

CHAPTER II

LITERATURE REVIEW

2.1 Definition of Solubility

Solubility is defined as the maximum equilibrium amount of solute that can normally dissolve in a certain quantity of solvent or solution at a specified temperature. Degree of saturation is categorized into three levels; i.e. saturated, unsaturated, and supersaturated solutions. The saturated solution contains the maximum amount of solute in that solvent. The unsaturated solution is a solution containing the dissolved solute in a less concentration than a saturated solution, while the supersaturated solution contains more than the maximum amount of solute and is considered as unstable condition. The additional solute in the supersaturated solution causes rapid crystallization.

The process of dissolution can be illustrated in Figure 2.1. It relates to the breaking of the intermolecular bonds of solvent molecules in the presence of solute, the separation of the solvent molecules to make space available for the solute, and the interaction between the solvent and solute.

Factors affecting solubility consist of temperature, pressure, and the nature of solute and solvent.

- *Temperature*: It generally relates to a certain amount of energy required to destroy the intermolecular forces between molecules. An increase in temperature of the solution causes an increase in the solubility of a solute. However, a few solid solutes are less soluble in warmer solution. For all gases, the solubility decreases as the temperature of the solution increases

- *Pressure*: Changes in pressure have little effect or practically no effect on solubility for liquid and solid solute, whereas an increase in pressure causes higher solubility for gaseous solutes.

- *The nature of solute and solvent*: The statement "Like dissolves like" is always used to describe the relationship between the nature of solute and solvent. Polar solutes dissolve well in polar solvents and nonpolar solutes dissolve well in

nonpolar solvents. Polar solutes do not dissolve well in nonpolar solvents and vice versa.

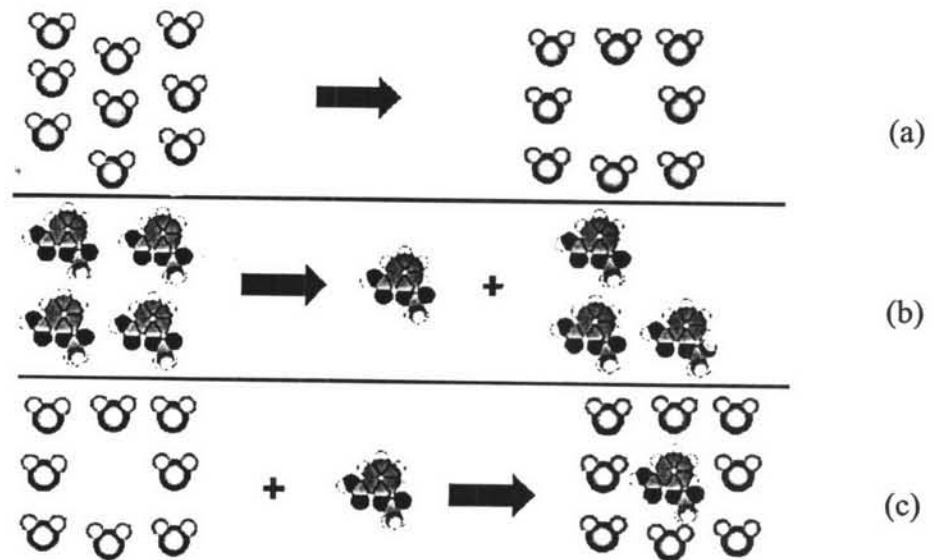


Figure 2.1 Steps of solute dissolves into solvent (a) opened hole in solvent molecules, (b) one molecule of solute breaks from the bulk, and (c) the free solute is integrated to the hole in solvent.

(<http://www.cop.ufl.edu/safezone/prokai/pha5100/solubility.htm>)

A parameter to measure how fast a solute dissolves is called the rate of dissolution. The factors affecting the rate of dissolution are temperature, agitation, surface area, and amount of solute already dissolved.

- Temperature: For solid and liquid solutes, increasing in temperature makes the solutes move faster and the process of dissolution occurs more rapidly. In case of gas solutes, the reverse is true.

- Agitation: The solutes can dissolve faster when the solution is agitated by stirring or shaking because agitation helps bring fresh portions of the solvent into contact with the surface area of solutes. As a result, more solute can dissolve and the rate of dissolution increases.

- Surface area: As the solvation process occurs at the surface of the solute, the higher the surface area of the solute is, the more opportunities for the solvent to attack the solute molecule take place. Thereby, solutes can dissolve faster.

- Amount of solute that already dissolved: If there is little solute already dissolved in the solution, the process of dissolution occurs relatively rapidly. As the solution approaches the point where no solute can be dissolved, this process takes place more slowly.

