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Temperature Stability of Naphthalene Sulfonic and Naphthalene Disulfonic Acids at Geothermal Conditions

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ABSTRACT

An experiment has been performed to investigate the stability of the four naphthalene disulfonic acids (2,6-NDS, 2,7-NDS, 1,5-NDS, 1,6-NDS) and two naphthalene sulfonic acids (1-NSA, 2-NSA) using a hydrothermal flow simulator. The experimental fluid was pH-modified, low pressure separator brine from the Nga Awa Purua power station at the Rotokawa geothermal field. The six tracers were added to this fluid and were reacted with crushed, sieved and clean fragments of greywacke sourced from well RK24 at Rotokawa. The temperature range of the experiments was 270 – 390°C. Experimental results show that 1,5-NDS begins to degrade at temperatures as low as 280°C while 1,6-NDS shows evidence of breakdown at about 330°C. The other disulfonic acids are relatively stable until about 340°C at which point evidence of degradation appears. The monosulfonic acid 2-NSA is the most stable and persists to about 380°C. Analysis of the rate of reaction for these breakdown reactions shows that the rate constants are dependent on residence time and not consistent with first order reactions. The reactions that occur in the industrial production of the sulfonic acids and napthol compounds may be analogous to the reactions found at high temperatures in geothermal systems. One these reactions shows that 2-NSA is produced at higher temperature consistent with the results from the experiments. Chemical equilibria calculations show how reaction rates may be different depending on the tracer concentration and the temperature of the system.

1. INTRODUCTION

Chemical tracers are used widely in the geothermal industry to measure enthalpies and to determine reservoir properties. In order for a tracer to be suitable for these studies, it must fulfill certain properties. These include low natural background concentration, detectability at low concentrations, non-adsorptive, low cost, low toxicity and high thermal stability. Naturally occurring tracers such as bromide are not suitable due to the large amounts of the tracer that must be injected and their high background concentrations. I^{131} and I^{125} radioactive tracers have low detection limits and are thermally stable; however, the half-lives of these isotopes are eight days and 60 days respectively, limiting their use over longer periods (McCabe et al., 1998). Also, during injection, it is necessary to deal with highly radioactive compounds in the field.

Fluorescent organic compounds can also be used as chemical tracers. Fluorescein and rhodamine have been used extensively in the study of flow patterns at ambient temperatures but they are not suitable at the temperature of geothermal systems because of their low thermal stability (Adams et al. 1992). The use of polyaromatic compounds including naphthalene sulfonic and disulfonic acids is a more recent technique that is now used extensively at geothermal systems throughout the world.

Naphthalene sulfonic (NSA), disulfonic (NDS) and trisulfonic (NTS) acids appear to meet all the necessary properties to be a suitable tracer in geothermal systems: their background concentration is low; they are detectable at very low concentrations (pg/kg); they are relatively inexpensive; have low toxicity and are reasonably thermal stable. Rose et al. (2001) perform experiments to study the thermal stability of these compounds including 2-NSA, 1,5-NDS, 2,7-NDS and 1,3,6-NTS. He used sealed quartz glass ampoules placed in a stainless steel autoclave to simulate geothermal conditions. Their results show that both 1,5-NDS and 1,3,6-NTS undergo moderate thermal decay over a period of one week at 330°C while 2-NSA and 2,7-NDS appear to be thermally stable at this temperature.

These experiments provided useful information on the relative stability of selected polyaromatic sulfonates and established guidelines for their use. However, four important issues remain that require resolution so that the maximum amount of data can be gleaned from tracer returns. These include: the temperature stabilities of the polyaromatic sulfonates; the kinetics of their breakdown depending on physico-chemical conditions in the fluid; the effects of adsorption, if any; and the breakdown products of the NSA and NDS.

In this study, laboratory experiments are being conducted in order to address these questions. The results will allow better interpretation of NSA and NDS tracer results through a more complete knowledge of the kinetics and products of the breakdown of these compounds.

