PROCEEDINGS, 42nd Workshop on Geothermal Reservoir Engineering
Stanford University, Stanford, California, February 13-15, 2017
SGP-TR-212

The pH dependent thermal stability of the naphthalene sulfonic acids 1,5-NDS and 2-NSA

Lucjan Sajkowski[1,2,*], Bruce W. Mountain[1] and Terry M. Seward[2]

[1]GNS Science, Department of Geothermal Sciences, Wairakei, New Zealand

[2]School of Geography, Environment and Earth Sciences, Victoria University of Wellington, New Zealand

[*]l.sajkowski@gns.cri.nz

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

ABSTRACT

The overall goal of our experimental studies is to investigate physicochemical factors that affect the stability of the naphthalene sulfonic acids under geothermal conditions. These organic compounds are heavily used in the geothermal industry as tracer chemicals, thus, understanding their thermal stability is crucial to their successful utilization. In our experiments, 1,5-naphthalene disulfonic acid (1,5-NDS), the least thermally stable of the NDS molecules, and 2-naphthalene sulfonic acid (2-NSA), the most thermally stable, were used. The objective was to investigate the effect of pH and ionic strength on the thermal stability and to determine the breakdown products.

The experiments were conducted using glass ampoules sealed by oxy-acetylene torch and placed in cold-seal autoclaves. Temperatures used were 200°C and 300°C, pH was varied and ionic strength (I) ranged between 0.001 M and 0.05 M. The duration of the experiments was 40 hours. Tracers were analyzed by high performance liquid chromatography (HPLC) using fluorescence detection and standard methods. The pH dependence of the thermal stability of 1,5-naphthalene disulfonate and 2-naphthalene sulfonate have been investigated.

The results show that:

1) 1,5-NDS is not stable at 300°C and 200°C, pH = 3.0 – 7.4, I = 0.001 M, = 0.05 M;
2) the low thermal stability of 1,5-NDS can be explained by two effects: steric hindrance and kinetics;
3) 2-NSA is stable at 200°C pH = 4.0 – 7.4, I = 0.05 M;
4) 2-NSA is stable at 200°C pH = 5.0 – 7.4, I = 0.001 M;
5) the stability of 2-NSA at 300°C is independent of ionic strength above pH = 4.2;
6) 2-NSA is thermally stable at 300°C and pH = 4.2 – 7.4, I = 0.05 M;
7) 1-NSA is a breakdown product of 1,5-NDS decomposition after 40 hours at pH 5.2 – 7.2, I = 0.05 M and 0.001 M, at 300°C.

Further experiments are underway to confirm and expand our knowledge of the thermal stability and kinetics of breakdown of these tracers.

1. INTRODUCTION

Well-managed geothermal resources are examples of clean, reliable, and renewable energy. The increasing demand worldwide for geothermal energy has driven an upsurge in the development of these energy sources. Nevertheless, constant improvements in technology and application of new scientific results are necessary to keep up with the rapidly changing needs and ensure more efficient use of geothermal energy.

Chemical tracers are a powerful tool used by the geothermal industry to manage geothermal reservoirs. A chemical compound can be used as the tracer if it meets several criteria, including thermal stability, low detection limit, low natural background concentration, non-absorptivity, non-toxicity and affordability. They are used in reservoir tests to track fluid flow between injection and production wells and to provide information on the hydrodynamics parameters of the reservoir. Return curves can be analyzed to understand reservoir properties relating to permeability, providing important inputs to numerical models and ultimately informing geothermal operators of the risks of thermal breakthrough.

In the last two decades, several studies have been conducted on the suitability 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 injecting different compounds or isomers into different wells. The compounds are easily differentiated by High Performance Liquid Chromatography (HPLC). Testing more than one well at a time reduces sampling and analysis cost per well when 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. Acid-dosed re-injection brine (from Nga Awa Purua power station) ~pH 5.0 (Winick et al, 2016) 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 380ºC, 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 deionized 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 utilized was 200-300ºC 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 containing solutions of different pH values. Each set includes the two ionic strengths (0.001 M and 0.05 M). 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).