2.2 Solubility Parameters

Due to the attempt to predict the information on mixtures from the thermodynamic properties of individual components, solubility parameters are enabled to calculate and interpret solubility in a semi-quantitative manner. The solubility parameter is a numerical value that shows the relative solvency behavior of a specific solvent. It is derived from the cohesive energy density (c) which indicates the energy of vaporization in calories per cubic centimeter, and it is a direct reflection of the degree of Van der Waals forces holding the molecules of the liquid together (Burke, 1984)

$$c = \frac{\Delta H - RT}{V_m} \quad (2.1)$$

where c = Cohesive energy density, cal/cm³ of liquid
 ΔH = Heat of vaporization, kcal
 R = Gas constant per mole
 T = Temperature, degree Kelvin
 V_m = Molar volume, cm³/mole.

In 1936, J. H. Hildebrand proposed the Hildebrand solubility parameter as a square root of the cohesive energy density (Burke, 1984):

$$\delta = \sqrt{c} = \left[\frac{\Delta H - RT}{V_m} \right]^{1/2} \quad (2.2)$$

where δ = Solubility parameter, (cal/cm³)^{1/2} or (MPa)^{1/2}.

The Hildebrand solubility parameters can adequately describe the solubility behavior in the nonpolar system, whereas they can give the unexpected results especially in the polar and hydrogen bonding system. To obtain more accuracy in predicting solubility behavior, Hansen (1966) proposed a practical extension of the Hildebrand parameter. Hansen parameters divide the total Hildebrand solubility parameters into three parts that are a dispersion force component, hydrogen bonding component, and a polar component. It is assumed that all parameters are valid simultaneously and the correlation can be written as follow (Burke, 1984):

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (2.3)$$

where δ_t = Hansen's total cohesion parameter
 δ_d = Dispersion component solubility parameter
 δ_p = Polar component solubility parameter
 δ_h = Hydrogen bonding component solubility parameter.

Generally, Hansen's total cohesion parameter should equal to the Hildebrand parameter, however, the differences of the two quantities may be derived from materials with specific interactions when they are determined by different methods.

2.3 Regular Solution Theory

The term "regular solutions" was first proposed by J.H. Hildebrand in 1929. The principle can be explained in the following statement (Hildebrand and Scott, 1962):

"A regular solution is one involving no entropy change when a small amount of one of its components is transferred to it from an ideal solution of the same composition, the total volume remaining unchanged."

The Hildebrand-Scatchard equation was proposed to calculate the solubility on binary mixture systems from data on individual components. It can be written as follow (Barton, 1991):

$$RT \ln^j f_x = RT \ln(^j a/^j x) = {}^j V^i \phi^2 ({}^i \delta - {}^j \delta)^2 \quad (2.4)$$

where ${}^j f$	=	Fugacity of solute j
${}^j a$	=	Activity of the solute j
${}^j x$	=	Mole fraction of the solute j
${}^j V$	=	Molar volume of solute j
${}^i \phi$	=	Volume fraction of solvent i
${}^i \delta$	=	Solubility parameter of solvent i
${}^j \delta$	=	Solubility parameter of solute i.

In case of infinitely dilute solutions, the volume fraction of solvent can be assumed to unity, ${}^i \phi = 1$, so

$$RT \ln^j f_x^\infty = {}^j V ({}^i \delta - {}^j \delta)^2 \quad (2.5)$$

For multicomponent mixture, a more general expression for the limiting infinite dilution activity coefficient of component j with molar volume ${}^j V$ is

$$RT \ln^j f_x^\infty = {}^j V ({}^i \delta - \bar{\delta})^2 \quad (2.6)$$

where $\bar{\delta}$	=	Volume fraction average Hildebrand parameter or the summation extending over all components, including the solute when its volume fraction is appreciable
	=	$\sum_i {}^i \phi^i \delta$.

(2.6a)

If the solute and solvent molecules are different considerably in size, the Flory-Huggins size effect term are taken into account. Equation (2.4) can be modified to, for solute j,

$$RT \ln^j f_x = {}^j V^i \phi^2 ({}^i \delta - {}^j \delta)^2 + RT [\ln {}^j V / {}^i V + {}^i \phi (1 - {}^j V / {}^i V)] \quad (2.7)$$

and for infinitely dilute solutions of solute j in solvent i where ${}^i \phi = 1$,

$$RT \ln^j f_x^\infty = {}^j V ({}^i \delta - {}^j \delta)^2 + RT [\ln ({}^j V / {}^i V) + 1 - {}^j V / {}^i V] \quad (2.8)$$

or

$$\ln^j f_x^\infty = \frac{{}^j V}{RT} ({}^i \delta - {}^j \delta)^2 + {}^j d \quad (2.8a)$$

where the Flory-Huggins combinatorial size effect term is

$${}^j d = \ln ({}^j V / {}^i V) + 1 - {}^j V / {}^i V \quad (2.8b)$$

2.4 Chemistry of Mercury

Mercury, also called quicksilver, is an element which is classified as a transition metal. It naturally occurs in the environment in the zero (elemental), +1 (mercury [I] or mercurous), or the +2 (mercury [II] or mercuric) valence states. In this research work, elemental mercury is in the area of interest. Elemental mercury or metallic mercury is a heavy, shiny, silver-white, odorless liquid at the room temperature. Table 2.1 shows some physical properties of elemental mercury.

