PROCEEDINGS, 47th Workshop on Geothermal Reservoir Engineering
Stanford University, Stanford, California, February 7-9, 2022
SGP-TR-223

The Use of Halogenated Benzene Sulfonates as Geothermal and Unconventional-Petroleum Tracers

Peter E. Rose[1], Michael Mella[1] and Philip Walker[2]

[1]Energy & Geoscience Institute at the University of Utah

423 Wakara Way suite 300, Salt Lake City, UT 84108

[2]Sino Chemsource Ltd

Keywords: geothermal energy, shale-oil, shale-gas, unconventional petroleum, halogenated benzene sulfonates, naphthalene sulfonates, solute tracers

ABSTRACT

Two halogenated-benzene-sulfonate compounds that show promise for use as geothermal and petroleum tracers were synthesized and then tested under laboratory conditions that simulate a hydrothermal environment. A decay kinetics analysis showed that the thermal stabilities of 4-fluorobenzene sulfonate and 2,5-dichlorobenzene sulfonate are comparable to those of Amino G and fluorescein, respectively—two compounds that have proven useful for geothermal tracing applications. An adsorptivity flow experiment indicates that both compounds respond conservatively when advected through a column flow reactor containing shale drill cuttings at 160 ºC. These preliminary experiments indicate that since many more compounds in this family of tracers are conceivable, the halogenated benzene sulfonates could significantly increase the number of tracers available for use in both petroleum and geothermal reservoirs.

1. INTRODUCTION

Fluid tracing in geothermal and unconventional-petroleum settings involves the tracking of fluids through subterranean reservoirs using solute tracers. In geothermal reservoirs, this flow is typically that of brine between injection and production wells, but can also involve injection and backflow through the same well, as is typical of unconventional (shale oil and shale gas) petroleum systems. In either case, the tracer is injected into an injection well, either initially as a slug or continuously in solution. Its concentration is subsequently measured over time in fluids sampled at production wells or at other places where fluids might emerge such as hot springs. Observers can then use the measured tracer concentrations and tracer-arrival times to interpret tracer-swept, interwell flow patterns throughout the reservoir.

Solute tracers can be characterized as belonging to either of two broad categories—conservative or reactive. Conservative tracers are defined as those that interact neither with the reservoir rock nor with the solvent as they are advected through the formation; their flow is therefore indistinguishable from that of the solvent. In contrast, reactive tracers engage in some fashion with either the rock or the solvent through thermal decay, reversible adsorption or diffusion. Their flow through the formation is either retarded or their concentration diminished relative to that of a conservative tracer. In order to determine whether a candidate tracer is conservative or reactive, it must be subjected to controlled laboratory experiments in order to determine its thermal stability and/or propensity for reversible adsorption under representative reservoir conditions.

Tracers for geothermal and unconventional petroleum applications must be sufficiently thermally stable to survive their passage through the reservoir. In addition, tracers must also be very detectable, environmentally benign, nontoxic, available in bulk and affordable. One family of compounds that meets these requirements and that has been used extensively in geothermal reservoirs around the globe is the naphthalene sulfonates (Rose et al., 2001). They possess excellent detectability by High Performance Liquid Chromatography/fluorescence, since the polyaromatic backbone provides a large fluorescence cross-section. A low detection limit in turn means that lower quantities are required for fullscale applications. These compounds are nontoxic, environmentally benign (Greim et al., 1994) and available in bulk (Lueng, 2013).

The naphthalene sulfonates have been shown to exhibit excellent resistance to thermal degradation in laboratory studies under conditions that simulate the reducing environment of a geothermal field (Rose et al., 2001). These laboratory results have been confirmed in numerous field tests (Rose et al., 2001; Rose et al., 2002a; Rose et al. 2002b; Rose et al., 2003). However, in a series of laboratory experiments that exposed the naphthalene sulfonate tracers to mineral surfaces and temperatures found in some of the world's hottest (>300ºC) geothermal reservoirs, they were shown to isomerize and/or degrade—especially when exposed to very high temperatures for long residence times (Sajkowski, 2020).

