CHAPTER II
LITERATURE REVIEW

2.1 Chemistry of Mercury

Mercury is an element being a liquid at ambient conditions. Its melting and boiling points are -38.87°C and 357°C, respectively. Elemental mercury is quite dense (13.5 times more than liquid water under ambient conditions). The high density, low saturation vapor pressure and high surface tension control the behavior of elemental mercury in solid, liquid and gaseous matrices. The common physical properties of elemental mercury are listed in Table 2.1 (Wilhelm, 2001).

Table 2.1 Physical properties of elemental mercury (Wilhelm, 2001)

Atomic number	80
Atomic weight	200.59 atomic mass units
Boiling point	357 °C (675°F)
Boiling point/rise in pressure	0.0746 °C/torr
Density	13.456 g/cm^3 at 20 °C (0.489 lb/in3 at 68 °F)
Diffusivity (in air)	0.112 cm^2/sec
Heat capacity	0.0332 cal/g at 20 °C (0.060 Btu/lb at 68 °F)
Henry's law constant	0.0114 atm m^2/mol
Interfacial tension (Hg/H$_2$O)	375 dyne/cm at 20 °C (68 °F)
Melting point	-38.87 °C (-37.97 °F)
Saturated vapor pressure	0.16 N/m^3 (pascal) at 20 °C (68 °F)
Surface tension (in air)	436 dyne at 20 °C (68 °F)
Vaporization rate (still air)	0.007 mg/cm^{2}hr for 10.5 cm^2 droplet at 20 °C

Mercury occurs in nature in the zero (elemental), +1 (mercury [I] or mercurous), or +2 (mercury [II] or mercuric) valence states. Mercurous compounds usually involve Hg-Hg bonds and are generally unstable and rare in nature.

Mercury occurs most prevalently in the elemental form or in the inorganic mercury form. Common mercuric compounds include mercuric oxide, mercuric chloride, mercuric sulfide and mercuric hydroxide. Organic mercury forms also exist and consist of two main groups: R-Hg-X compounds and R-Hg-R compounds, where R = organic species, of which methyl ($-CH_3$) is prominent, and X = inorganic anions, such as chloride, nitrate or hydroxide. The R-Hg-X group includes monomethylmercury compounds. The most prominent R-Hg-R compound is dimethylmercury.

Mercury is difficult to oxidize in the natural environment and spilled mercury (in soil for instance) retains the elemental form indefinitely in the absence of moisture and bacteria until evaporation. Mercury can be oxidized by the stronger oxidants including halogens, hydrogen peroxide, nitric acid and concentrated sulfuric acid. Mercury is oxidized and methylated in sediments by sulfate-reducing bacteria.

Selected solubility and volatility data for elemental mercury and some mercury compounds in water are presented in Table 2.2. It is important to note that mercury sulfides are largely insoluble in water (and oil) and, as pollutants are less available to receptors.

Under ambient conditions, silver, gold, copper, zinc, and aluminum readily form amalgams with elemental mercury. The solubility of these metals in elemental mercury is relatively low. The solubility of zinc in mercury is approximately 2 g Zn/100 g Hg, while gold solubility in mercury is only 0.13 g Au/100 g Hg. Silver, copper and aluminum have even lower solubility than gold. The affinity of mercury for gold is important in analytical procedures that trap vapor phase of mercury on gold collectors.

2.2 Mercury Species in Crude Oil

There are several chemical forms of mercury existing in geological hydrocarbons. Each of them has particular chemical properties. Table 2.2 presents the list of mercury compounds in petroleum.

Table 2.2 Solubility and volatility of mercury compounds (Wilhelm and Bloom, 2000)

Formula	State	Volatility	Solubility in H_2O at 25°C	Name
Hg^0	Liquid	Boiling Point 357°C Vapor Pressure 20 mg/m^3 at 25°C	50 ppb	Elemental
$HgCl_2$	Solid	Boiling Point 302°C	70 g/liter	Mercuric chloride
HgS	Solid	Sublimes under vacuum, Decomposes at 560°C	- log Ksp[1] = 52	Mercuric sulfide
$HgSe$	Solid	Sublimes under vacuum, Decomposes at 800°C	- log Ksp ~ 100	Mercuric selenide
$(CH_3)_2Hg$	Liquid	Boiling Point 96°C	< 1 ppm	Dimethyl-mercury
$(C_2H_5)_2Hg$	Liquid	Boiling Point 170°C	< 1 ppm	Diethyl-mercury

(1) Ksp = solubility product

Actually, the chemistry is much more diverse. Also, mercury in crude oil can be a chemical component of a variety of complex asphaltenic and sulfur–containing molecule.

Differentiation of the chemical forms of mercury in crude oil is difficult to accomplish. The development of operational methods set mercury in chemical categories which are determined by volatilities and phase solubility properties.

2.2.1 Dissolved Elemental Mercury (Hg^0)

Elemental mercury is a highly volatile compound to other metals. Also, it is soluble in crude oil and hydrocarbon liquids in atomic form to a few ppm. Elemental mercury is adsorptive and adsorbs on metallic components (pipes and

vessels), suspended wax, sand and other suspended solid materials in liquids. The measured concentration of dissolved elemental mercury typically decreases with distance from the wellhead due to adsorption, reaction with iron, conversion to other forms and loss of the suspended fraction.

