Kinetics of Triglyceride Solubilization by Micellar Solutions of Nonionic Surfactant and Triblock Copolymer. 1. Empty and Swollen Micelles

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By NMR and static and dynamic light scattering we investigated how the micelle size, shape, and aggregation number vary during the solubilization of triolein in mixed aqueous solutions of the nonionic surfactant $C_{12}E_n$ ($n = 5$ or 6) and the nonionic triblock copolymer Synperonic L61 (SL61). The latter was found to strongly accelerate the solubilization, although the copolymer alone is unable to solubilize triglycerides. A series of solutions containing different concentrations of surfactant and copolymer has been studied. The light scattering shows that we are dealing with giant micellar aggregates, each of them containing hundreds to thousands of surfactant molecules and dozens of copolymer molecules. Assuming that the micelles have the shape of prolate ellipsoids, we calculated their length and width. The results indicate that the initial, strongly elongated micelles transform into spherical or slightly ellipsoidal ones at the end of solubilization. The micelle aggregation number and hydrodynamic radius decrease by factors of 2−6 during the solubilization; i.e., one empty micelle splits into several smaller swollen micelles of radius 4−5 nm. The NMR measurements reveal that the equilibrium solubilization capacity (solubilized oil/mol of surfactant) is virtually not affected by the addition of SL61. Hence, the copolymer accelerates the process without influencing its final result; that is, SL61 acts as a promoter of solubilization. The results are used in the subsequent two papers of this series to develop a kinetic model of triglyceride solubilization and to verify it against experimental data.

1. Introduction

As known, under appropriate conditions the aqueous surfactant solutions are able to dissolve relatively large amounts of oil (as compared to oil solubility in pure water) by means of solubilization, that is by incorporation of oil molecules into surfactant aggregates.[1−3] The solubilization is an important element of detergency[4,5] and finds various applications in micellar enhanced separation,[6] emulsion polymerization, and the preparation of various cosmetic, pharmaceutical, and agricultural products.[1] Oils that are partially soluble in water (such as benzene, toluene, phenol, liquid alkanes, etc.) are efficiently solubilized by micelles of ionic surfactants.[1,2] The kinetic description of oil solubilization in these systems[7−12] involves dissolution of oil molecules into the aqueous phase and their subsequent capturing by the micelles, which are diffusing in the vicinity of the oil−water interface.

If water-insoluble oils (such as triglycerides) are to be solubilized, the ionic surfactants are rather inefficient. In contrast, it has been found[13−18] that some nonionics, close to their cloud point, can be good solubilizers of triglycerides. There is evidence that the nonionic micelles come in a direct contact with the triglyceride−water interface to capture oil molecules.[13,14] Such a process of micelle adsorption is improbable for ionic surfactants, because of the electrostatic (double layer) repulsion between the micelles and the oil−water interface, and this is the most probable reason for the inability of ionic surfactants to solubilize triglycerides. In contrast, a significant attraction has been detected between the partially dehydrated ethoxy groups of the nonionic surfactants at temperatures somewhat below their cloud point.[19] Consequently, adsorption of the micelles at the oil−water interface is possible under these conditions.

Close to the phase inversion temperature of the oil-in-water emulsions, more complicated mechanisms of solu-

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bilization are sometimes observed, including the formation of intermediate phases and dynamic Marangoni effects, which are caused by the partial surfactant solubility in the oil phase and the ultralow interfacial tension.[3,15−17,20]

To further clarify the process of triglyceride solubilization by nonionic surfactants, in this paper we investigate a system involving triolein (as a representative of the triglycerides), a nonionic surfactant $C_{12}E_n$ ($n = 5$ or 6), and the nonionic triblock copolymer Synperonic L61 (SL61, approximate formula $E_{2.5}P_{34}E_{2.5}$), where C_{12} = dodecyl group, E = ethylene oxide group, and P = propylene oxide group. These nonionic surfactants have been chosen because their micelles solubilize triglycerides at a detectable rate at room temperature. To reduce the cloud point of $C_{12}E_6$ and to accelerate the solubilization, we added 0.2 M Na_2SO_4 to the solutions of $C_{12}E_6$. Concerning $C_{12}E_5$, its micelles can solubilize triolein even without any added inorganic electrolyte. The polymer SL61 was used as an additive, because we found[21,22] that it strongly accelerates the solubilization process.

In this study we apply light scattering and NMR techniques to determine how the micelle properties (such as aggregation number, size, shape, diffusion coefficient, number concentration, and number of solubilized oil molecules/micelle) vary during the solubilization. This information is an important prerequisite for development of an adequate theoretical model of the kinetics of solubilization,[21] which takes into account the transformation of the empty micelles into swollen ones. Furthermore, the obtained data are used to test the theoretical model against kinetic experimental data for triolein solubilization.[22]

The micellar changes during solubilization are also a subject of independent interest.[4,23−35] It has been established by several research groups that the solubilization of various oils affects the surfactant micelles in different ways. The aliphatic hydrocarbons are found to increase the micelle radius if the initial empty micelles are spherical.[4,33−35] When the empty micelles are relatively large and nonspherical (e.g. rod- or wormlike), the solubilization of alkanes often causes a rod-to-sphere transition, accompanied with a significant decrease in the micellar size and aggregation number.[23,27] These transformations are explained with the predominant incorporation of alkanes inside the hydrocarbon core of the micelles.