2. METHOD

The experiment was conducted using a high temperature and pressure hydrothermal flow simulator (Fig. 1). Continuous fluid flow is maintained by a computer-controlled double-piston metering pump with a flow rate range of 0.001 – 15 ml/min. This pump injects distilled water into the bottom of the titanium accumulator which contains a piston that pushes upwards on the experimental fluid forcing it through the apparatus. The pressure vessel is constructed of titanium and has an internal diameter of 25 mm and an overall length of 150 mm encompassing 19.3 cm^3 internal volume. Mineral or rock substrates used in experiments are contained in the pressure vessel. It is heated externally in an insulated oven. Temperature is monitored by a thermocouple inserted directly into the pressure vessel. Pressure is maintained by a digitally-controlled back-pressure regulator. The exit valve and fluid path to the back-pressure regulator are heated using heating tape to prevent mineral precipitation. All wetted components are composed of titanium, except for the Teflon diaphragm located in the back-pressure regulator. Pressure, temperature and pumped volume are recorded at 10 minutes intervals throughout the experiment.

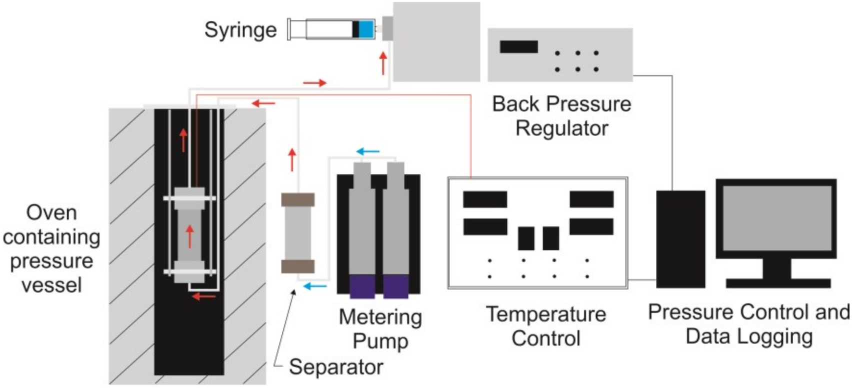

Figure 1: Schematic diagram of the high temperature and pressure hydrothermal flow simulator.

For the NDS experiment, the rock used was sourced from RK24 well from the Rotokawa geothermal field. It consisted of a composite sample of cuttings from an andesite unit. The cuttings were crushed and sieved, and cleaned with distilled water in an ultrasonic bath to remove highly reactive fine particles. The pressure vessel was filled with approximately 25 g of greywacke fragments of 1-2 mm in diameter. The pore fluid used was pH-modified (pH 6.1), low pressure separator brine from Nga Awa Purua power station at Rotokawa. The brine was spiked with the six naphthalene sulfonic acid tracers.

Fluid flow was commenced at room temperature at 1 ml/hr. After three days (to remove air from the pressure vessel) the temperature and pressure of the experiment were increased to 270^{o}C and 14 bar after which temperature was increased over the remaining experiment to 390^{o}C in 10 – 20^{o}C increments. Pressure was maintained at slightly above saturated water vapour pressure at each temperature and at 250 bars above the critical point. Four samples were collected at each temperature at three different flow rates (2 x 1.0 ml/hr, 1 x 0.5 ml/hr, 1 x 0.1 ml/hr). Samples for tracer measurement were untreated until analysis.

Tracers were analysed by high performance liquid chromatography (HPLC) using a Shimadzu Prominence HPLC by fluorescence detection. The mobile phase was 5 mM tetrbutyl ammonium phosphate in 25% methanol/water using isocratic flow. Detection limits are 0.04 µg/kg for NDS and 0.4 µg/kg for NSA.

2. RESULTS

Figure 2 shows the concentrations of NDS and NSA plotted versus temperature at three different flow rates. The tracers respond differently to temperature. All six appear stable at 270^{o}C. At 280^{o}C, 1,5-NDS already shows evidence of breakdown at the slowest flow rate (0.1 ml/hr). Up to 330^{o}C, 1,5-NDS and 1,6-NDS are decomposing resulting in an increase of 1-NSA and perhaps 2-NSA. The concentrations of 2,6-NDS and 2,7-NDS remain stable until approximately 330^{o}C and then they also begin to decay forming 2-NSA. At 330^{o}C, 1-NSA also begins to decay and decreases in concentration until the highest temperature of the experiment (390^{o}C). At approximately 380^{o}C, 2-NSA shows evidence of breakdown, particularly at the slowest flow rate. The total tracer concentration remains constant up to 330°C after which it begins to decrease (Fig. 3). At 390°C the rate of decomposition becomes more dependent on the flow rate.

