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ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY B · SEPTEMBER 2010

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Publisher's version / la version de l'éditeur:
Journal of physical chemistry, 114, 35, pp. 11489-11495, 2010-08-12

Web page / page Web
http://dx.doi.org/10.1021/jp105808j
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Solid Crystal Network of Self-Assembled Cyclodextrin and Nonionic Surfactant Pseudorotaxanes

Andrés Guerrero-Martínez,*,† David Ávila,‡ Francisco J. Martínez-Casado,§ John A. Ripmeester,⊥ Gary D. Enright,⊥ Luisa De Cola,† and Gloria Tardajos*,§

Physikalisches Institut, Wesfälische Wilhelms Universität Münster, Mendelstrasse 7, D-48149 Münster, Germany, Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040 Madrid, Spain, Departamento de Química Física I, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040 Madrid, Spain, and Steacie Institute for Molecular Sciences, National Research Council Canada, Ottawa, Canada

Received: June 23, 2010; Revised Manuscript Received: July 23, 2010

The title system allows the straightforward formation of three-dimensional crystals of self-assembled pseudorotaxanes formed by the nonionic surfactant Igepal CO-520 and β-cyclodextrin (β-CD) in aqueous solution. The work involves a combination of X-ray powder diffraction, high resolution electron transmission microscopy, and ^{13}C CP/MAS NMR studies of the solid crystal, supported by single crystal structural analysis. The results indicate a lamellar self-assembly of pseudorotaxanes with preferential orientation and disorder in the structure. For the single crystal, the unit cell was found to be triclinic ($P1$) and contains a β-CD dimer. The surfactant molecules are located in the channel formed by these dimers along the c axis of the crystal network. The individual pseudorotaxane structure is formed by a dimer of β-CDs threaded by the oxyethylene hydrophilic segment of Igepal CO-520, and a β-CD dimer that binds the hydrophobic region of the surfactant. Thus, as in a CD polyrotaxane structure, this system results in an ordered self-assembly of pseudorotaxanes through the formation of a network of hydrogen bonds between head-to-head β-CD dimers. Moreover, the analysis of the ^{1}H NMR spectra in solutions of pseudorotaxanes formed by β-CD and Igepals with different lengths of the hydrophilic tails indicates equal stoichiometry patterns of both oxyethyelene and hydrophobic regions for the different supramolecules. Whereas the common hydrophobic moiety threads two macrocycles, the ratio between complexed oxyehtlyene segments and β-CD is 2.5 for the hydrophilic tails. All these results show that nonionic surfactants can be used as alternative and effective linear threads to polymers and copolymers in the synthesis of supramolecular polyrotaxane solid crystals with CDs.

Introduction

In the past few years, supramolecular chemistry has focused on the design and synthesis of molecular systems, in which the functionalities of different species cooperate to form supramolecules that mimic the self-assembly strategy used by living systems to produce larger superstructures.[1] However, supramolecular systems have to be organized at the solid state and/or solid/liquid interfaces before they find applications as functional materials with spatially defined properties.[2−6] In the stepwise building of such materials, both reversible molecular assemblies to form supramolecules controlled by noncovalent interactions, ranging from weak van der Waals forces to more intense hydrogen bonds,[7] and nonreversible arrangements in the solid state to produce crystals with long-range order[3] are subjects of intensive research.

Two of the most appealing families of supramolecules due to their versatility toward chemical functionalization and application as artificial molecular machines are rotaxanes and pseudorotaxanes.[8] Whereas rotaxanes are interlocked molecules, basically consisting of a macrocycle trapped onto a linear thread by two bulky substituents, which usually demands the use of complex synthetic procedures for the chemical attachment of stopper molecules, pseudorotaxanes are supramolecular structures in which the macrocycle is directly entrapped by a molecular axis without bulky end groups, due to different affinities of the macrocycle for the diverse structural regions of the linear component.[9] The simplicity of pseudorotaxane synthesis, which in many examples relies on a direct mixture of the macrocycle and the molecular axis in solution,[10−12] makes them ideal candidates for self-organization at the solid state.[13] In this context, natural cyclodextrins (CDs) are known to exhibit unique inclusion characteristics as macrocycles with a wide variety of organic guest molecules. Many of their properties in aqueous solution, such as the high solubility, the hydrophobic character of the cavity, and the size tunability of this inner microenvironment, may allow exploitation of these capsules as hosts trapped onto linear organic molecules forming pseudorotaxanes of different stoichiometries.[14,15] Interestingly, several examples of these supramolecular pseudorotaxanes that form viscous solutions, fibrils, films, and gels have been reported.[16−19]

From the first report by Harada et al. in 1990 regarding the preparation of a pseudorotaxane supramolecular polymer consisting of α-CD and poly(ethylene oxide) (PEO),[20] many of these polyrotaxanes have been prepared in aqueous solution using CDs with different cavity sizes and polymers with different cross-sectional areas such as PEO derivatives,[21] polyesters,[22] poly-

* Corresponding author. E-mail: aguerrero@uvigo.es; tardajos@quim.ucm.es.
† Wesfälische Wilhelms Universität Münster.
‡ Departamento de Química Inorgánica, Universidad Complutense de Madrid.
§ Departamento de Química Física I, Universidad Complutense de Madrid.
⊥ National Research Council Canada.