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)
Melting point	- 38.87°C (- 37.97 F)
Density	13.546 g/cm ³ at 20°C (0.489 lb/in ³ at 68 F)
Saturation vapor pressure	0.16 N/m ³ (pascal) at 20°C (68 F)
Vaporization rate (still air)	0.007 mg/cm ² hr for 10.5 cm ² droplet at 20°C
Diffusivity (in air)	0.112 cm ² /s
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/H₂O)	375 dyne/cm at 20°C (68 F)

2.5 Mercury Species in Petroleum

There are several mercury forms existing in geological hydrocarbons. Each of them has their own chemical properties. Table 2.2 presents a partial list of mercury compounds identified to exist in petroleum. Mercury in natural gas is generally in the form of elemental mercury at the concentrations far below the saturation level. It can be inferred that no liquid mercury phase exists in most natural gas reservoirs. Organic mercury is another type of mercury species that presents in natural gas, but it is thought to be in a low level (less than 1 percent of total) according to the limited speciation data for gas condensates (Tao *et al.*, 1998). Organic mercury in produced gas is expected to partition to separated hydrocarbon liquids when the gas is cooled. Hence, if dialkylmercury (one example of organic mercury) is found in the reservoir, it would present mostly in gas condensates, less so in gas.

Table 2.2 Solubility and volatility of mercury compounds (Wilhelm, 2001)

Formula	State	Volatility	Solubility in H ₂ O 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 K _{sp} ⁽¹⁾ = 52	Mercuric sulfide
HgSe	Solid	Sublimes under vacuum, Decomposes at 800°C	- log K _{sp} ~ 100	Mercuric selenide
(CH ₃) ₂ Hg	Liquid	Boiling point 96°C	< 1 ppm	Dimethyl- mercury
(C ₂ H ₅) ₂ Hg	Liquid	Boiling point 170°C	< 1 ppm	Diethyl- mercury

(1) K_{sp} = solubility product

In crude oil or gas condensates, various forms of mercury species are likely to be discovered. Groups of mercury are chemically categorized by volatility and phase solubility properties so that the major categories are as follows:

2.5.1 Dissolved elemental mercury (Hg⁰)

Elemental mercury is soluble in crude oil and hydrocarbon liquids. It is highly adsorptive and can adsorb on metallic surfaces or on solid materials (sand) suspended in liquids. Elemental mercury is able to react with iron oxide which is the corrosion products from pipe and equipment walls. Its solubility in hydrocarbons depends strongly on temperature. Therefore, when saturated liquids are cooled, Hg⁰ can precipitate in the equipment.

2.5.2 Dissolved organic mercury (RHgR and RHgX, where R = CH₃, C₂H₅, etc. and X = Cl⁻ or other inorganic anion)

Dissolved organic mercury compounds are highly soluble in crude oil and gas condensate. They, also known as organometallic compound, are subdivided into two groups that are monoalkylmercury (RHgCl) and dialkylmercury (RHgR). Monoalkylmercury compounds, for example monomethylmercury halides (CH₃HgCl), tend to preferentially partition to water in primary separation whereas dialkylmercury compounds (RHgR), for example dimethylmercury (CH₃HgCH₃) and diethylmercury (C₂H₅HgC₂H₅), partition to hydrocarbon liquids during separations and to distillation fraction in accordance with their boiling point. The natural abundance of organometallic compounds in produced hydrocarbons is still now questionable. The existence of organic mercury compounds is inferred when analysis for total mercury in a liquid matrix does not satisfy the mass balance with operationally speciated forms.

2.5.3 Inorganic (ionic) mercury salts (Hg²⁺X or Hg²⁺X₂, where X is an inorganic ion)

The most common form of this mercury species is HgCl₂, which is normally more water-soluble than other forms of mercury. It partitions to the water phase in hydrocarbon/water separations. The distribution of HgCl₂ between water and liquid hydrocarbon depends on the salinity of the produced brine and its pH. The natural abundance of ionic compounds is uncertain because it was found that Hg⁰ can oxidize in hydrocarbon liquid samples exposed to oxygen and then Hg [II] is formed. (Bloom, 2000).

