THE pH DEPENDENT THERMAL STABILITY OF THE ORGANIC TRACERS 1,5-NDS AND 2-NSA

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Keywords: *Tracer studies, naphthalene disulfonic acid, naphthalene sulfonic acid, NDS, NSA, experimental geochemistry.*

ABSTRACT

The pH dependence of the thermal stability of 1,5-naphthalene disulfonate and 2-naphthalene sulfonate have been investigated. The experiments were conducted using batch autoclave reactors. Two experimental temperatures were investigated (200℃, 300℃). The pH ranged from 3 to 9.85 and two ionic strengths were used (0.001 M, 0.05 M). The duration of each experiment was 40 hours.

The results show that:

1) 1,5-NDS is not stable at 300°C, pH 3, 4, 9 and 9.85, I = 0.001M, 0.05M;
2) 1,5-NDS is stable at 200°C, pH 4, I=0.001 M;
3) the low thermal stability of 1,5-NDS can be explained by two mechanisms: steric hindrance and kinetics;
4) 2-NSA is stable at 200°C pH 3, 4, 9 and 9.85, I = 0.001M, 0.05M;
5) the stability of 2-NSA at 300°C is independent of ionic strength;
6) 2-NSA is thermally stable at 300°C and pH 9.85, I = 0.05 M;

Further experiments are underway to confirm and expand our knowledge.

1. INTRODUCTION

Well managed, geothermal energy sources are an example of clean, reliable, renewable energy. In the future, increasing demand for energy in New Zealand can be met by this relatively low-cost, local source of energy. However, constant improvement of technology and application of recent scientific results is required to keep up with the rapidly changing needs, and provide efficient use of this source of energy.

Chemical tracers are a powerful tool for the geothermal industry. A chemical compound can be used as the tracer when it meets several basic requirements, including thermal stability, low detection limit, low natural background concentration, non-absorptivity, safe and affordable. Tracers are used to track fluid flow between injection wells and production wells. Reservoir tracer tests provide information on the quantity of fluid from injection to each production well and the speed in which it returns. The return curve can then be analysed to understand reservoir properties relating to permeability, providing important inputs to numerical models.

In the two last decades, research has been conducted on the thermal stability of aromatic compounds for use as geothermal tracers including unsubstituted and substituted benzene sulfonic acids (Adams *et al.*, 1992), naphthalene mono- (NSA), di- (NDS), and trisulfonates (NTS) (Rose *et al.*, 1999; Rose *et al.*, 2001; Mountain and Winick, 2012). A significant advantage in using these compounds is the ability to investigate multiple injection wells during one test by putting specific compounds or isomers into each well. The compounds are easily differentiated on a High Performance Liquid Chromatogram (HPLC) and by testing more than one well at a time this reduces sampling and analysis costs per well compared to a discrete test for each injection well.

Rose *et al.* (2001) simulated hydrothermal conditions in batch autoclave reactors to test the thermal stability of 25 µg kg^{-1} of various tracers (1,3,6,8-pyrene tetrasulfonate, 1,3,6-NTS, 1,5-NDS, 2,7-NDS, 2-NSA) dissolved in 6.5 pH-buffered 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 experiments were performed by Mountain and Winick (2012) and re-examined by Dashkevich et al. (2014, 2015) to investigate the thermal stability of NDS and NSA with a hydrothermal flow simulator. 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. The pressure vessel was heated incrementally from 270 to 390ºC. 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 concentration. At 390ºC all tracers were thermally unstable.

Dashkevich *et al.* (2014) examined the stability of 1,5-NDS. The experiments investigated the effect of concentration using 100 µg kg^{-1}, 1.5 mg kg^{-1}, 25 mg kg^{-1} 1,5-NDS in deionised water, pH 6.5 phosphate buffer, geothermal brine and 0.4 mol kg^{-1} NaCl solution. Sealed quartz tubes were used at a temperature range of 260 - 350ºC for 10 and 40 hours. They reported that 1,5-NDS stability depends on the solution composition and pH but not on the tracer concentration. The degradation of 1,5-NDS to 1-NSA occurred near 300ºC.

In the current study, the stabilities of 1,5-NDS and 2-NSA were investigated at constant tracer concentration using solutions of differing pH and ionic strengths of 0.001 M and 0.05 M. The temperature range utilised was 200-300℃ and the experiment duration was 40 hours.

2. METHOD

The NDS analyses were performed using reverse-phase liquid chromatography with 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.

Eight sets of tubes were used representing different pH values. Each set includes the two ionic strengths (0.001M, 0.05M). Six duplicates of each tube were created. 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 40 hours (Fig. 1).

