

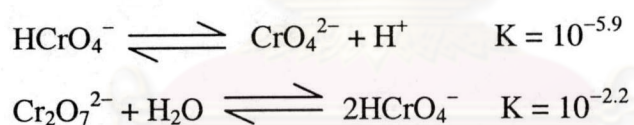
CHAPTER IV

RESULT AND DISCUSSION

In this chapter, we present the results and discussion of liquid-liquid extraction and solid-phase extraction of Cr(VI) anion by compounds **1b**, **2b**, **3** and **4**.

4.1 Liquid-liquid Extraction Studies

In the present work, we determined the strategic requirements for two-phase extraction measurements. The binding efficiencies of compounds **1b**, **2b**, **3** and **4** were carried out by solvent extraction of K_2CrO_4 from water into chloroform varying several parameters. One is the effect of initial pH of K_2CrO_4 solution. As we described in section 2.2.2.1, $HCrO_4^-$ and $Cr_2O_7^{2-}$ become the dominant species of Cr(VI) anion forms at high acidic condition. This is attributed to the following equilibria:

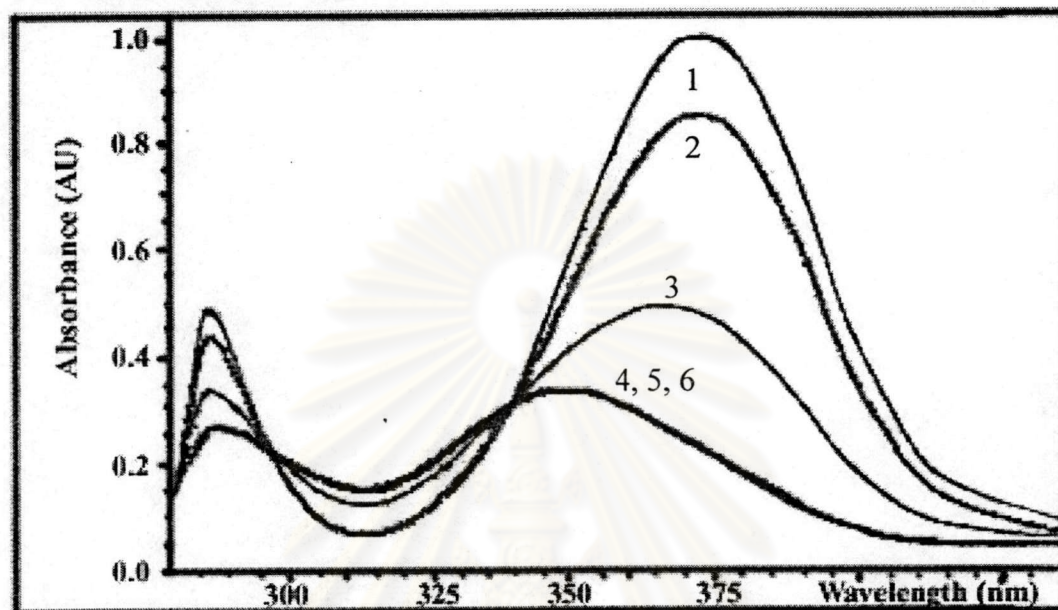


The spectrophotometric method is one good example of a precise method to distinguish Cr(VI) in $HCrO_4^-$ and $Cr_2O_7^{2-}$ based on their color. It may be based either on the yellow color of CrO_4^{2-} ions present in alkaline solution, or on the orange color of $Cr_2O_7^{2-}$ ions by acidification of the solution.

Figure 4.1 shows the experimental result of absorption spectra of Cr(VI) in 0.01M KCl solutions at different pH values. The absorption peaks at 350 nm and 373 nm correspond to CrO_4^{2-} and $Cr_2O_7^{2-}$, respectively. Both wavelengths were also found in the case of Cr(VI) in 1 M H_2SO_4 [153].

In this work, the wavelength of 373 nm was chosen for determination of Cr(VI) anion as CrO_4^{2-} in the aqueous phase in the presence of excess NaOH.

Overlaid Sample Spectra



Sample / Result table

Sample	Peak(nm)	Abs
1. K ₂ CrO ₄ 40 ppm at pH 7.84	373.0	1.00160
2. K ₂ CrO ₄ 40 ppm at pH 7.15	372.0	0.84997
3. K ₂ CrO ₄ 40 ppm at pH 6.51	366.0	0.48788
4. K ₂ CrO ₄ 40 ppm at pH 4.17	351.0	0.33465
5. K ₂ CrO ₄ 40 ppm at pH 3.31	350.0	0.33637
6. K ₂ CrO ₄ 40 ppm at pH 2.18	350.0	0.32970

Figure 4.1 Absorption spectra of Cr(VI) solutions at (1) pH 7.84, (2) pH 7.15, (3) pH 6.51, (4) pH 4.17, (5) pH 3.31, and (6) pH 2.18 in 0.01 M KCl.

4.1.1 Extraction Efficiency by Chloroform (Blank Test)

Chloroform was selected as the diluent (organic phase) because of the solubility of extractants and extracted species.

Solvent extraction studies with chloroform without the extractants were performed in the system of 0.257 mM K_2CrO_4 in a 0.01 M KCl solution at initial pH 2.37 (conditions described in section 3.3.1.1). The data listed in Table 4.1 showed no significant extraction into chloroform phase (% E < 1.8 for four replicating extractions).

Table 4.1 Extraction of Cr(VI) with chloroform.

No	[CrO ₄ ²⁻], ppm			% E
	initial	aqueous phase	organic phase	
1	50.18	49.29	0.89	1.77
2		49.55	0.63	1.26
3		49.76	0.84	0.84
4		49.55	1.26	1.26
Mean =				1.28 ± 0.38

4.1.2 Influence of Initial pH in K_2CrO_4 Solution

The extraction of Cr(VI) anions in 0.01 M KCl as a function of the initial pH of aqueous solution by four compounds (**1b**, **2b**, **3** and **4**) dissolved in chloroform was studied. The extraction results are shown in Figure 4.2 (conditions described in section 3.3.1.2, see data in Tables A.2a, A.2b, A.2c and A.2d in the appendix).

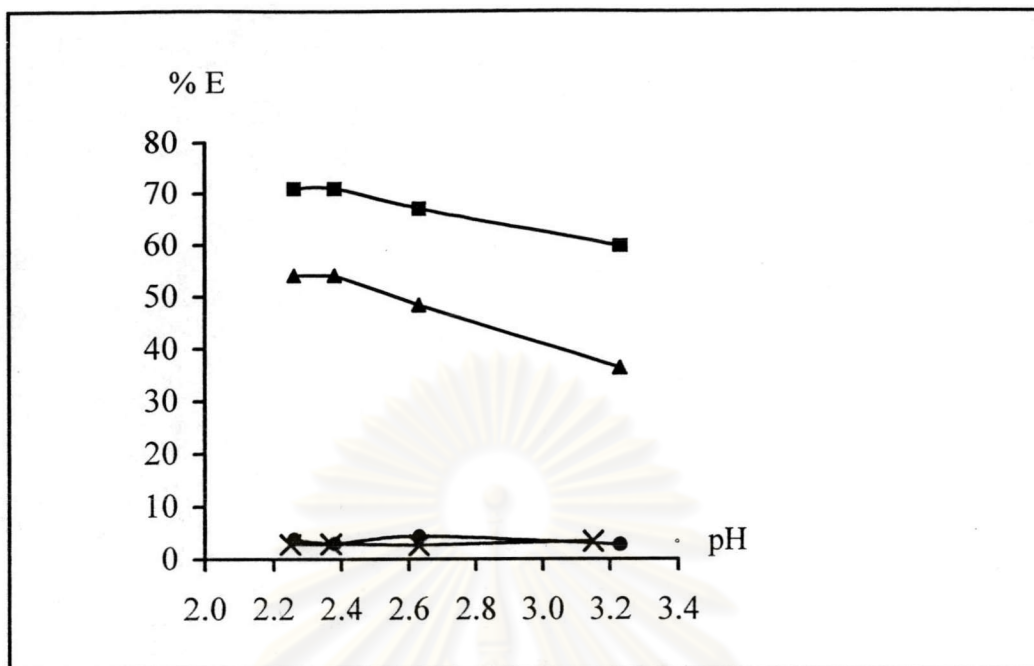


Figure 4.2 Effect of initial pH of aqueous solution on % E for Cr(VI).

[**1b**] = 0.257 mM, [**2b**] = 0.256 mM, [**3**] = 0.289 mM, [**4**] = 0.261 mM
 $[\text{CrO}_4^{2-}] = 0.257 \text{ mM}$. (\blacktriangle) = **1b**, (\blacksquare) = **2b**, (\bullet) = **3**, and (\times) = **4**.

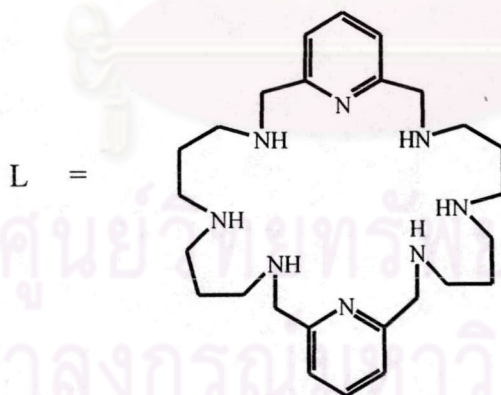
It is apparently clear that compounds **3** and **4** showed no significant extraction of Cr(VI). Two replicating extractions under pH range 2.25-3.24 showed % E < 5.1 and < 3.5 for compounds **3** and **4**, respectively. In contrast, the higher extraction efficiencies were found under similar pH range for compounds **1b** and **2b** with % E > 36 and > 59, respectively. This indicates that compounds **1b** and **2b** are the excellent extractant for Cr(VI) anion compared to compounds **3** and **4**. This remarkable increasing of extraction ability of compounds **1b** and **2b** may be due to more rigid structural features. Because both compounds contain cyclic amine binding sites which are appropriate for aggregation of anions. Moreover, the extraction efficiencies of these two compounds were at higher level of extraction at lower pH. The extraction property was enhanced in acidic medium showing that the protonated forms of both compounds were an effective host for Cr(VI) anions. The positive charge, resulting from protonation of amine groups, helps in coordination with anions as described in section 2.1.1. However, compound **2b** was more effective for Cr(VI) extraction than

compound **1b**. This might be due to the difference in (1) the cavity size of cyclic binding site and (2) the number of amine groups.

