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THE SOLUBILITY OF ELEMENTAL MERCURY IN WATER BETWEEN 30 AND 210°C

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ABSTRACT

The solubility of elemental mercury (Hg^0) at temperatures between 30 and 210°C was determined by direct sampling of mercury saturated water contained in a fixed volume stainless steel autoclave. The temperature dependence of the solubility was best represented by the equation

$$\log_{10} x_{Hg} = -11.879 + 0.01206T$$

where x_{Hg} is the mole fraction of dissolved Hg^0 and T is the temperature in degrees Kelvin.

At temperatures less than 100°C the best literature values are in good agreement with these results. At higher temperatures it is difficult to compare our data with previous studies as they show widely divergent results.

Comparison of field results for volatile mercury steam/water partitioning showed that up to 10^2 times more mercury was retained in solution than would have been indicated from the theoretical distribution coefficients calculated from the solubility data. A kinetic limitation to the mercury steam/water distribution in the Webre separator was the most likely explanation although the presence of other nonvolatile mercury species could not be discounted.

INTRODUCTION

The ability to predict the transport and partitioning behaviour of elemental mercury (Hg^0) during exploitation of geothermal reservoirs and power production requires reliable data for the vapour/liquid distribution coefficients. The distribution coefficient is derived from Henry's law constant which can be calculated from the solubility of elemental mercury. This study was undertaken because the large differences in Hg^0 solubility values between the few published experimental studies at temperatures above 100°C made it difficult to interpret field data collected at the Ohaaki geothermal field (Timperley and Mroczek 1989).

The importance of elemental mercury is that it appears to be the dominant chemical form of mercury found in chemical surveys of wells at New Zealand geothermal fields. This is in agreement with previous studies (Robertson et al. 1978) which showed that most if not all the mercury present in geothermal effluent is Hg^0, even at high H_2S gas levels. Chemical modelling (Varekamp and Buseck 1984) has also shown that mercury transport occurs largely as Hg^0 in dilute hydrothermal systems with moderate amounts of S (<0.01 mol/litre).

PREVIOUS WORK

At temperatures less than 100°C there have been numerous experimental solubility studies using a variety of measurement techniques. These studies also show a wide variation in values. The reason for the disagreement is not clear but trace contamination by air oxygen or not enough time allowed to attain the equilibrium solubility are commonly suggested reasons. Clever et al. (1985) reviewed and evaluated all available data and presented smoothed solubility data and smoothed Henry's constant equations over the temperature interval 273.15-393.15 K. The only high temperature study included in their evaluation was that of Sorokin (1973). Sorokin measured the solubility of mercury in water at temperatures of 573, 673 and 773 K at total pressures between 507 and 1013 bar. Samples were extracted from a flexible reaction cell autoclave at constant pressure and temperature. Clever et al. (1985) combined the hypothetical Henry's constant at the higher temperatures extrapolated to 1 bar with the Henry's constants calculated from the lower temperature data (277-346 K) of Glew and Hames (1971) to obtain an equation for Henry's constant over the temperature interval 393-773 K. Varekamp and Buseck (1984) also used the thermodynamic parameters calculated from Glew and Hames's (1971) data as well as Sorokin's (1973) data to calculate the solubility of Hg^0 to 250°C. Recently Gushchina et al. (1989) determined the solubility of mercury using a spectrophotometric technique at temperatures of 150, 200 and 250°C as well as evaluating previous work. Their results as well as those of Sorokin (1973), Sorokin's more recent experimental results and calculations as reported by Gushchina et al., Varekamp and Buseck's (1984) extrapolations, the smoothed literature interpolations of Clever et al. (1985) as well as selected low temperature

Table 1. Smoothed Mole Fraction Solubility, $-\log_{10}x_{Hg}$.