3. DISCUSSION

3.1 Implications

The results from the NDS/NSA stability experiment can give some preliminary guidelines to the use of fluorescent sulfonic acids in geothermal systems. A system dosed with either 2,6 or 2,7-NDS is not expected to show any depletion or generation of 2-NSA below a temperature of around 330°C. At temperatures greater than 330°C, 2-NSA may be the only isomer that would be expected to be returned unless the breakthrough time is very short. The injection of 1,5-NDS is not recommended for temperatures of 270°C or greater but if used in a system in this temperature range, one would expect to see mixed returns of 1-NSA and 1,5-NDS depending on the breakthrough time. This is assuming that there is no isomerization of 1-NSA to 2-NSA. Dosing with 1,6-NDS is expected to give a mixture of 1-NSA and 2-NSA depending on the temperature until about 340°C after which only 2-NSA is expected. In a system where the maximum temperature is 350°C or greater, only 2-NSA would be expected and above 380°C no returns would be found. This does not, however, preclude the appearance of other fluorescent by-products of the decay.

3.2 Kinetics

Figure 4 shows the rate constants of the breakdown for 1,5-NDS and 1,6-NDS depend on the residence time (flow rate). This is not consistent with a pattern of a first order breakdown reaction otherwise all the points would lie on the same straight line. In comparison with the data of Rose (2001), the dataset from this experiment have similar slopes which indicates that the activation energy of the breakdown reaction is similar in both experiments. The two data points at 270 and 290°C (furthest right in Fig. 4) do not lie on the same trend as the other temperatures. Possible explanations are analytical uncertainties because the change in concentration was small or there may have been another reaction mechanism at these temperatures.