Amphiphilic molecules, such as alkanols and amines, are solubilized with their polar groups preferentially located at the micelle surface.[2,4,23−26] Such substances reduce the optimal area/amphiphilic headgroup and thereby promote the formation of aggregates of lower mean surface curvature (rods, disks). Similar effects have been observed also with aromatic hydrocarbons solubilized by cationic micelles, in which a specific interaction between the positively charged headgroups of the surfactant and the highly polarizable π-electrons of the aromatic ring takes place.[28−32] This specific interaction leads to a preferential location of the aromatic hydrocarbons at the surface of the cationic micelles.

The triglyceride molecules have three long hydrocarbon tails connected to a polar group. For this molecular structure it is not easy to predict what would be the effect of the solubilizate on the micellar size and shape. The voluminous hydrocarbon tails render the triglyceride properties similar to those of the aliphatic substances, whereas the glyceride polar group could induce some specific interaction with the surfactant headgroups. The results obtained in this study show that the solubilization of triolein into nonionic surfactant micelles leads to effects, similar to those observed with normal (straight) aliphatic substances: the solubilization is accompanied with a splitting of the long rodlike micelles into smaller aggregates, and consequently, the micelle size significantly decreases.

This paper is organized as follows. Section 2 describes the materials used, experimental methods, and procedures of data processing. Section 3 presents our results for the micelle aggregation number, shape, composition, and amount of solubilized oil.

2. Experimental Details

2.1. Materials. The following substances were used in our experiments: pentaoxyethylene monododecyl ether, $C_{12}E_5$ (Fluka), molecular mass $M_w = 406.6$; hexaoxyethylene monododecyl ether, $C_{12}E_6$ (Fluka), $M_w = 450.6$; Synperonic PE/L61 (briefly SL61) with formula $(C_2H_4O)_{2.5}(C_3H_7O)_{34}(C_2H_4O)_{2.5}$ (ICI), $M_w \approx 2100$; triolein (Nu-Chek Prep. Inc.), $M_w = 885$; Na_2SO_4, analytical grade (Sigma); NaCl, analytical grade (Merck). All these substances were used as received, without additional purification.

In all experiments reported in this paper, we used 0.01 M NaCl solution for $C_{12}E_5$ and 0.2 M Na_2SO_4 solution for $C_{12}E_6$. NaCl was added to the $C_{12}E_5$ solutions just for having a well-defined ionic strength, whereas Na_2SO_4 was added to the $C_{12}E_6$ solutions for enhancing the solubilization rate owing to the salting-out effect.

The mixed solutions of $C_{12}E_n$ ($n = 5, 6$) and SL61 were prepared in the following way. First, the electrolyte was dissolved in water and the solution was filtered through a 100 nm filter (Millex VV, Millipore). Then stock solutions, containing a mixture of $C_{12}E_n$ and Synperonic L61 of a desired molar ratio, were prepared by dissolving the necessary amounts of the two surfactants in the respective electrolyte solution. On the next day, the stock solution was diluted to the required surfactant concentration. Thus, a set of solutions of different total surfactant concentration was prepared at constant electrolyte concentration and fixed $C_{12}E_n$ to SL61 ratio.

The solutions were stored at room temperature for several hours before dividing them into two parts. One of the two portions was stored for several hours in a thermostat at 27 °C and was, afterward, studied by dynamic and static light scattering (DLS and SLS) to determine the size, shape, and aggregation number of the empty micelles. A drop of triolein was added to the other portion of solution, which was then shaken by hand (to disperse the oil) and was stored for more than 10 days in a thermostat at 27 °C to accomplish the solubilization. The latter solutions

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were periodically studied by DLS, SLS, and NMR to analyze how the micelle properties changed with time.

As already mentioned, all measurements were performed at 27 °C. For comparison, the cloud-point temperature of 12 mM $C_{12}E_5$ is 31 °C; the cloud point of 12 mM $C_{12}E_6$ is 41 °C in the presence of 0.2 M Na_2SO_4. The addition of 0.1 wt % SL61 to the latter solution reduces the cloud point to 35 °C.

All glassware was cleaned by chromic acid and rinsed with deionized water from Milli-Q water purification system (Millipore Inc.).

2.2. Dynamic and Static Light Scattering. DLS is used to measure the translational diffusion coefficient of the micelles and to determine their hydrodynamic (Stokes) diameter, d_h. The latter can be calculated[36] from the measured micelle diffusion coefficient, D, by means of the Stokes–Einstein formula

$$d_h = kT/(3\pi\eta D) \tag{1}$$

where η is the viscosity of the disperse medium, T is the absolute temperature, and k is the Boltzmann constant.

SLS has been used to determine the molecular mass, M_p, and aggregation number of the micelles. In principle, one can apply SLS also for determining the second virial coefficient, A_2, and the radius of gyration, R_g, of colloid particles and polymer solutions.[37] However, in our systems this is impossible due to the following reasons. R_g cannot be determined because the micelles in the studied systems are too small, $d_h \ll \lambda_W$, where λ_W is the wavelength of the illuminating light. Likewise, A_2 cannot be measured because in these systems the micelle aggregation number increases with the surfactant concentration.[39] Therefore, one is not allowed to use the Zimm plot, which employs the assumption that the scattering entities do not change in size and shape upon variation of their concentration.[37]

For these reasons, we found the mass of the micelles (and their aggregation number) from the relation[39]

$$M_p = \frac{R(\theta \to 0)}{cK} \tag{2}$$

where $c = c_S - \text{cmc}$ (c_S is the total surfactant concentration, cmc is the critical micelle concentration), θ is the scattering angle, $R(\theta)$ is the Rayleigh ratio, which is proportional to the intensity of the scattered light, and K is an optical constant:

$$K = \frac{4\pi^2}{N_A} \frac{n_0^2}{\lambda_W^4}\left(\frac{dn}{dc}\right)^2 \tag{3}$$

N_A is the Avogadro number, n_0 and n are the refractive indices of the solvent (water) and solution, and dn/dc is measured independently by refractometer.

