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The Interactions Between Nonionic Surfactants and Cyclodextrins Studied by Fluorescence Measurements ⋆

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Abstract. The complex formation between some nonionic surfactants and α-, β- and γ-cyclodextrin was studied by fluorescence measurements. The relative fluorescence intensity of a solute containing a nonionic surfactant at a constant concentration far below the critical micelle concentration (CMC) are enhanced by the addition of cyclodextrins. Non linear type equations were derived to obtain stability constants by fluorescence measurements for inclusion complexes formed between cyclodextrins and the nonionic surfactants. In most cases 1 : 1- and 2 : 1-complexes (ratio of cyclodextrin to surfactant) are formed.

Key words: cyclodextrins, nonionic surfactants, complex formation, fluorescence

1. Introduction

Nonionic surfactants such as Triton X-100, NP-10 and Igepal CO-890 are molecules with aromatic components which can be used as self probes in fluorescence spectroscopy because they are naturally fluorescent [1, 2]. These surfactants are amphiphilic molecules that have the ability to aggregate in water and to form micelles above a critical micelle concentration (CMC). At nonionic surfactant concentrations far below the CMC the fluorescence spectrum shows a large peak centered around 305 nm and additional bands with maxima at 330 and 348 nm appear at concentrations above the CMC [3]. This appears from self-association, similar to dimeric species. Nonionic surfactants have the advantage of not being complicated by the influence of the dielectric constant of the medium on the CMC, or by the influence of the solvent on the activity coefficient of the free surfactant species [4].

Cyclodextrins (CDs) are polysaccharides made up of six to eight (α = 6, β = 7,γ = 8) D-glucose monomers linked covalently at the 1 and 4 carbon atoms. The internal cavities are relatively hydrophobic and have diameters ranging from 0.50 to 0.85 nm. This structure gives CDs the ability to include guest molecules within the

⋆ Dedicated to Professor Milan J. Schwuger on the occasion of his 60th birthday.
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hydrophobic cavity [5–9]. In these complexes, noncovalent, intermolecular forces play the primary role in complex formation and stabilization.

Fluorescence spectroscopy is an ideal measurement technique for the study of the binding ratio and the stability constant for the nonionic surfactant-cyclodextrin complexation because of its inherent sensitivity. The changes in absorbances at low surfactant concentrations, however, are so small that the stability constant K cannot be determined accurately by means of absorption spectroscopy. It is known from the literature that the fluorescence intensity of the nonionic surfactant Triton X-100 increases by complex formation with β-cyclodextrin [3]. Cyclodextrins are able to destroy micelles by complexing the surfactant molecules. Nuclear magnetic resonance (NMR) spectroscopy studies indicate that the phenyl group is included inside the cyclodextrin cavity. The linear Benesi–Hildebrand plots indicate the formation of a simple 1 : 1 complex between the nonionic surfactant Triton X-100 and β-cyclodextrin [3].

A calorimetic technique has also been used to study complex formation between α-, β-, γ-cyclodextrins and the surfactant TX-100 [10]. These investigations indicate that 2 : 1 (cyclodextrin/TX-100) complexes are formed at surfactant concentrations above the CMC.

In the present study a fluorescence model is developed for data analysis of 1 : 1 and 2 : 1 (cyclodextrin:surfactant) complex formation. To avoid any complication from the formation of micelles surfactant concentrations far below the CMC were used.

2. Experimental

The nonionic surfactants Triton X-100 (MW = 624.89 g/mol), NP-10 (MW = 660.90 g/mol), Igepal CO-890 (MW = 1982.5 g/mol) and as a test substance phenol were used in fluorescent measurements without further purification. The phenyl group of the nonionic surfactants is used as the fluorescing chromophore (see structure in Figure 1).

The α-, β- and γ- cyclodextrins were obtained from Wacker Chemie (München) and were used without further purification. The chemical structures are shown in Figure 1. All solutions were prepared in a 1 cm quartz cell with doubly distilled water at a temperature of 25 °C.

The fluorimetric investigations of complex formation between the nonionic surfactants and different cyclodextrins were measured at a constant surfactant concentration far below the CMC ($C_s \ll 2 \times 10^{-5}$ mol/l) in the presence of added cyclodextrin.