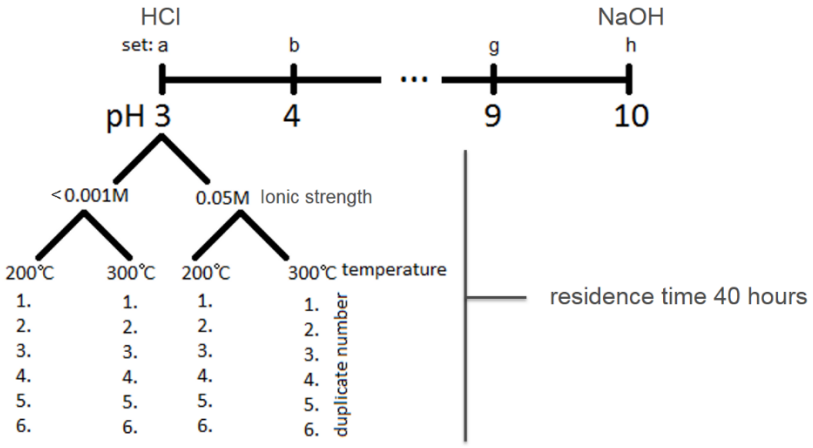

Figure 1: Experimental protocol.

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 tubes 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. Twenty-four 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 about 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 normalized combined concentrations of all sulfonate tracers after heating versus experimental pH. Each line represents solutions with different ionic strengths 0.05 M (blue) and 0.001 M (green). The pH was calculated using the Geochemist's Workbench® software package.

At 200°C and I = 0.05 M, total concentration of naphthalene sulfonates tracers is stable at pH = 5.0 – 7.4, below pH = 5.0 their stability decreases with decreasing pH (Fig. 2A). However, at 200°C and I = 0.001 M, total fluorescence suggests that tracers are stable only

above pH = 6.3. At 300°C total normalized tracer concentration is always below one (Fig. 2B), however, the rate of degradation is dependent on ionic strength and, in particular, the solution pH.

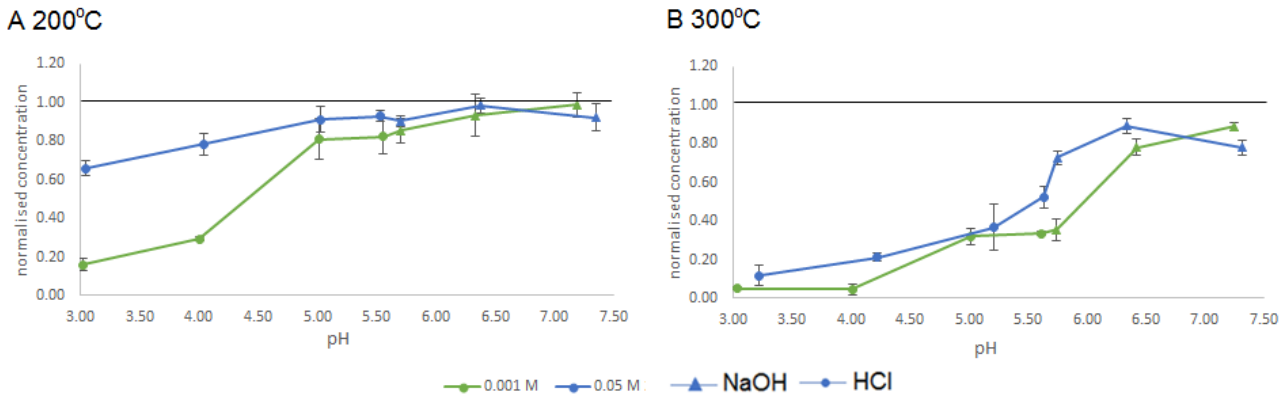

Figure 2: Normalized total fluorescence versus pH at 200°C (A) and 300°C (B). The blue line represents I = 0.05 M and the green line I = 0.001 M. Peak response was normalized using total fluorescence of the blank at 25°C. The black horizontal line represents no change in total fluorescence. Triangles represent solutions treated with NaOH, circles represent solutions treated with HCl. Vertical bars represent one standard deviation.

Normalized concentrations of individual sulfonates (2-NSA and 1,5 NDS) at 200°C and 300°C are shown in the Figure 3 plotted versus experimental pH. At 200°C and I = 0.001 M, 2-NSA is stable at pH = 5.0 – 7.4 (Fig. 3A). 1,5-NDS is not stable over the entire pH range. The stability of 1,5-NDS does increase with increasing pH, particularly between pH 4 and 5. At 200°C and I = 0.05 M, 2-NSA is stable from pH 4 to 7, in contrast to 1,5-NDS, which is unstable throughout this pH range (Fig. 3B).

At 300°C, all data show that 1,5-NDS has been significantly degraded. The stability of 2-NSA, however, appears variable with most lost at pH = 3.0 – 5.7, I = 0.001 M and pH = 3.2 – 4.2, I = 0.05 M. At pH = 4.2 – 7.4, I = 0.05 M, 2-NSA appears stable (Fig. 3D), likewise, at pH = 6.4 – 7.3, I = 0.001 M.

