

CHAPTER I

INTRODUCTION



1.1 Approaches to Ligand Design

Ligand for complexation of metal ions is needed in both industrial and analytical applications. This can be seen from continuous emerging reviews concerning ligand design for specific purpose such as chelation therapy [1], purification of metal [2-3] waste treatment [4], chemical catalysis [5] and analytical application such as ligand immobilized on solid for metal preconcentration [6] and in chemical sensor [7-9]. One common design feature of the developed ligand is its selective property.

Approach for designing selective ligand is frequently a trial and error process [9]. Other strategies include a *biomimic* design – the mimicry of a molecule from biological materials, and a *rational design* - a design consisting of incorporation of ligating groups of known binding characteristics into a new host molecule [10]. An optimal *preorganization* would lead to a ligand with high selectivity. The design may be followed by molecular modeling to achieve better understanding of interaction with metal ions. Publication on the use of computer modeling prior to synthesis is limited but one has been recently developed [11].

The level of preorganization increases from an open chain multidentate ligand to podands to macrocyclic compounds to spherands. While the hole-size effect dominates in the latter three, chelate ring size effect contributes to selectivity of multidentate ligands and to some extent on macrocyclic compounds [12]. The change in stability constants of complexes upon changing chelate ring size is demonstrated in Figure 1.1. It can be seen that passing from triethylenetetramine (TRIE) to 1,4,8,11-tetraazaundecane and in passing from ethylenediaminetetraacetic acid (EDTA) to trimethylenediaminetetraacetic acid (TMDTA) lead to greater decrease in complex stability with larger metal ions.

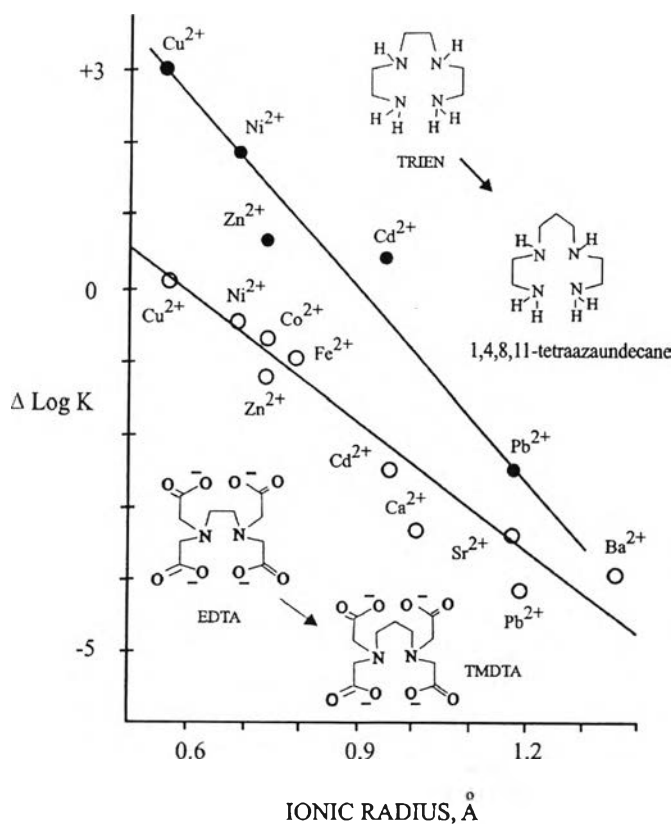


Figure 1.1 Effect on complex stability of increase chelate ring size from five-membered and six-membered in open chain ligands as a function of metal ion size (Redrawn from ref [12])

A platform for preorganizing ligating groups may be as simple as a benzene ring or larger molecule such as *calix[4]arene* (Figure 1.2a) [13] and *deoxycholic acid* (Figure 1.2b) [14]. The ligating groups may be as simple as ethyl ester or existing bidentate ligand such as bipyridyl. Of the two platforms, *calix[4]arene* is more popular possibly due to many advantages such as (i) easy and cheap synthesis (ii) amenability to chemical modifications such as substitutions at the *para*-position (wider rim) and at phenolic hydrogen (narrow rim), (iii) conformational mobility lead to a wide range of complexing abilities. Conformations of *calix[4]arene* are shown in Figure 1.3 and the numbering of substituents on *calix[4]arene* are shown in Figure 1.4.