From figure 4.2 it is noteworthy that the extraction abilities of compounds **1b** and **2b** decreased with increasing initial pH in aqueous phase. This result might be explained by the incomplete monoprotonated form (for compound **1b**) and diprotonated form (for compound **2b**), which occurs at higher pH and affect the extraction of Cr(VI) anion. The receptor containing less positive charge is capable to extract less anions than the receptor containing more positive charge. The similar explanation for complexation of selenate (SeO_4^{2-}) with hexaprotonated amine was described by Izatt and co-workers [154]. They showed that the formation constant of the 1:1 complexes decreased with decreasing positive charge (Table 4.2). It also means that the electrostatic interaction is demonstrated to play an important role in the complexation.

Table 4.2 The formation constants of the 1:1 complexes SeO_4^{2-} : L [154].

	6-protonated	5-protonated	4-protonated	3-protonated
log K	3.68	3.30	2.69	1.40



Therefore, a pH between 2.25-2.40 was selected as an initial pH of the aqueous solution for further studies because the highest extraction percentage was obtained under this condition.

4.1.3 Influence of Extraction Time

The extraction of 0.257 mM K_2CrO_4 in 0.01 M KCl at initial pH 2.37 with compounds **1b**, **2b** and **4** in chloroform at various extraction time was studied (conditions described in section 3.3.1.3.). The results Tables shown in A.3a, A.3b and A.3c in the appendix are represented in Figure 4.3.

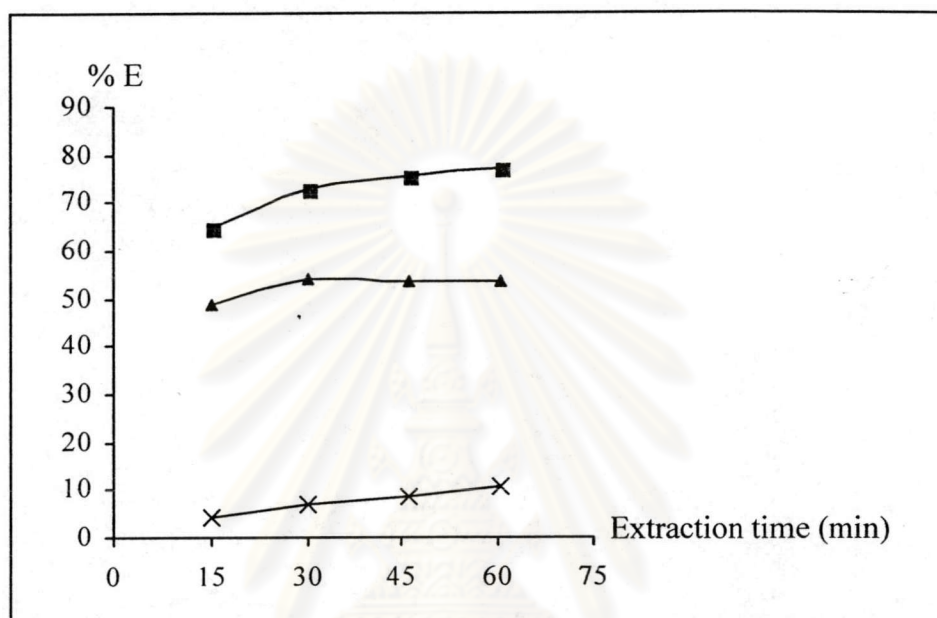


Figure 4.3 Effect of extraction time on % E for Cr(VI). [**1b**] = 0.257 mM, [**2b**] = 0.256 mM, [**4**] = 2.57 mM, $[CrO_4^{2-}] = 0.257$ mM. (▲) = **1b**, (■) = **2b**, and (×) = **4**.

From Figure 4.3 the change of % E after extraction time for 30 min were negligible, indicating that 30 min was sufficient to reach equilibrium, longer contact times caused no significant changes in the results.

Although the extraction ability slightly increased in the presence of compound **4** ten-folds over K_2CrO_4 , the extraction of Cr(VI) anion has been studied with compound **1b** and **2b** only because of poor extraction ability of compounds **3** and **4**.

4.1.4 Influence of Type and Concentration of Mediums

The studies of influence of types and concentrations of mediums were carried out at $\text{pH } 2.37 \pm 0.01$. The equivalent concentration of compounds **1b**, **2b** and K_2CrO_4 were used (conditions described in section 3.3.1.4). The data of extraction are shown in Tables A.4a, A.4b, A.4c and A.4d in the appendix. The results are shown in Figure 4.4.

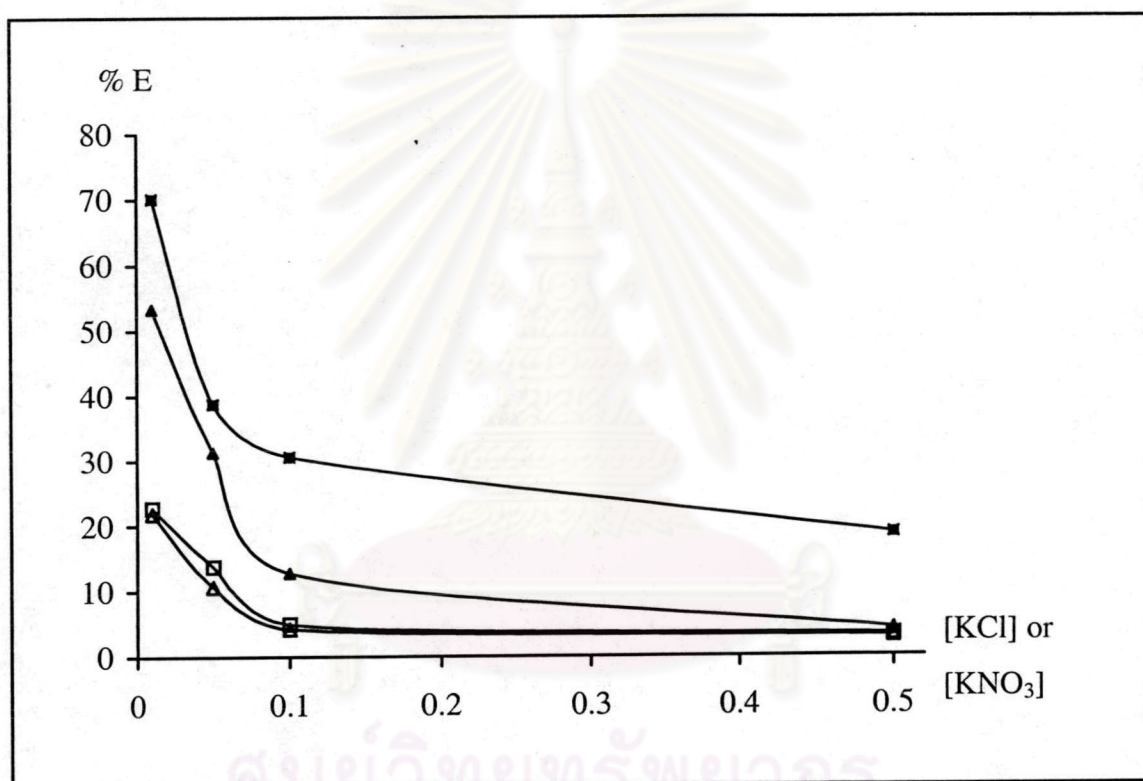


Figure 4.4 Effect of type and concentration of mediums on % E for Cr(VI).

$[\mathbf{1b}] = 0.257 \text{ mM}$, $[\mathbf{2b}] = 0.258 \text{ mM}$, $[\text{CrO}_4^{2-}] = 0.257 \text{ mM}$.

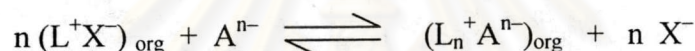
(Δ) = **1b** and (\blacksquare) = **2b** with KCl medium, (Δ) = **1b** and (\square) = **2b** with KNO_3 medium.

(a) Effect of type of medium

On comparison of KCl and KNO₃ mediums at similar concentration, % E of Cr(VI) anion from a chloride medium was higher than from a nitrate medium for both compounds. This indicates that nitrate species act as competitive anion to Cr(VI). This phenomenon suggests that both extractants have higher affinity for NO₃⁻ than for Cl⁻.

(b) Effect of concentration of medium

The extraction of Cr(VI) anion in different concentrations of KCl and KNO₃ solutions (0.01, 0.05, 0.1 and 0.5 M) was studied. From Figure 4.4, % E decreased when concentrations of mediums increased. It is reasonable to explain with the following equilibrium:



The equilibrium will go backwards in the presence of high concentration of X⁻ (where X⁻ = NO₃⁻, Cl⁻).

We could conclude that the highest extraction efficiency of Cr(VI) anions was found in a 0.01 M chloride medium.

4.1.5 Influence of Competitive Anions

Three kinds of oxyanions (nitrate (NO₃⁻), sulfate (SO₄²⁻) and dihydrogenphosphate (H₂PO₄⁻)) were individually added to 0.257 mM K₂CrO₄ in 0.01 M KCl. The concentration of the oxyanion in aqueous solution was maintained at 1.28 mM (five-fold excess of K₂CrO₄). The extraction studies were carried out at pH 2.37 ± 0.01. The results are shown in Figure 4.5 (see data in Tables A.5a and A.5b in appendix).

The extraction percentages of Cr(VI) with compounds **1b** and **2b** decreased in the presence of other oxyanions comparing to in the absence of other oxyanions. For both extractants, the presence of KNO₃ gave the lowest %E while the solution

containing K_2SO_4 and KH_2PO_4 gave the same % E. This indicates that the relative affinities of these three oxyanions to two extractants were in the order of $NO_3^- > H_2PO_4^- \approx SO_4^{2-}$. This finding is in a good agreement with the results in section 4.1.4.

