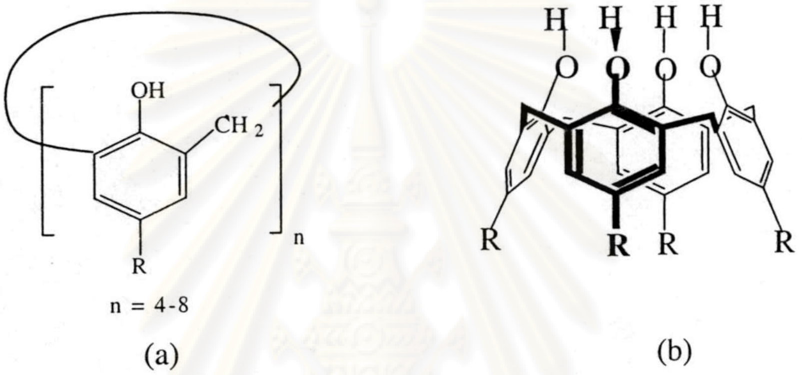
CHAPTER II

THEORY AND RELATED RESEARCH

2.1 Calixarenes

Calixarenes are macrocycles that made up of phenolic units meta-linked by methylene bridge [43] and possessing basket-shape cavities as shown in Figure 2.1.



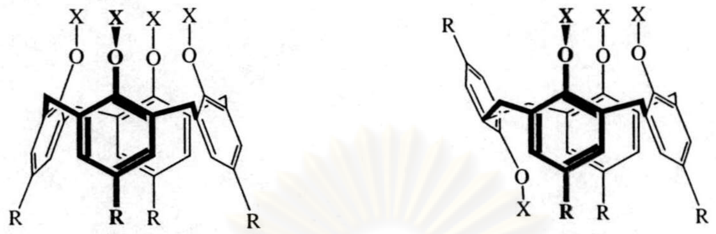
(a) (b)

Figure 2.1 General formula of calixarenes (a) and calix[4]arene (b).

The name "Calixarene" is given by Gutsche [44]. The word "calix" comes from chalice (in Greek : calix) and "arene" represents aryl rings in the molecular framework. Calixarenes can be prepared by base-catalyzed condensation of *p*-substituted phenol with formaldehyde [45]. Most common calixarenes have a number of phenol groups equal to 4, 6, or 8 while odd-number ring calixarenes are less studied due to the difficulty of their syntheses. Calixarenes have become one of the most attractive building blocks in supramolecular chemistry because they can be modified to gain numerous types of molecular receptors by many chemical reactions. The modification can be introduced at OH groups (which called "lower rim"), methylene bridge carbon or para position of aromatic ring (which named "upper rim") [13, 46-48].

The smallest member of calixarenes is calix[4]arene which has 4 phenolic units. Calix[4]arene is useful building blocks for host molecules with different properties [44], which are strongly influenced by the conformation of calix[4]arenes

[49]. Functionalization at lower rim of calix[4]arene with bulky substituents prevents the interconversion among the four conformations: cone, partial cone, 1,2-alternate and 1,3-alternate [50] as shown in Figure 2.2. The most stable conformation of calix[4]arenes is cone conformation because of intramolecular hydrogen bonding.



Cone

Partial cone

1, 2-Alternate

1, 3-Alternate

Figure 2.2 Four conformations of calix[4]arenes.

Modified calixarenes as anion receptors can be classified upon their functional groups such as amine or ammonium based anion receptors, amide based anion receptors, imine based anion receptors, or urea and thiourea based anion receptors.

2.1.1. Amine Based Anion Receptors

Aeungmaitrepirom W. and co-workers [42] have studied the solvent extraction of selenate and chromate using a diaminocalix[4]arene (calixarene **1**, Figure 2.3) in chloroform that was demonstrated to lead to an extraction of Se(VI) at pH 2.6 from a sodium chloride medium with a good selectivity over Cr(VI). The results showed that the extraction of divalent anions was favored compared to monovalent anions. The extraction order was $S_2O_3^{2-} > SeO_4^{2-} \approx SO_4^{2-} > HCrO_4^- > NO_3^-$ and no extraction of $H_2PO_4^-$, $H_2AsO_4^-$ and $HSeO_3^-$ was observed for all ligand concentration. An increase of pH or an addition of 5% or 10% decanol in chloroform favored the extraction of SeO_4^{2-} over $HSeO_4^-$ but led to a drastic decrease of selenium extraction.

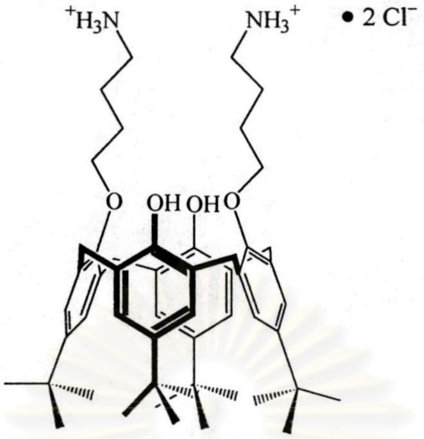


Figure 2.3 5, 11, 17, 23-tetra-*p-tert*-butyl-25,27-bis{butylammonium chloride-oxy}-26, 28-dihydroxy-calix[4]arene dichloride (calixarene **1**).

Tomapatanaget B. and co-workers [51] have investigated the complexation studies between an ammonium derivative of diaza benzo-crown ether-*p-tert*-butylcalix [4]arene (calixarene **2**, Figure 2.4) and some anions such as NO_3^-, CO_3^{2-}, PO_4^{3-}, CH_3COO^- and $C_2O_4^{2-}$ by ^1H NMR spectroscopy. It was found that only NO_3^- could form complex with this ligand. Because of hydrolysis of the other anions in aqueous solution, the generated OH^- would react with protons of the ammonium derivative. So, this ligand could not form complexes with other anions.

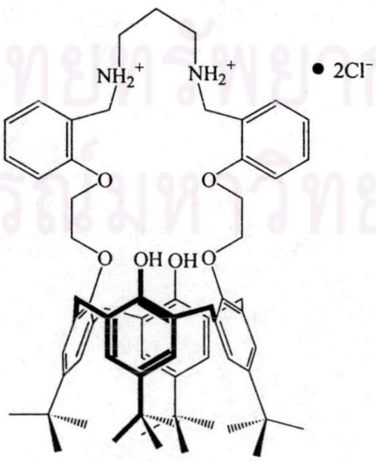


Figure 2.4 25, 27-*N, N*-di-((2-ethoxy)benzyl) propylenediamine-*p-tert*-butylcalix[4] arene dichloride (calixarene **2**).

Rojsajjakul T. and co-worker [52] have synthesized polyaza crown ether derivatives of calix[4]arene (calixarenes **3** and **4**, Figures 2.5 and 2.6). The anion complexation studies were carried out using ^1H - NMR spectroscopy. It was found that the anion selectivity of the calixarene **3** varied as follows: $CO_3^{2-} > NO_3^- > AsO_2^- > Cl^-$. The complex formation was found as 1:1 ratio. However, the synthesized calixarene **4** which contained methyl group on nitrogen atoms instead of protons did not show any sign of anion complexation as found in the precursor calixarene **3**. The result indicated that either hydrogen bonding between host-guest played an important role in this study or the steric hindrance form the methyl group might prohibit the inclusion of anions in calixarene **4**.

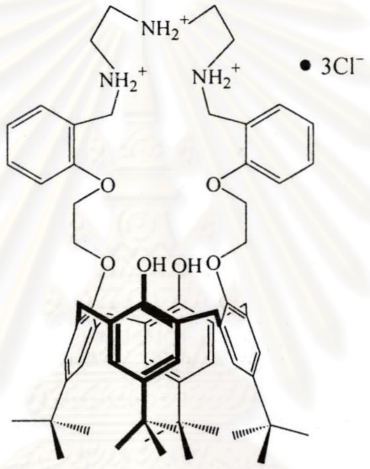


Figure 2.5 25, 27-{2, 2'- [2,2'- ((2,5,8-triammonium)nonyl)diphenxyl]diethyl}-*p*-*tert*-butylcalix[4]arene trichloride (calixarene **3**).

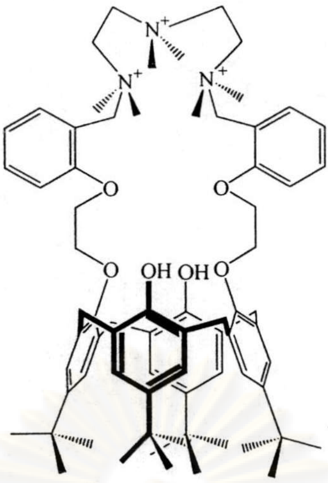


Figure 2.6 25, 27-{2, 2'- [2,2'- ((2,5,8-dimethylammonium)nonyl)diphenxyl] diethyl}-*p-tert*-butylcalix[4]arene (calixarene **4**).

Georgiev E.M. and co-workers [53] have synthesized a lower rim alkylammonium-substituted calix[4]arene (calixarene **5**, Figure 2.7) as extractant for both CrO_4^{2-} and $Cr_2O_7^{2-}$ from an aqueous solution into a chloroform layer. Furthermore, the extraction of CrO_4^{2-} and $Cr_2O_7^{2-}$ by the alkylammonium salts of butylamine, *N, N*-dimethylbutylamine, tributylamine, ethylenediamine and *N,N,N',N'*-tetra-methylethylenediamine were not observed. However, when the protonated alkylammonium salt of calixarene **5** was added, extraction of CrO_4^{2-} and $Cr_2O_7^{2-}$ into the chloroform layer occured. At ratios of CrO_4^{2-} : calixarene **5** of 1:0, 1:1, 1:2 and 1:20 the partition coefficients were 0, 0.5, 1.0 and 80, respectively. The extraction of CrO_4^{2-} and $Cr_2O_7^{2-}$ into chloroform by calixarene **5** in the presence of a ten-fold excess of Cl^- , SO_4^{2-}, CH_3COO^- , $H_2PO_4^-$, NO_3^-, $MoO_4^{2-}$and WO_4^{2-} has been investigated. The result showed that the monoanions with the exception of $H_2PO_4^-$ and the dianions had little effect on the extraction of CrO_4^{2-} and $Cr_2O_7^{2-}$. Moreover, according to addition of NaOH to the aqueous layer, the deprotonated calixarene **5** in the chloroform was no longer an effective host molecule for CrO_4^{2-} and the dianions then migrated back into the aqueous layer in a reversible process as show in equation 1.

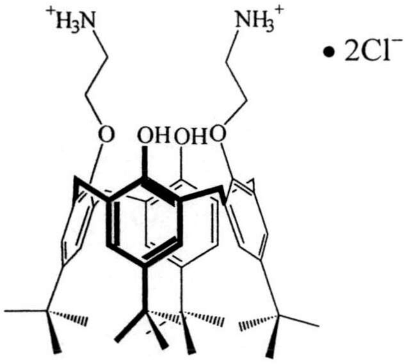
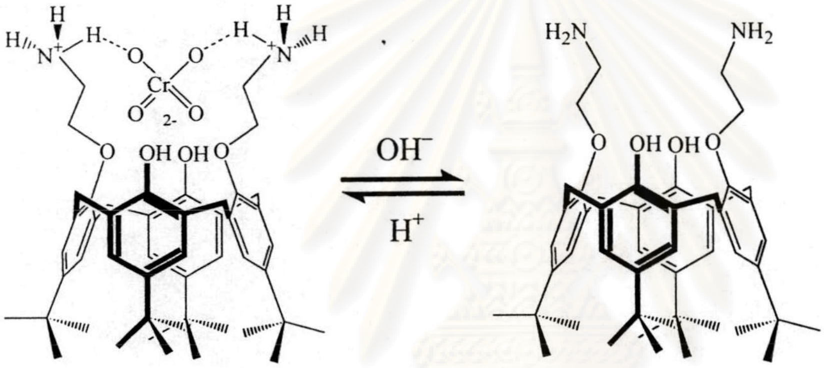


Figure 2.7 5, 11, 17, 23-tetra-*tert*-butyl-25, 27-bis(2-aminoethoxy)-26, 28, dihydroxycalix[4]arene bis hydrochloride (calixarene **5**).



