molecular and spatial organization of these particles. In this connection a complex analysis of all stages of the evolution of a spontaneous molecular self-organization, from micellization to aggregation into molecular blocks and further assembly into a liquid-crystalline structure, is of paramount importance.

Research on the supramolecular structure of lyotropic mesophases is based on studies of the structure, interactions, and packing of particular fragments of the system in question. Using a specified structure element and the rules of filling the volume, it is possible to model the architecture of the entire macrosystem. However, in the case of lyotropic systems containing the solvent as a consituent the single-crystal X-ray diffraction techniques are inapplicable and therefore corresponding information is scarce and of limited use. Here, a clear idea of the structure of the system under study, qualitative assessment of its architecture, and prediction of the properties of lyotropic mesophases can be made using quantum chemical calculations of molecular characteristics and parameters of the entire system.[19]

Earlier,[20] we reported the strategies of synthesis, the range of existence, and the liquid-crystalline behavior of the first representatives of new lanthanide-containing lyotropic mesophases. Studies of the micellar behavior of such systems as precursors of liquid-crystalline phases are of particular importance because the physicochemical characteristics and geometric parameters of micelles and micellar aggregates will affect the supramolecular organization in the lyotropic mesophase and can be used as criteria for control of self-organization processes.

The aim of this work was to study the formation of three-dimensional structures, as precursors of lyotropic mesophases, on the intermediate scale between the molecular and macroscopic levels. Namely, we studied the formation of micellar aggregates from molecules, model the geometries of these structures, and calculated their heometric parameters by quantum chemistry methods.

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Experimental

The systems under study were based on decaethylene glycol monododecyl ether $C_{12}H_{25}O(CH_2CH_2O)_{10}H$ ($C_{12}EO_{10}$) (Aldrich), a micelle-forming nonionic surfactant, and lanthanide nitrate crystal hydrates $Eu(NO_3)_3 \cdot 6H_2O$ and $La(NO_3)_3 \cdot 6H_2O$ (Aldrich).

Solutions were prepared using bidistilled water characterized by the standard specific conductivity ($(2-3) \cdot 10^{-8}$ S cm^{-1}) and surface tension (72 mN m^{-1} at 298 K). The $C_{12}EO_{10}$: $Ln(NO_3)_3 \cdot 6H_2O$ molar ratio in the solutions was 0.5 (at the $C_{12}EO_{10}$, $La(NO_3)_3 \cdot 6H_2O$, and $Eu(NO_3)_3 \cdot 6H_2O$ concentrations of 1.00, 1.36, and 1.38 g L^{-1}, respectively).

The ranges of existence of micellar aggregates and the critical micelle concentrations (CMC) of corresponding aqueous solutions were determined by measuring the surface tension according to Wilhelmi. The time taken to form the interface before establishment of the adsorption equilibrium was 45 min. Measurements were carried out at 298 K.

Quantum chemical calculations were performed by the MM+, AM1, and molecular dynamics methods using the HyperChem Version 6.03 software.

Results and Discussion

Surfactants are potential "building blocks" for the LLC design because their biphilic molecules form various self-organized structures showing a broad spectrum of morphologies in aqueous and organic solutions at concentrations higher than the CMC. Further increase in the surfactant concentration causes transformation of such structures into lyotropic mesophases. In this work we studied only the first stage of aggregation, namely, spontaneous formation of spherical micelles.

The concentration dependences of the surface tension of the solutions obtained for the nonionic surfactant—water and surfactant—lanthanide nitrate—water systems show a kink in the CMC region characteristic of micelle-forming surfactants.