Due to their successful use in hundreds of geothermal tracer tests around the world, the naphthalene sulfonates have recently served as the only reliable, thermally stable tracers for unconventional (shale-oil and shale-gas) petroleum applications, where reservoir temperatures can approach 200 ºC and conventional petroleum tracers fail (e.g., Horn River, Austin Chalk, Eagle Ford, and Permian Basin). In side-by-side tests between the naphthalene sulfonates and the halogenated benzoates in laboratory flow experiments under simulated reservoir conditions, using drill cuttings from a variety of shale reservoirs, the latter tracers were either thermally degraded or adsorbed to rock surfaces and therefore produced at only a few percent of a co-injected chloride control, whereas the naphthalene sulfonates showed no diminution in concentration relative to a chloride control (unpublished).

The halogenated benzoates were also used in conjunction with the naphthalene sulfonates in a field test in a shale-oil exploration well (unpublished). A distinct naphthalene sulfonate was injected with a distinct halogenated benzoate into each of the toe, middle and heel sets of stages—all at a common concentration of 750 parts-per-billion. In addition, a common naphthalene sulfonate (2,7-naphthalene disulfonate) was injected into all of the sets of stages, also at 750 ppb. Shown in Figure 1 are the concentrations of tracers sampled from the well during the first 115 days of flowback. The conservative tracers are shown in warm colors (red, orange, and yellow), whereas the fluorinated benzoates are shown in cool colors (blues and green). It is obvious that the fluorinated benzoates had largely disappeared—apparently due either to thermal degradation or adsorption or both. Otherwise, their concentrations would have overlain those of the naphthalene sulfonates. Since the fluorinated benzoates were assumed to behave conservatively, any interpretation of their production history is based on a false assumption, since "absence of evidence is not the same as evidence of absence".

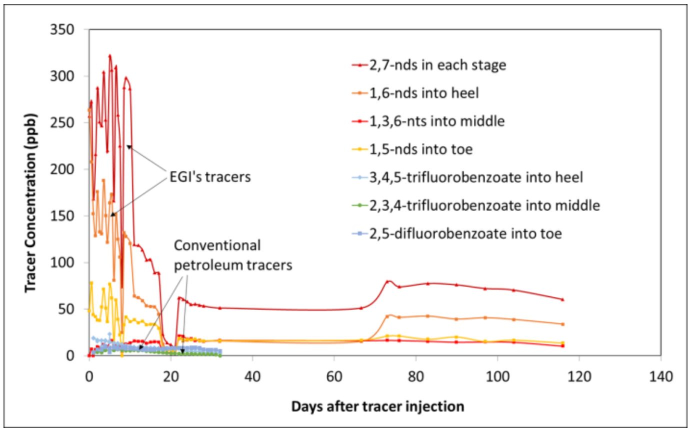

Figure 1. Concentrations of naphthalene-sulfonate and fluorinated-benzoate tracers measured in flowback samples from a shale-oil exploration well. All tracers had been injected at a concentration of 750 ppb. Given their low flowback concentrations, the halogenated benzoates had either thermally degraded or adsorbed onto reservoir rock.

In spite of the successful application of the naphthalene sulfonates as tracers in both geothermal and unconventional petroleum reservoirs, there are only eight that are available in bulk and, thus, reasonably affordable. Adams et al. (1992) attempted to address this shortage through an exhaustive study of 39 aromatic acids—primarily methylated and fluorinated benzoates—which had gained wide application in conventional, secondary-recovery petroleum applications such as waterfloods. Among the compounds tested were four benzene sulfonates: benzene sulfonate, 4-ethylbenzene sulfonate, 4-methyl benzene sulfonate, and 2,5-dimethylbenzene sulfonate. These four compounds were the most thermally stable of all the compounds tested, showing no decay after two weeks at 300 °C in simulated geothermal brine.

No halogenated benzene sulfonates were among the compounds tested in the Adams study, nor was any mention made of them as possible tracer candidates. However, since many halogenated benzoates are among the tracers that have been successfully used for decades in conventional petroleum applications, it was possible that halogenated benzene sulfonates would likewise possess all of the desirable tracer properties of the halogenated benzoates in addition to exhibiting better thermal stability. In this study, we investigated the thermal stabilities of two halogenated benzene sulfonates under conditions that simulate a geothermal reservoir.

