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Micellar Solutions of Octyl-18-crown-6

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The solution properties of the novel surfactant octyl-18-crown-6 ($C_8\Phi_6$) have been investigated with phase diagram, light-scattering, and surface tension measurements. This tenside is made up of an octyl hydrophobic chain attached to a 18-crown-6 ether and cyclic polar head-group that is highly selective for complexing K^+ ions. The results show that $C_8\Phi_6$ produces micellar structures in water and in KCl aqueous solutions, with a radius of about 30 Å. Addition of potassium ions in a molar ratio of 0.4 ($KCl/C_8\Phi_6$) increases the hydrophilicity of the surfactant, as shown by the increment of the phase separation temperature, and produces a slight shift in the critical micellar concentration value, as it results from surface tension measurements. The intermicellar interaction parameter α , obtained from QELS experiments, has been discussed. Pure $C_8\Phi_6$ micelles experience attractive intermicellar interactions overimposed to the hard-sphere interactions, while the K^+ complexation of the surfactant polar head-groups leads to a decrease of the average attractive component of the interaction. These results show that intermicellar interactions are selectively controlled and modulated by simply adding a proper salt that can be complexed by the polar head-groups of the surfactant.

Introduction

The synthesis and study of new surfactants with peculiar physicochemical properties is one of the most promising and ever expanding issues in colloid science. Ion transport across hydrophobic media, selective binding of ions in different solvents, electron transfer across micellar interfaces, enhancement of the quantum yield in photoionization processes, and more general host-guest molecular recognition processes have an increasing interest for scientific and industrial applications.^{1–5}

Crown ethers belong to the class of macrocycles and possess an outstanding ability to complex ions and small organic molecules, and to behave as ionophores capable of transporting ions across lipophilic barriers. The addition of a lipophilic long-chain alkyl group to a hydrophilic crown ether⁶ results in the formation of a crown ether-based surfactant that can form micelles or more complex supramolecular structures in water, similarly to the common nonionic surfactants. The production of new compounds that possess, in the same molecular structure, a hydrophilic and a lipophilic part, or at least two regions with different hydrophilicity, is of great interest for scientific and industrial purposes. For example, the supramolecular structures formed by different kinds of ligands (such as calix[*n*]arenes, cryptands, alkyl-crown ethers) and of macromolecules/polymers complexes including cyclodextrins, polyrotaxanes, and molecular nanotubes, are currently being studied for their potential use in host-guest systems.^{7–10}

In the most common cases, when a noncomplexing nonionic surfactant is dissolved in an aqueous solution of some electrolyte above the cmc, the micellar outer shell is formed by the polar head-groups, by the hydrating solvent molecules, and by a certain amount of ions that surround the hydrophilic groups. As far as the phase diagram is concerned, the addition of salts to nonionic micellar solutions generally produces little effects.¹¹

The nature and the behavior of alkyl-crown¹² and alkyl cryptand^{13–15} micellar systems are greatly affected by ion

complexation performed by the polar head-group of the surfactant. This surfactant will then carry an ion and its behavior will resemble that of an ionic tenside. In this way the micellar interface charge can be controlled by simply changing the surfactant/salt molar ratio,^{12,16} the pH can also be used to control the charge, especially when the complexing atom is nitrogen such as in azamacrocyclic cages.^{12,13} Therefore, the addition of specific ions or the variation of the pH determines a significant change in the micellar surface charge, that is from nonionic to fully ionic micelles.^{17,18} In previous papers^{12,16–18} we used a macrobicyclic cage, namely the 5,12,17-trimethyl-1,5,9,12,17-pentaazobicyclo[7.5.5]nonadecane, to complex lithium counterions in lithium dodecyl sulfate solutions. Besides the reduction of the micellar charge upon complexation of Li^+ , the addition of the macrocyclic ligand results in a strong increment in the aggregation number and in a change of the micellar shape from spheres to elongated ellipsoids.¹⁷ Moreover, the counterion distribution around the micellar surface has been calculated by SANS experiments, using a two-layer model for the micellar structure factor, and a multicomponent ionic solution theory due to Kahn and Ronis, for the intermicellar structure factor.¹⁸

