EXPERIMENTAL DETERMINATION OF THE THERMAL STABILITY OF THE ORGANIC TRACERS 1,5-NDS AND 2-NSA UNDER GEOTHERMAL CONDITIONS

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ABSTRACT

Naphthalene sulfonates are widely used in the geothermal industry as tracers. Experimental results show however, that these chemicals do have their temperature limits. Knowledge of the rate of thermal breakdown is essential to ensure successful tracer tests. In addition, knowledge of the breakdown products could be useful in interpreting fluid temperature history. The main goal of this project is to broaden the understanding of the processes taking place when these tracers are exposed to conditions found in the geothermal environment.

The experiments were conducted to measure the rate of the thermal breakdown reactions. Two tracers: 1,5-naphthalene disulfonate (1,5-NDS, least thermal stability of the compounds) and 2-naphthalene sulfonate (2-NSA, most thermally stable) were used. Aqueous solutions containing the tracers were sealed inside glass ampoules using an oxy-acetelyene torch and placed in cold-seal autoclave reactors. The reactors were exposed to 200°C and 300°C for different exposure times from 20 hours to 166 hours. The experimental pH was varied and ionic strength ranged between 0.001 and 0.05 M. Tracers were analysed by high performance liquid chromatography (HPLC) using fluorescence detection.

The rate constants were estimated by fitting a line through the data points. Results show that rate constants at 200°C are pH and ionic strength dependent. Increases in ionic strength slows the breakdown reactions while decreased pH increases the breakdown rate. Results at 300°C show similar trends, however, the overall rates of reaction are more rapid.

1. INTRODUCTION

The efficiency in geothermal energy production is improved by evaluating geothermal reservoir properties which results in better well planning. Tracer tests are the best tool to provide data on the flow of fluid from injection to production wells. The examination of tracer returns reveals reservoir properties such as permeability, providing important inputs to numerical models.

The naphthalene sulfonic acids are one group of compounds that are being used as tracers in the geothermal industry. Ideal tracers have to meet basic criteria, including thermal stability, low detection limit, low natural background concentration, non-absorptivity, non-toxicity and low-cost. The naphthalene sulfonic acids fit these criteria, however, a better understanding of their thermal stability is needed.

The different isomers of naphthalene sulfonates can be used simultaneously during one test. They can be easily differentiated and detected by high performance liquid chromatography (HPLC). Numerous tests have been conducted worldwide, including in New Zealand (e.g. Addison et al., 2015; Buscarlet et al., 2015).

The thermal stability of aromatic compounds used for geothermal tracers has been the subject of research during the last two decades. This includes: unsubstituted and substituted benzene sulfonic acids (Adams, 1992); naphthalene sulfonic acids (NSA); naphthalene disulfonic acids (NDS); and naphthalene trisulfonic acids (NTS) (Rose et al., 1999; Rose et al., 2001; Mountain and Winick, 2012).

In Rose et al. (2001) selected tracers (1,3,6,8-pyrene tetrasulfonate, 1,3,6-NTS, 1,5-NDS, 2,7-NDS, 2-NSA) were exposed to hydrothermal conditions in batch autoclave reactors to test their thermal stability. They used 25 µg kg^{-1} of each tracer dissolved in pH 6.5 buffer solutions sealed in quartz glass ampoules and heated to 330ºC for one week. Both 2-NSA and 2,7-NDS were stable in these experiments.

Further flow through experiments were performed by Mountain and Winick (2012) and re-examined by Dashkevich et al. (2014, 2015) to investigate the thermal stability of the NDS and NSA. The pH-modified brine (from Nga Awa Purua power station) with 100 µg kg^{-1} of the tracers was passed through crushed greywacke enclosed in a pressure vessel. This was heated incrementally from 270 to 390ºC. The residence time was in the range of 6 to 60 hours. They reported an increase in thermal stability in the order 1,5-NDS, 1,6-NDS, 1-NSA, 2,6-NDS/2,7NDS, 2-NSA. They noted that at 300-340ºC there was an increase in 1-NSA and up to 380 ºC, 2-NSA. At 390ºC all tracers were thermally unstable.

