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Cucurbituril and α- and β-Cyclodextrins as Ligands for the Complexation of Nonionic Surfactants and Polyethyleneglycols in Aqueous Solutions

H.-J. BUSCHMANN, K. JANSEN and E. SCHOLLMEYER
Deutsches Textilforschungszentrum Nord-West e.V., Frankenring 2, D-47798 Krefeld, Germany

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Abstract. The complexation of nonionic surfactants and polyethylene glycols by the ligands cucurbituril, α- and β-cyclodextrin was studied in aqueous solution. All the examined guest molecules form complexes with these ligands. Calorimetric titrations were performed to determine directly the stability constants and reaction enthalpies. The presence of an aromatic part in nonionic surfactants leads to more stable complexes with β-cyclodextrin than with the other ligands. If the surfactants contain no benzene group, the interactions with α-cyclodextrin are stronger compared to other ligands. The chain length of the polyethylene glycols has only an influence upon the values of the reaction enthalpy in the case of α-cyclodextrin.

Key words: cucurbituril, cyclodextrin, nonionic surfactants, complex formation

1. Introduction

Cyclodextrins are well known as host molecules for the complexation of a large number of organic molecules [1–3]. Some industrial applications have already been realized [1–5]. Cyclodextrins are rigid molecules with a fixed cavity compared to other macrocyclic ligands e.g. crown ethers or calixarenes. The selectivity of cyclodextrins is mainly governed by the hydrophobicity and the size of their cavities.

Comparable properties are relevant for another macrocyclic ligand. Cucurbituril is a rigid host molecule with a hydrophobic cavity. This ligand was firstly described in the literature in 1905 [6]. At that time the macrocyclic structure of the molecule was unknown. It took a long time for the structure of this molecule to be deduced [7]. In contrast to cyclodextrins only a few results about this ligand have been reviewed in the literature up to date [8–10].

The most important difference between cyclodextrins and cucurbituril is their water solubility. α-, β- and γ-cyclodextrin are quite soluble in aqueous solution [1]. In contrast cucurbituril is nearly insoluble in aqueous solution and dissolves in aqueous formic acid [11, 12] and in the presence of salts [6, 13–15]. Cyclodextrins form stable complexes with a large number of aliphatic and aromatic compounds. The complex formation between nonionic surfactants [16–24] and polyethylene

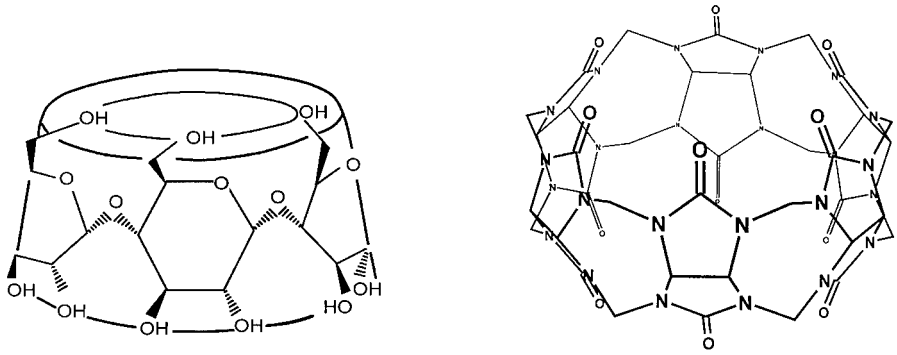


Figure 1. Structures of the macrocyclic ligands used.

glycols [25–31] and cyclodextrins has already been studied in detail. If the polyethylene glycol chain is long enough, more than one cyclodextrin molecule is complexed. This fact has been used for the formation of long chains with threaded molecules. The resulting molecules are named pseudorotaxanes [3, 25–32]. To date no results about the formation of pseudorotaxanes between polyethylene glycols and cucurbituril have been reported. Rotaxanes with cucurbituril are already known [33–36].