10.1021/jp105808j
Published on Web 08/12/2010

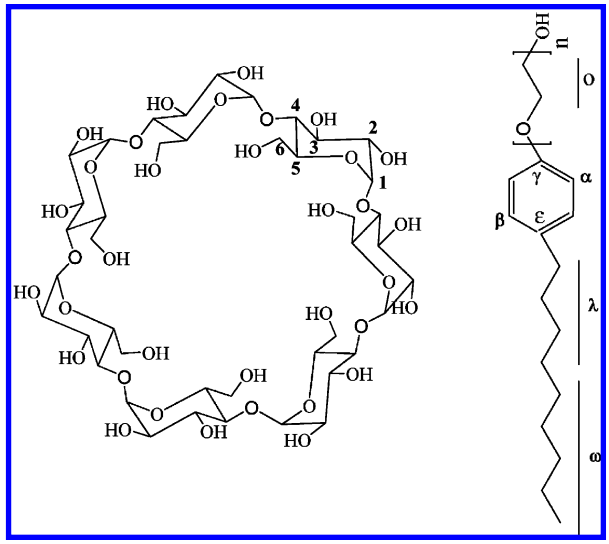

Figure 1. Chemical structures of β-CD (left) and Igepal surfactants (right).

amides and polyamines,[23,24] and block copolymers.[25] In all these examples, not only host−guest interactions but also cooperative effects resulting from the formation of networks of hydrogen bonds between head-to-head cyclodextrin dimers adds to the overall stability of these structures in aqueous solution.[26] This assisted complexation decreases the solubility of the adducts by reduction of the hydration states of both guests and hosts species[27] and usually leads to an organized pseudorotaxane aggregation and consequently to a macroscopic precipitation of the hydrated solid.[28]

Despite CD polyrotaxanes having been prepared as molecular organic solids with different levels of crystallinities, the degree of control to which such systems can be organized is still limited due to the high molecular weight and structural flexibility of polymeric species[26,29−31] Thus, we propose an alternative to overcome these structural limitations of polymeric pseudorotaxanes, using a shorter molecular axis with complexation behavior related to that of polymers and copolymers with CDs. Good examples are nonionic surfactants containing oligo(oxyethylene) groups as the polar heads, which show analogous amphiphilic properties to polymers with polyoxyethylene segments.[32] In the same manner, both families of surfactant and polymeric species may self-associate to form micelles in dilute aqueous solution and start to scatter light at higher concentrations according to complex liquid−liquid phase separation clouding phenomena.[33,34] Thus, these surfactants have been interesting hosts for the study of the role of hydration water in the complexation process with CDs.[35,36] As an example, oxyethylene nonionic surfactants with linear alkyl chains as the hydrophobic part have been used as guests to synthesize solid CD inclusion complexes at different hydration states.[37,38]

In this work, we highlight our approach to proceed from molecules in solution to the large self-assembly of CD pseudorotaxanes in the solid state. The attention is devoted to the nonionic surfactant Igepal CO-520 (polyoxyethylene(5) nonyl phenyl ether) as a linear thread for pseudorotaxane formation with β-cyclodextrin (β-CD) (Figure 1), with the aim of resembling the complexation of PEO derivatives with CDs. The use of this amphiphile is very suitable because its structure presents well-defined regions that show differential bindings with β-CD in aqueous solution.[39] Herein we report a combined X-ray powder diffraction (XRPD), high resolution electron transmission microscopy (HRTEM), and ^{13}C CP/MAS NMR study of the solid supramolecular polyrotaxane formed between Igepal CO-520 and β-CD, supported by single crystal structural analysis. Moreover, we confirm the obtained structure and stoichiometry by comparison of the ^{1}H NMR spectra of several β-CD pseudorotaxanes prepared from Igepals with different numbers of oligo(oxyethylene) groups (n = 5, 9, and 40) in solution.

Experimental Methods

Chemical and Sample Preparation. Nonionic surfactants Igepal CO-520 (n = 5), CO-630 (n = 9), and CO-890 (n = 40) and β-CD were purchased from Aldrich and used without further purifications. A water content of 13.5% by weight for β-CD, determined by thermogravimetric analysis, was considered in the calculation of the solution concentration. Freshly deionized water from a Millipore Q-System, with conductivities lower than 15 μS cm^{-1}, was used in the preparation of the samples. All the ^{1}H NMR samples were prepared in dimehtyl sulfoxide-d_6 (DMSO-d_6, Aldrich Chemical Co., 99.96% minimum deuterium).

From commercially available β-CD and Igepal surfactants with different oxyethylene chain lengths, polycrystalline pseudorotaxane samples were obtained by mixing both host and guest molecules in water at a high molar ratio of macrocycle 10:1 (10.0 mM and 1.0 mM of β-CD and Igepal surfactants, respectively). The fresh mixed solutions were continuously stirred at 25 °C, and after 24 h the resulting white precipitates were filtered and washed two times with water to remove excess reactants. Then the solids were exposed to a moderate temperature at 60 °C for 48 h.

X-ray Powder Diffraction Measurements. XRPD of β-CD and polycrystalline pseudorotaxane samples were recorded on a Siemens D-501 (Cu−K$_{\alpha 1}$ radiation λ = 1.5406 Å) over the angular range 10−100°, with a step scan of 0.04°.

Single Crystal X-ray Diffraction (SCXRD). The measurements were carried out on a Bruker Kappa APEXII CCD diffractometer (Mo−Kα). After several unsuccessful attempts to collect the data at 100 K, the cold stream temperature was changed to 200 K and the data quality was greatly improved. A full sphere of data (0.5°, 150 s/frame) was collected over a 5 day period.

The pseudorotaxane sample for the single crystal structural analysis was prepared from a fresh aqueous solution of Igepal CO-520 (1.0 mM) and β-CD (10.0 mM) after 10 weeks in an oven at 343 K.[26] The structure of the complex consists basically of the packing of β-CD macrocycles threaded by disordered Igepal molecules, the junction of these layers being very weak. The crystals thus obtained are very tiny and have the shape of a plate, so good quality crystals are very difficult to obtain due to their tendency to exfoliate. The data were collected from a clear, colorless, single crystal that had the shape of a plate (0.12 × 0.12 × 0.03 mm). As expected, the data were weak, dropping to I/σ of 1.0 at a resolution of ∼1 Å.

The β-CD molecules were refined with H-atoms in calculated positions and all non-hydrogen atoms refined with restrained, anisotropic thermal parameters. Within the β-CD molecules, the nearest- and second nearest-neighbor distances were restrained to expected values. No attempt was made to model disorder in the β-CD molecules (some minor disorder is usually seen and expected to be present, but the data is not of sufficient quality to resolve it). The electron density peaks located outside of the axial channels within the stacks of β-CD dimers are all assumed to be due to water molecules. The estimated number of these water molecules outside the β-CDs is approximately 23 (among

TABLE 1: Experimental Parameters and Main Crystallographic Data

empirical formula	2β-CD·Igepal·9H_2O ($C_{98.70}H_{140}O_{96.95}$)
M_r (g·mol^{-1})	2877.71
crystal system	triclinic
space group (no.)	$P1$ (1)
crystal size (mm)	0.12 × 0.12 × 0.03
temperature (K)	200 (2)
a (Å)	15.419 (4)
b (Å)	15.464 (5)
c (Å)	15.612 (4)
α (deg)	102.72 (1)
β (deg)	102.01 (1)
γ (deg)	104.31 (1)
V (Å^3)	3380.06 (16)
Z	1
λ (Å)	0.71073 (Mo−Kα)
D_c (g·cm^{-3})	1.414
μ (mm^{-1})	0.13
reflection collected	33753
unique reflections	6036
reflections with $I > 2\sigma(I)$	3823
parameters refined	1171
hydrogen treatment	H-atom parameters not refined (geom.)
R-factor	0.0849
wR-factor	0.2506
goodness of fit	1.051

4 fully and 34 partially occupied site). No attempt was made to find H-atoms attached to these O peaks. The axial Igepal guest extends over two unit cells, as the prominent electron density peaks correspond to half-occupied C or O atoms. An attempt was made to model the disordered guest, but it was not possible to solve it or to locate any associated H-atoms. The structure was solved by direct methods and subsequent Fourier syntheses using the SHELXS-97 program and was refined by the full-matrix least-squares technique against F2 in anisotropic approximation for indicated atoms.[40] The final agreement factors were reasonable (R1 = 0.0852 and wR2 = 0.2506) for such weakly diffracting, disordered crystal structures. The absorption was also corrected. The main crystallographic data and some experimental details are shown in Table 1. Further crystallographic details of the reported structure are in the Supporting Information.

High Resolution Transmission Electron Microscopy. HRTEM observations were performed in a Philips CM20 electron microscope working at 200 keV. Samples for TEM were prepared by ultrasonic dispersion of the polycrystalline pseudorotaxane sample in *n*-butanol and by depositing drops of this dispersion over a holey carbon-coated 3 mm copper grid. A preparation technique involving an embedding of the crystals in epoxy resin followed by slicing with an ultramicrotome was necessary to improve the stability of the specimen under the electron beam and to obtain crystals oriented with the stacking direction perpendicular to the incident beam.