The influence of pH conditions in the reservoir on the thermal stability of naphthol sulfonic esters at 100-130°C was investigated by Nottebohm et al. (2010). They showed a strong sensitivity of tracer stability to pH, with the reaction rate increasing up to four orders of magnitude with decreasing pH.

Further experiments, to examine the pH dependence of the thermal stability of 1,5-NDS and 2-NSA at higher temperatures, have been done using sealed glass ampoules (Sajkowski et al., 2017). Sets of ampoules with varying pH value and with ionic strengths (I) of 0.001 and 0.05 M were exposed for 40 hours to 200°C and 300°C. Results show that the stability of 1,5-NDS and 2-NSA increases, with increasing pH and the ionic strength. 1-NSA appears as a breakdown product at 300°C, pH = 5.2 - 7.2. Its increase in concentration is independent of ionic strength.

In the current study, the stabilities of 1,5-NDS and 2-NSA were further investigated at constant tracer concentration using solutions of differing pH and ionic strengths of 0.001 M and 0.05 M. The temperature range was 200 - 300℃ and the experiment duration was 10, 20, 40, 60 and 166 hours. The aim is to find rate constants for the thermal breakdown of the tracers in solutions with varying pH, I and temperature.

2. METHOD

2.1 Analytical method

The naphthalene sulfonic acids are analysed using HPLC by fluorescence detection (Shimadzu Prominence RF-20Axs). To protect the column from particulates, all samples are filtered through a 0.2 µm Minisart® NML surfactant-free cellulose acetate filters. The mobile phase is 5 mM tetrabutylammonium phosphate (Sigma-Aldrich) in 29:71% methanol:water. Methanol is HPLC grade from ThermoFisher Scientific. Ultrapure water with a conductivity of 0.055 µS cm^{-1} (18.2 MΩ cm^{-1}) is produced by Arium® pro-Ultrapure water system. Detection limits are 0.04 µg kg^{-1} for NDS and 0.4 µg kg^{-1} for NSA. The column is kept at 35°C. Sample injection volume is 50 µL and a 50 µL ultrapure water blank is run between each standard/sample.

2.2 Experimental method

Eight sets of tubes were used representing different pH values. Each set includes the two ionic strengths (0.001 M, 0.05 M). The solutions were prepared using ultrapure water. HCl and NaOH were used to fix pH and NaCl to adjust ionic strength. To each tube, 1,5-NDS and 2-NSA were added to obtain a concentration of 0.02 mg kg^{-1} and 0.01 mg kg^{-1} respectively. The tubes were heated to 200°C and 300°C for 10, 20, 40, 60 and 166 hours (Fig. 1).

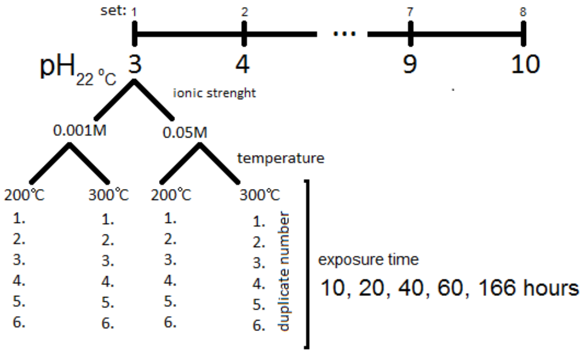


Figure 1. Experimental protocol.