t(°C) =	30	60	72	100	120	150	200	210	250	300
References										
This Study	8.22	7.86	7.72	7.38	7.14	6.78	6.17	6.05		
Sorokin (1973)*§				7.38			5.33			4.42
Sorokin calculated§	8.26	7.88	7.71	7.29	6.97	6.51	5.76	5.62	5.07	4.45
Gushchina et al. (1989)						5.45	4.83		4.21	
Reichardt and Bonhoeffer (1931)*					7.02					
Sanemasa (1975)	8.14	7.48								
Glew and Hames (1971)	8.23	7.91	7.76							
Varekamp, Buseck (1984)	8.23	7.91	7.77	7.38	7.12	6.67	5.97	5.95	5.39	
Clever et al. (1985)	8.23	7.85	7.70	7.36	7.13					

*Experimental Data
§As reported by Gushchina et al. (1989)

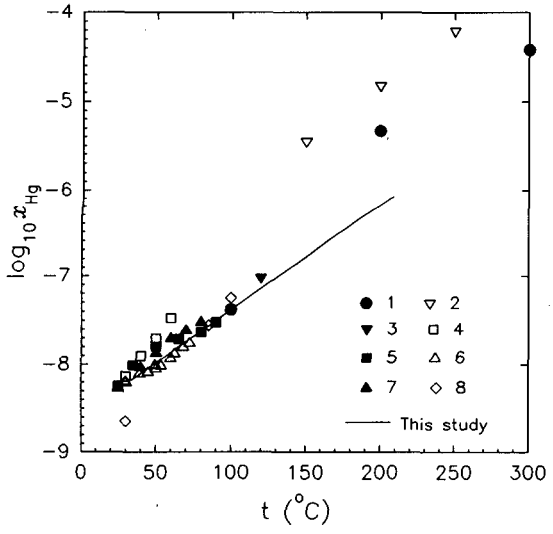

Figure 1. Comparison of experimental solubility values reported in the literature with the results from this study. 1 - Sorokin, 1973 (as reported by Gushchina et al, 1989), 2 - Gushchina et al., 1989; 3 - Reichardt and Bonhoeffer, 1931; 4 - Sanemasa, 1975; 5 - Choi and Tuck, 1962; 6 - Glew and Hames, 1971; 7 - Onat, 1974; 8 - Stock et al., 1934.

data are listed in Table 1. Figure 1 shows only the experimental data including more low temperature data below 100°C. As expected the Varekamp and Buseck's (1984) evaluations agree with Clever et al. (1985) due to the heavy weighting of the low temperature data of Glew and Hames (1971). At 150 and 200°C the solubility values of Gushchina et al. (1989) are significantly higher (1 log unit) than Sorokin's calculated values.

EXPERIMENTAL

Distilled water was degassed and purged with nitrogen (99.99% minimum purity). Traces of oxygen in the gas were removed by passing the gas through a heated tube packed with copper turnings. A 100 cm^3 capacity 316 stainless steel autoclave containing about 0.1 to 0.5 g metallic mercury (BDH "Analar") was filled under nitrogen with 75 ml of water. In all runs, except #2, the water contained 0.001 mol kg^{-1} hydrazine hydrate (BDH "Analar") to ensure no oxidation of mercury took place.

The autoclave was heated in a rocking furnace and the temperature was measured with a calibrated chromel-alumel thermocouple. The rocking was stopped 2 hours prior to sampling and the liquid was sampled through a short length of stainless steel capillary tubing using a low dead volume sampling valve directly into a weighed flask containing acidified 6% w/v potassium chromate solution. A pre-sample was first collected to clear the tubing of non-equilibrated fluid. Immediately after collection the sample was analysed for mercury using the flameless atomic absorption technique (Omang 1971).

At temperatures above 100°C equilibrium was only approached from below as the autoclave tended to leak with a reduction in temperature leading to higher but non-reproducible solubility values. In these experiments the liquid was equilibrated for between 4 and 31 days before sampling. The autoclave was thoroughly cleaned between runs including washing with hot nitric acid.

RESULTS

The raw experimental mercury solubility results at temperatures between 30 and 210°C are presented in Table 2. The total pressure would have been slightly above saturated vapour pressure as the autoclave was not evacuated after filling under nitrogen. However the change in solubility due to such a small pressure increase is negligible. At 300°C the decrease in solubility is 3.4×10^{-4} log units per bar (Sorokin, 1973). The standard deviation is a reflection of the uncertainties in the sampling and solubility method rather than the accuracy of the analytical technique (≈3%). The temperature

Table 2. Experimental Results, days = sampling time since commencement of run, n = No. of samples, t = temperature (°C), x_{Hg} = mole fraction of mercury, SD = standard deviation, H = Henry's constant (bar), B = vapour/liquid distribution coefficient.