^{13}C CP/MAS and ^{1}H NMR Measurements. Solid-state ^{13}C CP/MAS NMR spectra of polycrystalline pseudorotaxane samples were recorded at a 100.47 MHz on a 9.4 T Bruker Avance AV-400WB spectrometer (25 °C; 4 ms ^{1}H 90° pulses; 2.0 ms contact time; 12 kHz spinning rate; 4 s recycle delays).[40] The ^{13}C NMR signal assignments of the surfactants and β-CD were established from previous reports.[41,42]

All the ^{1}H NMR measurements were carried out at 298 K on a Bruker Avance AV-500 spectrometer (11.7 T). The proton spectra were recorded by averaging 32 scans, with a digital resolution of 0.30 Hz, and using a delay between pulses of 5 s that guarantees the complete relaxation of all the spectral resonances.[41] The signal assignments of the surfactants and β-CD were established by conventional NMR methods (correlation spectroscopy and total correlation spectroscopy).[44]

Figure 2. Evolution of a clouded solution of Igepal CO-520 in absence (1) and presence (2 and 3) of β-CD. Tubes 2 and 3 show the fresh mixture immediately after addition of β-CD and after 24 h.

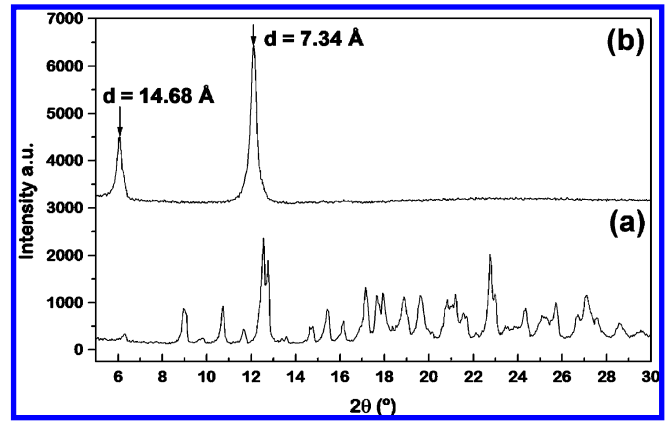

Figure 3. XRDP of the starting β-CD (a) and the Igepal CO-520 pseudorotaxane sample (b).

Results and Discussion

Crystallographic Analysis. The polycrystalline pseudorotaxane sample was precipitated by mixing β-CD and Igepal CO-520 in water at a high molar ratio of macrocycle 10:1 (see Experimental Methods). The initial cloudiness of the Igepal CO-520 solution, which is related to the presence of large micelles above the cmc of the surfactant (0.02 mM),[39] registered a remarkable fall as a consequence of the disruption of the aggregates by β-CD complexation (Figure 2). The resulting white powder was studied by X-ray diffraction measurements. The X-ray diffraction pattern (XRDP) of the pseudorotaxane sample reveals the disappearance of the original narrow and sharp peaks of the β-CD profile while two new broad reflections appear, indicating a decrease of the crystallinity after complexation (Figure 3). These results indicate a lamellar self-assembly of β-CD complexes (d value of the first peak is 14.68 Å) with preferential orientation and disorder in the structure. No significant changes of the crystal pseudorotaxane XRDP were

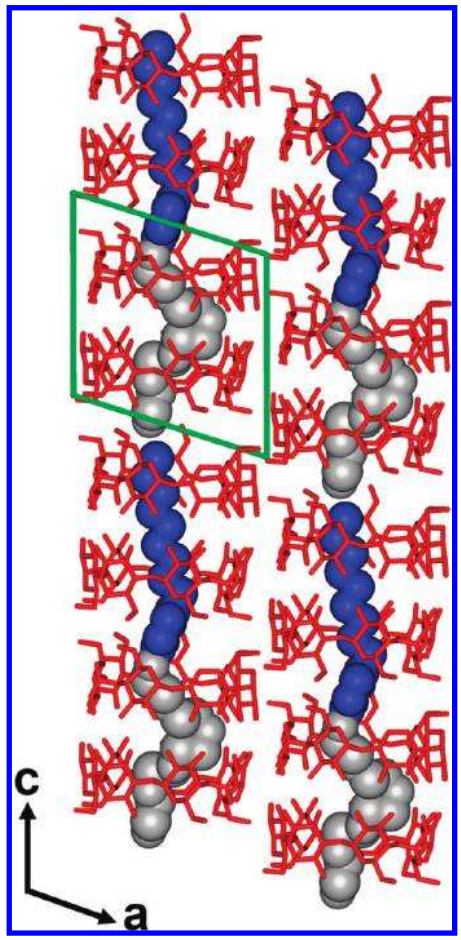

Figure 4. Structural refinement by single crystal X-ray of the Igepal CO-520 pseudorotaxane structure.

observed at different mixing molar ratios during the synthesis process (from 2:1 to 10:1 of macrocycle and surfactant, respectively), which points to a supramolecular complexation stoichiometry that does not depend on the mixing molar ratio. The intense preferential orientation and the structural disorder observed in the XRDPs make these data unuseful for any additional structural refinement.

In order to solve the structure of the pseudorotaxane, we grew single crystals (see Experimental Methods) and measured them by single crystal X-ray diffraction (SCXRD) (Figure 4). The unit cell was found to be triclinic (*P*1), similar to other β-CD complexes,[45,46] and to have a slightly distorted *C*2 polyrotaxane form.[26] The unit cell contains a well ordered β-CD dimer, with $\sim$23 water molecules distributed outside the β-CD channels. The surfactant guests are located in the channel formed by stacked β-CD dimers and extend into and overlap with other surfactant molecules in adjacent unit cells. As there is only room for one guest at a time, the occupancies are reduced.