The experimental solutions were bubbled with 0.01% H_2 in N_2 for 10 minutes in a 2 l flask and 2.5 ml aliquots of this solution were transferred to open quartz glass tubes (ID 7 mm, OD 9 mm). A blank was taken from the 2 l flask after deoxygenating. The headspace of the tubes was purged with nitrogen. They were evacuated using a vacuum pump and sealed using an oxygen-acetylene flame. This leaves ~2 ml headspace. The average time between transfer and sealing was about 20 seconds. Six duplicates were made for each set of experimental conditions. The duplicates were enclosed in 120 ml steel autoclaves which were half-filled with water to provide the confining pressure around the glass tubes. The autoclaves were placed into the preheated Carbolite LHT 5/60 oven. The time required to heat the autoclaves to the target temperature was ~2 hours while cooling down to 100℃ took about 2 hours. After heating, if the change of mass of the tube was more than 30 mg, it was concluded that the tube had leaked and it was discarded.

2.3 Determination of the rate constant

The values of the observed molal concentrations after different heating times are plotted as *ln*(concentration/molal) vs time/hour (Fig. 2 and 3). To obtain the rate constant k (hour^{-1}) the data were fitted using GraphPad Prism 7.03 software by the linear least squares method.

Experimental errors can lead to incorrect fitting, a single outlier can significantly influence calculations. Observations more than three standard deviations from mean were considered outliers. A statistical hypothesis test was applied:

- Null hypothesis: all data points are related, and all describe the observation.

- Alternative hypothesis: The most extreme value is not related to measured phenomena.

To test these hypotheses, the Extreme Studentized Deviate test was used (Ekezie and Ogu, 2013). When P-value for each datum point was calculated to be lower than 0.05 the null hypothesis was rejected.

