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Removal of azo dyes from aqueous solutions using calix[4]arene and β-cyclodextrin

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Abstract

A calix[4]arene-based oligomer **5** and a β-cyclodextrin polymer **6** were synthesized by the condensation of *p-tert*-butylcalix[4]arene and β-cyclodextrin, respectively, with hexamethylene diisocyanate. In their batch sorption of selected azo dyes, the β-cyclodextrin polymer **6** was found to be a better azo dye sorbent than the *p-tert*-butylcalix[4]arene-based oligomer **5**. In addition, oligomer **4** containing pendant calix[4]-arene units with crown-6 functionalities on the lower rim was synthesized and its complexation of the azo dyes was investigated by liquid–liquid extraction. The calix[4]crown-6 oligomer **4** showed the highest affinity for the azo dyes.

Keywords: β-Cyclodextrin; Calix[4]arene oligomer; Azo dye; Calix[4]crown-6

1. Introduction

Azo dyes represent a major group of all the dyes produced world-wide [1,2] and are important colorants having extensive applications in textiles, papers, leathers, gasoline, additives, foodstuffs and cosmetics [3]. Approximately 10–15% of the overall production of azo dyes is released into the environment, mainly via wastewater [4]. This is very dangerous because some of the azo dyes and their degradation products have a toxic, mutagenic or carcinogenic influence on living organisms. Therefore, the azo dye-containing wastewater should be treated before discharge [2]. Reduction of azo dyes leads to the formation of aromatic amines. Aromatic amines are generally not degraded and accumulate under anaerobic conditions [5], with the exception of a few aromatic amines characterized by the presence of hydroxyl and/or carboxyl groups [6]. Some aromatic amines pose health hazards to human beings either by direct contact and through the environment. The release of aromatic amines from consumer products, such as clothing and leather, has been reported [7]. Hence, it is necessary to ensure that our clothing, footwear, and other personal wear items are free from carcinogenic amines. Although azo dye molecules are biologically inactive, microorganisms in skin and in the environment can cleave the azo linkages and release the respective amines [8–10]. In view of these findings, some member states of the European Union (EU) have introduced a ban on azo colorants in consumer goods, which might release any of 20 listed harmful aromatic amines. At present, the German method DIN 53316 is the most accepted analytical method for the determination of azo colorants in leather and dyes [11].

In recent years, much attention has been paid to chemical separation techniques and the design and synthesis of new extraction reagents for ions and molecules. This attention results from environmental concerns and efforts to save energy and enhance recycling at the industrial level. In this respect, supramolecular chemistry has provided important avenues in the search for molecular structures that can serve as building blocks for the production of sophisticated molecules by anchoring functional groups oriented in such a way that they

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delineate a suitable binding site. This was achieved with the development of macrocyclic receptors, such as crown ethers, cryptands, spherands [12], natural cyclodextrins [13,14], and calixarenes [15,16].

It is known that calix[4]arenes can exist in cone, partial cone, 1,2-alternate, and 1,3-alternate conformations [12]. The available sites on these macrocyclic compounds can be easily modified to tailor them for many applications, such as ionophores in catalysis, heavy metal adsorption agents, and alkali metal and inclusion complexation agents [17–20]. Various attempts have been undertaken to incorporate calixarenes into different polymers, some of which are self-assembled systems [21–37]. Compared with calix-crown monomers, calix-crown polymers are a more recent innovation. Only a few examples have been reported [38–40]. Previously, we have synthesized two calix-crown monomers, along with their telomers, and investigated their ionophoric properties [41,42].

We now report the removal abilities of calix[4]arene oligomers **4** and **5** and their monomeric precursors **1** and **2**, as well as a β-cyclodextrin-based polymer **6**, (Fig. 1) for selected water-soluble azo dyes (Fig. 2).