The overall structure consists of Igepal CO-520 molecules that thread hydrogen-bonded head-to-head host dimers with four β-CDs for every surfactant molecule (Figure 4). The guest extends over two unit cells, as most electron density peaks correspond to half-occupied C or O atoms, and it is highly disordered about the channel that passes through a stack of CD dimers, making it impossible to resolve it. The proposed geometry shows two macrocycles threaded mainly by a twisted hydrophilic segment (five oxyethylene groups),[20,26] whereas two β-CDs bind the hydrophobic surfactant region (aromatic and aliphatic moieties) (Figure 1).[35,39] Each of these pseudorotaxanes is hydrogen-bonded to β-CD hydroxyl groups in the neighboring pseudorotaxane along the *c* axis with a head-to-head configuration of macrocycles, thus forming a network of hydrogen bonds that resemble a long CD polyrotaxane.[14] The packing between adjacent rows of pseudorotaxanes is driven by weak intermolecular interactions due to the characteristic spatial anisotropy of dielectric properties in CD polyrotaxanes.[28] This assisted complexation and packing strongly decreases the solubility of the supramolecular polyrotaxane by reduction of the hydration states of isolated pseudorotaxanes in aqueous solution, which leads to the precipitation of the polyrotaxane.

HRTEM Measurements. The low magnification TEM micrograph of the polycrystalline pseudorotaxane sample displayed in Figure 5 shows the packing of pseudorotaxane complexes along the *b* axis, consisting of a highly regular packing of wavy rows. In the enlarged area squared in yellow, we observe a repetition of 14.7 Å between the rows, which is the distance between two β-CDs along the *a* axis in the unit cell. This situation is clarified when the projected model along *b* is superimposed on the enlarged area of the experimental image (Figure 5). We should note that the measured distance could belong to any crystallographic axis because they are very close in length; however, the wavy nature of the rows suggests, taking in mind the structural model, that the Igepal CO-520 guest should be accommodated along this row which is then identified as the *c* direction. The wavy packing and the existence of defects (see the dislocation marked by red arrows in the image) indicate a high flexibility of the β-CD network to accommodate the Igepal CO-520 guest.

In order to confirm the refined structural model, we have performed for the first time to the best of our knowledge, a HRTEM study from a CD inclusion complex. Sensitive CD samples under the electron beam are very difficult to image, especially at high resolution.[47] The image in Figure 6 was recorded along the [111] zone axis of the pseudorotaxane sample. A HRTEM image represents the structure of the projected specimen under defined conditions of thickness and focus, and the thickness of the sample is always unknown; besides, obtaining the image in focus is very difficult due to the sensitive nature of the sample. For this reason the experimental image has been calculated using our crystallographic model described above as input and changing the focus and thickness. The best calculated image, which is obtained for a defocus of 50 nm and a 7 nm thickness, is represented together with the experimental image using the structural model built by single crystal refinement (Figure 6). We note that the simulated image shows a good match with the experimental image, confirming the results of the structural model obtained from single crystal data.

NMR Characterization. The polycrystalline Igepal CO-520 pseudorotaxane has been investigated and compared with pure β-CD by ^{13}C CP/MAS NMR spectroscopy.[43,48] The ^{13}C CP/MAS NMR spectrum of the pseudorotaxane can be described as two sets of signals with low and high intensities according to the presence of Igepal CO-520 and β-CD resonances, respectively. Regarding the macrocycle region (Figures 1 and 7), significant broadenings of the signals corresponding to C6 (62 ppm), C2−C3−C5 (75 ppm), C4 (84 ppm), and C1 (105 ppm) carbon atoms are observed after complexation. The characteristic broadness and lower resolution of the signals with respect to pure β-CD show a decrease of the number of structural conformations and indicate a dynamic dehydration process that macrocycles may undergo upon complexation with the surfactant.[43,48,49] Particularly relevant is the low resolution observed for C1 and C4 resonances, which reveals an important decrease

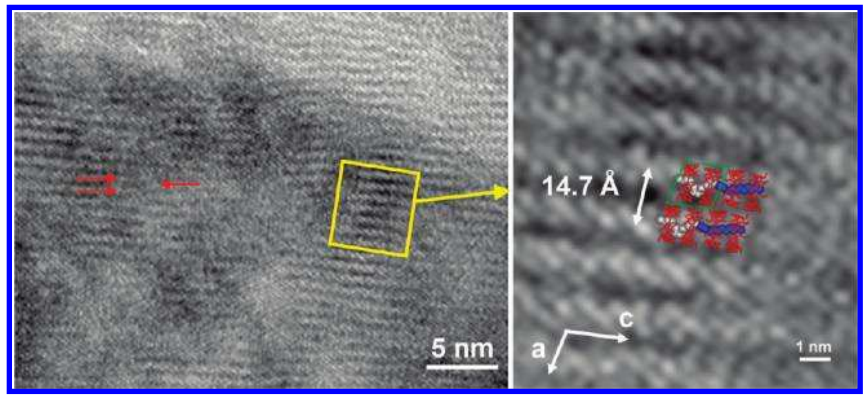

Figure 5. TEM image of a regular packing of Igepal CO-520 pseudorotaxane channels along the *c* axis. The sinusoidal packing and defects (see red arrows) show a high flexibility in the pseudorotaxane network.