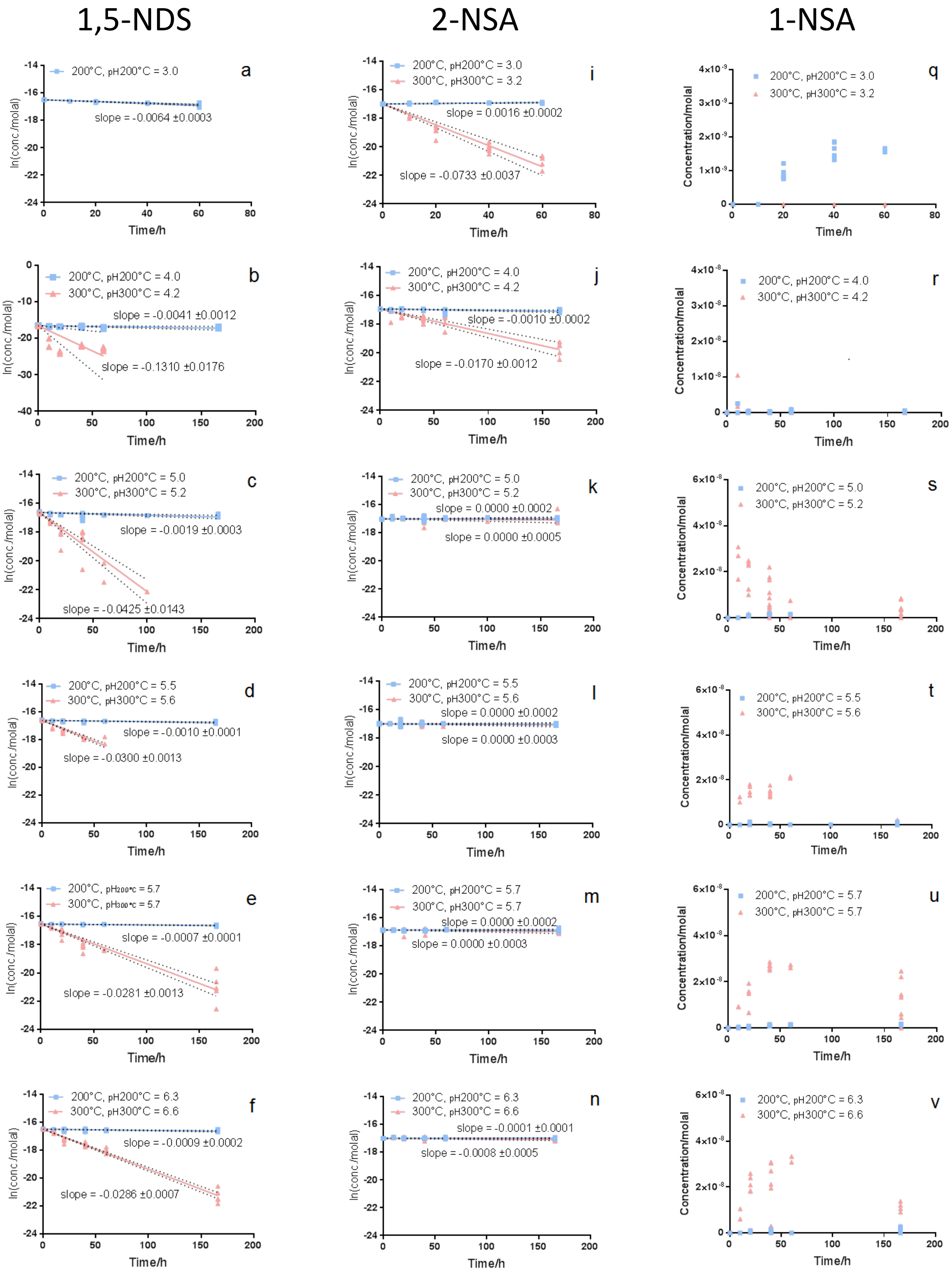
3. RESULTS

Figure 2a)-p) and 3a)-j) show the experimental results as the natural logarithm of the molal concentration of 1,5-NDS and 2-NSA after heating versus experimental pH. Figure 2q)-x) and 3k)-o) show molal concentration of 1-NSA versus exposure time. Figure 2 shows results for ionic strength 0.05 M and Figure 3, 0.001 M. The experimental pH was calculated using the Geochemist's Workbench® software package.

3.1 1,5-NDS Results

In Figure 2 (I = 0.05 M), the results (square symbols) show a correlation between pH and the rate constants k of 1,5-NDS breakdown at 200°C. The breakdown of 1,5-NDS is observed at all pH values. At pH = 3, the breakdown rate (the slope of the *ln* concentration versus temperature fit) is the fastest (-0.0064 hr^{-1}). With increasing pH, the breakdown rate decreases to a minimum value at pH = 5.7 (-0.0007 hr^{-1}) then increase again to -0.0017 hr^{-1} at pH = 8.2. At 300^{o}C (triangle symbols), no 1,5-NDS was detected at pH =3. Between pH = 4 to 8.2 the breakdown rate decreases with increasing pH (-0.1310 to -0.0052 hr^{-1}).

At I = 0.001 M and 200^{o}C (Figure 3), the fastest breakdown occurs at pH = 3 (-0.0195 hr^{-1}) and with increasing pH the breakdown rates decrease to near zero (~-0.003 hr^{-1}). Note, however, these breakdown rates are still faster than at I =0.05 M. At 300^{o}C, I = 0.001 M, there was complete breakdown of 1,5-NDS and it was not detected. Between pH = 5.6 – 8.2, the breakdown rate increases at near neutral pH values and then decreases toward pH = 8.2 (-0.0228 hr^{-1}).