Equation 2 can be used if the contribution of the interactions between the micelles is negligible. This is fulfilled when the interactions are short-ranged and the micelle concentration is not very high. The typical mean separation between the micelles in the studied solutions (for surfactant concentration 12 mM and aggregation number ≈ 1000) is about 50 nm, which is well above the typical hydrodynamic radius of the micelles (5–10 nm). The ionic strength of the studied solutions ensures a Debye screening length below 3.5 nm; i.e., the electrostatic interactions are relatively short-ranged.

The light scattering measurements were performed at 27 °C by means of a Malvern system 4700C (Malvern Instruments, U.K.), equipped with an argon laser operating with a vertically polarized incident beam at $\lambda_W = 488$ nm.

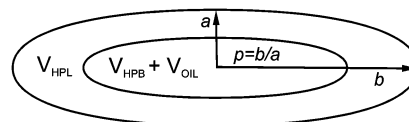**2.3. Nuclear Magnetic Resonance (NMR).** The aim of the NMR experiment was to determine the amount of solubilized

Figure 1. Sketch of a swollen micelle, which has the shape of a prolate ellipsoid with semiaxes a and b.

triolein in the micelles. For this purpose, the molar ratio triolein/$C_{12}E_n$ was determined from the areas of selected, well-resolved peaks in the ^1H NMR spectra of the swollen micelles (see section 3.2 for more details).

The spectra were recorded on a Bruker DRX-250 NMR spectrometer, operating at 250 MHz for protons, using a dual $^1H/^{13}C$ probehead. All spectra were measured at 300 K (27 °C). The temperature was controlled by a standard Bruker variable-temperature VT-1000 unit. The temperature of the sample was independently verified from the spectrum of the mixture CCl_3F, CD_3OD, CF_3COOH, and CH_2Cl_2 (volume ratio 8:6:1:1), which was closed in a narrow capillary and placed in the NMR tube. The internal temperature of the sample was calculated using the following equation[40]

$$T = 256.9 + 0.401\Delta\nu - 6.9696 \times 10^{-4}\Delta\nu^2 + \\ 1.728 \times 10^{-6}\Delta\nu^3 \tag{4}$$

where T is in Kelvin degrees and $\Delta\nu = \nu_{CH_2Cl_2} - \nu_{OH}$ Hz at 250.13 MHz frequency of the spectrometer. The accuracy of this measurement is better than ± 0.5 K.

2.4. Data Processing. The following two assumptions were made to interpret the experimental data: (1) The micelles have the shape of prolate ellipsoids. (2) The ratio of $C_{12}E_n$/SL61 in the micelles is equal to their ratio in the dissolved surfactant mixture. Assumption 2 implies that only one type of mixed micelles is formed in the $C_{12}E_n$/SL61 mixture; i.e., that there is no segregation of the micelles into $C_{12}E_n$ and SL61 enriched ones. Indeed, since $c_S \gg$ cmc, the micelle composition should be virtually the same as that of the total mixture, if only one type of mixed micelles is present. The good solubility of SL61 in the micellar solutions of $C_{12}E_n$ indicates that these two substances readily mix; therefore, only one type of micelles is expected.

Note that the above two assumptions are used only to characterize the change of the micelle shape, as a result of the solubilization of oil. The most important micelle characteristics (aggregation number, total number concentration, diffusion coefficient, and number of oil molecules/micelle) are directly determined by the used experimental methods and are not influenced by the above assumptions.

The calculation procedure is the following. The average mass of a micelle, M_p, is determined by SLS; see eq 2. The molar fractions of $C_{12}E_n$ and SL61 in the micelles are calculated by using assumption 2 above. Then we calculate the volume of the hydrophobic part of the surfactant molecules, V_{HPB}, in the micelle, which includes the aliphatic chains of the $C_{12}E_n$ molecules and the poly(oxypropylene) chains of the SL61 molecules (Figure 1). The mass density of the hydrophobic part was taken as 0.9 g/cm^3 in these calculations. From the NMR measurements we know the molar ratio $C_{12}E_n$/triolein in the micelle, which allows us to calculate the number of triolein molecules/micelle and the respective volume, V_{OIL}, occupied by triolein in the micelle.

To obtain the volume of the hydrophilic coat of the micelle, we calculate the mass of the ethoxy groups/micelle. On the basis of the experiments of other authors,[41,42] we assume that each ethoxy group binds 2 water molecules. Thus, we can determine the total mass of the hydrophilic coat. Assuming a mass density of ≈ 1 g/cm^3, we calculate the respective volume, V_{HPL}. The total volume of the micelle is $V_{MIC} = V_{HPB} + V_{HPL} + V_{OIL}$ (Figure 1).

