620 Russian Chemical Bulletin, International Edition, Vol. 50, No. 4, pp. 620—625, April, 2001

Complex formation between polyethylene oxide-containing nonionic surfactants and α- and β-cyclodextrins

E. I. Popova and I. N. Topchieva★

Department of Chemistry, M. V. Lomonosov Moscow State University,
Leninskie Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 939 0174. E-mail: kurganov@gagarinclub@ru

The inclusion complexes based on polyethylene oxide (PEO)-containing nonionic surfactants and α(β)-cyclodextrins (CD) were synthesized. Their composition and crystal structure were studied. The inclusion complexes of the surfactants with α-CD form a crystal structure similar to that of the α-CD—PEO complex. The inclusion complexes of the nonionic surfactants with β-CD form a structure similar to that of the β-CD—PEO complex. The structural models of the crystalline complexes were proposed. The micelle-forming abilities of the surfactants in dilute solutions in the presence of CD were studied. The CD binding to a surfactant molecule in aqueous solutions begins from the PEO fragment. Possible reasons for the formation of inclusion complexes between noncomplementary surfactant and β-CD molecules were discussed. The thermal stability was studied, and the possibility of thermal dissociation of the pseudo-complementary β-CD—surfactant complexes was shown.

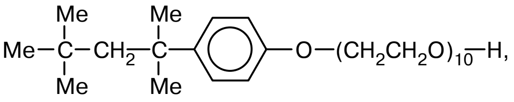
Key words: α-cyclodextrin, β-cyclodextrin, nonionic surfactants, micelle-forming properties of surfactants, X-ray diffraction analysis, differential scanning calorimetry.

Inclusion complexes (IC) of cyclodextrins (CD) and linear polymers are the most interesting objects in supramolecular chemistry. They are called "molecular necklaces" or pseudo-polyrotaxans and represent structures in which tens of CD molecules are threaded on the polymer chain. The complementary rule is fulfilled for the formation of these complexes: the size of the CD cavity corresponds to that of the cross-sectional area of the polymer chain. It has been shown that, in the case of polyalkylene oxides (PAO), the six-membered α-CD (diameter of the internal cavity 4.7—5.2 Å) interacts with polyethylene oxide (PEO),[1] the seven-membered β-CD (6—6.5 Å) interacts with polypropylene oxide (PPO),[2] and the eight-membered γ-CD (~8.5 Å) can be put on one PPO chain or two PEO chains.[2,3] The complexes are characterized by a specific stoichiometric ratio: one CD molecule per two PAO units for the α-CD—PEO and β-CD—PPO systems and one CD molecule per four PEO units for the γ-CD—PEO complex.

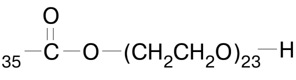
We have previously shown that nonionic surfactants containing PEO fragments as the hydrophilic part can also form inclusion complexes with α- and γ-CD.[4,5] The most pronounced effects of complex formation on the colloidal chemical properties of surfactants (Surf) were revealed for two systems: α-CD—octylphenyl PEO ether (Triton X-100) and α-CD—polyethylene oxide-1000 monostearate (PMS). A study of the crystalline complexes and micelle-forming properties of the α-CD—Surf systems in dilute solutions suggested that α-CD forms stoichiometric complexes with PEO fragments of the surfactant molecules. In this work, we studied the complex formation of the PEO-containing surfactants with "noncomplementary" β-CD and compared the micelle-forming abilities of the surfactants in the presence of CD of both types.

Experimental

Samples of α-CD and β-CD (Cyclolab, Hungary) were used as received. The following surfactants were used: Triton X-100 (octylphenyl PEO ether) (Sigma, USA)



polyethylene oxide-1000 monostearate (Schuchardt, Germany)



$$C_{17}H_{35}-\overset{\overset{\displaystyle O}{\|}}{C}-O-(CH_2CH_2O)_{23}-H,$$

Brij-35 (dodecyl PEO ether) (Merck, Germany)

$$C_{12}H_{25}-O-(CH_2CH_2O)_{23}-H.$$

All the surfactants were purified using the following procedure: the starting compound (1—2 g) was magnetically stirred for 2 h with diethyl ether (10—20 mL). The substance was isolated by the decantation of the ether or centrifugation.

