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Lyotropic Behavior of “3,4-(42-Crown-14)benzyl Dodecyl Ether” in Toluene in the Presence of Water

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ABSTRACT: The lyotropic behavior of an amphiphilic macrocrown ether (MC-12) with an average ring size of 42 atoms attached to a hydrophobic 12-carbon tail was studied in 70 wt % toluene in the presence of small amounts of water by a combination of polarized optical microscopy, ^{1}H-NMR, X-ray diffraction, and ^{13}C-NMR relaxation studies and by comparison to the lyotropic behavior of the corresponding solutions of Igepal-CO-720 [oligo(oxyethylene) nonylphenyl ether]. Igepal-CO-720 is a classic linear surfactant with a distribution of oligo(oxyethylene) lengths. MC-12 is a macrocyclic surfactant with a distribution of ring sizes. Since it was synthesized from poly(ethylene glycol) 600, 3,4-(42-crown-14)benzyl dodecyl ether is the predominant structure. Similar to Igepal-CO-720, MC-12 in 70 wt % toluene organizes into a lyotropic lamellar (L_α) mesophase, in which the macrocrown ethers are relatively flexible, when $[H_2O]:[EO] \leq 2.2$. When $[H_2O]:[EO] > 2.7$, the solutions macroscopically phase separate into an isotropic toluene layer containing only MC-12 and a water-enriched dense white emulsion in which MC-12 is organized in an L_α mesophase with its alkyl substituents interdigitated.

Introduction

In the previous paper in this series,[1] we proposed that homopolyrotaxanes that lack an enthalpic driving force for threading may potentially be synthesized in high yield by an amphiphilic approach. This approach is based on the ability of amphiphiles to form lamellae and columnar micelles in solvents that selectively solvate one of its components. We are developing and testing this concept using “3,4-(42-crown-14)benzyl dodecyl ether” (MC-12), in which a hydrophobic 12-carbon tail is attached to a hydrophilic macrocrown ether with an average ring size of 42 atoms. As outlined in Scheme 1, the amphiphilic macrocrown ether should aggregate into reverse micelles in hydrocarbon solvents due to selective solvation of the hydrophobic tails. If hydrophilic poly(ethylene oxide) (PEO), which is normally not soluble in hydrocarbon solvents, is then added to the organized solution of the micelles, it will be forced into their interior, thereby threading the crown ethers. In the simplest system of an amphiphilic macrocrown ether organized in a hydrocarbon solvent, the primary driving forces for threading should be the high concentration of macrocycles and their optimum alignment, as well as the increase in entropy which results from dilution of the macrocycles with linear thread.

Although MC-12 is almost insoluble in aliphatic hydrocarbon solvents, we have already demonstrated that it aggregates in toluene and benzene if small amounts of water are added.[1] To our knowledge, this is the first example of an amphiphilic macrocrown ether forming reverse micelles and/or inverse lyotropic mesophases. Oligo(oxyethylene) alkyl ether surfactants also aggregate in benzene and cyclohexane if water is added, but most form only isotropic solutions in these solvents in the absence of water.[2] As shown in Scheme 2, amphiphilic molecules form several different lyotropic liquid crystalline mesophases as a function of concentration.[3] Above the critical micelle concentration, amphiphilic molecules first aggregate into micelles with spherical, cylindrical, or plate shapes. If these isotropic micellar solutions are further concentrated, they form lyotropic solutions with nematic, cubic, columnar or lamellar mesophases. The amphiphiles crystallize at higher concentrations and/or in the absence of solvent.

We expect that the threading efficiency of MC-12 with poly(ethylene oxide) should vary with how MC-12 is organized and that, in general, threading should be higher in more ordered mesophases. The presence of water should also add an enthalpic component to threading. However, MC-12 is not a pure macrocycle. As discussed previously,[1] it was synthesized starting from poly(ethylene glycol) 600 (600 g/mol) and therefore has a distribution of ring sizes corresponding to the narrow polydispersity of PEG600. In addition, it contains approximately 17% of double ring sizes formed in the cyclization step. If polyrotaxanes are to find commercial applications, the polyrotaxane and both of its components must be synthesized inexpensively and in high yield. This precludes extensive separations and purifications. We have therefore determined the ability of MC-12, with its distribution of ring sizes, to form organized solutions.

This paper presents our first detailed study of the lyotropic phase behavior of MC-12 in toluene in the presence of water. It presents the ternary phase diagram in the organic-rich region where inverse micelles/phases are favored and then focuses on the lyotropic behavior of solutions composed of 30 wt % (MC-12/H_2O) / 70 wt % toluene.[4] The phase behavior of MC-12 is also corroborated by comparison with that of Igepal-CO-720 [oligo(oxyethylene) nonylphenyl ether], which is a classic linear surfactant with an average of 12 oxyethylene (EO) units. As shown by the structures in Scheme 3, the ratio of oxyethylene and hydrocarbon units of MC-12 ($EO:CH_2 = 1.08$, or 1.17 counting the aromatic C_2O unit) and Igepal-CO-720 ($EO:CH_2 = 1.33$) are similar, and both connect the hydrocarbon chain to the oligo(oxyethylene) unit through an aromatic ring.

Results and Discussion

Parts a and b of Figure 1 present the partial ternary phase diagrams of Igepal-CO-720/water in toluene and hexanes, respectively, at room temperature. In the

