CHAPTER II

THEORY

2.1 Secondary Chemical Equilibria Liquid Chromatography (SCE-LC)(73-80)

The retention of an eluite in liquid chromatography is based upon the distribution of the eluite between the stationary phase and mobile phase (primary equilibrium). By convention, any other equilibria that takes place in the mobile phase, or stationary phase, or both, are considered "secondary". In the past, manipulation of the mobile-stationary phase equilibrium distribution of the solute by using secondary chemical equilibria (SCE) was widely utilised in order to overcome low column efficiencies. The wide range of different chemistries that can be used to alter the mobile-stationary phase equilibrium to achieve better resolution or selectivity makes SCE a sensible alternative to the more conventional HPLC mode, some examples of SCE are shown in Table 2.1

Table 2.1: A general form and examples of secondary chemical equilibria

chemical equilibrium	analyte _	equilibrant
•AX - A + X •	AX, A	Х
HA A' + H'	weak acid	H ⁺
BH ⁺ ← B + H ⁺	weak base	H,
ML ← M + L	metal or ligand	ligand or metal
IP === I +P	ion	ion-pairing agent
SM === S + M	solute	micelle

^a General form of secondary chemical equilibrium.

Acid and base extraction provides some of the simplest examples of the use of SCE to facilitate distribution separation. The conversion of an organic acid or base into

a water-soluble salt permits its aqueous extraction from a water-immiscible organic phase. In this way, organic acids or bases can be separated from neutral organic compounds that are preferentially retained in the organic phase. In the same way, control of the pH of the aqueous phase permits the separation of strong acids or bases from weaker acids or bases.

2.1.1 Universal Retention Model of SCE-LC

One of the advantages of SCE-LC over conventional LC is the availability of a simple, accurate, universal retention model. The general equation for the capacity factor of an analyte A which participates with the equilibrant X in the equilibria shown below is

$$AX_{a} \longrightarrow AX_{a-1} \dots \longrightarrow A$$
 (2.1)

$$k' = F_{AX(a)}k'_{AX(a)} + F_{AX(a-1)}k'_{AX(a-1)} + ... + F_{A}k'_{A}$$
 (2.2)

where $F_{AX(n)}$, $F_{AX(n-1)}$, and F_A are the stoichiometric fraction of the analyte in each of its forms and $k'_{AX(n)}$, $k'_{AX(n-1)}$, and k'_A are the limiting capacity factors of each form of the analyte. Stated another way, the observed capacity factor of an analyte will be the weighted average of all the analyte's limiting capacity factors. For the single-step equilibrium (n=1), corresponding capacity factor equation are given below

$$AX \longrightarrow A + X \tag{2.3}$$

$$k' = F_{AX}k'_{AX} + F_{A}k'_{A}$$
 (2.4)

From equation (2.3), an analyte can exhibit one of three types of retention.

- 1. General retention. Both forms of an analyte (AX and A) are retained, but to a differing degree.
- 2. Partial retention. Either form AX or A of an analyte is retained.
- 3. Degenerate retention. Both forms of an analyte are equally retained or are unretained.

2.1.2 A Retention Model of Reversed-Phase Liquid Chromatography of Metal Complexes

One example of SCE is the use of complexing eluents for the separation of metal species. This method generally involves using one or more complexing agents in the mobile phase in order to resolve a few, or a group, of metal ions. Generally, the chromatographic resolution in these systems can be controlled by adjusting the concentration of the complexing agent(s) in the mobile phase. Other attractive features of this technique include the potential to generate high column efficiency and an improvement in detection properties of metal complexes over the free ions. A dilute solution of a weakly complexing ligand is the most frequently used mobile phase for this form of SCE, and these conditions generally favor the formation of one or more metal ligand species for each metal cation in the sample solution.