+ CrO_4^{2-} …….(1)

Wolf N. J. and co-workers [7] have synthesized and studied the extraction ability of amine and carbamoyl substituted calix[4]arenes (calixarenes **6-12**, Figure 2.8) for the anions HPO_4^{2-}, SeO_4^{2-}, VO_3^-, ReO_4^-, CrO_4^{2-}, WO_4^{2-} and MoO_4^{2-} from water into a chloroform layer. The remaining metal content in the aqueous layer was measured by ICP-AES.

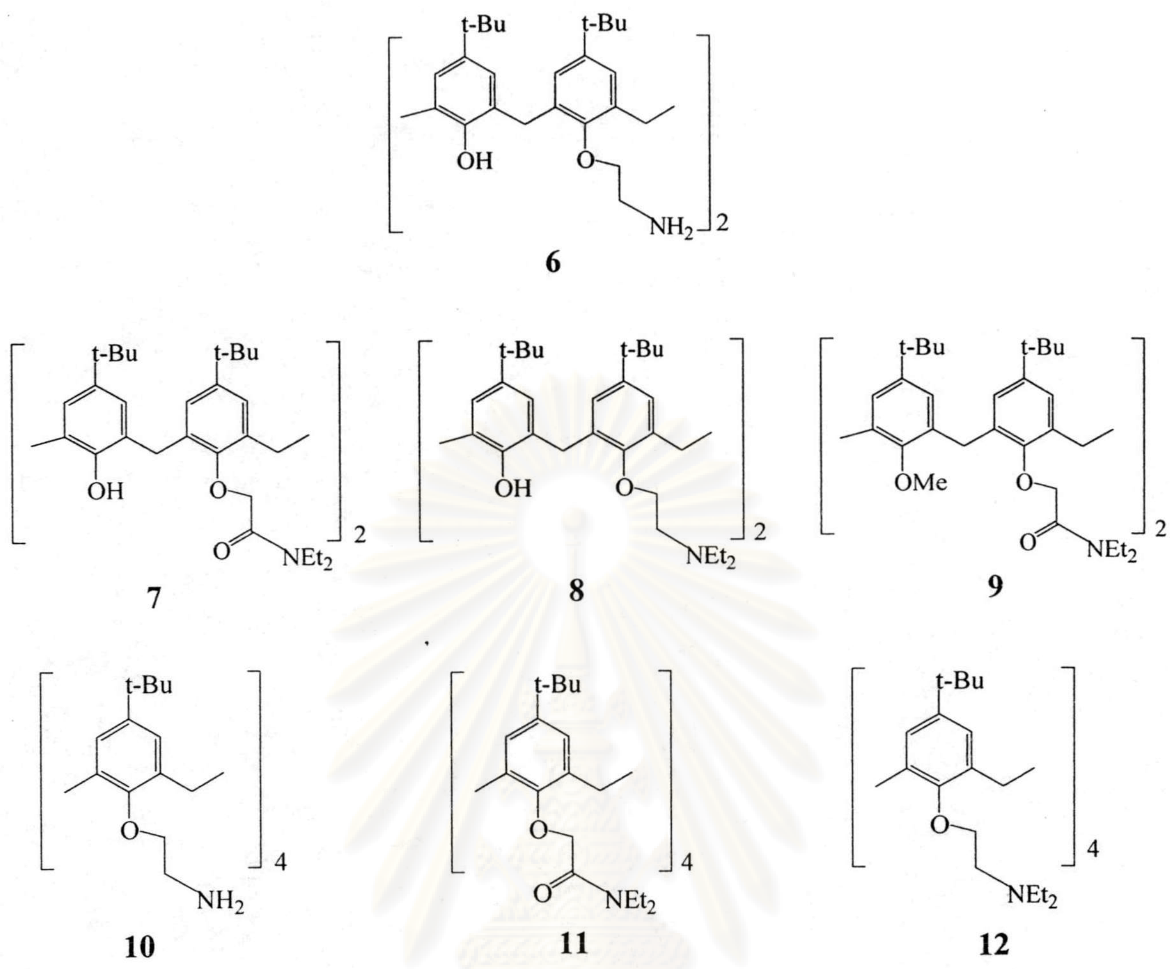


Figure 2.8 Structures of amine and carbamoyl substituted calix[4]arenes (calixarenes **6-12**).

The extraction studies under pH 0.85 and 7.0 showed that there was a higher level of extraction at the lower pH, which correlated with the protonated forms being the better extractants. However, the extraction of both HPO_4^{2-} and VO_3^- with all amines (with the exception of calixarene **8**) demonstrated that the protonated form was a poorer extractant than was the unprotonated form. In addition, the highest extraction percentages of all extractants for all anions were found at pH 7, amine **10** being the most effective. This indicated higher extraction ability in their unprotonated form. Since calixarene **10** has four 2-aminoethoxy substituents on the lower rim, the high extraction across the range of oxyanions tested may results from the presence of multiple amine sites for hydrogen bonding. Furthermore, the more hydrophobic *N, N*-diethyl substituted derivatives (calixarenes **8** and **12**) are not consistently better extractants than the unsubstituted derivatives (calixarenes **6** and **10**). Moreover, the results generally show that the calix[4]arene amines are better extractants than the calix[4]arene amides.

2.1.2. Amide Based Anion Receptors

Falana O.M. and co-workers [54] have synthesized dicarbamoyl butylcalix[4]arene derivatives (calixarenes **13-15**, Figure 2.9) and studied geometric and conformational effects of extraction ability for $Cr_2O_7^{2-}$ and $HSeO_4^-$ at pH 0.85. The concentration of Cr and Se was determined by ICP-AES.

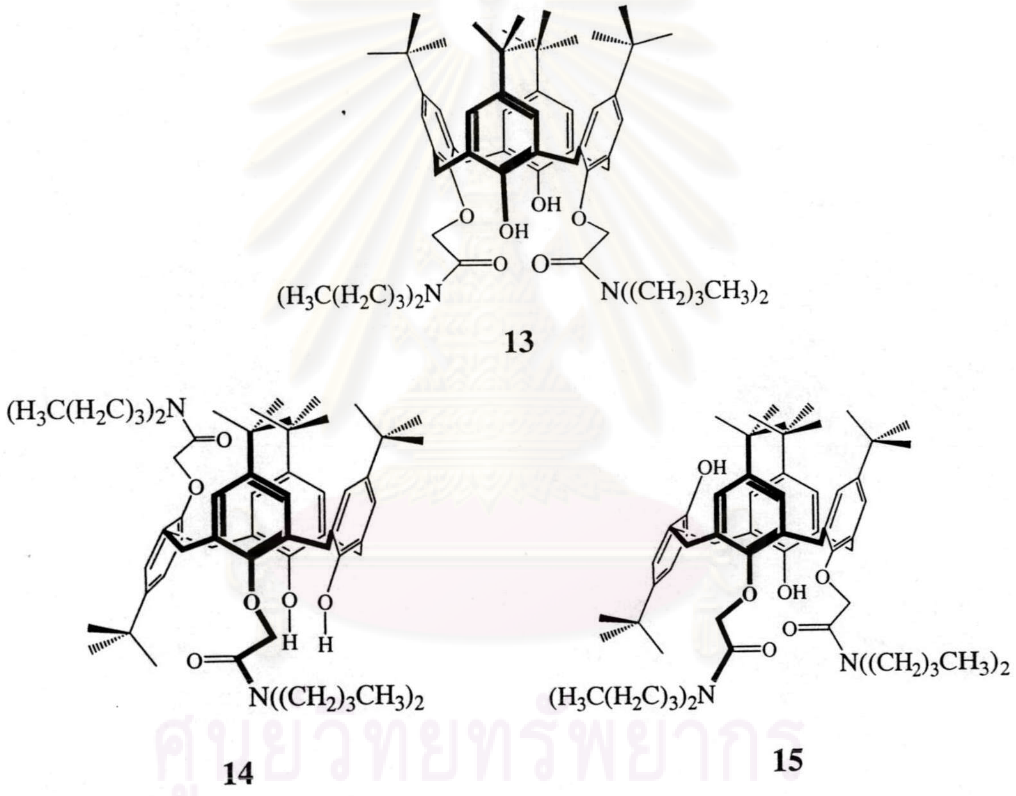
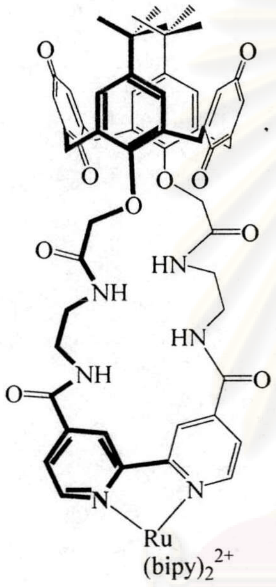


Figure 2.9 Structure of (dibutylcarbamoyl)methoxy-*tert*-butylcalix[4]arene derivatives (calixarenes **13-15**).

The results showed that calixarenes **13-15** were able to extract $Cr_2O_7^{2-}$ from water into toluene layer while calixarene **14** and **15** were able to extract $HSeO_4^-$. Unfortunately, the extraction studies from water into isooctane layer found that these three calixarene derivatives were not able to extract $Cr_2O_7^{2-}$. However, only calixarene **15** could extract $HSeO_4^-$ into isooctane layer.

Beer P.D. and co-workers [55] have synthesized the ruthenium(II) and rhenium(I) bipyridyl calix[4]diquinone receptors (calixarenes **16-17**, Figure 2.10). The results showed that these molecules selectively bound and sensed acetate anions via a remarkable luminescent emission intensity retrieval effect. Acetate addition to receptor **16** in acetonitrile caused a 500% emission intensity increase. This suggests that anion binding inhibited intramolecular oxidative electron transfer between the ruthenium(II) bipyridyl and calix[4]diquinone centers that would otherwise quench the emission.



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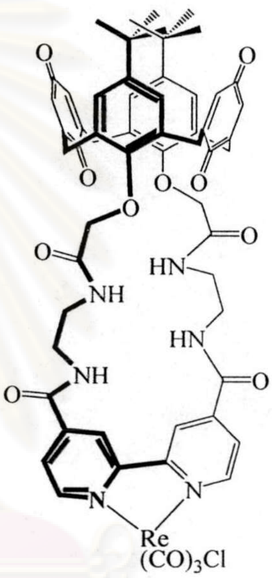