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Table 1. Properties of the Micelles after 0, 3, and 10 days of Contact of Triolein with Solutions Containing 12 mM $C_{12}E_6$ + 200 mM Na_2SO_4 or 12 mM $C_{12}E_5$ + 10 mM NaCl

type of surfactant	SL61 (wt %)	D_h (nm)	$N_{surfact.}$	N_{SL61}	$N_{triolein}$	V (nm^3)	p	a (nm)
			0 days (Empty Micelles)					
$C_{12}E_6$	0.0	25.5	1010	0	0	1178	17.0	2.6
	0.1	17.7	518	22	0	692	11.5	2.4
	0.2	15.0	356	30	0	517	9.3	2.4
$C_{12}E_5$	0.1	34.7	1841	77	0	2204	24	2.8
	0.2	26.8	895	74	0	1219	21	2.4
	0.3	24.0	726	90	0	1141	17	2.5
			After 3 days					
$C_{12}E_6$	0.0	20.3	853	0		996	11.9	2.7
	0.1	10.1	252	11	6	345	3.7	2.8
	0.2	9.8	195	16	7	304	3.9	2.7
$C_{12}E_5$	0.1	17.2	729	30	26	916	8.0	3.0
	0.2	14.5	437	36	16	620	7.0	2.8
	0.3	13.4	331	41	12	526	6.5	2.7
			After 10 days					
$C_{12}E_6$	0.0	13.7^a	555^a	0	12^a	681^a	4.8^a	3.2^a
	0.1	8.4	219	9	8	307	1.2	3.9
	0.2	9.1	198	16	9	311	2.6	3.1
$C_{12}E_5$	0.1	8.9	341	13	20	404	1	4.6
	0.2	9.1	261	22	15	377	1.3	4.1
	0.3	10.2	235	29	12	378	3.3	3.0

^{a} After 16 days.

The assumption that the micelles have the shape of a prolate ellipsoid allows us to determine the semiaxes a and b from the volume of the micelles, V_{MIC}, and their diffusion coefficient, D, determined by DLS. Note that the hydrodynamic diameter, d_h, calculated by eq 1 is an effective micelle diameter, which has a value between $2a$ and $2b$. When the data are processed, the eccentricity $p = b/a$ is determined as an adjustable parameter. It is related to the diffusion coefficient of the ellipsoid through the expression[43]

$$D = \frac{kT}{6\pi\eta a}\left[\frac{3}{4}p\beta + \frac{1}{8}p\alpha_{II} + \frac{1}{4}\frac{\alpha_I}{p}\right] \qquad (5)$$

where β is defined as

$$\beta = \frac{\cosh^{-1}p}{p(p^2-1)^{1/2}} \quad p > 1 \text{ (prolate ellipsoid)} \qquad (6)$$

α_{II} and α_I are the mobility functions for the ellipsoid in directions parallel and perpendicular to the main axis, respectively

$$\alpha_{II} = \frac{2(p^2\beta-1)}{p^2-1} \qquad \alpha_I = \frac{p^2(1-\beta)}{p^2-1} \qquad (7)$$

In addition, the small semiaxis can be expressed through the micellar volume V_{MIC},

$$a = \left(\frac{3V_{MIC}}{4\pi p}\right)^{1/3} \qquad (8)$$

which allows one to determine p from the comparison of the experimentally measured D with the theoretically calculated D (eqs 5–8). In this way, one can find the shape of the micelle from the light scattering and NMR data.

3. Results and Discussion

3.1. Hydrodynamic Diameter of the Micelles. A summary of the results obtained by DLS is presented in Table 1 and Figures 2 and 3. In particular, Table 1 shows the obtained values of the micelle hydrodynamic diameter, d_h, the average numbers of molecules of surfactant,
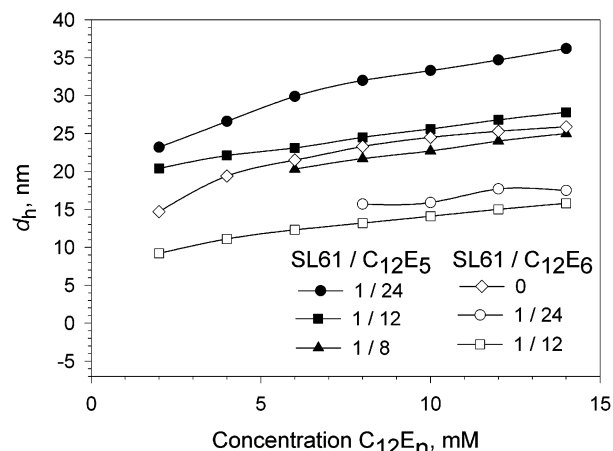
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Figure 2. Hydrodynamic diameter, d_h, of mixed SL61/surfactant micelles as a function of the surfactant concentration at several fixed ratios of polymer to surfactant (mol/mol). All solutions of $C_{12}E_5$ contain 0.01 M NaCl, while all solutions of $C_{12}E_6$ contain 0.2 M Na_2SO_4.
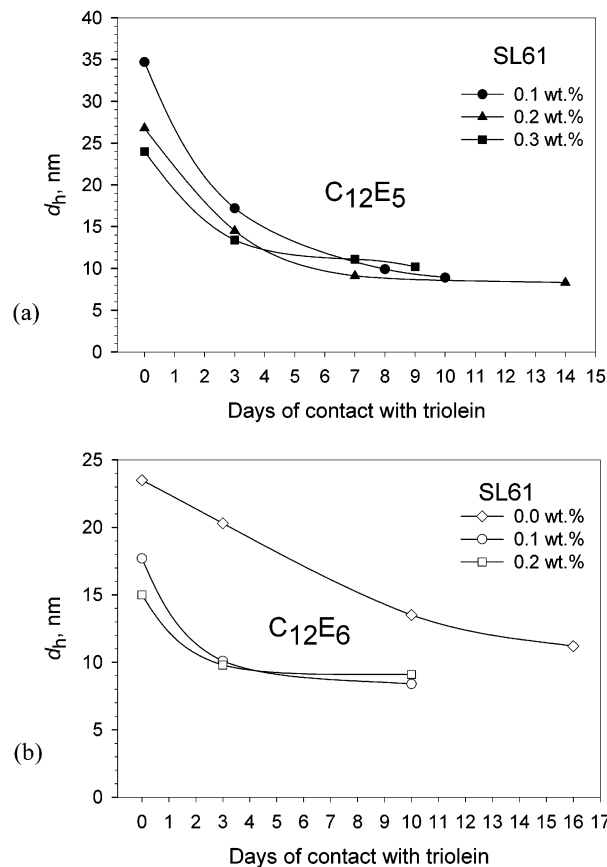