2.5.4 Complex mercury (HgK or HgK₂, where K is an organic sulfide, thiol, thiophene, or mercaptan)

It is claimed to exist in some crude oils and condensates. However, it can not exactly identify the specific complexes of mercury.

2.5.5 Suspended mercury compound

The most common examples are mercuric sulfide (HgS) and selenide (HgSe), mercury associated with asphaltenes, and mercury (elemental or compounds) adsorbed on solid particles such as sand or wax. These compounds are presented in unprocessed hydrocarbon liquids and many process streams as suspended solid particles of very small particle size. They must be separated before any operation otherwise they tend to remain in the residuum in the atmospheric and vacuum distillations.

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. Particulate HgS can be formed by mixing gas or condensate from sour and sweet reservoirs which the reaction of elemental mercury with S₈ or ionic mercury with H₂S can occur. That particulate HgS is able to precipitate in tanks and equipment. In addition, according to theory, the high temperature processing such as hydrotreating in refineries should be able to convert dialkylmercury and complex mercury to the elemental form.

The degree to which mercury partitions into products and effluent streams during the processing depends on the solubility of mercury. Table 2.3 provides the approximate solubility of the common species in several liquid matrices. The solubility of elemental mercury in normal alkanes as a function of temperature is also shown in Figure 2.2.

Table 2.3 Approximate solubility of mercury compounds in liquids at 25°C
(Wilhelm, 2001)

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	
CH ₃ HgCl	> 10,000	1,000	> 1,000

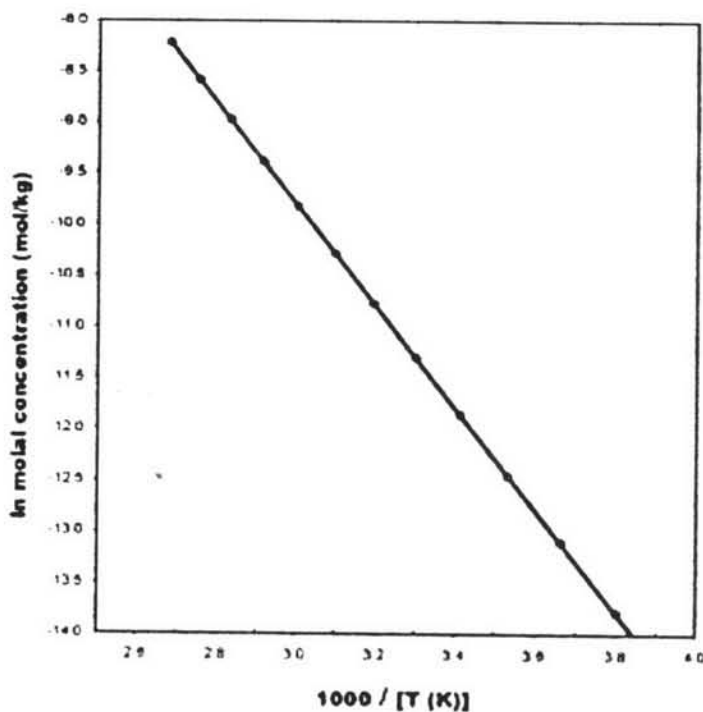


Figure 2.2 Solubility of elemental mercury in normal alkanes as a function of temperature (Wilhelm, 2001).

2.6 Effects of Mercury on Processing

Mercury has displayed its detrimental impacts on processing equipment. The effects of mercury can be described as follows:

- Mercury deposit in cryogenic equipment that sometime causes cracking of welded aluminum heat exchangers. McIntire *et al.* (1989) ascribed the failure of the aluminum heat exchangers in the ethylene plant of Cain Chemicals to mercury attack by processing Algerian condensate containing 26-40 $\mu\text{g/L}$ of Hg. As a result of this industrial accident, to develop an effective mercury removal technology from condensate then becomes an important topic in petrochemical industry because of the gradual shift of ethylene plant feed stock from naphtha to condensate.

- Mercury from gas processing operation affects downstream processes since gas plant products are normally used as feedstock for chemical manufacture, especially olefins, ethylene, aromatics and MTBE. The downstream

industry takes risk to mercury contamination in process feeds due to cited equipment problems and catalyst poisoning.

- Mercury contaminates the treatment processes, which are used in petroleum process, such as molecular sieve and glycol dehydration units, and amine acid gas removal systems. Contaminated treatment liquids and spent molecular sieve sorbents are difficult to dispose or regenerate.

- Sludge containing mercury from water treatment systems, separators, desalters, and heat exchangers is classified as toxic waste stream. It is difficult to store or process for disposal.

- Waste water streams that contain a significant amount of mercury have to be treated to remove mercury before discharging. Therefore, plant operational expense is increased due to the demands of mercury removal unit from waste water.