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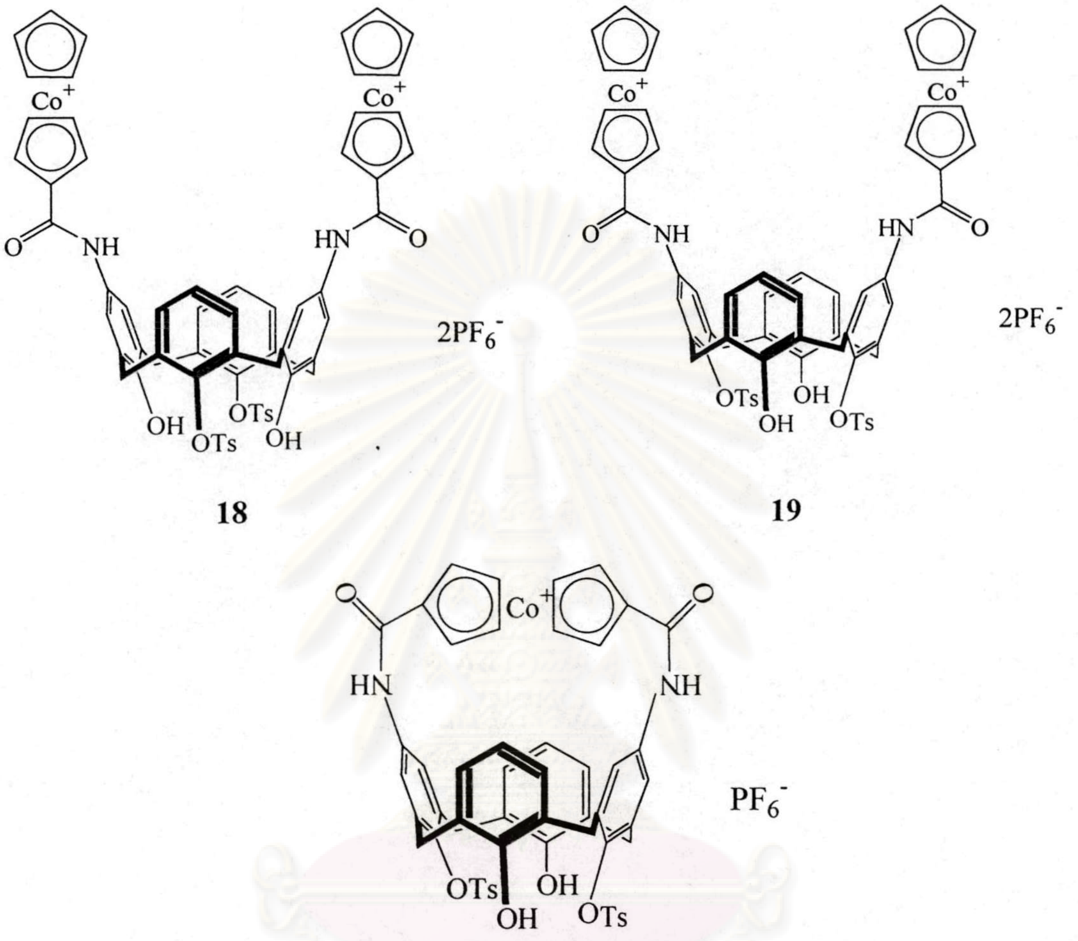
Figure 2.10 Structure of ruthenium(II) and rhenium(I) bipyridyl calix[4]diquinone receptors (calixarenes **16-17**).

Three upper-rim cobaltocenium calix[4]arene receptors (calixarenes **18-20**, Figure 2.11) have been synthesized by Beer P.D. and co-workers [56]. ^{1}H-NMR titration studies in deuterated dimethyl sulfoxide revealed that the isometric receptors **18** and **19** formed strong complexes with CH_3COO^- and $H_2PO_4^-$ anions dependent upon the positioning of lower-rim tosyl substituents. For example calixarene **18** displayed the selectivity trend $CH_3COO^- >> H_2PO_4^-$ whereas the selectivity preference was reversed with isomeric **19**. Cobaltocenium bridged calix[4]arene **20** formed thermodynamically stronger anion complexes with $MeCOO^-$ and $H_2PO_4^-$ anions than either **18** or **19**.



18 **19**

20

Figure 2.11 Structure of upper-rim cobaltocenium calix[4]arene receptors (calixarenes **18-20**).

A step forward in the field of ion complexation is the design and synthesis of heteroditopic receptors, which are able to complex simultaneously with cation and anion either as ion-pair or as free ion [57-59]. For example, Casnati A. and co-worker [60] have synthesized a heteroditopic calix[4]arene receptor (calixarene **21**, Figure 2.12) in 1,3-alternate conformation bearing two pentafluorophenyl amide group as anion binder and a crown-5 polyether for cation complexation. Surprisingly, in the presence of potassium acetate it formed an unusual 2:2:2 (ligand:cation:anion) complex, whose structure has been elucidated by x-ray crystallography.

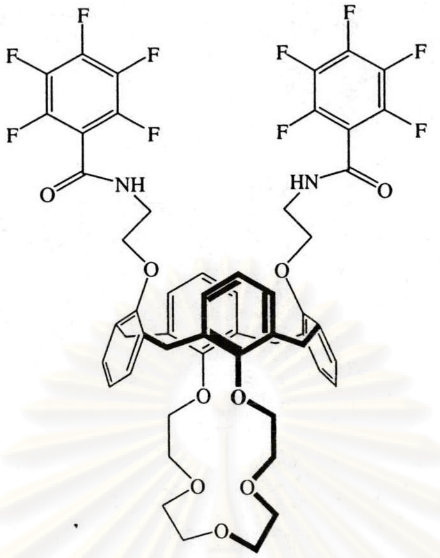
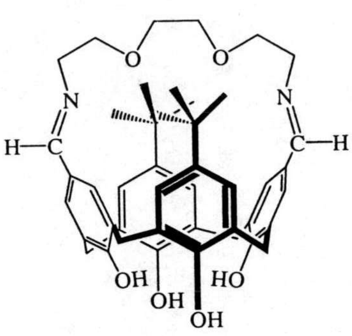


Figure 2.12 Structure of a heteroditopic calix[4]arene receptor (calixarene **21**).

2.1.3. Imine Based Anion Receptors

Yilma A. and co-workers [61] have synthesized two new calix[4]arene-bases azacrown ionophores (calixarenes **22-23**, Figure 2.13). The binding efficiencies of the extractants by solvent extraction of $Na_2Cr_2O_7$ from water into dichloromethane at different pH values were studied. They found that the introduction of two ester groups onto the 1,3-position of lower rim of calixarene **22** increased its extraction ability for $Cr_2O_7^{2-}$. The extraction efficiency of calixarene **23** was quite high at low pH due to protonation of the imine group.



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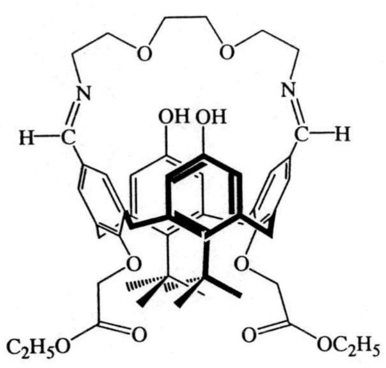
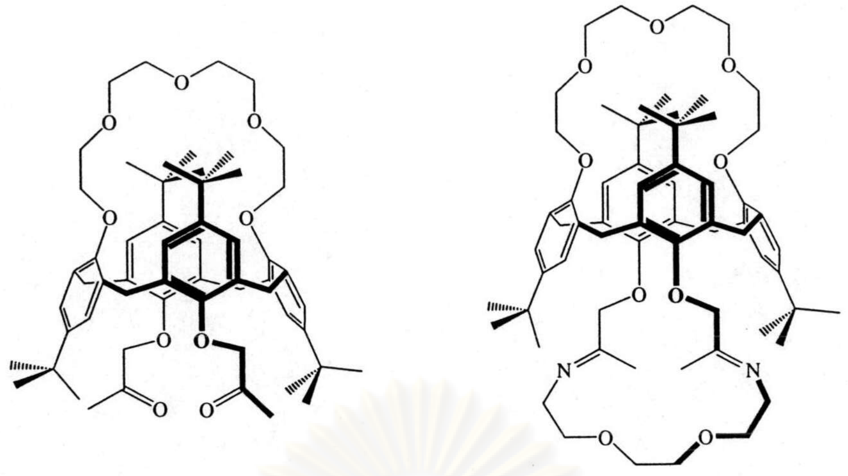


23

Figure 2.13 Structure of calix[4]arene-bases azacrown ionophores (calixarenes **22** and **23**).

Memon S. and co-workers [62] have synthesized two new 1,3 - alternate calix [4]arenes based bifunctional receptors (calixarenes **24-25**, Figure 2.14) for alkali or transition metal cations and $Cr_2O_7^{2-}$ anion from aqueous phase into dichloromethane. The complexation studies showed that calixarene **25** was an excellent receptor for both alkali and transition metal cations as compared to calixarene **24**. The higher complexation property of the ionophore **25** was due to the presence of hard and soft binding sites in its molecule (crown ether and azacrowns). Moreover, the receptor **25** was more effective for the extraction of $Cr_2O_7^{2-}$ anion as compared to the receptor **24** because receptor **25** contained a Schiff-base type cyclic binding site that was appropriate for aggregation of anions. The extraction property was enhanced in acidic medium, showing that the protonated form of receptor **25** was an effective host for $Cr_2O_7^{2-}$ anion.



24 **25**

Figure 2.14 Structure of 1,3 - alternate conformation calix[4]arene based bifunctional receptors (calixarenes **24** and **25**).

2.1.4. Urea and Thiourea Based Anion Receptors

Nam K.C.and co-workers [63] have synthesized calix[4]diquinone with appended urea groups (calixarene **26**, Figure 2.15). It has been shown to be selective for HSO_4^- over $H_2PO_4^-$, Cl^- and CH_3COO^-.

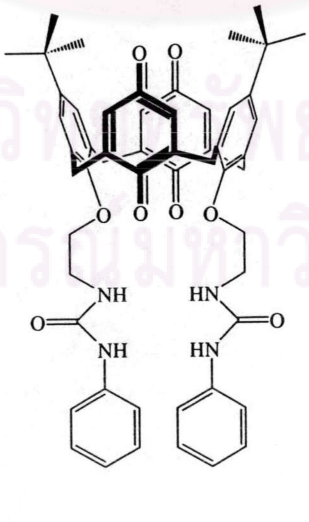
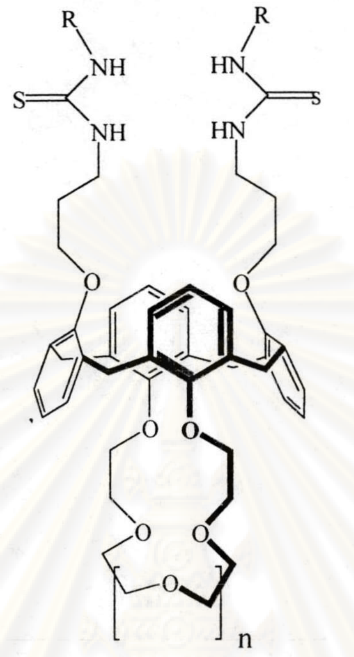


Figure 2.15 Structure of calix[4]diquinone with appended urea groups (calixarene **26**).

Reinhoudt D.N. and co-workers [64] have published a very detailed study of the transport of hydrophilic salts by mixtures of cation and anion receptors and by ditopic receptors. The ditopic receptors **27** and **28** (Figure 2.16) transported CsCl or KCl faster than other anion or cation receptors.



n = 1 R = 2-ethylhexyl
n = 2 R = 2-ethylhexyl

Figure 2.16 Structure of ditopic calix[4]arene based ion pair receptors (calixarenes **27** and **28**).

2.2 Chromium

2.2.1. Industrial Use and Sources of Chromium

While there are natural sources of chromium in the environment, mostly Cr(III), the majority of Cr(VI) originates from industrial activities. The industrial use-stream of chromium begins with its mining as chromite, usually ferrous chromite ($FeO \cdot Cr_2O_3$) [65-66].

Sodium chromate (Na_2CrO_4) traditionally has been produced by air roasting (oxidation) of chromite with sodium carbonate and calcium oxide (lime). Dichromates (Na_2 or $K_2Cr_2O_7$), chromicoxide (CrO_3), chromic acid ($H_2Cr_2O_7$), and other oxides of chromium (e.g. K_2CrO_4), including the chromate pigments (barium, calcium, lead, strontium, and zinc chromate) are in turn derived from Na_2CrO_4.

Most of chromium consumed by U.S. industry is for the production of metal alloy (about 70 % of the chromium usage) mainly wrought-stainless and heat-resisting steels [65-66]. However, chromium can be oxidized and leached from stainless steel into a water solution from [67]. Recycling of chromium is typically accomplished with stainless steel recycling [65-66, 68].

Cr(VI) chemicals, which typically make up about 10 to 15 % of chromium usage, are principally used for metal plating (which use $H_2Cr_2O_7$), as dyes, paint pigment, and leather tanning [65-66]. Cr(II) and (III) chemicals are also manufactured but in small amounts compared with Cr(VI). Chromium dichloride ($CrCl_2$) and chromium sulfate ($CrSO_4$) are examples of the former and chromium trifluoride (CrF_3), chromium trichloride ($CrCl_3$), and chromium nitrate ($Cr(NO_3)_3$) are examples of the latter.