2. CHEMICAL SYNTHESIS AND ANALYSIS

One of us (Walker) synthesized two compounds from among the many possible halogenated benzoates: 4-fluorobenzene sulfonate and 2,5-dichlorobenzene sulfonate (Figure 2.)

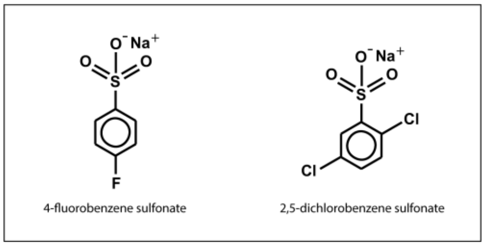

Figure 2. Structures of the two candidate tracers, 4-fluorobenzene sulfonate and 2,5-dichlorobenzene sulfonate.

The halogenated benzene sulfonates were analyzed using a Waters-2695 High Performance Liquid Chromatograph (HPLC) with absorption detection and paired-ion chromatography. We used a reverse-phase C-18 Waters XBridge column (4.6 x 50 mm and 3.5 um pore size). The mobile phase consisted of an isocratic, pH-7.5, phosphate-buffered, 5 Mmol solution of tetrabutyl ammonium phosphate (TBAP) in 70% water and 30% meOH. The absorbance detector was set at 230 nm. This HPLC method allowed for the separation of analytes both from each other and from reservoir interferences.

3. THERMAL DECOMPOSITION KINETICS

The decay kinetics of the two halogenated benzene sulfonate tracer candidates was studied using an autoclave batch reactor under conditions designed to simulate a geothermal environment. The compounds were dissolved in buffered aqueous solutions at target concentrations of 25 ppm by weight and adjusted to a room-temperature pH of 7. The buffer consisted of 0.747 gm/l of KH_2PO_4 and 0.403 gm/l of Na_2HPO_4.

Eighteen-ml aliquots of the buffered tracer solution were transferred to 30-ml quartz ampules and purged with argon in order to remove dissolved oxygen. The ampules were carefully sealed using an oxymethane flame, while still being purged with argon. For each experiment, four ampules were prepared, including one that would serve as a control.

The sealed vials were transferred to a water-filled, one-liter autoclave (Autoclave Engineers, Philadelphia, PA), which was heated to the target temperature. The time required for the autoclave to attain operational temperature was between 1.5 and 2 hours, whereas the cool-down time was about 4 hours. In all cases, the interior of the reactor was maintained within 1 °C of the target temperature for a duration of three days. The pressure inside the autoclave was the pressure of steam under saturated conditions at the target temperature. The control and was stored at 2 °C for the duration of the autoclave experiment.

The thermal decay kinetics of halogenated benzene sulfonate was modeled by the first-order differential equation:

$$-dC/dt = k \cdot C \qquad (1)$$

where C is the concentration of the halogenated benzene sulfonate and k is the first-order rate constant. Solution of this equation results in the following relationship between C and t:

$$ln\left(\frac{C}{C_0}\right) = -k \cdot t \qquad (2)$$

where C_0 is the initial concentration of the halogenated benzene sulfonate. The temperature dependence of k can be described by the Arrhenius relationship:

$$k = Ae^{(-E_a/RT)} \qquad (3)$$

where A is the pre-exponential factor, E_a is the energy of activation, R is the gas constant and T is absolute temperature. A linearization of the Arrhenius expression results in the following:

$$lnk = ln\,A - \frac{E_a}{RT} \qquad (4)$$

Figure 3 shows plots of equation 4 between 190 °C and 300 °C for the two compounds 4-fluorobenzene sulfonate and 2,5-dichlorobenzene sulfonate. The linearities of these plots indicate that the Arrhenius equation provides a reasonably good expression for the temperature dependence of the decay rate constant.