A Perkin-Elmer LS-3B fluorescence spectrometer was used to obtain the excitation-emission spectra. The excitation wavelength λ_{excit} was 275 nm. The fluorescent emission was measured at the maximum of the fluorescence spectra at the wavelength $\lambda_{\text{em.}}$ = 305 nm for TX-100, NP-10, Igepal CO-890 and 300 nm

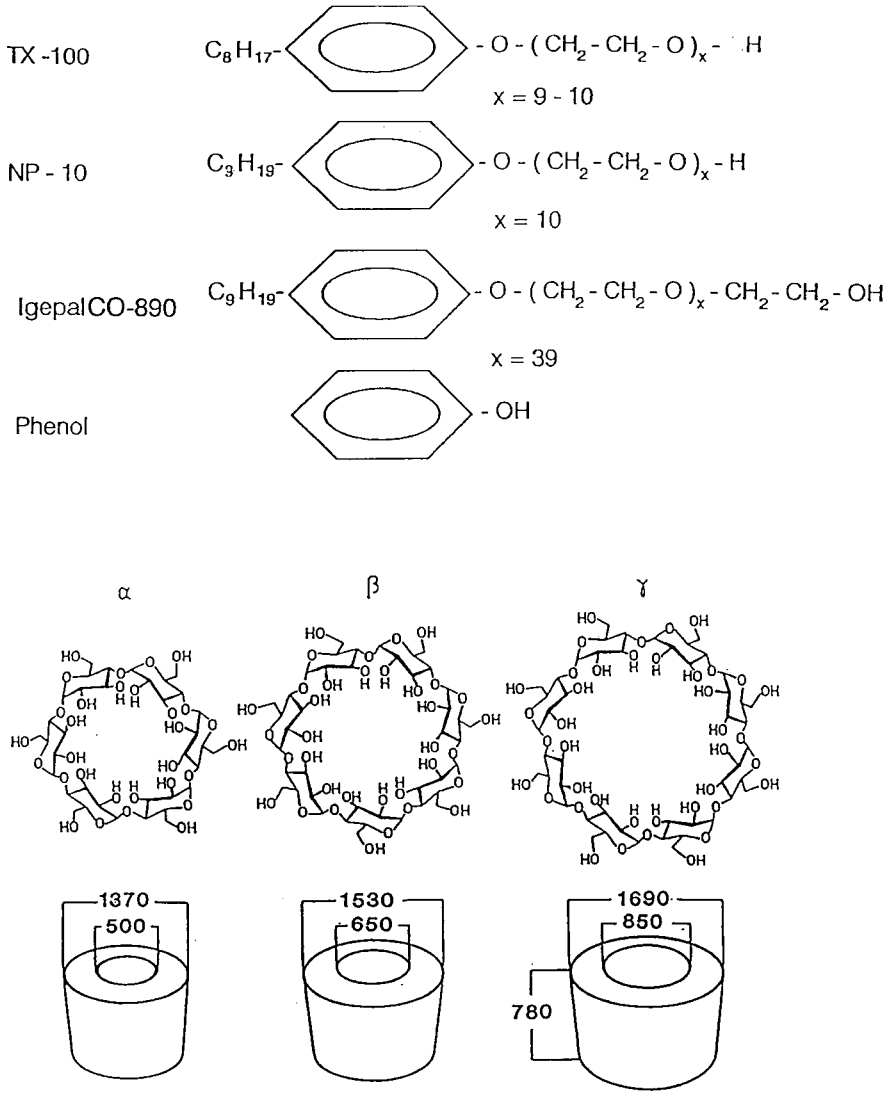

Figure 1. Chemical structures of the surfactants and cyclodextrins (cavity size in pm).

for phenol. The fluorescence spectra of Igepal CO-890 at different concentrations of β-cyclodextrin are shown in Figure 2.

3. Theory

Assuming that the cyclodextrins form 1 : 1 and 2 : 1 inclusion complexes with the surfactant as shown below,