Synthesis of CD—Surf complexes. *Crystalline α-CD—Surf complexes.* An aqueous solution of α-CD (100 mg mL^{-1}) was added to a weighed sample of the surfactant Triton X-100, PMS or Brij-35 (13.3, 11.6, or 10.7 mg, respectively). The mixture was thoroughly stirred till complete dissolution of the sample and stored for 1 day at ~20 °C. The crystalline residue that formed was separated by centrifuging, washed with water (1 mL), and dried in a vacuum desiccator to a constant weight. The yield of crystalline products was 46—48 %.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 594—599, April, 2001.

1066-5285/01/5004-620 $25.00 © 2001 Plenum Publishing Corporation

Crystalline β-CD—Surf complexes. A saturated aqueous solution of β-CD (10 mL, 20 mg mL^{-1}) was added to a weighed sample of the surfactant Triton X-100, PMS or Brij-35 (22.8, 19.9 or 18.4 mg, respectively). The mixture was thoroughly stirred and stored for 1 day at 5 °C. The crystalline complex was separated and dried under the conditions described above. The yield of crystalline products was 22—25 %.

X-ray diffraction analysis of samples was carried out on an URS-55 setup using an RKV-86 chamber with a planar film, Cu-Kα radiation filtered by Ni (λ = 1.54 Å).

Determination of composition of the crystalline complexes. *Polarimetry.* A weighted sample of the complex (~10 mg) was dissolved in a solution of 0.2 *N* NaOH (3 mL). The optical activity of solutions of the complexes was measured on a VNIEKIPRODMASh A1-EPO polarimeter in a cell with an optical path length of 2.5 cm. The CD content was calculated by the pre-plotted calibration in the coordinates specific optical activity (α_D)—CD molar concentration in an alkaline solution.

UV spectroscopy. A weighed sample of the CD—Triton X-100 complex (~10 mg) was dissolved in an aqueous solution (5 mL) of 0.2 *M* NaOH. The absorbance at the wavelength λ = 275 nm was measured on an Ultrospec 4050 instrument. The content of Triton X-100 in the complex was estimated by the pre-plotted calibration curve *D*—molar concentration of the surfactant in an alkaline solution.

Surface tension (σ) of dilute aqueous solutions of surfactants in the presence of CD was measured by the loop-detachment method from the solution surface using a torsion balance (BT type) in a cell with temperature maintaining at 25 °C.

Calorimetric studies of the β-CD—PMS complex were carried out on a TA-4000 thermoanalyzer (Mettler, Switzerland) with a heating rate of 20 deg min^{-1}.

Results and Discussion

Complex formation in the α-CD—Surf systems. The interaction of α-CD with surfactants in concentrated aqueous solutions results in the formation of crystalline complexes. X-ray diffraction analysis (Table 1) established that their structure is similar to that for the molecular necklace formed by the interaction of α-CD with PEO (hexagonal lattice with the unit cell parameters $a = b$ = 13.64 Å, c = 16.34 Å).[6] This indicates that molecular necklaces are formed in the α-CD—Surf systems.

A component of the complexes, CD, is an optically active substance. We determined its content (ω) by polarimetry under the consideration of complete water removal from the samples: ω(Surf) = 100% − ω(α-CD). The data on the composition of the complexes are given in Table 2. It follows from the presented results that the complexes under study have the following composition: α-CD—Triton X-100 (5 : 1), α-CD—PMS (11 : 1), and α-CD—Brij-35 (10 : 1). In the first two cases, the obtained correlations coincide within an experimental error with the calculated values under the assumption that α-CD is localized only on the PEO fragments of the surfactant obeying standard stoichiometry: one α-CD molecule per two PEO units. The proposed structure of the complexes is presented in Fig. 1.

It was of interest to reveal whether similar complexes exist in aqueous solutions or not. To answer this question, we studied the colloidal chemical properties of the surfactants in the presence of CD in dilute solutions. This approach gave an additional information about the specific features of the structure of the complexes, in particular, about localization of CD on the surfactant molecule. With this purpose, we determined the critical micelle concentrations (CMC) of the surfactants in the presence of CD and studied the plot of CMC of nonionic surfactants *vs.* α-CD content. The CMC was determined from the position of the break on the curve of the surface tension (σ) of an aqueous solution of the surfactant *vs.* logarithm of its concentration (c). Figure 2 presents a typical curve $\sigma = f(\log c)$ for Triton X-100.