In our studies we have so far used the complexing properties of different ligands to encapsulate the counterions and shield them from the micellar interface, in order to evaluate the macroion–macroion and the macroion–counterion interactions. More recently, our group focused its attention on those amphiphilic compounds, such as alkyl-crown ethers and calix[*n*]arenes, that join a significant surface activity and high selectivity for complexing specific cations or including small organic molecules in host-guest systems.^{7–9,12,16}

In this paper we report the properties of micellar solutions obtained from a novel surfactant, the octyl-18-crown-6 ether, herein after called $C_8\Phi_6$ (see Figure 1). This molecule is able to complex potassium ions in a highly selective way, and the properties of its aqueous solutions are expected to respond to the addition of salts unlikely the micellar systems formed by the conventional nonionic alkylpoly(oxyethylene) surfactants (C_iE_j). In fact, linear C_iE_j possess a $(OCH_2CH_2)_jOH$ tail that terminates with an $-OH$ residue and that is not able to give stable complexes with cations. On the other hand, the cyclic

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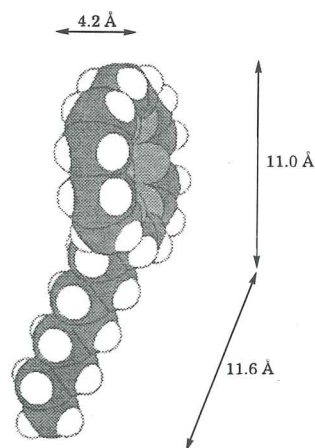


Figure 1. CPK molecular model for $C_8\Phi_6$.

homologues $C_i\Phi_j$ do not possess alcoholic groups but can easily form complexes with ions such as Na^+ , K^+ , Cs^+ , and Ba^{2+} , depending on the ligand's cavity size.⁴

The results, obtained from phase diagram investigation, and from surface tension and light-scattering experiments, show that micellar solutions are formed by the nonionic surfactant $C_8\Phi_6$ in water. The complexation of potassium ions operated by the polar cyclic head-groups results in a significant change in the phase diagram, in the cmc behavior, and in the micellar interactions.

Materials and Methods

Pentaethylene glycol, hydrochloric acid, sodium hydride, sodium hydroxide, potassium hydroxide, *p*-toluenesulfonyl chloride, methylene chloride, 1,4-dioxane, and potassium chloride were purchased from Fluka (Milan, Italy). 1,2-Epoxydecane was obtained from Aldrich (Milan, Italy). All chemicals were used as received, with the exception of 1,4-dioxane. $C_8\Phi_6$ was synthesized and purified as reported in the Appendix.

For all samples we used bidistilled water purified with a Millipore Milli-Q system. The density of $C_8\Phi_6$ (molecular weight 376) was found to be 1.10 g/cm³.