1,5-NDS
2-NSA
1-NSA
a
200°C, pH200°C = 3.0
slope = -0.0064 ±0.0003
b
200°C, pH200°C = 4.0
300°C, pH300°C = 4.2
slope = -0.0041 ±0.0012
slope = -0.1310 ±0.0176
c
200°C, pH200°C = 5.0
300°C, pH300°C = 5.2
slope = -0.0019 ±0.0003
slope = -0.0425 ±0.0143
d
200°C, pH200°C = 5.5
300°C, pH300°C = 5.6
slope = -0.0010 ±0.0001
slope = -0.0300 ±0.0013
e
200°C, pH200°C = 5.7
300°C, pH300°C = 5.7
slope = -0.0007 ±0.0001
slope = -0.0281 ±0.0013
f
200°C, pH200°C = 6.3
300°C, pH300°C = 6.6
slope = -0.0009 ±0.0002
slope = -0.0286 ±0.0007
i
200°C, pH200°C = 3.0
300°C, pH300°C = 3.2
slope = 0.0016 ±0.0002
slope = -0.0733 ±0.0037
j
200°C, pH200°C = 4.0
300°C, pH300°C = 4.2
slope = -0.0010 ±0.0002
slope = -0.0170 ±0.0012
k
200°C, pH200°C = 5.0
300°C, pH300°C = 5.2
slope = 0.0000 ±0.0002
slope = 0.0000 ±0.0005
l
200°C, pH200°C = 5.5
300°C, pH300°C = 5.6
slope = 0.0000 ±0.0002
slope = 0.0000 ±0.0003
m
200°C, pH200°C = 5.7
300°C, pH300°C = 5.7
slope = 0.0000 ±0.0002
slope = 0.0000 ±0.0003
n
200°C, pH200°C = 6.3
300°C, pH300°C = 6.6
slope = -0.0001 ±0.0001
slope = -0.0008 ±0.0005
q
200°C, pH200°C = 3.0
300°C, pH300°C = 3.2
r
200°C, pH200°C = 4.0
300°C, pH300°C = 4.2
s
200°C, pH200°C = 5.0
300°C, pH300°C = 5.2
t
200°C, pH200°C = 5.5
300°C, pH300°C = 5.6
u
200°C, pH200°C = 5.7
300°C, pH300°C = 5.7
v
200°C, pH200°C = 6.3
300°C, pH300°C = 6.6
ln(conc./molal)
Concentration/molal
Time/h
-14
-16
-18
-20
-22
-24
0
-10
-20
-30
-40
0
20
40
60
80
50
100
150
200
1x10^-9
2x10^-9
3x10^-9
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4x10^-8
6x10^-8

