



Full Length Article

The behavior of mercury in water, alcohols, monoethylene glycol and triethylene glycol



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HIGHLIGHTS

- Solubility of mercury is reported for water, several alcohols, MEG and TEG.
- Elemental Hg may be stripped from MEG solution by petroleum gas.
- Hg partitions to the distillate phase during regeneration of MEG.
- Hg after inlet separators in rich MEG is particulate HgS.

ARTICLE INFO

Article history:

Received 13 December 2016

Received in revised form 25 January 2017

Accepted 28 January 2017

Keywords:

Mercury solubility
Mercury partitioning
Alcohols
Monoethylene glycol
Triethylene glycol

ABSTRACT

The oil and gas industry is becoming aware of the effects of produced mercury on hydrocarbon processing systems, and that produced mercury contaminates processing equipment. The use of technical information is critical to planning for decommissioning, decontamination and waste minimization. To this end, the solubility of mercury in the polar solvents - water, alcohols, monoethylene glycol (MEG) and triethylene glycol (TEG) have been determined from approximately 243 to 373 K. Elemental mercury solubility in MEG and TEG is somewhat higher than that reported previously in the literature when a mass of mercury was agitated for several days in the respective solvent. Elemental mercury was nearly quantitatively stripped from water by natural gas in a small laboratory stripping column, and in a distillation experiment, about 75% of Hg⁰ in 40 vol% MEG partitioned to the distillate phase. Elemental mercury is present in process inlet flow lines and can drop out. This is expected if the reservoir is both hot and saturated with elemental mercury (common), and the pipeline is colder (common). However, in the inlet separator, any dissolved mercury is removed by the drop in pressure and the flashing of C1-C4 hydrocarbons. These light hydrocarbons are very effective in stripping Hg⁰ from the crude and condensate. What remains in the crude and condensate is particulate metacinnabar, β-HgS. In amine treaters and glycol dehydrators a portion of the Hg⁰ in the gas can react with traces of oxygen to form heat-stable salts. These can further react to form Hg-rich sludges. The success of the experiments will be useful to the industry in understanding the behavior of mercury in polar solvents, gas hydrate inhibition and in glycol and amine contactors.

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1. Introduction

The awareness of toxic volatile metals such as mercury (Hg) in the petroleum industry is steadily increasing. Drilling into deeper and hotter reservoirs increases the probability of encountering Hg in produced fluids. Mercury is a naturally occurring trace constituent of crude oil, natural gas, and natural gas condensate, and virtually all geologic hydrocarbons contain measurable quantities. Recent shale gas and coal bed methane Hg detection from the

Americas to Australasia have impacted the hydrocarbons processing industry's risk to midstream and downstream processing. Trace metals including Hg are scavenged by carbon/stainless steel (adsorbed/chemisorbed) into interfacial surfaces and can complex into scale/metal grain boundaries, requiring special chemistry and chemical application methods for successful decontamination [1,2]. The Hg forms primarily on the interior surface of the scale of the pipe, not in grain boundaries. It forms by a reaction between Hg⁰ and the scale oxides and sulfides. As the pipe corrodes and the scale gets thicker, the Hg layer stays on the interior surface. Since the reaction product, β-HgS is primarily on the interior, at least a portion can be removed by aggressive pigging [3].

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Hydrocarbons with elevated Hg levels traditionally have been associated with a limited number of regions around the world. The deep drilling now occurring is producing elevated Hg in hydrocarbons in regions that have not previously experienced the phenomenon [4]. Mercury impacts on the industry range from health and safety risks due to corrosion of aluminum and copper alloys (also known as liquid metal embrittlement), to toxicity to flora and fauna through emissions to the environment, to catalyst poisoning, and to contamination of process equipment that must be ultimately decommissioned [5].

Elemental mercury and its compounds are very toxic leading to severe poisoning symptoms in organisms, and sometimes death. Elemental mercury is a priority pollutant and as such is regulated in the United States due to toxicity, but the risk to personnel and the environment should be underscored by the overarching risk to processes, which can lead to catastrophic failure and explosion of cryogenic trains, which there have been ~10 in as many years. The presence of even trace levels of Hg in oil and gas feed stocks also can require additional environmental and health and safety controls that are well known throughout the industry, but have traditionally been implemented only in regions known to experience elevated Hg. Furthermore, elevated Hg-containing hydrocarbons frequently carry a significant price discount in world markets, since they must be processed using specialty equipment that is not common in most refineries.

The solubility of Hg in petroleum fluids has received much recent interest [6,7–10]. Several factors adversely affect the production, handling and processing of Hg-contaminated fluids. Therefore, it is important to understand the concentrations and forms of Hg that are present in not only produced fluids such as crude oil, natural gas, water and natural gas condensate, but also fluids that are used to process especially natural gas. Gas dehydration, acid gas removal, and chemical treatment processes, (for example, gas hydrate control using methanol or MEG), are all potentially impacted by Hg present in produced fluids. Several oil-field basins around world have Hg associated with gas, oil and water. These basins are often associated with the earth's mercuriferous and volcanic belts. Mercury ores usually occur in very young orogenic belts, where rocks of high density are forced to the crust of Earth, often in hot springs or other volcanic regions.