Table 1. Interplanar distances (d) in the crystalline α-CD—PEO, α-CD—Triton X-100, β-CD—PPO, and β-CD—Surf complexes

Reflection	*d*/Å				*hkl**	
	α-CD—PEO	α-CD—Triton X-100	β-CD—PPO	β-CD—Surf	α-CD	β-CD
1	16.60	16.50	15.24	—	001	002
2	11.82	11.82	14.58	14.59	100	100
3	8.28	8.18	12.26	12.33	002	$1\bar{1}0$
4	6.88	6.74	9.27	9.11	110	110
5	5.55	5.51	8.87	8.87	201	111
6	4.46	4.43	7.48	—	210	$0\bar{0}4$
7	3.91	3.90	7.42	7.39	300	$2\bar{1}0$
8	3.25	3.28	6.13	—	310	$2\bar{2}0$
9	—	2.67	6.08	6.05	321	$1\bar{2}3$
10			5.67	5.65		$2\bar{2}2$
11			5.03	5.04		$3\bar{1}0$
12			4.71	4.70		$2\bar{3}1$
13			4.49	—		033
14			4.33	4.32		131
15			4.16	4.21		034
16			3.73	3.77		040
17			3.42	3.39		$4\bar{3}0$

* Miller indices of reflections.

Table 2. Composition of the CD—Surf complexes determined by polarimetry (I), UV spectroscopy (II), and from the plot of the yield of complexes *vs.* composition of the initial mixture (III)

Complex	I		II		III, r**
	ω*(β-CD) (%)	r**	ω*(Surf) (%)	r**	
α-CD—Triton	90±3	5 : 1	—	—	—
α-CD—PMS	91±3	11 : 1	—	—	—
α-CD—Brij-35	90±3	10 : 1	—	—	—
β-CD—Triton	89±3	5 : 1	9.3±0.5	5.7 : 1	—
β-CD—PMS	86±3	7 : 1	—	—	9 : 1
β-CD—Brij-35	88±3	8 : 1	—	—	8 : 1

* Content of a component of the complex.
** Molar ratio CD : Surf.

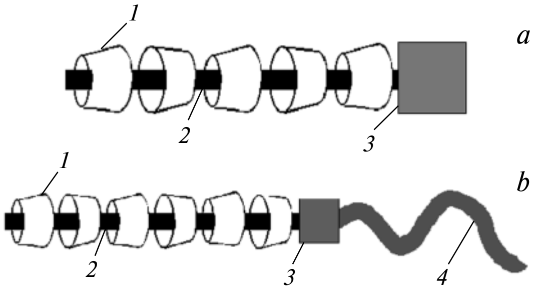


Fig. 1. Scheme of the structure of the α-CD—Triton X-100 (*a*) and α-CD—PMS complexes (*b*). *a*. *1*, α-CD; *2*, PEO; and *3*, octylphenyl group. *b*. *1*, α-CD; *2*, PEO; *3*, linker; and *4*, oligoethylene.

The introduction of α-CD into a solution of Triton X-100 was found to increase CMC (Fig. 3, curve *1*), which is likely due to the formation of a modified surfactant with a gradually increasing degree of filling of the PEO fragments with α-CD molecules. It can be assumed that the formation of molecular necklaces (MN) results in the hydrophilization of the polymeric fragment due to the introduction of many hydroxyl groups containing in the CD molecules. When reached the component ratio α-CD : Triton X-100 equal to 5 : 1, an increase in CMC ceases, which corresponds to the maximum filling of the PEO fragment of the Triton X-100 molecule. A further increase in the α-CD content in a surfactant solution does not substantially change CMC.

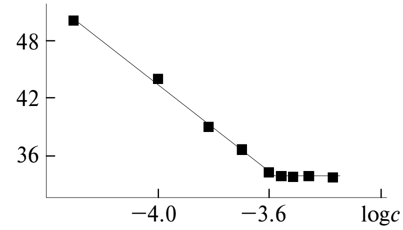


Fig. 2. Plot of the surface tension (σ) of an aqueous solution of Triton X-100 *vs.* surfactant concentration (*c*) at 25 °C.