The initial data were obtained in the tensiometric experiments carried out according to Wilhelmi (Fig. 1). At the surfactant concentrations higher than the CMC, the surface tension in the system changes only slightly. In this case a saturated monomolecular surfactant layer characterized by the limiting adsorption (Γ_∞) is formed on the surface. The Γ_∞ values were determined as follows. By combining the Gibbs equation and the Langmuir adsorption isotherms, we used the Shishkovsky equation (1) for the concentration dependence of the surface tension:

$$\Delta\sigma(b, \Gamma_\infty) = RT\Gamma_\infty \ln(1 - bC), \qquad (1)$$

where Γ_∞ is the limiting adsorption[21] and b is the adsorption equilibrium constant. The parameters Γ_∞ and b were determined by approximating the experimental dependence of $\Delta\sigma_{exp}$ on C at low concentrations using Eq. (1) and the methods of regression analysis and by minimizing the functional

$$\varepsilon(b, \Gamma_\infty) = \sum_{i=1}^{n}\left[\Delta(\sigma_{exp})_i - \Delta\sigma_i(b, \Gamma_\infty)\right]^2. \qquad (2)$$

The $\Delta\sigma$ values at different values of the parameters b and Γ_∞ were calculated using Eq. (1). The error functional ε was minimized using the Marquardt algorithm.[21]

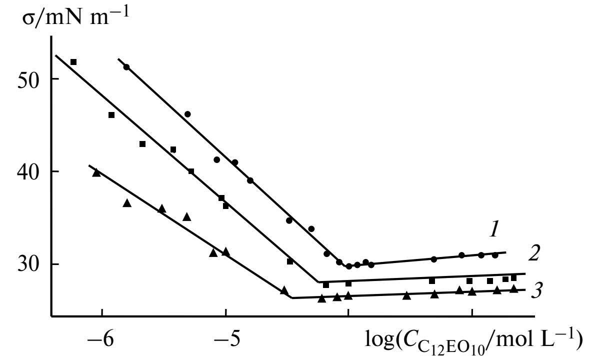

Fig. 1. Surface tension (σ) plotted *vs.* logarithm of $C_{12}EO_{10}$ concentration for the systems $C_{12}EO_{10}-H_2O$ (*1*), $C_{12}EO_{10}-Eu(NO_3)_3 \cdot 6H_2O-H_2O$ (*2*), and $C_{12}EO_{10}-La(NO_3)_3 \cdot 6H_2O-H_2O$ (*3*).

From the Γ_∞ values we determined the parameters of the adlayer S_0 and δ (S_0 is the surface area per adsorbed molecule equal to the surface area of the polar hydrophilic fragment of the molecule and δ is the adlayer thickness governed[22] by the length of the hydrophobic fragment of the molecule):

$$S_0 = 1/(\Gamma_\infty N_A), \qquad (3)$$

$$\delta = (M\Gamma_\infty)/\rho. \qquad (4)$$

Table 1 lists the micellization and adsorption parameters of the systems under study.

The results obtained for the binary system $C_{12}EO_{10}-H_2O$ are in agreement with the published data.[23—25] Introduction of lanthanide ions into this system causes a decrease in the surface tension and, therefore, reduction of the CMC and the limiting adsorption. Addition of eletrolytes to the solutions of nonionic surfactants leads to a decrease in the CMC due to desalina-

Table 1. Adsorption and micellization parameters of systems $C_{12}EO_{10}-H_2O$ (I), $C_{12}EO_{10}-Eu(NO_3)_3 \cdot 6H_2O-H_2O$ (II), and $C_{12}EO_{10}-La(NO_3)_3 \cdot 6H_2O-H_2O$ (III) at 278 K

System	$CMC \cdot 10^4$ /mol L^{-1}	$\Gamma_\infty \cdot 10^6$ /mol cm^{-2}	S_0/Å^2	δ/Å
I	0.915	2.280	72.82	14.29
II	0.6	1.569	105.81	16.63
III	0.315	1.539	107.85	16.52

tion effect among the lyotropic anions in the Hoffmeister series.[25] The effect of the lyotropic series in the interaction with the surfactant is most pronounced for monovalent metal anions, the nature of the cation being less important.[26—28] Recently,[29,30] the sensitivity of the Cl^-, NO^{3-}, and ClO_4^- anion constituents of transition-metal (Co, Ni, Mn, Zn, Cd) salts to their solubility in nonionic surfactants C_mEO_n (m = 12, 16; n = 4, 10, 23) and to formation of lyotropic liquid-crystalline system was reported. The authors pointed to an important role of coordination of the anion to the metal ion. Unlike the transition metals under study characterized by a coordination number (CN) of four, the lanthanide ions (La^{3+}, Eu^{3+}) are characterized by high CNs (8, 9), which makes their role in the reactions with the surfactants even more important. Also, in our case the interaction of oxyethylated groups with the lanthanide ion is to a greater extent due to the coordinating action of the ion. As a consequence, the polarizability increases due to the ion-dipolar interactions of the Ln ion with the polar groups of the surfactant and a decrease in the degree of hydration of these groups, which causes the CMC to decrease.