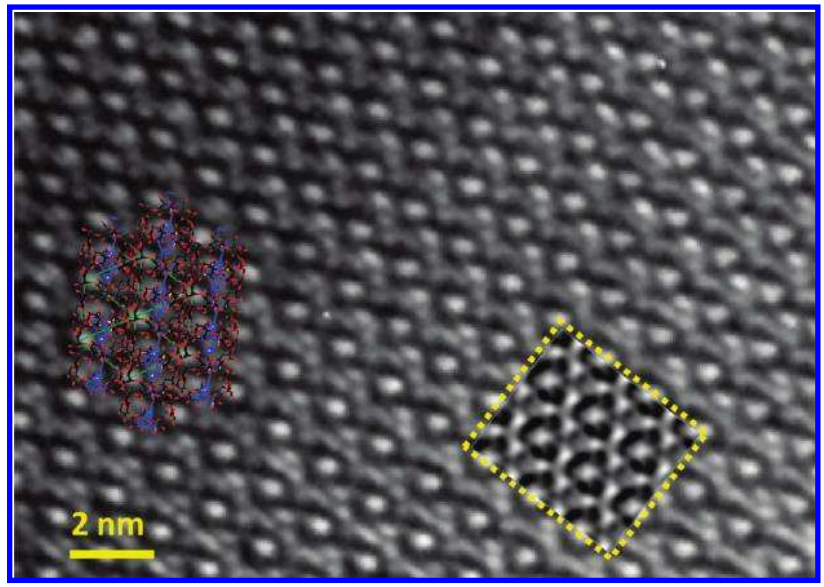

Figure 6. HRTEM image along the [111] zone axis. The corresponding calculated image (inset square) using the single crystal X-ray data as input shows a good match with the experimental image. The proposed model of the arrangement of pseudorotaxane complexes along the [111] zone axis is also depicted.

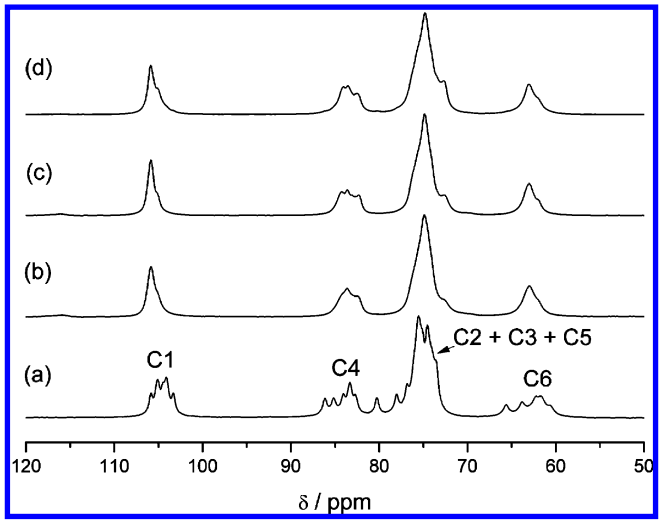

Figure 7. Expansions of ^{13}C CP/MAS NMR spectra, and β-CD resonance assignments for pure β-CD (a) and pseudorotaxanes formed by Igepals CO-520 (b), CO-630 (c), and CO-890 (d).

in the distributions that the α-1,4 glycosidic C1−C4 dihedral angle presents in the complexed structure. This conclusion agrees well with the C1−C4 dihedral value of 127 ± 4° obtained from the SCXRD measurements, by comparison with a typical distribution of 128 ± 13° for pure β-CD.[50] Additionally, the C6 resonance exhibits a loss of multiplicity that can be explained through a decrease of the number of conformations that primary hydroxyl groups have in the free macrocycle. This evidence suggests the formation of intense hydrogen bonds between β-CDs dimers along the axis of the pseudorotaxane structure, in good agreement with the crystallographic and HRTEM analysis. As for the surfactant region, low intensity groups of signals were observed at 32 ppm (carbon alkyl chain), and at 115, 128, and 158 ppm (aromatic carbon moiety), which could not be compared at solvent-free experimental conditions with the isolated Igepal CO-520 surfactant because of its liquid state at room temperature.