$$S + CD \Leftrightarrow CDS$$

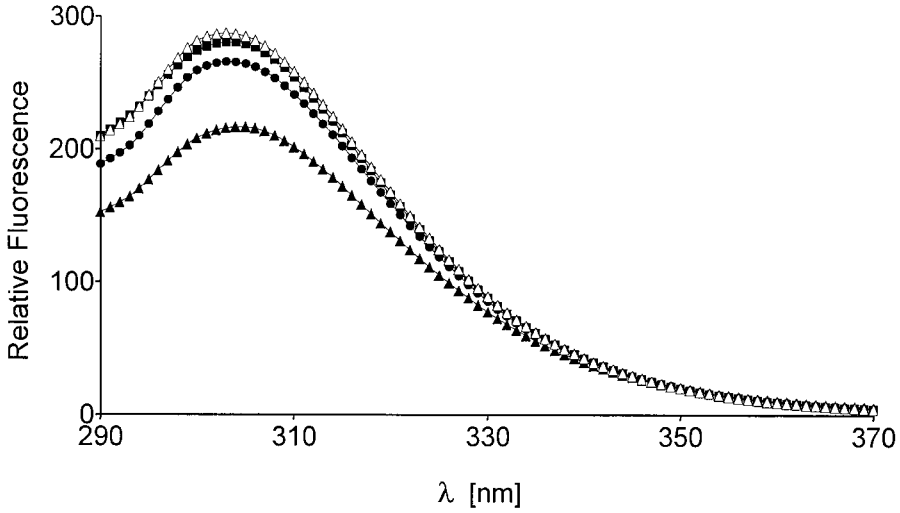

Figure 2. Fluorescence spectra of Igepal CO-890 (1×10^{-5} mol/l) at different concentrations of β-cyclodextrin (▲: without β-cyclodextrin; ●: 1×10^{-5} mol/l; ■: 3×10^{-5} mol/l; △: 4×10^{-5} mol/l).

$$CDS + CD \Leftrightarrow CD_2S$$

there are no interactions between the surfactant monomers and that the cyclodextrin is not fluorescent, the relative fluorescence ($F_{\text{rel.}}$) can be assumed to increase linearly with concentration of the surfactant. Then the observed fluorescence intensity will be given by the contributions from free surfactant and from surfactant-cyclodextrin complexes in the form:

$$F_{\text{rel.}} = k_1[S] + k_2[CDS] + k_3[CD_2S] \tag{1}$$

where k_1, k_2, k_3 are the proportionality constants, which include the geometrical arrangement of the instrument and the respective quantum yields. [CD], [S], [CDS] and [CD_2S] are the equilibrium concentrations of cyclodextrin, surfactant and the complexes.

The formation constants of the complexes are defined by:

$$K_1 = \frac{[CDS]}{[CD][S]}$$

$$K_2 = \frac{[CD_2S]}{[CDS][CD]}. \tag{2}$$

The total concentration of cyclodextrin c_D and of surfactant c_S is given by:

$$c_D = [CD] + [CDS] + 2[CD_2S] \tag{3}$$

$$c_S = [S] + [CDS] + [CD_2S] \tag{4}$$

Equation (4) can be rearranged to give:

$$1 = \frac{[S]}{c_S} + \frac{[CDS]}{c_S} + \frac{[CD_2S]}{c_S}. \tag{5}$$

Combining Equations (5) and (2), Equation (1) can be rewritten:

$$F_{rel} = k_1 c_S \alpha + k_2 c_S (1 - \alpha - \beta) + k_3 c_S \beta \tag{6}$$

with

$$\alpha = \frac{[S]}{c_S} = \frac{1}{1 + K_1[CD] + K_1 K_2 [CD]^2} \tag{7}$$

and

$$\beta = \frac{[CD_2S]}{c_S} = \frac{K_1 K_2 []^2}{1 + K_1[CD] + K_1 K_2 [CD]^2}. \tag{8}$$

The relative fluorescence is given by Equation (9):

$$F_{rel.} = F_0 \alpha + F_1 (1 - \alpha) + (F_2 - F_1)\beta \tag{9}$$

with

$$F_0 = k_1 c_S$$

$$F_1 = k_2 c_S$$

$$F_2 = k_3 c_S$$

The equilibrium concentration [CD] can be calculated from Equation (10):

$$c_D = [CD] + c_S \frac{K_1[CD] + K_1 K_2 [CD]^2}{1 + K_1[CD] + K_1 K_2 [CD]^2}. \tag{10}$$

The fluorescence intensities (F_0) of the surfactants in the absence of cyclodextrin are obtained by direct measurements. By using Equation (9) the experimental data can be directly fitted by nonlinear regression analysis. The sum of squares (S) between the experimental data ($F_{exp.}$) and the theoretical equation ($F_{rel.}$) is minimized by variation of the parameters K_1, K_2, F_1, F_2.