In a solution containing aquated metal ions M, and unidentate ligands L, there is a tendency for metal ions and metal complexes to engage in reactions which result in the addition or replacement of one or more of the ligands in the coordination spheres of the metal ions. The following equations and equilibrium constants can be used to describe such a system at equilibrium:

$$M + L \longrightarrow ML \qquad K_1 = [ML]/[M][L] \qquad (2.5a)$$

$$ML + L \longrightarrow ML_2 \qquad K_2 = [ML_2]/[ML][L] \qquad (2.5b)$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$ML_{n-1} + L \longrightarrow ML_n \qquad K_n = [ML_n]/[ML_{n-1}][L] \qquad (2.5c)$$

Where n represents the maximum coordination number of the metal. The K₁, K₂, and K_n are called stepwise formation constant (or stepwise stability constants). The magnitudes of these constants indicate the thermodynamic tendency of a species to exist (to be "stable") once equilibrium has been established in the system. If the pH and concentration of each ligand in solution are known, then these reactions and constants can be used to determine the equilibrium concentration of each metal species. In those instances in which the solution is also a liquid chromatographic chuent, such qualitative and quantitative information relates to the different types of chuite forms that are present in the mobile phase, free and complexed metal. This information is significant

because the retention that is observed for a particular chite is dependent upon the relative proportion of each different cluite forms present in solution.

The most valuable equilibria were selected on the basis of modern representations of the electronic and geometric structure of metal complexes, the nature of reversed-phase stationary phase, the character of intermolecular interactions and the retention mechanism for metal complexes.

Equilibria in a sorbent-eluent system: In using the binary water-organic mixtures as a mobile phase, the alkyl groups of the stationary phase (SiR) are solvated by molecules of an organic solvent (E) (eq.2.6) and unmodified (uncapped) silanol groups (SiOH) are hydrated (eq.2.7). The specific adsorption of the organic modifier should also be taken into account (eq.2.8).

SiR + E
$$\Longrightarrow$$
 SiR.E (2.6)
SiOH + H₂O \Longrightarrow SiOH.H₂O (2.7)
SiOH + E \Longrightarrow SiOH.E (2.8)

The dissociation of residual silanol groups can be assumed. However, in water-organic media this process might be suppressed to a considerable extent by the adsorption effects of strongly polar components of the mobile phase. Therefore, for this reason the decrease in concentration of SiOH groups and also the participation of SiO groups in the overall retention can be neglected.

Interphase distribution of metal complex: Addition of metal complex, ML_n, to the chromatographic system is accompanied by its solvation in the mobile phase followed by the distribution between the volume of mobile phase and a surface layer of the sorbent. These processes can be expressed by the following equations (eq.2.9-2.10)

$$MIL_n + E \iff ML_n.E$$
 (2.9)
 $ML_n + SiR \iff SiR. ML_n$ (2.10)

Solvation may take place by different mechanisms (interpheric or intrapheric) and the participation of both components of the mobile phase depending on the eluent composition and the type of complex. The reason for the retention of metal complexes in reversed-phase is the association of molecules of the mobile phase.

Reactions of metal complex in the chromatographic system: Among chemical reactions of metal complexes, which are possible under RP-LC conditions, the following were considered

Dissociation:

$$ML_a \leftarrow ML_{a-1}^+ + L^-$$
 (2.11a)

$$\dot{\mathbf{M}}^{(\mathbf{p}-1)^{+}} \stackrel{\cdot}{\longleftarrow} \dot{\mathbf{M}}^{\mathbf{p}^{+}} + \mathbf{L}^{-} \tag{2.11b}$$

Hydrolysis:

$$ML_n + H_2O \rightleftharpoons M(OH)L_{n-1} + HL$$
 (2.12a)

$$M(OH)_{a-1}L + H_2O \longrightarrow M(OH)_a + HL$$
 (2.12b)

Interaction with an electron-donor organic base:

$$ML_n + B \longrightarrow ML_n \cdot B$$
 (2.13)

In general, the last reaction can occur also by a ligand-exchange mechanism up to the formation of cationic complexes:

$$ML_n + mB \longleftrightarrow MB_n^{n+} + nL$$
 (2.14)

However, the replacement of ligands from the inner coordination sphere of the metal atom was observed experimentally only at high concentrations of donor-active compounds.

Other equilibria: Stabilization of metal complexes in the chromatographic process requires special methods such as the addition of the ligand or organic base to the mobile phase and using a buffer as its aqueous component.