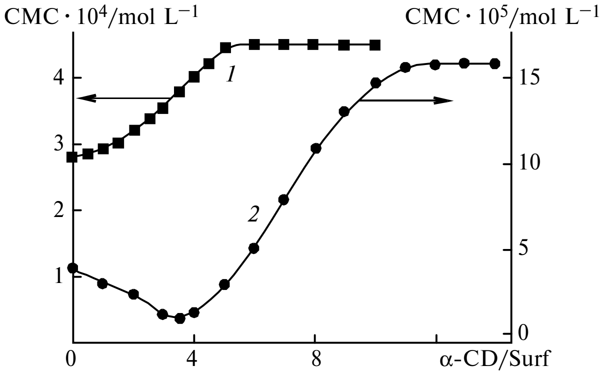


Fig. 3. Plot of the CMC value of aqueous solutions of Triton X-100 (*1*) and PMS (*2*) *vs.* α-CD/Surf molar ratio at 25 °C.

The data obtained indicate, in our opinion, that when the complex is formed the α-CD molecule is selectively threaded on the PEO fragment of the Triton X-100 molecule. This is possible because the internal cavity of α-CD cannot include the hydrophobic part of the Triton X-100 molecule for steric reasons (the diameter of the α-CD cavity is ~5 Å, and the cross-sectional area of the hydrophobic part of Triton X-100 is ~6.5 Å).

The cross-sectional area of the hydrophilic and hydrophobic fragments of PMS and Brij-35 molecules is the same (~4.8 Å). In this case, the structure of the complexes that formed can be suggested from the analysis of data on the micelle-forming properties of the surfactant in the presence of α-CD. The plot of the CMC value *vs.* α-CD : PMS ratio has a minimum at the ratio α-CD : PMS equal to 3.5, after which the CMC increases again and, when reached the limiting value, remains unchanged (see Fig. 3, curve *2*). The composition of the complex in the point corresponding to the achievement of a plateau coincides with the composition of the crystalline complex.

The primary decrease in CMC can formally be attributed to a partial "hydrophobization" of the PMS molecules due to the interaction with α-CD. However, this assumption contradicts the fact that the CD molecules formed of glucose groups are polar. The observed effect can have a more reasonable explanation as follows. According to the Kjellander theory,[7] the solubility of PEO in water is due to the incorporation of the polymer chain into the solvent structure. In addition, it is known from experimental works[8] that the conformation of the PEO chains is sensitive to the polarity of environment. The *gauche*-conformation of the C—C bonds of PEO predominates in an aqueous medium, whereas the *trans*-conformation is more stable in a nonpolar environment. The zone of contact between the free region of the PEO fragment and molecular necklace is schematically drawn in Fig. 4.

It can be assumed that due to steric hindrances and a local change in the medium polarity near the free region of the PEO chain the interaction between PEO and water should weaken. In other words, the region of the polymer chain of PEO adjacent to the molecular neck-

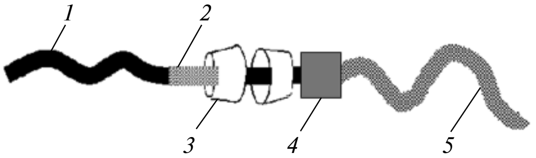


Fig. 4. Zone of contact between the free region of the PEO fragment and molecular necklace in the α-CD—PMS complex: *1*, PEO; *2*, zone of contact; *3*, α-CD; *4*, binding group; and *5*, oligoethylene.

lace must be more hydrophobic. It is most likely that at low CD : polymer ratios the contribution of the hydrophobization effect exceeds that of the hydrophilization effect from the CD molecules. However, with the further increase in the degree of filling of the surfactant molecules, the total hydrophilicity of the complex increases. This results in the situation where the CMC of the final product 11 α-CD · PMS becomes higher than the CMC of the starting surfactant.