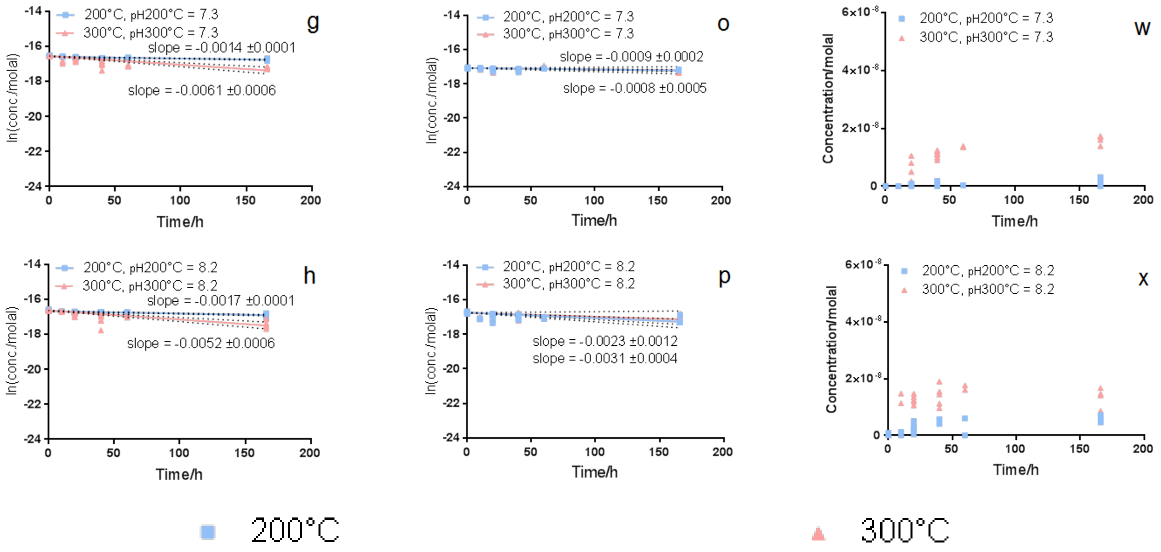
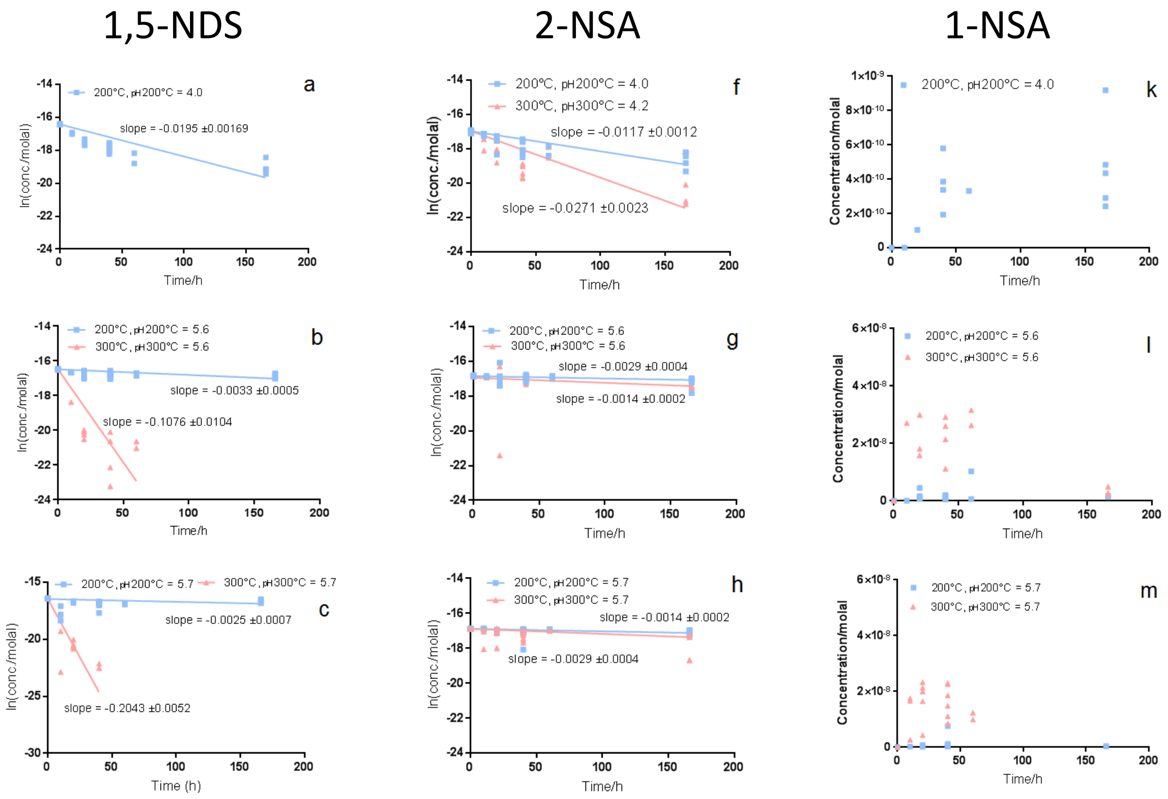


Figure 2. Concentrations of 1,5-NDS (a-h), 2-NSA (i-p) and 1-NSA (q-x) after heating at 200°C and 300°C and pH = 3.0 – 8.2, I = 0.05 M for 10, 20, 40, 60 and 166 hours. Results are converted to natural logarithm for 1,5-NDS and 2-NSA.