Run	days	t	n	x_{Hg}x10^9	SD	H	B
1	14	58.5	6	20	3	1794	9603
1	20	78.8	3	22	1	5434	11931
2	5	89.6	3	44	5	5319	7609
3	5	131.5	2	104	4	17132	5882
4	4	90.5	3	39	2	5958	8235
4	7	91.3	3	36	3	6880	9223
4	11	91.3	3	32	1	7483	10030
5	9	60.3	3	18	1	2121	10439
5	11	60.3	3	12	1	3138	15441
5	14	60.3	2	17	1	2281	11227
6	4	39.8	3	10	1	1007	13756
6	7	39.3	3	10	1	933	13092
7	2	134.8	9	92	4	22382	6959
7	4	134.5	6	91	4	22401	7028
8	7	102.0	3	38	3	11726	10606
8	9	102.0	3	38	1	11011	9959
8	14	102.0	3	40	1	10731	9706
9	4	161.8	6	208	10	30164	4420
9	9	163.8	6	218	6	30357	4223
9	14	163.3	9	279	31	25501	3594
10	6	34.0	3	6.5	0.2	851	15959
10	8	34.0	2	6.40	0.02	835	15643
10	10	34.5	2	8	1	808	14743
11	6	185.5	6	515	41	29927	2435
11	8	185.0	6	469	4	29996	2470
12	6	104.2	3	49	4	10162	8499
12	8	107.5	3	55	6	11262	8398
13	6	54.0	3	12	1	1956	12972
13	9	57.5	2	15	1	2132	11962
14	28	207.8	3	1369	205	25357	1245
15	31	208.8	6	992	50	32350	1555

dependence of $\log_{10}x_{Hg}$, where x_{Hg} is the dissolved mercury mole fraction, was linear within the experimental errors and the data is presented in Figure 2. The smoothed linear curve derived in this study is also shown in Figure 1 together with experimental results from previous work. The agreement at temperatures below 120°C is good but at 150 and 200 °C these results are over 1 log unit lower than those of Gushchina et al. (1989). The values are also lower than Sorokin's calculated results but the agreement is better, differing by about 0.4 log units at 150 and 200°C.

Henry's constant can be calculated from the solubility data assuming that Hg^0 is at equilibrium in the water and vapour phases, that the partial pressure of mercury (P_{Hg}) is such that the liquid mercury is in equilibrium with its aqueous solutions and assuming that the solubility of water in liquid mercury is negligible.

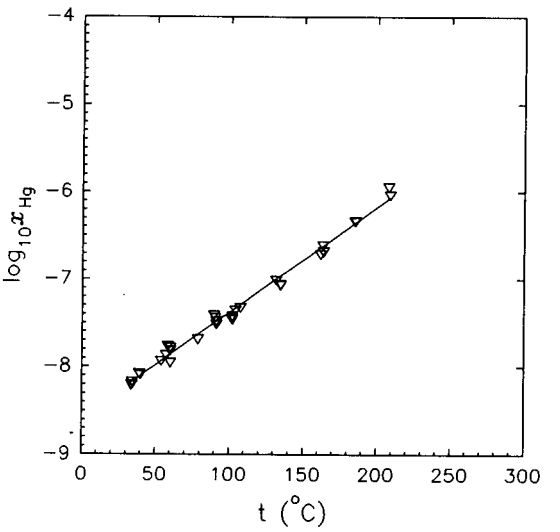

Figure 2. Temperature dependence of experimental and smoothed mole fraction solubilities.

Henry's constant (H) is calculated by

$$H = \frac{P^{o}_{Hg}}{x_{Hg_{(aq)}}} \qquad (1)$$

where P^{o}_{Hg} is the vapour pressure of pure liquid mercury. From the ideal gas law the vapour/liquid distribution coefficient (B) can be calculated by

$$B = \frac{H\,Z}{R\,T} \qquad (2)$$

where Z is the specific molar volume of steam, R is the gas constant and T is the temperature in degrees Kelvin.