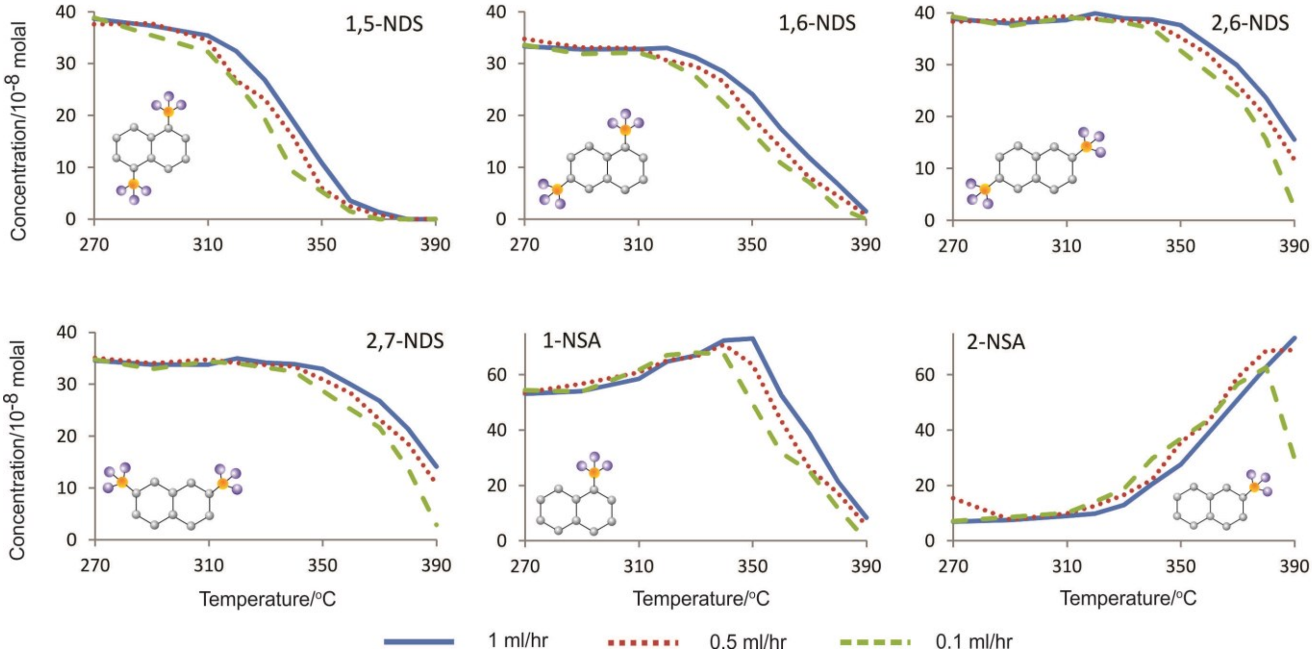

Figure 2. Concentrations of six naphthalene sulfonic acids (x10^{-8} molal) versus temperature at three different flow rates.

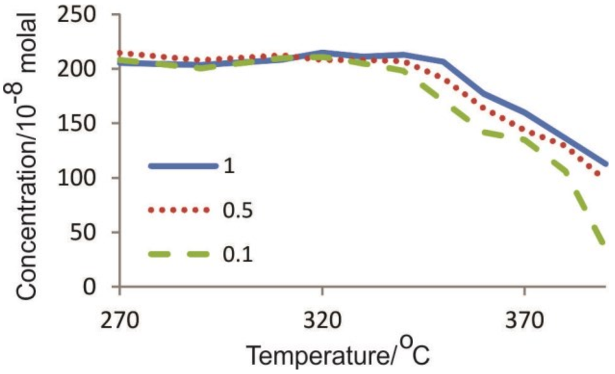

Figure 3. Total tracer concentration (x10^{-8}) at three different flow rates.

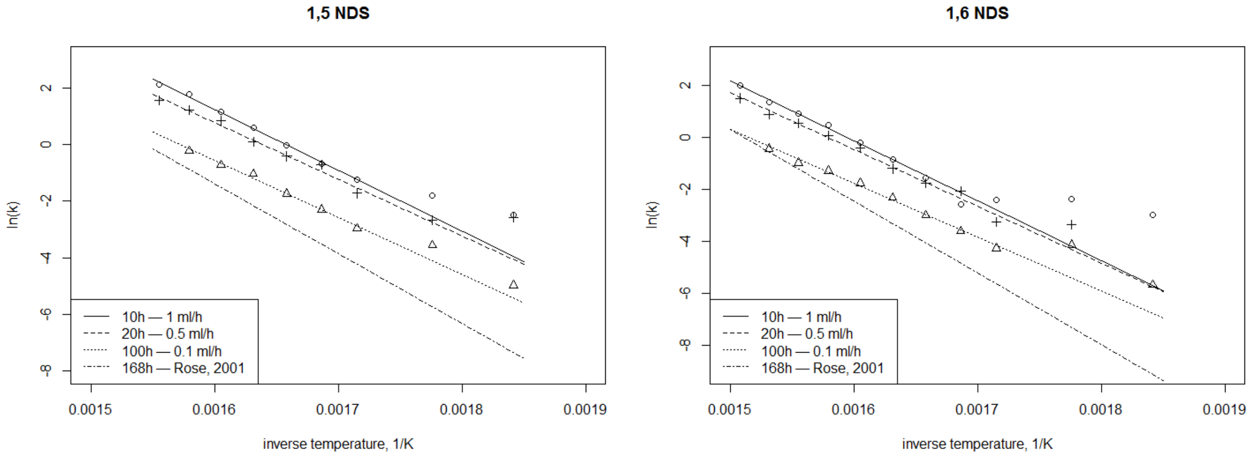

Figure 4. Arrhenius plot of ln(k) vs. inverse temperature for the breakdown of 1,5-NDS and 1,6 NDS at four different residence times. The two right most points were not used in the estimation of the linear dependence of ln(k) vs 1/T.