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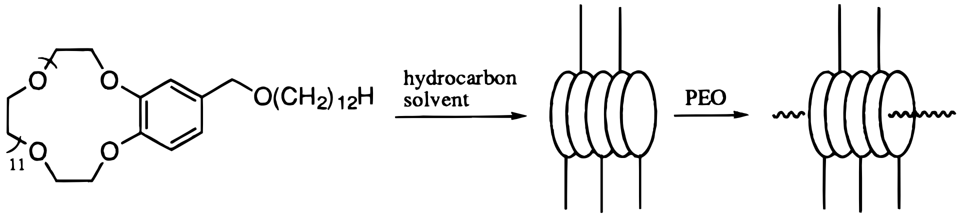
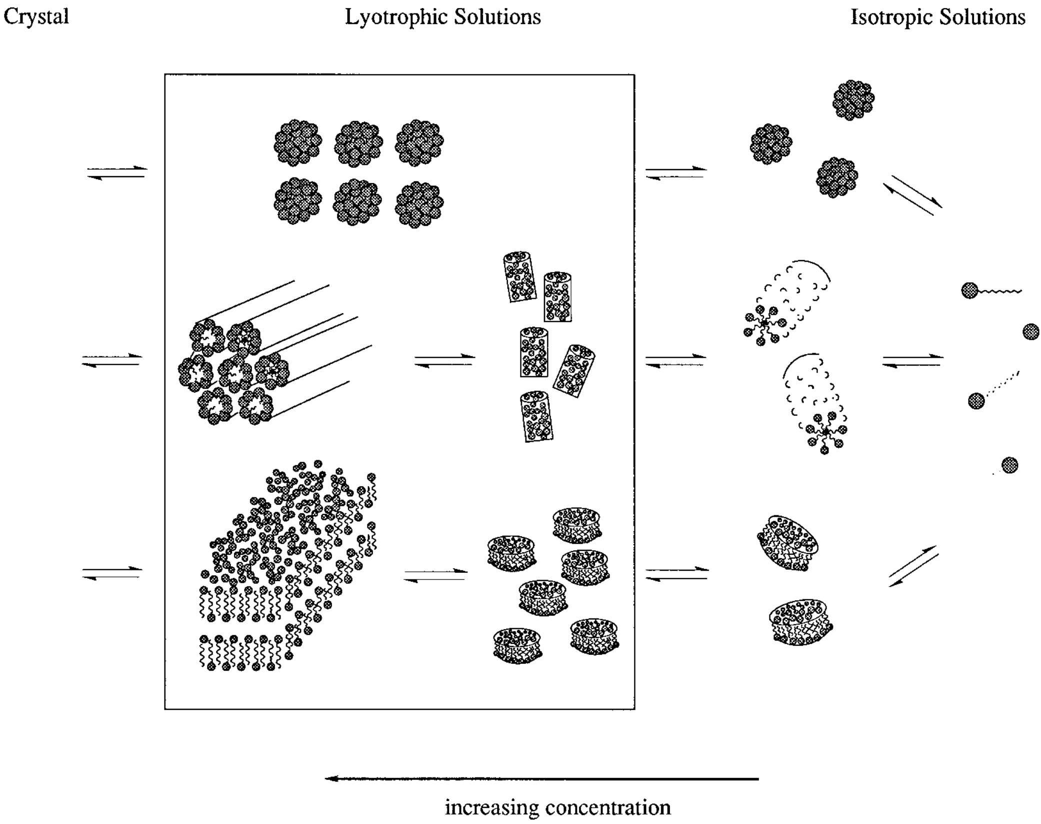
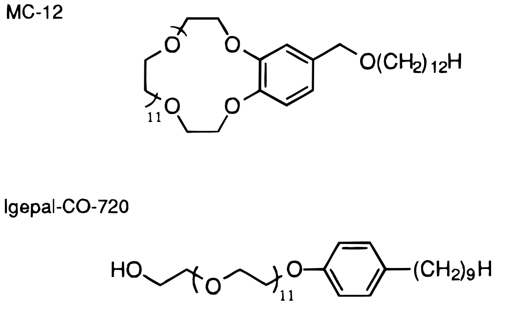
Scheme 1. Amphiphilic Approach for Preparing Homopolyrotaxanes, Such as 3,4-(42-Crown-14)benzyl Dodecyl Ether Threaded with Poly(ethylene oxide)



Scheme 2. Some of the Lyotropic Mesophases Formed by Amphiphilic Molecules as a Function of Concentration[3]



Scheme 3. Comparison of the Chemical Structures of MC-12 and Igepal-CO-720



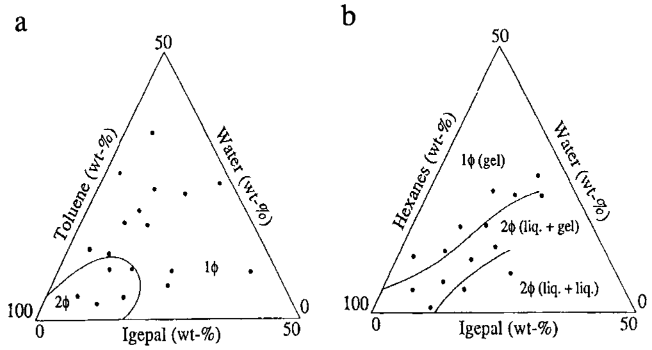


Figure 1. Partial ternary phase diagrams in the organic-rich region at room temperature: (a) Igepal-CO-720/water/toluene; (b) Igepal-CO-720/water/hexanes. 1*ϕ* = one phase; 2*ϕ* = two phases.

absence of water, the toluene solutions of Igepal-CO-720 are isotropic. That is, the difference in solubility of the hydrocarbon and oligo(oxyethylene) segments in toluene is not great enough to cause Igepal-CO-720 to aggregate. However, aggregation occurs when water is added. This is evidently because water forms hydrogen bonds with the oxyethylene units and hydroxy end-group, thereby decreasing their solubility in toluene. The aggregated solutions of Igepal-CO-720/water in 70 wt % toluene remain macroscopically homogeneous[5] up to [H_2O]:[EO] =7.5, in spite of the fact that water is only slightly soluble in toluene. In general, reverse micelles solubilize significant amounts of water, with the solubilized water referred to as a water pool.[6]

In contrast, oligo(oxyethylene) segments are much less soluble than hydrocarbon segments are in hexanes, and hexane solutions of Igepal-CO-720/water macroscopically phase separate at most [H_2O]:[EO] ratios. When the water content is low, the two liquid layers are isotropic, and both water and Igepal-CO-720 are in the lower layer. This is evidently because Igepal-CO-

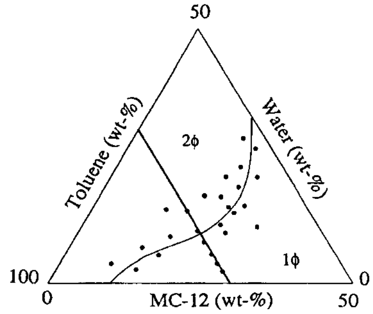


Figure 2. Partial ternary phase diagram in the organic-rich region at room temperature of MC-12/water/toluene. 1ϕ = one phase; 2ϕ = two phases.