Figure 3. Variation of the micelle hydrodynamic diameter, d_h, during the process of triolein solubilization in the presence of various concentrations of SL61 in solutions of (a) 12 mM $C_{12}E_5$ + 0.01 M NaCl and (b) 12 mM $C_{12}E_6$ + 0.2 M Na_2SO_4.

polymer, and triolein per micelle, $N_{surfact.}$, N_{SL61}, and $N_{triolein}$, the average volume, V, the eccentricity, p, and the small semiaxis, a, of the micelles. Note that no measurements with $C_{12}E_5$ without SL61 are included in this paper, because we expect that some of the assumptions used to interpret the data (section 2.4) might be inapplicable to the giant branched micelles of pure $C_{12}E_5$ (without SL61 and triolein). A detailed characterization of the micelles of $C_{12}E_5$ was made in ref 39 by light scattering and electron cryomicroscopy.

Light scattering and NMR measurements have been carried out (i) before solubilization, (ii) at the third day, and (iii) at the 10th day of contact between oil and surfactant solution, for various ratios $C_{12}E_n$/SL61; see Table 1. For the solutions of $C_{12}E_6$ without SL61, measurements were made also after 16 days of contact with triolein, because the solubilization in this system is very slow.

Figure 2 shows results about the size of micelles, which have not been in contact with triolein. It is seen that $C_{12}E_5$ forms larger micelles than $C_{12}E_6$, despite the lower ionic strength of the added inorganic electrolyte in the $C_{12}E_5$ solutions. This is due to the shorter (and consequently less hydrophilic) heads of the $C_{12}E_5$ molecules, which give rise to formation of larger micelles with smaller mean curvature (as compared to $C_{12}E_6$). It is seen also that the addition of SL61 to the solutions leads to a decrease of the micelle size by $\approx 30\%$ for $C_{12}E_5$ and by $\approx 40\%$ for $C_{12}E_6$. Upon the increase of the surfactant concentration from 2 to 14 mM, the size of the micelles increases by 40 to 80%.

As seen from Figure 3, the size of the micelles decreases during the solubilization of triolein. In all systems (except $C_{12}E_6$ without SL61), d_h decreases by a factor of about 2 after 3 days of contact of the surfactant solution with triolein. The subsequent contact of the micelles with oil (up to the 10th day) leads to a further, though less pronounced, decrease of the micellar size. After 7−8 days of solubilization, the micelles reach their final equilibrium size ($d_h \approx 8-10$ nm) which is almost the same for all systems, irrespective of the concentration of SL61 and the type of the used surfactant ($C_{12}E_5$ or $C_{12}E_6$).

For the solution of $C_{12}E_6$ without SL61, the decrease of the micelle size is much slower due to the lower rate of solubilization (Figure 3b). For this solution more than 16 days are needed to reach the final state with equilibrium swollen micelles.

3.2. Micelle Aggregation Number and Amount of Solubilized Oil. The main results from the SLS experiments, presented in Table 1 and Figure 4, show that we deal with giant micellar aggregates, each of them containing hundreds to thousands surfactant ($C_{12}E_n$) molecules and dozens of polymer (SL61) molecules. The numbers of surfactant and polymer molecules per micelle, $N_{surfact.}$ and N_{SL61}, are greater for the solutions with $C_{12}E_5$ in comparison to the ones with $C_{12}E_6$, at identical other conditions. $N_{surfact.}$ decreases, whereas N_{SL61} increases, with the rise of the concentration of SL61. During the process of solubilization, one observes a significant decrease of $N_{surfact.}$ and N_{SL61}, especially in the first 3 days. The changes in the solution of $C_{12}E_6$ *without* SL61 are much slower as compared to all other investigated solutions. Figure 4 shows that the micelles finally reach almost the same aggregation number, despite of the different ethoxy chain lengths and SL61 concentrations.

To determine the amount of solubilized oil in the micelles ($N_{triolein}$ in Table 1) we analyzed the NMR spectra of the surfactants and oil and assigned the signals to the respective molecular groups. Solutions of 5 wt % $C_{12}E_5$ in D_2O and 10 wt % triolein in $CDCl_3$ were used for this purpose. The recorded spectra, along with the peak assignment, are shown in Figure 5. The assignment of the signals was made by taking into consideration the magnetic anisotropy effect of the neighboring groups and was additionally confirmed by two-dimensional proton−proton correlated spectroscopy (2D COSY) and heteronuclear multiple-quantum coherence spectroscopy (HMQC).