2. Results and discussion

Structures of calix[4]arene monomers **1–3** and oligomers **4** and **5** and β-cylcodextrin polymer **6** are shown in Fig. 1. The syntheses of **1–4** are based on the reported procedures [43–45]. Oligomerization of **3** with hexamethylene diisocyanate (HMDI) in a minimum amount of DMF gave oligomer **5** in 65% yield. The average molecular weight (M_w) of oligomer **5**, as determined by GPC in THF against polystyrene standards, was 2150 g/mol. This indicates the presence of two calixarene units in the oligomeric skeleton. Oligomer **5** was also characterized by FTIR and ^{1}H NMR spectroscopy. The IR spectrum of **5** showed a band at 1715 cm^{-1} for the carbonyl group of the urethane units (–N–C=O) and a band at 2275 cm^{-1} for isocyanate end groups (N=C=O). The ^{1}H NMR spectrum of oligomer **5** exhibited only broad signals. Therefore, it was not possible to discern the conformation of the calixarene moieties in the oligomeric skeleton.

To allow the comparison of the extraction results obtained using the calixarene-based oligomers with those for a β-cyclodextrin (β-CD) polymer, cross-linked β-CD polymer **6** was prepared by reaction of β-CD with HMDI. The polymer precipitated in a short time when the molar ratio of reactants was 1:10 (β-CD:HMDI). The cross-linked polymer was insoluble in water, as well as organic solvents. Consumption of the isocyanate reactant was followed by observing the decrease in absorbance of the –N=C=O *anti*-symmetric stretching band at 2275 cm^{-1}. A band at 3350 cm^{-1} due to the free NH stretching absorption for the urethane group developed as the polymerization progressed. Upon completion of reactant mixing, urethane groups were present, as seen from an absorption at 1715 cm^{-1} for N–C=O.

The thermal stability of β-CD polymer **6** was evaluated by thermal gravimetric analysis (TGA) and compared with its β-CD precursor. It is found that the polymer undergoes two-step thermal degradation. The first step arises from decomposition of β-CD, while the second is due to the polymer. According to the literature [46], CD starts to decompose at temperatures ranging from 290 to 300 °C. The onset of degradation for CD polymer **6** was found to occur at 350 °C. This is quite high compared to conventional polyurethanes, which generally begin to decompose around 200–220 °C. The enhanced thermal stability of β-CD polymer **6** is attributed to its cross-linked nature, since it is well known that cross-linking leads to increased thermal stability. Differential scanning calorimetric (DSC) studies showed no transition up to 250 °C. The difference in decomposition temperatures for **6** as determined by TGA and DSC is due to the different heating rates utilized for the two techniques. A weight loss maximum of 44–45% during the first stage of thermal decomposition results from cleavage of the urethane linkage and volatilization of the resultant decomposition products. The absence of a glass transition is due to the highly cross-linked nature of polymer. A previously reported β-CD polymer exhibited no thermal transition before decomposition with an endothermic peak at around 272 °C [46].

2.1. Liquid–liquid extraction studies

Since removal of azo dyes from aqueous media is environmentally important, their extraction or sorption from aqueous samples was investigated. Azo dyes are expected to form inclusion complexes with 1,3-dialkyl-substituted calix[4]arenes and their oligomers. Liquid–liquid extraction of four water-soluble azo dyes (Fig. 2) by monomers **1** and **2** and by oligomer **4** was conducted. The results are presented in Table 1. These data were obtained using a dichloromethane solution of the extractant to remove the azo dye from an aqueous phase. The residual concentration of azo dye in the aqueous phase was then determined spectrophotometrically. From the results presented in Table 1, it can be seen that unsubstituted *p-tert*-butylcalix[4]arene (**1**) and its dinitrile derivative **2** were ineffective in transferring the azo dyes into the organic phase. In marked contrast, calix[4]arene-crown oligomer **4** exhibited high extraction levels for all four azo dyes.

For insoluble calix[4]arene-based oligomer **5**, solid–liquid batch sorption was utilized to assess its ability to remove the water-soluble azo dyes from aqueous solution. Compared with calix[4]arene monomer's extractants **1** and **2**, oligomeric calix[4]arene sorbent **5** showed enhanced extraction of two azo dyes (DB71 and MO), but not for the other two (TY and TP). DB71 and MO have amino/dialkylamino groups, whereas TY and TP do not.