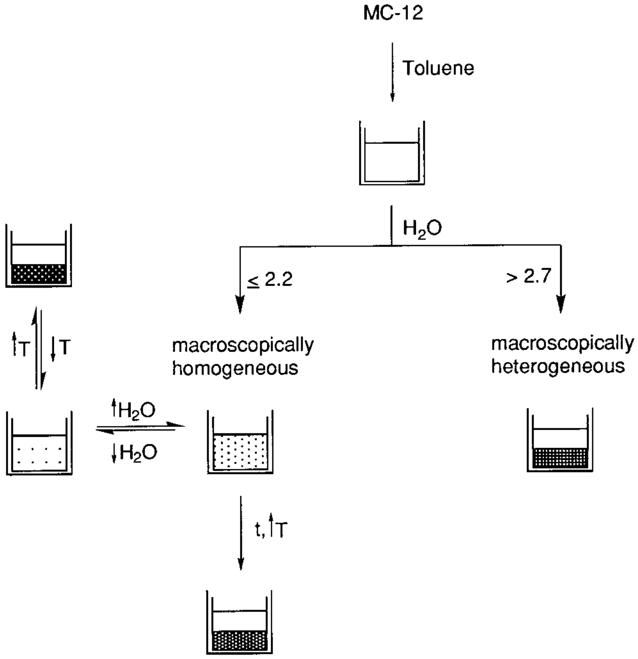
720 is much more soluble in water than in hexanes. As the water content increases, the layer containing Igepal-CO-720 initially becomes turbid but then forms a macroscopically homogeneous transparent gel. However, the macroscopically homogeneous gel becomes turbid when the water content is very high and the content of Igepal-CO-720 is very low.

MC-12 is almost completely insoluble in hexanes, but forms isotropic solutions in pure toluene. Figure 2 presents the partial ternary phase diagram of MC-12/water in toluene at room temperature. Since MC-12 lacks a hydroxy group, the intermolecular hydrogen-bonded associations of MC-12 and water are evidently weaker than in the Igepal-CO-720 system, and the miscibility limits are thus shifted to lower [H_2O]:[EO] ratios. Using the line drawn for the 30 wt % (MC-12/H_2O) / 70 wt % toluene system as an example,[4] Figure 2 shows that an initially clear solution of MC-12 in toluene gradually becomes increasingly turbid as water is added due to aggregation of the hydrated, hydrophilic oligo(oxyethylene) segments. When the water concentration exceeds a critical value at the biphasic boundary, the solution macroscopically phase separates into an isotropic solution and a dense white emulsion.

In order to simplify analysis of the ternary MC-12/water/toluene solutions into a binary system, we have focused on solutions containing 30 wt % (MC-12/H_2O), 70 wt % toluene.[4] As summarized in Scheme 4, the 30 wt % (MC-12/H_2O), 70 wt % toluene solutions with [H_2O]:[EO] > 2.7 macroscopically phase separate at room temperature into a slightly yellow isotropic layer and a more dense, white emulsion; [H_2O]:[EO] = 2.7 is therefore the upper critical water concentration relative to oxyethylene units. The solutions with [H_2O]:[EO] $\leq$ 2.2 are macroscopically homogeneous at room temperature, with their turbidity increasing as the concentration of water increases. However, even the homogeneous solutions phase separate into a yellowish isotropic layer and a more dense white emulsion if they are heated. This phase separation is reversible when [H_2O]:[EO] $\leq$ 0.6, and the biphasic systems become macroscopically homogeneous upon recooling. In contrast, the thermally-induced phase separation of solutions with [H_2O]:[EO] = 0.7−2.2 is irreversible unless the solutions are subsequently agitated.

Table 1 summarizes the ^{1}H-NMR-determined compositions of the isotropic layer and the white emulsion of the phase-separated solutions with [H_2O]:[EO] = 0.45 and [H_2O]:[EO] = 3.6. The solution with [H_2O]:[EO] = 0.45 phase separates reversibly at 90 °C, whereas that with [H_2O]:[EO] = 3.6 is biphasic at room temperature. The yellowish color of the clear upper layers corresponds to the color of MC-12. As summarized in Table 1, the upper isotropic layers contain only MC-12, whereas the lower white emulsion layer is enriched in water. This apparently corresponds to a phase inversion in which a lyotropic oil-in-water (o/w) solution becomes insoluble in the toluene-rich water-in-oil (w/o) parent solution, with some of the MC-12 remaining in toluene in the upper isotropic layer.

Scheme 4. Macroscopic Phase Separation Behavior of 30 wt % (MC-12/H_2O), 70 wt % Toluene at Room Temperature As a Function of [H_2O]:[EO][a]



[a] Shaded areas represent anisotropic/turbid solutions; unshaded areas represent isotropic/transparent solutions.

Table 1. Composition of the Two Layers of Thermally-Induced Macroscopic Phase-Separated 30 wt % (MC-12/H_2O), 70 wt % Toluene As Determined by ^{1}H-NMR at Room Temperature in $CDCl_3$[a]

original		visual	composition (wt %)		
[H_2O]:[EO]	layer	observation	MC-12	H_2O	toluene
0.45	upper	transparent	13	0	87
	lower	turbid	31	19	50
3.6	upper	transparent	26	0	74
	lower	turbid	20	39	41

[a] Original wt % composition of solutions before macroscopic phase separation. [H_2O]:[EO] = 0.45: 27% MC-12, 3% H_2O, 70% toluene. [H_2O]:[EO] = 3.6: 15% MC-12, 15% H_2O, 70% toluene.