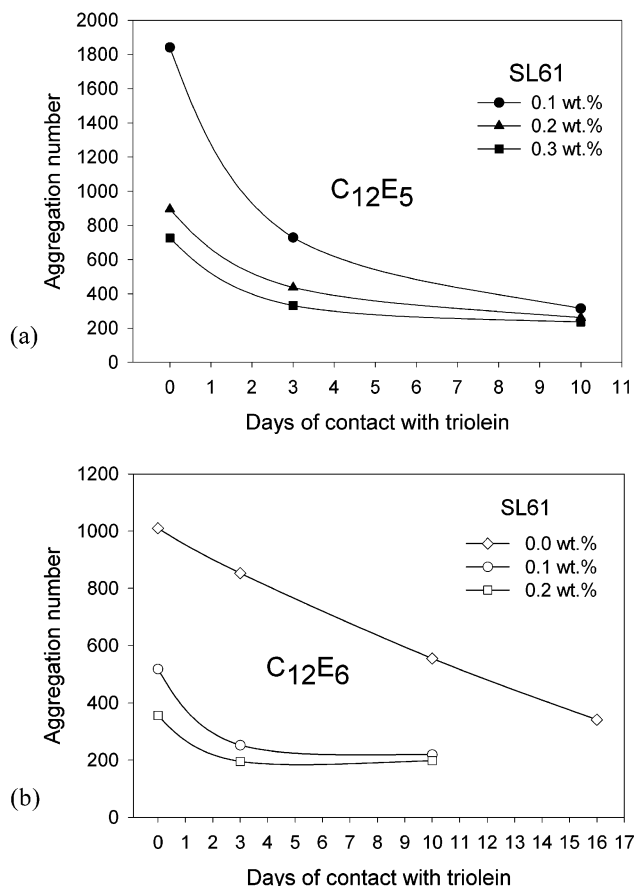The ^{1}H NMR spectrum of swollen micelles (containing triolein) of 12 mM $C_{12}E_5$ and 0.3 wt % SL61, in D_2O, is

Figure 4. Variation of the micelle aggregation number, $N_{surfact.}$, during the process of triolein solubilization in solutions of (a) 12 mM $C_{12}E_5$ + 0.01 M NaCl and (b) 12 mM $C_{12}E_6$ + 0.2 M Na_2SO_4, in the presence of various concentrations of SL61.

presented in Figure 5c. Most of the peaks of $C_{12}E_5$ and triolein are overlapped in the aliphatic region and cannot be used for determination of the surfactant/oil ratio. The most convenient signals for this purpose are those at 2.15 ppm from the $O-CO-CH_2$ groups of triolein and the compound signal at 1.5 ppm, which results from the β-CH_2 group of $C_{12}E_5$ (or $C_{12}E_6$) and $-O-CO-CH_2-CH_2$ groups of triolein. The fraction of this signal created by the triolein molecules can be estimated from the area of the peak at 2.15 ppm. As one can see from the individual ^{1}H NMR spectrum of triolein, the relative ratio of the two signals is 1:1. Therefore, the contribution of triolein can be subtracted from the total area of the 1.5 ppm peak, and the result gives the area corresponding to β-CH_2 group. In other words, the surfactant-to-oil ratio can be found from the following equation:

$$\frac{\text{molecules of } C_{12}E_n}{\text{molecules of oil}} = \frac{(I_{1.5} - I_{2.15})/2}{I_{2.15}/6} = 3\frac{(I_{1.5} - I_{2.15})}{I_{2.15}} \quad (9)$$

Here $I_{2.15}$ is the area of the signal at 2.15 ppm, corresponding to six protons from three $O-CO-CH_2$ groups in the triolein molecule; $I_{1.5}$ is the total area of the peak at 1.5 ppm, which corresponds to the overlapping signals of β-CH_2 group of $C_{12}E_n$ (for two protons) and of three $-O-CO-CH_2-CH_2$ groups (six protons).

