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BEHAVIOUR OF SULPHUR HEXAFLUORIDE IN WATER ABOVE 210 ^{O}C - IMPLICATIONS FOR ITS USE AS A GEOTHERMAL TRACER

E.K. MROCZEK **AND** R.B. GLOVER

Wairakei **Research Centre, IGNS, Taupo, NZ**

SUMMARY - The solubility sulphur hexafluoride (SF_6) has been recently measured in our laboratory between 75 °C and 230 "C. Increasing the temperatures above about 210 "C resulted in an unexpectedly rapid decrease in SF_6 gas partial pressure. Above this temperature departure from Henry's law was also observed. The decrease in SF_6 partial pressure and decrease in dissolved SF_6 suggests that depletion of SF_6 from the vapour and liquid water was occurring, perhaps to form a dense immiscible SF,-water phase. This also explains the anomalous behaviour of SF_6 as reported in recent tracer tests in high temperature geothermal aquifers.

INTRODUCTION

The use of SF_6 as a conservative groundwater and geothermal tracer for delineating hydrogeologic parameters has been well documented (Glover and Kim, 1993; Wilson and Mackay, 1993; Adams, 1995; Bixley et al., 1995; Upstill-Goddard and Wilkins, 1995). SF_6 is an inert, sparingly soluble and nontoxic gas, resistant to chemical and thermal degradation over a wide range of conditions. In addition the background concentrations of SF_6 are essentially zero and it is easily analysed to very low detection limits (3×10^{-17} moles) by gas chromatography using an electron capture detector (ECD). SF_6 is also inexpensive and requires no special handling precautions. This unique combination of properties confers many advantages to SF_6 over more conventional tracers such as radioactive ^{133}Xe (Wilson and Mackay, 1993; Upstill-Goddard and Wilkins, 1995).

In high temperature geothermal fields however, SF_6 tracer tests have given anomalous results. For example, Glover and Kim (1993) noted that SF_6 acted as liquid tracer at depth with similar dilutions as iodine and rhodamine but lower dilution than xenon. They found this difficult to explain as xenon is considerably less volatile than SF_6.

In recent simultaneous tracer tests in the liquid phase at Wairakei the breakthrough time for all the tracers was similar although the normalized response curve for SF_6 showed a sharper peak and considerably decreased tailing (Bixley et al., 1995). This could be explained either by removal of SF_6 in the aquifer or by higher absorption and subsequent release of all the other tracers resulting in an increase in their residence time. In contrast, injection trials of SF_6 - sodium fluorescein (Nafl) into low temperature (<40 "C) aquifers showed substantial evidence of increased SF_6 tailing with respect to Nafl and similar effects have been observed with other tracer pairs (e.g. noble gas - Nafl) in comparable experiments (Upstill-Goddard and Wilkins, 1995). The SF_6 tailing was explained by selective diffusion into stagnant or near stagnant zones of fracture fluid or the bulk rock matrix. The enhanced SF_6 residence times in the low temperature test is opposite to that observed at Wairakei, suggesting that removal of SF_6 is a plausible explanation for the decreased tailing at the higher temperatures.

Adams (1995) noted that dilution of SF_6 seems to be intrinsically higher in the liquid phase and suggested this could be due to its higher density or due to enrichment of SF_6 in steam during boiling in the aquifer. Glover and Kim (1993) also explained the apparent dilution of the liquid phase concentrations by aquifer boiling.

The lack of measured Henry's law constants for SF_6 above 50 "C made it difficult to interpret the results of tracer injection tests into high enthalpy single and two phase geothermal aquifers. The use of SF_6 in new applications, such as determining the conditions of injectate boiling, was based on data extrapolated from temperatures less than 50 °C (Adams, 1995).