The surface area per adsorbed molecule equal to the suarface area occupied by the polar hydrophilic fragment of the surfactant molecule is smaller than the corresponding values in the case of micellization involving lanthanide ions. The results obtained for the metal-containing systems are consistent with the ionic radii of lanthanides,[31] namely, R_{La} = 1.16 Å and R_{Eu} = 1.066 Å. Micellar aggregation in the presence of metal ion involves a change in the conformation of the oxyethylene units with predominance of the *trans-gauche-gauche-trans*-conformation, which provides the coordination to the lanthanide ion.[32] The flexible polar oxyethylated groups $C_{12}EO_{10}$ are formed around the lanthanide ion, which leads to an increase in the size of the polar fragment of the molecule. The adlayer thickness remains almost unchanged, because the presence of the metal ion in the surfactant solution has a little effect on the conformation of the hydrocarbon radical of the amphiphilic molecule.

To gain a better insight into spontaneous self-organization of surfactants in aqueous solution and their configurations, we modeled the geometries of system´s components.

A commonly accepted model of a molecular aggregate is the droplet model by Tanford,[33] in which the nucleus of an aggregate possesses the properties of a nonpolar liquid. The droplet model permits numerical studies of nonspherical micelles and polymorphism on going from spherical to globular and cylindrical equilibrium modifications.[34]

Geometry calculations were carried out for a spherical molecular aggregate formed by $C_{12}EO_{10}$ in water. The hydrocarbon chains of the surfactant molecules were assumed to form a quasi-liquid compact hydrocarbon nucleus containing no voids (small hydrocarbon droplet). If n is the aggregation number and V_r is the volume of the hydrocarbon radical, then the volume, V, of the hydrocarbon nucleus can be determined as follows:

$$V = nV_r. \tag{5}$$

At the same time the volume depends on the shape of the micelle and on the length of the radical L_r. In particular, for a spherical micelle one has

$$V = 4\pi L_r^3/3. \tag{6}$$

The aggregation number was calculated from Eqs (5) and (6) assuming that the density of the hydrocarbon nucleus equals that of the macroscopic hydrocarbon phase at the same temperature:

$$n = 4\pi L_r^3/(3V_r). \tag{7}$$

The maximum length and the volume of the hydrocarbon radical were determined as follows[35]:

$$L_r = 1.5 + 1.265N_C, \tag{8}$$

$$V_r = 54.3 + 26.9(N_C - 1), \tag{9}$$

where 1.5 and 1.265 (Å) is the length per CH_2 group and per C—C bond, respectively; 54.3 and 26.9 (Å^3) are the volumes of the terminal methyl and methylene groups, respectively;[36] and N_C is the number of carbon atoms in the chain fragment that is included in the hydrocarbon nucleus of the micelle.

Optimum geometric parameters of the surfactant molecule were calculated by the molecular mechanics (MM+) and molecular dynamics (MD) methods and by the semiempirical quantum chemical method AM1, which were chosen based on the optimum cost/performance ratio. The starting conformation of the surfactant molecule was determined after optimization by the MM+ and AM1 methods.

