

# CHAPTER I

## INTRODUCTION

### 1.1 Rationale

Recently, there are numerous examples of molecules that act as hosts and complexants for cations, but there are fewer examples of molecules that act as hosts for anions [1-4]. Because the design of selective receptors for anions is more demanding than that for cations owing to wide varieties of both geometries and sizes (Table 1.1).

**Table 1.1** The geometry and size of various anions [5].

Anions	Geometry	Size (Å)
F <sup>-</sup>	spherical	1.33
Cl <sup>-</sup>	spherical	1.81
Br <sup>-</sup>	spherical	1.96
I <sup>-</sup>	spherical	2.20
CO <sub>3</sub> <sup>2-</sup>	trigonal planar	1.78
NO <sub>3</sub> <sup>-</sup>	trigonal planar	1.79
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	tetrahedral	2.00
PO <sub>4</sub> <sup>3-</sup>	tetrahedral	2.38
SO <sub>4</sub> <sup>2-</sup>	tetrahedral	2.30
ClO <sub>4</sub> <sup>-</sup>	tetrahedral	2.50

The geometry is an important factor to account for the design of selective anion receptors because it is not easy to synthesize receptor molecules with complementary binding sites in a proper three-dimension arrangement [6]. Moreover, the complexation between hosts and anions depend on pH of the solution since anions may be pH-dependent species. (Table 1.2).

**Table 1.2** Structures of major oxyanions of P(V), Se(VI), V(V), Re(VII), Cr(VI), Mo(VI), and W(VI) at pH 1 and pH 7 [7].

<b>pH 1</b>	H <sub>3</sub> PO <sub>4</sub>	HSeO <sub>4</sub> <sup>-</sup>	VO <sub>2</sub> <sup>+</sup>	ReO <sub>4</sub> <sup>-</sup>	Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	MoO <sub>3</sub> .2H <sub>2</sub> O	WO <sub>3</sub> .2H <sub>2</sub> O
<b>pH 7</b>	HPO <sub>4</sub> <sup>2-</sup>	SeO <sub>4</sub> <sup>2-</sup>	V <sub>10</sub> O <sub>28</sub> <sup>6-</sup>	ReO <sub>4</sub> <sup>-</sup>	CrO <sub>4</sub> <sup>2-</sup>	MoO <sub>4</sub> <sup>2-</sup>	WO <sub>4</sub> <sup>2-</sup>

The challenge in the field of anion complexation is to design the best receptors with high selectivity and high stability. Thus, the molecular recognition of anionic guest species by positively charged or electron deficient neutral abiotic receptor is currently of intense interest [8-10].

Calixarenes have become one of the most attractive receptors in the design and synthesis of artificial receptors for anions because they can be modified to gain numerous types of molecular receptors by many chemical reactions. In particular, the lower or upper rim of the calix[4]arene unit can be modified to achieve more sophisticated structures to bind specific guest species [11-14]. Several excellent studies on anion coordination using calixarene based chelating units have been reported [15-19].

From an environmental viewpoint, a series of anions for which selective hosts would be useful are the oxyanions. One such anion is chromate, which is important because of high toxicity [20-23], and its presence in soils and waters [24].

Workplace exposed to Cr(VI) has been associated with a number of industrial source, such as metal plating, spray painting, welding, tanning, and abrasive blasting operations [25, 26]. Environmental sources of Cr(VI) include deteriorated or disturbed chromate containing paint, combustion sources such as automobiles and incinerators, and fugitive dusts from contaminated soil [27, 28].

Environmental chromium exist primarily in two valence states, Cr(III) and Cr(VI). The trivalent state is relatively nontoxic and is an essential trace nutrient in the human diet [29]. It is considered to be essential part of living organisms such as biologically active chromium for metabolism of glucose. A deficiency of chromium in animals can produce diabetes, arteriosclerosis, growth problems, and eye cataract [20]. On the other hand, Cr(VI) has been shown to be a human respiratory carcinogen [29, 30] and has been classified by the U.S. Environmental Protection Agency (EPA)

as a Group A inhalation carcinogen [31]. The danger of environmental contamination depends on the oxidation state of chromium, i.e. the hexavalent form is 100 to 1000 times more toxic than the most common trivalent form. Hexavalent chromium compounds can reduce plant growth and cause skin inflammation or eczema in fish, mammals and humans, and after a longer latent time, lung cancer [20]. In contrast, water soluble Cr(III) compounds are not considered carcinogenic, possibly because they do not cross plasma membranes [32, 33].

According to its toxicity as mentioned above, several approaches have been used for the environmental removal of Cr(VI). One approach is to reduce its oxidation state in the presence of oxide surfaces with  $\alpha$ -hydroxyl carboxylic acids such as mandelic acid [34], or alternatively with oxalic acid or substituted phenols [35]. An alternate approach couples the microbial reduction of Cr(VI) with the anaerobic degradation of benzoate [36]. However, treatment of Cr(VI) from waste water is usually accomplished by chemical reduction of Cr(VI) to Cr(III) and subsequent chemical precipitation [37, 38]. In this way the removal of Cr(VI) from the aqueous effluents generates a typically inert residual sludge which is usually disposed in land fills [37]. Although it can reduce the chromium concentration in the waste water to a low level, it is not possible to recycle the metallic element back to the industrial process [38].