$$S = \sum_{i=1}^{N} (F_{exp.} - F_{rel.})^2. \tag{11}$$

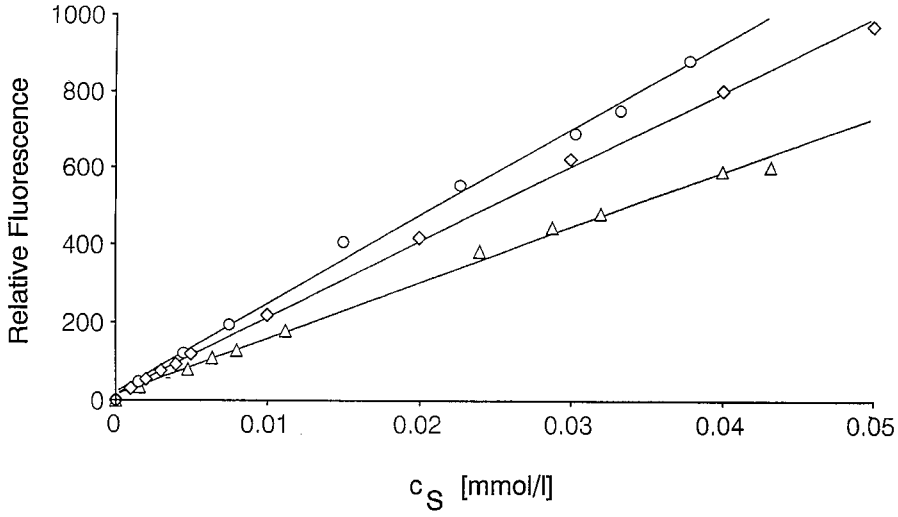

Figure 3. Relative fluorescence intensity at different concentrations (c_S) of the surfactants TX-100 (△), NP-10 (○) and Igepal CO-890 (◊) in doubly distilled water.

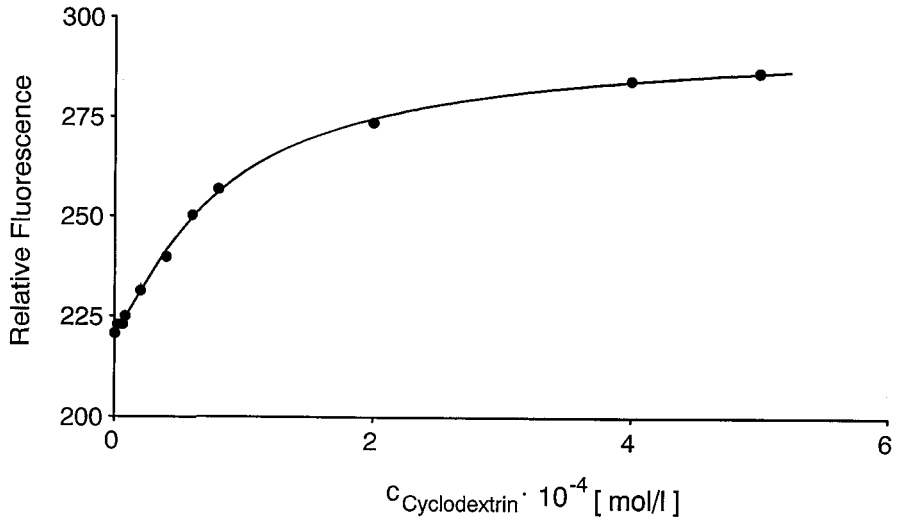

Figure 4. Relative fluorescence intensity of Igepal CO-890 (1×10^{-5} mol/l) at different concentrations of γ-cyclodextrin and the fitted curve using Equation (4).

4. Results and Discussion

In Figure 3 the standard calibration curves of the relative fluorescence intensity at low concentrations below the CMC for the surfactants TX-100, NP-10 and Igepal CO-890 are shown. The slopes are linear indicating that there are no interactions between the monomers of the surfactants. The experimentally measured relative fluorescence intensities together with a fitted curve for the nonionic surfactant