As Triton X-100, PMS retains its ability to form micelles at all the CD : Surf ratios. This indicates that α-CD binds only the hydrophilic part of the PMS molecule. The following factors are possible reasons for the preferential interaction of α-CD with the PEO fragment of the surfactant: a high steric accessibility of the hydrated PEO fragment compared to the hydrocarbon part of the PMS molecule; the ester group prevents the removal of the molecular necklace from the side of the PEO fragment to the hydrophobic block.

Indeed, in studying the α-CD—Brij-35 system (the bulky binding group is absent from this surfactant) in which the sequences of the CD molecules can freely move to the hydrophobic tail of the surfactant, we observed the abolition of micelle formation at a component ratio of 3 : 1 (Fig. 5). A schematic structure of the α-CD—Brij-35 complex is presented in Fig. 6.

Thus, the interaction of α-CD and surfactant in an aqueous solution results in the formation of inclusive complexes, and threading of the macrocycles on the surfactant molecules begins from the PEO fragments. When the surfactant contains bulky binding groups, molecular necklaces are formed only on the PEO block of the surfactant. If the size of this group is comparable with the diameter of the CD cavity, the tubes consisting of macrocycles move from the PEO fragment to the hydrophobic part of the surfactant molecules thus preventing micelle formation.

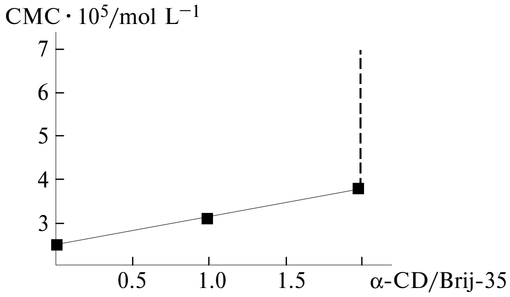


Fig. 5. Plot of the CMC value of an aqueous solution of Brij-35 *vs.* α-CD/Surf molar ratio at 25 °C.

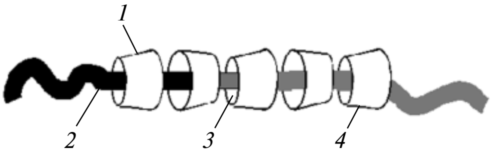


Fig. 6. Schematic structure of the α-CD—Brij-35 complex: *1*, α-CD; *2*, PEO; *3*, binding group; and *4*, oligoethylene.

Complex formation in the β-CD—Surf systems. We began to study the complex formation of the nonionic surfactants with β-CD from the β-CD—Triton X-100 system. It is known that the cross-sectional area of the hydrophobic fragment of the Triton X-100 molecule corresponds exactly to the diameter of the internal cavity of β-CD, and the length of the octylphenyl group is approximately equal to the depth of the CD cavity. Based on this, we could expect the formation of a complex with the 1 : 1 stoichiometric ratio of components. The data on the composition of the crystalline complex isolated from a mixture of concentrated aqueous solutions of β-CD and Triton X-100 (see Table 2) showed that in this complex ~6 CD molecules fall on the surfactant molecule, which corresponds to the complete filling of both the hydrophobic and hydrophilic fragments of the surfactant with cyclodextrin molecules. According to X-ray diffraction data (see Table 1), the structure of the β-CD—Triton X-100 complex is similar to that of the previously studied complexes of β-CD and PPO (crystals with the monoclinic system and following unit cell parameters: a = 15.13 Å, b = 15.55 Å, c = 30.34 Å, γ = 105.94°).[9] These data indicate unambiguously the formation of molecular necklaces of β-CD on the Triton X-100 molecule. It is most likely that the octylphenyl group of Triton X-100 acts as an "anchor," which holds the first threaded CD molecule. The further molecular necklaces form due to the hydrogen bonds between the hydroxyl groups of the "anchor" CD molecule with the hydroxyl groups of addional CD molecules.

Considering the interaction of β-CD with two other surfactants, PMS and Brij-35, one should keep in mind that they contain no fragment complementary to the β-CD cavity. Nevertheless, mixing of concentrated aqueous solutions also resulted in the formation of crystalline precipitates. X-ray diffraction analysis of these precipitates showed that all of them are identical in nature to the structure of the β-CD—PPO complex. To determine the composition of the complexes, we used, along with polarimetry, another approach based on a study of the plot of the yield of the complex (η) *vs.* ratio of components in the starting mixture. This plot for the β-CD—Brij-35 system is presented in Fig. 7. It is seen that the inflection of the curve corresponds to the component ratio β-CD : Brij-35 ≈ 8 : 1.