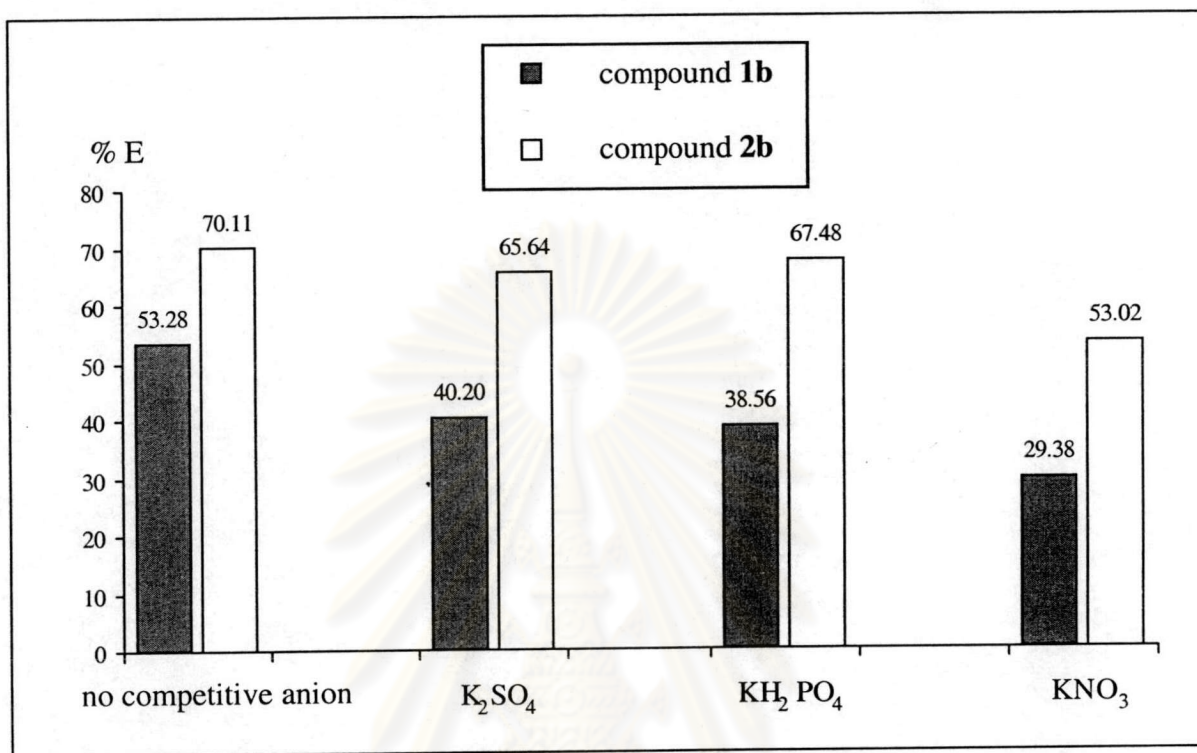


Figure 4.5 Diagram of % E of Cr (VI) in the presence of competitive anions.

$[1b] = 0.257$ mM, $[2b] = 0.258$ mM, $[CrO_4^{2-}] = 0.257$ mM,

$[SO_4^{2-}] = [H_2PO_4^-] = [NO_3^-] = 1.28$ mM in 0.01 M chloride medium.

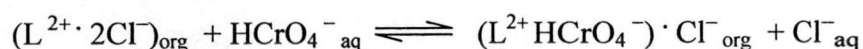
Although the results indicated that the extraction of Cr(VI) anion were influenced by the presence of other oxyanions, both extractants still retained high extraction efficiencies. It seems that both extractants gave a good selectivity to Cr(VI) anions over SO_4^{2-} , $H_2PO_4^-$ and NO_3^- .

4.1.6 Influence of Concentration of Extractant in Various Mediums

The extraction equilibrium studied to obtain the stoichiometry of the extracted species were carried out under 4 conditions of aqueous solution by using 5 different concentrations of extractants (conditions described in section 3.3.1.6.). The data was analyzed by using the classical slope analysis method as described in section 2.4.4.2.2.

As it is well known that HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ ions (from K_2CrO_4 : see section 2.2.2.1) become the dominant of Cr(VI) anion forms at high acidic conditions. Thus, in this section we consider two simple extraction mechanisms as follows:

Extraction equilibrium 1 is defined as ligand extracts only HCrO_4^- (1 : 1 ratio) :



where $\text{L}^{2+} \cdot 2\text{Cl}^-$ is the compound **1b**.

The extraction equilibrium 1 constant, K_{ex1} is

$$K_{\text{ex1}} = \frac{[(\text{L}^{2+} \text{HCrO}_4^-) \cdot \text{Cl}^-]_{\text{org}} [\text{Cl}^-]_{\text{aq}}}{[\text{L}^{2+} \cdot 2\text{Cl}^-]_{\text{org}} [\text{HCrO}_4^-]_{\text{aq}}}$$

Or one can define in term of distribution ratio, D:

$$D = \frac{K_{\text{ex1}} [\text{L}^{2+} \cdot 2\text{Cl}^-]_{\text{org}}}{[\text{Cl}^-]_{\text{aq}}}$$

Thus, the following equation can be obtained:

$$\log D = \log K'_{\text{ex1}} + \log [\text{L}^{2+} \cdot 2\text{Cl}^-]_{\text{org}} \dots\dots\dots (2)$$

where

$$K'_{\text{ex1}} = \frac{K_{\text{ex1}}}{[\text{Cl}^-]_{\text{aq}}}$$

Extraction equilibrium 2 is define as ligand extracts only $\text{Cr}_2\text{O}_7^{2-}$ (1 : 1 ratio):



The extraction equilibrium 2 constant, $K_{\text{ex}2}$ is:

$$K_{\text{ex}2} = \frac{[\text{L}^{2+} \cdot \text{Cr}_2\text{O}_7^{2-}]_{\text{org}} [\text{Cl}^-]_{\text{aq}}^2}{[\text{L}^{2+} \cdot 2\text{Cl}^-]_{\text{org}} [\text{Cr}_2\text{O}_7^{2-}]_{\text{aq}}}$$

Or one can define in term of distribution ratio, D:

$$D = \frac{K_{\text{ex}2} [\text{L}^{2+} \cdot 2\text{Cl}^-]_{\text{org}}}{[\text{Cl}^-]_{\text{aq}}^2}$$

Thus, the following equation can be obtained:

$$\log D = \log K'_{\text{ex}2} + \log [\text{L}^{2+} \cdot 2\text{Cl}^-]_{\text{org}} \dots\dots\dots(3)$$

where

$$K'_{\text{ex}2} = \frac{K_{\text{ex}2}}{[\text{Cl}^-]_{\text{aq}}^2}$$

Consequently, plots of $\log D$ vs. $\log [\text{L}^{2+} \cdot 2\text{Cl}^-]_{\text{org}}$ may lead to a straight line whose slope of 1 allows an access to the stoichiometry of the extracted species [42, 61] and K_{ex} can be calculated from intercept of the graph.

The plots of $\log D$ vs. $\log [\text{L}]_{\text{eq}}$ (for compound **1b**) are shown in Figures 4.6 and 4.7 correspond to extraction equilibria 1 and 2, respectively. The data calculated for these two graphs are shown in table A.6b, A.6d, A.6f, and A.6h in the appendix.

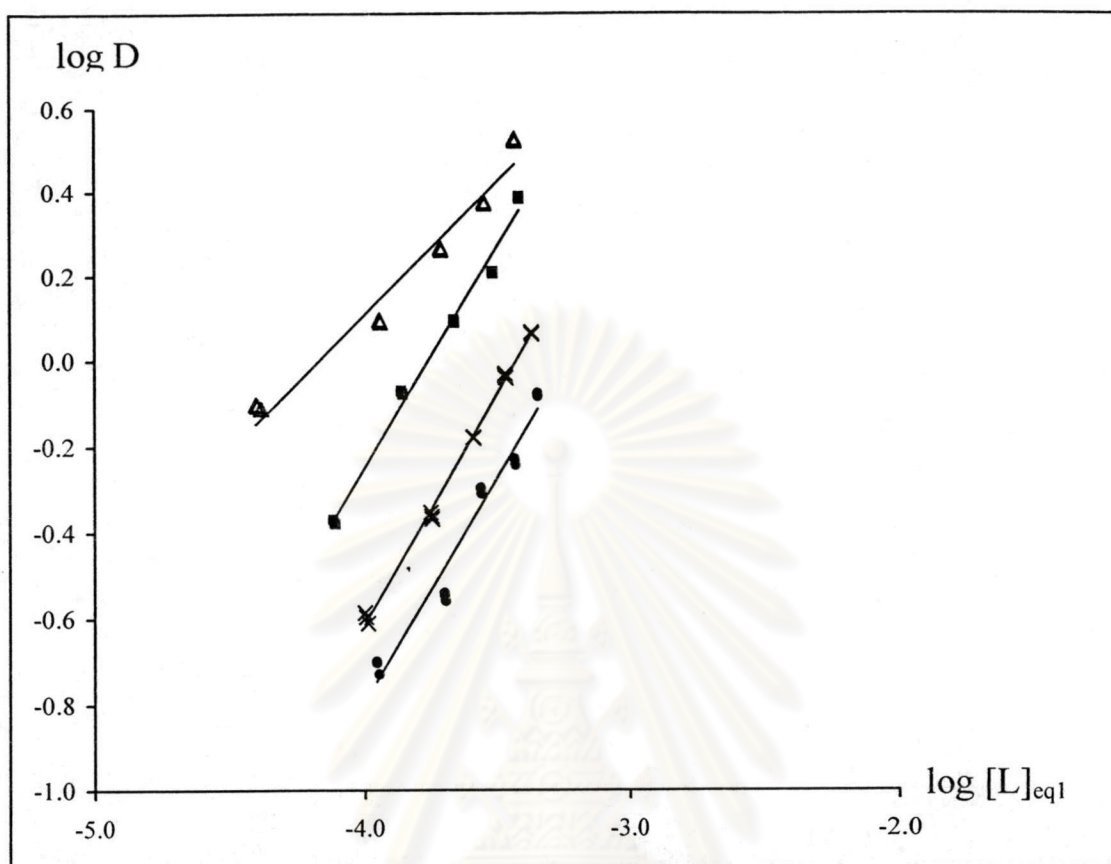


Figure 4.6 Extraction of HCrO_4^- anion by compound **1b** in chloroform at 25 °C.

Δ 50 ppm of K_2CrO_4 in 0.01 M KCl, pH 2.37

■ 50 ppm of K_2CrO_4 in 0.01 M KCl, pH 2.75

× 50 ppm of K_2CrO_4 in 0.05 M KCl, pH 2.37

● 50 ppm of K_2CrO_4 in 0.01 M KNO_3 , pH 2.37

where $[\text{L}]_{\text{eq1}}$ = concentration of free ligand (M), $[\text{L}^{2+} \cdot 2\text{Cl}^-]_{\text{org}}$, in equilibrium 1

$$= [\text{L}]_{\text{int}} - [\text{Cr(VI)}]_{\text{org}}$$

Figure 4.6 shows that by increasing the concentration of compound **1b** the distribution ratio increases. Plot of $\log D$ vs. $\log [\text{L}]_{\text{eq1}}$ yields straight line and its slope found to be nearly 1 for all four systems (Table 4.3).