By using the above procedure, we determined the molar ratio of $C_{12}E_n$ to triolein in the systems shown in Table 2. From the column "3 days" one sees that the solubilization is faster in $C_{12}E_5$ solutions, which is in agreement with the kinetic solubilization studies.[22] For solutions of $C_{12}E_6$,
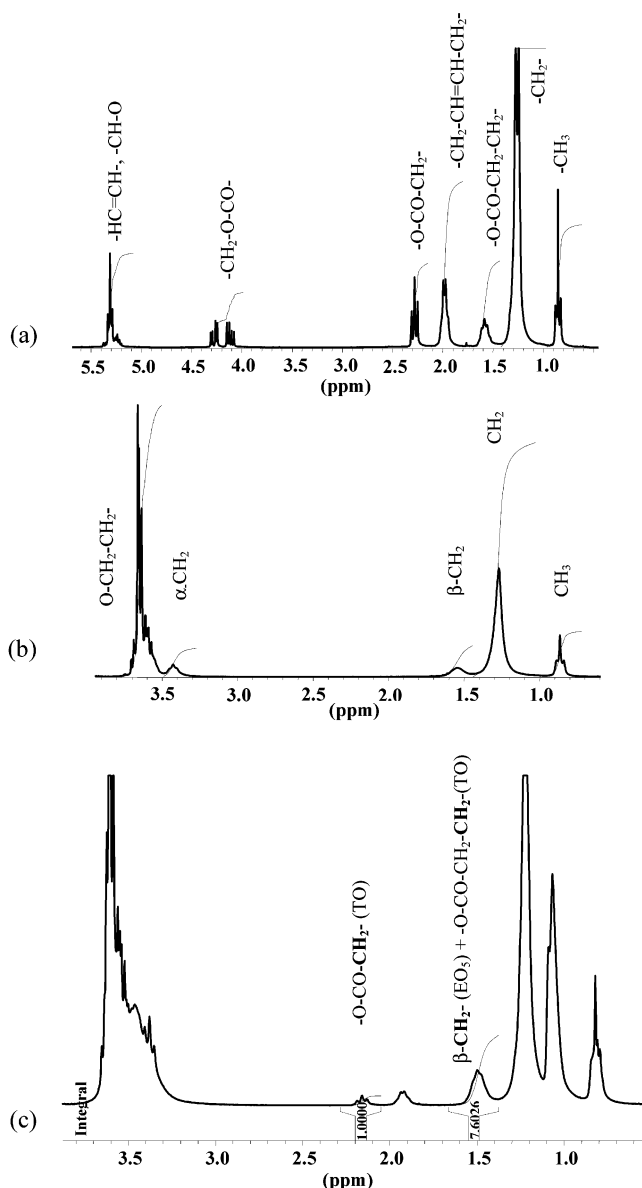
Figure 5. ^{1}H NMR spectra of (a) triolein in $CDCl_3$ with the assignment of the peaks indicated, (b) $C_{12}E_5$ in D_2O, and (c) swollen micelles in the mixture of 12 mM $C_{12}E_5$ and 0.3 wt % SL61 (0.01 M NaCl in D_2O). The peaks whose areas are used to determine the molar ratio of triolein to $C_{12}E_5$ are indicated.

Table 2. Molar Ratio of Triolein/$C_{12}E_n$ in the Micelles Measured by NMR

	wt % SL61	3 days	10 days
$C_{12}E_5$	0.1	1:31	1:17
	0.2	1:24	1:17
	0.3	1:26	1:17
$C_{12}E_6$	0.0	1:78	1:28[a]
	0.05	1:63	1:26
	0.1	1:42	1:25
	0.2	1:26	1:19

[a] After 16 days.

one sees that the solubilization is faster at higher concentrations of SL61, again in agreement with the kinetic studies presented in ref 22. On the other hand, no significant difference between the $C_{12}E_5$ solutions containing different concentrations of SL61 is noticed. This result can be explained by assuming that the solubilization process had been more or less accomplished in this systems at the third day, so that the kinetic effects were less pronounced at that time. Remarkably, the final ratio
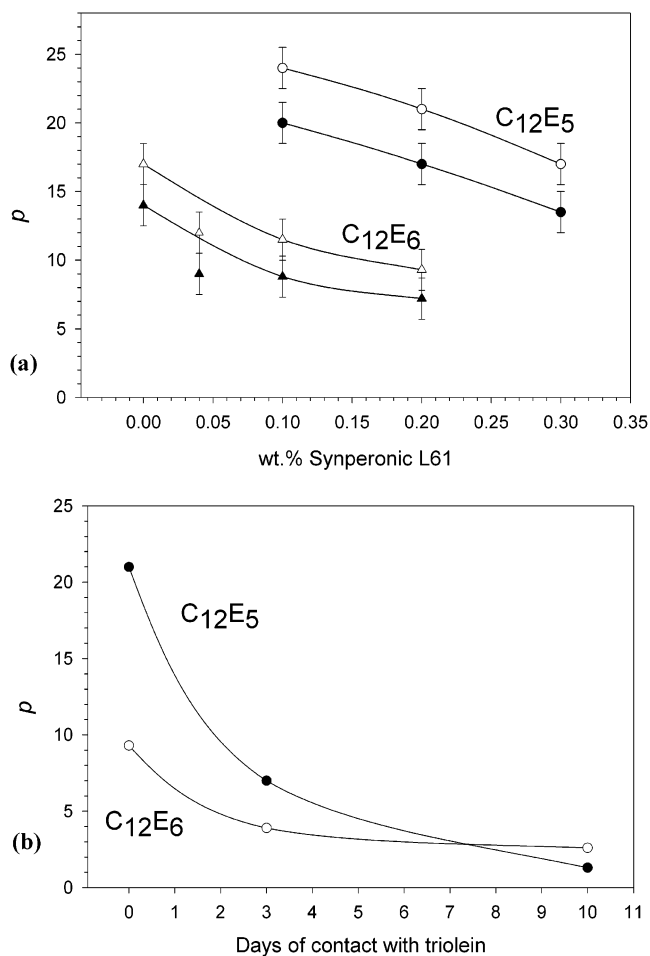

Figure 6. (a) Eccentricity $p = b/a$ of ellipsoidal empty micelles vs the concentration of SL61. p is calculated under the assumption that either 2 or 4 water molecules/ethoxy group are present (the solid and empty symbols, respectively). (b) Variation of p during the process of triolein solubilization at fixed 0.2 wt % SL61. The surfactant concentration is 12 mM $C_{12}E_n$; the inorganic salts are as in Figure 2.

triolein/surfactant turns out to depend very slightly on the concentration of SL61 for a given nonionic surfactant (see the column "10 days" in Table 2). This result shows that the main role of SL61 is to accelerate the solubilization process, without affecting significantly the solubilization capacity of the micelles. The data in Table 2 show also that the solubilization capacity of $C_{12}E_5$ is about 50% higher in comparison to that of $C_{12}E_6$. Using the results for $N_{surfact.}$, obtained by SLS, we recalculated the data from Table 2 to determine the number of triolein molecules/ micelle—see the data for $N_{triolein}$ in Table 1.