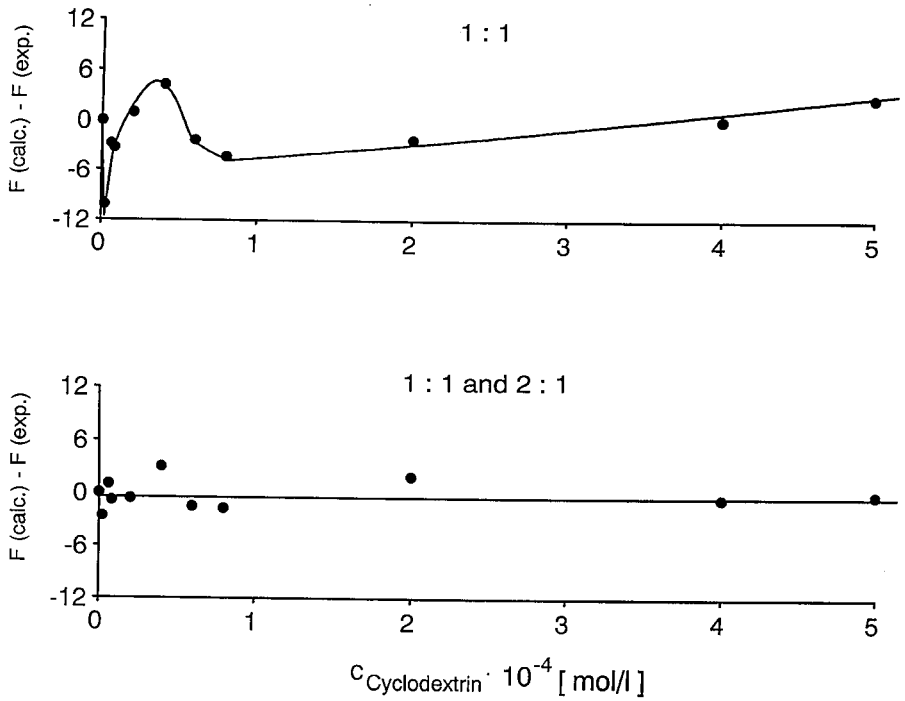

Figure 5. Difference between the calculated fluorescence intensity $F_{calc.}$ and the measured fluorescence intensity $F_{exp.}$ for a 1 : 1 and 1 : 1 and 2 : 1 model of complexation between γ-cyclodextrin and Igepal CO-890 at different concentrations of γ-cyclodexterin.

Igepal CO-890 at different γ-cyclodextrin concentrations are shown in Figure 4. There is a good agreement between the experimental values and the fitted theoretical equation. The fluorescence intensity increases sharply at low concentrations of γ-cyclodextrin and then reaches a constant level for higher concentrations.

A calculation for 1 : 1-complexes only shows a systematical error between the difference of $F_{calc.} - F_{exp.}$ (Figure 5) for this system. This indicates that 1 : 1 and 2 : 1-complexes are formed.

It is well known that nonionic surfactants consist of two distinct regions, a hydrophobic alkyl chain sometimes in connection with an aromatic ring and hydrophilic ethoxy groups with different chain lengths.

Phenol was used to prove that the aromatic components are taken inside the cyclodextrin cavity. The experiment shows that the fluorescence signal of phenol is enhanced by the addition of β-cyclodextrin. It forms the weakest complex with β-cyclodextrin of all the guest molecules examined. The stability constant of log K_1 = 1.90 (see Table I) determined from fluorescence measurement is of the same order as that determined calorimetrically (log K_1 = 1.97 [11]). This indicates that the phenol group is also accommodated inside the cavity of β-cyclodextrin. From fluorescence measurements there is no complex formation detectable with α- and

Table I. Values of the 1 : 1 and 2 : 1 stability constants (K_1, K_2 in mol/l) for the complex formation of nonionic surfactants and phenol with α-, β- and γ-cyclodextrin in aqueous solution at 25 °C

	Cyclodextrin	Surfactant-concentration c_S mmol/l	log K_1	log K_2
TX100	α	0.0064	2.88	0.53
	β	0.0064	3.71	1.03
	β		3.52[a]	
	γ	0.0064	4.58	2.31
NP 10	α	0.0030	2.57	1.14
	β	0.0030	4.53	1.99
	γ	0.0030	4.61	3.2
Igepal	α	0.010	–[b]	
CO-890	α	5.000	1.79[c]	
	β	0.010	4.68	3.27
	γ	0.010	4.79	4.08
Phenol	α	0.0040	–[b]	–
	α	5.000	2.62[c]	
	β	0.0042	1.90	–
	β		1.97[d]	
	γ	0.0042	–[b,e]	

[a] From Ref. 3.
[b] No increase in fluorescence intensity .
[c] From calorimetric titrations, Ref. 12.
[d] From Ref. 11.
[e] No heat produced during calorimetric titrations, Ref. 12.

γ-cylodextrin However, calorimetric titrations show the formation of complexes between phenol and Ipepal CO-890 and α-cyclodextrin [12].

The values of the stability constants for the 1 : 1 and 2 : 1 complex formation (cyclodextrin/surfactant) are summarized in Table I. The stability constant for the complexation of TX-100 with β-cyclodextrin is in a good agreement with an earlier published value (log K_1 = 3.52) [3]. A similar value (log K_1 = 3.72) has been determined in this work.

It can be see from Table I that the stability constants K_1 and K_2 increase with the cavity size of the cyclodextrins. These observations clearly demonstrate that the alkyl and benzoyl groups take part in complex formation. However, the chemical structure of these chains does influence the stability of the complexes significantly. Without the alkyl substituents phenol forms the weakest complexes of all mole-

cules examined. The stability constants for the formation of 2 : 1 complexes are always smaller when compared with the stability constants of the 1 : 1 complexes. The results indicate that both cyclodextrins are complexed at different parts of the nonionic surfactants. A further insight is possible using NMR or calorimetric measurements.

Acknowledgements

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