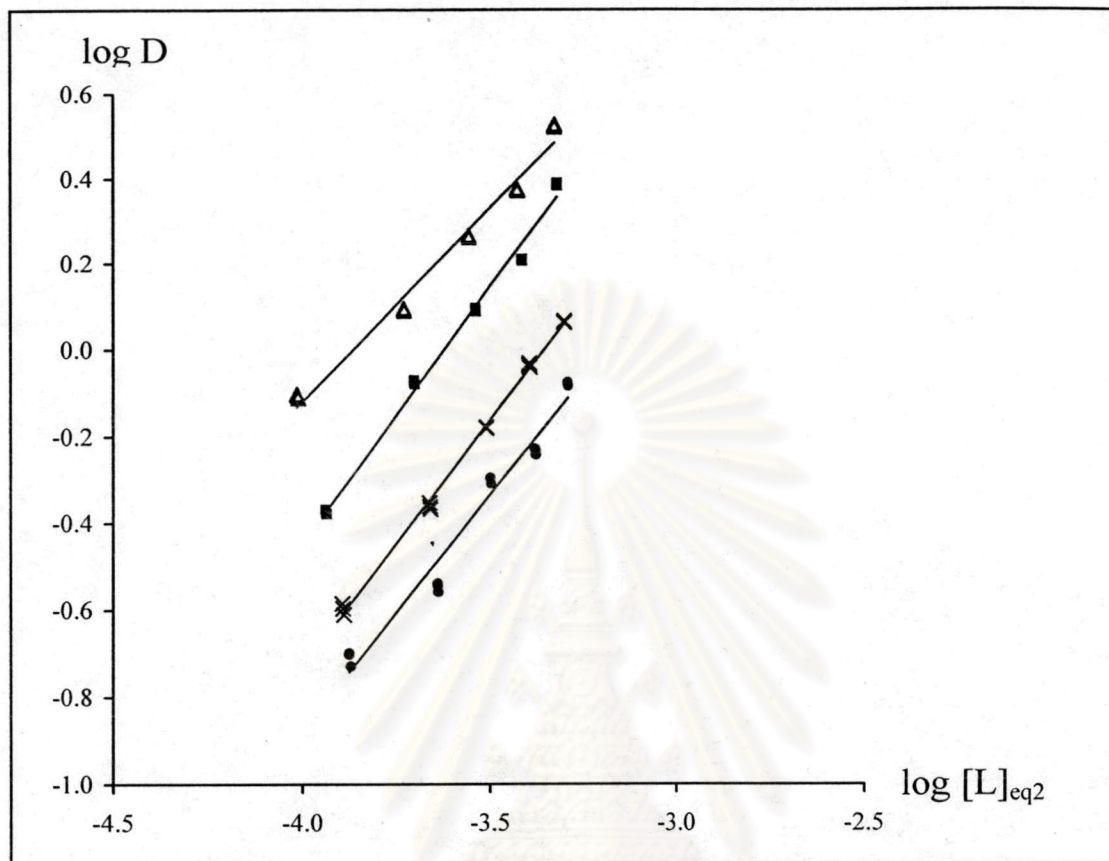


Figure 4.7 Extraction of $\text{Cr}_2\text{O}_7^{2-}$ anion by compound **1b** in chloroform at 25 °C.

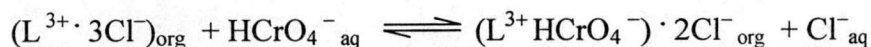
- Δ 50 ppm of K_2CrO_4 in 0.01 M KCl, pH 2.37
- 50 ppm of K_2CrO_4 in 0.01 M KCl, pH 2.75
- × 50 ppm of K_2CrO_4 in 0.05 M KCl, pH 2.37
- 50 ppm of K_2CrO_4 in 0.01 M KNO_3 , pH 2.37

where $[\text{L}]_{\text{eq}2}$ = concentration of free ligand (M), $[\text{L}^{2+} \cdot 2\text{Cl}^-]_{\text{org}}$, in equilibrium 2
 $= [\text{L}]_{\text{int}} - \frac{1}{2} [\text{Cr(VI)}]_{\text{org}}$

Similar to extraction equilibrium 1, Figure 4.7 shows that by increasing the concentration of compound **1b** the distribution ratio increases. The slope of $\log D$ vs. $\log [\text{L}]_{\text{eq}2}$ straight line is found to be nearly 1 for all four systems (table 4.3).

We have also studied the extraction of Cr(VI) anions using compound **2b** bearing three amine groups as anion binder. The extraction equilibrium is considered in the similar approach of compound **1b** as follows:

Extraction equilibrium 3 is defined as ligand extracts only HCrO_4^- (1 : 1 ratio) :



where $\text{L}^{3+} \cdot 3\text{Cl}^-$ is the compound **2b**.

Thus, the following equation can be obtained:

$$\log D = \log K_{\text{ex3}} + \log [\text{L}^{3+} \cdot 3\text{Cl}^-]_{\text{org}} \dots \dots \dots (4)$$

where

$$K'_{\text{ex3}} = \frac{K_{\text{ex3}}}{[\text{Cl}^-]_{\text{aq}}}$$

Extraction equilibrium 4 is defined as ligand extracts only $\text{Cr}_2\text{O}_7^{2-}$ (1 : 1 ratio):



Thus, the following equation can be obtained:

$$\log D = \log K_{\text{ex4}} + \log [\text{L}^{3+} \cdot 3\text{Cl}^-]_{\text{org}} \dots \dots \dots (5)$$

where

$$K'_{\text{ex4}} = \frac{K_{\text{ex4}}}{[\text{Cl}^-]_{\text{aq}}^2}$$

The results are shown in Figures 4.8 and 4.9 for extraction equilibria 1 and 2, respectively. The data calculated for these two graphs are shown in table A.6j, A.6l, A.6n and A.6p in the appendix.

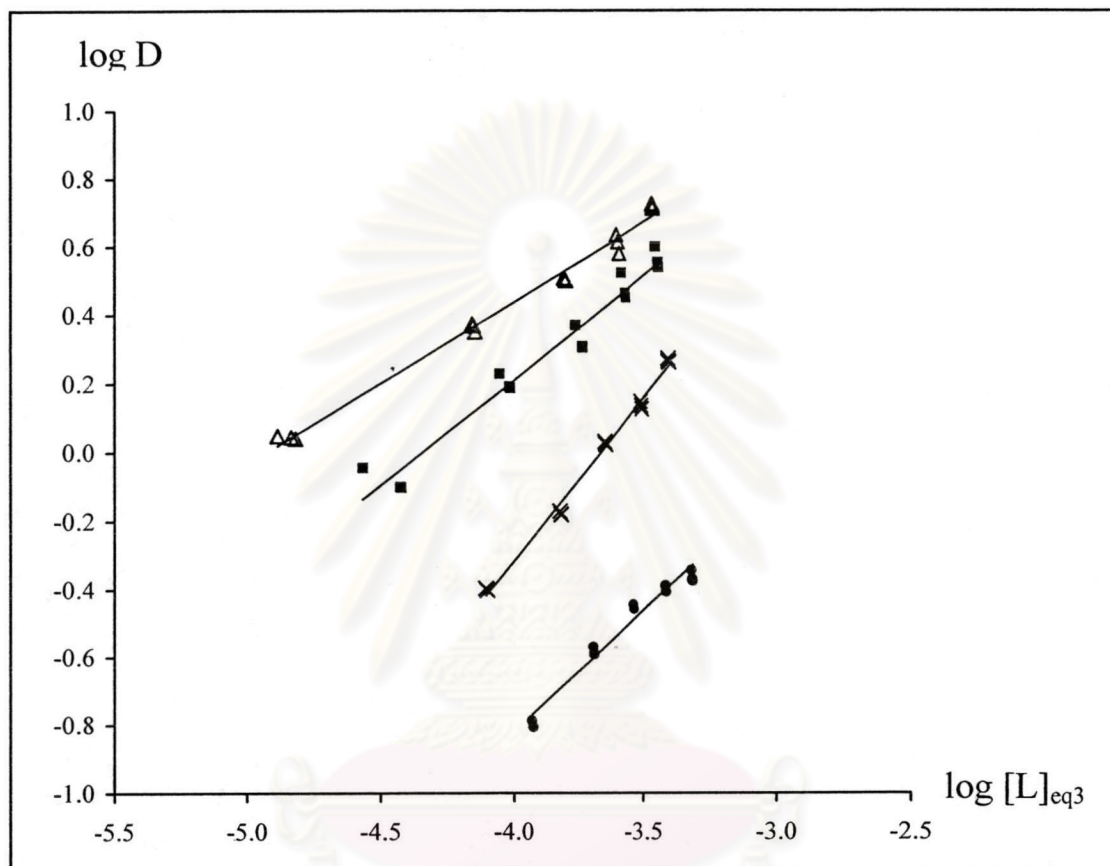


Figure 4.8 Extraction of HCrO_4^- anion by compound **2b** in chloroform at 25 °C.

Δ 50 ppm of K_2CrO_4 in 0.01 M KCl, pH 2.37

■ 50 ppm of K_2CrO_4 in 0.01 M KCl, pH 2.75

× 50 ppm of K_2CrO_4 in 0.05 M KCl, pH 2.37

● 50 ppm of K_2CrO_4 in 0.01 M KNO_3 , pH 2.37

where $[\text{L}]_{\text{eq3}} = \text{concentration of free ligand (M), } [\text{L}^{3+} \cdot 3\text{Cl}^-]_{\text{org}}$, in equilibrium 3
 $= [\text{L}]_{\text{int}} - [\text{Cr(VI)}]_{\text{org}}$

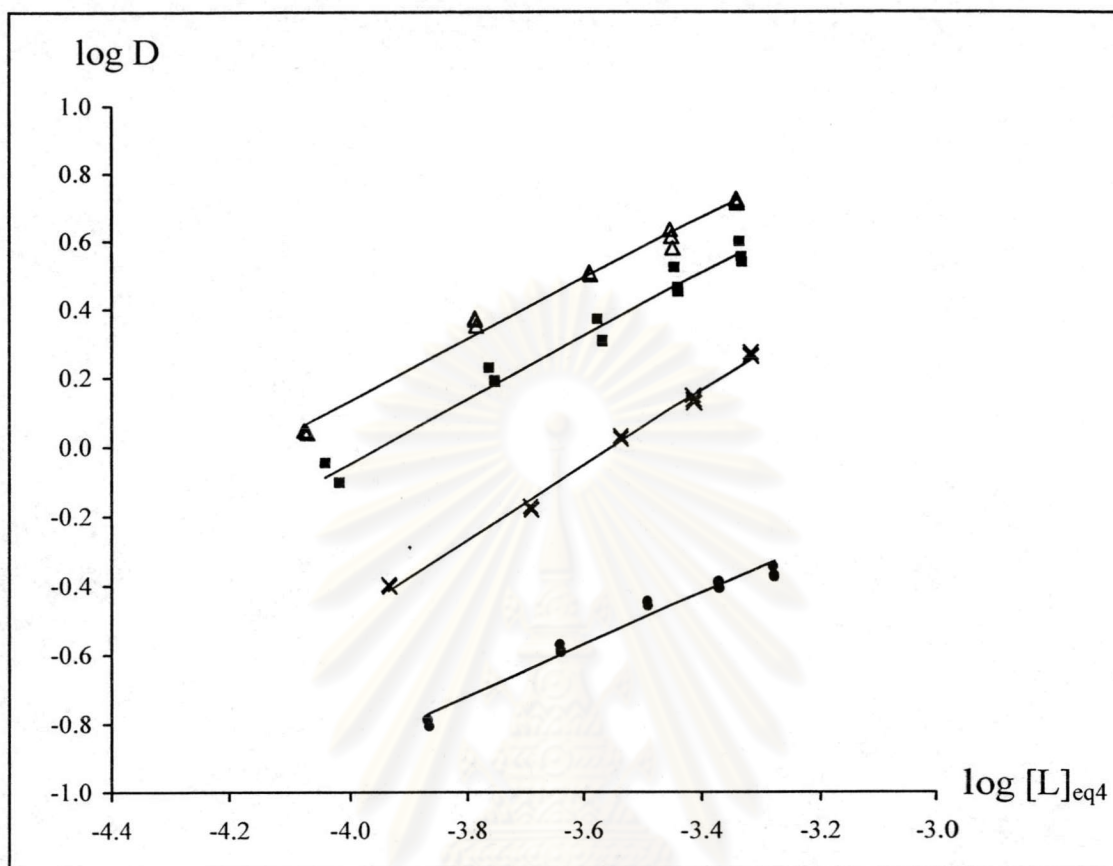


Figure 4.9 Extraction of $\text{Cr}_2\text{O}_7^{2-}$ anion by compound **2b** in chloroform at 25 °C.