In the present study we will present the first quantitative results for the complexation of nonionic surfactants and polyethylene glycols with cucurbituril.

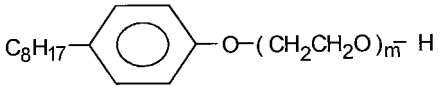
2. Experimental

The macrocyclic ligands α- and β-cyclodextrin (Wacker) were commercial samples and used without further purification. The ligand cucurbituril was synthesized and purified as described in the literature [6, 13]. The elemental analysis and the ^{1}H-NMR spectroscopic data are in accordance with published results [10, 13]. The ligands are shown in Figure 1.

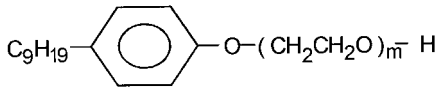
The nonionic surfactants Triton X100 (Serva), NP10, NP20 (both Hüls AG), Igepal CO-720 (Aldrich), Brij30, Brij56, Brij99 (Janssen) and different polyethylene glycols (PEG, Fluka) were used without further purification. The chemical structures of the nonionic surfactants are given in Figure 2. Bidistilled water was used as solvent. Due to the low solubility of cucurbituril in aqueous solution a mixture of water and formic acid (50/50 vol%) was used as solvent.

The stability constants and thermodynamic values were estimated by calorimetric titrations using a Tronac Model 458 calorimeter. During a calorimetric titration a solution of the ligand (0.03–0.08 mol/l) was added to a solution of the guest molecule (1–5·10^{-3} mol/l). After corrections of all non-chemical heat effects the heat Q produced during titration is related to the reaction enthalpy ΔH by the following equation:

$$Q = \Delta n \cdot \Delta H$$



m = 9 - 10 : **Triton X 100**



m = 10 : **NP 10**
m = 20 : **NP 20**
m ≈ 12 : **Igepal CO-720**

$CH_3(CH_2)_n(OCH_2CH_2)_mOH$

n = 11 , m = 4 : **Brij 30**
n = 15 , m = 10 : **Brij 56**
n = 17 , m = 10 : **Brij 99**

$H(OCH_2CH_2)_mOH$

PEG

Figure 2. Chemical structures of the nonionic surfactants and polyethylene glycols (PEGs) used in this work.

with the number of moles Δn of the complex formed. Δn depends upon the stability of the complex formed. The mathematical treatment of the experimental data has already been described in detail [37–39]. The reliability of the results obtained from calorimetric titrations compared with those from potentiometric and conductometric titrations has already been demonstrated [40]. Under the given experimental conditions only the formation of 1:1 complexes between cucurbituril and the PEGs examined was observed.

3. Results and Discussion

The results for the complexation of nonionic surfactants and polyethylene glycols by α-, β-cyclodextrin and cucurbituril are summarized in Table I along with the results taken from the literature.

All the three examined ligands form stable complexes with nonionic surfactants and PEGs. Obviously the chemical structures of the nonionic surfactants influence the values of the stability constants and of the reaction enthalpies in the case of cyclodextrins. Most of these reactions are favoured by enthalpic contributions.

Table I. Stability constants log K (K in l·mol^{-1}) and thermodynamic values ΔH and $T\Delta S$ (kJ·mol^{-1}) for the complexation of nonionic surfactants and PEGs with cucurbituril (in aqueous formic acid 50 vol%) and α- and β-cyclodextrin (in water, pH 5) at 25 °C