The MM+ method can be used for modification of the starting molecular conformation and as a preliminary stage for the determination of the optimum configuration of the system.[37,38] The method includes the potential fields of all atoms in the system and provides the most general treatment of problems among all the molecular mechanics methods.[39]

The conformation of the surfactant molecule in solution with allowance for hydrogen bonding was determined by the AM1 method. In most cases the quality of the results obtained approaches that of the *ab initio* calculations, being better that that provided by the MNDO method; this especially concerns the description of hydrogen bonds.[40]

The final structure of the surfactant molecule with allowance for thermodynamic parameters was determined by the MD method, which has been successfully used in

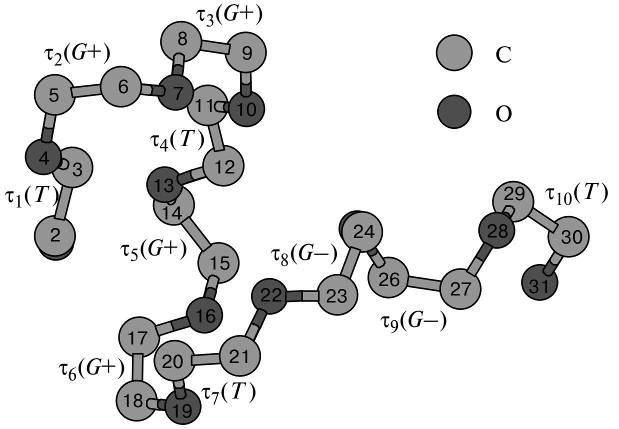

Fig. 2. Structure of the polar fragment of the surfactant molecule; shown are the conformations of O—C—C—O units; τ_n is the torsion angle (atoms are numbered from the chain head), T stands for the *trans*-conformation and ($G\pm$) stands for the (*gauche*+)- or (*gauche*–)-conformation.

modeling of micellar systems and for the determination of geometric parameters and thermodynamic characteristics.[41,42]

For convenience of calculations, processing of the results obtained, and reduction of the computing time, the effects of solvent on the polar and nonpolar fragments of the surfactant molecule were analyzed separately. The surfactant molecule was conditionally divided into two fragments, the hydrocarbon "tail" ($C_{12}H_{25}^-$) and the polar group ($-O(CH_2CH_2O)_{10}H$). A proton was attached to the former at the junction with the polar fragment and an ethyl radical was attached to the latter at the junction with the nonpolar group. This facilitated subsequent assembly of the hydrocarbon tail and the polar fragment with retention of the conformation at the junction.

Table 2. Geometric characteristics of nonpolar (C_{12}) and polar (EO_{10}) fragments of the surfactant molecule

Fragment	X	Y	Z
		Å	
C_{12}	2.61	2.48	15.86
EO_{10}	9.56	7.11	14.59

Geometry optimization of the polar fragment of the surfactant molecule by the MM+, AM1, and MD methods was carried out for $T = 298$ K with a unit cell (edge length 40 Å) containing a total of 2114 water molecules. As a result, we obtained the geometric parameters of the polar fragment of the surfactant molecule (Fig. 2) with the O—C—C—O torsion angles (τ/deg) listed below.

τ_1	τ_2	τ_3	τ_4	τ_5	τ_6	τ_7	τ_8	τ_9	τ_{10}
154	66	66	146	49	30	104	–67	–45	92

The configuration of the polar fragment of the surfactant molecule shows alternation of *trans-gauche-gauche-trans*-conformations (*T-G-G-T*) of the O—C—C—O units, which leads to gradual helical twisting of the structure.

The structure of the hydrocarbon fragment of the surfactant molecule was optimized by the MD method with inclusion of the solvent effect. Numerical experiment was carried out in a unit cell (edge length 20 Å) containing a total of 265 water molecules. The absence of imaginary vibrational frequencies for the transition states in the final step of calculations served a criterion for stability of the structure of the surfactant molecule in solution.

The geometric parameters of the modeled fragments of the surfactant molecule (Fig. 3) are listed in Table 2.