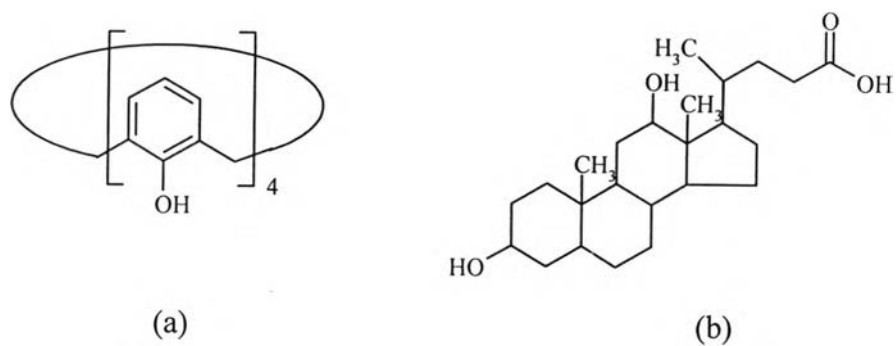


Figure 1.2 (a) calix[4]arene (b) deoxycholic acid

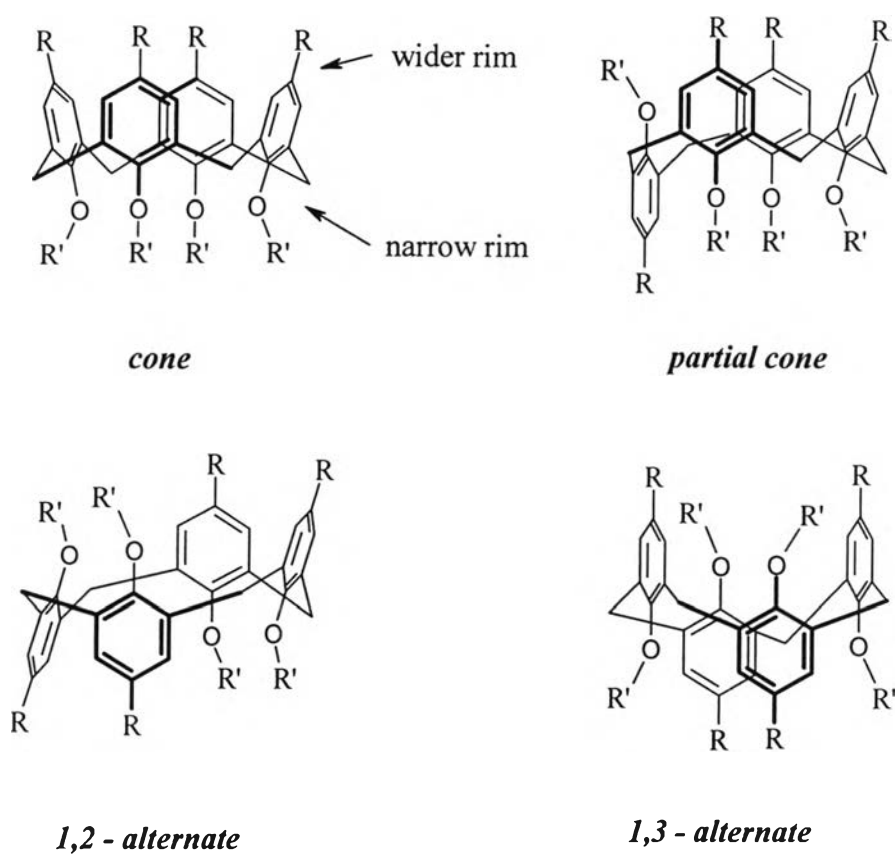


Figure 1.3 Four possible conformations of calix[4]arene

Calixarene-based ligands for complexing metal ion has been reviewed by Ludwig and Dzung [15]. Some structures are shown in Figure 1.5.

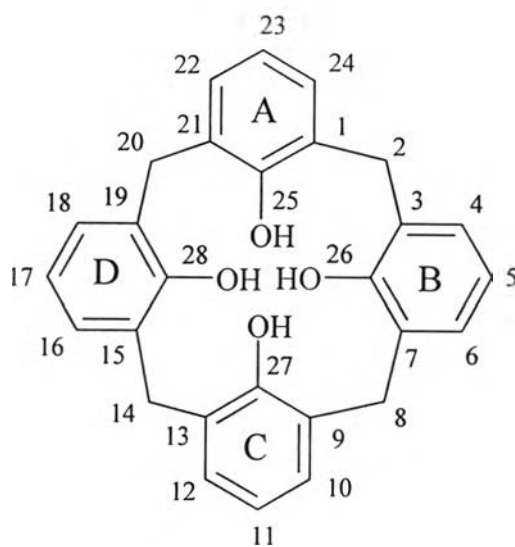


Figure 1.4 Numbering of substituents on calix[4]arene

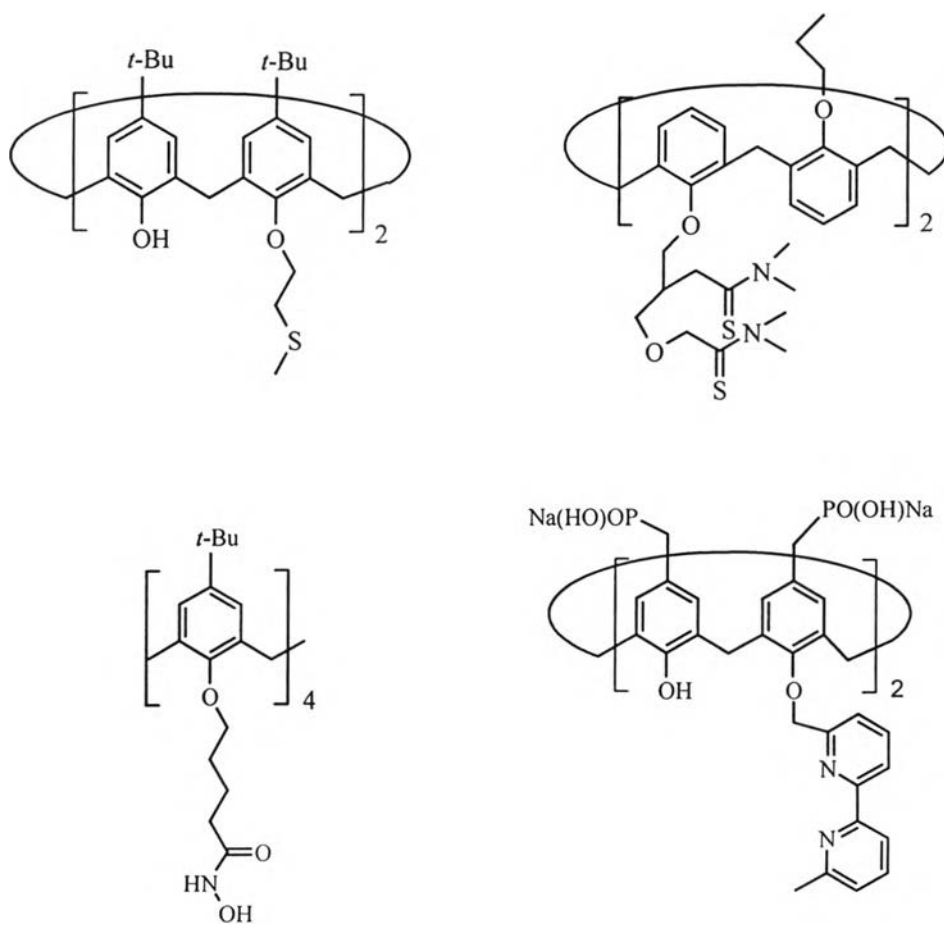


Figure 1.5 Some calixarene-based ligands for complexation of metal ions [16-19]

1.2 Ion-Selective Electrode

One of major driving forces for a new ligand is in sensor development, especially *ion selective electrode* (ISEs). According to IUPAC, ISE is an electrochemical sensor based on thin films or selective membranes as recognition elements and an electrochemical half cell [20]. They often contain a second kind electrode as the inner or internal reference electrode. The ISE membrane may be single crystal, glass, polymer-based crystalline material, liquid ion-exchanger or neutral molecule embedded in polymer matrix [21]. The polymer membrane gives an opportunity to obtain a variety of electrodes selective towards particular ions by judicious choice of ionophore. This type of electrode, called *carrier-based ISE*, find its major use in clinical diagnosis [22]. Recently, a research in this field led to an improvement in detection limit to picomolar level [23-25]. This places the potentiometry into one of analytical technique for trace element analysis [26].

Another benefit that can be obtained from of ISE is that it is amenable to *miniaturization* [27-28] which made it suitable for *in vivo* measurement [29-30]. Other applications include using as a detector in flow system such as ion chromatography [31] and flow-injection analysis [32-34].