2.7 Mercury Situation Associated with Offshore Production in Thailand

By 1982, Thailand's first gas field started. Then, in 1985, a trace of mercury contaminant in natural gas and condensate was first found at the Platong field in the Gulf of Thailand. Due to this finding, produced waters, which were discharged from the processing platforms into the sea, were of significant concern because these waters contained mercury that was scrubbed from natural gas and gas condensates. Three years later, there was a study on mercury concentrations in sediment which was carried out by Tetra Tech (1998). It was reported that samples that were collected at Erawan Platform contained average mercury concentration of 1404 $\mu\text{g/g}$ and 863 $\mu\text{g/g}$ (dry weight) in 1997 and 1998, respectively. Samples around the platforms were also taken. The concentrations ranged from 206-292 $\mu\text{g/g}$ (dry weight). At that time, three types of analysis relating to total mercury, particulate mercury, and the relative bioavailability of mercury were conducted. The results indicated that mercury in the sediments surrounding the Platong and Erawan platforms was present as mercuric sulfide (HgS).

In the offshore oil and gas industries, produced water occupies the highest volume of waste source. From the characterization of produced water, it is shown that mercury in the aquatic environment is present in elemental form of mercury (Hg^0), particulate mercury sulfide (HgS), inorganic mercury (Hg^{2+}), and methylated form such as monomethylmercury (CH_3Hg^+). Some of produced water is used to re-inject back into the depleted wells so as to resolve the mercury issue. The direct injection method of treated produced water was applied into Erawan field, 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 far from the estimated 300-400 kg/year that would have been released without the treatment and injection (Oil & Gas Journal; Nov 16, 1998; 96, 46, page 34-36)

Despite the re-injection approach utilized by the gas and oil operations in the Gulf of Thailand, the technologies for removing contaminants from produced water have been simultaneously developed to mitigate the impact of mercury. The treatment systems in oil and gas available in Thailand are separator, deoiler cyclone, chemical flocculation process, induced gas floatation, skim tank, and hydrocyclone. One of the most effective treatments is hydrocyclone, which primarily reduces dispersed and dissolved hydrocarbons from produced water, in which some mercury is believed to exist or absorbed onto suspended organic particles. In the future, desanding hydrocyclone and activated carbon adsorption will be implemented.

2.8 Analytical Methods for Mercury Determination in Hydrocarbon Matrices

A number of analytical methods for mercury and mercury compounds in hydrocarbon matrices have been introduced by the academic researchers and petroleum industry for a long time. Early measurements of the solubility of mercury were done by means of amalgamation or electrodeposition of the dissolved mercury. More recently, the measurement have been done by using the radioactive tracer Hg^{203} , atomic absorption spectroscopy, neutron-activation analysis, and etc. Each of analytical methods are differentiated by how the samplings are taken (collection), species conversion/separation (digestion, extraction, filtration, vaporization, and

combustion), and types of detection method. However, in order to achieve the accurate value of mercury concentration, taking sample from hydrocarbons containing mercury is the most concerned step due to the partitioning of mercury compounds among various phases, species conversion in sample containers, loss of nonpolar compounds in plastic vessels, and adsorption of mercury on sample container surfaces.

In gas matrices, elemental mercury (Hg^0) and some lesser amount of dimethylmercury ($\text{Hg}(\text{CH}_3)_2$) are the main types of mercury found. Since they are present in low concentrations, it is difficult to detect directly by only spectroscopic methods (UV, visible, IR, and X-Ray) because of the interference by hydrocarbons. Accordingly, pre-concentration of mercury in gas to a collector is required. The widespread methods of mercury determination in gas matrices are a wet collection method, a dry collection method, and activated carbon impregnated with iodide (Wilhelm, 2001).

- *The wet collection method* is to bubble gas that contains mercury through a permanganate solution where all mercury species are converted to mercuric ion (Hg^{2+}). Then, mercuric ion is reduced by stannous chloride (SnCl_2) to elemental mercury (Hg^0) and separated by volatilization into an inert gas stream for detection. Detection methods are typically UV atomic absorbance or UV atomic fluorescence. This method gives the accurate result and reasonable sensitivity if sufficient volume of gas is acquired. However, the apparatus used to collect the sample is cumbersome and large volume is required.

- *The dry collection method* involves amalgamation of elemental mercury (Hg^0) on Ag, Au, or Au/Pt (sputtered on quartz). Gas that contains elemental mercury (Hg^0) is passed through a metal collector at a very low flow rate for quantitative trapping. The mercury/metal amalgam is then heated in an inert gas stream in order to volatilize mercury for detection. This method is very effective for light and dry gas, but if the gas stream contains heavy hydrocarbons, heating the traps will help minimizing the hydrocarbon condensation to occur.