SF_6 SOLUBILITY

The solubility of SF_6 has been measured between 2.5 °C and 50 "C by Ashton et al. (1968) and between 5 "C and 40 °C by Cosgrove and Walkley (1981) and recently to 230 °C (Mroczek, 1996). The experimental methods and thermodynamic analysis used to derive Henry's constants (k_H) and the distribution coefficient (B) of SF_6 between the liquid and vapour phases have been presented elsewhere (Mroczek, 1996).

Within the experimental errors, estimated to be 10% at 75 °C and 20% above 200 °C, $\ln k_H$ and $\ln B$ are expressed by equations 1 and 2. The smoothed results are listed in Table 1. The form of equation 1 has been shown by Harvey (1996) to successfully predict the high-temperature Henry's constants for a number of solutes as the solvent's critical temperature is

Table 1 : Smoothed Henry's law constants (k_H) and vapour/liquid distribution coefficients (B).

t/°C	$\ln(P_s/\mathrm{MPa})$	$\ln(k_H/\mathrm{MPa})$	$\ln B$
25	-5.754	10.045	15.738
50	-4.394	10.458	14.836
75	-3.255	10.648	13.934
100	-2.289	10.679	13.032
125	-1.460	10.595	12.129
150	-.742	10.430	11.227
175	-.114	10.206	10.325
200	.441	9.941	9.423
225	.936	9.647	8.520
230	1.029	9.586	8.340
250 §	1.380	9.332	7.618
300 §	2.150	8.659	5.814

§ extrapolated values

$$\ln k_H = \ln P_s - 14.8637/T^* + 2.1337(1-T^*)^{0.355}/T^* + 18.82(T^*)^{-0.41}\exp(1-T^*) \quad (1)$$

$$\ln B = 26.4987 - 0.03609T \quad (2)$$

$$T = t + 273.15; \quad T^* = T/647.096 \quad (3)$$

where t is in degrees Celsius

approached. The solvent vapour pressure P_s for water was derived using the equation of Wagner and Pruss (1993), using a value of 647.096 K for the critical temperature.

The experimental and smoothed Henry's constant results are presented in Figure 1. For comparison, data for xenon, commonly used as a radioactive tracer, and nitrogen, one of the less soluble geothermal gases (Harvey, 1996), are also included in Figure 1. At 100 "C, SF_6 is approximately 4 and 14 times less soluble than xenon and nitrogen respectively, and at 200 °C, 3 and 7 times less soluble respectively.

The linear relationship between ln$B$ and temperature is shown in Figure 2. Adams (1995) derived from low temperature Henry's constant data, an equation for the SF_6 distribution coefficients at elevated temperatures. There is good agreement between the present results and his extrapolated values which are also shown in Figure 2.

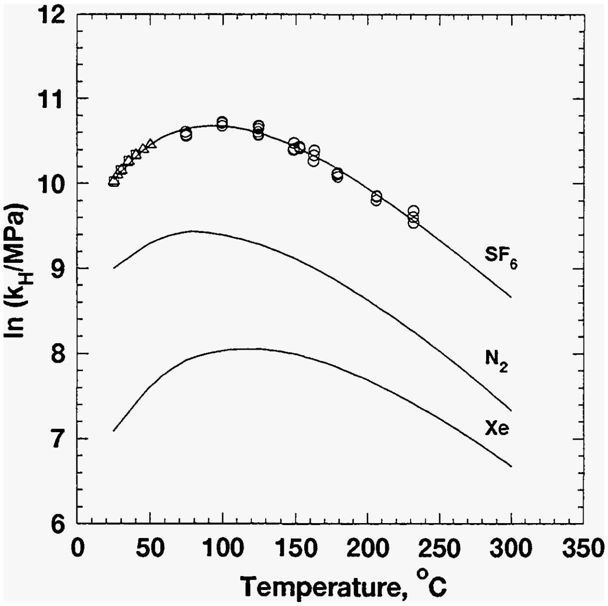

Figure 1 : Henry's law constants: —○— this work; A Ashton et al. (1968); ☐ Cosgrove and Walkley (1981); Xe and N_2 correlations from Harvey (1996).

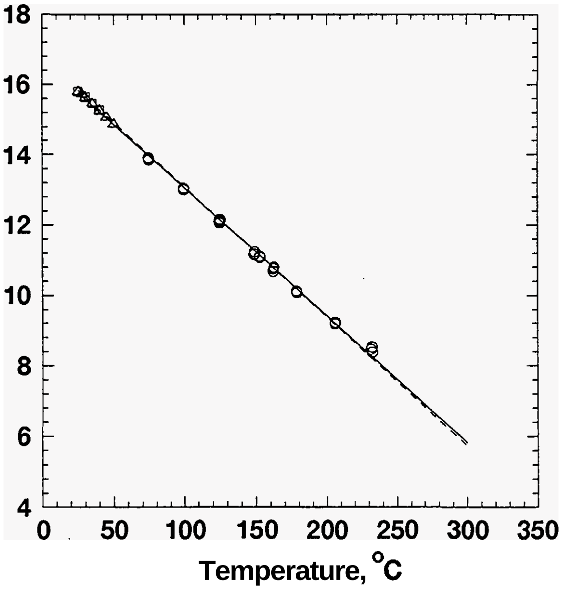

Figure 2 : Distribution coefficients: —○— this work; A Ashton et al. (1968); ☐ Cosgrove and Walkley (1981); ---- Adams (1995).

BEHAVIOUR AT HIGH TEMPERATURES

Increasing the mass of SF_6 in order to increase the precision of the pressure measurements above 200 "C failed because of an unusually abrupt drop in gas partial pressure. Increasing the mass also decreased the temperature at which there was an obvious departure from Henry's law. The readings were stable and reproducible when approached from a lower or higher temperature. This suggested that the deviation was not due to error in the experimental method.

The decrease in partial pressure was initially thought to be due to a leak in the autoclave plumbing but the pressures were reversible on decreasing the temperature. The effect is illustrated in Figure 3 which shows the change in $P(SF_6)$ on increasing the temperature to 267 "C. The autoclave, which was not sampled in this run, was filled with 60 cm^3 of water and 0.5 MPa of gas at room temperature. The mass of gas in the vessel was constant while the head space volume decreased with increased temperature due to the expansion of water in the vessel. The head space volume at 267 °C was approximately 46 cm^3, which included the volume of the tube fittings at the top of the vessel. At about 200 °C to 210 "C there was a sharp drop in partial pressure (Figure 3, Run 1). Eventually the partial pressure stopped decreasing so that between 230 °C and 267 °C the change was less than the uncertainties in the pressure measurement. With a smaller head space in the vessel (Figure 3, Run 2) the pressure appeared to stabilize at a higher final partial pressure of gas. The partial pressure curve for nitrogen matched the trend for SF_6 up to 200 °C but thereafter showed a much more gradual decline without any abrupt change in pressure. The change in the gas partial pressures for both gases should have followed a similar trend except that the nitrogen partial pressure was expected to decline at a faster rate due to the higher solubility of this gas.

The observed decrease in SF_6 partial pressure as well as a decrease in the solubility suggests that a dense immiscible SF_6 or SF_6/H_2O binary phase is forming and removing gas from the vapour and liquid water. The critical temperature of pure SF_6 is 45.6 °C (Cole and Palmer, 1990), well below the temperatures used in these experiments, so condensation of the liquid gas cannot account for the observed effect.

An unrecognized experimental artifact may still account for this unusual behaviour so further investigations into the PVT properties of SF_6/water mixtures at elevated temperatures and pressures are required to confirm these results.

Implication for Use as a Geothermal Tracer

The extremely low solubility and high volatility of SF_6 between 75 °C and 230 °C has been confirmed in these experiments but the data *per se* does not account for the anomalous behaviour of SF_6 reported in previous tracer tests. The data can be used to model the transport and partitioning of SF_6 during boiling in two phase geothermal aquifers. The results also confirmed the validity of the correlation derived by Adams (1995). His predicted distribution coefficients are well within the error of the experimentally derived values (Figure 2).

The deviation from Henry's law and the apparently unusual behaviour of SF_6/water mixtures could not have been predicted by extrapolation of data from lower temperatures. The formation of a denser SF_6 phase explains why the more volatile SF_6 appeared to behave as a better liquid tracer than xenon in Wairakei field tests (Glover and Kim, 1993) and also offers an alternative explanation, to boiling and steam enrichment, for the apparent removal of SF_6 from the liquid water phase (Glover and Kim, 1993; Adams, 1995; Bixley et al., 1995). It may also explain why in a steam zone injection and monitoring experiment (Glover and Kim, 1993) significantly lower returns of SF_6 (34.9%) were found compared with ^{133}Xe (82%) when the higher volatility of SF_6 would indicate the reverse should occur.

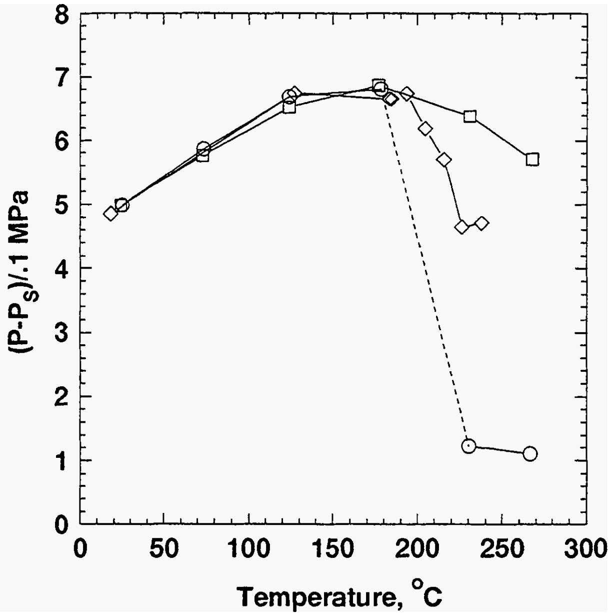

Figure 3 : Temperature dependence of partial pressure of SF_6 and N,. Run 1: 46 cm^3 head space at 267 °C (○ SF_6, □ N_2). Run 2: 38 cm^3 head space at 240 °C (◇ SF_6).

The results suggest that a steam phase formed at temperatures above about 210 °C and then separated from the liquid phase should be depleted in SF_6 however this effect could easily be masked by subsequent mixing and flashing. The removal most likely occurs soon after injection before the concentration is reduced by dispersion in the aquifer.

The formation of a dense phase at temperatures above 210 °C may confound the interpretation of the tracer results. Overall the properties of SF_6 still make it a very useful tracer, particulary in conjunction with other liquid and gas tracers, however conclusions based on SF_6 normalized response curves should be treated with caution until the properties of SF_6/water mixtures are further evaluated.

CONCLUSIONS

1. The solubility of SF_6 has been measured between 75 °C and 230 °C. Semiempirical equations, describing the temperature dependence of Henry's law constant and the vapour/liquid distribution coefficients have been derived between 25 °C and 230 °C. The form of the Henry's law equation is suitable for extrapolating values to temperatures approaching the critical point of water.

2. Above 210 °C deviation from Henry's law can occur, suggesting depletion of gas in the water vapour and liquid water to form a dense SF_6 phase. It is possible the deviation is an experimental artifact. However the formation of a dense phase can explain the anomalous behaviour of SF_6 reported in injection trials of this gas into high temperature geothermal fields. As a consequence SF_6 tracer results at these elevated temperatures need to be interpreted with caution.

3. The PVT properties of SF_6/water mixtures need further investigation at temperatures above 200 "C.

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