2.2.2 Dissolved Organic Mercury

Dissolved organic mercury compounds bounding to at least one carbon atom, RHgR and RHgX where R= CH_3, C_2H_5, etc. and X = Cl- or other inorganic anion are highly soluble in crude oil and gas condensate. Organic mercury compounds are similar to elemental mercury in adsorptive tendencies but differ in their boiling points and solubility. So, they partition to distillation fractions in a different fashion from Hg^0. This category includes dialkylmercury (i.e. dimethylmercury, diethylmercury) and monoethylmercury halides (or other organic ions).

2.2.3 Dissolved Inorganic (ionic) Mercury Salts

Mercury salts (mostly halides), $Hg^{2+}X$ or $Hg^{2+}X_2$ where X is an inorganic, are soluble in oil and gas condensate but preferentially partition to the water phase in primary separations. Mercuric chlorides have a reasonably high solubility in organic liquids (about 10 times more than elemental mercury). Ionic salts also may be physically suspended in oil or may be attached (adsorbed) to suspended particles.

2.2.4 Dissolved Complex Mercury

Mercury bound to atom other than carbon with sulfur being the most common, HgK or HgK_2. Typical compounds might include mercury complex by thiophenes, thiols, etc. Mercury is not thought to exist as a porphylin complex.

2.2.5 Suspended Mercury Compounds

The most common examples are mercuric sulfide (HgS) and selenide (HgSe), which are insoluble in water and oil but may be present as suspended solid particles of very small particle size.

2.2.6 Suspended Adsorbed Mercury

This category includes elemental and organic mercury that is not dissolved but rather adsorbed on inert particles such as sand or wax. Suspended mercury and suspended mercury compounds can be separated from liquid feeds to the plant by physical separation techniques such as filtration or centrifugation.

The distribution of mercury species in crude oil and gas condensate varies significantly. Some oil may have elemental mercury as the dominant species (>90 percent of the total mercury concentration) while others may exhibit mostly oxidized or suspended form. Typically, crude oil and unprocessed gas contain considerable amount of suspended mercury. The dominant dissolved species in those feeds are elemental and ionic halide. There is also dialkylmercury existing in hydrocarbon but it is in low concentration.

Gas and liquid processing are able to cause transformation of one chemical form of mercury to another. A well-known example is the reaction of elemental mercury with sulfur compounds. The mixing of gas and/or condensate from sour and sweet reservoirs allows the reaction of elemental mercury with S_8 or ionic mercury with H_2S to form particulate of HgS that can precipitate in tanks and deposit in equipment. In theory, the high temperature processing such as hydrotreating in refineries should convert dialkylmercury and complex mercury to the elemental form.

The partitioning of mercury into product and effluent streams during petroleum processing often, concentrating in specific distillation cuts are largely determined by its solubility. Table 2.3 provides the approximated solubility of the common species in several liquid matrices.

Table 2.3 Approximated solubility of mercury compounds in liquids at 25°C (Wilhelm and Bloom, 2000)

Species	Water (ppm)	Oil (ppm)	Glycol (ppm)
Hg^0	0.05	2	< 1
RHgR	?	miscible	> 1
$HgCl_2$	70,000	> 10	> 50
HgS	0.01	< 0.01	< 0.01
HgO	50	low	< 0.01
CH_3HgCl	> 10,000	1,000	> 1,000

2.3 Overview of Analytical Methods

There are many analytical methods of mercury and mercury compounds. Each of them is used to determine total mercury in liquid or gaseous hydrocarbons and to quantitatively specify mercury species. Analytical methods can be classified by collection (sampling), species conversion/separation (digestion, extraction, filtration, vaporization) and detection method (Wilhelm and Bloom, 2000).

Hydrocarbons containing mercury are difficult to sampling owing to partitioning of mercury compounds among the phases, species interconversion in some sample container, loss of non-polar compounds in plastic container and adsorption of mercury on sample container surface. Each position should be taken into account when mercury concentration in hydrocarbon is required.

Hg^0 and some lesser amount of $Hg(CH_3)_2$ mostly exist in gas matrices. The mercury concentration in gas is difficult to measure directly by spectroscopic method (UV, visible, IR and X-ray) because of interference by the hydrocarbons. There are three common methods to determine elemental mercury concentration in gas: wet collection method, dry collection method and activated carbon impregnated with iodide. A prevalent wet collection method is to bubble gas containing mercury through a permanganate solution where Hg^0 in gas was oxidized to Hg^{2+}. Then,