The data on the composition of the complexes obtained by different methods are summarized in Table 2. They agree satisfactorily with each other. It follows from

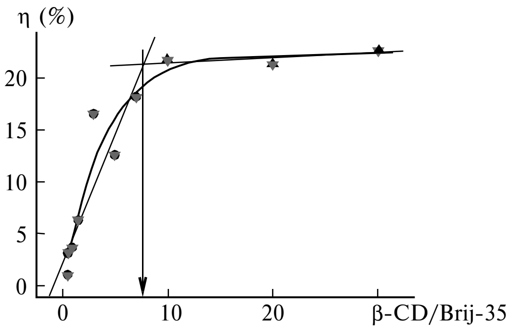


Fig. 7. Plot of the yield of the complex (η) *vs.* β-CD/Brij-35 molar ratio in the starting mixture.

these results that the filling of the PMS and Brij-35 molecules with macrocycles is incomplete. In fact, when requirements of standard stoichiometry (one CD molecule per six atoms of the main chain**[10]**) are fulfilled, the maximum number of CD molecules capable of being put on one surfactant molecule should be 14 and 13 for PMS and Brij-35, respectively, which is much higher than the experimental values.

The body of presented data does not establish unambiguously the localization of the macrocycles on the surfactant molecules. Hence, we studied the micelle-forming properties of the surfactants in the presence of β-CD. It turned out that, in all cases, micelles do not form at the component ratio β-CD : Surf ≥ 4 : 1 (Fig. 8).

The lack of micelle formation in the studied systems is related, most likely, to the hydrophilization of the alkyl fragments of the surfactant molecules due to their incorporation into the CD cavities. It can reasonably be assumed that cyclodextrins can also be localized in the crystalline complexes, at least partially, on the hydrophobic fragments of the surfactant. The assumed structure of the β-CD—Surf complexes is schematically presented in Fig. 9.

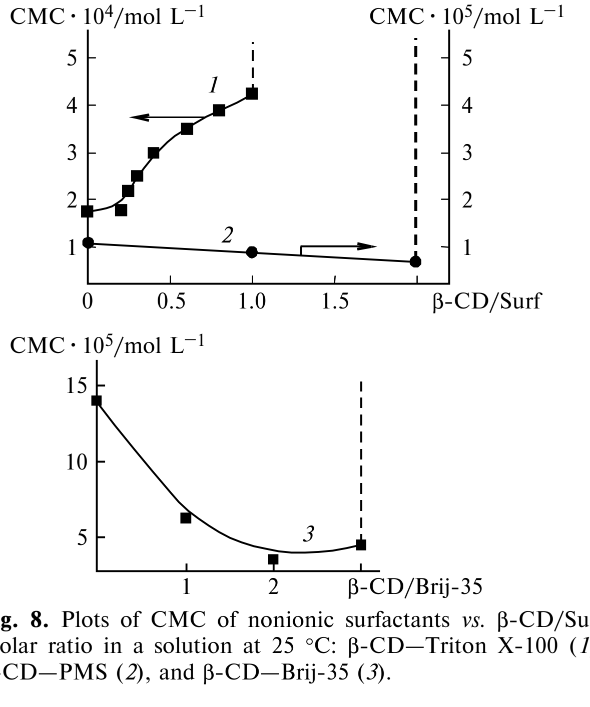


Fig. 8. Plots of CMC of nonionic surfactants *vs.* β-CD/Surf molar ratio in a solution at 25 °C: β-CD—Triton X-100 (*1*), β-CD—PMS (*2*), and β-CD—Brij-35 (*3*).

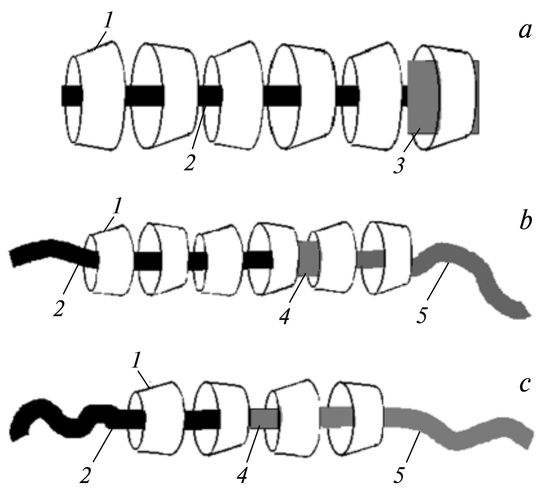


Fig. 9. Scheme of the structure of complexes: β-CD—Triton X-100 (*a*), β-CD—PMS (*b*), and β-CD—Brij-35 (*c*). *1*, β-CD; *2*, PEO; *3*, octylphenyl group; *4*, binding group; *5*, oligoethylene.

In discussion of reasons for the formation of complexes of PEO-containing surfactants with β-CD, we have to note that neither oligoethylene nor PEO apart form crystalline IC with β-CD.**[10]** By analogy to the model proposed for the β-CD—Triton X-100 complex, we may assume that at least one fragment corresponding geometrically to the diameter of the internal β-CD cavity must exist in the surfactant molecule for the formation of molecular necklaces on the PMS and Brij-35 molecules. This fragment is localized, most likely, in the zone of contact between the hydrophobic and hydrophilic parts of the surfactant. This assumption agrees with the findings**[11]** of a change in the conformation of the terminal fragments of PEO when a "foreign" substituent adds to them.

Thus, the synthesized crystalline IC based on α-CD and β-CD and nonionic PEO-containing surfactants can conventionally be grouped as follows: "*complementary*" (containing at least one fragment where the "guest" molecule fits exactly the sizes of the "host" cavity) and "*pseudo-complementary*" (complexes in which the geometric conformity between the both molecules is achieved by the corresponding change in the "guest" conformation). All the α-CD—Surf and β-CD—Triton X-100 complexes are assigned to the first group, and the second group is composed of β-CD—PMS and β-CD—Brij-35. It can be assumed that the complexes of different groups differ in their properties and, first of all, in stability. To check this assumption, we compared their thermal stability.

Thermostability of the CD—Surf inclusion complexes. A study of the α-CD-based complexes by differential scanning calorimetry (DSC) did not reveal any specific features compared to the molecular necklaces based on α-CD and PEO. On primary heating of the samples, the thermograms of the complexes exhibit an endothermic peak associated with water loss (~5%) in the temperature

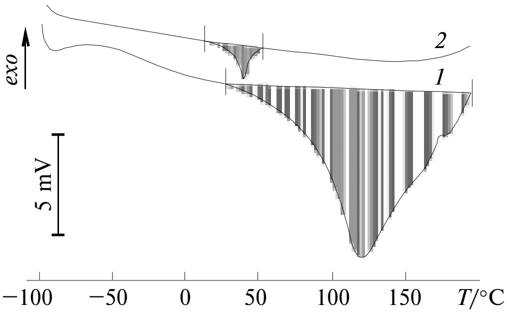


Fig. 10. Thermogram of the β-CD—PMS complex: primary (*1*) and repeated (*2*) heating of the sample.

region from 120 to 190 °C. Subsequent cooling of the complexes from +200 to −70 °C and repeated heating (from −70 to +200 °C) did not reveal any thermal effects.

The crystalline β-CD—Surf complexes behave in a different manner. Heating of all β-CD—Surf complexes to 200 °C results in the appearance of an endothermic peak of water loss with a maximum at ~120 °C. The content of water in the β-CD—PMS and β-CD—Triton X-100 complexes was 7.2 and 6.3%, respectively. Repeated heating gave no effect on the thermogram of the β-CD—Triton X-100 complex, like for the α-CD—Surf complexes. Meanwhile repeated heating the β-CD—PMS complex resulted in the appearance of the endothermic peak at 38 °C corresponding to melting of the free surfactant (m.p. (PMS) 35 °C; specific heat of melting 112.2 mJ mg^{-1}) on the thermogram (Fig. 10). This fact indicates a possibility of the thermal dissociation of this complex. The amount of PMS separated from the complex was estimated by the comparison of the measured endothermic effect with the specific heat of melting of the free surfactant. It was 6.2% of the sample weight, which is somewhat lower than the content of the surfactant in the complex (10.8%).