Chromium platers use heater baths of $H_2Cr_2O_7$ to chromium onto pieces of other metals. Under an electric current, the hydrated dichromate ions move toward the positive electrode, which is the metal to be plated. The hydrogen and oxygen gases formed escape the bath forming aqueous acidic chromate laden mists.

2.2.2 The Chemistry of Chromium

Although many different oxidation states of chromium exist in the environment, only Cr(III) and (VI) are the most stable [69]. The interconversion of Cr(III) and Cr(VI) is controlled by several factors, including the presence of concentrations of chromium species and oxidizing or reducing agents, the electrochemical potentials of the oxidation and reduction reactions, ambient temperature, light, sorbents, acid-base reaction, complexing agents, and precipitation reactions [70].

Cr(VI) exists as chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$), or chromium trioxide (CrO_3). Furthermore, only one Cr(III) compound, (Cr_2O_3), is an oxide, so the role of oxygen is central to the oxidation/reduction (redox) process for chromium. In a sense, the commonly used term hexavalent chromium is a misnomer because Cr(VI) does not exist as a free cation as does Cr(III). In fact, as all Cr(VI) species are oxides, they act like a divalent anion rather than a hexavalent cation [71].

2.2.2.1 The Chemistry of Cr(VI): Chromate and Dichromate Ions [72]

In basic solutions above pH 6, CrO_3 forms the tetrahedral yellow chromate ion, CrO_4^{2-}. Between pH 2 and 6, $HCrO_4^-$ and the orange-red dichromate ion, $Cr_2O_7^{2-}$, are in equilibrium. At pH values below 1 the main species is H_2CrO_4 . The equilibria are

$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+ \qquad K = 10^{-5.9}$$

$$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+ \qquad K = 4.1$$

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2\,HCrO_4^- \qquad K = 10^{-2.2}$$

In addition, there are also the base-hydrolysis equilibria as follows:

$$Cr_2O_7^{2-} + OH^- \rightleftharpoons HCrO_4^- + CrO_4^{2-}$$

$$HCrO_4^- + OH^- \rightleftharpoons CrO_4^{2-} + H_2O$$

The CrO_4^{2-} ion is tetrahedral but $Cr_2O_7^{2-}$ has the structure shown in Figure 2.17.

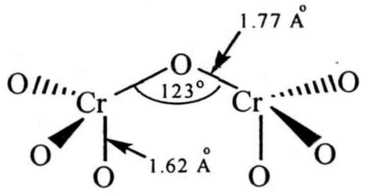


Figure 2.17 Structure of the dichromate ion as found in Na_2CrO_7.

2.2.2.2 General Oxidation and Reduction Reactions

Acid solutions of dichromate are strong oxidants [72]:

$$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \rightleftharpoons 2\,Cr^{3+} + 7\,H_2O \qquad E^O = 1.33\ V$$

In alkaline solution, the chromate ion is much less oxidizing agent [72]:

$$CrO_4^{2-} + 4\,H_2O + 3\,e^- \rightleftharpoons Cr(OH)_3(s) + 5\,OH^- \quad E^O = 0.13\ V$$

Table 2.1 shows a number of oxidation and reduction reactions of chromium with common environmental agents.

Table 2.1 Example of possible oxidation/reduction reactions [73].

Oxidation/Reduction Reactions	E (Volts)
A) $2Cr^{3+} + 5H_2O + 3O_3 \rightleftharpoons 2CrO_4^{2-} + 10H^+ + 3O_2$	0.87
B) $2Cr^{3+} + 2H_2O + 3H_2O_2 \rightleftharpoons 2CrO_4^{2-} + 10H^+$	0.58
C) $3MnO_2 + 2Cr(OH)_3 \rightleftharpoons 3Mn^{2+} + 2CrO_4^{2-} + 2H_2O + 2OH^-$	1.33
D) $2Cr^{3+} + 3H_2O + 2MnO_4^- \rightleftharpoons Cr_2O_7^{2-} + 6H^+ + 2MnO_2$	0.35
E) $2Cr^{3+} + 7H_2O + 6Mn^{3+} \rightleftharpoons Cr_2O_7^{2-} + 14H^+ + 6Mn^{2+}$	0.18
F) $2Cr^{3+} + H_2O + 3PbO_2 \rightleftharpoons Cr_2O_7^{2-} + 2H^+ + Pb^{2+}$	0.13
G) $HCrO_4^- + 3V^{2+} + 7H^+ \rightleftharpoons Cr^{3+} + 3V^{3+} + 4H_2O$	1.45

Table 2.1 (*continue*).

Oxidation/Reduction Reactions	E (Volts)
H) $HCrO_4^- + 3Fe^{2+} + 7H^+ \rightleftharpoons Cr^{3+} + 3Fe^{3+} + 4H_2O$	0.56
I) $2HCrO_4^- + 3H_2S + 8H^+ \rightleftharpoons 2Cr^{3+} + 5H_2O + 3S$	1.18
J) $2HCrO_4^- + 5H^+ + 3HNO_2 \rightleftharpoons 2Cr^{3+} + 5H_2O + 3NO_3^-$	0.35
K) $2HCrO_4^- + 5H^+ + 3HSO_3 \rightleftharpoons 2Cr^{3+} + 5H_2O + 3SO_4^{2-}$	2.12
L) $2CrO_4^{2-} / Cr_2O_7^{2-} + R_3CH \rightleftharpoons Cr^{3+} + R_3COH$	–
M) $2CrO_4^{2-} / Cr_2O_7^{2-} + RCH_3 \rightleftharpoons Cr^{3+} + RCH_2OH$	–
N) $2CrO_4^{2-} / Cr_2O_7^{2-} + RCHO \rightleftharpoons Cr^{3+} + RCOOH$	–
O) $2CrO_4^{2-} / Cr_2O_7^{2-} + PAH \rightleftharpoons Cr^{3+} + \text{Quinones}$	–
P) $2CrO_4^{2-} / Cr_2O_7^{2-} + 3HCOOH \rightleftharpoons Cr^{3+} + 3CO_2$	–
Q) $2CrO_4^{2-} / Cr_2O_7^{2-} + 2CH_3CH_2OH \rightleftharpoons Cr^{3+} + 2CH_3COOH$	–

2.2.2.3 Precipitation and Dissolution Reactions [71]

Chromium can also undergo precipitation-dissolution reactions. The solubility of chromium compounds and the kinetics of the dissolution govern these reactions. The water solubility of both Cr(III) and (VI) species various over many orders of magnitude as suggested by the equilibrium constants listed in Table 2.2.

However, most of the water-soluble Cr(III) species do not occur naturally and are unstable in the environment. The principal Cr(III) reaction in water is the formation of chromium hydroxides of varying water solubility. The degree of hydroxylation is pH dependent with the trihydroxide being least soluble. Cr(III) would then tend to precipitate in neutral aqueous solutions. This tendency is enhanced by the formation of mixed iron chromium hydroxide $(Cr,Fe)(OH)_3$, which has an even lower solubility than $Cr(OH)_3$ and rapid precipitation/dissolution kinetics that could make it an important solubility controlling compound [74].

Table 2.2 Example of solubilization and precipitation reactions [71].

Solubilization and Precipitation Reactions	**Equilibrium Constant, K**
A) $Cr(OH)_3\ (s) \rightleftharpoons Cr^{3+} + 3OH^-$	$10^{-30}\ M^{-4}$
B) $Cr_2(SO_4)_3\ (s) \rightleftharpoons Cr^{3+} + 3SO_4^{2-}$	$1.3 \times 10^{-7}\ M^5$
C) $CrCl_3\ (s) \rightleftharpoons CrCl_2^+ + Cl^-$	$1.5 \times 10^{-3}\ M^2$
D) $CrF_3\ (s) \rightleftharpoons CrF_2^+ + F^-$	$3.0 \times 10^{-3}\ M^2$
E) $Cr(NO_3)_3\ (s) \rightleftharpoons Cr^{3+} + 3NO_3^-$	$0.4\ M^4$
F) $CrO_3\ (s) \rightleftharpoons CrO_3\ (aq)$	$6.2\ M$
G) $BaCrO_4 \rightleftharpoons CrO_4^{2-} + Ba^{2+}$	$3.0 \times 10^{-10}\ M^2$
H) $CaCrO_4 \rightleftharpoons CrO_4^{2-} + Ca^{2+}$	$2.3 \times 10^{-2}\ M^2$
I) $CuCrO_4 \rightleftharpoons CrO_4^{2-} + Cu^{2+}$	$3.6 \times 10^{-6}\ M^2$
J) $K_2CrO_4 \rightleftharpoons CrO_4^{2-} + 2K^+$	$0.2\ M^3$
K) $Na_2CrO_4 \rightleftharpoons CrO_4^{2-} + 2Na^+$	$3.6\ M^3$
L) $(NH_4)_2CrO_4 \rightleftharpoons CrO_4^{2-} + 2NH_4^+$	$20\ M^3$
M) $PbCrO_4 \rightleftharpoons CrO_4^{2-} + Pb^{2+}$	$1.8 \times 10^{-14}\ M^2$
N) $ZnCrO_4 \rightleftharpoons CrO_4^{2-} + Zn^{2+}$	$1.1 \times 10^{-5}\ M^2$
O) $ZnCrO_4 \cdot 4Zn(OH)_2 \rightleftharpoons CrO_4^{2-} + Zn^{2+} + 4Zn(OH)_2$	$5.0 \times 10^{-17}\ M^2$
P) $SrCrO_4 \rightleftharpoons CrO_4^{2-} + Sr^{2+}$	$3.0 \times 10^{-5}\ M^2$
Q) $K_2Cr_2O_7 \rightleftharpoons Cr_2O_7^{2-} + 2K^+$	$4.9 \times 10^{-3}\ M^3$
R) $Na_2Cr_2O_7 \rightleftharpoons Cr_2O_7^{2-} + 2Na^+$	$5.1 \times 10^2\ M^3$
S) $(NH_4)_2Cr_2O_7 \rightleftharpoons Cr_2O_7^{2-} + 2NH_4^+$	$4.0\ M^3$

In contrast, the chromate (CrO_4^{2-}) and dichromate ions ($Cr_2O_7^{2-}$) are water soluble at all pH. However, chromate can exist as an insoluble salt of a variety of divalent cations, such as Ba^{2+}, Sr^{2+}, Pb^{2+}, Zn^{2+} and Cu^{2+} (Reactions G-I, and M-P in Table 2.2), and these salts have a wide range of solubility. The rates of precipitation/dissolution reactions between chromate, dichromate anions, and these cations vary greatly and pH dependent. An understanding of the dissolution reactions is particularly important for assessing the environmental effects of chromium because Cr(VI) often enters the environment by dissolution. Dissolution of sparingly soluble chromate salts (*e.g.*, $SrCrO_4$) is particularly important because they provide a continual source of chromate anions.

2.2.2.4 Sorption Reaction

Sorption process is important to understanding the fate and transport of chromium in the environment. Sorption refers to the removal of a solute from the aqueous phase of an environmental matrix to the surface of a solid. Chromium ions are attracted that have a net electric charge due to imperfections or substitutions in the crystal lattice or due to chemical dissociation reactions at the solid's surface [75]. For example, chromate ions can sorb to mineral solids that have exposed hydroxy group on their surface [76].

$$\text{Surface - OH} + H^+ + HCrO_4^- \rightleftharpoons \text{Surface - } OH_2^+HCrO_4^-$$

2.2.3 Absorption, Metabolism, and Toxicology of Chromium

Chromium can act directly at the site of contact or be absorbed into, or through, human tissues. One of the critical differences between Cr(VI) and (III) species is that the former can be a strong oxidant, while the latter is not. A second important difference is that the chromate ion passes through cellular membranes many orders of magnitude faster than do Cr(III) species [77, 78].

Cr(VI) can act as an oxidant directly on the skin surface or it can be absorbed through the skin, especially if the skin surface is damaged [79]. In fact, irritation of the skin is a most frequently reported human health effect from exposure to Cr(VI), taking the form of skin ulceration (dermatosis) and allergic sensitization (dermatitis) [80-82]. Skin ulceration involves the corrosion and removal of skin, forming ulcers and subsequent scars by gross exposure to chromates and moisture [83]. Indeed, dermatosis was the fist observed health effect associated with Cr(VI) exposure, although improved industrial hygiene practices have greatly reduced its incidence [81, 82, 84].

Chromium absorbed though the lung into the blood system is excreted by the kidneys and the liver. However, large doses of chromium into the blood can result in acute kidney and liver damage [85, 86]. Chronic liver and kidney damage due to long-term exposure of Cr(VI) has also been reported [87].

Absorption of Cr(VI) compounds through the upper respiratory system produces two different health effects. One is the ulceration or perforation of the nasal septum and the second is the irritation of the upper airways. Again, it is the oxidative power of chromates that corrodes the epithelium [80, 85], causing ulcers and perforations. Evidence of the above effects was documented in early studies for chromate workers, revealing mucosal irritation and papillomas in nasal cavity, oral cavity, and the larynx.

Respiratory cancer is the health effect of most concern and is the basis for the regulation of Cr(VI). There is also some indication that Cr(VI) may cause cancer of the upper airways and upper gastrointestinal tract, such as the esophagus, larynx, trachea, and stomach [88]. Cr(VI) appears to be a contact carcinogen to the respiratory system. It has not been implicated in skin cancer, where there is far more frequent and intense contact than for any other part of body. Also, Cr(VI) has not been reported to be a carcinogen for organs for which the only exposure to Cr(VI) is via the blood. Research on the carcinogencity of Cr(VI) has focused on that fact that chromate ion quickly pass through cellular and nuclear membranes, while the trivalent species are many orders of magnitude slower [89].

The rates of lung cancer among chromate workers were reported to be very high in a number of studies. However, the conclusion of almost all of the studies was that not all forms of Cr(VI) were carcinogenic, but rather that only the water–insoluble species were carcinogenic while water-soluble species were not. The results from animal studies and human epidemiology have led some authors to argue that water-soluble Cr(VI) should be considered as carcinogenic as the insoluble species [88, 90, 91]. Other authors believe that the issue cannot be resolved yet.

There is vast literature documenting the mutagenic and cytogenic effects of various chromium compounds [78, 92, 93]. Various studies have shown various Cr(VI) compounds cause many kinds of genetic damage in the laboratory. Chromate ions can either pass the nuclear membrane and be reduced to Cr(III) or be reduced in the cytoplasm [94]. Because neither Cr(VI) nor (III) reacts strongly with DNA, it is thought that the reduction of Cr(VI) to (III), either in the cytoplasm, nucleus, or the blood, produces free radicals (OH·, O, O_2^-, RS·, R· etc.), which in turn can bind to DNA [95].

Cr(VI) is both a powerful epithelial irritant and a confirmed human carcinogen [96]. Additionally, Cr(VI) is toxic to many plants, aquatic animals, and bacteria [80].

In contrast, Cr(III) is generally benign and even a known micronutrient in an organic form [97, 98].

The biologically important form of chromium is the trivalent ion. Cr(III) is required for proper carbohydrate and lipid metabolism in mammals. Trivalent chromium was present in RNA from all sources examined and probably contributes to the stability of the structure. Injected chromium trichloride ($CrCl_3$) accumulated in the cell nucleus (up to 20% of cellular chromium content), it enhanced RNA synthesis in mice and in regenerating rat liver, suggesting that Cr(III) is involved directly in RNA synthesis. On the hand, Cr(VI) inhibited RNA synthesis and DNA replication in several systems [99].

In food consumed by humans and animals it is important in which form chromium is present. Biologically active chromium can be found in unrefined sugar syrup from beet and corn, in wheat germ, in black pepper and in beer yeast, which therefore are useful to prevent chromium deficiency. A deficiency of chromium in animals can produce diabetes, arteriosclerosis, growth problems, and eye cataracts [20].

2.2.4 Policy and Regulation

The primary purpose of regulating chromium in the environment is to control and reduce the risk of lung cancer and dermatitis to the general public associated with the exposure to Cr(VI). Because Cr(VI) is also toxic to some aquatic organisms and microorganisms used in waste water treatment, it is also desired to reduce the release of Cr(VI) into these systems.

The policy decisions in some regulatory agencies to regulate the concentration of Cr(VI) differently from Cr(III) have been based on chemical, toxicological, and epidemiological evidence. For example, the United States Environmental Protection Agency (USEPA) [100-107] has proposed a “Health Based” clean–up concentration (Preliminary Remediation Goals or “PRGs”) for Cr(VI) in soil at much lower concentrations than Cr(III). The California EPA has proposed a modification of the Federal PRG for Cr(VI), but not for Cr(III), in soils at a concentration of below 1 mg/kg [108]. The California EPA likewise classifies a solid as hazardous based on the total and leachable Cr(VI) content (CCR Title 22, Section 66261.24).

2.3 Separations Technology for the Recycling and Reuse of Liquid Waste Streams

Companies are increasingly being forced both by regulatory and cost pressures to reduce the amount and environmental sensitivity of the liquid waste they produce. This has lead to a focus on their ability to clean up this waste and return or recycle a significant proportion. The use of recycled waste streams often also has the additional cost benefit of reducing the raw material requirement, thus again reducing costs.

Wastewater streams have traditionally been treated by a combination of physico-chemical processes such as flocculation, precipitation and filtration, and biological processes such as activated sludge and biofilm processes. Such treatments are usually effective in reducing organic pollutants to a level suitable for disposal into public sewerage or natural waterways. However, they often fail to reduce the concentration of heavy metals below permissible limits. Further, these technologies usually do not provide the selectivity necessary to create valuable product streams suitable for recycle or reuse, and as a consequence the by-product sludge can itself become a disposal problem [109].

Separation processes provide the means for approaching these latter objectives. The wastewater stream is fractionated into two or more liquid phases that are either process recyclable, saleable or waste. There are three separation technologies that facilitate such recycling: solvent extraction, membrane technology, ion-exchange and adsorption processes.

(a) Solvent Extraction

The most established separation technology for wastewater recycling is solvent extraction. This process is principally used for large-scale operations where the concentrations of contaminants are high (see Figure 2.18). Solvents are becoming increasingly selective, allowing specific molecules to be separated from the aqueous phase while other are retained.

A major commercial application of this technology has been in the selective removal of heavy metal ions from wastewater streams. A water insoluble metal-complexing agent in a non–polar organic solvent is contacted with the waste stream and the metal ions transfer into organic phase. This loaded organic phase is then further contacted with a second aqueous strip phase. The metal ions transfer back into this aqueous stripping solution which is returned as recycle to the industrial process.

Heavy metals can be present in wastewater as either cations or anions. Cations are usually extracted into an organic diluent by acidic or chelating extractants. Metal anions can be extracted by ion-pair formation with long chain alkyl amines in an organic diluent, as long as salts or acids are present in the aqueous phase [110]. Suitable metal–complexing agents include tri-*n*-octylamine (TOA) for the removal of Cr(VI) and Hg(II) [111, 112] and methyl tricaprylyl ammonium choride (Aliquat 336) for Cr(VI) removal [113-116].

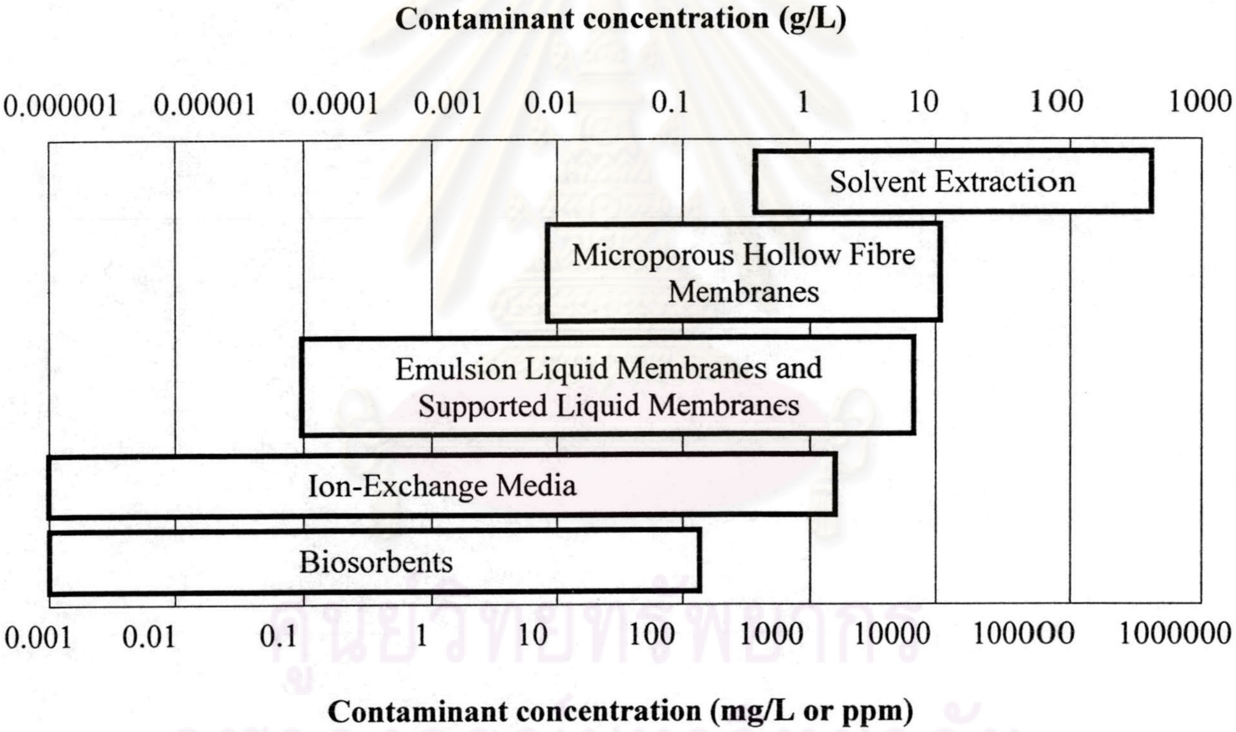


Figure 2.18 Solute concentration ranges for separation technologies [109].

(b) Membrane Technology

A membrane is a semi-permeable barrier through which only selected chemical species may diffuse. Historically, membrane technology has had wide applications in wastewater treatment and desalination through reverse osmosis. In this process, a pressure difference across a membrane is used to overcome the osmotic pressure gradient. The smaller water molecules are literally pushed through the semi-permeable membrane while the larger solute species retained. Cellulose acetate membranes are the most common, uses in either a spiral wound, hollow fiber, tubular or plate-and- frame configuration.

Nanofiltration is an emerging technology that combines such pressure filtration with the use of a negatively charged membrane. The more negatively charged multivalent anions and higher molecular weight organic are retained while monovalent salts pass through the membrane. Such an approach has been applied to the recovery and re-use of dairy [117, 118], tanning [119, 120], sugar [121, 122] and textile [123-125] industry effluents. Fouling and energy costs remain the major barrier to large–scale application of this technology.

With both reverse osmosis and nanofilitration, the membrane operates primarily through size exclusion and so the selectivity for specific metal ions is limited. Much greater selectivity in wastewater treatment can be obtained by combining the physically selective permeability of membranes with the chemically selective separation provided by the solvent extraction process. In this instance, a membrane is placed between a waste stream and a suitable solvent, and mass transfer of selected chemical species occurs across this barrier.

(c) Ion-Exchange and Adsorption Processes

At low solute feed concentrations, the use of solvent extraction or solvent–based membrane processes lose their advantage. Often under these conditions, the loss of solvent into the aqueous wastewater phase through solubility is greater than quantity of solute recovered. In this instance, an alternative technology is required.