- Δ 50 ppm of K_2CrO_4 in 0.01 M KCl, pH 2.37
- 50 ppm of K_2CrO_4 in 0.01 M KCl, pH 2.75
- × 50 ppm of K_2CrO_4 in 0.05 M KCl, pH 2.37
- 50 ppm of K_2CrO_4 in 0.01 M KNO_3 , pH 2.37

where $[\text{L}]_{\text{eq4}}$ = concentration of free ligand (M), $[\text{L}^{3+} \cdot 3\text{Cl}]_{\text{org}}$, in equilibrium 4

$$= [\text{L}]_{\text{int}} - \frac{1}{2} [\text{Cr(VI)}]_{\text{org}}$$

Figures 4.8 and 4.9 show the similar results as with compound **1b**. It means that when the concentration of compound **2b** increases, the distribution ratio also increases. The slope of $\log D$ vs. $\log [\text{L}]_{\text{eq}}$ for both equilibria is found to be nearly 1 for four systems similar to the case of compound **1b** (table 4.4).

Other assumptions of extraction equilibrium for compound **1b** and **2b** are listed in more details in Tables 4.3 and 4.4, respectively. The calculation of hypothesis 3-5 is similar to two extraction equilibria as described previously.

Table 4.3 Hypothesis of extraction equilibria for compound **1b**.

Hypothesis*	conditions	slope	
		theory	experiment
1) $L^{2+} + HCrO_4^- \rightleftharpoons L^{2+} HCrO_4^-$	0.01 M KCl, pH 2.37	1	0.63
	0.01 M KCl, pH 2.75	1	1.04
	0.05 M KCl, pH 2.37	1	1.07
	0.01 M KNO ₃ , pH 2.37	1	1.04
2) $L^{2+} + Cr_2O_7^{2-} \rightleftharpoons L^{2+} Cr_2O_7^{2-}$	0.01 M KCl, pH 2.37	1	0.90
	0.01 M KCl, pH 2.75	1	1.19
	0.05 M KCl, pH 2.37	1	1.14
	0.01 M KNO ₃ , pH 2.37	1	1.08
3) $L^{2+} + 2HCrO_4^- \rightleftharpoons L^{2+} 2HCrO_4^-$	0.01 M KCl, pH 2.37	1	1.47
	0.01 M KCl, pH 2.75	1	1.79
	0.05 M KCl, pH 2.37	1	1.53
	0.01 M KNO ₃ , pH 2.37	1	1.38
4) $2L^{2+} + HCrO_4^- \rightleftharpoons (2L^{2+})HCrO_4^-$	0.01 M KCl, pH 2.37	2	a
	0.01 M KCl, pH 2.75	2	a
	0.05 M KCl, pH 2.37	2	0.87
	0.01 M KNO ₃ , pH 2.37	2	0.92
5) $2L^{2+} + Cr_2O_7^{2-} \rightleftharpoons (2L^{2+})Cr_2O_7^{2-}$	0.01 M KCl, pH 2.37	2	0.63
	0.01 M KCl, pH 2.75	2	1.04
	0.05 M KCl, pH 2.37	2	1.07
	0.01 M KNO ₃ , pH 2.37	2	1.04

* the extraction equilibria present in simple term (without counter ions and subscript aq or org)

^a $\log [L]_{eq}$ cannot be obtained because $[L]_{eq} = [L]_{int} - 2[Cr(VI)]_{org}$ gives negative values.

Table 4.4 Hypothesis of extraction equilibria for compound **2b**.

Hypothesis*	conditions	slope	
		theory	experiment
1) $L^{3+} + HCrO_4^- \rightleftharpoons L^{3+}HCrO_4^-$	0.01 M KCl, pH 2.37	1	0.47
	0.01 M KCl, pH 2.75	1	0.61
	0.05 M KCl, pH 2.37	1	0.96
	0.01 M KNO ₃ , pH 2.37	1	0.72
2) $L^{3+} + Cr_2O_7^{2-} \rightleftharpoons L^{3+}Cr_2O_7^{2-}$	0.01 M KCl, pH 2.37	1	0.89
	0.01 M KCl, pH 2.75	1	0.92
	0.05 M KCl, pH 2.37	1	1.09
	0.01 M KNO ₃ , pH 2.37	1	0.75
3) $L^{3+} + 2HCrO_4^- \rightleftharpoons L^{3+}(HCrO_4^-)_2$	0.01 M KCl, pH 2.37	1	1.54
	0.01 M KCl, pH 2.75	1	1.54
	0.05 M KCl, pH 2.37	1	1.60
	0.01 M KNO ₃ , pH 2.37	1	0.90
4) $2L^{3+} + HCrO_4^- \rightleftharpoons (2L^{3+})HCrO_4^-$	0.01 M KCl, pH 2.37	2	a
	0.01 M KCl, pH 2.75	2	a
	0.05 M KCl, pH 2.37	2	0.35
	0.01 M KNO ₃ , pH 2.37	2	0.63
5) $2L^{3+} + Cr_2O_7^{2-} \rightleftharpoons (2L^{3+})Cr_2O_7^{2-}$	0.01 M KCl, pH 2.37	2	0.47
	0.01 M KCl, pH 2.75	2	0.61
	0.05 M KCl, pH 2.37	2	0.96
	0.01 M KNO ₃ , pH 2.37	2	0.72

* the extraction equilibria present in simple term (without counter ions and subscript aq or org)

^a $\log [L]_{eq}$ cannot be obtained because $[L]_{eq} = [L]_{int} - 2[Cr(VI)]_{org}$ gives negative values.

From Tables 4.3 and 4.4, the experiment slopes close to the theory slopes are found for hypothesis 1 and 2. This suggests that these two equilibria might occur. The extraction constants of compound **1b**, K'_{ex1} and K'_{ex2} in equations 2 and 3, are summarized in Tables 4.5 and 4.6 for extraction equilibria 1 and 2, respectively. In addition, the extraction constants of compound **2b** for equilibria 3 and 4, K'_{ex3} and K'_{ex4} in equation 4 and 5, are shown in Tables 4.7 and 4.8, respectively.

Table 4.5 K'_{ex1} of Cr(VI) extraction with compound **1b**.

Conditions	$\log K'_{ex1}$	K'_{ex1}
50 ppm of K_2CrO_4 in 0.01 M KCl pH 2.37	2.64	4.43×10^2
50 ppm of K_2CrO_4 in 0.01 M KCl pH 2.75	3.90	8.06×10^3
50 ppm of K_2CrO_4 in 0.05 M KCl pH 2.37	3.68	4.84×10^3
50 ppm of K_2CrO_4 in 0.01 M KNO_3 pH 2.37	3.37	2.36×10^3

Table 4.6 K'_{ex2} of Cr(VI) extraction with compound **1b**.

Conditions	$\log K'_{ex2}$	K'_{ex2}
50 ppm of K_2CrO_4 in 0.01 M KCl, pH 2.37	3.49	3.14×10^3
50 ppm of K_2CrO_4 in 0.01 M KCl, pH 2.75	4.30	2.03×10^4
50 ppm of K_2CrO_4 in 0.05 M KCl, pH 2.37	3.81	6.49×10^3
50 ppm of K_2CrO_4 in 0.01 M KNO_3 , pH 2.37	3.45	2.86×10^3

Table 4.7 K'_{ex3} of Cr(VI) extraction with compound **2b**.

Conditions	$\log K'_{ex3}$	K'_{ex3}
50 ppm of K_2CrO_4 in 0.01 M KCl, pH 2.37	2.32	2.10×10^2
50 ppm of K_2CrO_4 in 0.01 M KCl, pH 2.75	2.65	4.56×10^2
50 ppm of K_2CrO_4 in 0.05 M KCl, pH 2.37	3.50	3.19×10^3
50 ppm of K_2CrO_4 in 0.01 M KNO_3 , pH 2.37	2.05	1.12×10^2

Table 4.8 K'_{ex4} of Cr(VI) extraction with compound **2b**.

Conditions	$\log K'_{ex4}$	K'_{ex4}
50 ppm of K_2CrO_4 in 0.01 M KCl, pH 2.37	3.72	5.27×10^3
50 ppm of K_2CrO_4 in 0.01 M KCl, pH 2.75	3.65	4.50×10^3
50 ppm of K_2CrO_4 in 0.05 M KCl, pH 2.37	3.85	7.18×10^3
50 ppm of K_2CrO_4 in 0.01 M KNO_3 , pH 2.37	2.14	1.38×10^2

According to Tables 4.3 and 4.4 it is shown that the experiment slopes of hypothesis 1 and 2 are close to the theory slopes for both compounds. Because of the slopes of nearly 1 at pH 2.37 and 2.75, this allows us to consider the extraction of 1:1 complexes. The anion extracted might be either HCrO_4^- or $\text{Cr}_2\text{O}_7^{2-}$. However, Cr(VI) anion can present in different forms depending on pH and its concentration of Cr(VI) as shown in Figure 4.10 [155].