1.2.1 Electrode Component

A *membrane* is a layer consisting of semi-permeable (solid or liquid) material, which controlled permeability. In *carrier-based ISE*, a membrane is usually made from a polymer which contains built-in fixed charged sites or intentionally added hydrophobically trapped mobile site (*lipophilic ionic sites*) to make it permeable only to one charge type. For ion of the same charge type, *ionophore* is required for obtaining required selectivity. A typical membrane composition for the usual cations and anions consisted of PVC (~33 wt%), plasticizer (~65 wt%), ionic additive (~0-2 wt%) and ionophore (~1-5 wt%) [35].

Polymer matrix

The basic function of polymer is to provide mechanical stability and elasticity to membrane. The most commonly used polymer for ISE membrane is poly(vinylchloride) (PVC). Because its glass transition temperature (T_g) is high

(~80°C for high molecular weight PVC), a plasticizer must be used. However, the presence of plasticizer may result in shorter lifetime of a membrane due to exudation of plasticizer. The loss of selectivity and detection limit also will occur due to the leaching of dissolved ionophore upon prolonged use. This problem is more critical in miniaturized ISE. One way to avoid these problems is using a “internal plasticized polymer” such as methacrylic and acrylic resins [36]. Another problem of PVC is that it exhibits poor adhesion to silicon substrate and often fails due to electrolytic shunts around the membrane. Silicone rubber is an alternative in this case [37-38]. Another alternative to PVC is styrene-acrylonitrile copolymer which was claimed to enhance average lifetime of ISE due to higher hydrophobicity and dipole moment. The interference from anions was also lesser due to the fixed negative charged cyano groups in the polymer matrix. [39].

Plasticizer

Plasticizer is actually a solvent that is physically compatible with polymer. PVC plasticizer determines membrane polarity. Typical plasticizers are dioctyl sebacate (DOS) and *o*-nitrophenyl octyl ether (*o*-NPOE).

Lipophilic ionic sites

Lipophilic ionic additive is a salt of lipophilic anion/cation and an exchangeable counter ion. Ionic additive provides membrane *permselectivity* – ability of the membrane to allow only ions of the same charge sign as primary ion to pass (Donnan exclusion) which results in theoretical Nernstian response. Another advantage of using ionic additives is the reduction of membrane resistance which is especially important in microelectrodes. Typical ionic additive for cation selective electrode is tetraphenylborate derivatives [40].

Ionophore

The term *ionophore*, i.e., ion-carrier, has been coined in order to describe the ion transport activity of valinomycin and nigericin and to emphasize the dynamic aspects of the transport mechanism. But the term *ligand* was used to emphasize the association and coordination between the carrier molecule and the cation [41]. Ionophore is the key component determining the membrane *selectivity*. The ideal

ionophore should bind to only one ion, have fast exchange kinetics and lipophilic enough to ensure that it would not be leaching out easily from a membrane [7].

1.2.2 Electrode Response

A theoretical model on carrier-based ion-selective electrode has been reviewed by Bakker, Bühlmann and Pretsch [7].

Ion-selective electrode cell

The ion-selective electrode measuring cell (Figure 1.6) consists of ion selective electrode and outer reference electrode. A *reference electrode* is an electrochemical half cell which maintains a virtually constant potential with respect to a solution. Conventional drawing of the cell is

outer ref | test solution | membrane | inner ref.

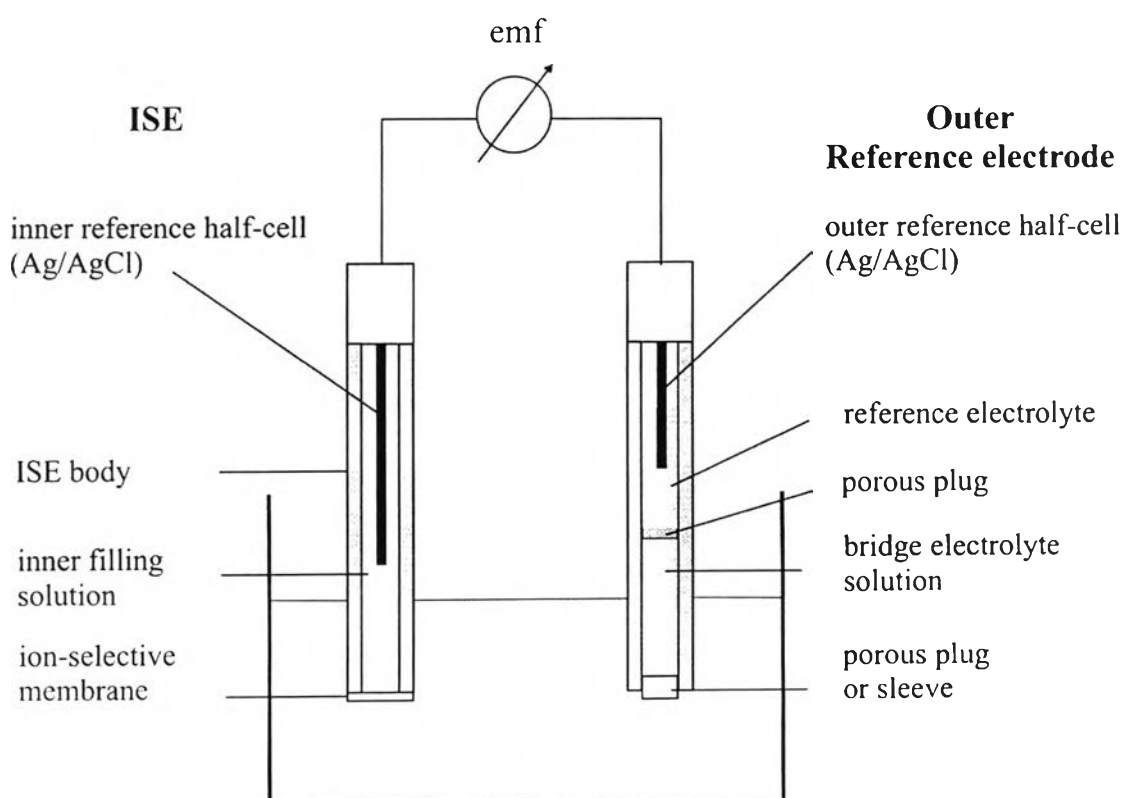


Figure 1.6 Schematic diagram of an ISE measuring cell and measuring circuit

The total potential difference (*electromotive force*, emf, E) across this cell can be measured by a high-impedance voltmeter and can be described as the sum of all individual potential component in the circuit as

$$E = E_{\text{const}} + E_J + E_M \quad (1)$$

where E_M is the membrane potential, E_J is the liquid junction potential at the sample/bridge electrolyte interface and E_{const} is potential that is sample-independent. To make E depends on E_M it is necessary to keep E_J small and constant. *Membrane potential*, E_M , consists of three contributions: two phase boundary potentials from the two membrane/solution interface and diffusion potential within the membrane. The latter is zero if no ion concentration gradient occurs. One of phase boundary potential, the potential at the membrane/inner filling solution interface, can be assumed to be independent on sample composition ($E_{\text{const},1}$). Therefore,

$$E_M = E_{\text{const},1} + E_{\text{PB}} \quad (2)$$

where E_{PB} is the phase boundary potential at the membrane-sample interface.