Fields producing elevated mercury concentrations in hydrocarbons and water typically exhibit characteristics such as low hydrogen sulfide, elevated carbon dioxide, abnormally high geothermal gradients, coaly or I-type tin granite or carbonate source rocks. High Hg crudes are not necessarily low sulfur crudes, however. They are low mercaptan crudes, and usually low H₂S crudes. Mercaptans react with Hg⁰ over time to form β-HgS which decorates the exterior of formation materials. The sulfur species that remain in the crude and do not react with the Hg⁰ to form HgS are thiophenic. Thermal degradation of carbonate source rocks often leads to fluid contamination with elevated Hg and carbon dioxide concentrations [11]. In sweet reservoirs, Hg⁰ and compounds may be present initially in gas, crude oil, condensate and produced water, whilst in sour reservoirs, Hg will almost always be present as β-HgS.

Bedded coals tend to concentrate Hg and arsenic. As Hg concentrations increase, the rank levels of these coals decrease. It is postulated that certain coal-forming land plants act as concentrators of Hg present in soils upon which they grow. Co-occurrence and correlations of mercury concentrations and total organic carbon (TOC) content in sedimentary rocks are referred to as “genetic origin.” Mineral origin of Hg in hydrocarbons and water is explained by volatilization of Hg in rock at high temperature followed by dissolution in liquids devoid of significant sulfur [12]. That Hg⁰ is soluble in both hydrocarbons and water results in contamination of natural gas, condensate, crude oil and water within a reservoir.

Elemental Hg⁰ solubility in liquid hydrocarbons follows the general trend of increases with increasing carbon number. Solubility is generally higher in straight chain hydrocarbons than branched hydrocarbons or olefins. Recent work has been published that is designed to allow the prediction of the thermodynamic behavior of Hg⁰ in a wide variety of solvents, solvent mixtures, and operating conditions where experimental data are unavailable [8,13,14]. Solubility is higher in aromatics than alkanes, and always increases with temperature [8]. It also follows the general order: alcohols > TEG > MEG > Amines > H₂O for these pure polar solvents. When the temperature-dependent solubility of Hg⁰ in natural gas or liquid hydrocarbons is exceeded, liquid Hg⁰ may “precipitate”. Several upstream oil and gas facilities have had to install low point drain systems, such as low temperature separators, slug catchers and other dewpointing system's vessels (cold process where most of the Hg⁰ will drop out) dedicated to drain off liquid Hg⁰. Mercury collection systems (Hg collection pots) may be drained manually or automatically. Liquid Hg⁰ tends to drop out of gas at about 8.7 °C [15]. Operators drain from the aforementioned pots regularly (sometimes as often as weekly or biweekly basis) to remove the liquid Hg⁰ from the system. The liquid Hg⁰ is collected in Bethlehem flask containers dedicated for Hg disposal. After the Bethlehem container is full, it is sold, disposed in dedicated injection wells, or transported to local waste treatment company for further disposal/treatment [16].

The solubility of Hg in hydrocarbons is important in understanding its partitioning and distribution in various phases and process fluids. It is important to understand the behavior of Hg prior to decommissioning and plant turnarounds. Furthermore, it is relevant in the pre-planning decommissioning phase, since many operators have not performed any studies, and a last resort is to attempt to understand mercury behavior just before decontaminating production platforms, floating-production-storage units (FPSOs), and midstream processing plants. Although many new assets are constructed with an understanding that Hg mass flux and distribution affect asset risks and risks to process, personnel and the environment change as systems equilibrate and evolve, many assets are in the aforementioned state and close to cessation of production. At this point, obtaining precise quantification, distribution and mass loading data is imperative to develop accurate decontamination and waste minimization plans [17,18].

Unless dynamic reactions occur in un-drilled reservoirs, one expects Hg⁰ to achieve vapor-liquid-liquid equilibrium (VLE) solubility. After penetration of the reservoir with the drill bit and eventual production, Hg⁰ is expected to co-migrate to the surface with petroleum either in aqueous solution, the gas phase or as a solute in liquid hydrocarbons. Mercury as β-HgS will accumulate on drill strings and production tubing, and therefore, will affect partitioning and distribution downstream of the wellhead. The change in temperature and pressure during migration of fluids to the surface likely re-distributes Hg⁰ in the phases. Fluid cooling from the wellhead to surface allows Hg⁰ to condense as liquid droplets, which may adsorb onto sand, clays and waxes. Much of the total mercury fraction, THg, in gas condensate is comprised of suspended particles in the 1–10 μm range. Dimethylmercury, although present in very low concentrations in condensate and produced water, but preferring those phases as the stream cools, requires measuring it upstream where the temperature is elevated (at first separation of the condensate). Note also that during the regeneration cycle of dehydrators, dimethylmercury can be measured in not only the gas phase, but also in the aqueous knockout vessel [6].