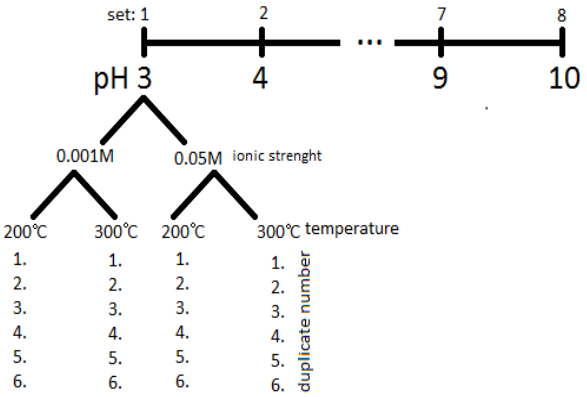


Figure 1. Experimental protocol.

The experimental solutions were bubbled with 0.01% H_2 in N_2 for 10 minutes in a 2 L flask, 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. Thirty-six tubes of each set were made (six for each concentration/matrix combination). 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 was discarded.

3. EXPERIMENTAL RESULTS

Figure 2 shows the experimental results to date. The figure shows the tracer concentrations before heating and average tracer concentration after heating.

At pH 3, I = 0.001 M and 200°C (Fig. 2a), 1,5-NDS was significant thermally degraded while 2-NSA remained unchanged. At higher ionic strength, thermal stability increased and less 1,5-NDS degraded (Fig. 2b). At pH 4, I = 0.001 M and 200°C (Fig. 2c), 1,5-NDS appears to be stable while at higher ionic strength, the stability decreases (Fig. 2d). The stability of 2-NSA is not affected at pH 4 and 200°C (Fig. 2c,d).

At pH 9.85, I = 0.001 M and 200°C (Fig. 2e), both 1,5-NDS and 2-NSA are relatively unaffected, nevertheless, detectable amounts of other tracers are formed, supposedly at the expense of 1,5-NDS. At higher ionic strength (Fig. 2f), degradation of 1,5-NDS is evident, however, because of small quantities of the other tracers in the blank it is not possible to gauge their formation. Again, the stability of 2-NSA is not affected at pH 9.85 and 200°C (Fig. 2 e,f).

At 300°C, at the above conditions (Fig. 2a-f), all experiments show that 1,5-NDS has been degraded. The stability of 2-NSA, however, appears variable with most lost at pH 3, I = 0.001 M and pH 9.85, I = 0.001 M. At pH 9.85, I = 0.05 M, 2-NSA appears stable (Fig. 2f).

Results for pH = 9, collected to date, indicate that 1,5-NDS and 2-NSA remain relatively stable to 300°C (Fig. 2g,h).

4. DISCUSSION

4.1 Protonation

Unlike most electrophilic aromatic substitution reactions, sulfonation/desulfonation is reversible. According to Bruckner (2010), benzene sulfonic acid can be protonated by addition of protons and heat (Fig. 3). Benzenesulfonic acid ($C_6H_6O_3S$) is a strong acid with the pK_a = -2.7 (Guthrie, 1977) which dissociates to electrophilic $C_6H_5SO_3^-$ and H^+. Excess protons attach to electrophile to create the carbocation. The addition of heat causes replacement of SO_3^- with H^+ creating benzene and sulfur trioxide (Fig. 3). The process that occurs is dependent on the concentration of protons. A large excess of protons causes the reverse reaction where bezenesulfonic acid is formed. It is assumed that the naphthalene sulfonic acids act similarly.

Figure 2a shows the percentage of tracers in a pH 3 solution at low ionic strength. At 200°C, 2-NSA is thermally stable. However, at 300°C both 1,5-NDS and 2-NSA are being degraded. This may be the consequence of the extra enthalpy required for the protonation mechanism. Solutions at the same pH but higher ionic strength show the same pattern (Fig. 2b), except 1,5-NDS at 200°C where the salt effect stabilises the acid molecule (Dashkevich *et al.*, 2014).

Solutions at pH 4 indicate that the necessary catalytic amount of protons in solution was not achieved to commence naphthalene protonation. At 300°C 1,5-NDS, as the lowest stable isomer, undergoes degradation at both ionic strengths. The low stability of 1,5-NDS at 0.05 M ionic strength solution needs to be explained.

