Available online at www.sciencedirect.com
ScienceDirect
Reactive & Functional Polymers 68 (2008) 125–132
REACTIVE & FUNCTIONAL POLYMERS
www.elsevier.com/locate/react

The synthesis and metal cation extraction studies of novel polymer-bound calix(aza)crowns

Gülderen Uysal Akkuş [a,*], Shahabuddin Memon [b], Dilek Erol Gürkaş [a], Selma Aslan [a], Mustafa Yilmaz [c]

[a] Department of Chemistry, Afyon Kocatepe University, Afyonkarahisar 03200, Turkey
[b] National Center of Excellence in Analytical Chemistry, University of Sindh, Jamshoro 76080, Pakistan
[c] Department of Chemistry, Selçuk University, Konya 42031, Turkey

Received 23 May 2007; received in revised form 1 October 2007; accepted 13 October 2007
Available online 24 October 2007

Abstract

This article describes the synthesis and extraction properties of new calix(aza)crown monomers and their polymer-bound analogues. These compounds have been synthesized by reacting calix-(aza)crowns (**4a, 4b** and **4c**) with Merrifield's resin. Their cation phase-transfer studies were performed by using liquid–liquid extraction procedure. It has been inferred from the observations that monomer **4a** shows a good extraction behavior toward selected alkali (Na^+, K^+, Cs^+) and transition metal cations (Cu^{2+}, Co^{2+}, Cd^{2+}, Ni^{2+}, Hg^{2+}, Pb^{2+}), while **4b** and **4c** prefer Na^+ and K^+ among alkali metal cations, respectively. The polymer analogues **5a** and **5b** are efficient extractants for all the selected metal cations; whereas **5c** is selective only for transition metal cations.

Keywords: Calixarene; Calix(aza)crowns; Polymeric calixarene; Solvent extraction; Metal cations

1. Introduction

The design of macromolecules with high ionic affinities is important for numerous applications in chromatography, catalysis and separations [1–3]. Immobilization of ion selective ligands to form polymer-supported reagents results in an extended set of applications [4–7]. Several studies have been carried out to synthesize new complexants for charged and neutral molecules. Among these, 'Calixarenes' after cyclodextrins and crown ethers are an important class of macrocycles widely used in supramolecular chemistry as useful basic skeleton and an excellent 'platform' for the design of receptor sites for the specific recognition of guests [8–10]. During the past decades scientists have made to include crown rings on calixarene skeleton to combine the unique properties of both species in one molecule. Thus, calixcrowns are a family of macropolycyclic molecules in which the subunits of calixarene and crown ether are combined through the bridging of phenolic oxygen atoms of the calixarene moiety by polyoxyethylene chains.

* Corresponding author. Tel.: +90 2722281339x200; fax: +90 2722281235.
E-mail address: guakkus@gmail.com (G. Uysal Akkuş).

1381-5148/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.reactfunctpolym.2007.10.005

Calixcrowns with a linkage in 1,3- and 1,2-position, calixspherands double or triple calixarenes with various connecting chains have been reported [11,12]. An alternative strategy has been developed for the synthesis of calix(aza)crowns in which the distal positions on the lower rim of calix were linked with 1,3-diamide bridges [13]. The complexation properties of these molecules appear to be highly dependent upon the nature, number of donor groups, and the conformation of the calix[4]arene moiety [11–14]. The interesting properties shown by these cyclic oligomeric molecules stimulated the exploitation of useful methods towards their incorporation into polymeric matrices, which are interesting for the development of ion selective electrodes and membranes, chemical and biochemical sensors and selective extraction of ions and neutral molecules [15–19]. Previously, to increase the affinity of calixarenes toward metal ions and anions, two main strategies have been followed: first, different ionophoric groups including carbonyl, amide, and nitrile have been incorporated onto the calix-platform; second, the calixarene units have been fixed in a polymeric matrix [20–29]. We have also reported the synthesis of calix(aza)crowns and their corresponding oligomers along with their extraction behavior towards toxic metal cations [30]. Herein, we report the synthesis and extraction studies of calix(aza)crowns and their polymer-supported resins.

2. Experimental

2.1. Apparatus

Melting points were determined on a Barnsted/Electrothermal apparatus in a sealed capillary and are uncorrected. ^{1}H NMR spectra were recorded on a Bruke Avance DPX 400 spectrometer in $CDCl_3$ with TMS as an internal standard. IR spectra were recorded on a Perkin–Elmer 1605 FTIR System Spectrum BX spectrometer as KBr pellets. UV–vis spectra were obtained on a Shimadzu 160A UV–vis recording spectrophotometer.

2.2. Materials

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. Merrifield's resin was purchased from Fluka (No. 63862). NaH was used as 60% dispersion in oil and washed twice with *n*-hexane before use. Generally, solvents were dried by storing them over molecular sieves (Aldrich; 4 Å, 8–12 mesh). Toluene was dried with calcium hydride and stored over Na wire. Acetone was distilled from $CaSO_4$; MeOH was distilled over Mg and stored over molecular sieves. The drying agent employed was anhydrous sodium sulphate. All aqueous solutions were prepared with deionized water that had been passed through a Milli-Q Plus water purification system.

2.3. Synthesis

p-tert-butylcalix[4]arene **1**, calix[4]arene **2** and its diester derivative **3** were synthesized according to the literature procedures [31–34]. Below are given the synthetic methodologies adopted for new compounds (**4a, 4b** and **4c**) and their corresponding polymeric resins (**5a**, **5b** and **5c**) employed in this work as illustrated in Scheme 1. The following general procedure was adopted to transform calix[4]arene diester **3** into the corresponding calix-(aza)crowns (**4a–c**).

2.4. General procedure

A solution of **3** (10 g; 17.60 mmol) and 1,8-diaminooctane/1,8-diamino-3,6-dioxaoctane/diethylenetriamine (17.60 mmol) in methanol/toluene (600 mL) was refluxed with continuous stirring for 38 h. Then another portion of 1,8-diaminooctane (2.52 g; 17.60 mmol) in methanol (15 mL) was added and the reaction mixture was further refluxed for 78 h. The reaction mixture was then cooled to room temperature, the solvent was removed under reduced pressure and a pure product of **4a** was obtained by flash column chromatography using dichloromethane:acetone (4:1) as eluent.

2.4.1. Treatment of 25,27-dimethoxy-carbonylmethoxy-26,28-dihydroxycalix[4]arene 3 with 1,8-diaminooctane (**4a**)

Yield: 70%, mp: 190 °C, IR(KBr) 3360 cm^{-1} (OH), and 1645 cm^{-1} (NHCO). ^{1}H NMR ($CDCl_3$); δ 1.3–2.1 (m, 12H, CH_2), 3.45(d, 4H, $J = 12.8$ Hz, Ar-CH_2-Ar), 4.10(d, 4H, $J = 12.8$ Hz, Ar-CH_2-Ar), 4.3–4.9 (m, 8H, C–CH_2–NH, CH_2O), 6.07 (br s, 2H,OH), 6.97 (t, 4H, ArH), 7.31–7.51 (m, 8H, ArH), 7.9 (br s, 2H, NH). Calculated for $C_{40}H_{44}O_6N_2$, C, 73.9; H, 6.78; N, 4.31. Found: C, 70.23; H, 5.10; N, 3.89.