The relationship of E_{PB} and sample composition can be derived from thermodynamical considerations. For aqueous solution containing ion I in equilibrium with the membrane, electrochemical potential, $\tilde{\mu}$, of the ion I in aqueous phase is:

$$\tilde{\mu}(\text{aq}) = \mu(\text{aq}) + zF\phi = \mu^\circ(\text{aq}) + RT \ln a_1(\text{aq}) + zF\phi(\text{aq}) \quad (3)$$

and for the contacting organic phase:

$$\tilde{\mu}(\text{org}) = \mu(\text{org}) + zF\phi = \mu^\circ(\text{org}) + RT \ln a_1(\text{org}) + zF\phi(\text{org}) \quad (4)$$

where μ is the chemical potential, μ° is chemical potential under standard conditions, z is the charge of the ion I, a_1 is the activity of ion I, ϕ is the electrical potential, and R , T and F are the universal gas constant, the absolute temperature and the Faraday constant, respectively.

Under the assumption that the interfacial ion transfer and complexation process between ionophore and ion I in membrane are relatively fast so that the

equilibrium holds at the interface, the electrochemical potentials for both phases are the same. This leads to

$$E_{PB} = \Delta\phi = -\frac{\mu^\circ(\text{org}) - \mu^\circ(\text{aq})}{zF} + \frac{RT}{zF} \ln \frac{a_1(\text{aq})}{a_1(\text{org})} \quad (5)$$

where $\Delta\phi = \phi(\text{org}) - \phi(\text{aq})$. If $a_1(\text{org})$ is constant, it could be combined with other sample-independent terms into $E_{const,2}$ and equation (5) reduce to the form of the Nernst equation

$$E_{PB} = E_{const,2} + \frac{RT}{z_1F} \ln a_1(\text{aq}) \quad (6)$$

Substitution of E_{PB} into equation (2) and (1) gives an equation describing the response of the ion-selective electrode towards ion I in aqueous solution:

$$E_I = E_1^\circ + \frac{RT}{z_1F} \ln a_1(\text{aq}) \quad (7)$$

Where E_1° is a new constant including all sample-independent potential in a cell. The

Nernstian slope of the response function is $2.303 \frac{RT}{z_1F} = \frac{59.16 \text{ mV}}{z_1}$ at 25°C.

1.2.3 Electrode Characteristics

Selectivity of ISE membrane

The selectivity is one of the most important characteristics of the ISE as it measures reliability of measurement of an analyte in a sample. According to Nicolskii-Eisenmann formalism, the effect of an interference ion J can be described by replacing the activity term in the Nernst equation by a sum of selectivity-weighted activities:

$$E = E_1^\circ + \frac{RT}{z_1F} \ln (a_1(I) + K_{IJ}^{\text{pot}} a_J(I)^{z_I/z_J}) \quad (8)$$

where a_I (IJ) and a_J (IJ) are the activities of ion I and J in the mix sample and K_{IJ}^{pot} is *potentiometric selectivity coefficient* for I over J.

The effect of membrane component to the selectivity of the membrane has been proposed [7]:

$$K_{IJ}^{pot} = K_{IJ} \frac{(\beta_{JL_{nl}})^{z_1/z_2}}{\beta_{IL_{nl}}} \frac{R_T^-}{z_1 [L_T - n_1 (R_T^- / z_1)]^{n_1}} \times \left(\frac{z_2 [L_T - n_2 (R_T^- / z_2)]^{n_2}}{R_T^-} \right)^{z_1/z_2} \quad (9)$$

where

$\beta_{IL_{nl}}$ is the overall complex formation constant for the primary cation-ionophore complex with the stoichiometric factor n_1 .

$\beta_{JL_{nl}}$ is the overall complex formation constant for the primary cation-ionophore complex with the stoichiometric factor n_2 .

R_T^- is the total membrane concentrations of anionic sites.

L_T is the total membrane concentrations of ionophore.

K_{IJ} is the equilibrium constant for the ion exchange between uncomplexed primary I and interfering ion J between the sample and organic phase:

$$K_{IJ} = \left(\frac{a_I(aq)}{[I^{z_1+}]} \right) \left(\frac{[J^{z_2+}]}{a_J(aq)} \right)^{z_1/z_2} \quad (10)$$

where the bracket denote the concentration of free ions in organic phase.

For a simple case where I and J have equal charge and forming equal stoichiometry of their complexes ($z_1 = z_2$ and $n_1 = n_2$), equation (9) reduce to

$$K_{IJ}^{pot} = K_{IJ} \frac{\beta_{JL_{nl}}}{\beta_{IL_{nl}}} \quad (11)$$

In this case, the observed selectivity is directly proportional to the ratio of the stability constants of the involved complexes.

The methods for determination of the potentiometric selectivity coefficient of an ISE are classified into two main categories: *mixed solution methods* and *separate solution methods* [42] as follows:

Mixed Solution Method

- Fixed interference method (FIM)
- Fixed primary ion method (FPM)
- Two solution method (TSM)
- Matched potential method (MPM)

Separate solution method

- Separate solution method (SSM, $a_i = a_j$)
- Separate solution method (SSM, $E_i = E_j$)

Fixed interference method, FIM, the emf of an ISE cell is measured with solution of constant activity of interfering ion, a_j , and varying activity of primary ion. The emf values obtained are plotted vs. the logarithm of the activity of the primary ion a_i . The intersection of the extrapolation of the linear portions of this plot indicates the value of a_i which is used to calculate from:

$$K_{IJ}^{pot} = \frac{a_i}{(a_j)^{z_i/z_j}} \quad (12)$$

In *fixed primary ion method, FPM*, the emf of an ISE cell is measured with solution of constant activity of primary ion, a_i , and varying activity of interfering ion a_j . The emf values obtained are plotted vs. the logarithm of the activity of the interfering ion. The intersection of the extrapolation of the linear portions of this plot indicate the value of a_j which is used to calculate from equation (12)