2.1.3 A Retention Model of Ion-Pair Reversed-Phase Liquid Chromatography

The application of reversed-phase ion-pair chromatography to the separation of charge solutes has gained wide acceptance as an alternative to ion-exchange. It is found that the addition of long-chained alkyl ions to the mobile phase gave enhanced separation of oppositely charged solute ions. This technique has been called "soap chromatography", "ion-pair chromatography", "solvent-generated (dynamic) ion-exchange chromatography", "solvophobic-ion chromatography", "surfactant chromatography", and "ion-interaction chromatography". The variety of nomenclature indicates the uncertainty which exists concerning the retention mechanism in this mode of liquid chromatography. There are three models describing the retention on the

surface of a reversed stationary phase. Notable among these are the "ion pairing model", the "dynamic ion exchange model", and the "ion interaction model".

lon-pairing model: It is known that the attraction between oppositely charged ions will lead to an association between them. Any association between two solutes will lower the chemical potential of both of them. To understand the influence of ion pairing on solute distribution consider first the two phase system, consisting of phase A and phase B, at equilibrium with the two species in the absence of ionic association. The ionic modifier will be distributed between the phases, as will the sample ion. Now, if association occurs between the ionic modifier and the sample ion in phase A only, the chemical potential of both species is reduced in phase A. As a result, the tendency of the sample ion and the ionic modifier to dissolve in phase A is increased, and some of each ion will move from phase B to phase A.

The model of ion pairs, which simply accounts for the electrostatic attraction between ions, shows that the formation constant for ion pair depends on the cube of the dielectric constant. Thus the coulombic association of ions because of electrostatic effects is greatly influenced by the solvent dielectric constant, and more weakly influenced by the presence of other ions. The association of ions with each other may also be promoted by chemical forces, in addition to simple coulombic attraction. For example, hydrophobic association of ions may occur in water, while hydrogen bonding can direct ion pair formation in non-polar media.

In a two-phase system, in which ions associate in both phases, it may be that the chemical force responsible for the joining together of a pair of ions in one phase are not the same forces that cause the ion-pair formation in the other phase. Therefore, the formation of ion pairs in the stationary phase of a chromatographic system does not necessarily mean that there will be ion pairs in the mobile phase. The role of ion pairs in reversed-phase chromatography is difficult to determine using chromatography alone. The formation constant for ion pair formation in both phases must be known, as well as the concentration of the ionic modifier and its activity coefficient in the stationary phase. The formation of ion pairs in the mobile phase alone decreases the retention of the sample ion, while the formation of ion pairs alone in the stationary

phase will increase it. In the presence of both influences, retention may increase, decrease, or remain constant in the presence of an ionic modifier.

Dynamic ion-exchange model: A dynamic ion-exchange model has the reversed-phase surface covered with modifier ion reagent (ion-pair agent), so the surface becomes like that of an ion exchanger. The sorption of the ionic modifier is assumed to follow a Langmuir isotherm if the buffer concentration is high. If the concentrations of buffer and ionic modifier are in the same range, the assumed isotherm is more complex, because the sorption is pictured as an equilibrium distribution of the ionic modifier and the prevailing counterion. For the case in which the modifier ion is an anion M and the sample ion is a cation S⁺ the minimum number of equilibria to describe the distribution of solute is given as follow:

Adsorption of sample ion onto L:

$$S_m^+ + Y_m^- + L_s \rightleftharpoons SYL_s$$
 (2.15)

Ion-pair formation in mobile phase:

$$S_m^+ + M_m^- \longrightarrow SM_m \qquad (2.16)$$

Adsorption of modifier ion into L:

$$X_m^+ + M_m^- + L_1 \rightleftharpoons XML_2 \qquad (2.17)$$

Adsorption of sample ion and modifier ion giving ion pair in stationary phase:

$$S_m^+ + M_m^- + L_1 \iff SML_1$$
 (2.18)

For in this case, L is the unoccupied "ligand" sites in/on the reversed-phase; X⁺ is the electrolyte cation in bulk solution; Y is the electrolyte anion in bulk solution. The lower case subscripts m and s refer to bulk solution mobile phase and to reversed-phase stationary phase, respectively.

Ion interaction model: In the proposed model, the ion-interaction reagent ions (ion pairing ions), are adsorbed and create a charged primary ion layer on the reversed-phase surface. The oppositely charged ions form a secondary ion layer. The bulk eluent contains ion-interaction reagent ions and oppositely charged. The solute with the same charge as ion-pairing agent will experience an electrostatic repulsion by the primary ion layer which will tend to keep the solute ions away from the stationary phase and will cause them to be eluted rapidly by the mobile phase. However, the ion-interaction

reagent distribution equilibrium is dynamic so that ion-interaction reagent is constantly desorbing, and an equivalent amount of ion-interaction reagent is adsorbing at the same rate. If the ion-interaction reagent concentration in the eluent is increased, the amount of adsorbed ion-interaction reagent will increase; if the eluent concentration is decreased, the amount adsorbed will decrease.

