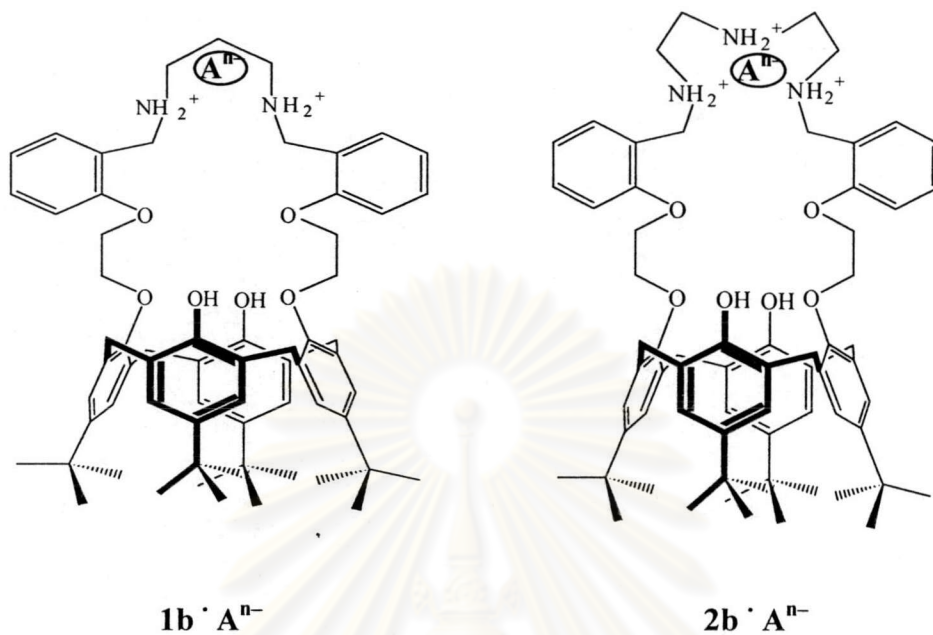


CHAPTER V

CONCLUSION

Three calix[4]arenes (25, 27-*N*, *N*-di-((2-ethoxy)benzyl) propylenediamine-*p*-*tert*-butylcalix[4]arene dichloride (**1b**), 25, 27-{2, 2'-[2,2'-((2,5,8-triammonium)nonyl) diphenoxyl]diethyl}-*p*-*tert*-butylcalix[4]arene trichloride (**2b**) and inclusion of 25, 27-di-((2-ethoxy)benzylamine)-calix[4]arene (**3**) and one urea (3,3'-dihexylurea azobenzene (**4**)) were used as extractant for the extraction studies of Cr(VI) anion.

A preliminary evaluation of Cr(VI) anions binding efficiencies of compounds **1b**, **2b**, **3** and **4** were carried out by liquid-liquid extraction of K_2CrO_4 from water into chloroform. The results showed that the protonated forms of **1b** and **2b** had higher extraction efficiencies than **3** and **4** (% E > 36, > 59, < 5.1 and < 3.5 for **1b**, **2b**, **3** and **4**, respectively). The distinction of extraction ability of **1b** and **2b** may be due to more rigid structural features and protonation of amine groups of **1b** and **2b**, which help in transferring anions when compared to compounds **3** and **4**. However, compound **2b** was more effective for Cr(VI) extraction than compound **1b**. This might be due to the difference in the cavity size of cyclic binding site and the number of amine groups. The highest extraction efficiency of Cr(VI) anions was found in a 0.01 M chloride medium at pH 2.37. The relative affinities of oxyanions, as competitive anion, to **1b** and **2b** were in the order of $NO_3^- > H_2PO_4^- \approx SO_4^{2-}$. The extraction mechanisms were determined by the classical slope analysis method. The indicate that the 1:1 extracted species between extractant and Cr(VI) were obtained (figure 5.1) and the anion extracted might be either $HCrO_4^-$ or $Cr_2O_7^{2-}$.



where Aⁿ⁻ is HCrO₄⁻ or Cr₂O₇²⁻.

Figure 5.1 Structures of **1b · Aⁿ⁻** and **2b · Aⁿ⁻**.

The extraction efficiency at 7 extraction cycles showed quite high retained extraction ability (% E > 44 and > 54 for compounds **1b** and **2b**, respectively).

The solid-phase extraction studies with dynamic coating of **1b** and **2b** on silica as solid-support showed higher extraction percentages than in liquid-liquid extraction. These drastic increasing of extraction ability because enormous surface area of calixarenes coated on SiO₂ to contact the aqueous phase and more hydrophilic in the presence of silanol groups. **1b** and **2b**, retained quite high extraction ability at three extraction cycles.

Potential applications and suggestions for future works:

From all aforementioned results and discussion, the knowledge of extraction properties (liquid-liquid extraction and solid-phase extraction) of aminocalix[4]arenes towards chromate ions could lead to potential applications such as preconcentration of Cr(VI) in waste water or the possibility of employing calix[4]arene derivatives as basic structure for construction of HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ ion sensors. Future works should be focused on:

1. X-ray crystal structures of both ligands **1b** and **2b** as well as their anion complexes in order to understand the nature of coordination mode of synthetic receptors towards ions.

2. Studies of the extraction abilities of both ligands towards Cr(VI) anion with flow rate in solid-phase extraction mode by packing the ligand-coated SiO_2 in a minicolumn, cartridge, glass fiber or paper filter disks.



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