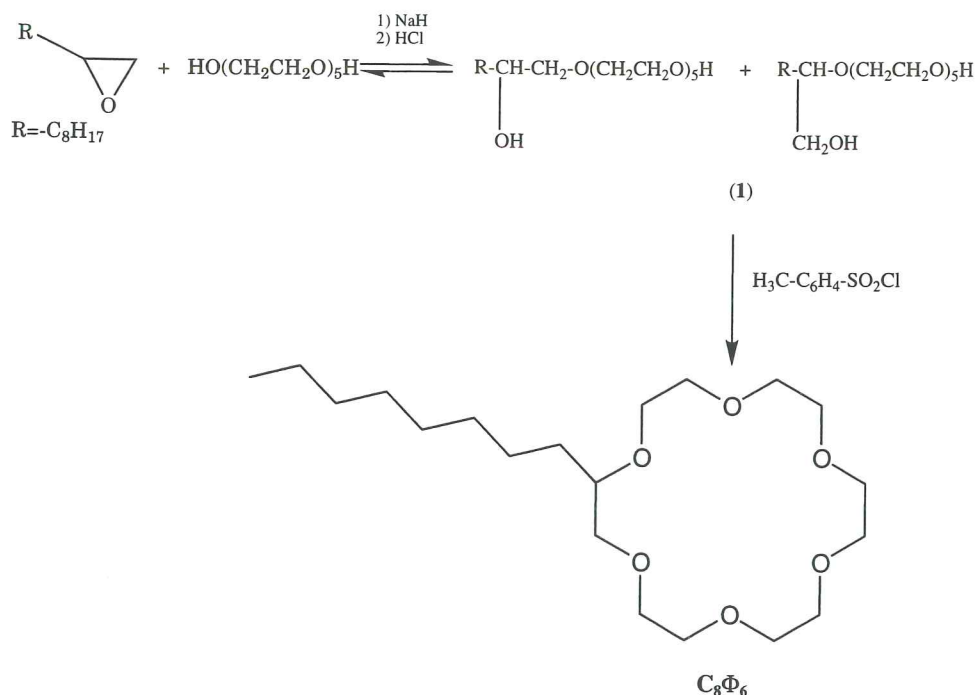


Figure 2. Reaction path for the synthesis of $C_8\Phi_6$.

Phase Diagram. The phase behavior for each sample was studied using a thermostatic bath stabilized within ± 0.1 °C. Samples were prepared in NMR glass tubes and flame sealed.

Surface Tension. Surface tension at the air-solution interface was measured by the Du-Noüy ring method using a Sigma 70 instrument (KSV Instruments, Ltd.). The temperature of the solution was kept at 20 ± 0.1 °C with a thermostatic bath.

Light Scattering. QELS experiments were carried out on a Brookhaven Instrument apparatus (BI 9000AT correlator and BI 200 SM goniometer). The signal was detected by an EMI 9863B/350 photomultiplier. The light source was a Coherent Innova 90 Ar⁺ laser, at $\lambda = 514$ nm, linearly polarized in the vertical direction, with a power attenuated in order to avoid sample heating. The laser long-term power stability was $\pm 0.5\%$. Homodyne detection was recorded using decahydronaphthalene as cell matching liquid. The data were collected in multiple-sample time detection, and the autocorrelation function of the scattered light intensity was expanded about an average line width Γ as a polynomial function of the sample time with cumulants as parameters to be fitted, stopped to the second moment. A weighed least-squares technique was applied to the second-order polynomial function to determine the constants and their standard deviation.^{19,20} The average mutual diffusion coefficient D is related to Γ by the relationship

$$D = \Gamma/K^2 \quad (1)$$

where

$$K = (4\pi n/\lambda)\sin(\theta/2) \quad (2)$$

K is the scattering wave vector, n the index of refraction of the sample, and θ the scattering angle. The deviation of the experimental curve from a single-exponential decay, that is, the degree of polydispersity in the sample, is usually given by μ_2/Γ^2 , where μ_2 is the second moment of the distribution.²⁰

The index of refraction of the samples was measured with the Abbé refractometer (Atago 3T) with an accuracy of ± 0.0002 . The dust-free samples were stabilized at 20 ± 0.1 °C.

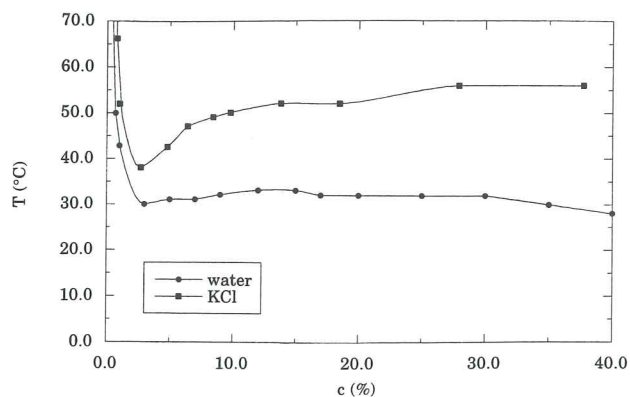


Figure 3. Phase diagram of the $C_8\Phi_6$ aqueous micellar solutions without KCl (lower consolution line) and with KCl (upper consolution line) in molar ratio $KCl/C_8\Phi_6 = 0.4$.

Results

Phase Diagram. When a clear and homogeneous water dispersion of $C_8\Phi_6$ surfactant is slowly heated up, the solution suddenly becomes turbid and eventually it separates into two coexisting phases. Cooling down the sample, the original clear system is restored and the process is fully reversible. Plotting the temperature at which the phase transition occurs versus the surfactant concentration, one can obtain the phase diagram for such a system. For nonionic surfactants like C_iE_j the addition of a salt in the dispersing medium slightly affects the phase transition temperature. In our case, the phase diagrams of $C_8\Phi_6/H_2O$ and of $C_8\Phi_6/H_2O/KCl$ systems were recorded (see Figure 3) as a function of $C_8\Phi_6$ concentration, in the range between 1.0% and 40% w/w of surfactant. In all $C_8\Phi_6/H_2O/KCl$ samples the $KCl/C_8\Phi_6$ molar ratio is always equal to 0.4; this value ensures that all the present K^+ ions are complexed by the polar cyclic head-groups. In Figure 3, the continuous lines represent the consolution curves between the monophasic region at the bottom of the diagram and the biphasic region at the top. For the $C_8\Phi_6/H_2O$ system the phase diagram shows that a temperature increment results in phase separation around 30 °C (cloud point temperature, T_{cp}) for a surfactant concentration of about 3% w/w. Once phase separation occurs and samples are stable, the lower phase is weakly opalescent, while the upper phase is transparent. For the $C_8\Phi_6/H_2O/KCl$ system, the consolution line is located at higher temperatures and the cloud-point region is narrower with respect to the system without potassium chloride: T_{cp} is about 38 °C for a $C_8\Phi_6$ concentration of 3%. In both cases, when the temperature approaches the cloud point, the samples show critical opalescence and require a very long stabilization time before phase separation is complete, about 1 week.

Surface Tension. The surface tension (γ , mN/m) of $C_8\Phi_6/H_2O$ and $C_8\Phi_6/H_2O/KCl$ solutions was measured as a function of $C_8\Phi_6$ concentration at 20 °C, and the critical micellar concentrations were determined from the γ vs $\log C$ curves. The critical micellar concentration of $C_8\Phi_6$ in water (0.020 mol/L) is higher than the value of the linear homologue C_8E_6 (0.010 mol/L),²¹ and in the presence of KCl, cmc is 0.025 mol/L. The area per molecule (A , Å²/molecule) at the gas/liquid interface is obtained from the slope of the $\gamma/\log C$ curve, according to Gibbs' equation²²

$$\Gamma_0 = \frac{-1}{2.303RT} \frac{\partial \gamma}{\partial \log c} \quad (3)$$

$$A = 10^{16}/N_A \Gamma_0 \quad (4)$$

and the value obtained for pure $C_8\Phi_6$ is 51 ± 4 Å²/molecule.

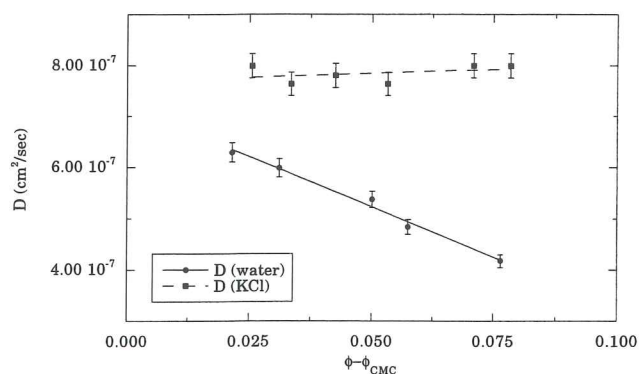


Figure 4. Diffusion coefficient vs volume fraction of micelles in solution for aqueous solutions of $C_8\Phi_6$ and with KCl at 20 °C.

TABLE 1: Experimental Values of D_0 (cm²/s), α , R_h (Å), and Polydispersity (P) for $C_8\Phi_6/H_2O$ and $C_8\Phi_6/H_2O/KCl$ Micellar Solutions at 20 °C

solvent	$D_0(10^{-7})$	α	R_h	P
H ₂ O	7.50 ± 0.13	-5.2 ± 0.3	28.6 ± 0.5	0.1
H ₂ O/KCl	7.74 ± 0.14	$+0.3 \pm 0.3$	27.8 ± 0.5	0.1

Light Scattering. QELS experiments were performed on the monophasic samples of the phase diagram at 20 °C to determine the size and shape of micellar aggregates in solution. In order to avoid multiple scattering, the $C_8\Phi_6$ concentrations in the investigated samples are close to cmc. In this case, the diffusion coefficient D of the micelles does not depend on the scattering angle θ and is a function of the surfactant volume fraction, according to the following relation

$$D(\phi) = D_0(1 + \alpha\phi) \quad (5)$$

where D_0 is the self-diffusion coefficient, α is the second virial coefficient related to the intermicellar interactions, and ϕ is the volume fraction of the dispersed phase.²³ It is important to recall that the dispersing phase of micellar solutions contains solvent molecules (pure water or KCl aqueous solution) and surfactant monomers at a concentration that equals the cmc; thus ϕ is the volume of the assembled surfactant over the total volume of the solution.^{24,25}

At infinite dilution, when $C \rightarrow \text{cmc}$, QELS experiments provide the value of the self diffusion coefficient of the micelles. Once D_0 is known, the hydrodynamic radius of the micelles, R_h (Å), can be calculated according to Stokes–Einstein's formula

$$R_h = k_B T / 6\pi\eta D_0 \quad (6)$$

where k_B is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of the medium in which the micelles are dispersed.²⁶ In Figure 4, the diffusion coefficient D is plotted versus ϕ at 20 °C for $C_8\Phi_6/H_2O$ and $C_8\Phi_6/H_2O/KCl$ micellar solutions. In both cases D_0 , and α have been calculated with a least-squares linear fitting of the experimental data, according to eq 5. The hydrodynamic radius R_h was obtained from eq 6, and the values are reported in Table 1.

It is important to underline that the concentration of $C_8\Phi_6$ monomers in equilibrium with the micelles is large, since the cmc is quite high (0.76% w/w for the $C_8\Phi_6/H_2O$ system). This implies that the monomers contribute to the scattered intensity autocorrelation function $C(t)$ with a relevant single-exponential decay of very short time constant that corresponds to objects smaller than 15 Å in size. To subtract the monomer contribution from the total signal, we performed the calculation of the micellar time constant starting from a channel that corresponds

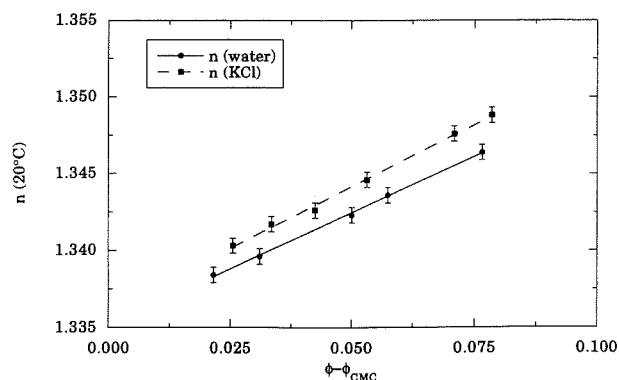


Figure 5. Index of refraction as a function of volume fraction of micelles for aqueous solutions of $C_8\Phi_6$ and with KCl at 20 °C.

to the region in the $C(t)$ curve where the autocorrelation function decay produced by the scattering monomers is asymptotic. We also verified that such subtraction did not result in a loss of information on the micelle time constant. The polydispersity degree (P) is calculated from the second moment of the distribution and reported in Table 1.