Uncharged molecules do not experience electrostatic repulsion (or attraction), their transfer across the primary and secondary ion layer is relatively unaffected by the presence of the ionic ion-interaction reagent. The secondary ion layer is also in dynamic equilibrium and other charged ions (the oppositely charged ions of primary layer) can compete for a position in this layer. If an ion with an adsorbophilic (or ehrophobic) functional group gets into the secondary ion layer, it will tend to be pushed from the secondary ion layer to the mobile phase-stationary phase interface. The addition of an oppositely charge to the primary ion layer has the net effect of neutralizing the charge for this layer. The net result is that a pair of ions (not necessarily an ion pair) has been adsorbed onto the stationary phase.

2.2 Mercury Compounds (81-86)

2.2.1 Chemistry and Production.

Mercury is the only metallic element, which is silvery-white liquid at ordinary temperature and pressure. Mercury was found in Epytain tombs of 1500 BC. Mercury is a transition element (group IIB in periodic table) and electron configuration as [Xe]4 f¹⁴5d¹⁰6s². The characteristics of mercury are atomic weight 200.59, atomic number 80, melting point -38.842 °C, boiling point 356.58 °C, specific gravity 13.546 (at 20°C), and has three oxidation state, Hg(0), Hg(I), and Hg(II). Hg(0) is the state with the inert pair, and Hg(I) and Hg(II) are formed by loss of one or two electrons, respectively. Mercury is obtained by heating cinnabar (HgS) in a current of air and by condensing the vapor.

$$2HgS + 3O_2 \longrightarrow 2HgO + 2SO_2 \qquad (2.19)$$

2HgO
$$\longrightarrow$$
 2Hg + O₂ (2.20)

Cinnabar was also reduced with iron and copper (or brass). Both metals were often used for holding the sulfide during heating.

$$HgS + Fe \longrightarrow FeS + Hg$$
 (2.21)

$$HgS + 2Cu \longrightarrow Cu_2S + Hg$$
 (2.22)

Mercury is purified from solids by allowing it to pass through perforated paper or leather. Dissolved metals are remove by passing a thin stream of the metal through dilute nitric acid, and then either distilling or electrolyzing. Mercury is measured in unit of flasks, and one flask contains 34.5 kilogram.

Mercury(I): The experimental strongly suggests that two mercury atoms are bonded together to give the dimeric species, Hg_2^{2+} . Presumably, the bond, 250 pm., is formed by the overlap of the 6s orbital achieving electron pairing and a diamagnetic species. The Hg_2^{2+} ions are moderately stable towards disproportionation in solution which has potential for reaction -0.115 V and equilibrium constant 1.15 x 10^{-2} . Most Hg(I) compounds are insoluble except the nitrate, chlorate, and perchlorate. Hence, reagents such as OH, S^2 , CN, and R_2S produce Hg(II) compounds from a solution containing Hg(I). The four Hg(I) halide, Hg_2X_2 , are known and have a linear structure. The chloride, bromide, and iodide are insoluble and precipitate from solution by adding an alkali metal halide to mercurous nitrate.

Mercury(II): Hg(II) is readily produced by oxidation of mercury with nitric acid,

$$3Hg + 8H^{+} + 2NO_{3}^{-} \longrightarrow 3Hg^{2+} + 2NO + 4H_{2}O$$
 (2.23)

Hg(II) is polarisable and is a soft acid associates strong with soft base, such as the S^2 ion. The four halides of Hg(II) are known and are prepared by direct action of the halogen on the metal or by the following reactions, where X=Cl, Br, and I.

$$HgSO_4 + 2NaX \longrightarrow Na_2SO_4 + HgX_2$$
 (2.24)

$$HgO + 2HX \longrightarrow HgX_2 + H_2O$$
 (2.25)

The chloride structure is linear. The aqueous solution of HgCl₂ (Cl⁻ concentration 0.01-1.00 x 10⁻⁶ mol/L) contains mainly the dichloride, but may also contain small amounts of Hg²⁺, HgCl⁺, HgCl₃, and HgCl₄²⁻ as shown in Figure 2.1. In aqueous system in pH range 2-6, Hg(II) can be hydrolysed giving Hg(OH)₂

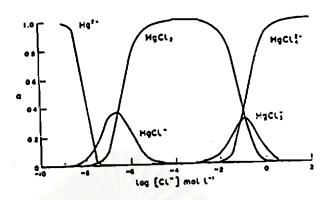


Figure 2.1: Distribution diagram for mercury-chloro species.