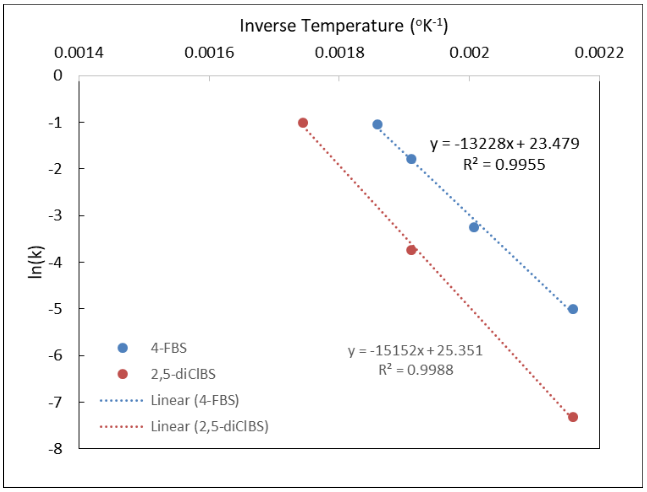

Figure 3. Arrhenius plot of ln (k) vs. inverse temperature between 190 °C and 300 °C for each of the two compounds 4-fluorobenzene sulfonate and 2,5-dichlorobenzene sulfonate. The dotted lines represent the least squares regressions for each.

Using the Arrhenius data, the half-lives of the two compounds were calculated as functions of temperature (Figure 4). For comparison, the half-lives of other geothermal tracers, including amino G and the two xanthene dyes fluorescein and rhodamine WT, are also plotted.

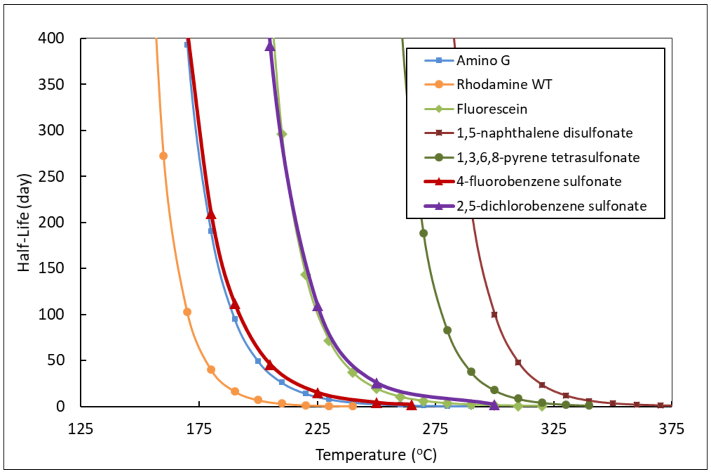

Figure 4. Plots of half-life vs. temperature based upon the Arrhenius plot shown in Figure 3. Shown for comparison are the half-lives of other tracers that have been used in geothermal reservoirs. The plot for 4-fluorobenzene sulfonate shows its stability is similar to that of Amino G, and that the stability of 2,5-dichlorobenzene sulfonate is similar to that of fluorescein. Both Amino G and fluorescein have been used successfully in several geothermal tracer tests.

REVERSIBLE ADSORPTION

An important property of tracers—particularly for tracers used in unconventional petroleum applications—is reversible adsorption. As tracers are advected through a geothermal reservoir, the progress of reversibly-adsorbing tracers is slowed relative to that of conservative tracers due to electrostatic interactions with fracture surfaces. Conservative tracers, by definition, react neither with the solution nor with the fracture surfaces and thus are advected indistinguishably from water molecules. And whereas conservative tracers are used to constrain interwell flow patterns and reservoir-pore volume (Rose et al., 1997; Rose et al., 2004), the use of reversibly adsorbing tracers *in combination with conservative tracers* can potentially provide additional valuable information about the reservoir fracture surface area for heat transfer (Rose et al., 2012; Dean et al., 2015; Wu et al., 2021).

The flow retardation of reversibly adsorbing tracers relative to conservative tracers was measured in a flow reactor whose schematic is shown in Figure 5. First, a solution was prepared containing a mixture of conservative tracers that are used in geothermal and unconventional-petroleum applications, including the conservative tracers 2,6-naphthalene disulfonate; 1,5-naphthalene disulfonate; and chloride. To this solution was added the candidate tracers 4-fluorobenzene sulfonate and 2,5-dichlorobenzene sulfonate. Also included in the solution was the tracer 2-naphthalene sulfonate, which has been shown to be slightly adsorptive on some shales—especially at lower temperatures.