The speciation of Hg is critical to the development of methods to manage it. This is an active area of research. Elemental Hg can drop out if the temperature of the separator (or pipe) is less than the reservoir temperature (this is common). Prior to stabilization

(in the flowline and in the inlet separator) both volatile Hg^0 and particulate Hg can be present in the liquid phases. But during stabilization, the lower pressure and evolving light gases appear to be very effective in stripping dissolved Hg^0 from the crude and condensate. In the resulting stabilized crudes, condensates, and produced water Hg has been found to be present as nanometer particulate $\beta\text{-HgS}$ on the exterior of micron-sized solids from formation sand and other solids [19]. Additional Hg cannot be stripped from the stabilized fluids, thus Hg^0 appears to report predominantly to the stripped gas products and potentially to sediments from inlet separators. Elemental Hg is either not present in stabilized crudes or is at very low levels. Details of this analysis will be published shortly [20].

For aqueous treating solutions used to dehydrate gas or remove acidic impurities, a portion of Hg^0 can adsorb in the solution and be desorbed in the regeneration process. This Hg^0 is then present in the regeneration off-gas from these units. In addition to this route of Hg transfer, Hg can also end up as a stable form in the treating solution from these processes. This species of Hg is part of the heat stable salts which form from a reaction between traces oxidants in the gas and sulfur or nitrogen compounds [21]. In high-pH amine solutions, the Hg is probably in the form of HgS_2H^- and HgS_2^{2-} .

The proportion of mercury which is adsorbed as Hg^0 versus heat-stable salt complexes is not known. Most likely, the simple adsorption of Hg^0 dominates; otherwise the Hg content of the solutions would rapidly increase. While there are two potential routes for Hg to transfer in gas-treating plants, the focus of this discussion will be on the simple process of adsorption and desorption of Hg^0 .

The study of amounts and forms which Hg is present in petroleum is important when analyzing and risking health, environmental and safety issues, and when selecting removal technologies. Wilhelm et al. [17], have traditionally divided forms of Hg into basic categories, but new research is re-defining this view. The simplest categorization is dissolved vs. insoluble. Dissolved Hg is that passing through a pressure filter of arbitrary pore size usually ranging between 0.2 and 0.8 μm (preferably 0.45 μm), whilst insoluble Hg is that which will not pass through the filter. Insoluble Hg is often termed, “particulate Hg” because there are several Hg compounds that are soluble and several that are insoluble in water and hydrocarbons. Since this is a functional definition, any particulate Hg having sizes less than the filter would be classified as “dissolved”. In practice, varying the filter size (or centrifuge speed) removes different amounts of Hg. However, this traditional definition relies on the use of a filter with the arbitrarily-selected size. Recent studies have found that the particulate Hg in crudes and condensates consists of a range of particle sizes [19]. Furthermore, using ever smaller filters, or increasingly intense centrifuge conditions removes more Hg. The Hg in the recovered solids has been found to be predominantly $\beta\text{-HgS}$ and devoid of Hg^0 . The interpretation of these results is that there is no true “dissolved” Hg in crude and petroleum. Rather the portion that passes through filters is simply small particles of $\beta\text{-HgS}$.

As with crude and condensate, the species of Hg found in produced water has been determined to be particulate $\beta\text{-HgS}$ of various sizes. The portion of Hg in aqueous solutions which passes through a filter can be misidentified as inorganic Hg salts, which imply their presence as ionic species in solution [22].

The predominant Hg specie present in natural gas is the element, Hg^0 . Due to their volatility, most dialkyl mercury species, R_2Hg , will also report to the gas phase near the wellhead in higher temperature gas. Fortunately, only traces of the very toxic dialkyl mercury compounds have been detected in oil and gas samples. In glycols and amines, THg is present in other forms as well. Some Hg will be in transit through the gas processing plants as Hg^0 . However, other forms are also present. In high pH amines, a stable form is HgS_2H^- . In glycol dehydrators a species like $\text{Hg}(\text{SR})_2$ is pre-

sent. These species are part of the heat stable salts in these units. Other species include cyanides, hydrosulfides, etc. [19]. These heat stable salts form from traces of oxidants in the gas that react with H_2S , mercaptans and other species. Depending on the regenerator temperature, some of the Hg-complexes can decompose. The Hg-complexes also continue to react and make Hg-rich sludges containing 100's of ppm Hg. The Hg in these sludges is $\beta\text{-HgS}$, and related species.