In *two solution method, TSM*, the emf of an ISE cell is measured with a pure solution of primary ion, E_i and a mixed solution of the primary and interfering ion E_{i+j} . Then

$$K_{IJ}^{pot} = \frac{a_i (e^{\Delta E z_i F / (RT)} - 1)}{(a_j)^{z_i/z_j}} \quad (13)$$

where $\Delta E = E_{I+J} - E_I$

In *matched potential method*, MPM, the potentiometric selectivity coefficient is defined as the activity ratio of primary and interfering ions that give the same potential change under identical conditions. This method does not depend on the Nicolskii-Eisenmann equation at all. The determination starts by first adding a specified amount of the primary ion solution into a reference solution that contains a fixed activity (a_I) of primary ions to give the *total activity* a_I' and the corresponding potential change (ΔE) is recorded. Next, a solution of an interfering ion is successively added to another reference solution in separate experiment until the same potential change (ΔE) is recorded. The change in potential at constant background of the primary ion must be the same in both cases. If the final activity of J in solution is a_J , then

$$K_{IJ}^{pot} = \frac{(a_I' - a_I)}{a_J} \quad (14)$$

In *separate solution method* (SSM, $a_I = a_I$), the emf of an ISE cell is measured with each of two separate solutions, one containing the ion I with activity a_I (but no J), the other containing the ion J at the same activity a_I (but no I). If the measured values are E_I and E_J respectively, the value may be calculated from the equation:

$$\log K_{IJ}^{pot} = \frac{(E_J - E_I)z_I F}{2.303 RT} + \left(1 - \frac{z_I}{z_J}\right) \log a_I \quad (15)$$

In *separate solution method* (SSM, $E_I = E_J$), the $\log a$ vs E relations of an ISE for the primary and interfering ions are obtained independently. Then, the activities that correspond to the same electrode potential value are used to calculate

$$K_{IJ}^{pot} = \frac{a_I}{(a_J)^{z_I/z_J}} \quad (16)$$

Response time

The response time is another important characteristics of the ISE. According to IUPAC, response time ($\Delta E/\Delta t$) is the time which elapses between the instant when an ISE and a reference electrode are brought into contact with a sample solution (or at which the activity of the ion of interest in a solution is changed) and the first instant at which the emf/time slope ($\Delta E/\Delta t$) becomes equal to a limiting value selected on the basis of the experimental conditions and/or requirements concerning the accuracy (e.g. 0.6 mV/min). The graphical definition is shown in Figure 1.7.

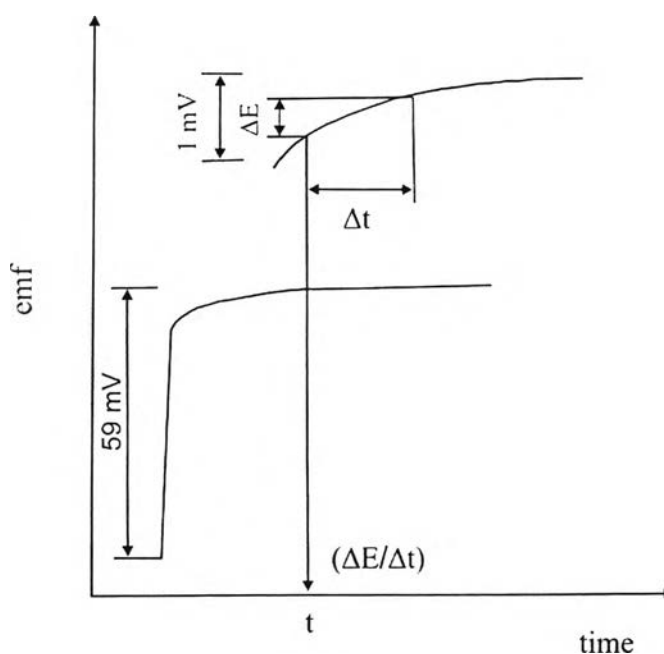


Figure 1.7 Definition and determination of response time. Redrawn from [43]

The possible process responsible for the length of the response time is the interfacial ion-exchange and the diffusion-controlled equilibration of the sample with the aqueous side of the membrane. For electrodes equilibrated with the salt of an ion to which they respond according to the Nernst equation, diffusion through a stagnant aqueous layer is the slowest process which defines the response time in this situation. Fast stirring of aqueous solution reduces the thickness of a stagnant layer which result in faster response time than the unstirred solution. For electrode with a change in membrane composition after measurement such as when use with a sample of different composition or use in selectivity determination, the internal diffusion in membrane may be a limiting process.

Detection limits

In practice, a calibration plot (a plot of cell emf vs. the logarithm of the single ionic activity or concentration of a given species) has the shape as shown in Figure 1.8. The *detection limit* may be taken as the activity (or concentration) of I at the point of intersection of the extrapolate linear midrange and final low concentration level segments of the calibration plot. At too high ionic activity, the ISE becomes insensitive to activity so that the slope of the curve changes.

There are two main reasons for the deviation from Nernstian slope at lower ion activity: (a) in the absence of interfering ion or ISE is highly selective, a constant release of a low amount of primary ions from the membrane into the sample. The result is that the activity of primary ion at membrane-sample interface is higher than that in the bulk so the response of the electrode becomes insensitive to sample activity changes. (b) in the presence of interfering ions and ISE has limited selectivity, the interfering ion compete with primary ion. By rearranging equation (12)

$$a_1(\text{DL}) = K_{IJ}^{\text{pot}} (a_j)^{z_j/z_1} \quad (17)$$

that is, the detection limit of the ISE in a solution with a given interfering ion activity can be predicted from the potentiometric selectivity coefficient.

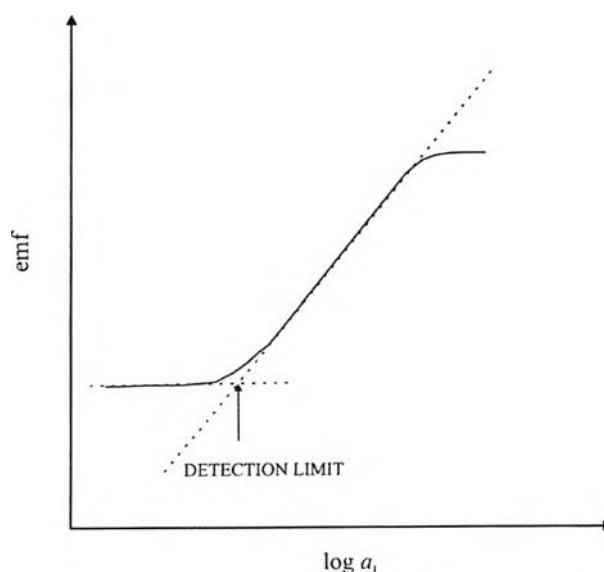


Figure 1.8 Calibration plot of an ISE showing practical definition of detection limit. a_1 denote the single ion activity of single primary ion I

1.3 Ligand for Copper(II) Ion Selective Electrode

Ionophore for copper(II) ion used in ion-selective electrode (ISE) has been extensively reviewed and categorized [42,44]. Some ionophores published later are cited in Table 1.1 and the corresponding structure of some ionophores is followed at the end of the table. Although it is not a complete collection, it at least reflects diversity of ionophores and the trend in the design for the ligand selective for Cu^{2+} ion. Because of a limited space, only some characteristics of interest are shown.