Guest molecule	Cucurbituril			α-Cyclodextrin			β-Cyclodextrin		
	log K	$-\Delta H$	$T\Delta S$	log K	$-\Delta H$	$T\Delta S$	log K	$-\Delta H$	$T\Delta S$
TX100	2.80	1.1	14.8	2.44	7.5	6.4	4.50	62.6	−37.0
				2.88[a]			3.71[a]		
							3.52[b]		
NP10	3.08	2.6	14.9	2.46	9.0	5.0	4.74	62.1	−35.1
				2.57[a]			4.53[a]		
NP20	3.17	3.7	14.3	2.56	2.4	12.2	4.96	67.2	−39.0
Igepal CO-720	2.84	1.1	15.0	3.71	5.3	15.8	4.91	38.1	−10.2
Brij30	2.44	2.7	11.1	–[c]			3.23	20.6	−2.3
Brij56	2.81	1.8	14.2	>5	26.7		>5	5.6	
Brij99	2.31	2.8	10.3	>5	26.8		>5	7.2	
PEG300	1.43	1.8	6.3	2.51	6.4	7.9	3.17	1.3	16.7
PEG400	3.13	3.3	14.5	3.78	6.1	12.4	3.03	0.7	16.5
PEG600	3.19	3.3	14.8	3.83	14.9	6.9	3.15	1.3	16.6
PEG1000	3.12	3.7	14.0	4.25	48.1	−24.0	3.24	0.5	17.9
PEG1500	3.17	4.1	13.9	4.43	48.8	−23.6	–[d]	2.1	

[a]Ref. [41],
[b]Ref. [19].
[c]Formation of a precipitate.
[d]Not calculable from the thermogram.

Only the complexation of the PEGs with β-cyclodextrin is favoured by entropic factors.

The stability constants and reaction enthalpies for the complexation of nonionic surfactants containing a benzene group with the different ligands are not influenced by the number of ethylene oxide groups. However, the cavity size of the ligands influences the values of the reaction enthalpy. During the complexation with β-cyclodextrin the highest values of the reaction enthalpy with these nonionic surfactants are observed. This is surprising because phenol forms a complex with α-cyclodextrin which is more stable than with β-cyclodextrin [41].

In contrast the complex formation of nonionic surfactants without a benzene group with α-cyclodextrin gives the highest values of the reaction enthalpy compared with the other ligands. The increasing chain lengths of the polyethylene glycols only has an influence upon the stability constants and reaction enthalpies in the case of α-cyclodextrin.

Surprisingly no influence of the chemical structures of the nonionic surfactants or the PEGs upon the complexation reaction is observed with the ligand cucurbituril. A schematical structure of this complex is given in Figure 3. With all the

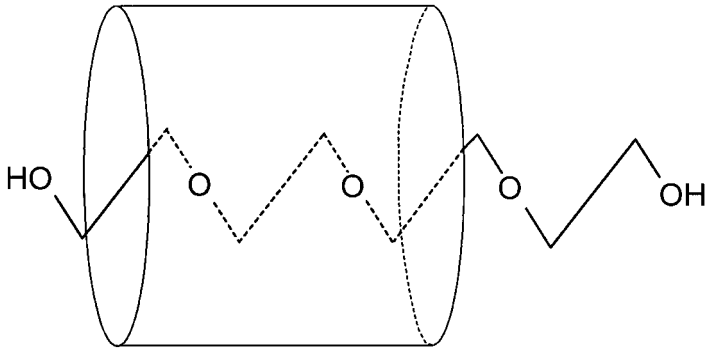


Figure 3. Schematical structure of a complex between a PEG and cucurbituril.

examined guest molecules the complexation is strongly favoured by entropic contributions. The differences in the solvations of the ligands are mainly responsible for these observations. Cucurbituril is dissolved mainly in the protonated form whereas cyclodextrins are only solvated by water molecules. In the case of cucurbituril these protons are located at both portals of the cavity due to the carbonyl groups. In contrast the hydroxyl groups of the cyclodextrins are located anywhere at the surface of these molecules. To be complexed inside the cavities of these ligands the guest molecules have to replace the strongly bound protons at the carbonyl groups of cucurbituril. In the case of the cyclodextrins only a few and also weakly bound water molecules are set free during the complex formation. This explains the different behaviour of cucurbituril and cyclodextrins during the complexation reactions.

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