The polarized optical micrographs of the macroscopically homogeneous solution of 30 wt % (MC-12/H_2O), 70 wt % toluene with [H_2O]:[EO] = 0.45, and the dense white emulsion that separates from it at 90 °C are shown in parts a and b of Figure 3, respectively. The fanlike texture and homeotropic regions of the dense white emulsion (Figure 3b) are characteristic of a lamellar (L_α) phase.[7−11] The birefringent texture with oily streaks in a homeotropic background of the macroscopically homogeneous phase (Figure 3a) is less distinctive but is also characteristic of an L_α lyotropic mesophase.[7−9] As shown in Figure 4, the texture of the macroscopically homogeneous solution of 30 wt % (Igepal-CO-720/water), 70 wt % toluene with [H_2O]:[EO] = 0.8 is nearly identical, albeit brighter. Lyotropic solutions of cholesterol-derivatives of diazacrown ethers in dilute aqueous HCl also exhibit similar textures.[12]

The X-ray data in Table 2 confirms that the macroscopically homogeneous solution of 30 wt % (MC-12/

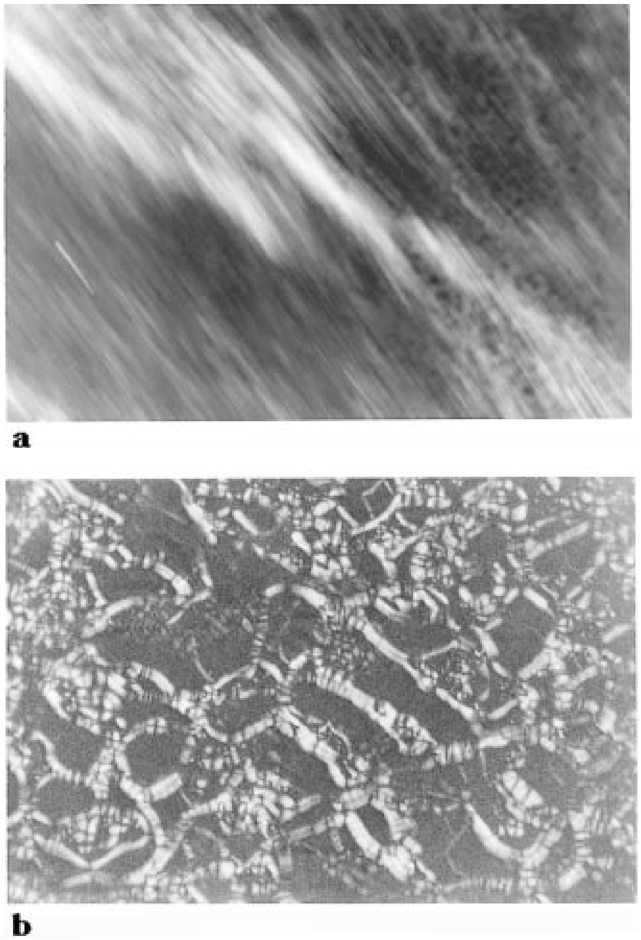


Figure 3. Polarized optical micrographs (200×) of 30 wt % (MC-12/H_2O) / 70 wt % toluene with [H_2O]:[EO] = 0.45 at room temperature: (a) macroscopically homogeneous solution (the picture is blurred due to the movement of the solution); (b) dense white emulsion that separates at 90 °C.

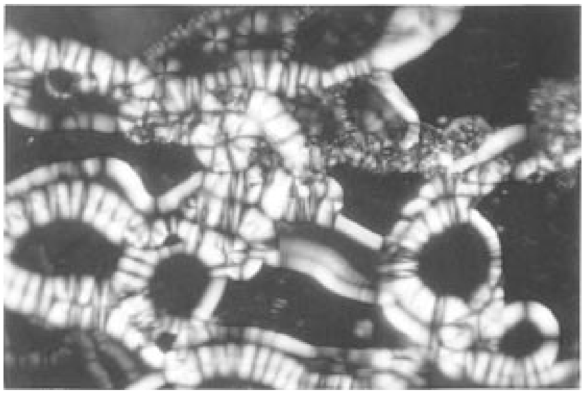


Figure 4. Polarized optical micrograph (200×) of the macroscopically homogeneous solution of 30 wt % (Igepal-CO-720/water), 70 wt % toluene with [H_2O]:[EO] = 0.8 at room temperature.

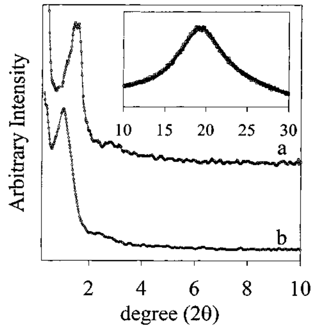
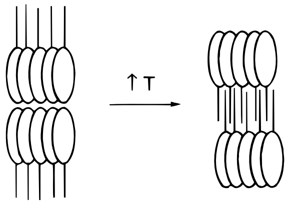


Figure 5. X-ray diffractograms of 30 wt % (MC-12/H_2O), 70 wt % toluene with [H_2O]:[EO] = 0.89 at 12 °C: (a) macroscopically homogeneous solution; (b) dense white emulsion that separates from it at 60 °C. The inset is of the macroscopically homogeneous solution at wider angles.

Table 2. X-ray Scattering Results of 30 wt % (MC-12/H_2O), 70 wt % Toluene

		bragg spacing (Å)	
original [H_2O]:[EO]	temp (°C)	macroscopically homogeneous solution	phase-separated emulsion
0.45	ambient	56.1	
		28.1	
0.89	12	60.0	85.7
		30.0	42.9

Scheme 5. Model of the Interdigitated MC-12 o/w Lamellae after Temperature-Induced Phase Separation



H_2O), 70 wt % toluene with [H_2O]:[EO] = 0.45 is lamellar. The diffractions at small angles correspond to Bragg spacings of 56.1 and 28.1 Å, and are therefore in the typical 2:1 ratio of the first- and second-order reflections of lamellar periodicity.[8,13,14] The X-ray results of the corresponding solution with [H_2O]:[EO] = 0.89 are also summarized in Table 2 and plotted in Figure 5, both before and after temperature-induced phase inversion. We recorded this data at 12 °C instead of at room temperature in order to produce more intense diffractions. The interlamellar spacing of this macroscopically homogeneous solution is 4 Å larger than that with [H_2O]:[EO] = 0.45. This is apparently due to both the greater amount of solubilized water and the expansion of water with decreasing temperature, both of which should produce larger water pools. Other than the slightly larger *d*-spacings of the solution with [H_2O]:[EO] = 0.89, the diffractograms of the two systems are essentially identical. That is, the first- and second-order reflections of the solution with [H_2O]:[EO] = 0.89 are also in the 2:1 ratio of a lamellar structure. The diffuse reflection centered at 19.5° in the wide angle X-ray diffractogram shown in the inset of Figure 5 demonstrates that MC-12 is disordered within the lamellae.