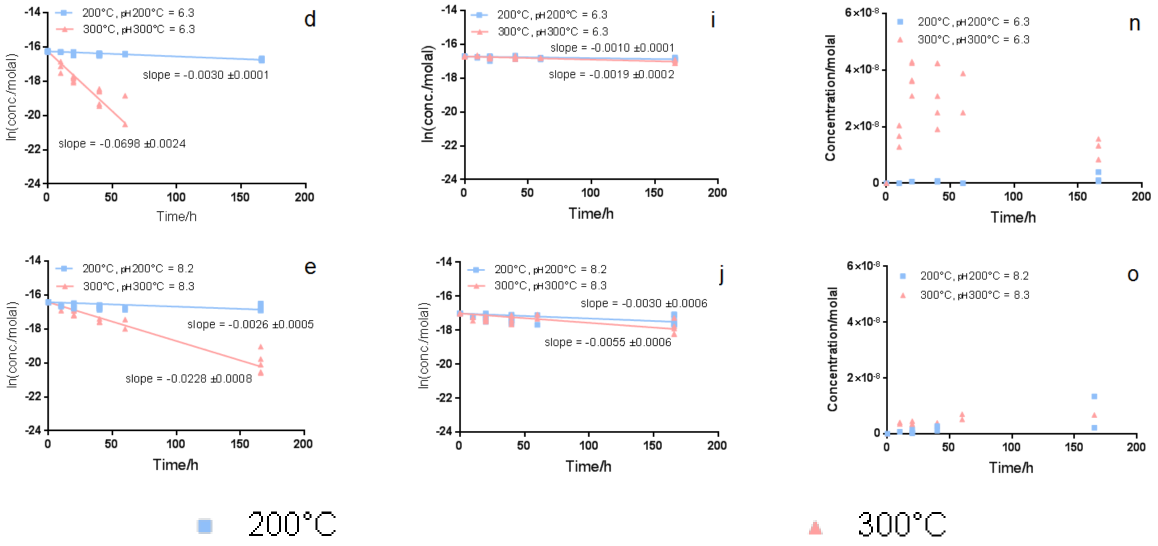


Figure 3. Concentrations of 1,5-NDS (a-e), 2-NSA (f-j) and 1-NSA (k-o) after heating at 200°C and 300°C and pH = 4.0 – 8.2, I = 0.001 M for 10, 20, 40, 60 and 166 hours. Results are converted to natural logarithm for 1,5-NDS and 2-NSA.

3.2 1-NSA Results

The isomer, 1-NSA, has been observed as a decomposition product in previous experiments (Mountain and Winick, 2012). In the current study, 1-NSA was measurable at all pH conditions but there was no discernible relationship between pH and 1-NSA concentration at 200°C (Figure 2). At 300°C, 1-NSA was not detected at pH = 3, while at higher pH values, measurable concentrations of 1-NSA were found. However, the maximum 1-NSA concentrations were detected at about 40 hours after which, it decreased. An exception is at pH 8.2 where the 1-NSA remained stable up to 166 hours.

At lower ionic strength (Figure 3), similar results were found at both temperatures.

3.3 2-NSA Results

Figure 2 (I = 0.05 M) shows that 2-NSA is stable at 200°C at pH = 5 – 6.3 (for at least 166 hours). At 300°C, 2-NSA appears stable at pH = 5 – 5.7.

At 200°C and lower ionic strength (Figure 3), breakdown of 2-NSA was measurable, but was most noticeable at pH = 3. At 300°C, similar results are observed.

4. DISCUSSION

4.1 Implications for tracer testing

The results from these experiments can be used as guidelines for future tracer tests. The stability of 2-NSA appears to extend up to 300°C in solutions with ionic strength equal to 0.05 M (~ionic strength of a New Zealand geothermal fluid) and pH ranging between 5.0 – 6.3 The injection of 1,5-NDS, however, is not recommended at 300°C. However, at 200°C, I = 0.05 M and neutral to alkaline pH, 1,5-NDS could be used. Also, the breakdown of 1,5-NDS to 1-NSA can occur, however, it appears to be a transient product and would not persist in the time frame of a field test, except possibly under alkaline conditions.