Normalized 1-NSA concentrations versus pH are shown in the Figure 4. 1-NSA appears as a breakdown product at 300°C after 40 hours, pH = 5.2 – 7.2. At 300°C, I = 0.05 M, the highest concentration of 1-NSA is found at pH = 5.8 (Fig. 4A), and pH = 6.3 for I = 0.001 M (Fig. 4B). After 40 hours at 200°C 1-NSA is not present.

There was no evidence of isomerization of 1,5-NDS to 2-NSA.

4. DISCUSSION

4.1 Protonation

Unlike most electrophilic aromatic substitution reactions, sulfonation/desulfonation is reversible. According to Bruckner (2010), benzenesulfonic acid can be protonated by addition of protons and heat (Fig. 5). Benzenesulfonic acid ($C_6H_6O_3S$) is a strong acid with the pKa = -2.7 (Guthrie, 1977) which dissociates to electrophilic $C_6H_5O_3S^-$ and H^+. Excess protons attach to the electrophile to create a carbocation. The addition of heat causes replacement of $-SO_3^-$ with H^+ creating benzene and sulfur trioxide (Fig. 5). The process that occurs is dependent on the concentration of protons. It is assumed that the naphthalene sulfonic acids act similarly.

At 200°C, pH = 3.0 – 5.0, 2-NSA and 1,5-NDS are not thermally stable, however, above pH = 5.0, 2-NSA is stable (Fig. 3A). At 300°C both 1,5-NDS and 2-NSA are being degraded at pH = 3.0 – 6.5 for 2-NSA and pH 3.0 – 7.4 for 1,5-NDS (Fig. 3C). This may be attributed to the extra enthalpy required for the protonation mechanism. Solutions at the same pH but higher ionic strength show different results (Fig. 3B, D), except pH = 3.0 – 4.2 where both tracers are not stable. Stability of molecules in higher ionic strength solution can be explained by the salt effect that stabilizes the acid molecule (Dashkevich et al., 2014). High salt concentrations "shield" the negative charges on each sulfonate. When the charges are not shielded at low salt concentrations, the stability of naphthalene sulfonates decreases due energetically more favorable breakdown products.

For solutions above pH = 5.0 at 200°C and low ionic strength (Fig. 3A), the necessary catalytic amount of protons in solution was not available to cause naphthalene protonation. At 300°C 1,5-NDS, however, is sufficiently unstable that it undergoes degradation at both ionic strengths (Fig. 3C, D).