3.3 Possible Reaction Mechanisms

The process used to produce NDS and NSA involves the sulfonation of naphthalene by reaction with concentrated sulfuric acid. Sulfonation is an electrophilic substitution and the sulfonating reagent is $H_3SO_4^+$. The reaction occurs as follows:

$$RH_X + xHSO_3^+ = R(SO_3H)_x + xH^+$$

where R represents the naphthalene moiety. In the industrial process a mixture 1-NSA and 2-NSA are produced from the same reagents (naphthalene and sulfuric acid). At 60°C 1-NSA predominates while at 160°C 2-NSA is the dominant product. This is because the energy of activation is lower for 1-NSA than for 2-NSA; however, 2-NSA is more stable. Heating 1-NSA with sulfuric acid leads to isomerization to 2-NSA. Further sulfonation of 1-NSA produces a mixture of 1,5-NDS and 1,6-NDS while sulfonation of 2-NSA produces mainly 2,7-NDS with admixture of 2,6-NDS.

Another industrial process which involves sulfonic acids treats them with NaOH at temperatures around 300-350°C to produce aromatic alcohols, for example:

$$R(SO_3H) + 2NaOH = ROH + Na_2SO_3 + H_2O$$

and

$$R(SO_3Na) + 2NaOH = RONa + Na_2SO_3 + H_2O$$

In both of these reactions, if R is naphthalene the products will be naphthol and naphthol sodium salt, respectively. Similar reactions could be expected to occur at depth in a geothermal system. This suggests that naphthol could be a by-product of sulfonic acid breakdown.

3.4 Effect of Concentration

If any of the above reactions are responsible for tracer breakdown then the rate of their decomposition will depend on pH and/or pOH which are the functions of temperature and tracer concentration. In order to address this question we have performed some chemical equilibria calculations to determine the effect of these variables on tracer stability.

We simulated three situations: the present experiment, the experiment of Rose (2001), and at the time of a field tracer injection. We use 2-NSA for these calculations where pKa at 25°C is +0.3 and for sulfuric acid is -3. We have assumed that the temperature dependence of the pKa for 2-NSA is the same as sulfuric acid, therefore the pKa at any temperature is 10000 times lower than sulfuric acid. pKw values are taken from Bandura and Lvov, 2005. pKa for HCl and pKa2 for H_3PO_4 (pH buffer) were taken from Geochemist's Workbench© (Bethke, 2008).

Figure 5a shows the concentration of 2-NSA of 100 µg/kg in pure water (pH=7). Even though the pH and pOH increase with temperature the concentration of dissociated 2-NSA does not change because it is completely dissociated. In Figure 5b, at the same 2-NSA concentration, the pH and temperature conditions of our experiment are shown. The pH is simulated by addition of HCl to give 6.1. In this experiment the sulfonic acid is also completely dissociated but pOH is several orders of magnitude less than pH up to approximately 200°C. Above 200°C, pH and pOH are the same as in Figure 5a which means the initial pH of the solution is not important. Figure 5c shows the conditions of Rose (2001) where 2-NSA concentration was 25 mg/kg and the solution was buffered using a phosphate buffer to pH=6.5. It shows that the pH varies little over the temperature range but pOH increases five orders of magnitude from 0 to 250°C after which it remains constant. The 2-NSA is completely dissociated and its concentration is similar to that of the hydrogen ion and, as a consequence well below the concentration of the OH^- ion. Figure 5d shows the same conditions with the exception that 2-NSA concentration is 100 µg/kg. If the reactions proposed above are the possible mechanisms of tracer decomposition then its rate will be affected by its concentration. Figure 5e shows the conditions of a field injection experiment where the concentration of 2-NSA is 100 kg/m^3. In this case the concentration of dissociated 2-NSA is 0.3 molar and the sulfonic acid is not completely dissociated. The amount of dissociated 2-NSA decreases with temperature increase (0.03 molar at 400°C). The pH of the solution is controlled by dissociated tracer and varies from 0.3 to 1.6 and OH^- concentration is several orders of magnitude below that of the tracer. This means that if the above reactions take place during a field injection the decomposition rate is quite different depending on dilution and temperature.

4. CONCLUSIONS

An experimental study has been undertaken to investigate the stability of the naphthalene disulfonic acids (2,6-NDS, 2,7-NDS, 1,5-NDS, 1,6-NDS) and the naphthalene sulfonic acids (1-NSA, 2-NSA) under geothermal conditions of 270 – 390°C and 14 – 250 bars. The results of this experiment showed that:

a) 2,6 and 2,7-NDS are thermally stable until approximately 330°C above which there is noticeable degradation;

b) 1,5-NDS begins to degrade at a temperature as low as 280°C;

c) 1,6-NDS shows degradation beginning at 330°C;

d) 1-NSA begins to increase in concentration at 280°C and reaches peak concentration between 330 - 350°C, depending on the flow rate;

e) 2-NSA shows a continual increase in temperature reaching a maximum at about 370°C after which it begins to rapidly degrade.