Thus, a β-CD polycrystalline pseudorotaxane was prepared from the Igepal CO-890 (polyoxyethylene(40) nonyl phenyl ether) surfactant, which is an amorphous solid surfactant at room temperature. The ^{13}C CP/MAS NMR spectrum of the Igepal CO-890 pseudorotaxane is depicted in Figure 7, showing similar results to those obtained previously with the Igepal CO-520 derivative. A general broadening of the highly intense β-CD signals indicates a more rigid structural conformation of the macrocycles within the pseudorotaxane due to the stacking of β-CD dimers. By contrast no significant broadness and changes of the multiplicity of the aliphatic signals Cλ and Cω (31 ppm) and the aromatic resonances Cα (116 ppm), Cβ and Cε (129

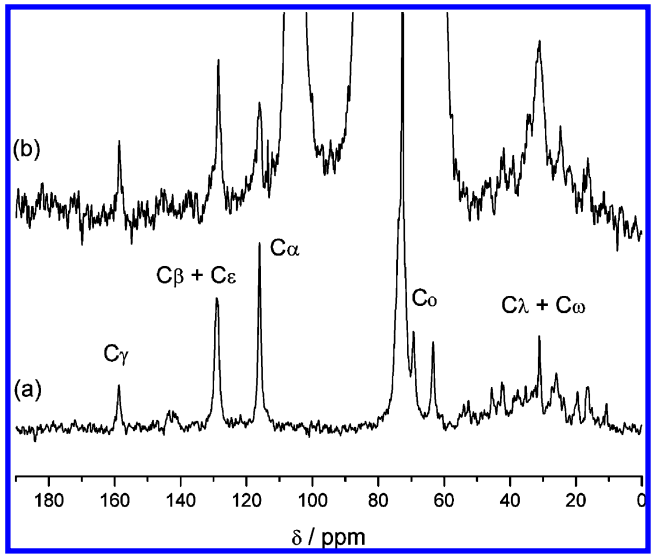

Figure 8. Expansions of ^{13}C CP/MAS NMR spectra, and surfactant resonance assignments for pure Igepal CO-890 (a) and its β-CD pseudorotaxane (b).

ppm), and Cγ (159 ppm) of the surfactant are observed after complexation (Figures 1 and 8). This evidence suggests the preservation of the native amorphous ordering of pure Igepal CO-890 in the pseudorotaxane network, which agrees well with the high disorder of surfactant molecules observed along the *c* axis in the Igepal CO-520 pseudorotaxane single crystal.

The stoichiomerty of both solid Igepal CO-520 and CO-890 surfactant pseudorotaxanes have been studied by ^{1}H NMR spectroscopy in solution using DMSO-d_6 as solvent.[51] Additionally, the β-CD pseudorotaxane formed by a nonionic surfactant with an intermediate oxyethylene chain length, such as Igepal CO-630 (polyoxyethylene(9) nonyl phenyl ether), has been prepared and used for the stoichiometric analysis. As a comparison, the ^{13}C CP/MAS NMR spectrum of the Igepal CO-630 pseudorotaxane has been included in Figure 7, which reveals the formation of a supramolecular system analogous to those obtained for their counterparts of 5 and 40 oxyethylene groups. Figure 9 shows the ^{1}H NMR spectra of pure β-CD and the pseudorotaxane samples in DMSO-d_6. No significant shifts of the Igepal surfactants and β-CD resonances have been observed for the pure and pseudorotaxane solutions, thus indicating a complete disruption of the supramolecular complexes by solvent solvation. The quantitative analysis has been carried out using the ratio between the integration intensities of the H1 resonance of the macrocycle, and the Hα and Hβ signals of the respective surfactants, which are compiled in Table 2 and Figure 9. From these results, it can be seen that the number of macrocycles ($n_{\beta\text{-CD}}$) of the supramolecular structures increases linearly with the number of oxyethylene groups of the surfactant (n_{oxyeth}), with a linear fit of $n_{\beta\text{-CD}} = 1.9 + 0.43 \times n_{\text{oxyeth}}$ ($R^2 = 0.996$). This fit shows that the common hydrophobic region in Igepal surfactants, formed by the aliphatic tail and the aromatic moiety (Figure 1), threads two macrocycles ($n_{\text{oxyeth}} = 0$, $n_{\beta\text{-CD}} = 1.9$), which confirm previous complexation studies and stoichiometric calculations in aqueous solution (the values of the 1:1 and 2:1 binding constants are $K_{1:1} = (1.9 \pm 0.2) \times 10^4$ L mol^{-1} and $K_{2:1} = (1.1 \pm 0.1) \times 10^3$ L mol^{-1}, respectively),[35,39] whereas each extra β-CD is threaded on the oxyethylene chain with 2.5 oxyethylene segments ($n_{\text{oxyeth}} = 4.9$, $n_{\beta\text{-CD}} = 4$), results that are in good agreement with the stoichiometry obtained for the Igepal CO-520 pseudorotaxane by SCXRD. Thus for different Igepal pseudorotaxanes, periodicity between guest and host is achieved

