



Synthesis of tetra-substituted calix[4]arene ionophores and their recognition studies toward toxic arsenate anions



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ABSTRACT

The article displays the synthesis of a family of novel tetra-substituted calix[4]arene ionophores bearing furyl, phenyl, and pyridyl units in the cone conformation. In the synthesis, the lower rims of calix[4]arene scaffold were modified in order to establish the influence of the molecular structure of calixarene on recognition of toxic anions as arsenate by liquid–liquid extraction process. In addition, the effects of solvent, solution conditions (mainly pH), and counter ions (Cl^- , NO_3^- , and SO_4^{2-}) on the extraction abilities of the ionophores were studied. From the liquid–liquid phase extraction studies, it was observed that the structures of the tetra-substituted calix[4]arenes influenced the extraction percentage of selected toxic anion. Also, thermodynamic parameters, such as the free energy (ΔG°) and enthalpy (ΔH°) indicated an exothermic nature of extraction and a spontaneous and favorable process.

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1. Introduction

Arsenate anions are important because of their high toxicity and because of their presence in soils and waters.^{1,2} At sufficient concentrations, these anions can be highly toxic to many organisms and carcinogenic to humans.³ Natural conditions as well as anthropogenic activities (input of pesticides, combustion of fossil fuels or mining) are responsible for increased As concentrations.⁴ Arsenic represents an acute problem for drinking water quality in many countries world wide, for example, in Western India, Bangladesh or Taiwan.^{5–7} Arsenic is an omnipresent eco-toxin; the presence of arsenic in water is a serious threat for more than 100 million people in the world.⁸ Humans are clearly sensitive to arsenic carcinogenesis; prolonged exposure to arsenic damages the central nervous system and results in diverse types of cancer in liver, lung, bladder, and skin.^{9,10} In this regard, treatment of wastewater containing arsenate [As(V)] prior to discharge is essential. Several methods, such as precipitation, co-precipitation, ion-exchange, adsorption, ultra filtration, and reverse osmosis are available to remove these species from water.^{11,12} Among them, depending on adsorption solvent extraction is one of the most commonly used treatment methods and employs a selective complexant especially for ions in aqueous solution. In this field, calixarenes are useful ionic receptors due to their

important functionalization possibilities. This can be largely attributed to the fact that they are attractive host molecules that can be easily functionalized in terms of bearing suitable binding sites for target guest species.¹³ The hosts can be neutral, containing urea,^{14–16} thiourea^{17,18} or amide functions.¹⁹ They can also be positively charged, containing pyridinium,²⁰ polyammonium²¹ or quaternary ammonium²² binding sites. Calixarenes are cyclic oligomers made of several phenolic units bound with methylene bridges.^{23,24} The phenolic–OH groups of the calixarene lower rim can be further functionalized to feasibly give various ionic receptors for anions, cations, as well as hosts of neutral molecules.^{25,26} On the other hand, the molecular recognition of anionic guest species by positively charged or electron deficient neutral abiotic receptor molecules is an area of intense current interest. The importance of favorable amine, amide, or imide hydrogen bonding interactions for anion binding has recently been exploited in the design of calix[4]arene anion receptors. Although there are numerous examples of molecules that act as hosts and complexants for cations, relatively few molecules have been reported as hosts for anions.²⁷ Thus, the development of efficient extractants for anions has received considerable attention in recent years.²⁸ Compared to the number of reports on the binding of anions with calixarenes, reports on the binding of oxoanions are still limited.^{29–31} From this point of view calixarene derivatives bearing anion binding receptors are at the center of interest.

In a previous study,³¹ we reported a di-substituted calix[4]arene ionophore bearing pyridinium units, which acted as a receptor for both dichromate and arsenate anions, and observed that

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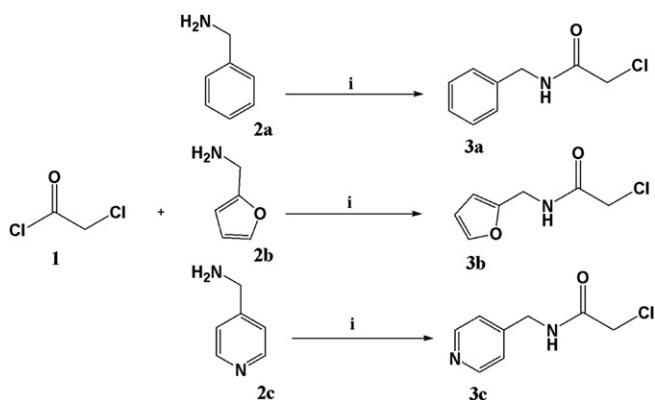
pyridinium units were effective binding sites for these ions. However, there are no further articles showing the effect of the both number and type of substituents on lower rim of calixarenes on extraction of arsenate anions in the literature. Thus, in this study, we aimed to synthesize new tetra-substituted calix[4]arene receptors bearing pyridyl, furyl, and phenyl units on their lower rim in order to systematically study the influence of the molecular structure (Schemes 1 and 2). Furthermore, their recognition

abilities were investigated toward arsenate anions by means of liquid–liquid phase extraction processes. To evaluate the thermodynamic feasibility and to confirm the nature of the extraction system, basic thermodynamic parameters, standard free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°) were calculated.