Organomercury compounds: organomercury compounds are historically important, and methylmercury was found in 1851 by Frankland, from the reaction,

$$Hg^{2+} + CH_3I \longrightarrow CH_3Hg^+\Gamma$$
 (2.26)

The Hg-C bond is not strong, but is stronger than the Hg-O bond Organomercury compounds have been used for the preparation of more stable organometallic system because of the weakness of Hg-C bond. Dialkylmercury, R₂Hg are prepared by reacting a Grignard reagent, or alkyllithium, or alkylaluminium with HgX₂. The organo compounds are typically covalent bond, and (CH₃)₂Hg (b.p. 92.5 °C) and (CH₃CH₂)₂ Hg (b.p. 170 °C) are liquid. The chlorocompounds, e.g. CH₃HgCl (m.p. 170 °C) and CH₃CH₂Hg (m.p. 193 °C) are solids.

2.1.2 The Uses of Mercury Compounds and the Occurrence in Environment

Mercury and organomercury are used in variety of products and industrial processes (see also Table 2.1). The main use of mercury, though declining, is as the mobile cathode in the chloroalkali industry, for the production of chlorine and caustic soda from the electrolysis of brine. Two separate cell reactions occur as below;

Electrolyser cell

At carbon cathode: $Cl_{(aq)} \longrightarrow 1/2 Cl_{2(g)} + e^{\circ} = -1.358 V$

At mercury anode: $Na^{+}_{(eq)} + e^{-} + xHg \longrightarrow NaHg_x$ $E^{\circ} = -1.868 \text{ V}$

:

Decomposer cell

At NaHgx cathode:

 $NaHg_x \longrightarrow Na^+_{(aq)} + e^- + xHg$

At carbon anode

 $H_2O + e^- \longrightarrow 1/2H_2 + OH_{(eq)}$

Caustic soda is produced in the last cell, and the mercury recycled back to the first cell. The large quantities of mercury were lost to the environment from these cells. In 1972 UK chloroalkali plants produced 850,000 tones of chlorine and discharged 34 tones of mercury, and in 1983 produced 810,000 tones of chlorine and discharged 12 tones of mercury. Also, mercury is used in electrical and measuring apparatus, such as mercury discharge lamps, power rectifiers, mercury batteries, thermometers, barometers and electrical switches. Mercury salts are used as catalysts in the industrial production of vinyl chloride, vinyl acetate and acetaldehyde from acetylene. In this process Hg(II) is reduced to Hg(0) but regenerated with iron(III).

Table 2.2: The use of organomercury compounds

compound	use	
CH ₃ HgX	Agricultural seed dressing, fungicide	
C ₂ H ₅ HgX	Cereal seed treatment	
RHgX	Catalyst for urethane, vinyl acetate production	
C ₆ H ₅ H _g X	Seed dressings, fungicide, slimicide, general	
	bactericide. For pulp and paper paints	
p-CH ₃ C ₆ H ₅ HgX	Spermicide	
ROCH ₂ CH ₂ HgX	Seed dressings, fungicides	
ClCH2CH(OCH3)CH2HgX	Fungicide, pesticide, preservative	
Thiomersal	Antiseptic, C ₂ H ₅ Hg derivative	
mercurochrome	Antiseptic, organomercury fluorescein derivative	
Mersalyl	Diuretic, methoxyalkyl derivative	
	RCH ₂ CH(OCH ₃)CH ₂ HgX	
Mercurophylline	Diuretic	

Mercury is also used as dental filling. A dental alloy of Ag (66.7-74.5%), Sn (25.3-27.0%), Cu (0.0-6.0%), and Zn (0.0-1.9%) is mixed with elemental mercury (approximately 1:1 weight ratio) to give a dental amalgam, a past which soon hardens in the tooth cavity. The amalgam is strong, resistant to abrasion, adheres strongly to the tooth, is of very low solubility and impermeable to saliva.