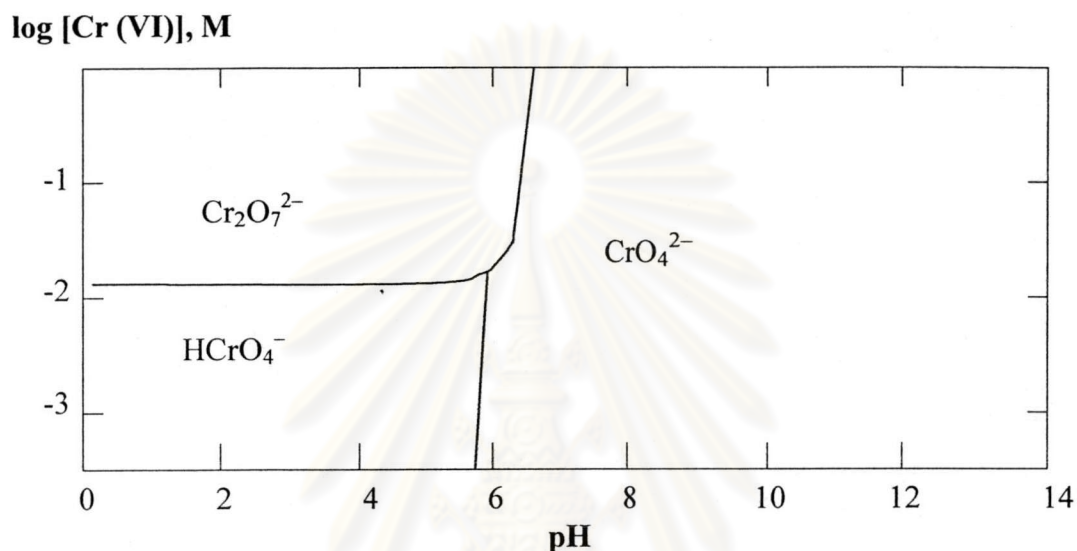


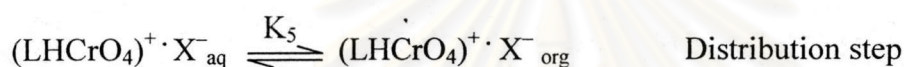
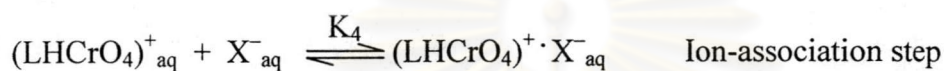
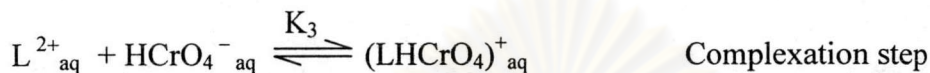
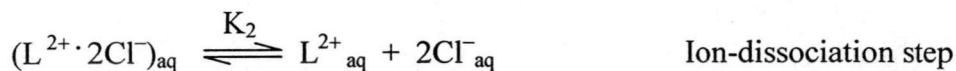
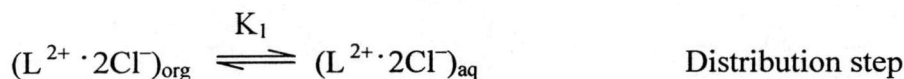
Figure 4.10 The different species of Cr(VI) anions in water as a function of pH and its concentration [155].

Figure 4.10 indicates that at pH 2.37 and 2.75 for the concentration of 0.257 mM of K_2CrO_4 ($\log [\text{Cr(VI)}] = -3.6$, condition used in this work), the majority of Cr(VI) is found in HCrO_4^- form. Therefore, the extraction equilibrium 1 and 3 (extracted species is extractant- HCrO_4^-) is likely to occur than the extraction equilibrium 2 and 4 (extracted species is extractant- $\text{Cr}_2\text{O}_7^{2-}$).

According to the aforementioned discussion in sections 4.1.2 and 4.1.6, and also the classification of solvent extraction system as described in sections 2.4.4.2.2 and 2.4.4.2.3, the possible assumption of extraction mechanism of HCrO_4^- or $\text{Cr}_2\text{O}_7^{2-}$ with the **1b** or **2b** could be proposed in many different cases as follows:

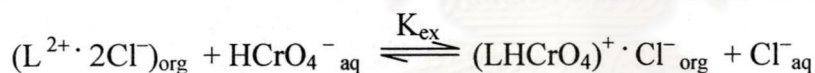
A. diprotonated form of compound 1b

(a) the extraction mechanism of HCrO_4^- might consist of 5 steps:



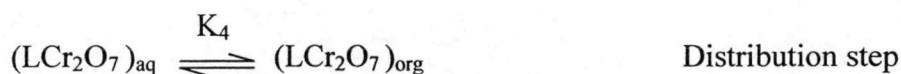
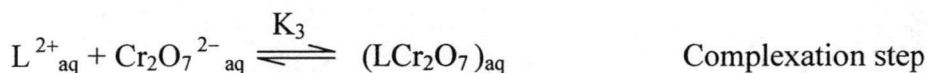
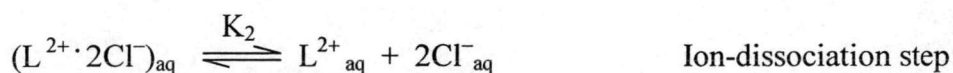
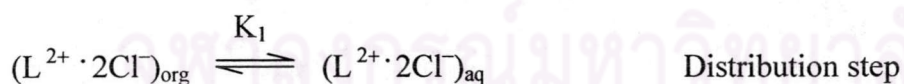
where X^- is Cl^- or NO_3^- .

Thus, The extraction equilibrium can be obtained:

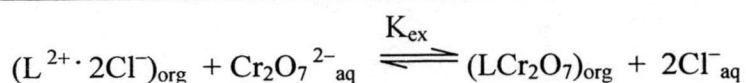


where the extraction constant, $K_{\text{ex}} = K_1 \times K_2 \times K_3 \times K_4 \times K_5$

(b) the extraction mechanism of $\text{Cr}_2\text{O}_7^{2-}$ might consist of 4 steps:



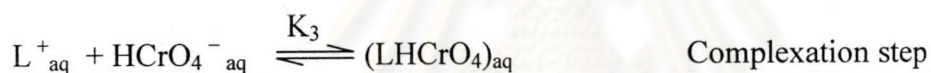
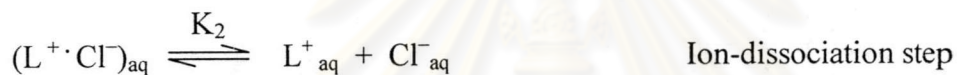
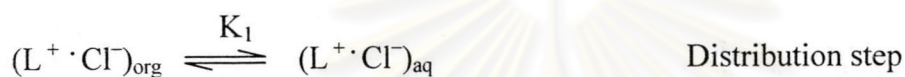
Thus, the extraction equilibrium can be obtained:



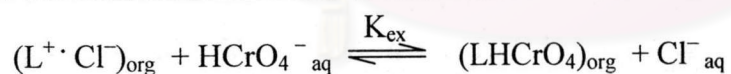
where the extraction constant, $K_{ex} = K_1 \times K_2 \times K_3 \times K_4$

B. monoprotonated form of compound 1b

(a) the extraction mechanism of $HCrO_4^-$ might consist of 4 steps:



Thus, the extraction equilibrium can be obtained:

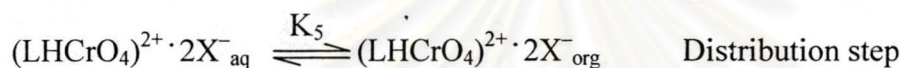
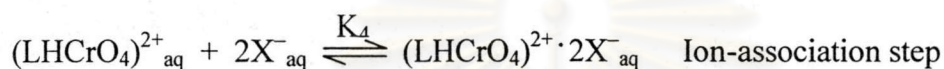
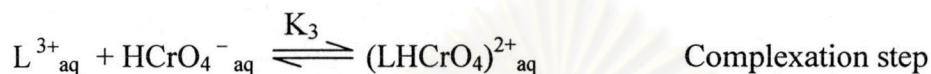
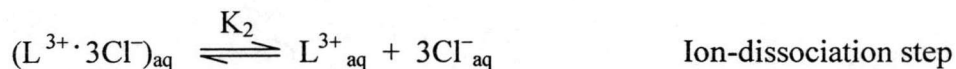
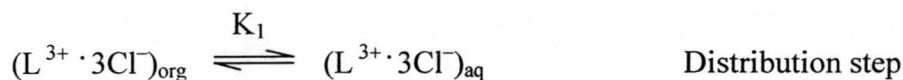


Where the extraction constant, $K_{ex} = K_1 \times K_2 \times K_3 \times K_4$

In case of extraction with **2b** the extraction mechanism could be proposed in similarly approach.

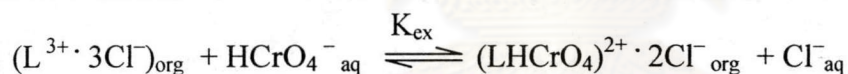
C. triprotonated form of compound 2b

(a) the extraction mechanism of HCrO_4^- might consist of 5 steps:



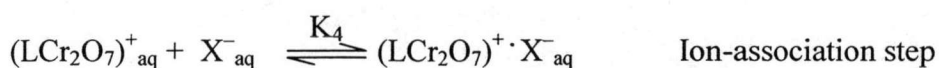
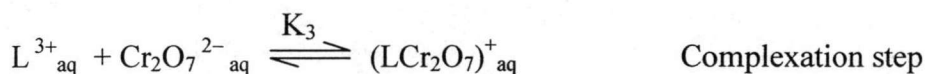
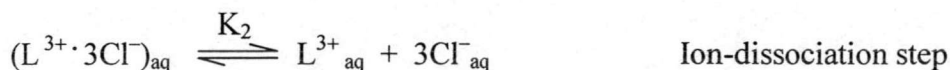
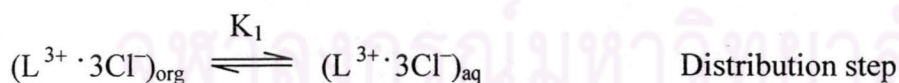
where X^- is Cl^- or NO_3^-

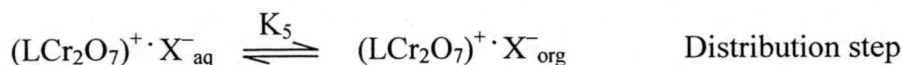
Thus, The extraction equilibrium can be obtained:



where the extraction constant, $K_{\text{ex}} = K_1 \times K_2 \times K_3 \times K_4 \times K_5$

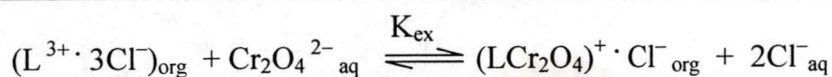
(b) the extraction mechanism of $\text{Cr}_2\text{O}_7^{2-}$ might consist of 5 steps:





where X^- is Cl^- or NO_3^-

Thus, The extraction equilibrium can be obtained:



where the extraction constant, $K_{\text{ex}} = K_1 \times K_2 \times K_3 \times K_4 \times K_5$

D. diprotonated form of compound 2b

The extraction mechanism of HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ might consist of 5 and 4 steps respectively, similar to the case of diprotonated form of **1b**.