A stainless-steel reactor flow cell having a length of 25 cm was filled with shale drill cuttings and heated to 160 °C; an aqueous conditioning solution of constant ionic strength was flowed through the column at 2 ml/min. After the column was equilibrated, valves were switched and the solution containing the tracer mixture was pumped through the reactor.

Shown in Figure 6 are the concentrations of tracers as measured at the exit of the reactor. The data show that all of the tracers eluted at approximately the same time, indicating that, within the parameters and resolution of this experiment, none of the compounds adsorbed.

SUMMARY AND CONCLUSIONS

Two halogenated benzene sulfonate compounds—4-fluorobenzene sulfonate and 2,5-dichlorobenzene sulfonate—were synthesized and tested for use as novel tracers in geothermal and petroleum applications. The decay kinetics of the two compounds was studied over a temperature range of 190 °C to 300 °C in order to determine its Arrhenius parameters for first-order thermal decay under conditions that approximate those of a geothermal reservoir. A plot of half-life vs. temperature indicates that 4-fluorobenzene sulfonate is comparable in stability to Amino G and that 2,5-dichlorobenzene sulfonate is comparable in stability to fluorescein. Both Amino G and fluorescein have been used successfully in several geothermal reservoirs.

The adsorptivities of the two benzene-sulfonate compounds were investigated using a column flow reactor under conditions that simulate those of a high-temperature, unconventional petroleum (shale) reservoir. They were shown to elute indistinguishably from known conservative compounds, indicating that within the parameters and resolution of the experiment they were non-adsorptive.

We plan to synthesize and test several more compounds from this family of halogenated benzene sulfonates for thermal stability and adsorptivity. If successful, these tests will serve to significantly increase the number of compounds currently available for use as tracers in geothermal and unconventional-petroleum reservoirs.

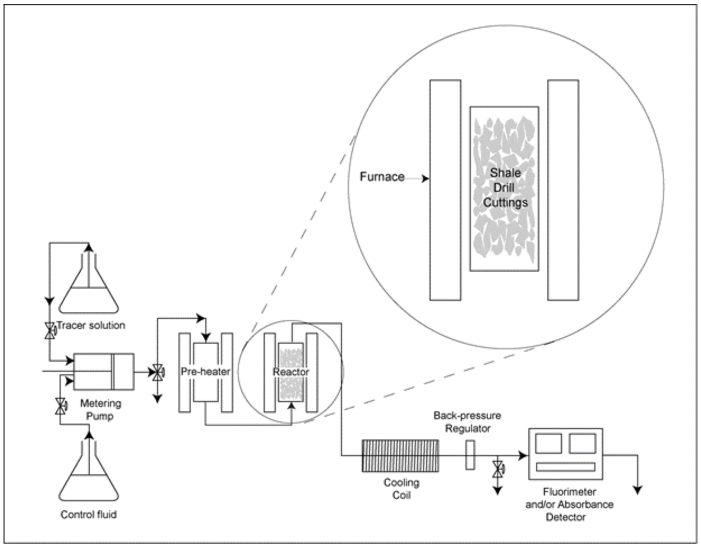

Figure 5. Schematic of the flow reactor used to characterize tracer reversible adsorption.

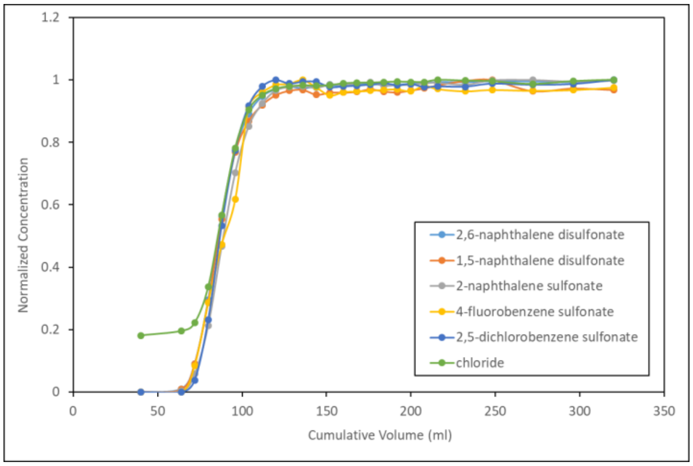

Figure 6. Concentrations of tracers as measured after flowing through a 160 °C column that was filled with shale cuttings.