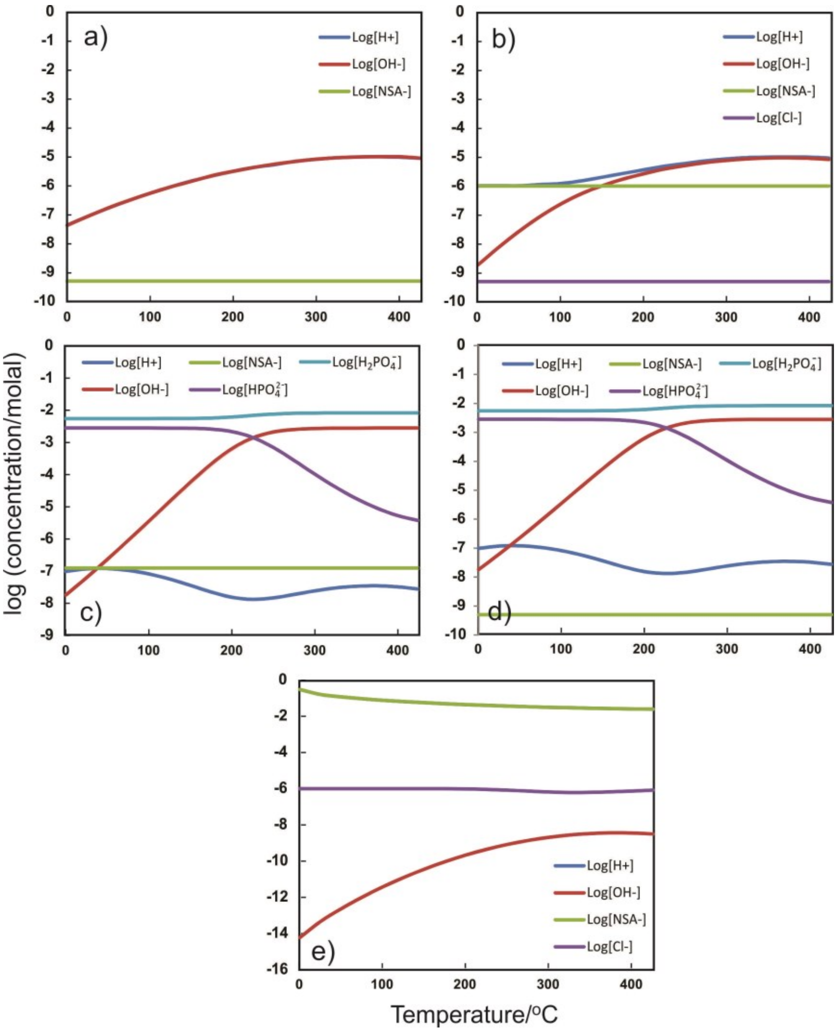

Figure 5. Chemical equilibrium models of solution composition vs. temperature: a) 2-NSA 100 µg/kg and pure water; b) 2-NSA 100 µg/kg and pH = 6.1; c) 2-NSA 25 mg/kg, phosphate buffer, pH = 6.5; d) 2-NSA 100 µg/kg, phosphate buffer, pH = 6.5; e) 2-NSA 100 kg/m^3 pH = pNSA$^-$.

Analysis of the rate of reaction for the sulfonic acids shows that the rate constants are dependent on residence time and not consistent with first order reactions. We proposed reaction mechanisms that are based on the industrial processes involving these compounds. These mechanisms are pH and pOH dependent which means that the rate of tracer decomposition in a geothermal system would be affected by temperature, initial concentration and dilution. Chemical equilibria calculations confirms this dependence which implies that they should be taken into account when performing laboratory experiments. Our current research plan is to investigate the mechanisms and kinetics of the breakdown of the sulfonic acids in the laboratory using a combination of hydrothermal simulations, both batch and continuous-flow, and UV-Vis spectroscopy.

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