Table 1.1 Ionophore and some characteristics of Cu^{2+} ion-selective electrode

ligand [reference]	membrane composition (weight percent)	method $\log K_{\text{Cu}, \text{M}^{n+}}^{\text{pot}}$	linear range (M)	slope (mV decade ⁻¹) at 25°C	response time
L1 [45]	L1 (0.5 %) NaTPB (5.0 %) <i>o</i> -NPOE (61.0%) PVC (33.5 %)	FPM Mn^{2+} -2.29 Fe^{3+} -1.34 Co^{2+} -2.13 Zn^{2+} -2.10 Ag^+ n.d Cd^{2+} -2.09 Hg^{2+} -1.19 Pb^{2+} -2.39 Na^+ -1.34 K^+ -3.89 Mg^{2+} -3.03 Ca^{2+} -3.00 Sr^{2+} -3.09 Ba^{2+} -3.14	5.0×10^{-6} – 5.0×10^{-2}	29.8	5 s
L2 [46]	L2 (5 %) oleic acid (10 %) benzyl acetate (55%) PVC (30%)	TSM Mn^{2+} n.d Fe^{3+} n.d Co^{2+} -1.62 Ni^{2+} -2.01 Zn^{2+} -2.35 Ag^+ n.d Cd^{2+} -1.59 Hg^{2+} -2.41 Pb^{2+} -2.20 Li^+ -1.49 Na^+ -0.48 K^+ -0.89 Cs^+ -0.80 Mg^{2+} n.d Ca^{2+} -1.64 Sr^{2+} -1.03 UO_2^{2+} -2.39	3.2×10^{-5} – 1.0×10^{-1}	30	< 20 s

Table 1.1 Ionophore and some characteristics of Cu²⁺ ion-selective electrode (cont.)

ligand [reference]	membrane composition (weight percent)	method $\log K_{Cu, M^{z+}}^{pot}$	linear range (M)	slope (mV decade ⁻¹) at 25°C	response time
L3 [47]	L3 (1.0%) KTCIPB (0.75 mol%) <i>o</i> -NPOE (66%) PVC (33%)	MPM	3.2×10^{-5} – 3.2×10^{-3}	28.5	-
		Mn ²⁺	n.d		
		Fe ³⁺	-1.17		
		Co ²⁺	n.d		
		Ni ²⁺	-1.72		
		Zn ²⁺	n.d		
		Ag ⁺	n.d		
		Cd ²⁺	-1.92		
		Hg ²⁺	n.d		
		Pb ²⁺	n.d		
		Li ⁺	n. r		
		Na ⁺	n.r		
		K ⁺	-1.6		
		Cs ⁺	n.r		
		Mg ²⁺	n.d		
Ca ²⁺	n.d				
Sr ²⁺	n.d				
Rb ⁺	-1.11				
L4 [48]	L4 (1.0%) DBP (66.5 %) PVC (32.5%)	FPM	7.0×10^{-7} – 5.0×10^{-2}	30	10 s
		Mn ²⁺	n.d		
		Fe ³⁺	-3.27		
		Co ²⁺	<-4.12		
		Ni ²⁺	<-3.5		
		Zn ²⁺	<-4.12		
		Pd ²⁺	-0.28		
		Cd ²⁺	<-3.5		
		Hg ²⁺	<-3.5		
		Pb ²⁺	<-4.12		
		Li ⁺	<-4.12		
		Na ⁺	<-4.12		
		K ⁺	n.d		
		Cs ⁺	n.d		
		Mg ²⁺	<-		
		Ca ²⁺	4.12 <-4.12		
		Sr ²⁺	n.d		
		Ba ²⁺	<-4.12		
		Cr ³⁺	-4.01		
		Al ³⁺	<-4.12		
V ⁺⁵	<-4.12				
Mo ⁺⁶	<-4.12				
L5 [49]	L5 (5 %) oleic acid (15%) <i>o</i> -NPOE (55%) PVC (30%)	MPM	1.0×10^{-6} – 1.0×10^{-1}	29.8	10 s
		Mn ²⁺	n.d		
		Fe ³⁺	n.d		
		Co ²⁺	-3.70		
		Ni ²⁺	-3.70		
		Zn ²⁺	-3.40		
		Ag ⁺	-4.00		
		Cd ²⁺	-3.52		
		Hg ²⁺	n.d		
		Pb ²⁺	n.d		
		Li ⁺	-4.40		
		Na ⁺	-4.00		

Table 1.1 Ionophore and some characteristics of Cu²⁺ ion-selective electrode (cont.)

ligand [reference]	membrane composition (weight percent)	method $\log K_{Cu, M^{z+}}^{pot}$	linear range (M)	slope (mV decade ⁻¹) at 25°C	response time	
L5 (cont.)		K ⁺	-3.70			
		Cs ⁺	-4.15			
		Mg ²⁺	-3.52			
		Ca ²⁺	-3.40			
		Sr ²⁺	n.d			
		Ba ²⁺	n.d			
L6 [50]	L6 (3.2 %) NaTPB (1.6%) DOP (64.9%) PVC (30.3 %)	MPM		6.3 × 10 ⁻⁷ – 2.0 × 10 ⁻²	30	< 10 s
		Mn ²⁺	n.d			
		Fe ³⁺	n.d			
		Co ²⁺	n.d			
		Ni ²⁺	-5.00			
		Zn ²⁺	-3.34			
		Ag ⁺	n.d			
		Cd ²⁺	-2.66			
		Hg ²⁺	-2.92			
		Pb ²⁺	-2.37			
		Tl ⁺	-3.92			
		Li ⁺	n.d			
		Na ⁺	n.d			
		K ⁺	n.d			
		Cs ⁺	n.d			
		Be ²⁺	n.d			
		Mg ²⁺	n.d			
		Ca ²⁺	n.d			
		Sr ²⁺	n.d			
		Ba ²⁺	n.d			
L7 [51]	L7 (6 %) oleic acid (8%) <i>o</i> -NPOE (56%) PVC (30 %)	Co ²⁺	-3.03			
		Ni ²⁺	-2.19			
		Zn ²⁺	-1.49			
		Ag ⁺	-2.11			
		Cd ²⁺	-2.28			
		Hg ²⁺	-3.72			
		Pb ²⁺	-1.38			
		Li ⁺	n.d			
		Na ⁺	n.d			
		K ⁺	n.d			
		Cs ⁺	n.d			
		Be ²⁺	-3.12			
		Mg ²⁺	n.d			
		Ca ²⁺	n.d			
		Sr ²⁺	-4.30			
		Ba ²⁺	n.d			
		Tl ⁺	-2.19			
Al ³⁺	-3.13					
La ³⁺	-4.07					
UO ₂ ²⁺	-3.16					