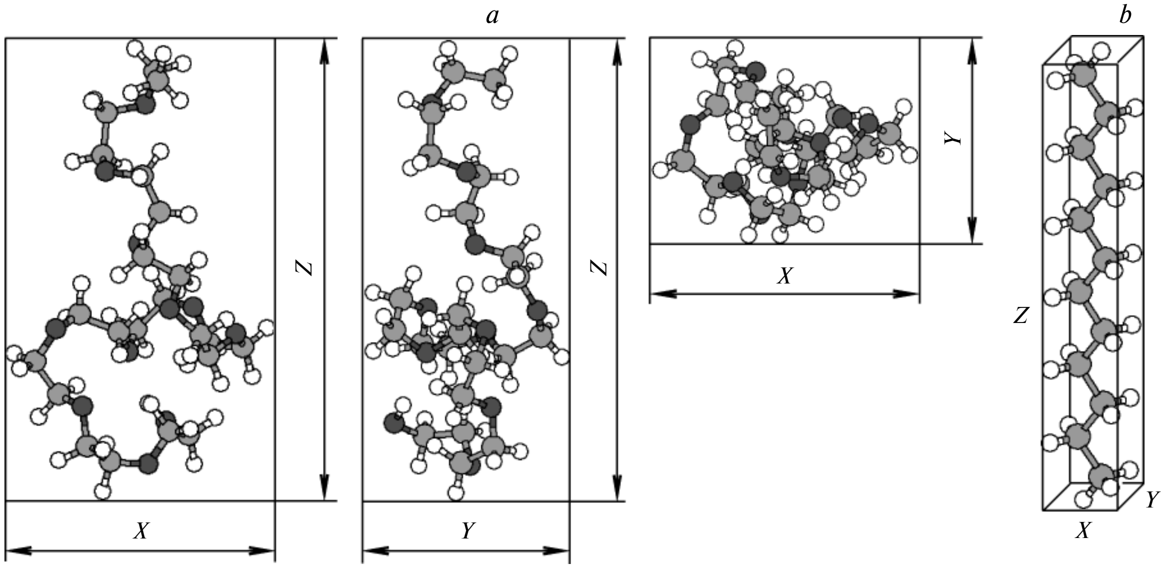

Fig. 3. Two-dimensional projections of the structure of the polar fragment (*a*) and three-dimensional structure of the nonpolar fragment (*b*) of the $C_{12}EO_{10}$ molecule.

Table 3. Calculated characteristics of the micelle structure and its fragments for the $C_{12}EO_{10}$—H_2O* system

Computational method	V	V_r	V_0	L_r/Å
		Å^3		
Molecular modeling	12034.07	216.83	429.43	15.86
From Eqs (5), (7)—(9)	19429.27	350.20	467.45**	14.29

* n = 55.5.

** The volume of the polar fragment of the molecule was calculated using the experimentally determined S_0 value (see Table 1).

Considering a micelle as a self-closed monomolecular layer and knowing the geometric characteristics of a single surfactant molecule, one can estimate the size of the micelle and the adlayer. Table 3 lists the parameters obtained from Eqs (5) and (7)—(9) and the values obtained from modelig of the fragments of the surfactant molecule in solution. The molecular volumes in the HyperChem program were determined using the QSAR (Quantitative Structure—Activity Relationships) module incorporated into the program.

Analysis of the data listed in Table 3 shows different volumes of the hydrocarbon radical and, hence, the volume hydrocarbon nucleus compared to the results of modeling. This is due to some admissions in the Tanford method[34] concerning the nonpolar fragment of the surfactant molecule, in particular, ignoring the lengths of interatomic bonds of neighboring methylene groups. The Tanford procedure uses summation of the volumes of the methylene groups, which leads to an increase in the total volume of the hydrocarbon radical (V_r = 350.20 Å^3; *cf.* V_r = 216.83 Å^3 as shown by the results of modeling with inclusion of the atom-atom interaction of the neighboring methylene groups and the overlap of the AOs of adjacent carbon atoms).

By comparing the experimental and theoretical adlayer thicknesses we can determine the orientation of the molecules in the monomolecular layer. Similarity between the adlayer thickness (δ = 14.29 Å) and the length of the hydrocarbon molecular fragment (L_r = 15.86 Å) indicates a vertical orientation of the molecules in the adlayer.

Thus, in spite of our approximations, the model of the surfactant molecule proposed in this work provides a quite correct description of the structure of spherical micelles and the method used here for the studies of micellization and adsorption at the air—solution interface leads to reliable description of the initial stage of formation of lyotropic mesophases. The characteristics determined in our study can be used in the design of LLC-based materials with preset morphology and functionality.

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