The calculated[15] length of the linear analog of chain-folded MC-12 with the oligo(oxyethylene) segment in the most extended conformation is 59 Å. This corresponds within experimental error to the lamellar thickness (60 Å) determined by X-ray diffraction of the macroscopically homogeneous solution of 30 wt % (MC-12/H_2O), 70 wt % toluene with [H_2O]:[EO] = 0.89 (Figure 5). However, the lamellar spacing of the dense white emulsion that separates from it at 60 °C is 86 Å. This lamellar spacing is similar to the calculated spacing (91.3 Å) for a bilayer organization of MC-12 in which the hydrocarbon substituents are interdigitated (Scheme 5). Interdigitation of the hydrocarbon substituent in the dense white emulsion is also consistent with an o/w aggregation of MC-12. The diffractogram of the macroscopically homogeneous sample also has a shoulder that corresponds to a Bragg spacing of 86 Å. This

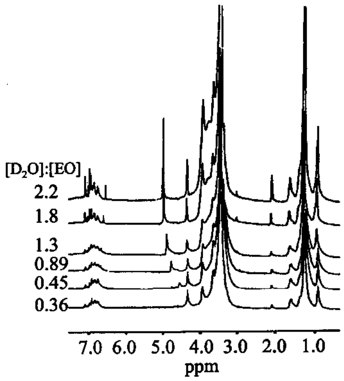


Figure 6. ^{1}H-NMR spectra of 30 wt % (MC-12/D_2O), 70 wt % toluene-d_8 solutions at room temperature as a function of [D_2O]:[EO].[16]

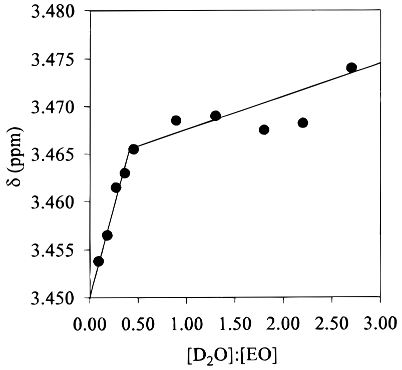


Figure 7. Shift of the oligo(oxyethylene) $-OCH_2-$ ^{1}H-NMR resonance of 30 wt % (MC-12/D_2O), 70 wt % toluene-d_8 at 3.45 ppm as a function of [D_2O]:[EO].

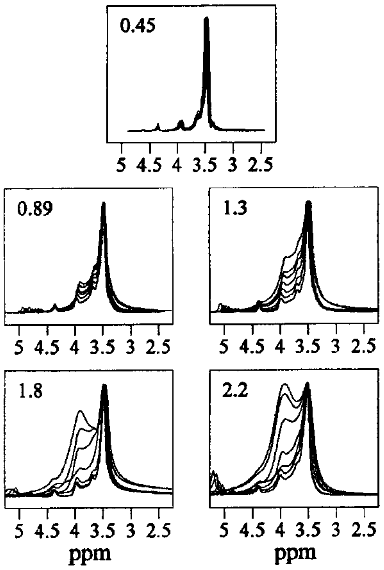


Figure 8. ^{1}H-NMR spectra in the oxyethylene region of 30 wt % (MC-12/D_2O) / 70 wt % toluene-d_8 solutions as a function of temperature at [D_2O]:[EO] = 0.45, 0.89, 1.3, 1.8, and 2.2. Numbers above each set of spectra correspond to [D_2O]:[EO]; within each set of spectra, the resonance at ~4 ppm increases in intensity with each 5 °C decrease in temperature (35, 30, 25, 20, 15, and 5 °C).

indicates that the lamellar phase of the macroscopically homogeneous solution of MC-12 is partially biphasic, at least at higher water contents.

Figure 6 presents the ^{1}H-NMR spectra of 30 wt % (MC-12/D_2O), 70 wt % toluene-d_8 solutions at room temperature as a function of the water content. When [D_2O]:[EO] $\leq$ 0.4, the ^{1}H-NMR spectra of these transparent solutions are similar to that of the isotropic solution of MC-12 in 100% toluene.[16] The resonances of the slightly turbid solution with [D_2O]:[EO] = 0.45 are also narrow. However, the oxyethylene resonances at 3.5−4.3 ppm begin to broaden when [D_2O]:[EO] = 0.45. This broadening may be due to the changing environment of the oxyethylene segments, such that the three partially resolved resonances become more chemically inequivalent in the presence of water. Alternatively, the downfield shift of the three partially resolved oxyethylene resonances may be due to an equilibrium between unimers in bulk solvent and lamellar aggregates of MC-12 in which they are exchanging rapidly on the NMR time scale.[6,17,18] In this case, the shift of each resonance should be the weighted average of the distinct resonances of the unimer and aggregate. Figure 6 also shows that all of the solutions containing D_2O have a resonance at 4.5−5.0 ppm due to solubilized water;[19,20] the HOD resonance of this water pool shifts downfield and increases in intensity as the water content increases.

As shown in Figure 7 using the $-OCH_2-$ resonance at 3.45 ppm as an example, essentially all of the ^{1}H-NMR resonances of MC-12 and HOD shift downfield as the concentration of D_2O increases, but with an abrupt change in the dependence of the shift at [D_2O]:[EO] = 0.45. Similarly, the oxyethylene ^{13}C-NMR resonances of Pluronic L64 [poly(oxyethylene-*block*-oxypropylene-*block*-oxyethylene), $PEO_{13}PPO_{30}PEO_{13}$] shift upfield in *o*-xylene as the water content increases, with different slopes of the dependence for [D_2O]:[EO] < 0.5 and [D_2O]:[EO] > 0.5.[19] The concentration at which such changes in the slope occur is often considered the critical micelle concentration. For example, the $CH_3CH_2CO_2^-$ ^{1}H-NMR resonances of anhydrous alkylammonium propionates in benzene and carbon tetrachloride also shift downfield and upfield, respectively, as their concentration increases, with a change in the slope at the "operational" critical micelle concentration.[6,17] However, we have already demonstrated by polarized optical microscopy and X-ray diffraction that the solution with [D_2O]:[EO] = 0.45 is organized in a lamellar mesophase. The concentration of water is therefore well above the critical micelle concentration. The abrupt change in the dependencies of the downfield shifts of all of the ^{1}H-NMR resonances of MC-12 at [D_2O]:[EO] = 0.45 may therefore correspond to the transition from the isotropic or nematic micellar solution to the lamellar mesophase.