Metacinnabar is also the most common form detected in liquid hydrocarbons, and can predominate in other solvents. It should be noted that the solubility of Hg^{2+} salts is significant, so Hg^{2+} in theory could be present in non-polar hydrocarbons and polar solvents such as alcohols and glycols [7a,7b]. Cationic Hg would be stable only under acidic conditions, however. Under neutral or caustic conditions, other species are present. When HgCl_2 dissolves in pH 7 water, it does not dissociate, but remains as HgCl_2^0 molecular species. Elemental Hg^0 solubility in liquid hydrocarbons follows the general trend of increases with increasing carbon number. Solubility is generally higher in straight chain hydrocarbons than branched hydrocarbons or olefins. Solubility is generally higher in aromatics than alkanes, and always increases exponentially with increasing temperature [8].

2. Review of previous measurements

Sabri et al. [8,9] have examined the partitioning of Hg into glycols that are used in gas processing facilities (dehydrators) and as gas hydrate inhibitors in wells and pipelines. They report that the solubility of Hg^0 in MEG solutions ranges from 0 to 60 ppbv (ng/mL) with a slight increase to ~80 ppb when the pH was reduced from ~9 to ~6 at room temperature. They utilized 10, 50 and 90 wt% laboratory reagent grade MEG, 50 wt% lab-MEG with added salts, and 50 wt% MEG supplied by industry in their solubility and partitioning studies. Elemental mercury vapor in dry nitrogen was bubbled into solutions of MEG for 17 h at room temperature. Testing showed that Hg^0 apparently reached equilibrium saturation in MEG in this timeframe. Mercury concentrations were determined by inductively coupled plasma mass spectroscopy (ICP-MS) [8,9]. The solubility of Hg in TEG was previously reported to be 2.90 ppm [23]. A lean amine solution from a refinery acid gas scrubber was reported to contain 250 ppb THg probably HgS_2H^- given the pH of the solution [24]. The concentration of Hg^0 in a simulated lean flue gas desulfurization solution of monoethanolamine was reported to be 27 ppb [25]. The solubility of Hg^0 in methanol, isopropanol, *n*-octanol and water were previously examined by Clever [26]. The reported concentrations for Hg^0 solubility in these solvents at 298 K are 722, 682, 924 and 60 ppbw, respectively, but these appear to be THg measurements and not necessarily Hg^0 concentrations.

The solubility of Hg^0 and THg in methanol and water were previously examined by Bloom and Gallup [7a,7b], with reported concentrations of 640 and 52.1 ng/g at 298 K, respectively. The solubility of HgCl_2 was also examined in polar and non-polar solvents and found to be significant, as expected. While HgCl_2 dissolves in pH 7 water, its disassociation constant is very low and not a good model for Hg species from petroleum. When the pH drops by the addition of acid, then the HgCl_2 disassociates. A number of the solvents examined by Bloom and Gallup [7a,7b] reacted with a Hg droplet to form Hg “corrosion” products that produced THg levels far higher than the true Hg^0 concentration. Most simple alcohols were seen to tarnish the Hg^0 droplet – growing darker with increasing molecular weight in the absence of a reducing agent. The presence of “corrosion” products appeared to be due to the reaction between Hg^0 and trace solvent impurities. For example, significant levels of dissolved

Hg^{2+} compounds appeared to result from almost every oxygen-containing solvent in the absence of a reducing agent and after treating the solvent with copper filings [7a]. In an extension of that work, the solubility of Hg^0 in several alcohols, MEG and TEG is reported here. THg concentrations were essentially the same as Hg^0 concentrations due to added stannous citrate reducing agent, *vide post*.

Because the concentration of mercury in these solutions is below the limit of spectroscopic techniques, an implicit assumption in these VLE experiments is made that the mercury remains in the elemental state and is not oxidized or complexed. Alekhin et al., have presented results which show that the solubility of elemental mercury is lowered when oxygen is excluded or removed by reduction [27].

3. Experimental

3.1. Materials

Analytical grade solvents and acid were purchased from Sigma Aldrich. Distilled water was obtained from the laboratory still. Reagent grade stannous chloride and citrate were also obtained from Sigma Aldrich. Triply-distilled elemental mercury was obtained from Strem Chemicals Inc. The best way to obtain clean droplets of Hg^0 was to use a 100 mL gas-tight syringe with a fine gauge stainless steel needle to pull liquid from the center of a larger mass, where the Hg was more than a centimeter deep.

3.2. Analytical methods

THg in the solvents was determined after first digesting ~0.4 g of sample with 3.0 mL of concentrated nitric acid using an Anton Paar high pressure asher [7a]. Samples were wet combusted for 2 h in ultra-clean quartz tubes at 573 K and 125 atm of pressure. After dilution with reagent water, aliquots were analyzed using SnCl_2 reduction, purge and trap on gold, electrochemical desorption of the mercury as Hg^0 , and detection/quantification via a BrooksRand cold vapor atomic fluorescence spectrometer (CVAFS). Elemental mercury was independently determined after dilution with hexane. Diluted samples were purged directly after floating up to 200 mL of sample on the surface of 100 mL pre-purged 0.2 wt% HCl in water contained in a bubbler that has never been in contact with Sn^{2+} . Purging the sample results in the evaporation of the hexane and the release of Hg^0 onto a gold trap [28,29]. Quality assurance parameters of the results are the same as those previously reported in Table 1 of Ref. [7a], where the minimum detection limit was 0.5 ng/g).