The much higher levels of azo dye removal by calix[4]arene-crown oligomer extractant **4** than calix[4]arene oligomer sorbent **5** suggests a role of Na$^+$ complexation by the polyether units in the former. To probe this possibility, the levels of residual Na$^+$ in the aqueous phases following liquid–liquid extraction of the azo dyes were determined by atomic

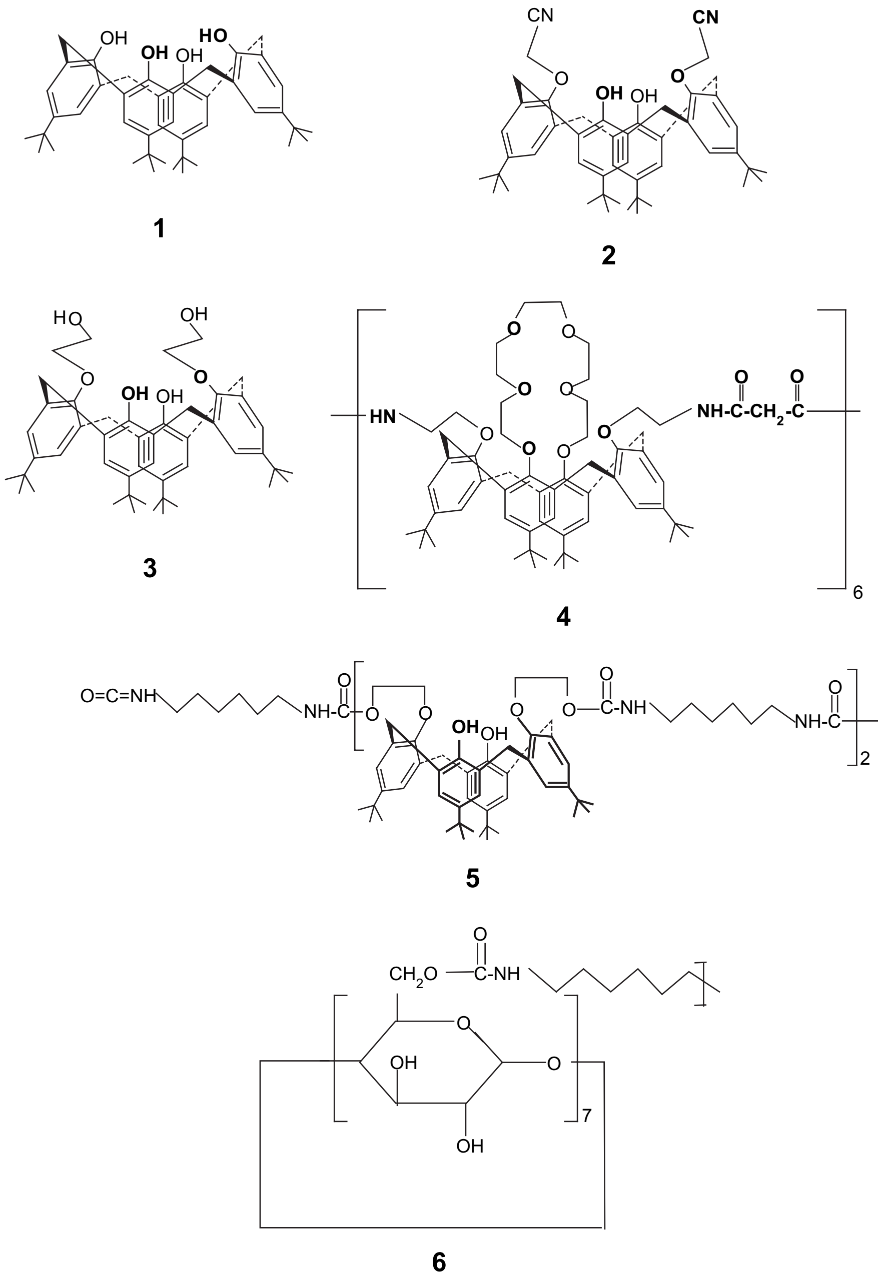

Fig. 1. Chemical structures of extractants.

absorption. The results are given in Table 2. The pronounced Na^+ extraction suggests an ion-pair extraction mechanism in which Na^+ coordinates with the polyether ring, while the azo dye anion inserts into the hydrophobic calixarene cavity.