Hg^{2+} is reduced to Hg^0 by using stannous chloride and separated by volatilization or sparging into an inert gas stream for quantitative detection which are usually UV atomic absorbance or UV atomic fluorescence. These methods are accurate and reasonably sensitive if adequate volumes of gas are used; however, the equipment employed to collect the sample is quite difficult and also required a large volume of sample. The amalgamation of Hg^0 on Ag, Au or Ag/Pt (sputtered on quartz) was applied in dry collection method. The metal collector is used to quantitatively collect the Hg^0 in gas which flow through the collector at very low flow rate. Also, the organomercury is trapped on collector but the gas flow rate is lower than that of Hg^0. To release mercury for detection, the amalgam is heated in an inert gas and it is very effective for light and dry gas. Heating the traps at 50°C to 150°C is required to prevent hydrocarbon condensation without compromising the collection efficiency, if heavier components contain in gas stream. Iodated carbon impregnated with potassium iodide is also used to trap mercury from gas metrics. The trap is then utilized in routine digestion analysis when Hg is already collected from the certain volume of gas; however, iodated carbon traps are less sensitive than gold trap and required a higher volume of collection. It is also used for moist gas which maintains at temperature above the condensation temperature of water and unprocessed gas where reasonably high concentrations are expected.

In case of liquid hydrocarbons, the mercury concentrations are usually determined as total mercury instead of mercury species determination. Analytical methods include combustion, wet (hot) digestion and wet extraction. The combustion techniques oxidized the entire liquid hydrocarbons and mercury in the combustion gas is then trapped by amalgamation on gold. The amalgam is heated to desorb mercury for detection which is similar to that employed in gas. Acid digestion methods chemically oxidize all mercury species to mercuric ion (Hg^{2+}) that partitions to the aqueous phase. The mixture of nitric, hydrochloric, sulfuric acids and perchloric acids are employed for acid digestion. These methods should carefully be operated to avoid loss of mercury via vaporization. In the similar way, BrCl is used in extractive method for light hydrocarbon liquid. These methods do not chemically decompose the matrix. Less heat is required and loss of mercury due to volatile does not occur. Both digestion and extraction methods have treatment procedure in the

same way. The aqueous solutions are treated with stannous chloride or sodium borohydride to convert Hg^{2+} to Hg^0 and then sparged (Ar). The sparged gas is either sent directly to a detector or collected on a metal trap and then thermally desorb mercury into inert gas stream for detection. The most common forms of detection are cold vapor atomic absorbance (CVAA) and cold vapor atomic fluorescence (CVAF). CVAF is a very sensitive method and the detection limit 100 to 700 pg can be achieved. It allows accurate determination of trace amount of sample and also significantly reduces matrix interference by extreme dilution prior to analysis. Other types of total mercury analysis methods include inductively couple plasma (ICP) or microwave induced plasma (MIP) followed by mass spectrometry or atomic emission spectrometry (AE) detection and Neutron activation analysis (NAA). The ICP/MIP techniques and NAA method in which samples are irradiated in a nuclear reactor and the decay radiation (gamma) is quantitatively counted avoid digestion of the sample and also minimize some of potential errors that can occur in multi-step wet chemical processing of liquid sample. NAA method avoids wet processing of sample as well. NAA method has been used successfully to measure the total mercury concentration in crude oil.

Operational speciation of liquid sample includes multiple and sequential analyses for the various forms and a mass balance exercise (Wilhelm, 2001).

$$THg = Hg^0 + (RHgR + HgK) + Hg^{2+} + \text{suspended Hg} \quad (2.1)$$

Suspended mercury is quantitatively determined by measuring total mercury of an agitated sample followed by measuring total mercury of a filtered portion of the agitated sample. Ionic forms are determined by non oxidative extraction. The volatile elemental form (Hg^0) is determined by sparging and collecting the volatile component on a trap. The combustion techniques, extraction and acid digestion are typically used to determine total mercury concentration. The sum of the concentration of dialkylmercury and complexed mercury (RHgR + HgK) is often estimated by the discrepancy in the mass balance. Sophisticated techniques (GC-CVAF, GC-ICP/M) are required to determine the exact concentration of the organic mercury forms.

2.4 Study of Mercury Solubility in Water and Hydrocarbons

The dissolution of elemental mercury in water has been known since 1929. The first attempt to determine the solubility of mercury in water was done by Bonhoeffer and Reichardt (1929). They found that the existence of soluble mercury can absorb spectrum and showed the characteristic resonance line at 253.7 nm. The mercury solubility in pure water at various temperatures was conducted by using ultraviolet spectrophotometer in 1974 (Onat, 1974). This method used mercuric ion (Hg^{2+}) to convert the soluble mercury (Hg^0) into mercurous ion (Hg_2^{2+}) that presents the strong absorbance in the detector. It can quantitatively determine the mercury in water. Also, the results estimated by Beer's law were consistent with the experiment results. Moreover, it was found that the mercury solubility in water increased with increasing temperature. The solubility data and solubility curve as a function of temperature were depicted in Table 2.4 and Figure 2.1, respectively.

Secondly, total mercury dissolved in hydrocarbon has been studied in many research works. The various hydrocarbons were studied at constant temperature by using optical density (OD) technique (Kunt and Main, 1964). The saturation of mercury was obtained in 20 minutes by vigorous shaking. The optical density at 2560 °A of saturated solution of mercury in hydrocarbon was used to calculate the solubility. The experimental results were compared with one obtained from the thermodynamic calculation. The solubility measured from another technique also reported in this work. All solubility data are compiled in Table 2.5.