These simple relationships are expected to hold in these experiments and under most geothermal conditions because of the very low solubilities, vapour concentrations and partial pressures.

Henry's constants and distribution coefficients were calculated for each experimentally determined Hg^0 solubility using liquid mercury vapour pressures from Douglas et al. (1951). A least squares fit of the data showed that the best equation describing the temperature dependence of the data to be of the form

$$\log_{10}H = a + bT + c\log_{10}T + \frac{d}{T} \qquad (3)$$

where T is the temperature in degrees Kelvin. The regression for the distribution coefficients included the

Table 3. Regression Coefficients for Fitting Experimental Data in Table 2.

	a	*b*	*c*	*d*	r^2
$\log_{10}x_{Hg}$	-11.88	0.012056	-	-	0.990
$\log_{10}H$	-535.94	-0.13814	215.438	13944.2	0.992
$\log_{10}B$	-402.57	-0.10581	161.042	11877.4	0.995

Table 4. Smoothed Elemental mole fraction Solubilities - x_{Hg}, Henry's Constants - H (bar) and Vapour/Liquid Distribution Coefficients - B. σ = Standard Error of Estimate.

t	$-\log_{10}x_{Hg}$	σ	$\log_{10}H$	σ	$\log_{10}B$	σ
30	8.22	0.02	2.83	0.03	4.18	0.03
50	7.98	0.02	3.20	0.02	4.11	0.01
75	7.68	0.01	3.62	0.02	4.04	0.01
100	7.38	0.01	3.97	0.01	3.96	0.01
125	7.08	0.01	4.24	0.02	3.85	0.01
150	6.78	0.02	4.41	0.02	3.70	0.01
175	6.48	0.02	4.49	0.02	3.50	0.02
200	6.17	0.03	4.47	0.03	3.25	0.02
210	6.05	0.03	4.44	0.04	3.14	0.02

theoretical data value of 1 at the critical point of water. The regression coefficients for Equation 3 are listed in Table 3 and the smoothed calculated data is presented in Table 4.

The experimental and smoothed Henry's constants and distribution coefficients are presented in Figures 3 and 4 as well as the literature evaluations of Clever at al. (1985) and the experimental results of Gushchina et al. (1989). The agreement with the values of Clever et al. at low temperatures is good with greater deviations at high temperatures. The differences between Henry's constants and distribution coefficients calculated from Gushchina's et al. (1989) data are substantial because their solubility values are so much higher than found in this study.

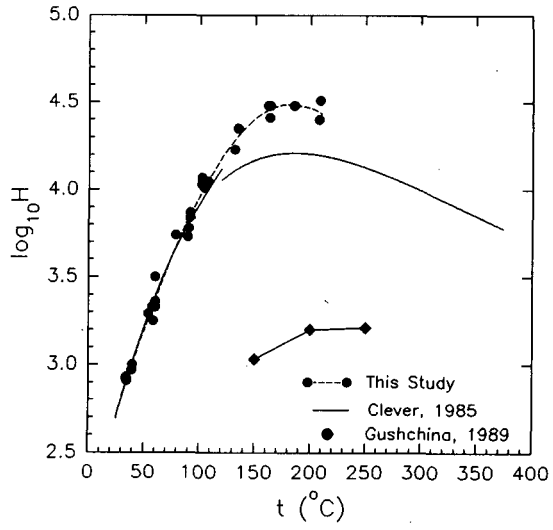

Figure 3. Temperature dependence of Henry's constant, H (bar) for dissolved elemental mercury.