3.3. Experimental setup

Solubility. Samples for analysis were made by completely filling 125 or 250 mL borosilicate bottles with solvent, injecting ~1.0 to 2.0 g of clean liquid Hg^0 , and tightly replacing the Teflon™-lined screw caps. Stannous citrate was added and bottles were incubated at temperatures ranging from 243 to 373 K with constant gentle agitation or periodic vigorous agitation. Periodically, the agitation was stopped, and the samples were allowed to settle for at least 4 h prior to aliquoting. As a buffer against temperature fluctuations, sample bottles were kept in 400 mL plastic beakers filled to 70% with a temperature-appropriate inert liquid. The beakers were used to carry the sample from the incubator to and from the analytical balance. The entire handling process generally took less than 2 min, resulting in trivial changes in temperature, and therefore, the Hg^0 concentration of the sample. The Hg^0 concentration in at least one of the samples per temperature was periodically

Table 1
 Hg^0 equilibrium solubility (ng/g or ppbw) in water and alcohols.

T (°C)	Water	μ , Uncertainty	Methanol ^a	μ , Uncertainty
-30			21.22	2
-20			45.08	2
-10			90.44	4
0	28.3	1	172.4	5
10	37.5	2	314.1	8
20	49.9	2	549.3	15
30	66.2	4	925.7	28
40	88.7	3	1508.9	52
50	118.2	4	2386.4	73
60	157.1	6	3671.6	86
100	481.4	16	16,330	94
T (°C)	n-Propanol	μ , Uncertainty	n-Octanol	μ , Uncertainty
-30	22.03	4	24.33	3
-20	45.96	5	51.38	3
-10	90.68	7	102.5	6
0	170.2	10	194.4	7
10	305.7	14	352.5	12
20	527.4	12	798.5 ^b	15
30	877.8	38	1317.7 ^c	33
40	1414.2	61		
50	2212.1	98	2635.3	101
60	3368.5	94		
100	14,455	387	17,759	520
T (°C)		96% Octanol		μ , Uncertainty
-30		9.62		2
-20		19.68		5
-10		38.1		9
0		70.28		12
10		124.2		11
20		271.4 ^b		23
30		438.2 ^c		42
40				
50		850.4		89
60				
100		5275.1		166

^a Average of two separate studies.

^b 25°.

^c 35°.

monitored over days to months, until a constant concentration was observed. The actual quantitative data produced for the study were then collected in replicate digestions two or more days after equilibrium was verified.

A special procedure was employed for the determination of the solubility in water, alcohols and glycols, owing to the ease with which Hg^0 is oxidized to Hg^{2+} (likely HgO) even in extremely carefully prepared solvents, yielding results that can be many orders of magnitude too high [7b]. Bloom and Gallup [7a,7b] also noted that some solvents or impurities therein reacted with the mercury resulting in “tarnishing” of the droplet, *vide supra*. In these instances, the THg concentration significantly exceeded the Hg^0 concentration. Therefore, a droplet of clean Hg^0 was placed into the bottles filled to the top with ultra-pure argon-purged solvent to which 100 ppm of stannous citrate (pH 7.0) was added, and the cap sealed. By adding Sn^{2+} to the aqueous samples, the redox potential was forced down to a point where only Hg^0 can exist. Aliquots from these samples were then analyzed in the same manner as discussed above.

At temperatures exceeding or approaching the boiling point of the solvents, coated stainless steel pressure vessels were used to reach equilibrium solubility. In these instances, the vessel was opened through a valve and the sample was bled into gold-coated sand-containing tubes which were then analyzed in a specially-designed furnace with CVAFS detection [29].

Gas Stripping. Mercury saturated water (46 ppb at 293 K) was counter-currently contacted with hydrocarbon gas in a specially designed, packed glass column of 500 mL capacity to evaluate

the efficiency of gas stripping to remove dissolved Hg^0 into the vapor phase. The column was packed with a plastic mesh. The residence time of the water in the column was set at 8 s. The water and gas flow rates were set to mimic an actual stripping tower at a gas field (76 kg/min water and 0.46 kg/min hydrocarbon gas). Samples of water were collected before, during and after the stripping operation for THg and Hg^0 analysis.

Distillation. The 40 vol% MEG sample at 293 K, containing 67 ppb of THg and Hg^0 , was placed into a round bottom flask attached to a water-cooled condenser. The mixture, which had been treated with stannous citrate to limit oxidation of the Hg^0 was heated to 398 K and the distillate was collected at room temperature and monitored for volume. Volumetrically, the 40 vol% MEG was concentrated up to 80 vol% when the distillation was terminated. The concentrations of THg and Hg^0 were determined in both the distillate and the concentrate.