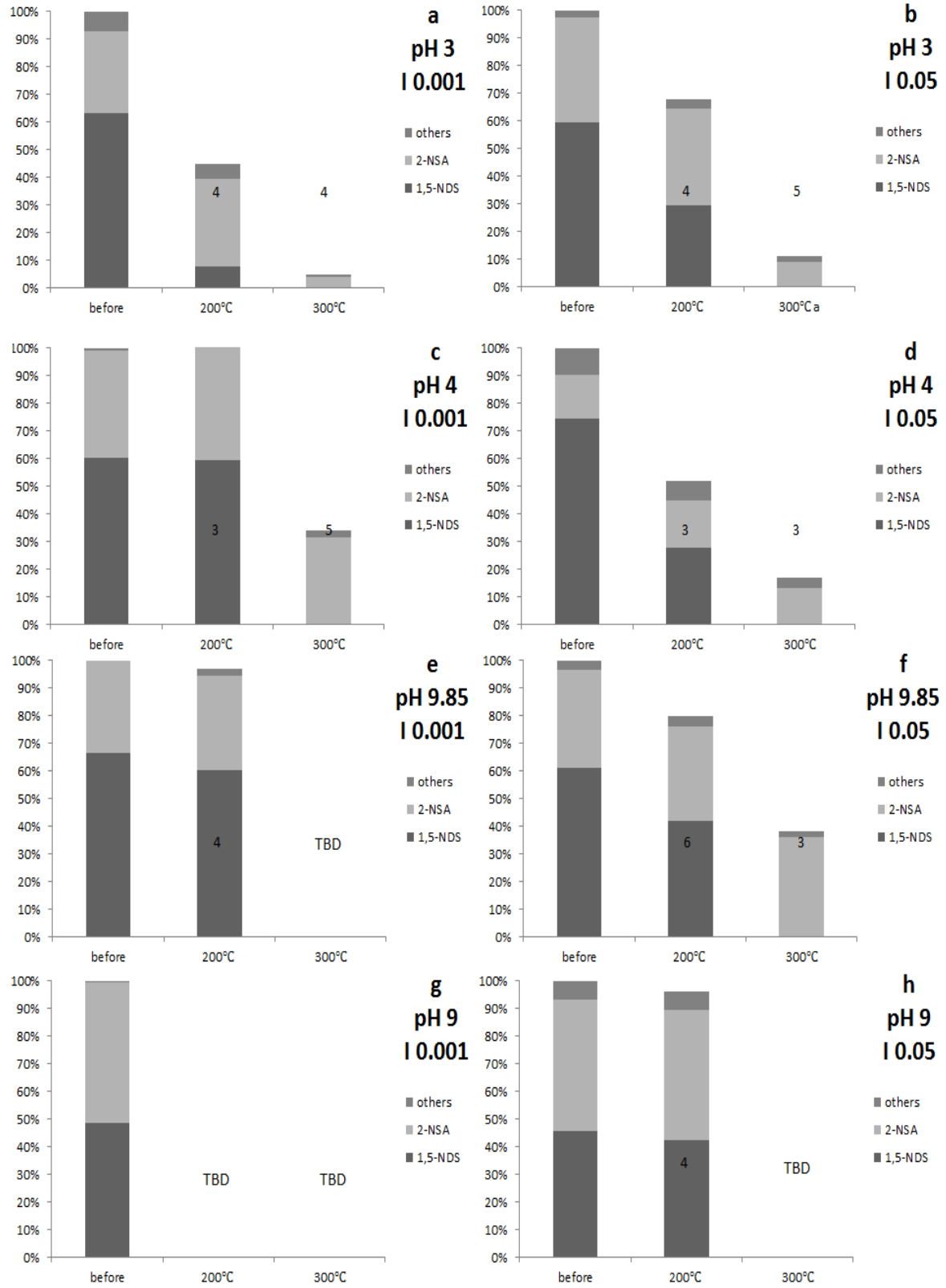


Figure 2. Percentage of tracers in sample before and after heating at 200°C and 300°C for 40 hours. Other tracers found include 2,6-NDS, 2,7-NDS, 1,6-NDS, 1-NSA. Numbers on bars = number of replicates. I = ionic strength (M). TBD = to be done.