Although this result shows no evidence to predict the accurate extraction equilibrium, it is viable to use these extractants for the phase transfer of Cr(VI) anion.

4.1.7 Recycling of Ligand

The purpose of this study is to prove that compounds **1b** and **2b** can be reused several times. The experiment was carried out with equivalent molar concentrations of 2.57×10^{-4} M of extractants and K_2CrO_4 solution in 0.01M KCl solution at initial pH 2.37 ± 0.01 . The equal volume of aqueous and organic phase was used.

The stripping process was performed by using 0.01 M NaOH in order to migrate Cr(VI) anion back into aqueous phase. The stripped extractant was protonated by 0.02 M HCl solution in order to regenerate the extractant for reuse. The extraction time for each cycle was 30 min and the stripping and protonation time was 60 min,

which was longer than the extraction time to ensure that the equilibrium of stripping and protonation was reached (more details described in section 3.5.1).

The extraction percentages of Cr(VI) after several extraction and stripping cycles with compound **1b** and **2b** were shown in Figure 4.11. The data calculated for these two graphs are shown in Tables A.7a and A.7b in the appendix.

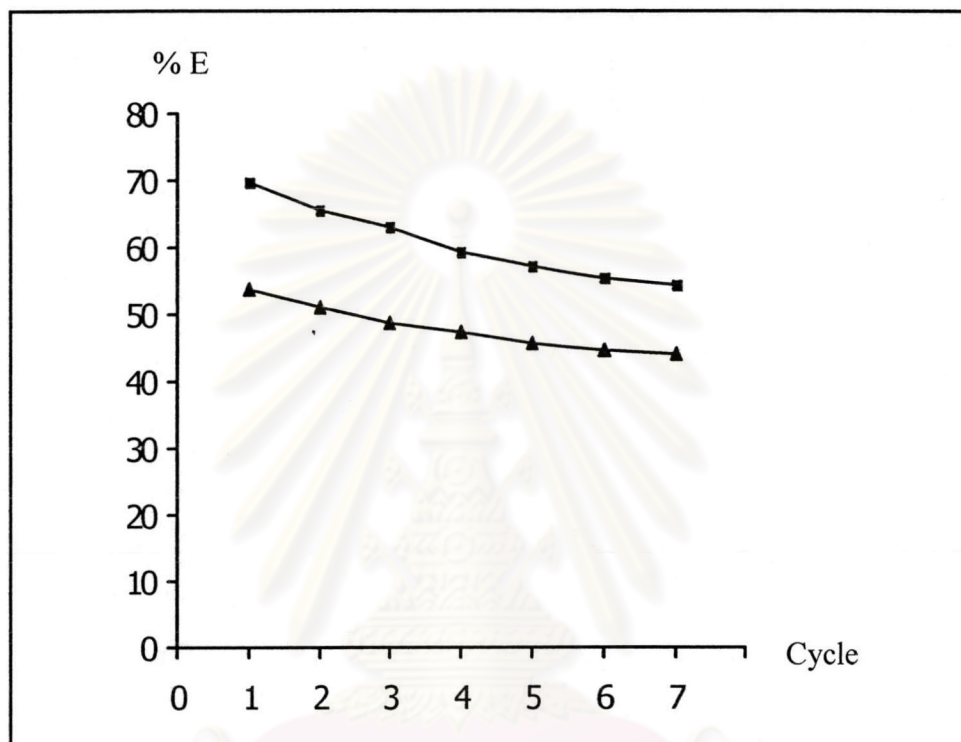


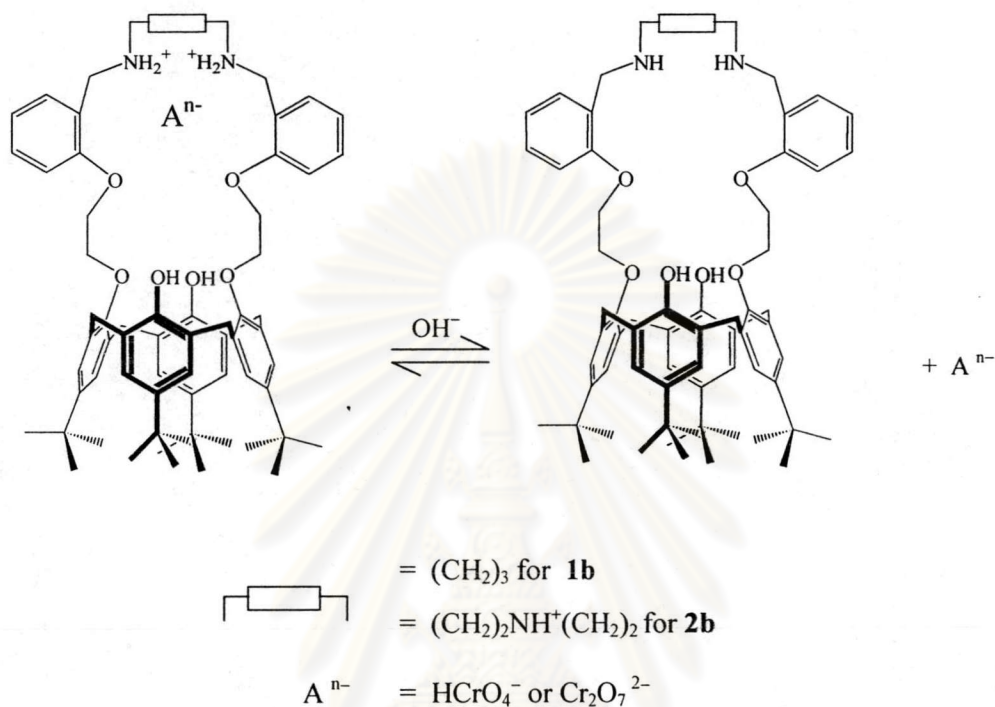
Figure 4.11 Results of 7 extraction cycles of 0.257 mM K_2CrO_4 in 0.01 M KCl at initial pH 2.37 ± 0.01 using 0.01 M NaOH as strippant.

(▲) = **1b**, and (■) = **2b**.

The extraction percentage of 54-44 and 70-54 were obtained from 7 extraction cycles for compounds **1b** and **2b**, respectively. It means that the extraction efficiency decreases with increasing number of extraction cycle. In addition, the decreasing of extraction percentages of compound **1b** is slightly than compound **2b**. However, both extractants retained quite high extraction ability at 7 extraction cycles.

The decreasing of extraction percentages with increasing number of extraction cycles could ascribe to the stripping efficiency seen from recovery percentage. (87 % and 65 % for compound **1b** and compound **2b**, respectively) (see table A.7a and A.7b in appendix) The higher recovery percentage of Cr(VI) was found for compound **1b**,

indicating that Cr(VI) was released from compound **1b** more than **2b**. This can be explained by the deprotonated calixarenes, resulting from the addition of NaOH to the aqueous phase, which were no longer effective host molecule for Cr(VI) as shown in the following equilibrium:



However, the partial deprotonated forms of **1b** and **2b** might occur depending on their protonation constants. These forms containing positive charge were effective host for Cr(VI). So, the recovery percentage < 100 % were obtained.

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4.2 Solid-phase Extraction Studies

4.2.1 Extraction by SiO₂ (Blank Test)

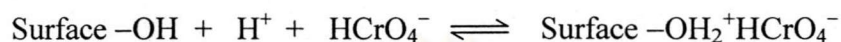
The extractions of Cr(VI) anions with 0.01-1.0 g SiO₂ in the absence of the extractant (conditions described in section 3.3.2.1) were investigated. The extraction results are shown in Table 4.9.

Table 4.9 Extraction percentages of Cr(VI) by SiO₂.

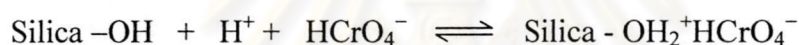
Extraction time (min)	Weight of SiO ₂ (g)	[CrO ₄ ²⁻] _{int} (ppm)	pH int.	pH final	[CrO ₄ ²⁻] _{aq} (ppm)	% E
30	0.0171	53.70	2.38	2.38	56.49	0
30	0.0330			2.39	54.21	0
30	0.2005	50.27	2.38	2.50	50.32	0
60	0.2007			2.56	50.38	0
30	0.5002			2.93	45.65	9.19
60	0.5003			2.96	45.64	9.21
30	1.0006	49.70	2.37	3.30	41.93	15.63
30	1.0008			3.32	41.98	15.53
30	1.0018	48.27	2.38	3.34	40.98	15.10
30	1.0018			3.35	40.96	15.14
60	1.0008	49.70	2.37	3.39	42.32	14.85
60	1.0007			3.37	42.36	14.77
60	1.0018	48.27	2.38	3.42	41.07	14.92
60	1.0018			3.42	41.06	14.94

The results show no significant extraction for 0.01-0.20 g SiO₂. The extraction percentages of 9.2 and ~15 were obtained for 0.5 and 1.0 g SiO₂, respectively, where the number of moles of SiO₂ were > 3,000- fold over that of K₂CrO₄.

These results suggest that SiO₂ has little ability to extract Cr(VI) anions. Nevertheless, as described in section 2.2.2.4, chromate ions can sorb to mineral solids that have hydroxyl groups exposed on their surface as follows:

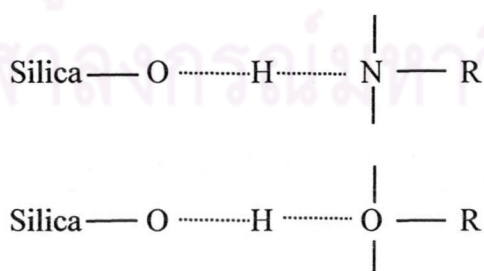


Thus, it could be concluded that chromate ions sorb to SiO₂ because the surface chemistry of silica is dominated by the presence of hydroxyl groups commonly referred to as silanols (see section 2.5.1). In addition, as the extraction was done in acidic condition (pH 2.37), Therefore, the equilibrium of chromate ion sorb to silica could be provided as follows:



4.2.2 Extraction with Ligand Coated on SiO₂

A possible assumption of interaction between the calixarenes and SiO₂ is the hydrogen bonding because free silanol groups on silica can attract amine, hydroxyl groups or ethoxy group (as described in section 2.5.1) giving the calixarenes coated on SiO₂.



where means the hydrogen bond interaction.