4. Results

4.1. Solubility

Multiple determinations at each of three or more temperatures were measured for each Hg^0 /solvent pair. The concentrations of THg and Hg^0 were similar for each pair and averaged to yield the reported values. The Hg concentrations obtained for the water and alcohol experiments together with estimated uncertainties are shown in Table 1. The Hg concentrations for the MEG and TEG solubility studies together with standard deviations are provided in Table 2. Mercury solubilities in solvents are expressed as an exponential function of temperature (typically 243–333 K) as shown in Table 3. The form of the exponential function is consistent with those reported by Bloom and Gallup [7a,7b]. At temperatures higher than 333 K, the exponential expressions do not accurately reflect the measured concentrations. In some solvent systems, the higher temperature data at 373 K was obtained in sealed Siltec™-coated pressure vessels when the boiling point was less than 373 K. Some values at 373 K are included in Table 1.

For reference and comparative purposes, the calculated solubility from the exponential expressions at 298 K is included in Table 3. *n*-Octanol (>99 wt%) yields the highest Hg solubility followed by methanol, propanol, TEG, MEG, and water. In two independent studies, the solubility of Hg in methanol was essentially equivalent at 298 K; i.e., 627 and 640 ppb thereby showing reproducibility of experiments. Fig. 1 compares some mercury solubilities in alcohols, which shows good agreement between the present study and prior literature values. Similarly, in two separate studies of solvent water, the Hg concentrations at 298 K are calculated to be 57.4 and 52.1 ppb. These values are closely equivalent to a literature-reported concentration of ~60 ppb at 298 K [9]. In the studies of 99%, 80%, and 40% TEG the Hg concentrations at 293 K are 344, 151 and 94 ppb, respectively. By comparison, the Hg solubilities in 99%, 80%, and 40% MEG at 293 K are 182, 96 and 67 ppb, respectively. Solvents diluted with water, representing rich and lean glycols, and water/octanol exhibit lower Hg solubilities than the nearly pure (99%) solvents. As more water is added to the glycols, the mercury concentrations decrease, as expected [26].

Table 2
 Hg^0 equilibrium solubility (ng/g or ppbw) in glycols.

T (°C)	99% MEG	80% MEG	40% MEG	99% TEG	80% TEG	40% TEG
1.5	62.7 ± 4	31.9 ± 1	17.6 ± 2			
20	182 ± 3	96.2 ± 3	66.7 ± 4	344 ± 20	151 ± 11	93.6 ± 9
50	1020 ± 15	707 ± 8	320 ± 16			

Table 3
 Hg^0 solubility relationships (ng/g) for solvents between about –30 and +50 °C, where T is degree Celsius.

[Hg ⁰] at 25 °C	Solvent	Hg ⁰ solubility	R ²
57.4	Water	28.1e ^{0.0286T}	1.00
52.1	Water [7a]	17.0e ^{0.0448T}	0.979
627	Methanol (Study 1)	151e ^{0.0569T}	0.992
640	Methanol (Study 2)	156e ^{0.0565T}	0.990
715	Methanol [26]	206e ^{0.0498T}	0.999
677	Isopropanol [26]	186e ^{0.0517T}	1.00
601	<i>n</i> -Propanol	150e ^{0.0555T}	0.992
736	<i>n</i> -Octanol	171e ^{0.0584T}	0.993
252	96 vol% <i>n</i> -Octanol	62.2e ^{0.0559T}	0.993
246	99 vol% MEG	56.4e ^{0.0589T}	1.00
142	80 vol% MEG	27.7e ^{0.0655T}	0.999
78	40 vol% MEG	16.7e ^{0.0616T}	0.999

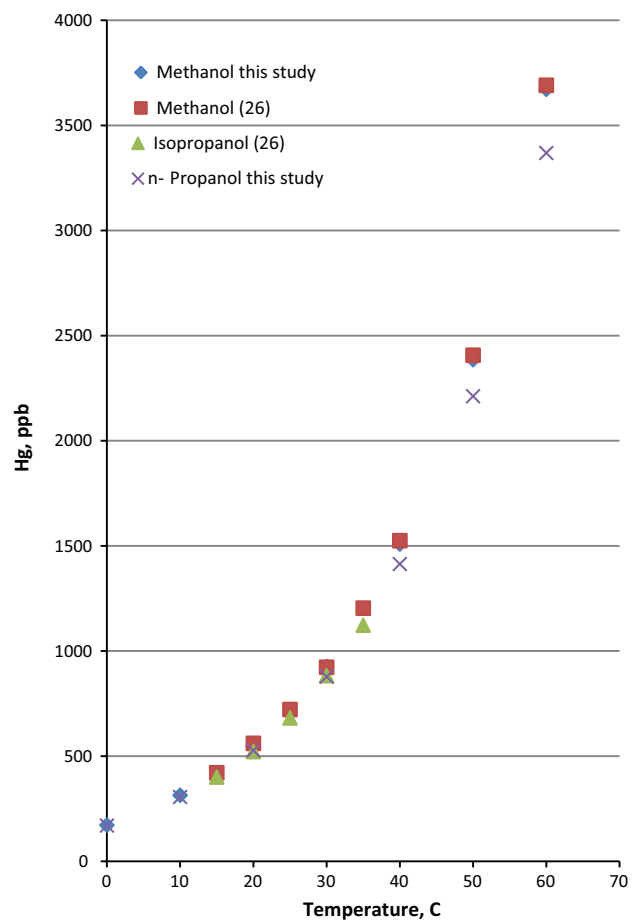


Fig. 1. Comparison of mercury solubilities in alcohols.