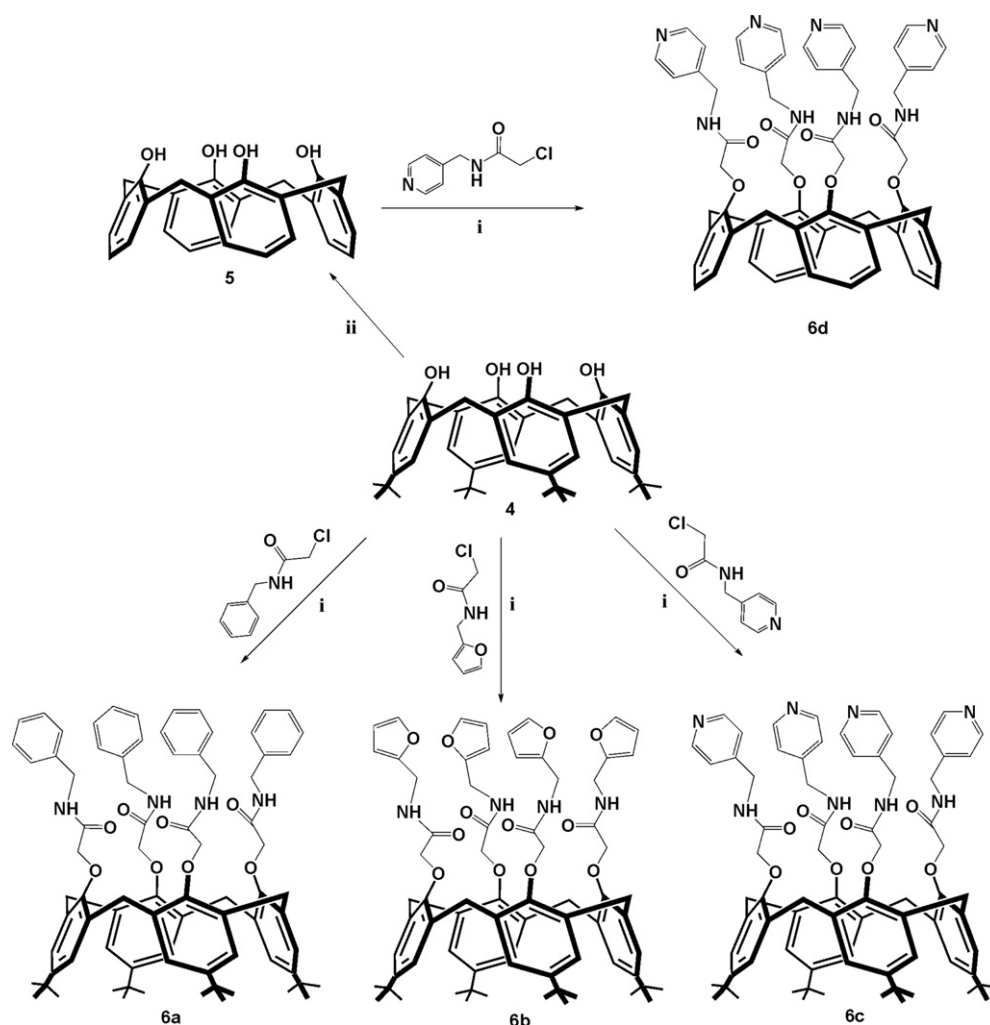
2. Results and discussion

2.1. Synthesis

As mentioned above, a set of new calix[4]arenes bearing pyridyl, furyl, and phenyl units on their lower rim were prepared. The binding properties of calix[4]arene derivatives were explored toward arsenate anions. The synthesis of the new calix[4]arene derivatives is given in Scheme 1. For the synthesis of calix[4]arenes based on different functional units **6a–d**, the parent compounds (**4** and **5**) were prepared according to published literature procedures.^{23,24} Corresponding chloroacetamide derivatives (**3a–c**) were synthesized according to modified literature methods as mentioned Scheme 1 or follows.^{32–34} All of the structures were clarified through ^1H NMR, FTIR (ATR), and elemental analyzes. Firstly, chloroacetamides (**3a–c**) were obtained simply by the direct reaction of chloroacetyl chloride with suitable amine compounds, such as benzylamine for **3a**, furfurylamine for **3b**, and/or 4-pyridylmethylamine for **3c**, respectively, in CH_2Cl_2 solution at



Scheme 1. The synthetic route for preparation of acetamides **3a–c**. Reaction conditions: (i) Et_3N , CH_2Cl_2 , rt, 2–3 h.



Scheme 2. A schematic representation of the synthesis of tetra-amido calix[4]arene ionophores **6a–d**. Reaction conditions: (i) NaH , THF/DMF , NaI , reflux, 72 h; (ii) AlCl_3 , phenol, toluene, rt, 1 h.

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