Figures 8 and 9 show the ^{1}H-NMR spectra of the macroscopically homogeneous solutions of 30 wt % (MC-12/D_2O), 70 wt % toluene-d_8 in the oxyethylene and benzylic region as a function of temperature at fixed water content, and as a function of water content at fixed temperature, respectively. When [D_2O]:[EO] = 0.45, the oxyethylene resonances remain almost constant with decreasing temperature; all of the spectra are only slightly broader than that of the isotropic solution of MC-12 in 100% toluene.[16] However, when [D_2O]:[EO] $\geq$ 0.89, the oxyethylene resonances broaden significantly and shift downfield with decreasing temperature. Figure 8 clearly shows that the broadening with decreasing temperature is greater when more water is present. Since water is required for MC-12 to form organized solutions in toluene, the extent of this broadening may be correlated with the degree of order within the system and/or the amount of MC-12 that is aggregated.

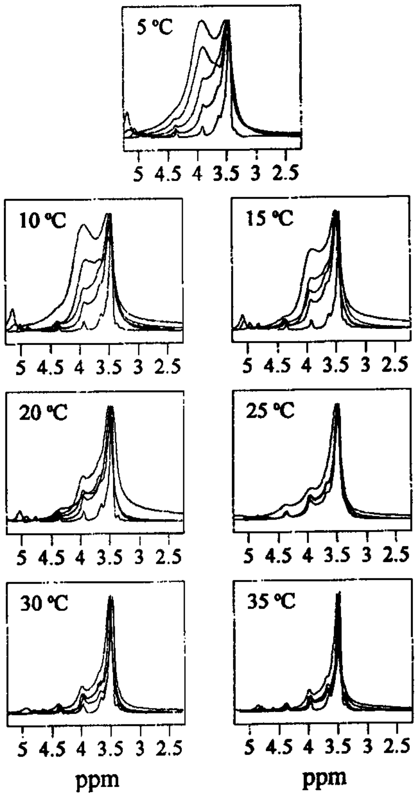


Figure 9. ^{1}H-NMR spectra in the oxyethylene region of 30 wt % (MC-12/D_2O) / 70 wt % toluene-d_8 solutions as a function of [D_2O]:[EO]. Within each set of spectra, the resonance at ~4 ppm increases in intensity with each [D_2O]:[EO] = 0.45 incremental increase ([D_2O]:[EO] = 0.45, 0.89, 1.3, 1.8, and 2.2).

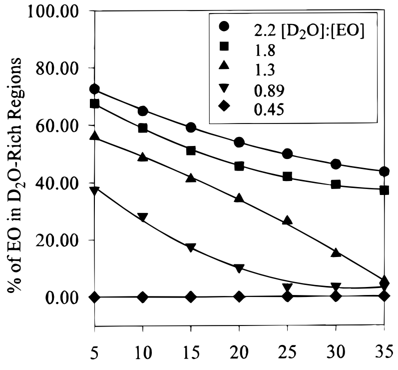
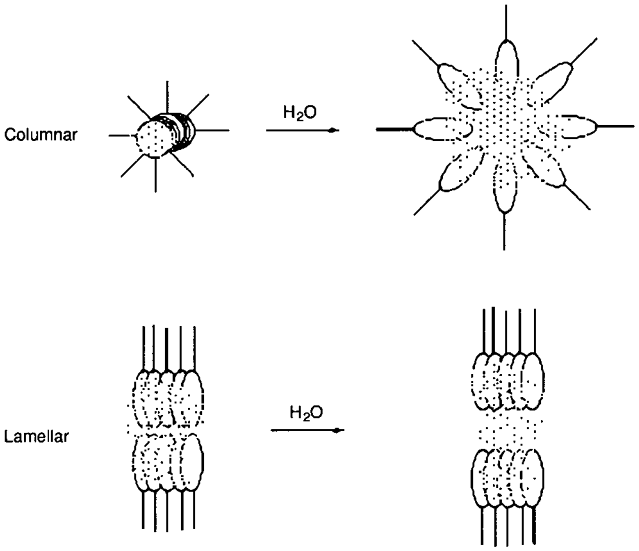


Figure 10. Percent shift of the oligo(oxyethylene) $-OCH_2-$ ^{1}H-NMR resonances of 30 wt % (MC-12/D_2O)/70 wt % toluene-d_8 as a function of temperature.

Figure 10 plots the percent shift of the oxyethylene resonances of the macroscopically homogeneous solutions of 30 wt % (MC-12/D_2O), 70 wt % toluene-d_8 as a function of temperature and [D_2O]:[EO]. Since the shift of the lamellar solution with [H_2O]:[EO] = 0.45 was too small to accurately measure, we assigned it a nominal value of 0.0%. Figure 10 demonstrates that there is less shift as a function of temperature at both extremes in [D_2O]:[EO]. When the water content is high, the addition of more water evidently has less of an effect on the local environment of oxyethylene since more of the water is in the water pool. However, the extent of the broadening of the oxyethylene resonances increases as the water content increases, which may mean that the degree of order in these systems is also increasing and/or that the amount of aggregated MC-12 is increasing.

Scheme 6. Effect of Increasing Water Content on the Columnar and Lamellar Mesophases of an Amphiphilic Macrocrown Ether Such as MC-12 in a Hydrocarbon Solvent



As discussed in the introduction, we expect that the threading efficiency of MC-12 with poly(ethylene oxide) should be higher in more ordered mesophases, which is presumably controlled by the amount of water present. However, we also believe that there will be an optimum amount of water necessary to maximize the threading efficiency within a given phase. This is illustrated in Scheme 6. Although a minimum amount of water is necessary to force the macrocrown ethers to aggregate, the macrocycles should lose some of their alignment as more water is added. More importantly, a water pool develops which can solubilize the added poly(ethylene oxide) and thereby decrease the concentration of threads in the vicinity of the macrocycles.