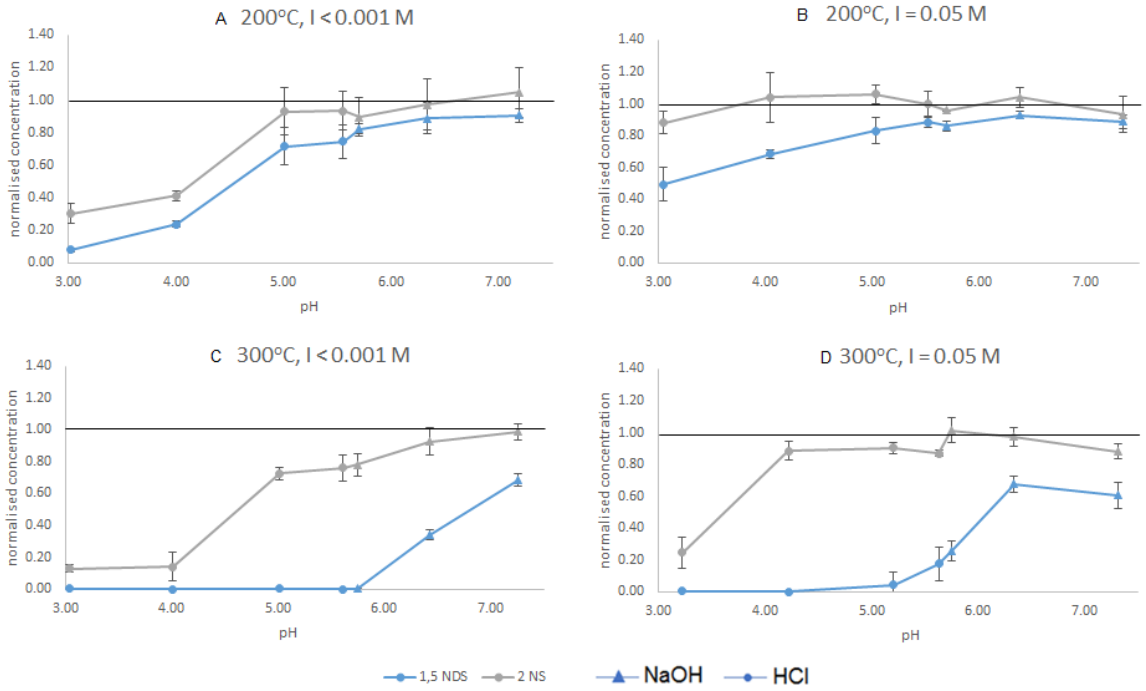

Figure 3: Normalized 2-NSA and 1,5-NDS concentrations versus experimental pH at 200°C and 300°C, I = 0.001 and 0.001. Blue lines represent 1,5-NDS and grey, 2-NSA. Peak response was normalized using total fluorescence of the blank at 25°C. The black horizontal line represents zero change in total fluorescence. Triangles represent solutions treated with NaOH and circles represent solutions treated with HCl. Vertical bars represent one standard deviation.

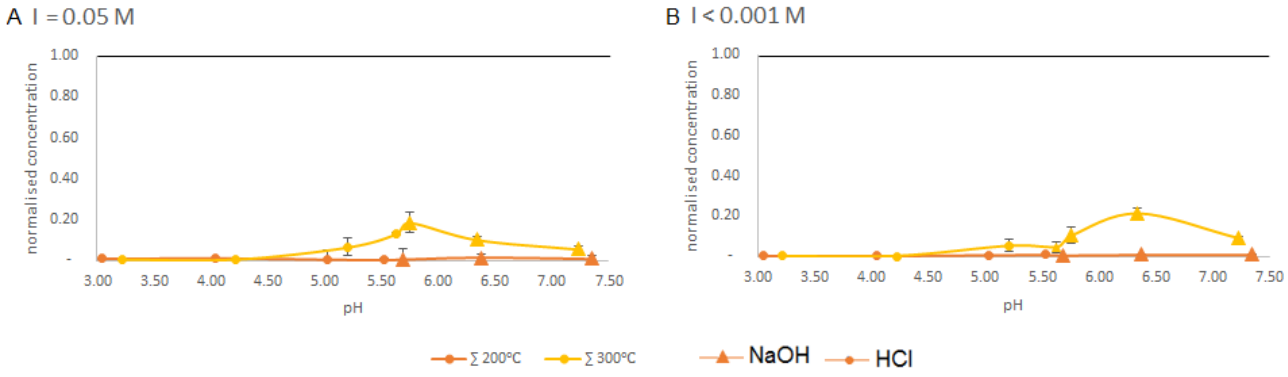

Figure 4: Normalized 1-NSA concentration versus pH at 200°C and 300°C, I = 0.05 M and I = 0.001 M (B). The yellow line represents concentrations at 300°C and the orange at 200°C. Peak response was normalized using total fluorescence of the blank at 25°C. The black horizontal line represents no change in total fluorescence. Triangles represent solutions treated with NaOH. Circles represent solutions treated with HCl. Vertical bars represent one standard deviation.

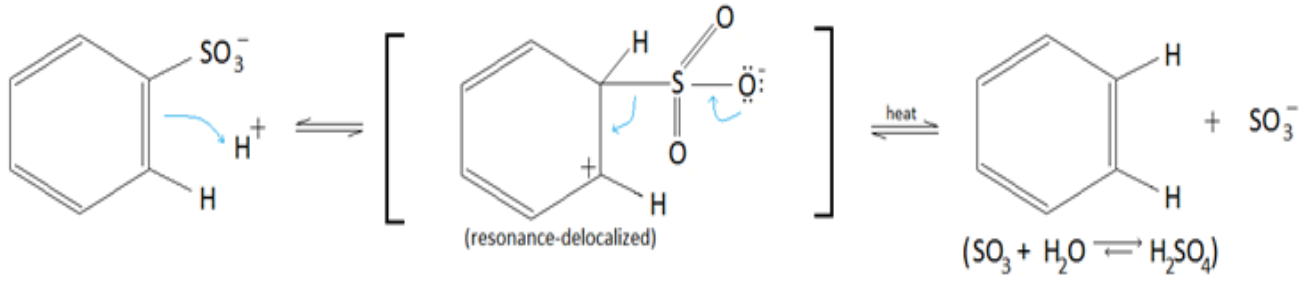

Figure 5: The benzenesulfonic acid desulfonation reaction mechanism (Bruckner, 2010).

