PROCEEDINGS, Twenty-Fifth Workshop on Geothermal Reservoir Engineering
Stanford University, Stanford, California, January 24-26, 2000
SGP-TR-165

THERMAL STABILITY OF THE VAPOR-PHASE TRACER R-134A

Michael C. Adams and Phaedra M. Kilborn

E&GI
423 Wakara Way
Salt Lake City UT 84108 U.S.A
e-mail: madams@egi.utah.edu

ABSTRACT

The vapor-phase tracer R-134a has been used in several tracer tests in vapor-dominated and two-phase geothermal systems. This paper describes laboratory studies designed to produce kinetic parameters for the decay of R-134a in the system water-steam-nitrogen-tracer are described. The kinetic parameters calculated from the experimental data were used to extrapolate to conditions in The Geysers steam reservoir. The results indicate that R-134a is sufficiently stable to be used in tracer tests conducted in the normal Geysers reservoir, but that a correction for thermal decay should be applied if R-134a is used in the high-temperature reservoir.

INTRODUCTION

Vapor-phase tracers are useful in nearly all types of geothermal systems. They have been used in liquid-dominated (Upstill-Goddard and Wilkins, 1995), two-phase (Bixley et al., 1995; Moore et al., 2000), and vapor-dominated fields (Adams et al., 1991a; Beall et al., 1994; Beall et al., 1998). Vapor-phase tracers are of particular and immediate importance at The Geysers because the large quantities of injected water are being increased. Artificial (Adams et al., 1991a; Adams et al., 1999; Beall et al., 1994; Beall et al., 1998; Gulati et al., 1978; Voge et al., 1994) and natural (Beall, 1993; Beall et al., 1989) tracers have been used at The Geysers to identify and track the flow of injected water and to evaluate the recovery of injectate (Goyal, 1999). However, the natural tracers have become ineffective as the surface facilities were adapted to conserve steam for reinjection, and the most successful artificial tracers, chlorofluorocarbons, were taken off the market because of their deleterious effect on ozone concentrations in the upper atmosphere (UNEP, 1993). R-134a and R-23, both hydrofluorocarbons, were proposed in 1997 as substitute geothermal tracers for the chlorofluorocarbons (Adams, 1997). Several successful field tests have now been performed using R-134a and R-23 (Adams, 1999; Beall et al., 1998). In this paper, we report the results of laboratory tests undertaken to evaluate the thermal stability of R-134a and present some of its physical and thermodynamic properties. A similar report will be published on R-23 at a later date.

PROPERTIES OF R-134A

R-134a is a replacement for some of the chlorofluorocarbons previously used in refrigeration, air conditioning, foam blowing, pharmaceutical inhalers, and fire suppressants. Like the chlorofluorocarbons, many of the hydrofluorocarbons are inflammable, non-toxic, and relatively inert. The toxicity of hydrofluorocarbons is generally even lower than that of corresponding brominated and chlorinated hydrocarbons because of the higher stability of the carbon-fluorine bond. R-134a has a very low acute and sub-chronic inhalation toxicity, has no chronic toxicity, and is neither a developmental toxicant nor genotoxic (Booth and Bixby, 1932). Hydrofluorocarbons are, however, somewhat less stable at high temperatures than the chlorofluorocarbons. They are also less detectable using an electron capture detector, which was the preferred method for the chlorofluorocarbon tracers. However, an analytical method has been developed by Thermochem, Inc., which yields detection limits on the order of 10 to 100 parts per trillion (Adams et al., 1999). This method uses an enrichment procedure coupled with gas chromatography. A megabore porous polymer capillary column is used to separate the tracers from each other and from potentially interfering compounds. A modified Halogen-Specific Detector is used for detection.

Hydrofluorocarbons do not contribute to ozone depletion in the atmosphere because they do not contain chlorine or bromine atoms. Their vapor pressures are similar to their chlorofluorocarbon analogues, but they are considerably more soluble. Several properties of R-134a and R–23, another potential hydrofluorocarbon tracer (Adams et al., 1991b; Yagi et al., 1997), are listed in Table 1. Some data for the chlorofluorocarbon R-13 are also listed for comparison. A more comprehensive list of hydrofluorocarbons and their properties can be found in Adams et al. (1991b).

Table 1. Properties and uses of R-134a and R-23. A chlorofluorocarbon, R-13, is shown for comparison. The properties were taken from McLinden et al. (1998), exposure limits from the respective MSDS's, and ozone depletion potentials from Albritton et al. (1994) and UNEP (1993).

	R-134a	R-23	R-13
Formula	CF_3CH_2F	CHF_3	$CClF_3$
CAS Number	811-97-2	75-46-7	75-72-9
CAS Name	1,1,1,2-Tetrafluoroethane	Trifluoromethane	Chlorotrifluoromethane
General Uses	Refrigerant, Foaming Agent	Refrigerant	Low-temperature Refrigerant
Chronic Exposure Limits	1000 ppmv	1000 ppmv	1000 ppmv
Boiling Point (9.83 kPa)	-26.1^{o}C	-82.1^{o}C	-81.3 K
Vapor Pressure (20^{o}C)	571.5 kPa	4201.9 kPa	3182.0 kPa
Solubility in Water (25^{o}C)	0.15 % by wt.	0.1 % by wt.	0.009% by wt.
Critical Temperature	374.25 K	299.05 K	302.35 K
Critical Pressure	4059 kPa	4836 kPa	3915 kPa
Critical Volume	1.95 L/kg	1.90 L/kg	1.74 L/Kg
Critical Density	512 kg/m^3	525 kg/m^3	576 kg/m^3
Ozone Depletion Potential	<0.0005	<.0004	0.1

The liquid-steam distribution coefficients of most hydrofluorocarbons have not been measured at temperatures above 100^{o}C. For the purposes of this study the low-temperature solubility data were extrapolated to higher temperatures by transforming the Henry's Law constants (Kh) to volatility ratios (B), which represent the ratio of the molal concentration in the gas to that in the liquid. It has been shown empirically that log(B) is an approximately linear function of temperature (Drummond, 1981). The compressibility factors required for the transformation of Kh to B were calculated from the critical constants compiled in Adams et al. (1991b) using the three-parameter corresponding states correlation of Lee and Kesler (1975). The solubility functions obtained in this manner are listed in Table 2 and are calculated using the relationship:

$$Log(B) = aT + b \quad (1)$$

where B is the gas to water ratio in steam divided by the gas to water ration in water, T is the temperature in degrees Celsius, and a and b are constants.

Table 2. Coefficients used to calculate the liquid-steam distribution of the tracers. The data used to calculate the coefficients for R-13 and R-23 were taken from Wilhelm et al, (1977), data for 134a were obtained from the manufacturer.

Tracer	a	b
R-134a	-0.01145	5.293
R-23	-0.00835	5.324
R-13	-0.1507	6.641

EXPERIMENTAL METHOD

R-134a was obtained as a 55 ppm by weight mixture with nitrogen from the Matheson Gas Company. Thirty milliliter quartz ampules were used to test the gas for thermal stability in a one-liter, stationary Autoclave Engineers pressurized autoclave. The ampules were first filled with 5 mls of distilled water. The purpose of the water was to fix the internal pressure of the ampule during the test, and to provide water as a reactant, reproducing in part the situation encountered by a tracer in a vapor-dominated reservoir. Air was then purged from the water and the ampule by inserting a small-diameter tube into the water at the bottom of the ampule and bubbling argon through it. The air was purged because oxygen is not present as its reactive diatomic form in geothermal waters. The ampule was filled with the 55 ppmw mixture of R-134a in nitrogen through the same tube. The tube was withdrawn to a position near the top of the ampule neck while an oxy-acetylene flame was used to seal the neck. Four ampules were prepared for each experimental run. Three were heated in the autoclave and one was stored in a refrigerator for use as an experimental control during analysis.

Analysis of the R-134a was carried out by transferring the contents of the ampule to a vacuum line. The line was connected to the gas chromatograph via an automated six-way valve, which transferred 0.25 mls of sample to the chromatography column for each analysis.

The peak area of each sample was referenced to the control rather than a standard to avoid any bias that might occur when the vial is filled or purged. Standards were also run by filling the vacuum line from the gas source at a similar pressure in order to track variations in precision due to the analytic setup and not the vial-filling procedure.

The experimental runs were conducted at three temperatures, 270°, 290°, and 310°C, and for at least three times at each temperature (Table 3). The temperatures chosen were a reflection of the decay rate, as our analytic methods work best where decay is between 20 and 90%. Several of the runs were repeated after six months in order to check for analytical drift and to establish the precision of the overall method.

Table 3. Experimental data

Temp. (°C)	Time (days)	Fraction Remaining	Relative St. Dev.
270	7	0.90	0.017
270	7	0.92	0.009
270	7	0.91	0.009
270	11	0.86	0.013
270	11	0.80	0.010
270	11	0.88	0.017
270	14	0.72	0.019
270	14	0.78	0.015
270	14	0.75	0.010
270	14	0.81	0.016
270	14	0.80	0.021
270	14	0.80	0.020
270	19	0.73	0.002
270	19	0.78	0.022
270	19	0.77	0.010
290	7	0.74	0.078
290	7	0.74	0.013
290	11	0.57	0.015
290	11	0.61	0.072
290	11	0.63	0.023
290	11	0.65	0.060
290	11	0.63	0.047
290	11	0.60	0.030
290	14	0.53	0.051
290	14	0.61	0.034
290	14	0.61	0.013
290	14	0.50	0.028
290	14	0.54	0.020
290	14	0.55	0.036
310	3	0.73	0.053
310	3	0.73	0.029
310	3	0.73	0.005
310	6	0.56	0.050
310	6	0.45	0.096
310	6	0.52	0.030
310	9	0.28	0.037
310	9	0.32	0.048
310	9	0.28	0.091

DISCUSSION

The results indicate that the decay of R-134a in pure water follows a pseudo-first order rate law, given by the relationship:

$$\frac{C}{C^0} = e^{-kt} \qquad (2)$$

where C is the tracer concentration after heating, C^0 is the initial concentration, k is the rate constant, and t is time. The fit of the data to equation 1 for each temperature is shown in Figure 1.

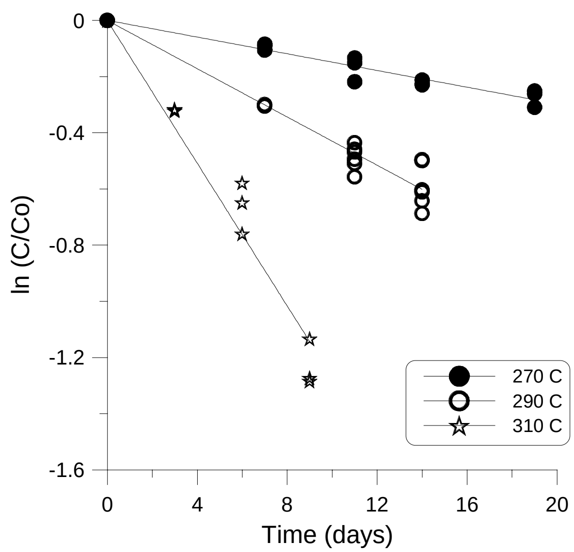

Figure 1. Experimental data for the decay of R-134a with time in pure water. C/C^o is the fraction remaining after decay.

The temperature dependence of the decay rate is given by the Ahrrenius equation:

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A_0 \qquad (3)$$

where k is the rate constant, E_a is the activation energy, R is the Universal Gas Constant, T is temperature is degrees Kelvin, and A_0 is the collision frequency factor. The fit of the ln k values to the inverse of temperature is shown in Figure 2.

The kinetic parameters were derived from the raw data using linear least squares regression. These constants and the fit statistics are listed in Table 4.

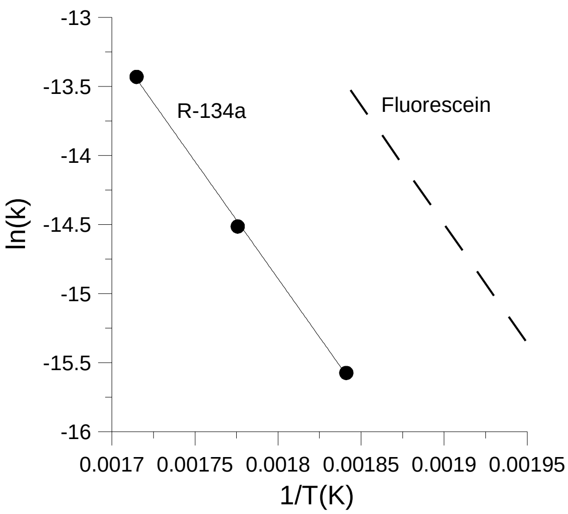

Figure 2. Ahrrenius plot of the variation of the decay rate with inverse temperature. The slope of the line indicates the activation energy of the reaction. Fluorescein data from Adams and Davis (1991) are shown for comparison

Table 4. Summary of kinetic parameters derived from the data in Table 3 .

270°C: $k = 1.72 \times 10^{-7}\ s^{-1}$
Coefficient of Determination, $r^2 = 0.92$
13 data points

290°C: $k = 4.97 \times 10^{-7}\ s^{-1}$
Coefficient of Determination, $r^2 = 0.90$
15 data points

310°C: $k = 1.47 \times 10^{-6} s^{-1}$
Coefficient of Determination, $r^2 = 0.90$
15 data points

E_a = 140,916 J/mol
ln (A) = 15.65 s^{-1}
Coefficient of Determination, $r^2 = 0.999$
3 data points

The constants in Table 4 can be combined into the simplified expression:

$$\ln(k) = 27.02 - \frac{16{,}969}{\left(T(c) + 273.15\right)} \quad (4)$$

where temperature is in degrees Celsius and **k is in days^{-1}**. The rate can then be used with equation 2 to calculate the amount of decay expected at a given temperature. A plot such as Figure 3 can also be used to estimate the amount of decay during a tracer test at a given temperature. For example, a tracer test conducted in the normal reservoir at The Geysers (~240°C) lasting 50 days at a maximum temperature would result in approximately 12% decay of R-134a.

The same test conducted in the high-temperature reservoir (>300°C) would result in 90% decay. However, R-134a may still be useful at high temperatures because of its excellent detection limit.

The indications from our initial tests of R-23 are that it is as stable or more stable than R-134a. Consequently, the diagram in Figure 3 could be used for R-23 until better data are available.

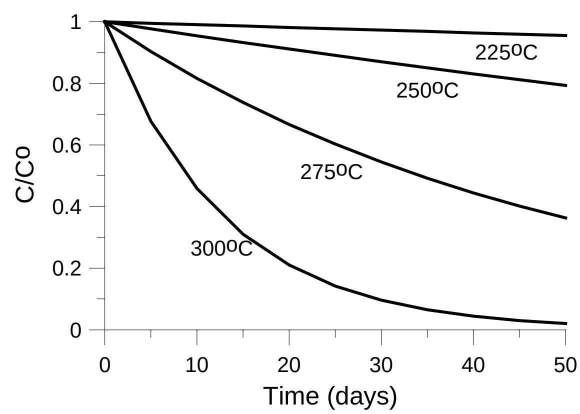

Figure 3. Time-decay plot for various temperatures. The plot was made using the kinetic parameters listed in Table 4.

SUMMARY

Kinetic parameters for the decay of the vapor-phase tracer R-134a in the system water-steam-nitrogen-tracer have been calculated from experimental data. The results indicate that R134a is sufficiently stable to be used in tracer tests conducted at The Geysers with little loss from thermal decay.

ACKNOWLEDGEMENTS

Funding for these experiments was provided by the Department of Energy under contract No. DE-AC07-95ID13274. Such support does not constitute endorsement by the DOE of the opinions, findings, conclusions, or recommendations contained within this manuscript.

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