Since MC-12/H_2O is organized in an L_α phase in 70 wt % toluene rather than in a phase in which its rings are open, such as perhaps a columnar mesophase, the chain-folded macrocrown ether should be more easily threaded if it is flexible. The dynamics of a molecular structure can be studied by NMR relaxation techniques; shorter spin−lattice relaxation times generally correspond to higher order or greater rigidity.[21] For example, the ^{13}C spin−lattice relaxation times (T_{1C}) of the crown ether portion of a copolymer of styrene and 4-vinyl-benzo-24-crown-8 in DMSO-d_6 decrease after it is complexed with potassium thiocyanate.[22] Similarly, the ^{13}C spin−lattice relaxation times of the aliphatic $-CH_2-$ groups of poly(oxyethylene) alkyl ethers decrease by 38% (1.6 times faster relaxation) upon going from an isotropic $CDCl_3$ solution to a lyotropic D_2O solution.[23] However, the oxyethylene relaxation times decrease by only 23% (1.3 times faster relaxation), which the authors consider the same within experimental error.[23]

Table 3 summarizes the T_{1C} spin−lattice relaxation times of a solution of 30 wt % (MC-12/D_2O), 70 wt % toluene-d_8 at 20 °C, both in the presence and absence of water. The aliphatic carbons of MC-12 relax approximately twice as fast when water is present ([D_2O]:[EO] = 0.89) as when it is absent, which confirms that the hydrocarbon segments are more ordered in the former case. In contrast, the oxyethylene resonances relax 1.3−1.7 times slower in the presence of water. Although this demonstrates that the macrocrown ethers

Table 3. ^{13}C-NMR (T_{1C}) Spin−Lattice Relaxation Times of 30 wt % (MC-12/D_2O), 70 wt % Toluene-d_8 at 20 °C

	chem shift (ppm)	T_{1C} (ms)	
		$[D_2O]:[EO] = 0.0$	$[D_2O]:[EO] = 0.89$
Aliphatic	15.5	3700	2100
	24.2	3100	1500
	33.5	2400	1100
Oxyethylene	70.0	300	390
	71.9	500	860
	73.9	505	760
Aromatic	115.3	450	630
	121.6	450	440
	133.4	1700	1200
	150.0	3400	1800

have more motion when water is present, and therefore seems to contradict the organization of MC-12 into an L_α mesophase, it is consistent with the macrocrown ethers being solvated by water in a water pool. That is, water is a better solvent than aromatic hydrocarbons for oligo(oxyethylene).[24] It also demonstrates that the chain-folded macrocrown ethers are relatively flexible in this lamellar mesophase, and may therefore allow threading relatively easily.

Conclusions

Solutions of 30 wt % (MC-12/H_2O), 70 wt % toluene form lyotropic lamellar (L_α) mesophases when $[H_2O]:[EO] \leq 2.2$. The L_α mesophase is one of the two most common mesophases formed by aqueous dispersions of oligo(oxyethylene) alkylphenyl ethers,[13,14,25] such as Igepal-CO-720. Therefore, replacement of the oligo(oxyethylene) segment with a macrocrown ether has little effect on the organization of oligo(oxyethylene) alkylphenyl ethers in a lamellar mesophase, even though the macrocycle contains a distribution of ring sizes. When $[H_2O]:[EO] > 2.7$, solutions of 30 wt % (MC-12/H_2O), 70 wt % toluene macroscopically phase separate into an isotropic toluene layer containing only MC-12 and a water-enriched dense white emulsion in which MC-12 is interdigitated to form an L_α mesophase. This is the result of a w/o to o/w phase inversion. Although MC-12 is organized in an L_α mesophase in toluene in the presence of water, the oxyethylene segments are more mobile in the presence of water, which indicates that the macrocrown ethers are sufficiently flexible to be threaded via an entropic driving force.

Experimental Section

Materials. "3,4-(42-Crown-14)benzyl dodecyl ether" (MC-12) was synthesized as described previously,[1] and dried in vacuo at room temperature for several days. Igepal-CO-720 (Aldrich) was thoroughly dried in vacuo at room temperature for several days. Toluene was dried by distillation from purple sodium benzophenone ketyl under N_2. HPLC grade hexanes and deionized water were used as received from EM Science. Chloroform-*d* (99.8% D), toluene-d_8 (99.6% D), and deuterium oxide (99.9% D) were used as received from Cambridge Isotope Laboratories.

Sample Preparation. All calculations involving MC-12 used the molecular weight corresponding to PEG600 with 13.2 repeat units (872.42 g/mol). Predried MC-12 or Igepal-CO-720 was placed in a vial equipped with a stir bar. After adding the appropriate amount of toluene, the mixture was vigorously stirred for several minutes. Water was then added all at once, and the mixture was stirred until use. The Igepal-CO-720/water/hexanes mixtures were prepared by initially dissolving the Igepal-CO-720 in H_2O, then adding hexanes all at once while vigorously stirring; this inverse procedure was necessary due to the limited solubility of Igepal-CO-720 in hexanes.

Techniques. A Leitz Laborlux 12 Pol S polarized optical microscope (magnification 200×) equipped with a Mettler FP82 hot stage and a Mettler FP90 central processor was used to analyze the anisotropic textures. A drop of sample was placed on a glass slide, and a cover slip was slowly placed on top of it such that the drop did not spread completely towards the edges. The cover plate was then fixed onto the glass slide with epoxy resin to prevent evaporation.

X-ray diffractograms were obtained using a Rigaku Rotaflex RU-200BH rotating anode, with Ni-filtered Cu Kα radiation, operating at 55 kV/190 mA. Collimation was affected with a Soller slit and a 1 mm pinhole, giving an instrumental resolution of 1°. SAXS profiles were recorded at 0.1° (2θ)/min and WAXS profiles at 1° (2θ)/min, using SC-30 Rigaku scintillation counters coupled to pulse-height analyzers. In all cases, the samples were injected with a syringe into 1.5-mm glass capillary tubes (Charles Supper) and sealed. A water/refrigerant cooled oven, constructed by the chemistry department at Laval University, was used and set at 12−13 °C. The temperature was stable to ±1 °C. A baseline profile obtained with an empty capillary tube was subtracted from all sample profiles.

The ^{1}H-NMR spectra were recorded on a 360 MHz Bruker Aspect 3000. The temperature was controlled by using a variable-temperature control unit equipped with liquid nitrogen. For the phase-separation studies, solutions were placed in a glass ampule, frozen in liquid nitrogen, and sealed under vacuum. The ampules were then heated to 90 °C for several hours. The ampules were scored and opened, and aliquots of both the white emulsion and the isotropic layer were removed using a syringe and diluted into $CDCl_3$. For the variable-temperature studies, the samples were spun at each temperature for a minimum of 15 min before acquisition. The variable-temperature series were run from 5 to 35 °C with increasing increments of 5 °C. A total number of 64 scans were acquired for each spectrum. The spectra were then digitized and analyzed quantitatively using Spectra-Calc (Galactic Industries). The average oxyethylene signals of the ^{1}H NMR spectra were curve-fitted using the FIT sub-program of Spectra-Calc. An offset baseline was set and a Gaussian/Lorentzian sum was chosen as the band shape for all. The band maxima were chosen after analyzing the first derivative of the region. After an initial computer-generated estimate of the band shape, which fixed the peak centers, the curve-fits were obtained by allowing peak heights and widths to vary consecutively. A maximum of 1000 iterations was sufficient to converge the minima.