Phenylmercury was used as a slimicide in the pulp and paper industry that has been abandoned in Europe and North America. In agriculture organomercury are used, mainly phenylmercury and methoxyethylmercury but also small quantities of ethylmercury. Some mercury compounds (HgCl₂, HgO, Hg(CN)₂, HgNH₂Cl, HgI₂, and organomercury compounds) have antiseptic and preservative qualities which are still used in pharmaceutical and cosmetic. Mercury oxide is used in eye ointments to treat irritation, and HgI₂ is used to treat skin diseases. Organomercury compounds are also employed as diuretics and in the treatment of syphilis. Details are given in Figure 2.2, which all compounds are antiseptic, apart from mercuophylline, general formula for diuretics is RCH₂CH(OCH₃)CH₂HgX.

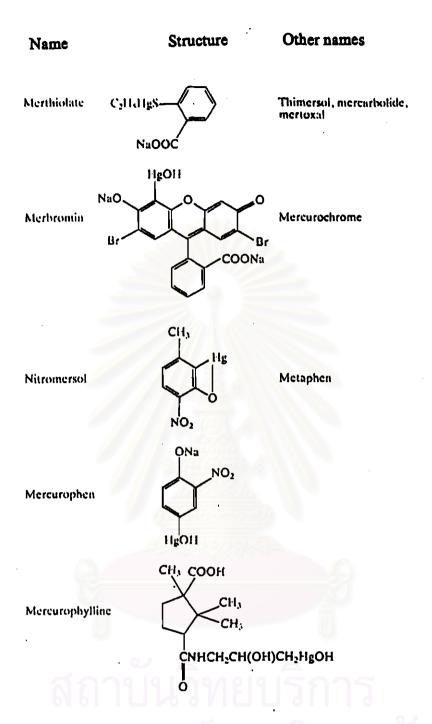


Figure 2.2: Some mercury antiseptics and diuretics.

Mercury compounds can contaminate the environmental resulted from misuse or spillage in both inorganic and organic forms. Moreover, the interconversion of inorganic and organomercury species can be occurred in the environment, and in some cases bacteria. Some of the important environmental interconversions given in Figure 2.3 and will be discussed below.

HgS_(s)

$$c \downarrow d$$

$$Hg^{o}_{(t)} \xrightarrow{a} Hg^{2+}_{(aq)} \xrightarrow{e} CH_{3}Hg^{-}_{(aq)} \xrightarrow{g} (CH_{3})_{2}Hg$$

$$f \downarrow h$$

$$C_{2}H_{5}Hg^{-}_{(aq)}$$

Figure 2.3: The interconversion of mercury species in the environment

reaction (a): The oxidation of mercury to Hg(II) can be achieved by dioxygen, and reagents that coordinate to the Hg(II) assist the reaction.

reaction (b): The reduction is achieved in aerobic condition by bacteria, such as the Pseudomonas genus.

reaction (c): The very low solubility of HgS drives the reaction to the right, especially in anaerobic conditions where H₂S, SH, and S² exist, but excess sulfide takes some mercury back into solution in the complex HgS₂²

reaction (d): In aerobic condition reaction occurred by removal of sulfide by its oxidation to sulfite and sulfate.

reaction (e) to (h): Methylation of mercury is achieved in the environment by methylcobalamine, a methyl derivative of vitamin B_{12} , and the degradation of methylmercury is also achieved by bacteria.

It is important that the methylation of inorganic mercury can be converted to more toxic methylmercury and may occur in various environmental matrices, such as in sediment, in the water column, in soil and by humic and fulvic material. Once formed, methylmercury may be further methylated by methylcobalamine to dimethylmercury. In aqueous solution, the second step is 6000 times slower than the first. Further methylation may also occur in the presence of sulfide ions or hydrogen sulfide by a dismutation process (see equation below).

$$2CH_3Hg^+ + S^2 \longrightarrow (CH_3Hg)_2S \xrightarrow{hv} (CH_3)_2Hg + HgS (2.27)$$