Table 1.1 Ionophore and some characteristics of Cu²⁺ ion-selective electrode (cont.)

ligand [reference]	membrane composition (weight percent)	method $\log K_{Cu, M^{z+}}^{pot}$	linear range (M)	slope (mV decade ⁻¹) at 25°C	response time
L8 [52]	L8 (5.0 %) oleic acid (16.4 %) <i>o</i> -NPOE (51.2%) PVC (27.4 %)	MPM	2.0×10^{-6} – 5.0×10^{-2}	29.5	5 s
		Mn ²⁺	-2.87		
		Fe ³⁺	n.d		
		Co ²⁺	-2.52		
		Ni ²⁺	-2.61		
		Zn ²⁺	-2.88		
		Ag ⁺	-0.10		
		Cd ²⁺	-3.04		
		Hg ²⁺	-1.58		
		Pb ²⁺	-3.28		
		Na ⁺	-2.82		
		K ⁺	-1.97		
		Cs ⁺	-2.41		
		Mg ²⁺	-3.10		
		Ca ²⁺	-3.25		
Sr ²⁺	n.d				
Ba ²⁺	-3.65				
L9 [53]	L9 (5.5 %) KTCIPB (3.7 %) <i>o</i> -NPOE (63%) PVC (27 %)	MPM	1.0×10^{-6} – 1.0×10^{-2}	29.1	10 s
		Mn ²⁺	n.r		
		Fe ³⁺	n.d		
		Co ²⁺	n.r		
		Ni ²⁺	n.r		
		Zn ²⁺	n.r		
		Ag ⁺	n.d		
		Cd ²⁺	-6.41		
		Hg ²⁺	n.d		
		Pb ²⁺	n.r		
		Li ⁺	n.d		
		Na ⁺	n.d		
		K ⁺	n.d		
		Cs ⁺	n.d		
		Mg ²⁺	n.d		
Ca ²⁺	n.d				
Sr ²⁺	n.d				
Ba ²⁺	n.d				
L10 [54]	L10 (5%) oleic acid (8%) benzyl acetate (57%) PVC (30%)	MPM	1.0×10^{-6} – 1.0×10^{-1}	29.0	5 s
		Mn ²⁺	n.d		
		Fe ³⁺	n.d		
		Co ²⁺	-3.6		
		Ni ²⁺	-4.0		
		Zn ²⁺	-4.0		
		Ag ⁺	-2.9		
		Cd ²⁺	-3.7		
		Hg ²⁺	n.d		
		Pb ²⁺	-2.7		
		Li ⁺	-3.2		
		Na ⁺	-4.2		
		K ⁺	-3.4		
		Cs ⁺	-2.7		
		Mg ²⁺	-3.9		
Ca ²⁺	-3.3				
Sr ²⁺	-4.3				

Table 1.1 Ionophore and some characteristics of Cu²⁺ ion-selective electrode (cont.)

ligand [reference]	membrane composition (weight percent)	method $\log K_{Cu, M^{z+}}^{pot}$	linear range (M)	slope (mV decade ⁻¹) at 25°C	response time
L10 (cont.)		Ba ²⁺ Tl ⁺	n.d -2.6		
L11 [55]	L11 (1%) NaTPB (1%) DOP (65%) PVC (33%)	MPM Mn ²⁺ Fe ³⁺ Co ²⁺ Zn ²⁺ Ag ⁺ Cd ²⁺ Hg ²⁺ Pb ²⁺ Li ⁺ Na ⁺ K ⁺ Cs ⁺ Be ²⁺ Mg ²⁺ Ca ²⁺ Sr ²⁺ Ba ²⁺ Ce ³⁺	n.d n.d -1.14 -1.10 -2.09 -0.27 -1.09 -0.35 n.d -2.35 -1.07 -1.22 n.d n.d -1.21 -1.20 -1.09 -1.25 -1.08	5.0 × 10 ⁻⁶ - 1.0 × 10 ⁻¹	29.6 30 s
L12 [56]	L12 (4 %) oleic acid (10%) <i>o</i> -NPOE (55%) PVC (31%)	SSM Mn ²⁺ Fe ³⁺ Co ²⁺ Ni ²⁺ Zn ²⁺ Ag ⁺ Cd ²⁺ Hg ²⁺ Pb ²⁺ Li ⁺ Na ⁺ K ⁺ Cs ⁺ Mg ²⁺ Ca ²⁺ Sr ²⁺ Ba ²⁺ Cr ³⁺	n.d n.d -2.41 -2.25 -3.41 -3.92 -3.60 -2.72 -2.72 n.d -3.72 n.d n.d n.d -3.20 n.d n.d -2.30	1.0 × 10 ⁻⁵ - 1.0 × 10 ⁻¹	29.2 < 10 s
L13 [57]	L13 (2 %) NaTPB (4.5%) <i>o</i> -NPOE (63.5%) PVC (30%)	SSM Mn ²⁺ Fe ³⁺ Co ²⁺ Ni ²⁺ Zn ²⁺ Ag ⁺ Cd ²⁺ Hg ²⁺ Pb ²⁺ Li ⁺ Na ⁺	-3.07 -2.09 -2.39 -2.66 -2.64 -2.68 -2.30 -2.07 -2.85 -2.07 -2.10	1.0 × 10 ⁻⁶ - 1.0 × 10 ⁻¹	29.3 < 20 s

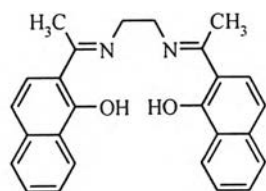
Table 1.1 Ionophore and some characteristics of Cu²⁺ ion-selective electrode (cont.)