The use of a solid matrix for adsorption and ion-exchange of contaminants provides such an alternative. The volume of adsorbent material required increases proportionately with the solute load, so that at higher solute concentrations, equipment size makes such processes economically unfeasible. Applications are typically limited to levels of contaminants in the ppm range (see Figure 2.18).

Activated carbon is the most widely used adsorbent for organic impurities in wastewater. Its non-polar surface, and low cost has made it the adsorbent of choice for a range of pollutants such as aromatics and pesticides. Tailored bentonite clays have been trailed as a more selective alternative [126].

Synthetic ion-exchange resins have long been used in commercial scale applications for the softening of demineralization of water. Again, while effective in reducing ionic contaminant levels to low levels, such resins have traditionally suffered from a lack of selectivity. Research has therefore been directed towards improving this selectivity. Experimental and pilot scale research has targeted the use of new ion-exchange resins and zeolite materials for the selective removal of specific heavy metal cation from wastewater [127-129].

Furthermore, biosorption is an emerging technology that also attempts to overcome the selectivity disadvantage of adsorption processes [130-132]. In this instance, biological materials, such as chitosan [133, 134], marine algae or alginates [135-137], fungi [132] or bacterial biomass [138, 139] are used as a chelating ion–exchange medium. These biopolymers and their derivatives contain a variety of functional groups, which can chelate ionic species of a specific size and charge. Such biomass is thus often much more selective than traditional ion-exchange resins and can reduce heavy metal ion concentrations to ppb levels. The biomass can be immobilized on to an inert framework in order to reduce is fragility under industrial conditions [137-139].

According to wide range of chromium usage as described in section 2.2.1. Therefore, it presents of high level in wastewater. Thus, the appropriate method for separation should be solvent extraction that is based for large-scale operation (see Figure 2.18). This technology is discussed in more detail in section 2.4.

2.4 Solvent Extraction

Solvent extraction or liquid-liquid extraction (LLE) is useful for separation analytes from interference by partitioning the sample between two immiscible liquids of phases. One phase in LLE is aqueous and the second phase is an organic solvent. More-hydrophilic compounds prefer the polar aqueous phase, whereas more hydrophobic compounds will be found mainly in the organic solvent [140].

To carry out an extraction, the extractive solvent is added to the aqueous sample solution, the vessel is tightly stoppered, and the vessel is shaken vigorously to create a temporary emulsion. The emulsion consists of very small spherical droplets of the extractive liquid suspended in the aqueous phase. The interfacial contact area between the two phases must be quite large in order to promote rapid mass transfer of the desired solutes from one phase to another. Even so, it is sometimes necessary to continue shaking for several minutes to attain a true equilibrium of the solutes between the two phases. When shaking is terminated, the emulsion should break up and the two liquid coalesce to form two continuous but immiscible liquid phases. A practical difficulty of liquid-liquid extraction is that emulsions sometimes break up very slowly or incompletely [141].

When chemical analysis of the extracted solutes cannot be carried out directly in the organic liquid, it is necessary to do a back-extraction or stripping. This can often be accomplished with an aqueous solution under conditions (e.g., changed pH) causing the solutes to prefer the aqueous phase [141].

2.4.1 Factors Affecting the Extractability of Solutes [142-143]

How the physical and chemical properties of a substance may influence its behavior in a solvent extraction system or how different solutes might distribute themselves between aqueous and organic solvents.

The two most important factors to be considered are (a) the solubility of the solute in each of the solvents, (b) any chemical equilibria that the solute might be involved in either solvent.

(a) Solubility

What kinds of solutes are soluble in aqueous phases and what kinds are soluble in organic phases? The principle "like dissolves like" works well here, and the ability of the solvent to solvate the solute is also very relevant.

Solvation is a process whereby solvent molecules are attracted to solute molecules with the formation of weak bonds between them. Thus a solvated molecule can be visualized as having a sphere of solvent molecules arranged round and weakly bonded to it. Solvation has a very fundamental effect on solubility. When the solvent is water it is called hydration and often the bonds (hydrogen bonds in this case) are relatively strong.

To predict qualitatively how a solute might be extracted from an aqueous phase into an organic phase, the following principles are useful guidelines but are not infallible.

For an uncharged species, the less polar is easier to extract quantitatively from an aqueous phase into a non-polar organic solvent.

Charged (ionic) species are generally difficult to extract into any organic phase from an aqueous phase, if indeed any extraction occurs at all, unless they are able to form an ion-pair with a counter ion.

The ability of either solvent to solvate the solute strongly will cause the solute to be retained by that solvent. This applies to water and its ability to hydrate ions and also to solvent such as diethyl ether which solvate various complex ions that are then extracted as solvated ion-pairs.

Polar solutes are more efficiently extracted into polar organic solvents than into non-polar organic solvents. This generally makes their extraction from aqueous phases more difficult because polar solvents are more likely to be miscible with water.

(b) Chemical Equilibria

The extractability of any solute will depend on its precise chemical form and this in turn is in part expressed in terms of the position of any relevant chemical equilibrium in either phase.

Selectivity in solvent extraction is most often achieved by judicious manipulations of appropriate chemical equilibria to produce either organic solvent-soluble or water-soluble species, rather than simply relying on natural differences in extractability of different solutes.

For example, neutral organic compounds do not ionize and so are potentially extractable at all values of pH. Acidic substances will be ionized at high pH, might be partially ionized at neutral pH but will tend to exist in the unionized form at low pH. Hence, acidic substances will be retained in the aqueous phase at high pH but are potentially extractable at low pH. Exactly the opposite argument applies to basic compounds by virtue of their protonation at low pH.

2.4.2 The Distribution Coefficient and Distribution Ratio [142-144]

The fundamental law of quantitative basis governing the distribution of a solute between two immiscible solvents is known as the *Nernst Distribution Law*.

This can be stated as follow:

" At equilibrium the activities in the two solutions of a substance distributed between two immiscible solvents will bear a constant ratio to one another, provided that temperature and pressure remain constant ". Analytical chemists as a rule do not like working with activities, and prefer to work with an expression involving concentrations. Therefore the *Distribution Coefficient*, K_D is defined as follows:

$$\boxed{K_D = \frac{\text{concentration of a substance in solvent A}}{\text{concentration of a substance in solvent B}} \quad \text{at equilibrium}}$$

Normally for aqueous/organic systems, solvent A is the organic solvent. Square brackets refer to molar concentrations, the subscript aq and org for the aqueous and the organic phase respectively, the substance being distributed, X, then:

$$\boxed{K_D = \frac{[X]_{org}}{[X]_{aq}} \quad \text{at equilibrium}}$$

K_D is thus a ratio and a dimensionless quantity, i.e. it has no units.

It is important to realize that K_D refers to one specific species only. If a substance is involved in chemical equilibria in either phase, then each species present will be characterized by its own value of K_D. As such, K_D is a constant provided that temperature, pressure and activity coefficients remain constant (the last is specified because K_D is defined in terms of concentrations and not activities. This assumption is reasonable at low concentrations provided that ionic strength remains constant).

If concerned the distribution between two phases of a species, X, that exists in solution in a number of chemical forms, and then we use the *Distribution Ratio*, D, which is defined as follows:

$$\boxed{D = \frac{\text{total concentration of X in solvent A}}{\text{total concentration of X in solvent B}} \quad \text{at equilibrium}}$$

The distribution ratio thus gives us information about the ratio of the total concentrations of the solute in each phase irrespective of its precise chemical form, and so the distribution ratio is of much greater practical use than the distribution coefficient.

An example for K_D and D of the extraction of an organic acid from water into an organic solvent. Assume that the acid HA is monoacid and that it dissociates into H^+ and A^- in water. Only HA is extracted into the organic solvent. K_D and D are defined as follow:

$$\boxed{K_D = \frac{[HA]_{org}}{[HA]_{aq}}}$$

$$\boxed{D = \frac{[HA]_{org}}{[HA]_{aq} + [A^-]_{aq}}}$$

D is not a constant and can vary widely indeed with experimental conditions, such as pH, that might affect the chemical equilibria. Nevertheless it is important to remember that the values of the equilibrium constants for each individual equilibrium do remain constant. This is the principle behind evaluation D in complex equilibrium systems.

2.4.3 Extraction Percentage [142]

How much material would actually be extracted? E, the percentage extraction, gives this.

$$\boxed{E\ (\%) = \frac{\text{amount of extracted substance}}{\text{total amount of substance present in both phases}} \times 100}$$

Or can be defined as follows:

$$\boxed{E\ (\%) = \frac{w_o - w_l}{w_o} \times 100}$$

Where w_o = substance contained at the beginning

w_l = substance left in the aqueous phase

2.4.4 The Extraction of Metal Ions [142-144]

The most important and useful area of application of solvent extraction in analysis is the extraction of metal ions from water into an organic solvent. Some important applications of the solvent extraction of metal ions are listed below and show the wide scope of the technique:

(a) Preconcentration step for atomic absorption analysis.

(b) To improve selectivity in spectrophotometric and other forms of analysis by using a selective extraction step.

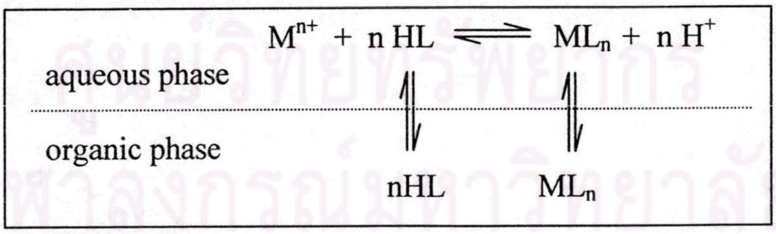
To extract metal ions from water into an organic solvent must convert them into an extractable complex. These complexes may be broadly classified into two types: (a) Neutral, coordinatively saturated, chelate complexes, (b) Ion-association complexes (ion pairs).

2.4.4.1 Neutral–chelate Extraction Systems [142-144]

In these systems, the metal ion reacts with an organic chelating ligand to form a neutral chelate complex. In these complexes the ligand molecules occupy all the metal's coordination sites, so that no water of coordination is present. The neutral complex should be free of polar groups not involved in coordination. One would expect chelate complexes that satisfy these conditions to be extractable into organic solvents with very high distribution coefficients, since one would expect the solubility properties of such a molecule to be similar to those of a relatively non-polar organic compound.

In order to neutralize the charge, the ligand should be a weak acid and should complex with the metal as the anion, thus hydrogen ions will be released on complex formation. Normally, the ligands act as weak monoacid and complex with the metal ion in the ration of one ligand molecule per metal ion per unit charge on the ion. Note also that the uncharged, neutral ligand is often significantly extractable into the organic solvent.

Many such systems are adequately described by the following equilibria in which M^{n+} represents a metal ion in the oxidation state n, HL is the neutral form of the complexing ligand, and L^- is the anionic form. The top half of the box below represents the aqueous phase and the bottom half represents the organic phase. Horizontal two–way arrows represent chemical equilibria, vertical two-way arrows represent transfer between phases.