Factors affecting methylation extent and rates include total inorganic mercury concentration, organic content, pH, redox potential (E_b), temperature, the nature of the micro-organisms present, sulfide levels, and the nature of the complexation of mercury by natural ligands. Sulfide is a particularly important controlling factor. This is due to formation of intractable mercuric sulfide, which is hardly methylated and to removal of any methylmercury by dismutation promoted by sulfide ions. Following methyltion, methylmercury does not usually build up in sediments to more than about 1.5% if the total mercury present. This is an approximate equilibrium level between formation and removal. The demethylation of methylmercury to Hg(0) and methane may occur in either photolytic decay in the atmospheric or the demethylation by micro-organism occurring in water, sediments, soil or the testine is to Hg(II) then Hg(0). A number of organomercury/ inorganic mercury cycles within the sediment/water/air system have been proposed be given in Figure 2.4

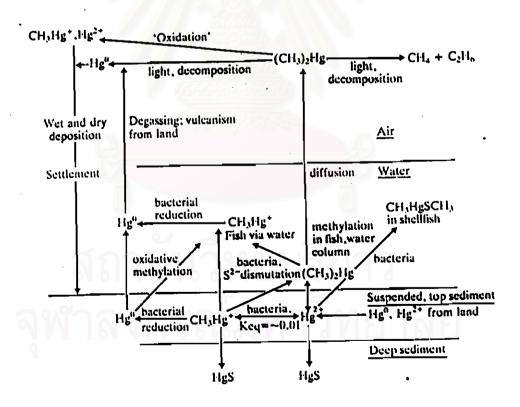


Figure 2.4: An environmental mercury cycle

2.1.3. The Toxicity of Mercury Compounds to Human Health

The toxicity of mercury occurs at three levels, depending on the chemical form. The order of decreasing toxicity is alkylmercury (esp. methylmercury) > Hg metal vapor > Hg(II) salts and phenyl and methoxy mercury salts. Mercury has well characterised toxic effects on both the physiological and the neurological systems of the body.

Mercury metal: The volatility of elemental mercury, and its use in a number of circumstances, means it's a serious toxin. The critical organs are the hings, kidneys and the brain. The vapor crosses the blood-brain barrier, and the metal is oxidized in the brain and in the blood stream. Once oxidized the mercury remains in the brain, whereas the free metal may move out again. The effects of mercury vapor on the respiratory tract are coughing, acute bronchial inflammation, chest pains, and in severe cases respiratory arrest. The exposures of mercury vapor have indicated a range of effects including loss of appetite, tremors, insomnia, shyness, diarrhea, voniting, and soreness in the oral cavity. Some of these effects indicate disorders of the central and peripheral nervous systems. Renal effects from high levels of mercury vapor exposure are proteinuria.

Inorganic mercury salts: Inorganic mercury is absorbed into the body less than mercury vapor, but the amount depends on the solubility of the species. The critical organ from intake by inhalation or ingestion is the kidney and the effect has been called sublimate nephrosis. Inorganic mercury also has an adverse effect on the central nervous system. Acute ingestion of inorganic mercury can cause precipitation of protein in the gastrointestinal tract and produce gastric pain, vomiting and bloody diarrhea. Renal damage can occur, including oliguria, severe anuria with azotemia and in severe cases renal failure. For chronic exposure, the renal effects recorded are proteinuria, albuminuria and oedema. The neurological effects are much the same as reported for other chemical forms of mercury. These include tremors, erethism fatigue, loss of memory and self confidence, and development of idiosynerasy. In severe case delirium with hallucinations and manic-depressive disorders have been reported.

Methylmercury: The most serious mercury toxin is methylmercury because of the solubility and binding ability of methylmercury to biological ligands results in a large half-life in various organisms for this species, e.g. 60-70 days in man, much longer than for inorganic forms (3-4 days). In addition to the direct toxicity of methylmercury, a slow decomposition to inorganic mercury may lead to secondary toxic effects as for inorganic mercury. Methylmercury readily crosses the placental and blood-brain barriers and it causes disintegration (lysis) of cells within the brain. This may involve a CH3Hg-S interaction. Of the methylmercury ingested and absorbed into the body, 90-95% became associated with the red cells and 5-10% with the plasma and gets into the brain. The main areas of brain function that are damaged by methylmercury are those that control sensory, visual, auditory, and coordination. The effects observed on human beings are, initially loss of sensation at the extremities and around the mouth (paresthesia) followed by loss of coordination in movement, loss of hearing, restricted visual field, blindness, coma, and death. Pregnant women, and unborn children, are most sensitive to methylmercury toxicity, especially the developing brain system of the child. Infants born to mothers with high intakes of mercury have had serious mental disturbances, including retardation of mental and physical development.