The index of refraction, n , of the micellar solutions measured as a function of ϕ is reported in Figure 5. n linearly increases with ϕ in the investigated range. The value of n for pure $C_8\Phi_6$ is 1.4648 at 20 ± 0.1 °C.

Discussion

$C_8\Phi_6$ in water is soluble at room temperature like linear nonionic surfactants, and the surfactant solubility decreases with temperature. A miscibility gap is shown at higher temperatures, with a lower critical point (cloud point). Similarly to linear nonionic surfactants, $C_8\Phi_6$'s solubility in water decreases with temperature, as expected from the lower consolution curve.^{27,28} When salts are added to micellar solutions formed by linear nonionic surfactants, T_{cp} lowers, as a result of the weaker hydrogen-bonding network in the bulk solvent that lowers the head-group hydration. Ionic surfactants show an opposite behavior; in fact their solubility in water usually increases as temperature raises. This phenomenon has been reported in the literature as the effect of stronger interactions between the micelles and the solvent.^{29,30}

However, when the salt interacts specifically with the head-group, as in the case of $C_8\Phi_6$, the cloud point is shifted to higher temperatures.^{29,31} For 3% $C_8\Phi_6$ in water the lower consolution point increases from 30 to 38 °C, supporting that K^+ ions are complexed by the surfactant head-groups and therefore that the surfactant is more hydrophilic and more soluble in water, so that a higher temperature is required for phase separation to occur. From surface tension measurements, the cmc of the $C_8\Phi_6$ in water is higher than that of the corresponding linear surfactant C_8E_6 ,²¹ in spite of the absence of a primary OH residue at the end of the ethylene oxide polar group in $C_8\Phi_6$, that should decrease both its solubility as well as its cmc. This result can be explained by considering that the polar head-group of $C_8\Phi_6$ is quite large and steric effects become predominant. Regarding the cmc value of $C_8\Phi_6$, there is a discrepancy between our data (0.020 mol/L) and the value reported in the literature by Kuo et al.³² In linear nonionic surfactants, the activity coefficient of the monomer changes, depending on the electrolyte concentration and on the nature of the added salt. Micellization is thermodynamically favored when surfactant monomers are salted out by the electrolyte,³³ due to the weaker interactions between the surfactant and solvent molecules, and cmc is lowered. The opposite situation applies when the monomers

are salted in.³³ In our case, the addition of salt produces a slight increase of the cmc from 0.020 and 0.025 mol/L, indicating an effect similar to the above-mentioned salting in.³⁴ This indicates that a thermodynamically disfavored micellization occurs, as a result of the higher repulsive interactions among the charged polar head groups. A deeper investigation of this behavior is the object of current studies.³⁴

Micelles of $C_8\Phi_6$ in water have a radius of about 30 Å as determined from QELS experiments. After addition of KCl the average radius remains unchanged. Furthermore, the polydispersity is similar, and quite low. The analysis of the second virial coefficient (as shown in Figure 4) indicates that for $C_8\Phi_6$ aggregates the α parameter is negative ($\alpha \approx -5$), and has a large absolute value,^{25,35} suggesting that $C_8\Phi_6$ micelles establish attractive interactions. Nonionic micelles experience the well-known volume excluded interactions as expected from the hard-sphere theory, and the van der Waals long-range intermicellar interaction (core-core and shell-shell) that play the opposite role producing attractive forces.^{36,37} In the case of the ionic system, electrostatic repulsions among charged micelles must be taken into account along with the above-mentioned interactions. For ionic micelles produced by linear surfactants, such as sodium dodecyl sulfate, the electrostatic repulsive component strongly dominates over the attractive contribution. In our case, the complexation of KCl by the alkyl-crown ether headgroups produces a decrease of the attractive component ($\alpha \approx 0$). In the KCl/ $C_8\Phi_6$ system (molar ratio 0.4) the balance between these different forces results in the overall averaged interaction parameter obtained from the second virial coefficient. This finding is interesting, as it means that interactions in micellar solutions can be modulated and controlled by simply adding a proper salt that is selectively complexed by the polar head-groups of the surfactant, and without changing the chemical structure of the surfactant itself.