To allow the comparison of solid–liquid batch sorption extraction results for the calixarene-loaded oligomer **5**, extractions were performed with the β-CD-polymer **6**. The results shown in Table 1 and Fig. 3 clearly establish that polymer **6** is a better sorbent for azo dyes than the calix[4]arene-based oligomer **5**. Other researchers have found that alkylated β-CD exhibited stronger binding ability for an azo dye (orange II) than the parent β-CD [47]. This stronger inclusion ability was attributed to enlargement of the larger opening of the β-CD cavity and contraction of the smaller opening by the alkyl groups, which destroys the strong hydrogen-bond network and makes it easier for a guest molecule to gain access to the β-CD cavity. Similarly we propose that incorporation of β-CD units into cross-linked polymer **6** serves to enhance their azo dye inclusion properties.

The sorption mechanisms of polysaccharide-based materials are different from those of other conventional adsorbents. These mechanisms are, in general, complicated because they may involve several different interactions [45,48,49]. Some of the reported interactions include: ion-exchange, complexation, coordination/chelation, electrostatic interactions, acid–base interactions, hydrogen bonding, hydrophobic

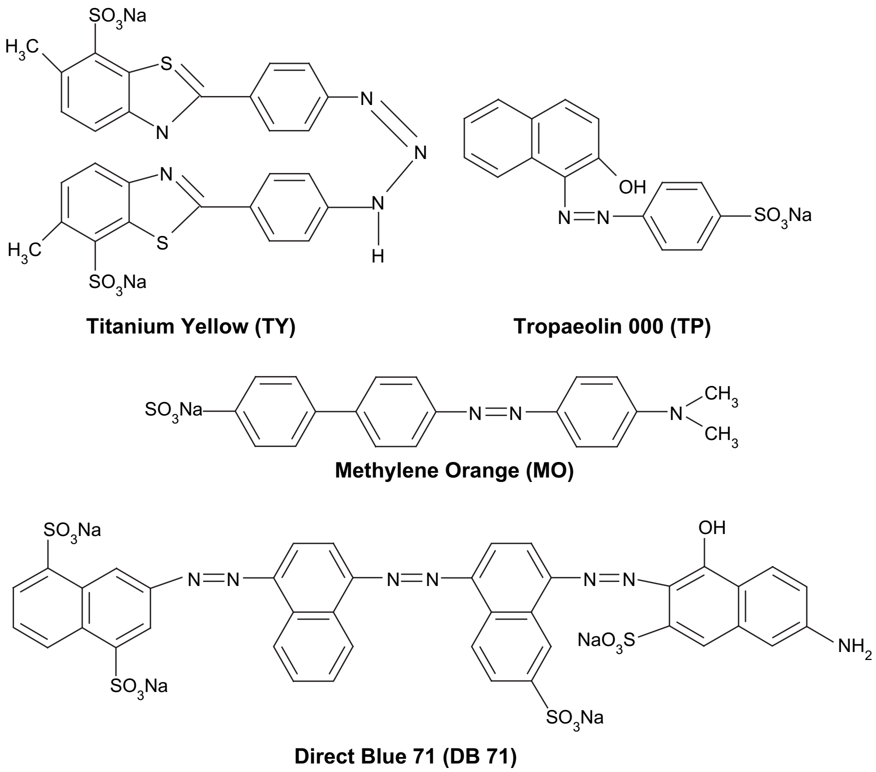

Fig. 2. Structures of the water-soluble azo dyes.

interactions, and physical adsorption. An examination of the literature data indicates that it is quite possible that at least some of these mechanisms are of varying degrees acting simultaneously depending on the chemical composition of the sorbent, the nature of the pollutant, and the solution environment.