- *The activated carbon impregnated with iodide* is also used to trap mercury from gas matrices. After collecting mercury from a known volume of sample, carbon/KI traps are subject to routine digestive analysis to determine the

total mercury concentration. Iodated carbon trap is less sensitive to contaminants in hydrocarbons than gold trap, so it is allowed to examine large volume of sample. This type of trap is appropriate for unprocessed gas where reasonably high concentration is expected.

In case of liquid hydrocarbons, various forms of mercury can exist, and it is typically measured as total mercury in liquid instead of individual mercury species. Common analytical methods include combustion/vaporization technique, wet (hot) digestion method, and wet extraction method.

- The combustion method entire liquid matrix is oxidized and vaporized, whereas the liquid hydrocarbon is not combusted but retained in vapor form in vaporization technique. Then, mercury in the vapors is trapped and analyzed by using the similar procedure to those utilized for natural gas.

- The wet digestion method uses strong acids (for example nitric acid, hydrochloric, sulfuric acid, and perchloric acid) and heat to chemically oxidize all mercury species in the liquid hydrocarbon matrix to mercuric ion (Hg^{2+}) that separates to aqueous phase. Mercuric ion (Hg^{2+}) in acid solution is quantified by acid neutralization, reduction by stannous chloride (SnCl_2) or sodium borohydride to generate elemental mercury (Hg^0) and then sparged by inert gas (Ar). This sparge gas will be either sent directly to a detector or collected on a trap to form an amalgam. The important constraints for wet digestion method are the acid solution temperature and the purity of chemicals that are going to be used. If the temperature of acid solution is high, it provides a risk of mercury losses due to vaporization. Additionally, if the associated chemicals in the analysis already contain small amount of mercury, the result of mercury concentration will be unreliable.

- The wet extraction method BrCl is used as an oxidant to digest only mercury species but not chemically decompose the liquid matrix. Thus, less heat is required for this process, and losses due to vaporization are eliminated. The mercuric ion (Hg^{2+}) in the aqueous extract is treated in the same way as the wet digestion method. An important consideration for this method is the duration for extracting solution contacting the sample. It must be long enough to reach complete oxidation and separation of all mercury existing in the sample. The typical forms of detector after the extraction are cold vapor atomic absorbance (CVAA) and cold

vapor atomic fluorescence (CVAF). Cold vapor atomic fluorescence (CVAF) is a very sensitive detection method with reported absolute detection limits 100 to 700 pg. This low detection limit allows accurate quantification of very small samples and dramatically reduces matrix effects.

Other methods for analyzing total mercury are inductively coupled plasma (ICP) or microwave induced plasma (MIP) followed by mass spectroscopy (MS) or atomic emission spectroscopy (AES) detection. The ICP/MIP techniques avoid process on digestion of sample, so it helps reducing the potential errors from multi-step wet chemical processing of liquid samples. Neutron activation analysis (NAA) is another type of method, which also avoids wet processing of samples. It has been used successfully to examine total mercury concentration in crude oil. With NAA, ICP/MIP, and MS/AES, the detection limit is reported to be lower than 0.1 pg.

More recently, a Nippon Instruments Corporation (NIC) Mercury Analyzer became well known in the petroleum industry with its ability to determine total mercury in any sample matrices (solid, liquid, or gaseous). This mercury analyzer is employed in the method UOP 938-00 (Total Mercury and Mercury Species in Liquid Hydrocarbon). With this mercury analyzer, the sample pretreatment procedure happens to be negligible and the detection limit of 0.1 ppb can be achieved.

2.9 Speciation of Mercury Compounds

In order to specifically define the amount of each mercury compounds in hydrocarbon sample, it involves multiple and sequential analysis for the various forms and a mass balance exercise.

$$\text{Total Hg} = \text{Hg}^0 + (\text{RHgR} + \text{HgK}) + (\text{HgCl}_2 + \text{RHgCl}) + \text{suspended Hg} \quad (2.9)$$

Total mercury concentration is determined by oxidative extraction method. Suspended mercury is quantitatively determined by measuring total mercury of an agitated sample and followed by measuring total mercury of a filtered portion of the agitated sample. In case of ionic and monoalkyl form ($\text{HgCl}_2 + \text{RHgCl}$), non-oxidative extraction of filtered samples by dilute acids is applied. The volatile

element form (Hg^0) is determined by sparging and collecting the volatile component on a trap. The sum of the concentrations of dialkylmercury and complex mercury is often estimated from the discrepancy in the mass balance. However, the exact concentration of the organic forms can be measured by more sophisticated techniques such as GC/CVAF or GC-ICP/MS.