REFERENCES

Adams, M.C., Moore, J.N., Fabry, L.G. and Ahn, J.H. (1992) “Thermal stabilities of aromatic acids as geothermal tracers”, *Geothermics,* **21(3),** pp. 323-339.

Dean, C., Reimus, P., Oates, J., Rose, P.E., Newell, D., and Petty, S. (2015) “Laboratory experiments to characterize cation-exchanging tracer behavior for fracture surface area estimation at Newberry Crater, OR”, *Geothermics,* **53**, pp. 213-224.

Greim H., Ahlers, R., Bias, R., Broecker, B., Hollander, H., Gelbke, H.P., Klimisch, H.J., Mangelsdorf, I., Paetz, A., Schon I., Stropp, G., Vogel, R., Weber, C., Ziegler-Skylakakis, K., and Bayer, E. (1994) Toxicity and Ecotoxicity of Sulfonic Acids: Structure-Activity Relationship: *Chemosphere*, **28(12)**, 2203-2236.

Leung, V. (2013) Yick-Vic Chemicals and Pharmaceuticals, yickvic@hkstar.com

Rose, P.E., Faulder, D.D., and Apperson, K.D. (1997) Fluid volume and flow constraints for a hydrothermal system at Beowawe, Nevada: *SPE 38762*.

Rose, P.E., Benoit, W.R., and Kilbourn, P.M., (2001) The application of the polyaromatic sulfonates as tracers in geothermal reservoirs: *Geothermics*, **30(6),** 617-640.

Rose, P.E., Johnson, S.D., and Kilbourn, P.M. (2001) Tracer testing at Dixie Valley, Nevada, using 2-naphthalene sulfonate and 2,7-naphthalene disulfonate: *Proc. Twenty-Sixth Workshop on Geothermal Reservoir Engineering*, Stanford University, SGP-TR-168, pp. 60-65.

Rose, P.E., Capuno, V., Peh, A., Kilbourn, P.M., and Kasteler, C. (2002a) The Use of the Naphthalene Sulfonates as Tracers in High Temperature Geothermal Systems, *Proceedings 23rd PNOC Geothermal Conference.*

Rose, P.E., Johnson, S.D., and Kilbourn, P.M., and Kasteler, C. (2002b) Tracer Testing at Dixie Valley, Nevada Using 1-Naphthalene Sulfonate and 2,6-Naphthalene Disulfonate: *Proc. Twenty-Seventh Workshop on Geothermal Reservoir Engineering*, Stanford University, SGP-TR-171.

Rose, P.E., Mella, M., and Kasteler, C., (2003) A new tracer (1,3,5-naphthalene trisulfonate) for use in liquid-dominated, high-temperature geothermal reservoirs: GRC Transactions, 27, pp. 403-406.

Rose, P.E., Mella, M., Kasteler, C., and S.D. Johnson, (2004) The Estimation of Reservoir Pore Data from Tracer Data: *Proceedings, 29th Workshop on Geothermal Reservoir Engineering*, Stanford University SGP-TR-175.

Rose, P.E., Leecaster, K., Clausen, S., Sanjuan, R., Ames, M., Reimus, P., Williams, M., Vermeul, V., and Benoit, R. (2012) A Tracer Test at the Soda Lake, Nevada Geothermal Field Using a Sorbing Tracer, *Proceedings, 37th Workshop on Geothermal Reservoir Engineering*, Stanford University SGP-TR-194.

Sajkowski, L. (2020) “The thermal stability of the naphthalene sulfonic acids under geothermal conditions”, Ph.D. dissertation, Victoria University of Wellington; Wellington, New Zealand.

Wu, H., Fu, P., Hawkins, A.J., Tang, H., and Morris, J.P. (2022) “Predicting thermal performance of an enhanced geothermal system from tracer tests in a data assimilation framework”, *Water Resources Research*, in press.