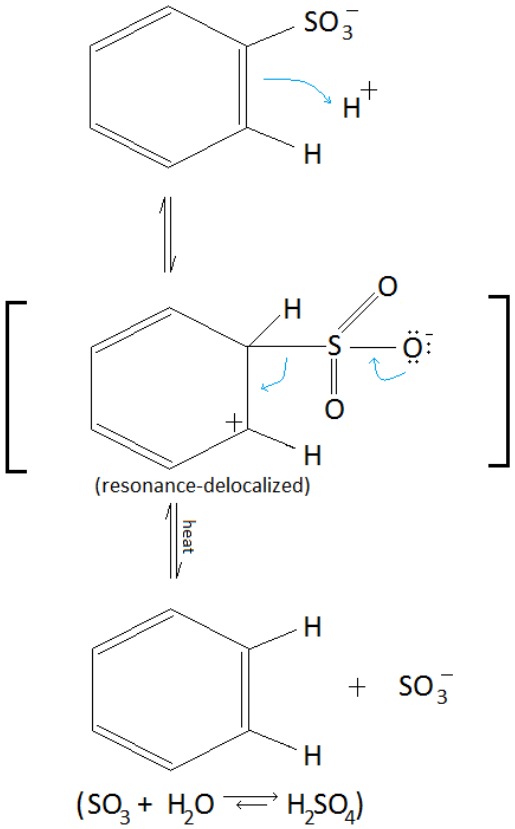


Figure 3. Benzenesulfonate acid desulfonation reaction mechanism (Bruckner, 2010).

4.2 Steric hindrance and the kinetics of reaction

The low thermal stability of 1,5-NDS can be explained by two mechanisms: steric hindrance and kinetics. The SO_3 substitution on C^1 interacts with C^8-H bond, at the same time, the SO_3 group attached to C^5 interacts with C^4-H, hence steric hindrance which causes 1,5-NDS to be more unstable (Fig. 4). Substitutions in positions C^1 and C^5 are favoured under kinetic control as α-substitution has a lower activation energy. With the increase in temperature, the C^2 position is favoured as it requires a higher activation energy.

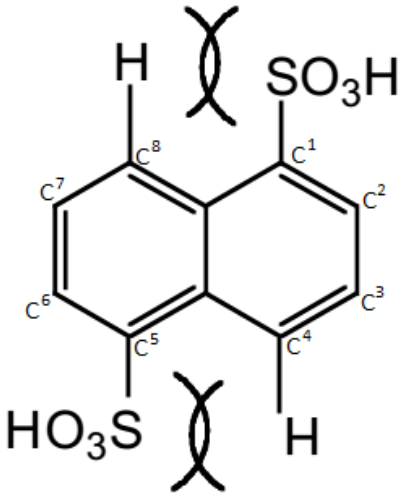


Figure 4. The steric hindrance in 1,5-NDS.

Table 1. Tracers concentration in the blank samples (ug kg^{-1}). ∑= 2,6-NDS + 2,7-NDS + 1,6-NDS + 1-NSA + 2-NSA. I- ionic strength (M).

pH	I	2,6-NDS	1,5-NDS	2,7-NDS	1,6-NDS	1-NSA	2-NSA	∑
3	0.001	0.37	20.14	0.62	1.13	0.16	9.46	0.37
3	0.050	0.80	19.35	0.00	0.00	0.00	12.34	32.49
4	0.001	0.05	20.73	0.05	0.15	0.00	13.38	34.36
4	0.050	1.33	19.55	0.44	0.63	0.17	4.07	26.19
9	0.001	0.00	9.66	0.02	0.04	0.01	10.20	0.00
9	0.050	1.34	9.14	0.00	0.00	0.00	9.43	1.34
10	0.001	0.00	21.18	0.00	0.00	0.00	10.58	31.76
10	0.050	1.14	19.30	0.00	0.00	0.00	11.13	31.57

5. CONCLUSIONS

An experimental study of 1,5-NDS and 2-NSA stability at pH = 3, 4, 9, 9.85 at 200 and 300°C and two ionic strengths (0.001M, 0.05M) has been conducted. The exposure time was 40 hours.

The results show the following:

1) 1,5-NDS is not stable at 300°C, pH 3, 4, 9 and 9.85, I = 0.001M, 0.05M;
2) 1,5-NDS is stable at 200°C, pH 4, I=0.001 M;
3) the low thermal stability of 1,5-NDS can be explained by two mechanisms: steric hindrance and kinetics;
4) 2-NSA is stable at 200°C pH: 3, 4, 9 and 9.85, I = 0.001M, 0.05M;
5) the thermal stability of 2-NSA at 300°C is independent of ionic strength;
6) according to the results to date, 2-NSA is thermally stable at 300°C and pH 9.85, I = 0.05 M;
7) there is no isomerisation of 1,5-NSA to 2-NSA;

8) significant concentrations of isomerisation products were not observed.

Further investigations of the stability at pH between 3 and 10 and varying ionic strength and temperature are underway.

ACKNOWLEDGEMENTS

The authors would like to thank Mercury for providing funding for this work. LS benefits from a Victoria University of Wellington Scholarship. Support was also provided by the Government of New Zealand through funding for the GNS Geothermal Resources of New Zealand research programme.

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