Table 2.4 Solubility of metallic mercury in water and the comparison of the results obtained from Beer's equation (Onat, 1974)

Temperature (^{o}C)	Concentration of soluble mercury		average deviation from mean	
	g.atom/l*	g.atom/l**	mg/100mg	%
25	3.05×10^{-7}	3.09×10^{-7}	0.0002	3.3
40	5.12×10^{-7}	5.19×10^{-7}	0.0002	1.9
50	7.43×10^{-7}	7.47×10^{-7}	0.0006	4.0
60	10.78×10^{-7}	10.87×10^{-7}	0.0008	3.0
70	13.33×10^{-7}	13.37×10^{-7}	0.0008	3.0
80	16.37×10^{-7}	16.40×10^{-7}	0.0002	0.6

*   Obtained from experiment,

**   Calculated from Beer's equation c= A/ab
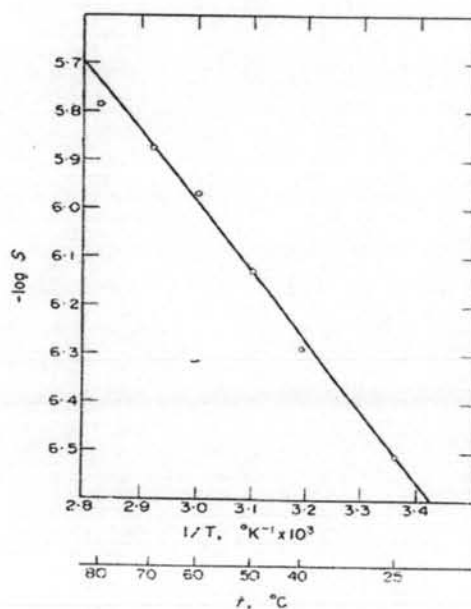
Figure 2.1 The solubility curves of mercury in water as the negative logarithm of molar solubility plotted against the reciprocal of absolute temperature (Onat, 1974).

Table 2.5 The solubility of mercury in some organic solvents (Kunt and Main, 1964)

Solvent	T (°C)	Solubility, μ moles/l		
		Experi-mental value*	Calculated from OD at 2650 A°	Calculated from thermodynamic equation
n-Pentane	25	-	5.8	5.0
n-Hexane	25	-	6.4	5.9
Isopentane	25	-	5.5	3.3
3- Methylpentane	25	-	5.1	7.4
2,2-Dimethylbutane	25	-	5.0	4.3
2,3- Dimethylbutane	25	-	6.0	6.0
n-Decane	25	-	5.5	1.5
Cyclohexane	25	11	-	15.8
Toluene	25	12.5	-	43.7
Benzene	25	12.0	-	66.7
Water	25	-	0.1	15.7×10^6
Methanol	25	-	1.52	0.97
Perfluorodimethyl-cyclobutane	25	-	0.34	0.46

* Radiotracer technique

According to Table 2.5, the solubility data quite agree with the calculated one from thermodynamic calculation (Hildebrand equation) except in cyclic aliphatic, aromatic hydrocarbon and water. It means that the thermodynamic equations are suitable for non-polar compounds. Four years later, the mercury solubility in various series of hydrocarbons such as aliphatic, aromatic hydrocarbon, and ether were mainly studied. Radiotracer technique was performed to measure the solubilities of mercury at 25 °C (Spencer and Voigt, 1968). The equilibrium was reached by shaking about 24 hours. The solubilities of mercury in aromatic and

aliphatic hydrocarbons were about 10^{-6} mole/l in water and in perfluorodimethylcyclobutane were for about 10^{-7} mole/l. The experiments were also conducted over the temperature range from 0 °C to 40 °C and the results were plotted into the logarithm correlation as log X = Alog T + B where X is the mole fraction of mercury and T is the absolute temperature. Hildebrand equation was calculated in order to compare with the experiment results. The coefficient of logarithm equation and solubilities of this work are presented in Table 2.6 and Table 2.7, respectively.

It can be concluded that the results are similar to the Kunt's results as shown in Table 2.5. The solubility calculated and listed in Table 2.7 are seen to agree well with experiment for aliphatic solvent, less for cyclic hydrocarbon, slightly less for aromatic and not at all for water. The determination of mercury solubility as a function of temperature in linear hydrocarbons was studied by treating with oxidizing solutions and using the cold vapor atomic absorption as detector. The experiments were performed in the temperature range from 5 to 40 °C (Okouchi and Sasaki, 1981). The temperature dependence of the mercury solubility in each hydrocarbon is shown in Figure 2.2 where X is mole fraction of the solute and T is the absolute temperature.

The result for pentane at 25°C was found to agree well with Kunt's results (Table 2.5). While the results for hexane, heptane, and octane agree well with those of Spancer results (Table 2.7). Six years later, solubilities of mercury in normal alkane was studied again. Pentane, hexane, heptane, octane and decane were selected in the experiment over the range of 0°C to 63°C (Clever and Iwamoto, 1987). It was observed that the molal solubility (mol kg^{-1}) of mercury is nearly independent of the normal alkane carbon number 5 -10 between 0°C and 63°C. The result can be fitted as shown in Figure 2.3 to the equation ln(S) (molality) = 5.1057 − 497090/T (absolute temperature). The obtained equation can also be used at other temperatures.