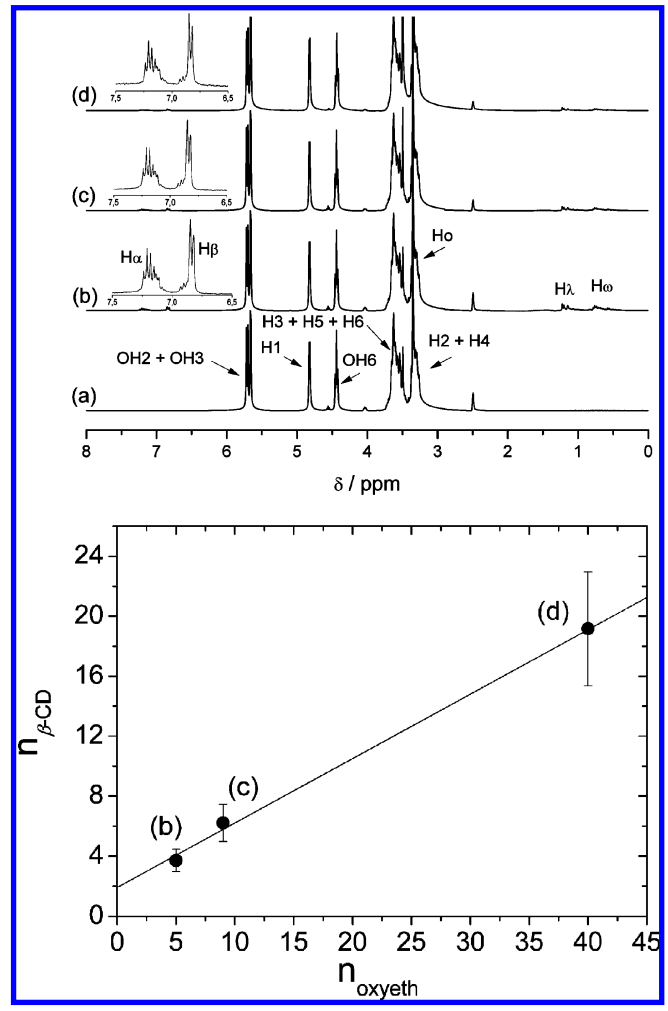

Figure 9. ^{1}H NMR spectra in DMSO (up), and β-CD and surfactant resonance assignments for pure β-CD (a) and pseudorotaxanes formed by Igepals CO-520 (b), CO-630 (c), and CO-890 (d). Correlation between the total number of complexed β-CD macrocycles and the surfactant oxyethylene groups (down), for pesudorotaxanes formed by Igepals CO-520 (b), CO-630 (c), and CO-890 (d). The error bars have been estimated from the phasing process of the ^{1}H NMR spectra.

TABLE 2: Normalized Resonance Integrals and Stoichiometric Ratios Obtained for Different β-CD and Igepal Pseudorotaxanes

	integrals		
pseudorotaxane	H1	Hα + Hβ[a]	stoichiometric ratio β-CD:Igepal
β-CD:Igepal CO-520	6.5	1 ± 0.2	4:1
β-CD:Igepal CO-630	10.9	1 ± 0.2	6:1
β-CD:Igepal CO-890	33.8	1 ± 0.2	19:1

[a] Errors estimated from the phasing process of the ^{1}H NMR spectra.

in the same way for the oxyethylene chain complexation, as there is the same number of oxyethylene segments per macrocycle. From a simple CPK model and taking into account the single crystal structure (Figure 4), the β-CD complexation between 2.5 oxyethylene groups may occur because the oxyethylene chain bunches up regularly in the Igepal structure, probably in the wide part of the H-bonded dimers,[26] whereas in the toroidal cavity itself and between adjoining β-CD sections the chain is extended.

Conclusions

A straightforward method for solid crystal complexation of Igepal oxyethylene nonionic surfactants and β-CD is presented

and investigated. Different techniques such as X-ray powder diffraction, single crystal X-ray diffraction, high resolution electron transmission microscopy, and ^{13}C CP/MAS NMR have been successfully employed for the structural analysis of single pseudorotaxanes in hydrated solid crystal structures. Moreover, the stoichiometries of such complexes have been determined by ^{1}H NMR in solution. The pseudorotaxane structures show a head-to-head β-CD dimer complexed with the hydrophobic region of the surfactants, whereas β-CDs are threaded tightly on the oxyethylene chain with 2.5 oxyethylene segments. This evidence suggests that the oxyethylene chain bunches up in the wide part of the H-bonded dimers of the pseudorotaxane structure due to a close packing of β-CDs. Thus, for different Igepal pseudorotaxanes, periodicity between guest and host is achieved in an analogous way. These results confirm that nonionic surfactants can be used as an alternative to polymers and copolymers for the preparation of supramolecular polyrotaxanes with CDs and may lead to the synthesis of numerous other less traditional solid CD pseudorotaxanes via complexation of nonionic amphiphiles such as Igepal or Triton derivatives with different oxyethylene chain lengths.

Acknowledgment. This work has been supported by the Ministerio de Educación y Ciencia (AGM and project CTQ2010-18564) and Universidad Complutense (UCM-BSCHGR58/08/921628).

Supporting Information Available: Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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JP105808J