2.10 Study on Mercury Solubility

The history of the study on solubility of metallic mercury first started in 1929 by Bonjoefffer and Reichardt. They attempted to measure the solubility of metallic mercury in water. What they had discovered was the existence of soluble mercury in water from the absorption spectrum of the solution. Mercury showed the characteristic resonance line at 253.7 nm. In a few years later, several methods of the solubility of mercury analysis were developed such as amalgamating the soluble mercury on a gold foil, electrodepositing on a copper wire, and developing a colored compound with organics or inorganic agents. In 1973, Onat conducted the experiment which was involved with in studying the solubility of metallic mercury in pure water at various temperatures ranging from 25°C-80°C. This work is based on the reverse of the disproportionation reaction of the mercurous ions.



The soluble mercury was converted to the mercurous form in the presence of mercuric ions. Mercuric ions are almost transparent to the radiation of wavelength 236.5 nm, while mercurous ions show a maximum absorbance peak. With this fact, the wavelength of 236.5 nm was used to determine the amount of mercury in water. According to the equilibrium mentioned above, this work was not only aimed to determine the solubility of metallic mercury in water, but to find an optimum concentration of mercuric solution which was sufficient to transform all the metallic mercury into mercurous ions also. The results of the solubility of metallic mercury in water from this research were in close agreement with other experiments. Additionally, a solubility curve was constructed based on the data of this work, then,

the solubility of mercury at any temperature in the range of 25-100°C can be estimated. From this research, amount of the metallic mercury in pure water at the concentration levels as low as 0.06-0.3 ppm can be detected by using common laboratory equipment.

A few decades later after the first attempt, the solubility of mercury in hydrocarbon solvents became interesting to the thermodynamicist in order to understand the nature and the extent of solvent-solute interaction, and to the photochemist to study the mercury photosensitization of liquid hydrocarbons. Kuntz and Mains (1964) made use of the optical density at 2560°A of a saturated solution of mercury in hydrocarbon at 25°C accompanied with the assumption of the Beer-Lambert absorption equation to evaluate the solubility of mercury in some organic solvents that were *n*-pentane, *n*-hexane, isopentane, 3-methylpentane, 2,2-dimethylbutane, 2,3-dimethylbutane and *n*-decane. Furthermore, the estimation of the mercury solubility in the selected hydrocarbon solvents using the Hildebrand equation for regular equation was also studied. The results from the experiments and the equation are shown in Table 2.4. The agreement between these two results was not at all bad, but it is better to consider the results from the Hildebrand equation as an "order of magnitude" approximation.

Table 2.4 The solubility of mercury in some organic solvents at 25°C (Kuntz and Main, 1964)

Solvent	Solubility, $\mu\text{moles/l}$	
	Calculated from O.D. at 2560 °A	Calculated from from Hildebrand equation
<i>n</i> -pentane	5.8	5.0
<i>n</i> -hexane	(6.4)	5.9
Isopentane	5.5	3.3
3-methylpentane	5.1	7.4
2,2-dimethylbutane	5.0	4.3

2,3-dimethylbutane	6.0	6.0
<i>n</i> -decane	5.5	1.5

Spencer and Voigt (1968) studied temperature dependence of the solubility of mercury in sixteen hydrocarbon liquids and water. A radiotracer technique was used in this experiment. The solubilities at 25°C were found to vary from about 10^{-6} mole/l for aromatic, aliphatic hydrocarbons and ethers. For water and perfluorodimethylcyclobutane, the solubilities were about 10^{-7} mole/l. The Hildebrand and Scatchard equation was also used to calculate the values of mercury solubilities at 25°C, and the results turned out to be in agreement with the experiments. In addition, their research focused on the thermodynamics of the solution of metallic mercury, thus, the partial entropies and heats of solution of mercury were determined from the temperature dependence of the mercury solubilities. In 1981, Okouchi and Sasaki reported the metallic mercury solubility in hydrocarbon liquids by means of the Cold Vapor Atomic Absorption Spectroscopy (CVAAS). The solubilities in *n*-pentane, *n*-hexane, *n*-heptane, and *n*-decane were observed in the temperature ranging from 5°C to 40°C. The results for pentane at 25°C were found to agree well with Kuntz's (1964) result, which was obtained by using the ultraviolet absorption measurement at 256 nm, whereas, the solubilities of metallic mercury in *n*-hexane, *n*-heptane, and *n*-octane were agreed well with those of Spencer (1968), which were acquired from the radioactive tracer Hg^{203} in the temperature range from 5°C to 40°C. In this work, a liquid-liquid distribution constant for metallic mercury between the selected hydrocarbons and water was measured at 25°C also. It is found that the distribution constant was equal to the ratio of the independent mercury solubility in hydrocarbons and water. During the review of the literature of the solubility of mercury in organic liquids, Clever and Iwamoto (1987) observed that the molal solubility (mol/kg) of mercury was nearly independent of the solvent at a given temperature (0 - 63°C or 273.15 - 336.15 K) for the normal alkane ($\text{C}_5 - \text{C}_{10}$), while the molar solubility (mol/l) was also nearly independent of the normal alkane solvent but in a slightly larger ambiguity. They plotted the natural logarithm of molal solubility against the inverse of the absolute