Table 2.6 Coefficients of logarithm equation giving the temperature dependence of the mercury solubility (Spencer and Voigt, 1968)

| Solvent	A	B
n-Hexane	17.084 ± 0.420	-48.366
n-Heptane	17.462 ± 0.301	-49.234
n-Octane	16.583 ± 0.228	-47.003
Isooctane	16.377 ± 0.451	-46.698
2,2-Dimethylbutane	14.905 ± 0.380	-43.089
Cyclohexane	13.140 ± 0.359	-38.405
Methylcyclohexane	16.011 ± 0.226	-45.563
Cyclohexene	17.148 ± 0.230	-48.294
Benzene	17.407 ± 0.360	-49.047
Toluene	16.034 ± 0.538	-45.567
o-Xylene	17.635 ± 0.316	-49.473
Isopropylbenzene	15.957 ± 0.235	-45.307
t-Buthylbenzene	16.689 ± 0.388	-47.140
Isopropyl ether	15.633 ± 0.578	-44.855
n-Butyl ether	15.666 ± 0.650	-44.696
Perfluorodimethyl Cyclobutane	29.921 ± 0.347	-73.746
Water	8.600 ± 0.575	-29.597

Table 2.7 Experiment and calculated solubilities at 25 °C (Spencer and Voigt, 1968)

| | Solubility | | |
| | μ moles/l | Mole fraction x 10^7 | |
Solvent	Experiment	Experiment	Equation
n-Hexane	6.3 ± 0.3	8.3	9.17
n-Heptane	6.6 ± 0.2	9.7	11.10
n-Octane	6.7 ± 0.1	11.0	12.80
Isooctane	4.2 ± 0.2	7.0	5.62
2,2- dimethylbutane	4.7 ± 0.3	6.3	4.73
Cyclohexane	12.1 ± 0.3	13.2	26.80
Methylcyclohexane	9.1 ± 0.1	11.7	17.60
Cyclohexene	13.3 ± 0.3	13.6	37.80
Benzene	11.9 ± 0.6	10.6	78.10
Toluene	12.0 ± 0.1	12.8	59.80
o-Xylene	12.0 ± 0.3	14.5	64.80
Isopropylbenzene	10.6 ± 0.3	17.3	39.10
t-Buthylbenzene	9.6 ± 0.3	14.9	32.10
Isopropyl ether	4.8 ± 0.2	6.8	6.41
n-Butyl ether	7.1 ± 0.2	12.1	12.9
Perfluorodimethyl-cyclobutane	0.38 ± 0.01	0.7	1.52
Water	0.28 0.01	0.05	2.5x10^4
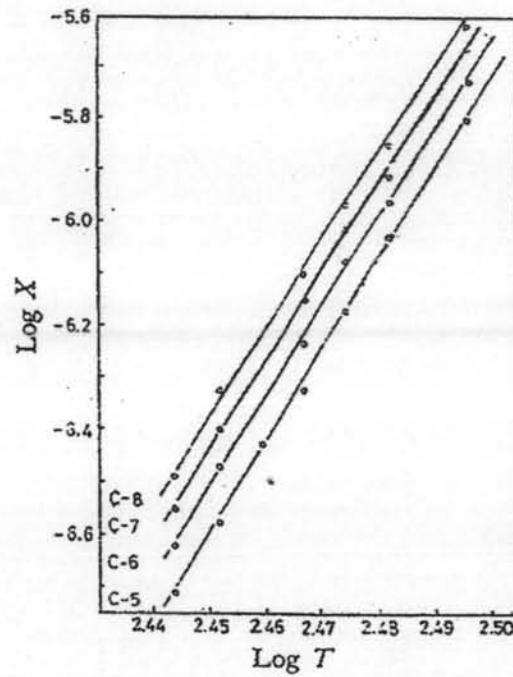
Figure 2.2 Temperature dependence of the mercury solubility in hydrocarbon
C-5: Pentane, C-6: Hexane, C-7: Heptane, C-8: Octane (Okouchi and Sasaki, 1981).
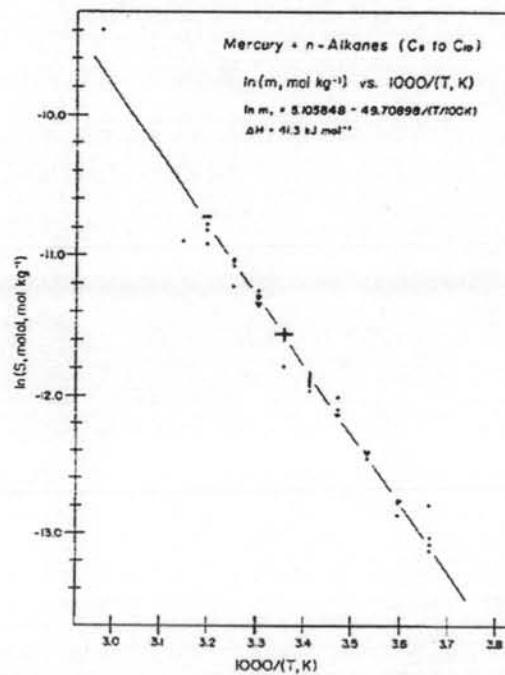
Figure 2.3 Solubility of mercury in normal alkane (Clever and Iwanoto, 1987).