3.3. Shape of the Micelles. As explained in section 2.4, in our analysis of the light-scattering data we assume that the micelles have the shape of prolate ellipsoids. In this model, the micelle shape is characterized by two parameters, e.g. the length of the short semiaxis, a, and the ratio of the long and short semiaxes, the eccentricity p; see Figure 1. The results for these parameters, obtained by processing of the light-scattering data, are presented in Table 1 and Figure 6. In Figure 6a one sees that $C_{12}E_5$ forms about twice longer micelles than $C_{12}E_6$ before the solubilization, which is consonant with the results for $N_{surfact.}$ (Table 1). The length of the micelles decreases with the rise of the concentration of SL61 in the mixture.

To evaluate how important is the assumption that 2 water molecules are bound to each ethoxy group in the hydrophilic layer of the micelles (section 2.4), we made
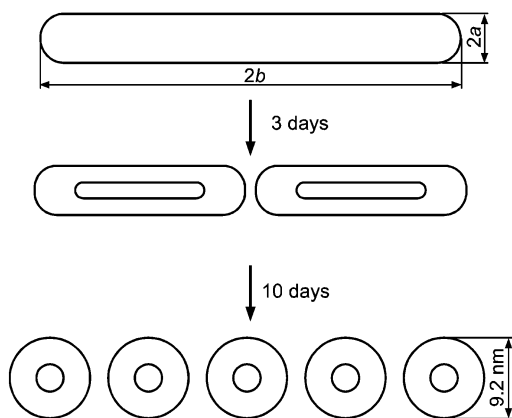
Figure 7. Sketch of the changes in the average micelle size and shape during the solubilization in a solution of 12 mM $C_{12}E_5$ + 0.1 wt % SL61 + 0.01 M NaCl. The ratio of the long to the short semiaxes is drawn to the real scale.

the same calculations by assuming that 4 (instead of 2) water molecules are bound/ethoxy group. The results of these calculations are also shown in Figure 6a with empty symbols. One sees that the eccentricity p increases slightly (with about 20%), but the main conclusions remain qualitatively the same. All other calculations are made using the assumption that 2 water molecules are bound to one ethoxy group.

From Table 1 and Figure 6b one sees that the initial, strongly elongated empty micelles ($p = 10-25$) transform into spheres ($p \approx 1$) or smaller ellipsoids ($p = 2-3$) as a result of the solubilization. The results for the small semiaxis a (see Table 1) show that the change of $p = b/a$ is due mostly to the decrease of b, i.e., to the shortening of the micelles. The increase of a is only about 50−70% at the end of the solubilization, whereas p decreases about 10 times. In other words, we may conclude that one empty micelle splits into several smaller swollen micelles. The ratio

$$m = [N_{\text{surfact.}}(\text{before solubilization})]/$$
$$[N_{\text{surfact.}}(\text{after solubilization})] \quad (10)$$

gives the number of equilibrium swollen micelles obtained by the splitting of an empty micelle owing to the solubilization. m is an important parameter in our kinetic model of solubilization.[21,22] The results in Table 1 show that m is between 2 and 6 and depends on the initial size of the micelles: m is larger for bigger empty micelles. The overall picture of the micelle size and shape transformation upon solubilization is illustrated in Figure 7.

4. Conclusions

The mixed micelles of $C_{12}E_n$ ($n = 5$, 6) and Synperonic L61 (with and without solubilized triolein) were characterized by light scattering and NMR. The aggregation number, diffusion coefficient, and size and shape of the micelles, as well as the number of solubilized oil molecules/micelle, were determined. The main results can be summarized as follows:

(1) The mean number of surfactant molecules incorporated in a micelle, $N_{\text{surfact.}}$, decreases by a factor of 2−6 during the process of solubilization (Table 1, Figure 4). In other words, one empty micelle splits into several swollen micelles (Figure 7).

(2) The hydrodynamic diameter of the micelles, d_h, also decreases significantly as a result of the solubilization. Although for the empty micelles d_h depends strongly on the composition of the $C_{12}E_n$/SL61 mixture (d_h is larger for the higher surfactant concentration and in the absence of SL61), the final value of d_h is found to be almost the same for the equilibrium swollen micelles in all studied solutions.

(3) Assuming that the micelles have the shape of prolate ellipsoids, we calculated their length and width. The results indicate that the initial, strongly elongated micelles transform into spheres or slightly elongated ellipsoids at the end of solubilization.

(4) The NMR data show that the ratio surfactant/triolein in the swollen micelles is slightly affected by the addition of SL61; i.e., the equilibrium solubilization capacity of the surfactant solution is insensitive to SL61. On the contrary, the results presented in Table 2 and in the subsequent parts of this series[21,22] demonstrate that SL61 strongly accelerates the solubilization process. In this respect, SL61 acts like a catalyst.

(5) The effect of the solubilized triolein on the size and shape of the surfactant micelles resembles that of *n*-alkanes. Therefore, one may expect that the triglycerides are incorporated preferentially inside the hydrophobic core of the surfactant aggregates.

As mentioned above, we use the obtained information about the micelle transformations to construct a theoretical model of the solubilization kinetics in part 2 of this study.[21] Furthermore, in part 3 the determined micelle properties have been utilized to test the model against experimental data for the solubilization kinetics of triolein.[22]