4.2. Gas stripping

The concentrations of THg and Hg^0 in effluent water resulting from the gas stripping tests in the columnar test were obtained. The gas stripping experiment was designed to simulate a field

stripping tower operating at 343 K. However, in the laboratory test, the column temperature could not be well-maintained and the average outlet water temperature was only 321 K. The initial concentrations of THg and Hg⁰ in the feed water were initially saturated at 46 and 45 ppb, respectively, at 293 K. At 321 K, the stripping efficiency ranged from about 70 to 80% with effluent THg and Hg⁰ concentrations ranging from 8 to 13 ppbw. A second run conducted at 293 K (due to difficulties in operating the laboratory column at elevated temperature), not unexpectedly, yielded only about 40–65% stripping efficiency (effluent Hg concentrations of 16–26 ppbw).

Given these results and the deficiencies in the stripping experiments, it is expected that a field or pilot stripping tower operating at 343 K will reduce the concentration of Hg⁰ (if present) in effluent water by a much higher efficiency. Even if the inlet Hg⁰ concentration is saturated at 343 K (and the corresponding solubility is extrapolated to be >200 ppb), it is expected that the stripped water is likely to contain very low concentrations of Hg⁰ at the field stripping tower conditions. We were unable to measure the Hg concentration in the hydrocarbon gas exiting the laboratory column due to the short duration of the tests. However, the stripping gas will be contaminated with Hg as a result of stripping if Hg⁰ is present, and thus will need to be treated by a mercury removal unit (MRU) to avoid any contamination of the stripper gas in downstream processes.

4.3. Distillation

The distillation experiment was designed to simulate MEG regeneration as practiced in the field. Approximately 26% of the Hg in the original 40 vol% MEG sample remained in the round bottom flask consisting of 80 vol% MEG. Approximately 74% of the Hg in the original 40 vol% MEG sample reported to the distillate. In both the distillate and the remaining 80 vol% MEG, the concentrations of THg and Hg⁰ were essentially equivalent. The presence of stannous citrate in the original 40 vol% MEG apparently prevented any oxidation of Hg during the distillation process. The initial concentration of Hg⁰ in the 40 vol% MEG was ~67 ppbw.

5. Discussion

The present study shows that the solubility of Hg⁰ in alcohols, TEG, MEG, and H₂O is less than a few ppmw at temperatures <333 K. Although the concentrations are quite low, they are still significant when considering that these Hg levels are much greater than drinking water (2 µg/L), or other standards for disposal of fluids to the environment. The concentrations of THg and Hg⁰ reported here for MEG are generally significantly greater than those reported by Sabri et al. [9,10]. In the present study, the solubility of Hg⁰ in 40 vol% MEG at 293 K (67 ppb) is similar to that previously reported (0–60 ppb). The concentrations reported herein for 99 and 80 vol% MEG at approximately room temperature are much greater than water and MEG (as reported by Sabri et al. [9,10]). However, Khalifa and Lue [13] predict that the solubility of Hg⁰ in MEG is 57.7 ppb (temperature and % MEG not reported). In contrast, the concentration of mercury in 99% TEG at room temperature is much less in the present study (344 ppb) than that reported by Carnell [23]. The value reported by Carnell is as high as the solubility of Hg⁰ in non-polar solvents at room temperature, [26] and is believed to be THg perhaps from reaction of Hg⁰ with TEG under oxidizing conditions to yield some of the more highly soluble Hg²⁺. The results of the present study also show that methanol used for gas hydrate control will be contaminated with much more Hg than MEG, if equilibrium solubility is reached.

Gas stripping experiments of Hg⁰ in water has tended to show that the Hg⁰ is effectively removed from the water into the gas phase. This result is not surprising since the analytical method for measuring Hg⁰ in solvents calls for purging with an inert gas and trapping on a gold-coated substrate. The laboratory stripping experiments were prone to problems maintaining desired temperatures. Pilot or field testing at 343 K with very large volumes of water should improve the results. Hayashi et al. [30] showed that Hg²⁺ may be stripped at 343 K from high dissolved solids content wastewater using air after reducing the cationic Hg to Hg⁰ with hydrazine. Effluent gas from strippers will contain Hg⁰ if it is initially present in the water. Stripping of oxidized Hg (Hg⁺ or Hg²⁺) will not occur unless there is water droplet carryover into the gas. At any rate, gas used for stripping Hg from water will become contaminated and must be handled with care to avoid emissions to the environment or contaminating downstream processes/piping.