2.5 Study of Mercury in Petroleum

The knowledge of the total mercury content presenting in natural gas and crude oil is quite important in terms of environmental concerns and plant operations. The treatment and digestion with oxidizing solution or high temperature reaction with air or oxygen are typically practices for determination of total mercury in petroleum. Their solutions or gas will then be sent to a spectrometric detector for mercury determination. The extraction method has been developed for the determination of mercury in gasoline and other petroleum products (Liang *et al.*, 1996). An oxidant or acid solution (BrCl or HCl) is used to oxidize the organomercury compounds in gasoline to inorganic mercury and extract to their phase (aqueous phase). Therefore, the extracted mercury is reduced to Hg^0 by $SnCl_2$ and detected by cold vapor atomic fluorescence spectrometer (CVAFS). The analytical results are independent of the mercury species. This method presents a robust analytical technique and has detection limit about 0.01 ng/ g. The report has recommended that BrCl is suitable to convert all organic mercury into inorganic mercury. Kelly *et al.* (2003) determined mercury in SRM crude oil and refined products. Isotope dilution cold vapor ICP/MS using closed system combustion was perform. Sample of approximately 0.3 g was spiked with stable ^{201}Hg and wet ash in closed system using 6 g of high purity nitric acid. The method detection limit is approximately 10 pg/g for a 0.3 g sample. The large amounts of reagents and procedures are required for treatment methods. Also, the procedures are often complicated and time consuming, increasing the risk of analytical errors and debasing detection limits through high and valuable blank levels. Another method of mercury determination is collecting on the trap. In 1998, the gold trap (Amasil) was studied on seven mercury species which are dimethylmercury (DMM), diethylmercury (DEM), diphenylmercury (DPM), methylmercury chloride (MMC), ethyl mercury chloride (EMC), phenylmercury chloride (PMC) and mercury (II) chloride (MC) (Shafawi *et al.*, 1998). They were spiked individually as well as their mixture of them into gas condensate. The experiments were accomplished by vaporizing of the sample at 400 °C with adsorption of mercury species on a gold trap held at 200 °C. Then, the trap is heated at 900 °C to release metallic mercury, which

is determined by an atomic fluorescence. The mercury recovery was found to be in the range of 80 – 100%. In the similar way, the thermal decomposition was applied to determine mercury in crude oil (Liang et al., 2000). The equipment is simple and available in laboratory. Sample was directly introduced into the system without the use of chemical and digestion procedure. After 4 minutes, matrices and mercury compounds were decomposed and its elementary was collected on the gold sand trap and then detected by atomic fluorescence spectroscopy (AFS). The detection was approximately 0.2 ng/g for 0.04 g of crude oil introduced into the system. Results are similar to the previous works that were independent of mercury species and sample type. However, the adjusting factors of the equipments such as flow rate of carrier gas have to be optimized..

Additionally, mercury species data are also important. Several mercury species have different properties which are in term of mobility, reactivity and bioavailability. Therefore, knowledge of mercury speciation is very useful for some decision considering plant design, Hg extraction and pollution control. Chromatographic separation by GC or HPLC, normally coupled to units to produce Hg^0 followed by element select detectors based on atomic or mass spectrometry has been developed for mercury determination. Schickling and Broekaert (1995) determined mercury species ($HgCl_2$, MeHgCl, PhHgAc, and Ph_2Hg) in gas condensate by on-line coupled HPLC with CVAAS. When the solution mixture was injected into HPLC, transphenylation occurs suddenly between $HgCl_2$ and Ph_2Hg and produces MeHgCl, indicating that the transphenylation of mercury species interferes HPLC analysis of the organic and organomercury. Bloom (2000) conducted the experiment for Hg speciation by using wet chemical method. Hg^0, dissolved and particulate total Hg, Hg(II) and methyl Hg was determined by specific extraction and procedure. For each species, detection limits of approximately 0.1 ng/g were obtained. This method requires many reagents and the procedures are quite complex. The large quantity of one species could give the error in another, resulting in risk of inaccuracies. Bouyssiere et al. (2002) developed the method for determination of atomic mercury, nonpolar dialkylated mercury compounds, polar monoalkylated species and inorganic mercury complexes in natural gas. ICP/MS was employed as a detection method for capillary gas chromatography and compared with microwave

induced plasma (MIP). Both ICP/MS and MIP favor nonpolar species. Hg^0 and Hg(II) are the major mercury species detected over 90% in gas condensate.