Conclusions

In this paper we report a study on the micellar solutions of a novel nonionic surfactant, the octyl-18-crown-6 ($C_8\Phi_6$) in water and in KCl aqueous solutions. Phase diagrams investigation, QELS, and surface tension measurements indicate that $C_8\Phi_6$ forms nearly spherical aggregates in solution and that K^+ ions are complexed by the cyclic polar head-groups of the surfactant. In the case of nonionic $C_8\Phi_6$ micelles, the cmc is about 0.020 mol/L, and upon addition of KCl ($KCl/C_8\Phi_6 = 0.4$ mol/mol) the cmc is slightly shifted toward higher values (0.025 mol/L). Micelles have a radius of about 30 Å in water and in KCl and experience volume excluded interactions in both cases. In particular, the analysis of the second virial coefficient obtained from light-scattering experiments indicates that pure $C_8\Phi_6$ micelles are not charged and experience attractive interactions. When the nonionic head-groups complex the cation of a proper salt (KCl), the intermicellar interactions can be varied by simply changing the amount of salt.

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Appendix

Purification of 1,4-Dioxane. In order to remove water and organic impurities from commercial dioxane, we proceeded as follows. A 1200 mL volume of dioxane was heated under reflux with 150 mL of hydrochloric acid 1 N for 4 h, with a gentle stream of nitrogen. The aqueous phase was then discarded, while the organic layer was vigorously shaken with some solid

potassium hydroxide several times, and left over solid KOH for 24 h. Dioxane was finally distilled in the presence of sodium and then used right a way.

Synthesis of $C_8\Phi_6$. Figure 2 shows the reaction procedure.⁶ A 152.5 g (0.64 mol) quantity of pentaethylene glycol was added dropwise to a dispersion of 6.4 g (0.32 mol) of sodium hydride in 200 mL of freshly distilled anhydrous dioxane, kept in an ice bath and under magnetic stirring. When the formation of hydrogen had ceased, 50 g (0.32 mol) of 1,2-epoxydecane was slowly added and the final mixture was refluxed for 24 h. After cooling at room temperature, 28 mL of concentrated hydrochloric acid was added, and the resulting solid was filtered off. Dioxane and pentaethylene glycol in excess were removed by distillation under vacuum, so that a thick yellow viscous oil was obtained. The product (1) was purified by molecular distillation (pressure = 5×10^{-4} mmHg, temperature = 120 °C, dropping rate = 15 drops/min, rotation speeds = 450 rpm), with a yield of 60% (72 g, 0.18 mol).

To a suspension of 30.4 g (0.76 mol) of finely ground sodium hydroxide in 900 mL of anhydrous dioxane, 72 g (0.18 mol) of product (1) was added. The mixture was kept under vigorous magnetic stirring for at least 10 h, and in the meanwhile 36.2 g (0.19 mol) of *p*-toluenesulfonyl chloride dissolved in 570 mL of anhydrous dioxane was added dropwise. When the addition was complete, the reaction mixture was kept at 60 °C for 10 h and then cooled down to room temperature. The solid precipitate was filtered off and washed with methylene chloride. From the combined liquid phases the solvents were removed with a rotavapor, obtaining a brown viscous oil that was purified twice by molecular distillation (pressure = 5×10^{-4} mmHg, temperature = 130 °C, dropping rate = 12 drops/min, rotation speed = 500 rpm). The final octylcrown ether ($C_8\Phi_6$) was obtained as a clear liquid with a yield of 46% (33 g, 0.09 mmol).

The purity of the final product was checked by GLC, NMR, MS, IR, and elemental analysis.

Differential scanning calorimetry (DSC) experiments were performed in order to determine whether $C_8\Phi_6$ absorbs water molecules during storage or not. The results indicate that water absorption is negligible.

The presence of sodium ions in the final $C_8\Phi_6$ was checked with atomic absorption analysis and we obtained a value lower than 10^{-5} M.

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