3. Conclusions

Calix[4]arene-based oligomers **4** and **5** and a β-CD-based polymer **6** were synthesized and utilized to extract selected water-soluble azo dyes. Oligomer **4** was found to be an efficient extractant for the azo dyes. Its effectiveness in transferring azo dyes by the calix[4]crown-6 oligomer indicates that Na^+ plays an important role by enhancing ion-pair complexation of Na^+ and the negatively charged azo dye. Batch sorption studies showed calix[4]arene-based oligomer **5** to be a poorer sorbent in solid–liquid extraction than the β-CD-based polymer **6**.

Table 1
Percent extraction of azo dyes by extractants **1**, **2**, and **4**–**6** (%)[a]

	DB71	TY	TP	MO
1	<1.0	<1.0	<1.0	1.9
2	<1.0	5.6	<1.0	6.1
4	71	91	96	94
5[b]	21	<1.0	<1.0	10
6[b]	35	52	41	37

[a] Aqueous phase, [azo dye] = 2×10^{-5} M, at pH 11; organic phase, dichloromethane, [ligand] = 1×10^{-3} M; at 25 °C for 1 h.

[b] Solid–liquid batch sorption from an aqueous solution of the azo dye.

4. Experimental

4.1. Apparatus

Melting points were determined on a Gallenkamp apparatus in a sealed capillary and are uncorrected. ^{1}H NMR spectra were recorded with a Bruker 400 MHz spectrometer in $CDCl_3$ with TMS as internal standard. IR spectra were recorded with a Perkin–Elmer 1605 FTIR spectrometer as KBr pellets. UV–vis spectra were obtained with a Shimadzu 160A UV–vis recording spectrophotometer. Elemental analyses were performed with a Leco CHNS-932 analyzer. TGA was carried out with Perkin–Elmer–Pyris 1 thermogravimetric analyzer. The sample weight was 13–15 mg. Analysis was performed from room temperature to 800 °C at a heating rate of 20 °C/min in a nitrogen atmosphere with a gas flow rate of 40 mL/min. DSC was performed from 0 to 300 °C at a heating rate of 10 °C/min under a nitrogen atmosphere with a gas flow rate of 40 mL/min. The analysis was carried out in sealed aluminum pans and the amount of the sample was 8–10 mg. Molecular weight determinations were conducted by gel permeation chromatography (GPC) in THF at 30 °C using an Agilent (HP) GPC

Table 2
Removal of Na^+ from the aqueous layer by extraction with calix[4]arene-crown **4**, (%)[a]

Azo dye	DB71	TY	TP	MO
Extraction %	69	70	71	69

[a] Aqueous phase, [azo dye] = 2×10^{-5} M, at pH 11; organic phase, dichloromethane, [ligand] = 1×10^{-3} M; at 25 °C for 1 h.

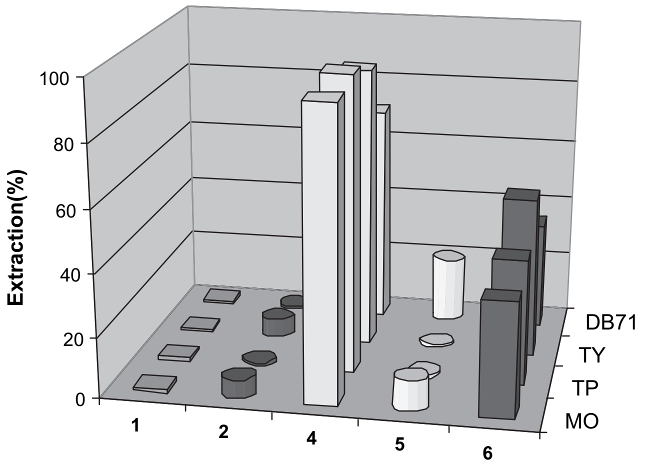

Fig. 3. Extraction percentages of the azo dyes with **1**, **2**, and **4−6**.

with refractive index detector, a solvent flow rate of 0.6 mL/min, and a sample concentration of 2.0 mg/mL. The micro columns were calibrated using a set of narrow polydispersity polystyrene standards. M_n and M_w were calculated with customary by using routine Millennium software installed on a PC, which controlled the entire GPC apparatus.