2.6 Mercury Situations in Thailand Associated with Offshore Oil and Gas Production

The exploration concession in Thailand for oil and gas companies was awarded in 1962. By 1982, Thailand's first gas field was started by a company. The trace amount of mercury was first found at the Platong field in 1985. Then the produced waters discharged from the process to the sea were of significant concern since this water contains mercury that has been scrubbed from natural gas and gas condensate. There was a study of the company on mercury concentration in sediment that was carried out by TetraTech. It was reported that the sample collected at Erawan Platform contained average mercury concentration of 1404 μg/g (dry weight) in 1997 and 863 μg/g (dry weight) in 1998. Sample around surrounding stations were also analyzed and found in the range of 206 – 292 μg/g (dry weight). The amount of mercury discharged into Gulf from oil and gas operation between 1991 and 1996 was estimated monthly by sampling produced waters at four different platforms (Erawan, Platong, Satun, and Funan). These values ranged between 40 and 330 kgs per year, the average value over this period of time was 197 kgs per year (Chongprasith et al., 2001). The mercury in produced water can be characterized in many species. It is shown that mercury in aquatic environment is present in elementary form (Hg^0), including particulate mercury sulfide (HgS), inorganic mercury (Hg^{2+}), and methylated forms, such as monomethyl mercury (CH_3Hg) which is rapidly absorbed by aquatic organisms, other contaminants are present in water soluble forms. For example, mercury in sediments surrounding the Platong and Erawan platforms is present as metacinnabar (mercuric sulfide) (Chongprasith et al., 2001). It was also reported that less than 0.2 percent of the total mercury in the sediments could be considered bio available and 95 to 98 percent of that was present as either crystalline or strongly bound amorphous mercury. In addition, an earlier report also describes the impact of total mercury released during gas production in

Bongkot field, Lower Gulf of Thailand, on marine organism (Windom and Cranmer, 1996).

Produced water is the highest volume waste source in offshore oil and gas industries. There are two techniques available to solve mercury problem: water treatment and water injection. However, the re-injection of all produced water is not completely feasible because the availability of geologic formations is not uncertain for receiving injected produced water. The technologies for removing contaminants from produced water have been simultaneously developed to reduce the impact of mercury. The treatment systems in oil and gas industries available in Thailand are separator, deoiler cyclone, chemical flocculation process, induced gas flotation, skim tank, and hydrocyclone. One of the most effective treatments is hydrocyclone which is primarily reducing dispersed and dissolved hydrocarbons from produced water in which some mercury is believed to exist or be absorbed onto suspended organic particles. In the future, de-sanding hydrocyclone, and activated carbon absorption will be implemented (Chongprasith et al., 2001).

The company has applied direct injection of treated produced water into Erawan field (Anonymous, 1998), the oldest gas field in the Gulf of Thailand. Since implementing the water treatment and re-injection scheme, the company has reduced the amount of mercury discharged into the Gulf to merely 13 – 14 kg/year, which is so far from the estimated 300 – 400 kg/year that would have been released without the treatment and injection.

2.7 Principle of Solubility

The solubility is the maximum amount of solute which can normally dissolve per amount of solvent (or solution) at a specified temperature (Chang, 1998). The process of dissolution was depicted and described in Figure 2.4. The process consists of the breaking of intermolecular bonds in solute, the separation of molecule of the solvent that provides space in the solvent for solute and the interaction between the solvent and solute molecule.
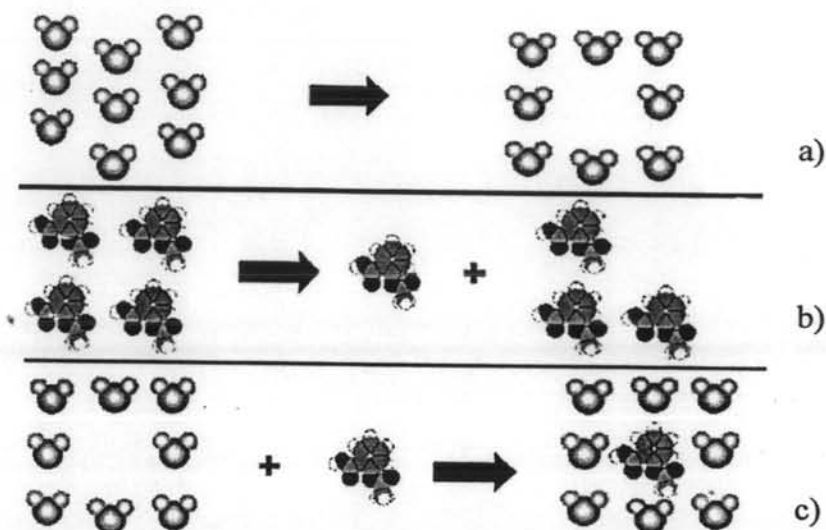
Figure 2.4 Step of solid dissociation: a) a hold opened in the solvent, b) a solute molecule of solute breaks away from its bulk and c) a free solute molecule was integrated in the available hole of solvent (http://en.wikipedia.org/wiki/Solubility).

The solution can be classified as the degree of saturation into 3 levels: a saturation solution, an unsaturation solution and a supersaturation solution. The saturation solution is a solution containing the maximum amount of solute and additional solute will not dissolve while the unsaturated solution contains solute that is less than the maximum level. The supersaturation solution is solution that contains more of the dissolved solute than normal level at a specific temperature and the extra amount of solute is caused fast crystallization. The main factors that have an effect on the solubility are as follows:

- *Temperature*

The rising temperature is the certain amount of energy for breaking intermolecular force of solute bulk. An increasing temperature of solution typically increases the solubility in solid and there is some solid compound that is less soluble at higher temperature. For all gases, solubility decreases with increasing temperature.

- Pressure

For solids and liquid solutes, changes in pressure have practically no effect on the solubility while gases become more soluble as the pressure above the solution increases.

- Natural of the solute and solvent

It is often expressed as "Like Dissolves Like". The solute and solvent must be alike in term of polarity. It means that polar solutes dissolve well in polar solvents and non polar solutes dissolve well in non polar solvents and polar solutes do not dissolve well in non polar solvents.

There are also various factors that influence how fast a solute dissolves which is called the rate of solution *i.e.* temperature, agitation, surface area and amount of solute already dissolved.

- Temperature

For liquids and solid solutes, increasing the temperature not only increase the amount of solute but also accelerate the rate of solute dissolved since solvent molecules moves faster and solvation occur more rapidly. For gases, the reverse is true.

- Agitation

When the solution is agitated by stirring or shaking, solutes will dissolve faster. It is because the solvent immediately surrounding the solute can quickly become saturated and agitation helps bring fresh solvent into contact with the surface of solute so that more solute can dissolve faster.

- Surface area

Solvation occurs at the surface of solute. The greater surface area gives more opportunities for the solvent to attack the solute. So, the total surface area of the solute is increased, the solute dissolves more rapidly

- Amount of solute already dissolved

When the solvent have a little of solute dissolved, dissolving process take place relatively rapidly. On the other hand, dissolving process take place more slowly, no solute dissolves in the solvent.

2.8 Solubility Parameter

A solubility parameter is a kind of cohesion parameter that describes the interactions between molecules in condensed phase. It can be used to predict and interpret solubility in quantitative manner. Hildebrand (Hildebrand *et al.*, 1992) proposed the solubility parameter or Hildebrand parameter that is the square roots of the cohesive energy densities:

$$\delta = \left(\frac{\Delta U}{V} \right)^{1/2}$$

(2.2)

Where δ = the solubility parameter $(MPa)^{1/2}$

ΔU = the molar internal energy of vaporization (J/Mol)

V = the molar volume (cm^3/Mol)

The Hildebrand parameter was intended for nonpolar and nonassociating system. To extend to the polar and hydrogen-bonding systems, two component of interaction were introduced into the solubility parameter. Barton (1991) reported a three – component solubility or Hansen parameter which are consisted of dispersion, polar and hydrogen bonding parameter. Each component was determined empirically on the basis of many experimental observations:

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$

(2.3)

Where δ_t = the total solubility parameter

δ_d = the dispersive component solubility parameter

δ_p = the polar component solubility parameter

δ_h = the hydrogen bonding component solubility parameter

A number of liquids and polymers have been tabulated for Hansen parameter. The Hansen's total cohesion parameter, δ_t, should equal the Hildebrand parameter, although the two quantities may differ for materials with specific interaction when they are determined by different methods.

A good multicomponent may be blended of a simple solvent and it is important to be able to evaluate the solubility parameter of mixed solvent which is so called the effective solubility parameter. The effective solubility parameter is usually determined by the properties of the pure component. The general expression of the effective solubility parameter is defined as follows (Barton, 1991):

$$\bar{\delta} = \sum_i {}^i\phi\, {}^i\delta \tag{2.4}$$

$$ {}^i\phi = {}^iV^i x / \sum_j {}^jV^j x \tag{2.5}$$

Where $\bar{\delta}$ = the effective solubility parameter

$^i\delta$ = the solubility parameter of component i

$^i\phi$ = the molar volume fraction of component i in total j component

^iV = the molar volume of component i

^ix = the mole fraction of component i

2.9 Regular Solution

The regular solution (Hildebrand et al., 1962) is a system involving no entropy change and constant total volume when a small amount of one component is transferred to such system from an ideal solution at the same composition. This theory is able to predict the temperature effecting to the solvation. Hildebrand – Scatchard equation was proposed. It provided a very simple prediction of liquid solubility and is defined by:

$$- RT \ln {}^{j}x_{s} = {}^{j}V({}^{j}\delta - {}^{i}\delta)^{2} \qquad (2.6)$$

Where ${}^{i}\delta$ = the solubility parameter of solvent i or the volume fraction average of solubility parameter.

${}^{j}\delta$ = the solubility parameter of solute j

${}^{j}x_{s}$ = the mole fraction solubility of j in i

${}^{j}V$ = the molar volume of component j (cm^{3}/Mol)

If molecule of the component i and component j differs substantially in size, the Flory-Huggin size effect will be taken into consideration. The Hildebrand – Scatchard equation was modified as follows:

$$- RT \ln {}^{j}x_{s} = {}^{j}V({}^{j}\delta - {}^{i}\delta)^{2} + RT(\ln({}^{j}V/{}^{i}V) + 1 - ({}^{j}V/{}^{i}V)) \qquad (2.7)$$