For the extraction equilibrium: $M^{n+}_{aq} + n\,HL_{org} \rightleftharpoons (ML_n)_{org} + n\,H^+_{aq}$

Thus, given the extraction equilibrium constant, K, as follow:

$$\boxed{K = \frac{[ML_n]_{org}\,[H^+]^n_{aq}}{[M^{n+}]_{aq}\,[HL]^n_{org}}}$$

Or can be defined in term of distribution ratio, D:

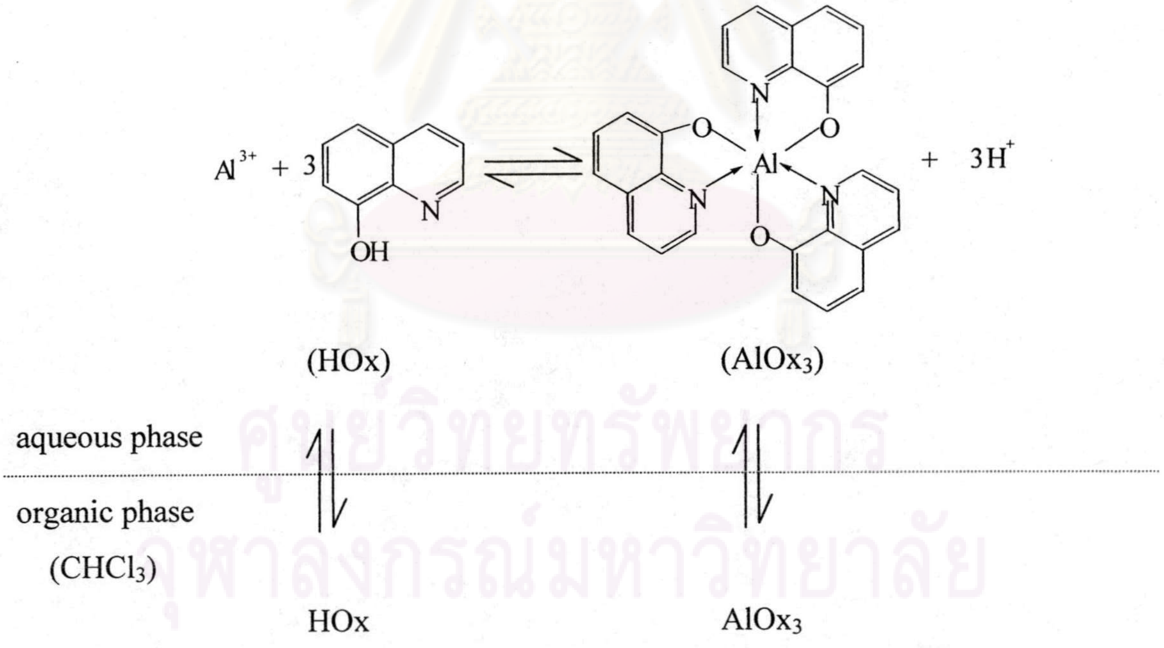
$$D = \frac{K\,[HL]^{n}_{org}}{[H^{+}]^{n}_{aq}}$$

Thus, this equation can be obtained:

$$\log D = \log K + n \log [HL]_{org} + n\,pH$$

The relationships between log D and pH is a straight line of slope, n.

An example of such a system is the extraction of Al (III) with 8–hydroxyquinoline (HOx) into trichloromethane.



Because of the release of H^{+} on complex formation, these extraction systems are highly pH dependent, complex formation and therefore extraction being suppressed at low pH. However, extraction is also often suppressed at high pH. This, however, is for a different reason, i.e. that the anionic form of the ligand has to compete with a high concentration of hydroxide ions which will preferentially react with the metal ion to form non–extractable hydroxide complexes if the pH is high enough.

There are many areas of application of neutral chelate extraction system, but the conditions under which they work best are given below:

(a) At low concentrations of metal ions (therefore for such processes as preconcentration). Their usefulness at high concentrations is limited by the solubility of the complex in the organic phase.

(b) Under conditions where extremes of pH are avoided (because under conditions of extreme pH complex formation is inhibited).

2.4.4.2 Ion-association Extraction System [142-144]

The alternative approach to the extraction of metal ions is to use an ion–association extraction system. An ion–association complex, normally formed between a large, bulky organic ion and a suitable counter–ion. The large, bulky ion may simply be added to the system as a component of a reagent, it may be formed by complex formation or it may be formed by solvation. The metal may be incorporated in this large ion or it may be incorporated in the counter–ion. The ionic species containing the metal, as well as the large ion may be cationic or anionic. These complexes are held together by relatively weak electrostatic forces, but are sufficiently stable to be efficiently extracted into organic solvents under appropriate conditions. The stability of these ion-association complexes is generally higher in the organic phase than in the aqueous phase.

Under these conditions the neutral–chelate extraction systems are generally most effective: (1) when extremes of pH (especially low pH) are avoided, (2) when the metal ion being extracted is not subject to hydroxide formation at relatively low pH, (3) when the concentrations of the metal ions involved are not too high, (4) when the metal ions involved are of the type to form stable complexes.

So, these ion–association extraction systems often work efficiently under conditions where the neutral–chelate extraction systems are less than satisfactory. For example:

(a) Ion association–extractions can be made from strongly acidic media.

(b) Extractions of high–valency transition–metal ions are often effective, because these ions can be extracted form acidic media.

(c) Extractions are available for alkali–metal ions.

(d) Extractions are applicable to wide concentration ranges of metal ion. Neutral–chelate extractions are normally effective only at low concentrations.

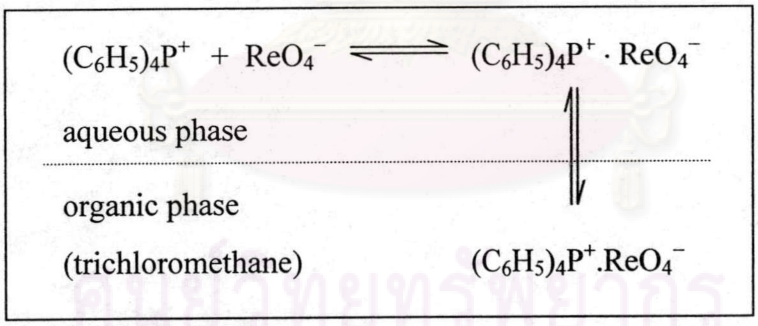
However, the chemistry of such systems is diverse and often very complex, because of the wide variety of conditions and concentrations.

Some representative examples of ion–association extraction systems are listed below.

2.4.4.2.1 Extractions Involving No Chelation or Solvation

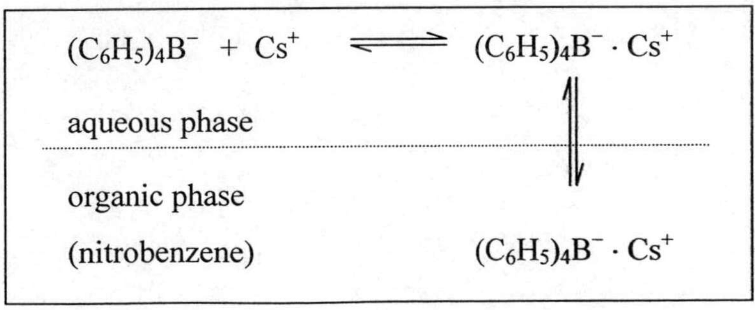
A bulky organic counter–ion is added to the system to form ion–association complexes with non–solvated/non–chelated cations or anions. These then can be quite small and relatively simple.

Here is an example of a bulky cation being used in this way:



$(C_6H_5)_4$ As^+ is another cation which can be used similarly. Other extractable anions include MnO_4^-, $HgCl_4^{2-}$ and $FeCl_4^-$.

Here is an example of a bulky anion being similarly used:

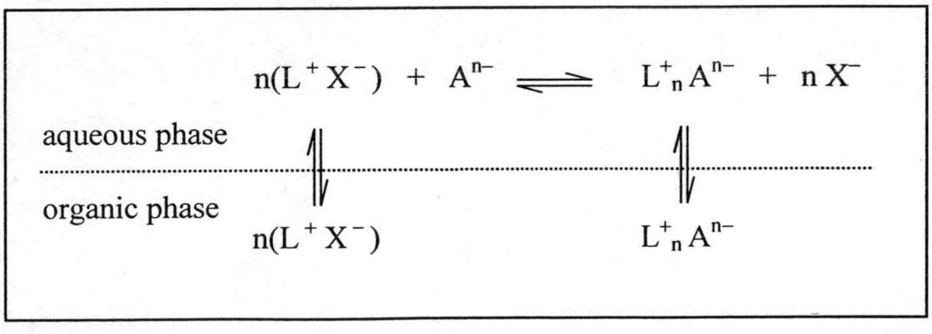


2.4.4.2.2 Liquid Ion Exchanges

Certain acidic phosphate esters such as butyl dihydrogen phosphate ($C_4H_9OPO_3H_2$), dibutyl hydrogen phosphate ($((C_4H_9)_2OPO_2H)$) and di(2–ethylhexyl) phosphate are liquids, themselves immiscible with water, or they can be dissolved in inert diluents immiscible with water. If these liquids or solutions are equilibrated with aqueous solutions containing certain cations, the phosphate esters can exchange protons with the cations in the aqueous phase, chelating and solvating the cations. Lanthanum (III) and high–valency actinides are examples of such cations to be extracted. These systems are known as liquid cation exchanges.

Similarly, amines of high molar mass that are protonated in the presence of acid, or alternatively tetra–alkylammonium salts of high molar mass, can also exist as liquids immiscible with water, or can be dissolved in diluents immiscible with water. Likewise, if these liquids or solutions are equilibrated with aqueous phase containing certain metal ions present as complex anions, exchange of anions between phase can occur and the metal is extracted as an ion–pair with the tetra–alkyammonium cation. Example of extractants such as Aliquat 336-S (tricaprylmethylammonium chloride). Anions extracted include species such as $FeCl_4^-$. These systems are known as liquid anion exchanges.

The following equilibria of anion exchange extraction systems are adequately described in which A^{n-} represents a metal ion in form of anion with the charge n such as $FeCl_4^-$, L^+X^- is the ion-association complexing ligand, and L^+ is the protonated ligand form, X^- is counter anion. The metal anion (A^{n-}) is extracted as an ion-pair in form of $L^+_n A^{n-}$. The top half of the box below represents the aqueous phase and the bottom half represents the organic phase. Horizontal two–way arrows represent chemical equilibria, vertical two-way arrows represent transfer between phase.



A mathematical treatment that calls " *slope analysis method* " [42] can be used for finding stoichiometry of the extracted species as described below:

Consider the extraction equilibrium: $n\,(L^+X^-)_{org} + A^{n-}_{aq} \rightleftharpoons (L^+_n A^{n-})_{org} + n\,X^-_{aq}$

Thus, given the extraction equilibrium constant, K, as follow:

$$\boxed{K = \frac{[L^+_n A^{n-}]_{org}\,[X^-]^n_{aq}}{[L^+X^-]^n_{org}\,[A^{n-}]_{aq}}}$$

Or can be defined in term of distribution ratio, D:

$$\boxed{D = \frac{K \cdot [L^+X^-]^n_{org}}{[X^-]^n_{aq}}}$$

Thus, this equation can be obtained:

$$\boxed{\log D = \log K + n \log [L^+X^-]_{org} - n \log [X^-]_{aq}}$$

Consequently, plots of log D vs. log $[L^+X^-]_{org}$ may lead to a straight line whose slope n allows access to the stoichiometry of the extracted species [42].

2.4.4.2.3 Chelate Systems

A good example is the extraction of Cu^+ ion with neocuproine into trichloromethane. A bulky organic chelate cation is formed as follows.

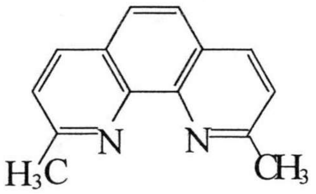
$$Cu^+ + 2\,L \rightleftharpoons CuL_2^+$$

$$CuL_2^+ + NO_3^- \rightleftharpoons CuL_2^+ \cdot NO_3^-$$

aqueous phase $\updownarrow$

organic phase

(trichloromethane) $CuL_2^+ \cdot NO_3^-$



Neocuproine = L

Note that the neocuprine regent differs from those reagents used in neutral-chelate extract systems in that it has no acidic hydrogen atoms. The complex still has no polar groups or water of hydration but does have a residual charge, which must be neutralized by ion-association complex formation with the nitrate anion.

2.4.4.2.4 Oxonium Systems

A very important group of systems in which metal ions, often in relatively high oxidation states, are extracted from acidic media into oxygen containing organic solvents such as ethers, ketones, or esters. The extraction involves conversion of the metal ion into a complex anionic form by reaction with the anion of the acid. Protons from the acid are then solvated by the oxygen containing extracting solvent. The complex anion and the solvated proton (the "oxonium" ion) then form an ion–pair (ion–association complex), and this is the species that is extracted.

An excellent example of an oxonium extraction system is the extraction of Fe(III) from a 6M–hydrochloric acid into diethyl ether.