Sabri et al. [9,10], have performed experiments to demonstrate the behavior of Hg during MEG regeneration. This has been performed on laboratory-grade, salted and industrial MEG. They examined the transfer and partitioning of mercury species in an unpressurized laboratory-scale distillation apparatus at 443 K. They reported that ionic Hg (Hg²⁺) was not stable in industrial MEG (50 wt%) due in part to an elevated pH (>8) and various additives in the sample. Amines or sodium carbonate is added to keep the pH high enough to avoid corrosion in pipelines where the gas contains high concentrations of CO₂. The Hg is not disassociated Hg²⁺ but is particulate β-HgS. The extent of the decomposition back to Hg⁰ depends on the temperature and time. In refinery crude furnaces ahead of the main column, essentially all the β-HgS decomposes in a few seconds at temperatures near 645 K. In practice, the MEG distillation takes place in two steps. The first is MEG regeneration which is performed at modest temperatures with the goal of removing some of the water. A portion of the remaining liquid is then sent to a vacuum distillation reclaimer which recovers the MEG (but not the amine) as an overhead stream. The β-HgS in both distillation steps remains intact in the bottoms and accumulates in the paste residue from the reclaimer. Therefore, β-HgS accumulated in a solid tar residue during distillation [9,10]. Decomposition (reduction) led to Hg⁰ partitioning into the gas phase and collecting in the distillate. About 50% of the THg reported to the distillate from the industrial MEG, whereas only about 10% left their laboratory MEG as Hg⁰. The partition percentage was highly dependent on the salt and organic content of the MEG solution.

In the present study of MEG regeneration by distillation, the laboratory MEG was 60 vol% water and contained added stannous citrate. (It was the remaining solution from the solubility study and contained an initial THg and Hg⁰ concentration of 67 ppbw at 293 K.) Although industrial MEG is expected to contain significant salts and additives, and perhaps several different species of Hg, we examined the distillation behavior of our laboratory MEG solution. The solution was heated to 398 K, and as discussed above, resulted in ~26% of the Hg in the original 40 vol% MEG sample remaining behind in the regenerated 80 vol% MEG, whilst ~74% of the Hg partitioned to the distillate water. The distillation was only performed in duplicate due to the limited amount of 40 vol% MEG remaining after the solubility studies, but concentrations of THg and Hg⁰ were similar in both experiments.

During glycol and amine regeneration a portion of the Hg⁰ gets tied up with sulfur compounds as part of the heat stable salts in solution [24]. A portion of these can decompose back to Hg⁰ in the high temperatures of the regenerator, while other portions react further to make Hg-rich sludges [31]. The THg in the sludges from amine and glycol plants is composed of fine particles of β-HgS, and a mercury dithiol precursor.

6. Conclusions

This study examined the equilibrium solubility of Hg^0 in polar solvents such as water, alcohols, MEG and TEG over the temperature range, 243–373 K. The solubility of Hg^0 in water was similar to that previously reported in the literature. The solubility of mercury in three alcohols, MEG and TEG at 293 K approached 200–600 ppb, which is significantly greater than water. In solvents diluted with water, the equilibrium solubility decreased, as expected. Solubility decreased further with increasing water dilution.

Water saturated with Hg^0 was stripped using petroleum gas in a small laboratory packed column. The Hg^0 was nearly quantitatively stripped from water as expected. Pilot or field scale stripping should partition all or most of the Hg^0 into the gas phase. The gas phase containing Hg^0 will need to be handled properly and may require treatment through a mercury removal unit.

The distillation of 40 vol% MEG containing 100 ppm of stannous citrate and equilibrated with 67 ppb of Hg^0 was performed in duplicate at 398 K and atmospheric pressure. Approximately 26% of the Hg in the original 40 vol% rich MEG sample remained in the round bottom flask of reconstituted 80 vol% lean MEG. Approximately 74% of the Hg in the original 40 vol% MEG sample reported to the distillate. In both the distillate and the remaining 80 vol% MEG contained equal concentrations of THg and Hg^0 . The presence of stannous citrate in the original 40 vol% MEG apparently prevented any oxidation of Hg during the distillation process. We concur with Sabri et al. [9] that Hg partitioning during MEG regeneration is a complicated process, and the results presented in theirs and our studies are specific to the experimental conditions employed. Further, the interpretation of results should be considered with regard to the specific conditions at which experiments were conducted.

Removal of Hg as close as possible to production wells is recommended in order to minimize contamination in downstream processes. Mercury removal catalysts are available to remove Hg from natural gas [16]. Mercury may be removed from produced water via filtration, adsorption or thiol precipitation, but removal from methanolic, MEG or TEG solutions may be more difficult [23,32,33].

Acknowledgement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

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