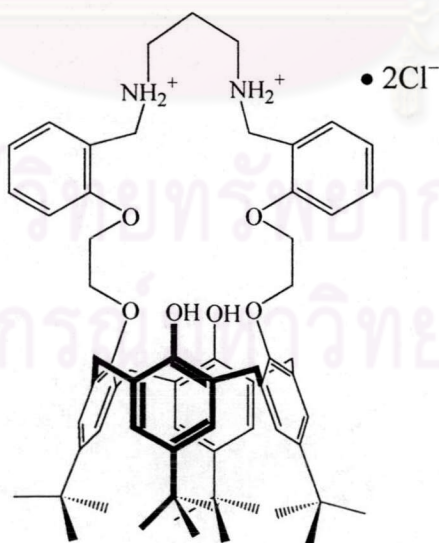
An alternate approach such as solvent extraction or liquid-liquid extraction by amine extraction applied to the Cr(VI) recovery has been extensively investigated [37-41]. The first step in the process of recovery of Cr(VI) is the extraction of the chromate anion from the acidic aqueous phase into the organic phase containing amine extractant. As a result, the complex amine-chromate is formed in the organic phase. Quantitation of the chromate anion was achieved in the stripping step by stripping reagents such as hydroxide anion [41, 42]. This method recover not only Cr(VI) but also the extractant. Moreover, the extractant after regeneration can be reused and retains quite high extracting ability [41].

## 1.2 Objectives

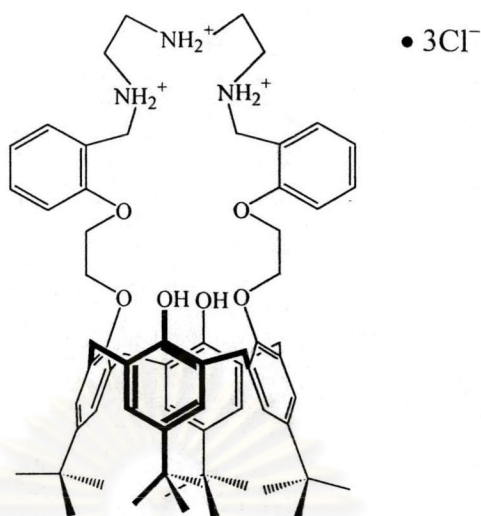
The aims of the present study are: (1) to study extraction properties of aminocalix[4]arenes toward chromate ion and (2) to study the parameters and the optimal conditions for chromate extraction.

## 1.3 Scope

In this article we report the ability of aminocalix[4]arene derivatives (compound **1b** and **2b**, Figures 1.1 and 1.2) as extractant for chromate ion from water into a chloroform layer. The influence parameters such as extraction time, pH, extractant concentration, types and concentration of spectator ions in the medium on the extraction have investigated in order to determine the optimal conditions for extraction. The mole ratio of extracted species and extractant was determined by slope analysis method. The effects of other oxyanions were also studied by individually adding three competitive oxyanions (potassium salts of  $\text{SO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$  and  $\text{NO}_3^-$ ) to  $\text{K}_2\text{CrO}_4$  solution. Furthermore, we studied the ability of extractant regeneration for several extracting cycles by using NaOH as strippant.

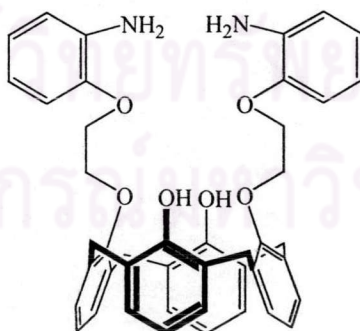


**Figure 1.1** 25, 27-*N, N*-di-((2-ethoxy)benzyl) propylenediamine-*p*-*tert*-butylcalix[4]arene dichloride (compound **1b**).

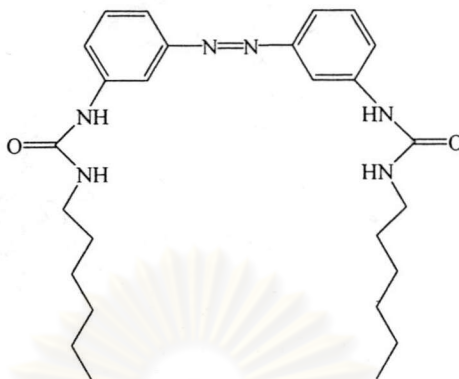


**Figure 1.2** 25, 27-{2, 2'- [2,2'- ((2,5,8-triammonium)nonyl)diphenxyl]diethyl}-*p*-*tert*-butylcalix[4]arene trichloride (compound **2b**).

Moreover, the extraction of Cr(VI) anion with compounds **3** and **4** (Figures 1.3 and 1.4 ) were studied in order to compare other influence parameter, which might be affect to the extraction efficiency such as the comparison of cyclic binding site (**1b** and **2b** ) to open binding site chain (**3**) and the amine functional group (**1b** and **2b**) to urea functional group (**4**) on the receptors.



**Figure 1.3** 25, 27-di-((2-ethoxy)benzylamine)-calix[4]arene (compound **3**).



**Figure 1.4** 3, 3'-dihexylurea azobenzene (compound 4).

Besides the liquid-liquid extraction studies, we also studied the ability of solid-phase extraction by compounds **1b** and **2b** with dynamic coating on silica as solid-support.

## 1.4 Potential Applications

To apply the knowledge of extraction properties (liquid-liquid extraction and solid-phase extraction) of aminocalix[4]arenes toward chromate ions for other applications such as preconcentration of Cr(VI) in waste water.

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย