**AROMATIC HYDROCARBONS ASSOCIATED WITH BRINES FROM
GEOPRESSURED WELLS**

FINAL REPORT

August 1983 - December 1989

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**Prepared by
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***HYDROCARBONS ASSOCIATED WITH BRINES
FROM GEOPRESSURED WELLS***

CONTRACT: DE-AS07-83NV10338

August, 1983 to December, 1989

FINAL REPORT

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HYDROCARBONS ASSOCIATED WITH BRINES

FROM GEOPRESSURED WELLS

This report presents the work completed under U.S. D.O.E. contract DE-AS07-83NV10338 during the period August 1983 to December, 1989. A new contract which continued this work in essentially its same form was issued in early 1990. This is a final report in form only, since the research continues.

Summary of Research Goals:

To determine the concentration of the cryocondensates in fluids of the various USDOE Geopressured wells as a function of production volume. To correlate the production of these compounds with reservoir and well production characteristics. To precisely measure solubilities of cryocondensates components in water and sodium chloride solutions (brines) as a function of ionic strength and temperature and the component's distribution coefficients between these solutions and oil.

To monitor the wells for the production of aliphatic oils and relate any such production with the cryocondensate yields.

To determine various $^{12}\text{C}/^{13}\text{C}$ ratios of well produced hydrocarbons.

To develop models of the geopressured reservoirs which are consistent with the data obtained.

To measure cryocondensate concentration in various depleted oil and gas wells as they became available.

To develop a harsh environment pH probe for use in well brines at surface temperatures and pressures.

SOLUBILITY AND DISTRIBUTION COEFFICIENT MEASUREMENTS

The measurement of basic physical chemical properties of the brine components produced in the U.S.DOE geopressured wells is necessary to provide the fundamental data necessary for an understanding of the mechanisms by which constituents of petroleum migrate and are partitioned into different phases in various geologic strata. The cryocondensate materials, which we sample, are present in the geopressured brines of all the wells observed to date. These materials are a complex mixture of aromatic compounds ranging in complexity from benzene to alkyl substituted anthracenes. A review of the literature concerning the solubility and thermodynamic distribution coefficients (see for example Keeley, Hoffpauir & Meriwether, *J. of Chem and Eng Data*, 33: 87-89, 1988) reveals that while data is available for room temperature and for solutions of pure water, there is little earlier information on these compounds in saline solutions and at elevated temperatures. Our work, reported in the reference noted above (a copy of which is attached to this section), extended the basic solubility data for benzene and toluene (two of the major aromatic constituents of the geopressured brine) to higher sodium chloride concentrations. To accomplish these measurements, new techniques and new equipment were developed. Some of these were reported in articles in the open literature (copies of which are attached): "Headspace Attachment for a Varian model 3700 Gas Chromatograph", Dean F. Keeley and John R. Meriwether, *Reviews of Scientific Instruments*, 57(7), 1986, p. 1434-1435 and "Sorption of Benzene and Toluene by Poly(tetrafluoroethylene) during Headspace Analysis", D.F. Keeley, M.A. Hoffpauir and J. R. Meriwether, *Analytical Chemistry*, 58, 1986, p. 1258-1259.

The measurements were extended to C₂ substituted benzenes which are

also found as constituents in the cryocondensates. The solubilities, Henry's Law constants and distribution coefficients for ethylbenzene, 1,2-dimethylbenzene (o-xylene), 1,3-dimethylbenzene (m-xylene) and 1,4-dimethylbenzene (p-xylene). These data are also to be published in the open literature.

The techniques we have developed during the course of this work allows us to make solubility measurements with precision and to make major contributions to the basic literature. It is important to realize that reliable data on these fundamental quantities comes only with great attention to detail and an insistence on consistency and reproducibility.

Headspace attachment for a Varian model 3700 gas chromatograph

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A headspace analysis attachment for a Varian model 3700 gas chromatograph is described. The attachment differs from most commercial headspace attachments in the size sample bottle that it can accommodate. Graphical data obtained using the attachment is given.

Headspace analysis is an analytical technique in which vapor in equilibrium with a condensed phase is analyzed. The condensed phase may contain one or more components which have appreciable vapor pressures. Analysis is generally done by gas chromatography (GC).^{1,2}

Most commercial headspace attachments for gas chromatographs use relatively small sample vials.³ The maximum size is about 25 cm³, of which only about 10 to 15 cm³ is available for the condensed phase. Such a size limitation can produce measurement problems if, as was our case, headspace analysis was the method of choice to determine solubilities of volatile compounds with limited solubilities.⁴ The best solution is to have a headspace attachment that will accommodate larger sample vials. This prompted us to build our own headspace attachment for a Varian model 3700 gas chromatograph.

The features which we designed into our headspace attachment include:

(1) The ability to accommodate up to a 125-cm³ septum bottle.

(2) Use of a tempering beaker (a double-walled beaker through which water is passed) to thermostat the sample bottle.

(3) Sample pressurization separate from the headspace attachment for simplicity of design. Pressurization is done through a hypodermic needle which is attached by tubing to an inert gas line and Heise precision pressure gauge.

(4) Use of a needle holder assembly and sidehole needle, a fine metering valve to control sample flow, and the GC's Valco gas sampling valve and sample loop to inject a constant size sample (240 mm³) into the GC.

(5) A thermostatically controlled heating element inside the headspace attachment to heat the headspace attach-

FIG. 1. Schematic diagram of headspace attachment. G = gas sampling valve (shown in the load position), R = resistance heater, P = thermistor probe, F = fine metering valve, N = needle assembly, B = pancake blower, C = proportional temperature controller, S = sample loop, V = vent.

FIG. 2. Headspace attachment, perspective view. G = gas sampling valve, R = resistance heater, P = thermistor probe, F = fine metering valve, N = needle assembly, B = blower compartment, C = to proportional temperature controller, S = sample loop, V = vent, T = thermometer, A = air vent with baffle.

ment and the pneumatic compartment of the GC in order to minimize sample adsorption.

Figure 1 is a schematic diagram of the headspace attachment. The attachment was constructed on a piece of 1.14-mm stainless steel, which replaced the pneumatic compartment cover of the GC. Holes were cut in this baseplate to allow for air circulation between the attachment and the GC pneumatic chamber. A pancake blower was used for air circulation. The remainder of the attachment was fabricated from 0.64-mm stainless steel bent to form two boxes. A port was cut between the two boxes for air circulation. The fine metering valve, sampling needle, thermistor probe, thermometer, and heater were installed in the upper box and the blower in the lower. The inside of both boxes was lined with 1.27-cm Ceramfab insulation. The front of the upper box was removable to facilitate needle and/or sample loop replacement. The tubing used throughout the attachment was 1.6-mm-o.d. small bore stainless steel. The heater was a 660-W cone glocoil type. Due to their tendency to absorb organic compounds, the use of plastics in a headspace attachment must be kept to a minimum.⁵ To prevent bending of the needle, a plastic needle guide was placed on a sample bottle prior to its attachment to the headspace unit.

Figure 2 is a perspective drawing of the headspace attachment.

The headspace attachment has been used to provide the experimental data to calculate the solubilities of several aromatic compounds in aqueous sodium chloride solutions.⁶

Figure 3 is a plot of integrator response for a series of five samples containing benzene vapor at different partial pressures and is typical of the quality of the data we obtain.

FIG. 3. Integrated peak area as a function of benzene vapor partial pressure at 25.00 °C. Linear correlation coefficient = 0.999.

This work was supported by the United States Department of Energy under Contract No. DE-AS08-83NV10338.

¹H. Hachenberg and A. P. Schmidt, *Gas Chromatographic Headspace Analysis* (Wiley, New York, 1977), pp. 3-4.

²B. V. Ioffe and A. G. Vitenberg, *Head-Space Analysis and Related Methods in Gas Chromatography* (Wiley, New York, 1984), Chap. 1.

³B. V. Ioffe and A. G. Vitenberg, *Head-Space Analysis and Related Methods in Gas Chromatography* (Wiley, New York, 1984), Chap. 2.

⁴H. A. Massaldi and C. J. King, *J. Chem. Eng. Data* 18, 393 (1973).

⁵D. F. Keeley and J. R. Meriwether, *Anal. Chem.* (in press).

⁶D. F. Keeley, M. A. Hoffpauir, and J. R. Meriwether (unpublished).

DEPLETED OIL AND GAS WELLS

Through out this contract, we have had a low priority task to sample the conate waters from some depleted or near depleted commercial oil and/or gas wells.

In this task we sought to broaden our aromatic hydrocarbon database on the geopressured-geothermal resource. The only wells which were available to us were those designed for the geopressured program. The design wells: the L.R. Sweezy, the Amoco Fee, the Gladys McCall, the Pleasant Bayou and, most recently, the Hulin contain a complex mixture of aromatic hydrocarbons. These hydrocarbons are now referred to as the "cryocondensates" because they are quantitatively sampled cryogenically from the gas streams of the wells. The hydrocarbon mixture contains more than ninety different compounds ranging from the simplest - benzene - to alkyl substituted anthracenes. Some of the compounds are very rare and have probably not been synthesized in the laboratory nor are their physical chemical and physiological properties know. Little information exists concerning the extent to which these compounds occur in conate waters.

Generally the opportunity to sample commercial wells comes infrequently. Many companies consider analyses of their well systems to be proprietary information. Fortunately, we had two former graduate students working in the oil and gas industry who were able to secure the cooperation of their companies.

We sampled seven Chevron wells located in the Tuscaloosa trend near New Roads, Louisiana (we appreciate the assistance of Mr. Francis Broussard and Mr. Dave Mistretta). The wells sampled were:

C.A. Lorio # 1
C.A. Lorio # 2

Albritton # 1
Alma Plantation
Lowman Merrick
J.V. Rougeou
I.J. Major #3

All of the wells were on the order of 19,000 feet deep and were making large amounts of brine. The water was not simply condensing water but formation brine advancing as the gas cap was exhausted. We sampled the brine output from the separators at each well. The sampling procedure involved passing a slow stream of brine through a coil of stainless steel tubing immersed in an ice bath. The procedure prevented the loss of the more volatile components of the brine. The samples were sealed in glass bottles and returned to the laboratory for analysis.

In the laboratory a one liter aliquot of each brine sample was equilibrated with 25 mL of hexane to remove the organic components. A portion of the extracted sample was injected into a gas chromatograph and the resulting spectrum compared to the spectra of standards materials and with our library of U. S. DOE geopressured well spectra.

Each of the deep, Tuscaloosa wells which are located below the geopressured horizon contained an aromatic hydrocarbon spectrum quite similar to the DOE design wells.

We also sampled five producing gas wells from Tenneco's (since sold) Ship Shoal Block 198 in the Gulf of Mexico. We are grateful to Mr. Kenneth Roy for Tenneco's hospitality on their production platforms. As with the Chevron wells, the Tenneco wells were making large quantities of water and were near the end of their useful productive lifetime. The brine being produced was taken as representative of the original formation water. The sampling and analysis procedures were the same as described above.

There were no aromatic hydrocarbons detected in any of the Tenneco

wells, which ranged in depth from 6745 to 9278 feet. All of these wells were above the geopressured horizon.

We were also able to add to our data base by analyzing some archived brine samples from the U.S. DOE Wells-of- Opportunity Program. We were not sampling wells for aromatic hydrocarbons during this program. Mr. Terry Osif of IGT provided the archived samples of brine from:

- the Saldana, in south Texas,
- the Girouard, in Lafayette Parish, LA,
- the Prairie Canal, in Calcasieu Parish, LA,
- the M.C. Zellerback, in Livingston Parish, LA,
- and the G.M. Koelemay, Jefferson County, TX.

The gas chromatographs of the hexane extract from the brine from each of these geopressured wells showed an aromatic hydrocarbon spectrum like that of the design wells.

In summary, the aromatic hydrocarbon spectrum in the U.S.DOE design wells is a fingerprint for all wells we have sampled that were producing from the deep, hot regions below the local geopressured horizon. None of the shallower wells from above the horizon contained any aromatic hydrocarbons. These observations are consistent with the generally accepted theory of petroleum maturation.

Full cryogenic sampling were done on the following occasions:

Date	Well	Flow rate (bbls/day)
10-10-83	Gladys McCall	13,000
11-23-83	Sweet Lake	2,222
11-30-83	Sweet Lake	6,528
12-12-83	Gladys McCall	15,800
1-1-84	Sweet Lake	2,820
1-12-84	Gladys McCall	20,000
1-30-84	Sweet Lake	2,230
2-3-84	Gladys McCall	22,200
3-6-84	Sweet Lake	2,064
3-21-84	Gladys McCall	20,000
5-24-84	Gladys McCall	25,050
6-13-84	Gladys McCall	20,184
7-9-84	Gladys McCall	20,208
7-12-84	L.Koelernay	
8-23-84	Gladys McCall	25,000
10-12-84	Gladys McCall	19,640
11-26-84	Gladys McCall	15,710
12-28-84	Gladys McCall	15,300
1-30-85	Gladys McCall	15,600
2-18-85	Gladys McCall	15,560
3-22-85	Gladys McCall	15,560
4-29-85	Gladys McCall	15,710
6-5-85	Gladys McCall	15,690
7-16-85	Gladys McCall	25,740
8-26-85	Gladys McCall	31,070
10-5-85	Gladys McCall	29,420
11-18-85	Gladys McCall	24,520
12-22-85	Gladys McCall	25,320
1-20-86	Gladys McCall	10,540
2-12-86	Gladys McCall	30,710
3-26-86	Gladys McCall	30,940
4-30-86	Gladys McCall	28,370
6-2-86	Gladys McCall	27,670
7-14-86	Gladys McCall	27,000
9-4-86	Gladys McCall	26,125
10-21-86	Gladys McCall	25,580
3-2-87	Gladys McCall	24,170
3-2-87	Gladys McCall	24,480
4-21-87	Gladys McCall	23,800
4-27-87	Gladys McCall	19,120
5-4-87	Gladys McCall	14,060
5-11-87	Gladys McCall	8,990
5-18-87	Gladys McCall	4,540
5-28-87	Gladys McCall	9,980
6-16-87	Gladys McCall	10,000
7-16-87	Gladys McCall	9,900
8-19-87	Gladys McCall	10,000

DOE WELL SAMPLING

The U.S. D.O.E. design wells were sampled on a monthly basis for the yield of the cryocondensate hydrocarbons. During the early part of the contract this was primarily the Gladys McCall and, toward the end of this contract, the Pleasant Bayou #2. The hydrocarbons of interest are distributed, in the separator, between the gas and liquid phases, both phases are sampled to obtain a quantitative analysis. A portion of the gas stream passes (60 ft³ over about a three hour period) through a cryogenic system and removes all materials which have partial pressures that allow for their condensation at -78.5 °C: hence the term "cryocondensates" to distinguish them from "condensates", a term commonly used in the oil and gas industry. A second procedure is used to recover the cryocondensate which was not exolved from the brine with the gas. This is accomplished by slowly passing brine from the separator through a coiled tube in an ice/water bath at 0 °C. The lower temperature is used to prevent the loss of the volatile components. In the laboratory the brine is extracted with hexane and the cryocondensate content determined by gas chromatography. From this data the cryocondensate content of the original well brine is determined and the yield corrected to oil field standard conditions: 1 atm pressure and 60 °F.

We have designed and installed (June, 1989) a gas scrubbing system at the Pleasant Bayou Well to collect a daily sample of the benzene and toluene components of the cryocondensates. The device is usually simply referred to as the "scrubber". This is not a quantitatively complete sample, but should be relatively correct on a day-to-day basis.

9-23-87	Gladys McCall	9,980	
10-19-87	Gladys McCall	9,980	Gladys Shut-in
6-17-88	Pleasant Bayou	20,460	
6-30-88	Pleasant Bayou	20,200	
7-27-88	Pleasant Bayou	19,180	
8-23-88	Pleasant Bayou	19,670	
10-7-88	Pleasant Bayou	19,020	
10-28-88	Pleasant Bayou	19,460	
12-7-88	Pleasant Bayou	18,500	
1-18-89	Pleasant Bayou	18,300	
2-17-89	Pleasant Bayou	18,070	
3-31-89	Pleasant Bayou	17,840	
5-4-89	Pleasant Bayou	12,530	
6-8-89	Pleasant Bayou	18,460	
7-5-89	Pleasant Bayou	16,000	
8-15-89	Pleasant Bayou	16,520	
11-1-89	Pleasant Bayou	16,510	
12-6-89	Pleasant Bayou	15,850	

WELL SAMPLE ANALYSIS

The regular cryocondensate samples and the scrubber samples (one for each day since the last visit to the well beginning in June, 1989) referred to above are returned to the laboratory and analyzed by gas chromatography and the yield of these products determined. The monthly cryogenic result is reported in terms of the cumulative brine production. A daily quantitative result is obtained by normalizing the scrubber sample data to the monthly quantitative sample taken as described above.

Figure 1 displays the yield of cryocondensates as a function of production volume for the Gladys McCall well. One should note the steady increase in the yield over approximately the first 8 million barrels (1.27 hm^3). During this period we predicted that the well would begin to produce oil (see models below); at just over 8 million barrels, oil production began.

The Sweet Lake well was erratic and unproductive and was capped after only a short production period

Figure 2 displays the total cryocondensate yield, from the cryogenic measurements, as a function of production volume from the beginning of the current long-term test on the Pleasant Bayou Well. The daily cryocondensate yield determined from the scrubber samples up to early January of 1990 is shown in Figure 3. The filled circles indicate dates on which the daily samples were normalized to the cryosamples.

Gladys McCall Well

Figure 1

Figure 2

Figure 3

ALIPHATIC HYDROCARBON MONITORING

Both the L. R. Sweezy and the Gladys McCall wells produced a heavy aliphatic oil after a large initial brine production (~ 8 million barrels in the case of Gladys McCall). The production of this oil was monitored throughout the production of the McCall and is shown graphically in Figure 4. During the induction period, the concentration of the cryocondensates increased. These observations led to our proposal of a model of the geopressed reservoir in which brine production drew heavy hydrocarbons from the neighboring shales to the production formation. These heavy hydrocarbons were considered to be the source of additional aromatics extracted into the water phase of the reservoir. A complete review of this model can be found in our paper published in the *Journal of Energy Resources Technology* (Vol. 110 pp. 177-182, 1988), a copy of which is attached. Each month we monitored the various fluid phases from the separators at the production wells for aliphatic oils. Thus far the Pleasant Bayou well has not shown signs of aliphatic oils. The behavior of the Pleasant Bayou has differed from the earlier wells in that the cryocondensate concentration has not systematically increased as a function of cumulative brine production.

$^{12}\text{C}/^{13}\text{C}$ MEASUREMENT

The various hydrocarbons from the various well were submitted for $^{12}\text{C}/^{13}\text{C}$ analyses to provide clues for sources of these hydrocarbons. The results are given in the following article.

Gladys McCall Well

Figure 4

HARSH ENVIRONMENT pH PROBE

Background

The U. S. Department of Energy has in the past sponsored several attempts to develop a device to measure the pH in the brine stream of geothermal wells and in other harsh environments. (for example, see Taylor and Phelan, PNL-3593). As recently as January, 1988, DOE solicited, through its Small Business Innovation Research (SBIR) program, proposals for the development of a similar device. This did not result in funding.) Such a device is desirable so as to provide in-situ data for general analysis of brines (and other chemical streams) and in particular to provide data for the understanding of scaling and corrosion.

We became aware of a new device that was being marketed by the CHEMFET Corporation (Bellvue, WA) to measure pH under normal laboratory conditions and were encouraged by Mr. Ray Fortuna (DOE - Wash) to pursue this possibility.. This device was based on the ISFET - the Ion Sensitive Field Effect Transistor. Under this Task, we are studying the application of these devices under conditions corresponding to those found in typical geopressured brines. CHEM-FET, Corp has been cooperating with us in this effort by donating the ISFETs for tests.

The goal of this task is to produce and field test an operational probe on a geopressured well.

During 1989 several milestones were reached:

- 1) A low pressure test cell was designed and constructed. The temperature was maintained at constant values by immersing the cell in a controlled water bath. All of the data reported here were obtained in this test cell.
- 2) A Ag/AgCl reference electrode has been developed to operate in the NaCl brines.

- 3) As shown in Figure 5, the ISFET probe produces a linear output as a function of the pH of brine solutions. Each of the solutions was prepared as standard buffer solutions of known pH.
- 4) The long term stability of the ISFET is an important characteristic of any successful instrument for the measurement of pH in brine solutions. Figure 6 shows the output of the ISFET as a function of time in a buffer of pH = 3.96. The temperature was maintained at 25.0 C. The stability of the probe is quite obvious.
- 5) The output of ISFET was measured as a function of the temperature of the water bath. The stability of the probe over the practical range of the water bath is shown in Figure 7.
- 6) A high pressure test cell has been designed and is under construction. This heated cell will allow the tests to be conducted up to 6,000 psi and to 150 C.

Figure 5

Figure 6