4.2. Reagents

Analytical TLC was performed on precoated silica gel plates (SiO_2, Merck PF_{254}), while silica gel 60 (Merck, particle size 0.040−0.063 mm, 230−240 mesh) was used for preparative column chromatography. NaH was used as 80% dispersion in oil and washed twice with hexane before use. Generally, solvents were dried by storage over molecular sieves (Aldrich; 4 Å, 8−12 mesh). Dichloromethane was distilled from $CaCl_2$. MeOH was distilled from Mg and stored over molecular sieves. All chemicals were purchased from Merck. All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system.

4.3. Synthesis

Monomers **1−3** and oligomer **4** were prepared according to literature procedures [43−45]. Calixarene oligomer **5** and β-CD polymer **6** were synthesized by the following methods.

4.3.1. Preparation of calix[4]arene oligomer *5*

Simultaneously a solution of 5,11,17,23-*tert*-butyl-25,27-(2-hydrocyethoxy)calix[4]arene **3** (2.00 g, 2.73 mmol) in dry DMF (25 mL) and a solution of hexamethylene diisocyanate (HMDI) (4.59 g, 27.32 mmol) in dry DMF (20 mL) were added to a stirred, 100-mL, three-neck flask via two dropping funnels at 70 °C under nitrogen. The stirring was continued for 1 h. The solvent was removed in vacuo to give a semisolid, which was stirred with ice-cold water to furnish a precipitate. This precipitate was stirred with hexane, and then with MeOH. It was filtered and dried under vacuum for 12 h. Yield: 65%, m.p. 260 °C (dec). IR (KBr) 2275 cm^{-1} (N═C═O) and 1715 cm^{-1} (C═O), ^1H NMR (DMSO) δ (ppm) 0.85−1.50 (m, 84H), 2.5 (m, 12H), 2.80−4.50 (m, 44H), 6.50−7.40 (m, 26H).

4.3.2. Preparation of β-CD polymer *6*

To a solution of β-CD (2.00 g, 1.76 mmol) in dry DMF (10 mL) in a 100-mL round-bottom flask at room temperature was added dropwise hexamethylene diisocyanate (HMDI) (2.96 g, 17.6 mmol) and the mixture was stirred at 70 °C for 4 h. The precipitate was filtered, washed with water and EtOH several times, and dried in vacuo for 24 h. Yield 87%. IR (KBr) 3350 cm^{-1} (NH) and 1715 cm^{-1} (C═O).

4.4. Liquid−liquid extraction

Azo dye extraction experiments were performed following Pedersen's procedure [50]. A mixture of 10 mL of 2.5×10^{-5} M aqueous azo dye solution and 10 mL of 1.0×10^{-3} M solution of ionophore calix[4]arene derivatives **1** and **2** or a 1×10^{-3} M solution of calix[4]arene unit/g of resin for oligomer **4** in dichloromethane was vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 min, magnetically stirred in a thermostated water bath at 25 °C for 1 h, and finally left to stand for an additional 30 min. The concentration of azo dye remaining in the aqueous phase was then determined spectrophotometrically by UV−vis analyses. Blank experiments showed that no azo dye extraction occurred in the absence of an extractant/sorbent. The residual concentration of azo dye was calculated by Eq. (1) with absorbance values recorded at λ_{max} for each azo dye solution (at 484 nm for tropaeolin 000 (TP), 586 nm for direct blue 71 (DB71), 463 nm for methyl orange (MO), and 407 nm for titan yellow (TY)

$$E\% = 100(A_0 - A)/A_0 \qquad (1)$$

where A_0 and A are the initial and final concentrations of azo dye before and after extraction, respectively.

4.5. Solid−liquid extraction

The adsorption capacities of the synthesized oligomer **5** and polymer **6** were determined by the following technique [14]: 25 mg of the sorbent was mixed with 10 mL of an aqueous solution of the azo dye (concentration 2×10^{-5} M) in a stopped flask that was shaken at room temperature. The sorbent was removed by centrifugation or filtration before measurements. The residual concentration of organic solute was determined spectrophotometrically by UV−vis analyses. The percentage sorption ($E\%$) was calculated from the absorbance (A) of the aqueous phases according to Eq. (1). The experiments were performed in triplicate.

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