temperature by using the data from several papers. The graph was somewhat similar to Figure 2.2 and the linear regression from the plot was obtained. The equation is

$$\ln S (\text{molality}) = 5.1059 - 4970.90/T \quad (2.11)$$

The above equation is valid for the experimental range of 5-10 carbon atoms in normal alkanes at a temperature range from 0 -63°C (273.15 - 336.15 K), but it might give a higher than actual results for branched alkanes for the reason that solubility of mercury in the branched chains depends on the chain branching. They also suggested that this equation can be used to estimate the solubility of mercury in normal alkanes of other carbon atoms at other temperature; however, it must be done with caution.

From the previous works mentioned above, it is noticeable that there was no study of mercury solubility in a mixed system of hydrocarbon liquids at that period of time. Furthermore, no study of mercury solubility and mercury species in petroleum fluids (crude oil, natural gas, and gas condensate) was reported. Most unfortunately, there was a report of a catastrophic failure of an aluminium heat exchanger occurred in the Skikda liquefied natural gas plant in Algeria. As a consequence, numerous research was conducted in the 90's. Stockwell and Corns (1993 and 1994) investigated the mercury species in natural gas by collecting the species on special gold impregnated silica traps or gold wire. The adsorbed mercury species was then released by heating to high temperature (900°C) and was detected by means of an atomic detector. However, the restriction for this work is that the collection efficiency of the adsorbent may be affected by the condensation of hydrocarbons on the amalgamating surface. With this method, the very low detection limit can be achieved accurately. In 1999, Shafawi *et al.* designed an experiment for the determination of total mercury in gas condensate by vaporizing the sample with mercury adsorption on a gold trap (Amasil). The trap was heated and metallic mercury was released, and then detected by atomic fluorescence spectrometry. Seven species of organomercury compounds; dimethylmercury (DMM), diethylmercury (DEM), diphenylmercury (DPM), methylmercury chloride

(MMC), ethylmercury chloride (EMC), phenylmercury chloride (PMC), and mercury (II) chloride (MC), were used as representatives for contaminants in gas condensate. When each of them was spiked individually into gas condensate, its recovery was in the range of 80-100%. The recovery was in the range of 88-97% if the mixture of mercury species were added in equal amount into the system. This method avoids the use of chemicals/additives and complicated digestion processes. However, the detection limits for this approach depends on the volatility of gas condensate and the mercury species in the sample, together with the effect of any matrix sample condensing on the trap. Though the wet collection methods may provide the risk of analytical error, Bloom (2000) developed a sequence of simple wet chemical extractions and combined with a robust and sensitive detector such as Cold Vapor Atomic Fluorescence Spectrometer (CVAFS). The accurate quantifications of total Hg (THg), dissolved Hg, particulate Hg, Hg(II), Hg⁰, and monomethylmercury (CH₃Hg) were able to reach the detection limits of less than 0.1 ng/g. In his work, sample stability tests were also performed on various types of container. These materials included borosilicate glass bottles with Teflon-lined caps, Teflon FEP bottles, polyethylene bottles, stainless steel (#316) vials, and glass vials lined on the inside with aluminum foil to be a representative of aluminium shipping containers. The results showed that organomercury compounds were stable for at least 30 days in all containers except the container made of polyethylene, while Hg⁰ was stable in all containers except the one made of stainless steel or polyethylene. Hg (II) rapidly lost from all containers except those made of aluminium.

In some research, chromatographic separation by GC or HPLC, which is coupled to units to produce Hg⁰ followed by element selective detectors, was employed. Schickling and Broekaert (1995) determined the mercury species in gas condensate by on-line coupled high-performance liquid chromatography and cold-vapor atomic absorption spectroscopy. This method did not require the use of any solvent extraction or chemical derivatization steps. However, it was found that the chemical reactions between mercury (II) chloride (HgCl₂) and diphenylmercury (Ph₂Hg) and between methylmercury chloride (MeHgCl) and diphenylmercury (Ph₂Hg) were able to occur. It indicated that transphenylation of mercury species

interfered HPLC analysis of the inorganic and organomercury compounds. The detection limit for this method was reported at the 10 ng/ml level.

From the literature review, it was apparent that solubility study was done only in single-solvent systems and no study of hysteresis on mercury solubility has ever been performed. In this study, mercury solubility in single-solvent and mixed-solvent systems with more up-to-date technology on mercury analysis in small concentrations was investigated.