ligand [reference]	membrane composition (weight percent)	method $\log K_{Cu, M^{z+}}^{pot}$	linear range (M)	slope (mV decade ⁻¹) at 25°C	response time	
L13 (cont.)		K ⁺	-2.19			
		Cs ⁺	n.d			
		Mg ²⁺	-2.17			
		Ca ²⁺	-2.12			
		Sr ²⁺	-2.19			
		Ba ²⁺	-2.60			
		Cr ³⁺	-3.27			
		La ³⁺	-3.06			
		Ce ³⁺	-3.12			
		Al ³⁺	-3.48			
L14 bis(acetyl acetonato) copper(II) [58]	L14 (1 %) NaTPB (1%) TBP (65%) PVC (33%)	MPM		2.0×10^{-6} - 1.0×10^{-1}	29.3	9 s
		Mn ²⁺	-1.74			
		Fe ³⁺	-2.08			
		Co ²⁺	-1.37			
		Ni ²⁺	-1.32			
		Zn ²⁺	-1.54			
		Ag ⁺	-1.92			
		Cd ²⁺	-1.92			
		Hg ²⁺	-2.06			
		Pb ²⁺	-1.47			
		Li ⁺	-2.02			
		Na ⁺	-1.82			
		K ⁺	-1.96			
		Cs ⁺	n.d			
		Ca ²⁺	-2.13			
		Mg ²⁺	-2.04			
		Sr ²⁺	-2.15			
		Ba ²⁺	-2.26			
L15 [59]	L15 (1.6 %) NaTPB (1.9%) DBBP (64.3%) PVC (32.1%)	FIM		1.0×10^{-3} - 1.0×10^{-1}	30	10 s
		Mn ²⁺	n.d			
		Fe ³⁺	-1.49			
		Co ²⁺	-1.66			
		Ni ²⁺	-1.62			
		Zn ²⁺	-1.46			
		Ag ⁺	-1.68			
		Cd ²⁺	-0.92			
		Hg ²⁺	-1.52			
		Pb ²⁺	-1.60			
		Li ⁺	-1.70			
		Na ⁺	-1.62			
		K ⁺	-1.42			
		Cs ⁺	n.d			
		Mg ²⁺	n.d			
		Ca ²⁺	-1.48			
		Sr ²⁺	n.d			
		NH ₄ ⁺	-1.59			
Al ³⁺	-1.52					

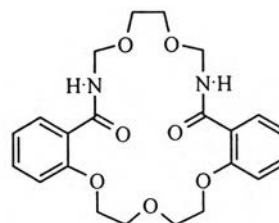
Table 1.1 Ionophore and some characteristics of Cu²⁺ ion-selective electrode (cont.)

ligand [reference]	membrane composition (weight percent)	method $\log K_{Cu, M^{2+}}^{pot}$	linear range (M)	slope (mV decade ⁻¹) at 25°C	response time
L16 [60]	L16 (5%) NaTPB (2%) DOP (48.9 %) PVC (48.9 %)	MPM Mn ²⁺ n.d. Fe ³⁺ n.d. Co ²⁺ -2.00 Ni ²⁺ -1.20 Zn ²⁺ -1.92 Ag ⁺ -1.17 Cd ²⁺ -1.49 Hg ²⁺ -2.03 Pb ²⁺ -1.19 Li ⁺ -1.20 Na ⁺ -2.00 K ⁺ -1.20 Cs ⁺ -2.00 Mg ²⁺ n.d. Ca ²⁺ -1.42 Sr ²⁺ n.d. NH ₄ ⁺ -2.72 Tl ⁺ -3.00	4.4 × 10 ⁻⁶ - 1.0 × 10 ⁻¹	29.3	8 s

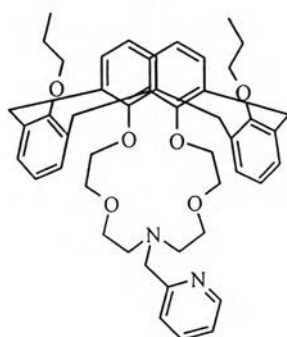
n.d = not determined n.r = no response



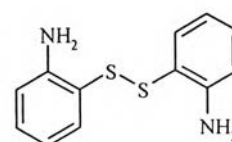
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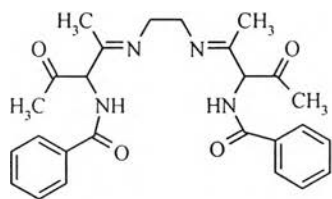
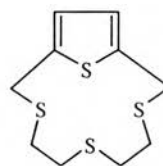
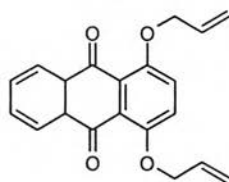
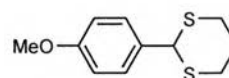
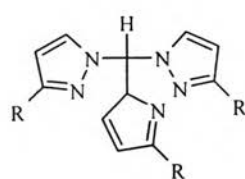
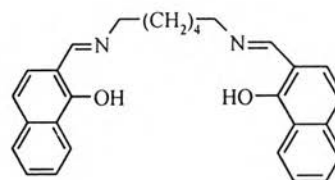
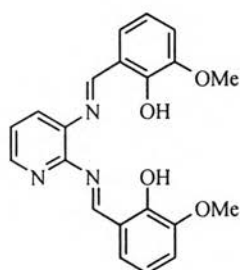
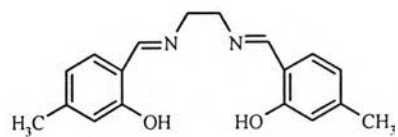
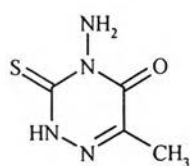
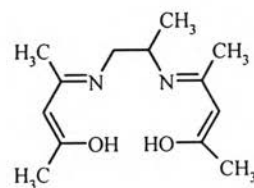
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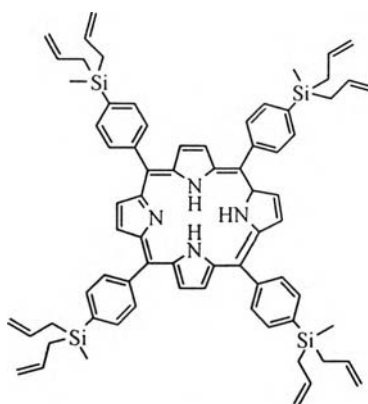


L3



L4

**L5****L6****L7****L8**R = *i*-Pr**L9****L10****L11****L12****L13****L15**

**L16**

1.4 Objective and Scope of This Research

The objective of this research is to design and synthesize calix[4]arene-based ligands for some transition metals such as copper(II) ion. The binding ability and selectivity of the synthesized ligands towards copper ions will be determined by means of UV-Vis spectrometry. The potentiometric selectivity of carrier-based ion selective electrodes based on the ligands will be evaluated.