The ^{13}C spin−lattice relaxation times (T_{1C}) at 293 K were obtained using a Bruker AMX500 spectrometer (^{13}C = 125.7038584 MHz), using the standard T_1 inverse recovery inverse gated t1irig subprogram. The exponential multiplication line broadening was set to 0.820 Hz in all cases. A total of 14 (256 scans) and 9 (800 scans) time delays were used for the $[H_2O]:[EO] = 0.0$ and 0.89 samples, respectively, with the longest time delays being 12 and 7 s.

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References and Notes

(1) Pugh, C.; Bae, J.-Y.; Scott, J. R.; Wilkins, C. L. *Macromolecules* **1997**, *30*, 8139.
(2) Kon-no, K. In *Surface and Colloid Science*; Matijevic, E., Ed.; Plenum Press: New York, 1993; Vol. 15; Chapter 3 and references therein.
(3) See for example: (a) Ringsdorf, H.; Schlarb, B.; Venzmer, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 113. (b) Israelachvili, J. N. In *Physics of Amphiphiles: Micelles, Vesicles and*

Microemulsions; Degiorgio, V., Corti, M., Eds.; North Holland Physics Publishing: Amsterdam, 1985.

(4) All of the solutions are composed of 70 wt % toluene, with the total weight of water plus MC-12 fixed at 30 wt %.

(5) We are defining homogeneous solutions as those that do not macroscopically phase separate at room temperature within 2 weeks or after centrifugation.

(6) Fendler, J. H. *Acc. Chem. Res.* **1976**, *9*, 153.

(7) Rosevear, F. B. *J. Am. Oil Chem. Soc.* **1954**, *31*, 628.

(8) Winsor, P. A. *Chem. Rev.* **1968**, *68*, 1.

(9) (a) Kratzat, K.: Finkelmann, H. *Colloid Polym. Sci.* **1994**, *272*, 400. (b) Kratzat, K.; Finkelmann, H. *J. Colloid Interface Sci.* **1996**, *181*, 542.

(10) Funari, S. S.; Holmes, M. C.; Tiddy, G. J. T. *J. Phys. Chem.* **1992**, *96*, 11029.

(11) Auvray, X.; Perche, T.; Anthore, R.; Petitas, C.; Rico, I.; Lattes, A. *Langmuir* **1991**, *7*, 2385.

(12) Xie, M.-G.; Liu, S.-K.; Liu, G.; Li, L.-Z.; Jiang, Q. *Liq. Cryst.* **1996**, *21*, 313.

(13) Rong, G.; Yang, J.; Friberg, S. E.; Aikens, P. A.; Greenshields, J. N. *Langmuir* **1996**, *12*, 4286.

(14) François, J.; Gilg, B.; Spegt, P. A.; Skoulios, A. E. *J. Colloid Interface Sci.* **1966**, *21*, 293.

(15) Biosym was used to calculate the molecular length of *p*-[oligo(oxyethylene)]benzyl dodecyl ether [7 oligo(oxyethylene) units] as a model of chain-folded MC-12 in its most extended conformation.

(16) MC-12 ^{1}H-NMR (toluene-d_8, ppm): 0.93 (t, $-CH_3$), 1.27 (m, $-[CH_2]_9-$), 1.65 (m, $-OCH_2CH_2CH_2-$), 3.48 (m, $-OCH_2CH_2O-$ and $-OCH_2[CH_2]_{11}H$, 46.8 H), 3.68 (br s, $-CH_2CH_2OAr$, 4 H), 3.97 (br s, $-CH_2OAr$, 4 H), 4.46 (s, $-OCH_2Ar$), 7.00 (m, 3 aromatic H).

(17) (a) Fendler, J. H.; Fendler, E. J.; Medary, R. T.; El Seoud, O. A. *J. Chem. Soc., Faraday Trans.* **1973**, *69*, 280. (b) Fendler, E. J.; Fendler, J. H.; R. T. Medary; El Seoud, O. A. *J. Phys. Chem.* **1973**, *77*, 1432. (c) El Seoud, O. A.; Fendler, E. J.; Fendler, J. H.; Medary, R. T. *J. Phys. Chem.* **1973**, *77*, 1876. (d) Fendler, E. J.; Constien, V. G.; Fendler, J. H. *J. Phys. Chem.* **1975**, *79*, 917.

(18) Okano, L. T.; El Seoud, O. A.; Halstead, T. K. *Colloid Polym. Sci.* **1997**, *275*, 138.

(19) Chu, B.; Wu, G. *Macromol. Symp.* **1995**, *90*, 251.

(20) Robeiro, A. In *Reverse Micelles*; Luisi, P. L., Straub, B. E., Eds.; Plenum Press: New York, 1984; p 113.

(21) (a) *NMR Spectroscopy of Polymers*; Ibbett, R. N., Ed.; Blackie Academic & Professional: New York, 1993. (b) Koenig, J. L. *Spectroscopy of Polymers*; American Chemical Society: Washington, DC, 1992.

(22) Buchanan, G. W.; Moghimi, A.; Ratcliffe, C. I. *Can. J. Chem.* **1996**, *74*, 1437.

(23) Heatley, F.; Teo, H. H.; Booth, C. *J. Chem. Soc., Faraday Trans. I* **1984**, *80*, 981.

(24) For example, the second virial coefficient of PEO in water at 25 °C is much higher than that in benzene: water, $A_2 = 62 \times 10^{-4}$ mol cm^3/g^2 ($M_n = 10.1 \times 10^3$); benzene, $A_2 = 27 \times 10^{-4}$ mol cm^3/g^2 ($M_n = 7.7 \times 10^3$). *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1989; p VII/132.

(25) Husson, F.; Mustacchi, H., Luzzati, V. *Acta Crystallogr.* **1960**, *13*, 668.

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