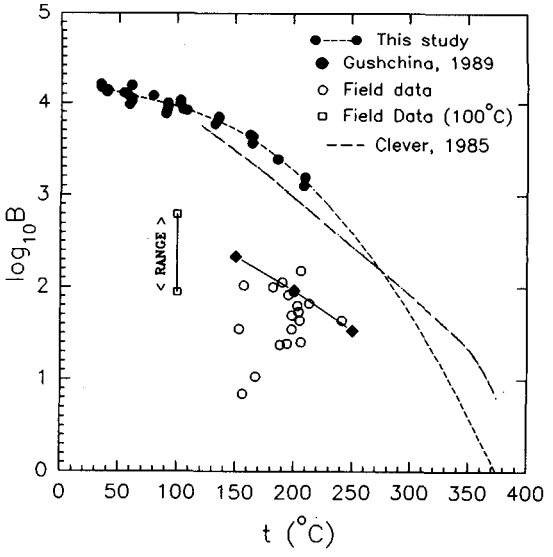

Figure 4. Experimental and field data for the temperature dependence of the distribution coefficient (B) of elemental mercury between aqueous vapour and liquid phases.

DISCUSSION

Experimental Solubility Values

Elemental mercury solubility values at temperatures above 100°C derived in this study are lower and the distribution coefficients higher than had been determined in previous experimental work. The attainment of equilibrium is critical for reliable solubility measurements. Glew and Hames (1971) showed that equilibrium at temperatures between 4 and 72°C was reached in less than 1 day under continuously stirred conditions while in the experiments of Gushchina et al. (1989) equilibrium at 150 and 250°C was attained in 8 and 2 hours respectively. Since the high temperature data of Gushchina et al (1989) and the mean literature value at 25°C was linear (log solubility vs. 1/T) they assumed their values were correct and suggested that equilibrium was not attained in all the other studies. This explanation seems unlikely given the equilibration times used in this study were between 2 and 31 days.

In this study hydrazine was used to ensure the mercury was not oxidized. Glew and Hames (1971) found that solubility was not affected by reducing agent (sodium

sulphite, hydrazine hydrate or sodium borohydride) concentrations between 0.001 and 0.02 mol kg^{-1}. At the higher temperatures association or complexing that might have occurred between the zerovalent elemental mercury and hydrazine or its decomposition products is likely to be negligible (Cobble, 1987) and obviously did not result in elevated total mercury solubilities. Sorokin (1973) took precautions to exclude oxygen and relied on the autoclave titanium to maintain reducing conditions relative to mercury and observed no oxidized mercury products. In the spectrophotometric method used by Gushchina et al. (1989) oxidized mercury would not have contributed to the Hg^0 absorption spectrum. However in their technique dissolved $HgCl_2$ was heated to 150°C and above to provide a known dissolved Hg^0 concentration. Oxidation may have affected the calibration which would have resulted in apparently higher Hg^0 solubility values. If this were the case they should not have obtained a consistent set of calibration data. According to the results of this study the lowest $HgCl_2$ concentration used would have resulted in oversaturation with respect to Hg^0 at 200 and 150°C. Gushchina et al. did not discuss the possibility of mercury oxidation by air affecting their results.

Comparison of Calculated Distribution Coefficients With Field Data

The major purpose of the study was to derive reliable mercury vapour/liquid distribution coefficients which can be used to calculate the steam and water mercury concentrations during boiling of geothermal fluid. The experimental data was compared with field data collected prior to the commissioning of the Ohaaki geothermal power plant (Timperley and Mroczek, 1989). In their study a portable Webre cyclone separator was used to collect steam and water samples of two phase fluid from a number of wells on the west bank of the Ohaaki geothermal field. An atmospheric (weirbox) water sample was collected at the same time as the samples at higher pressure. They found wide variations in mercury concentration between the wells, ranging from 16 to 181 ppb in the steam, 0.24 to 2.3 in high pressure separated water and 0.033 to 0.33 ppb in the weirbox water samples. High concentration in the Webre separated water samples were not correlated with high steam mercury concentrations, e.g. two samples separated at low pressure had 16 ppb steam concentrations and water concentrations of 2.3 and 1.5 ppb respectively. The results were not considered completely reliable. Possible reasons for the unreliability included imperfect separation in the Webre separator, slow kinetics for steam/water distribution in relation to fluid flow, the presence of non volatile mercury-sulphur species or oxidation of mercury during separation and sampling. However the data did not allow them to distinguish between these four effects. The mercury vapour/liquid distribution coefficients of these samples are plotted in Figure 4. The coefficients at atmospheric pressure were derived from the total discharge concentrations, which were calculated from mercury concentrations in steam and water from the Webre separated samples, and weirbox water mercury concentrations. The data shows wide scatter and the coefficients are significantly lower than the coefficients found in this study. The data is closest to the coefficients calculated from the solubility data of Gushchina et al. (1989) but in view of the previous discussion the agreement is considered to be fortuitous rather than an indication of the reliability of their results. If the experimentally derived ratios are to be of any use it is necessary to assess which of the reasons suggested by Timperley and Mroczek (1989) can best account for the discrepancy between the field and experimentally derived ratios.