2.4.4.2.5 Extractions Involving Solvation/Coordination by Organic Compounds

Certain ketones (e.g. 4-methylpentane-2-one), trialkyl phosphates (e.g. tributryl phosphate) and phosphine oxides (e.g. tri–octylphosphine oxide), either used as extracting solvents or as organic reagents diluted with an inert extracting solvent (e.g. kerosene) can bring about the extraction of metal ions by direct coordination and/or solvation of the metal ion or of the proton. Uranium (VI) can be extracted in this way from a nitric acid medium by using tributyl phosphate (TBP).

2.5 Solid–phase Extraction

It is well known that liquid-liquid extractions are very useful, but have certain limitations. The extracting solvents are limited to those that are water immiscible (for aqueous samples). Emulsions tend to form when the solvents are shaken, and relatively large volumes of solvents are used which generates a substantial waste disposal problem. The operations are often manually performed, and may require a back extraction [144]. Moreover, for wastewater with low concentrations of metal ions, such technology is limited by the need for high aqueous to organic phase ratios. This leads to high organic losses though entrainments in the aqueous phase. And there is also the potential for cross-contamination of the aqueous stream with the organic solution [109]. Many of these difficulties are avoided by the use of solid-phase extraction.

Some of the concepts of liquid–liquid extraction apply to solid–phase extraction (SPE). Instead of a temporary liquid emulsion, the extractive material in SPE is a suspension of spherical solid particles in the aqueous sample. The extractive particles typically are ~10-50 μm in diameter with a very large surface area, often ~200–800 m^2/g [141]. A large interfacial area between the particles and the sample solution is needed for rapid mass transfer of the extracted solutes from one phase to the other. The extractive particles must be sufficiently dense and large enough in diameter to settle rapidly when agitation of the solid and liquid phases is terminated [141]. In this technique, hydrophobic organic functional groups are chemically bonded to a solid surface, for example, powdered silica [144]. Most sorbents used for SPE are based on silica as the support material [145] and therefore an understanding of the properties of silica will provide an insight into the selection of an appropriate SPE sorbent.

2.5.1 Chemical and Physical Properties of Silica

The silica that is used in most chromatographic applications and in typical SPE procedures is an amorphous porous solid with a surface area of between 50–500 m^2/g and pore diameters of 50 – 500 A^0 [145]. The primary advantages of silica are its availability in a wide range of well–defined surface areas and pore sizes as well as its relatively low cost. While a very specific surface area and pore size (narrow distribution) is important in most HPLC applications, such stringent specifications are not necessary in SPE. These reduced requirements make the cost of the silica even lower and account for its popularity as a sorbent material in SPE [145].

The silica gel cannot be used directly with aqueous solvent mixtures because the water deactivates the silica to such an extent that it has only weak interactions with most substances during the isolation process. So weak, in fact, that there is essentially no retention. Thus, it is necessary for the silica surface to be made hydrophobic in nature for it to be functional with aqueous solvent [146].

The surface chemistry of silica [147, 148] is dominated by the presence of hydroxide groups commonly referred to as silanols. The silica particles contain unreacted silanols and siloxanes. The silanols are considered to be strong adsorption sites [149], while the siloxanes are hydrophobic. Silanols on the surface may be single, geminal, or vicinal in form (Figure 2.19).

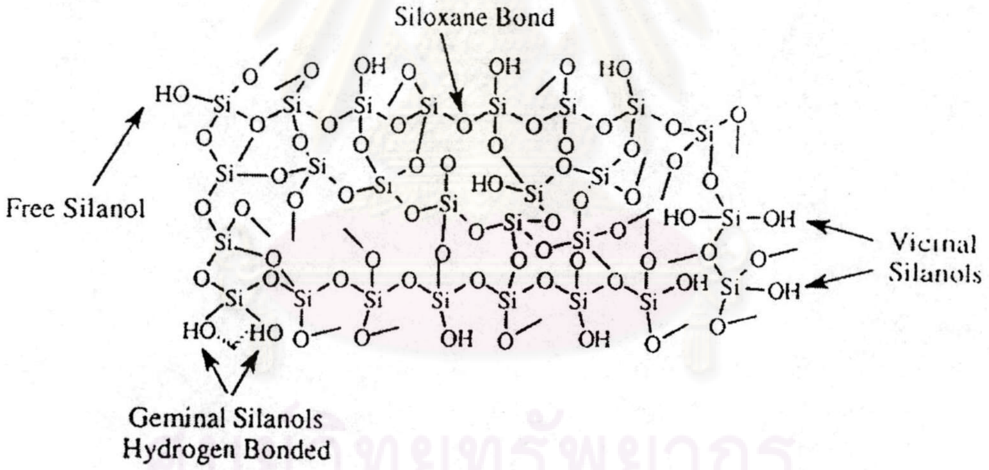


Figure 2.19 Structure of a silica gel showing siloxane bond, single free silanol, geminal silanols, and vicinal silanols [146].

A single silanol is simply an isolated hydroxyl group on the surface of silica gel. A vicinal silanol pair is two hydroxyl groups on adjacent silicon atoms, while the geminal silanols are two hydroxyl groups on the same silicon atom (Figure 2.19). A pair of vicinal or geminal silanols can form a bonded pair because of the ability for them to hydrogen bond to each other. The significance of these groups is that the three types of underivatized silanols may be reactive, with at least three different strengths for hydrogen bonding of weak cation exchange with any solute that may be bound to the bonded phase of the sorbent [148].

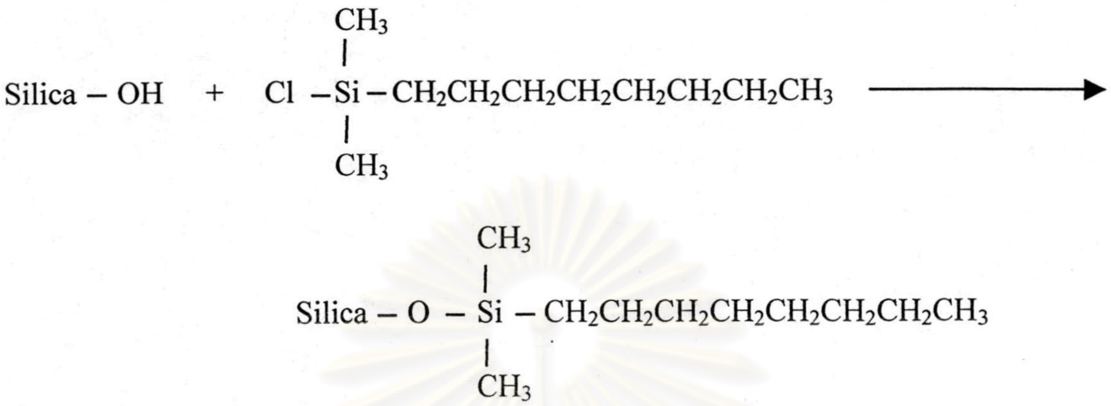
Another characteristic of the silica particle that should be considered is its stability as a function of pH. The solubility of the silica particles increases rapidly at pH above 7.0, with pH 7.5 considered the upper limit of usefulness. Similarly, the solubility of the silica will increase rapidly at pH below 2.0. Thus, this simple understanding of the silica surface is useful when designing methods for SPE and affect the choices of solvents for washing and eluting the SPE sorbents [148].

Several supply houses offer a full line of silica particles for SPE. The major types are listed in Table 2.3. The materials in this table are listed in their approximate order (top to bottom) of increasing polarity.

Table 2.3 Bonded-phase silica-modified materials used in solid-phase extraction [141].

Phase	**Polarity of Phase**	**Designation**
Octadecyl, endcapped	Strongly non-polar	C18ec
Octadecyl	Strongly non-polar	C18
Octyl	Non-polar	C8
Ethyl	Slightly polar	C2
Cyclohexyl	Slightly polar	CH
Phenyl	Slightly polar	PH
Cyanopropyl	Polar	CN
Diol	Polar	2OH
Silica gel	Polar	SiOH
Carboxymethyl	Weak cation exchanger	CBA
Aminopropyl	Weak anion exchanger	NH_2
Propylbenzene sufonic acid	Strong cation exchanger	SCX
Trimethylaminopropyl	Strong anion exchanger	SAX

The desired major functional group is introduced into porous silica particles by reaction of silanol groups on the silica with chloro- or methoxyorganosilane. For example, the C8-bonded phase material has the following structure [141]:



$$\text{Silica}-OH \quad + \quad Cl-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3 \longrightarrow$$

$$\text{Silica}-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$$

The nature of the extracting phase can be varied to allow extraction of different classes of compounds. Figure 2.20 illustrates bonded phases based on van der Waals forces, hydrogen bonding (dipolar attraction), and electrostatic attraction

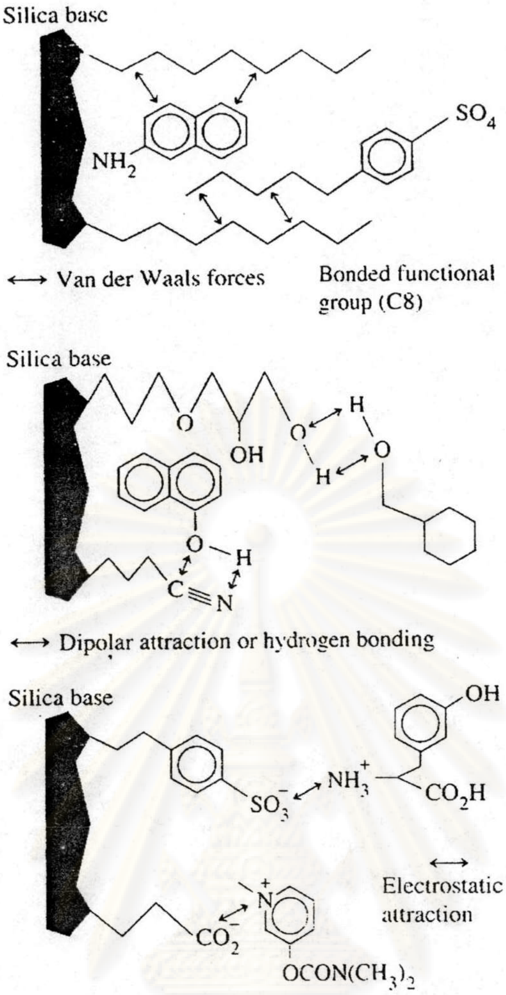
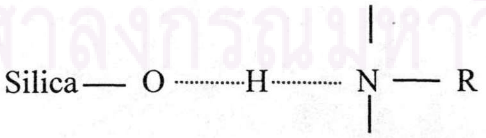
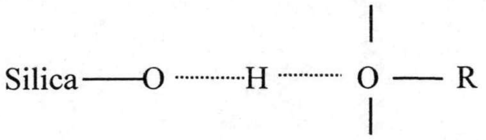


Figure 2.20 Solid-phase extractants utilizing non-polar, polar, and electrostatic interactions [144].

The free silanol groups can attract polar analytes that might not otherwise be extracted by hydrogen bonding (········). Alcohols and amines are example [141]:



$$\text{Silica}—\text{O}\cdots\cdots\text{H}\cdots\cdots\overset{|}{\underset{|}{\text{N}}}—\text{R}$$



$$\text{Silica}—\text{O}\cdots\cdots\text{H}\cdots\cdots\overset{|}{\underset{|}{\text{O}}}—\text{R}$$

The bulk of the chloro alkyl silanes is used in the derivatization reaction to prevent their reaction with all of the SiOH groups on the silica.

2.5.2 SPE on a Batch Basis

When SPE is performed on a batch basis, small, porous particles of solid extractant are added to the liquid sample. Some agitation is helpful in speeding up the extraction step when SPE is carried out on a batch basis. When equilibrium has been attained between the two phases, the solid particles can be separated by filtration or simply by carefully pouring off the liquid phase [141]. Although SPE can be done in a batch equilibration similar to that used in liquid-liquid extraction, it is much more common to use a small tube (minicolumn) or cartridge packed with the solid particles.