4.2 Decay Kinetics

Exponential decrease in the concentration of 1,5-NDS, characteristic for first order reaction, was observed in all samples. This was also observed by Rose et al. (2001). If the decay of 1,5-NDS follows a first order reaction then:

$$\frac{-dC_t}{dt} = k \cdot C_t$$

where C_t is the concentration of naphthalene sulfonate at time t and k is the first order rate constant. Using the laws of logarithms, we can obtain following equation:

$$ln\left(\frac{C_t}{C_0}\right) = -kt$$

$$ln(C_t) = -kt + C_0$$

simplifying the equation we obtain the final form of the rate law:

$$C_t = C_o e^{-kt}$$

which can be used to calculate concentration of reactant after any time.

4.3 Breakdown products

The experiments show that the breakdown of 1,5-NDS does produce some 1-NSA. This reaction appears to be independent of the ionic strength of the solution. The 1-NSA produced was stable for only about 60 hours at 300°C when pH was between 4.0 and 6.6 (Fig. 2r)-v), 3l)-n)). At 200°C, the reaction is too slow or does not occur during heating as is expected due to slower rate of 1,5-NDS decomposition at this temperature. In solutions with pH = 7.2 or greater, 1-NSA was stable for more than 166 hours. This suggests that 1-NSA persists at these conditions (Fig. 2w),x), 3o)). For pH = 4.0 or lower (Fig. 2o), 3k)) 1-NSA appears only at 200°C. This is explained by rapid 1,5-NDS decomposition under these conditions. No measurable breakdown projects of 2-NSA were observed in these experiments.

4.4 Protonation

The pH dependence of tracer stability can be explained by the desulfonation mechanism, as suggested by Bruckner (2010) and Sajkowski et al. (2016). According to Bruckner (2010), similar reactions occur with benzene instead of naphthalene as the aromatic ring in the compound. The addition of heat in the presence of excess protons causes replacement of SO_3^- by H^+ creating benzene and sulfur trioxide. The rate of this process is dependent on the concentration of protons hence breakdown occurs faster the lower the pH. It is conjectured here that naphthalene sulfonic acids act similarly.

Figures 2a),b), 2i),j), 3a),3f) show molal concentration of 1,5-NDS and 2-NSA over time at pH = 3.0 and 4.0. At 200°C, only 2-NSA is thermally stable in a solution with I = 0.05 M. However, at 300°C both 1,5-NDS and 2-NSA are being degraded. This can be explained by the position of the sulfonate groups in 1,5-NDS (α-substitution) as opposed to its position in 2-NSA (β-substitution) in addition to the extra enthalpy at higher temperature required for the desulfonation mechanism.

5. CONCLUSIONS

An experimental study of 1,5-NDS and 2-NSA stability at pH = 3.0 – 8.2, at 200 and 300°C and two ionic strengths (0.001M, 0.05M) has been conducted. The exposure time range between 10 and 166 hours.

The results show the following:

- 1,5-NDS is not stable at 200 - 300°C, pH 3.0 – 8.2, I = 0.001 M, 0.05 M;
- 1,5-NDS breakdown rate increases with decreasing pH and decreasing ionic strength;
- 2-NSA is stable at 200°C pH: 3.0 – 6.3, I = 0.05 M;
- 2-NSA is not stable at 300°C pH 3.0 – 4.2 and 6.3 – 8.2, I = 0.05 M;
- 2-NSA is stable at 300°C pH 5.0 – 5.7, I = 0.05 M;
- 2-NSA is not stable at 200°C and 300°C, pH 4.0 – 8.2 at low ionic strength;
- 1-NSA is a breakdown product of 1,5-NDS thermal decay and may persist at alkaline pH;

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