Excluding two values which had significantly lower distribution coefficients the rest of the 21 Webre separated water samples were on average 48 times more concentrated than would have been expected from the experimentally derived coefficients. Imperfect steam/water separation in the Webre is an unlikely reason as the samples would have needed to be diluted by steam (carrying mercury with it) by an average of 2%. This level of dilution would require steam to water volume ratios of about 7 at 150 °C and 2 at 200°C. Separations better than 0.1% are possible with a mini Webre separator operated in the appropriate manner (Ellis and Mahon, 1977).

The presence of mercury species other than Hg^0 or oxidation of Hg^0 during sampling could also explain the lower distribution coefficients. Comparison of total steam mercury concentrations with on-line measurements using a mercury Zeeman spectrophotometer strongly supported the assumption that the steam phase species was elemental (Christenson and Persson, 1992). The on-line measurements taken over 1 hour varied between 21 to 23 ($\pm$1) ppb compared to 22 ppb for a total mercury steam sample collected during this period.

The Webre separated water phase total mercury concentrations were always higher than corresponding weirbox samples. This suggested that the elevated Webre separated water mercury concentrations were not due to insoluble mercury sulphide as then the concentration would have been expected to increase on further flashing to atmospheric pressure. It is possible that aqueous mercury-sulphur species which are stable at the higher pressure but destabilize on flashing to atmospheric pressure could account for the nonvolatile fraction. It is not intended to present the results of chemical modelling here, but one preliminary calculation using the program SOLVEQ (Spycher and Reed, 1989) on an atmospheric BR9 water sample (typically pH 7.9 at 100°C, Hg(total) 0.033 ppb, H_2S(total) 2 ppm, ionic strength = 0.05) showed the water to be undersaturated (log Q/K = -3.3) with respect to cinnabar and except for Hg^0 all other mercury species were insignificant. For

this fluid at 100°C the equilibrium concentration of elemental mercury should have been less than 0.005 ppb.

Even if the formation of insoluble mercury sulphide was thermodynamically favoured the kinetics of the process are likely to be much slower than the time taken for separation and sample collection. In the Ohaaki power station only about 2 to 11% of the total incoming elemental mercury appears to be oxidized in the direct contact condenser and direct contact cooling tower (aerated condensate to steam ratio about 30:1). The amount of oxidized mercury is not constant and appears to be directly dependant on the colloidal sulphur burden in the circulating fluid (Timperley and Mroczek, 1989). The power station results suggest that the amount of mercury oxidation by sulphide may be much smaller than predicted thermodynamically because of slow kinetics compared to the rate of fluid flow through the system. In the field sampling situation the samples are collected quickly, directly into preservative and unlike the power station circuit water there is no sulphur due to the reducing conditions.

The reason for discrepancies between the experimentally derived distribution coefficients and the field work cannot be answered without further work but at this time the most favoured explanation is that there is a kinetic limitation on the mercury steam/water distribution.

CONCLUSIONS

1. The temperature dependence of the solubility of elemental mercury in water is linear within experimental errors between 30 and 210°C.

2. The values above 150°C are lower than found in previous studies but equilibration times were long and a reducing agent was used to limit oxidation of mercury.

3. The derived steam/water distribution coefficients did not compare well with concentration ratios calculated from Webre steam and water separated samples collected at Ohaaki Geothermal field. The exact cause for this discrepancy has not been determined although a kinetic limitation on the steam/water distribution during separation appears to be the most likely answer.

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