We attribute the underestimated amount of the nonionic surfactant isolated upon heating to the partial decomposition of PMS at high temperatures (decomp. (PMS) ~150 °C) at which the complex dissociates. This can be confirmed by the fact that an additional storage of the sample at 200 °C decreases the heating effect of surfactant melting due to its decomposition. An attempt to perform complex dissociation under milder conditions (at temperatures ≤ 150 °C) did not either increase the detected thermal effect likely due to the incomplete decomposition of the complex.

We also detected the thermal dissociation of IC with decomposition to the starting components for the β-CD—Brij-35 complex. On repeated heating of the sample, the melting peak at 39 °C (m.p. (Brij-35) = 36 °C) appears in the thermogram. The amount of the isolated and crystallized surfactant was ~2.8% of the sample weight. Note that the thermal dissociation of "*pseudo-complementary*" inclusion complexes in the solid state was found by us for the first time. Dissociation is likely reasoned by the capability of the surfactant molecule, weakly fastened in the β-CD cavity, of releasing from the tunnel formed by CD. At ~200 °C the surfactant exists as a melt and decompose partially. Subsequent cooling of the sample to −100 °C results in the crystallization of the released "guest."

Thus, we established for the first time that the PEO-containing surfactants interact with CD of all types to form inclusion complexes, which exist in both the crystalline state and dilute solutions. Among them, β-CD- and PMS-based (Brij-35) IC are most interesting. These surfactants contain no fragment geometrically corresponding to the diameter of the internal β-CD cavity. It is most likely that complex formation in these systems becomes possible due to a change in the conformation of the fragment of the PEO chain in the zone of contact with the hydrophobic part of the surfactant ("*pseudo-complementary*" complexes). The composition of the β-CD—PMS- and β-CD—Brij-35-based IC does not obey stoichiometry of molecular necklaces: six atoms of the main chain per CD molecule. They contain 11 and 10 atoms, respectively, of the main chain per CD molecule. We also demonstrated the different thermal stabilities of the standard, "*complementary*," and "*pseudo-complementary*" complexes. On heating to 200 °C, the latter dissociate to the starting components (under these conditions, standard molecular necklaces are stable).

The authors thank Prof. V. I. Gerasimov for fruitful discussion of XRD data of the complexes.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 00-03-32770).

References

1. A. Harada, J. Li, and M. Kamachi, *Macromolecules*, 1993, **26**, 5698.
2. A. Harada, M. Okada, J. Li, and M. Kamachi, *Macromolecules*, 1995, **28**, 8406.
3. I. G. Panova, V. I. Gerasimov, F. A. Kalashnikov, and I. N. Topchieva, *Vysokomol. Soedin.*, *B*, 1998, **40**, 2077 [*Polym. Russ. Sci.*, 1998, **40** (Engl. Transl.)].
4. I. N. Topchieva and K. I. Karezin, *Kolloid. Zh.*, 1999, **61**, 552 [*Russ. J. Collid. Chem.*, 1999, **61** (Engl. Transl.)].
5. I. N. Topchieva and K. I. Karezin, *J. Coll. Interface Science*, 1999, **213**, 29.
6. I. G. Panova, V. I. Gerasimov, F. A. Kalashnikov, and I. N. Topchieva, *Dokl. Akad. Nauk*, 1997, **355**, 641 [*Dokl. Chem.*, 1997 (Engl. Transl.)].
7. R. Kjellander and F. E. Kobertsson, *J. Chem. Soc., Faraday Trans.*, 1981, **77**, 1, 2053.
8. T. Ahlnäs, G. Karlström, and B. Lindman, *J. Phys. Chem.*, 1987, **91**, 4030.
9. I. G. Panova, Author´s Abstract, Ph. D. (Chem.) Thesis, Department of Chemistry, Moscow State Univ., Moscow, 2000.
10. A. Harada, S. Suzuki, M. Okada, and M. Kamachi, *Macromolecules*, 1996, **29,** 5611.
11. M. Björling, P. Linse, and G. Karlström, *J. Phys. Chem.*, 1990, **94,** 471.

Received June 27, 2000;
in revised form September 13, 2000