The effect of extraction time in the extraction of K_2CrO_4 (5 mL of 0.257 mM or 1.28×10^{-6} mole) from 0.01 M chloride medium at initial pH 2.37 ± 0.01 by ligand **1b** and **2b** coated on SiO_2 was investigated. The ligand capacity and the number of moles of ligand used in the extraction are summarized in Table 4.10. The extraction results are shown in Figure 4.10. (More details of the data, see Tables B.1b, B.2a, B.2b, B.2c, and B.2d in the appendix.)

Table 4.10 The ligand capacity and moles of ligand used in the extraction.

Compound*	Ligand loading ^a in SiO_2 ($\mu\text{mole/g}$ of SiO_2)	Ligand capacity ^b ($\mu\text{mole/g}$ of compound)	Weight of ligand coated SiO_2 used (g)	Mole $\times 10^{-6}$
1b-LC	36	34.7	0.0369 ± 0.0001	1.28 ± 0.01
1b-HC	105	94.5	0.0138 ± 0.0001	1.30 ± 0.01
2b-LC	40	38.3	0.0334 ± 0.0001	1.28 ± 0.01
2b-HC	149	127.6	0.0102 ± 0.0001	1.30 ± 0.01

Remark: mw. of **1b** = 1060.28 and **2b** = 1125.78

*Ligand coated on SiO_2 , LC = Low Capacity, HC = High Capacity.

^a Calculated by:

$$\text{Ligand loading in } SiO_2 = \frac{\text{mole of ligand loading in } SiO_2}{\text{Weight of } SiO_2 \text{ used}}$$

^b Calculated by:

$$\text{Ligand capacity} = \frac{\text{mole of ligand loading in } SiO_2}{\text{Weight of } SiO_2 \text{ used} + \text{Weight of ligand used}}$$

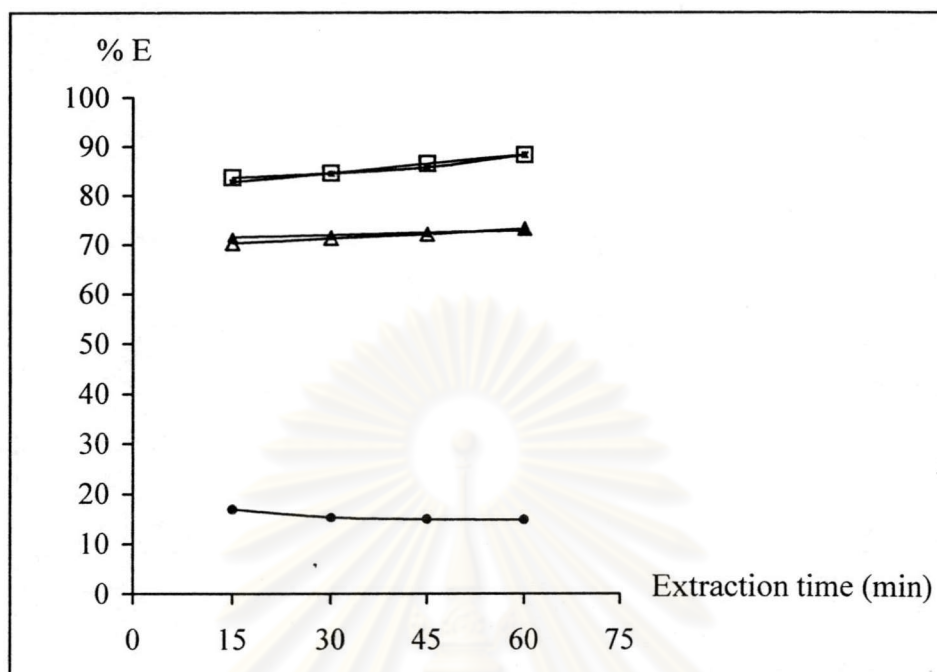


Figure 4.12 Effect of extraction time on extraction percentages of Cr(VI) for SPE.

(●) = SiO₂, (Δ) = **1b**-LC, (▲) = **1b**-HC, (□) = **2b**-LC, (■) = **2b**-HC.

Considering compound **1b**, either low capacity or high capacity, the extraction percentage curves show no difference of extraction ability. Compound **2b** shows similar phenomenon. It is clear that compound **2b** is more effective to extract Cr(VI) anion than compound **1b**.

The extraction percentage curves show no significant change with increasing extraction time. Thus, an extraction time of 15 min was sufficient to reach equilibrium.

It is interesting that the results show extraction behaviors of compounds **1b** and **2b** correspond with the results of LLE in section 4.1.3. It means that both compounds showed similar characteristic of Cr(VI) extraction ability either in LLE or SPE. However, two remarks are noted:

- (1) The equilibrium time in SPE was less than in LLE, and
- (2) The extraction percentages of both compounds in SPE were higher than in LLE.

These can be explained as follows:

- (1) HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ accessibility. When the calixarenes are coated on solid support, they have enormous surface area to contact the aqueous phase. This environment can provide a higher accessibility of HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ than that of calixarene in liquid phase.
- (2) The hydrophilic influence of liquid or solid matrix environment. The calixarenes coated on SiO_2 have more hydrophilic environment because the surface chemistry of silica is dominated by the presence of silanol groups. In contrast, calixarenes present in chloroform have more hydrophobic environment, therefore the distributions of HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ to the calixarenes in silica environment were higher than in chloroform environment because it is well known that the anions favor hydrophilic conditions.

4.2.3 Recycling of Ligand Coated on SiO_2

The purpose of this study is to prove that compounds **1b** and **2b** coated on SiO_2 can be reused several times. The results are shown in Figure 4.13. (More details of the data from graphs: see Tables B.3a and B.3b in the appendix.)

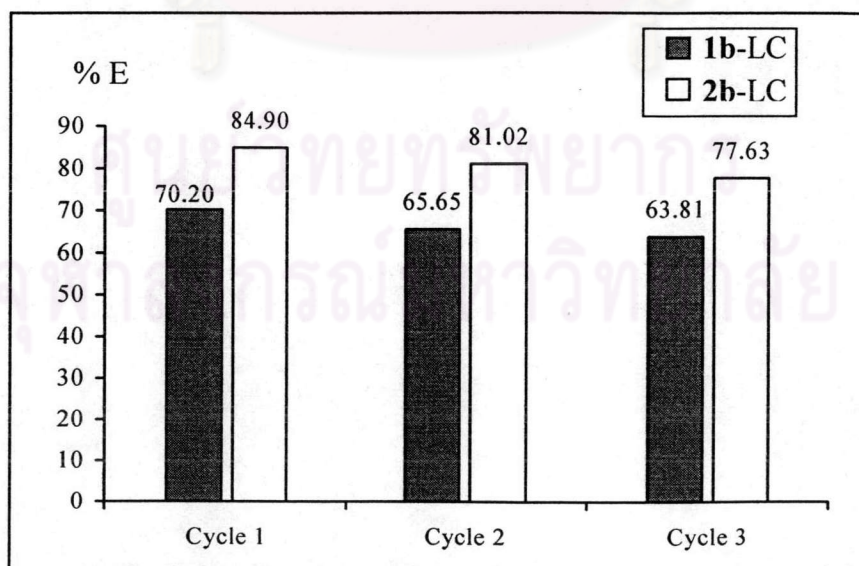


Figure 4.13 Results of three extraction cycles for SPE.

When the stripped extractants was reused for Cr(VI) extraction, the extraction efficiency decreased with increasing number of recycling times. However, after three extraction cycles, both extractants retained quite high extraction ability. The decreasing of extraction percentages with increasing numbers of extraction cycles could be explained by the same reason as in section 4.1.7.

Fortunately, the results shows that compounds **1b** and **2b** coated on SiO₂ can be reused several times and retains high extraction ability.

4.2.4 Leaching of Ligand from SiO₂ by Chloroform

To test the strength of the hydrogen bonding interaction between the calixarenes and SiO₂, 0.05 g of compounds **1b**-HC and **2b**-HC were agitated with chloroform at different time. The results are shown in Figure 4.14. (More details of the data see table B.4a and B.4b in the appendix.)

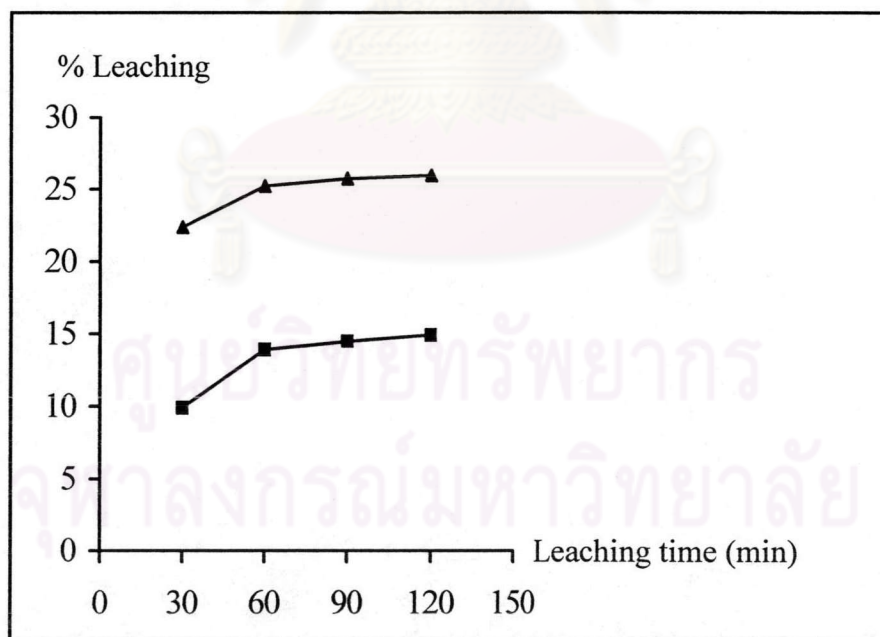


Figure 4.14 Leaching percentage of compounds **1b**-HC and **2b**-HC by chloroform.

(▲) = **1b**-HC, and (■) = **2b**-HC.

Consider both compounds, the leaching percentage curves increased sharply from 30 to 60 min and slightly increased with the time after 60 min. The results indicates that the leaching time of 60 min is sufficient to reach the leaching equilibrium.

Comparing both compounds, it is clear that compound **1b** has weaker hydrogen bonding interaction than compound **2b** because it had higher leaching percentage while compound **2b-HC** had higher ligand capacity. (See Table 4.10: ligand capacity of compound **1b-HC** and **2b-HC** were 94.5 and 127.6 $\mu\text{mole/g}$, respectively.)

Although the results shows that compounds **1b** and **2b** can be leached from SiO_2 , leaching percentages are low. (% Leaching < 26 and <15 for compound **1b-HC** and **2b-HC**, respectively. See table B.4a and B.4b in appendix.)

It is found that the extraction properties (SPE) of compounds **1b** and **2b** could be developed for other applications such as the preconcentration of Cr(VI) in waste water.



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