4.2 Steric hindrance and reaction kinetics

The low thermal stability of 1,5-NDS can be explained by two effects: steric hindrance and kinetics. Steric hindrance occurs when atoms in a molecule physically interfere with each other. This can lower the molecules thermal stability. 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. This causes 1,5-NDS to be more unstable (Fig. 6). Substitutions in positions C^1 and C^5 are favored by kinetics as α-substitution has a lower activation energy then β-substitution. With the increasing temperature, the C^2 position is favored as it requires a higher activation energy.

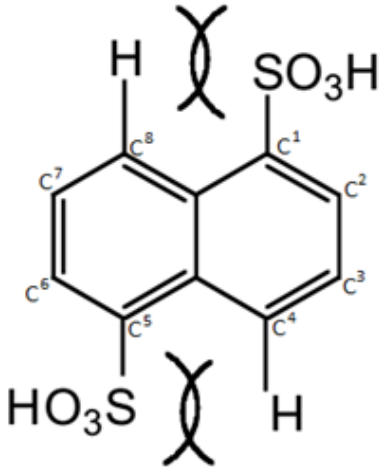

Figure 6: Steric hindrance in the 1,5-NDS molecule.

5. CONCLUSIONS

An experimental study of 1,5-NDS and 2-NSA stability at pH = 3.0 – 7.4, 200°C and 300°C, and two ionic strengths (0.001 M and 0.05 M) has been conducted. The length of all experiments was 40 hours.

The results show the following:

1) 1,5-NDS is not stable at 300°C, pH = 3.0 – 7.4, I = 0.001 M, 0.05 M;
2) the low thermal stability of 1,5-NDS can be explained by two effects: steric hindrance and kinetics;
3) 2-NSA is stable at 200°C pH = 4.0 – 7.4, I = 0.05 M;
4) 2-NSA is stable at 200°C pH = 5.0 – 7.4, I = 0.001 M;
5) 1-NSA is a breakdown product of 1,5-NDS decomposition after 40 hours at pH 5.2 – 7.2, I = 0.05 M and 0.001 M, at 300°C;
6) there is no detectable isomerization of 1,5-NSA to 2-NSA;
7) stability of 1,5-NDS and 2-NSA increases with increasing pH and ionic strength of the solution.

Further investigations of the stability at pH between 3.0 and 7.4 with extended experiment duration are underway.

ACKNOWLEDGEMENTS

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

REFERENCES

Adams, M.C., Moore, J.N., Fabry, L.G., and Ahn, J. H.: Thermal Stabilities of Aromatic Acids as Geothermal Tracers, *Geothermics*, **21** (3), (1992), 323–339.

Bruckner, R: Organic Mechanisms, Reactions, Stereochemistry and Synthesis. Springer-Verlag Berlin Heidelberg. (2010).

Dashkevich, Y.G., Mountain, B.W., Seward, T.M. and Winick, J.A.: Temperature Stability of 1,5-Naphthalene Disulfonate at Simulated Geothermal Conditions, *Proceedings,* New Zealand Geothermal Workshop, 2-6. (2014).

Dashkevich, Y.G., Mountain, B.W. and Winick, J.A.: Temperature Stability of Naphthalene Sulfonic and Naphthalene Disulfonic Acids at Geothermal Conditions, *Proceedings,* World Geothermal Congress Melbourne, 3–7. (2015).

Guthrie, J.P.: Hydrolysis of Esters of Oxy Acids: P K A Values For Strong Acids; Brønsted Relationship for Attack of Water at Methyl; Free Energies o Hydrolysis of Esters of Oxy Acids; And A Linear Relationship Between Free Energy Of Hydrolysis And P K A Holding Over a Range Of 20 P K Units, *Canadian Journal of Chemistry*, **56** (17), (1978), 2342-2354.

Mountain, B.W. and Winick, J.A.: The Thermal Stability of the Naphthalene Sulfonic and Naphthalene Disulfonic Acids Under Geothermal Conditions: Experimental Results and a Field-Based Example, *Proceedings*, New Zealand Geothermal Workshop, Auckland, New Zealand 19-21 November (2012).

Rose, P.E., Benoit, D. and Kilbourn, P: The Application of the Polyaromatic Sulfonates as Tracers in Geothermal Reservoirs. *Geothermics*, **30**, (2001), 617 – 640.

Rose, P. E., Goranson, C., Salls, D. and Kilbourn, P: Tracer Testing at Steamboat Hills, Nevada, Using Fluorescein and 1,5-Naphthalene Disulfonate, *Proceedings*, 24th Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, CA. (1999).

Winick, J.A., Addison, S., Sewell, S., Buscarlet, E., Hernandez, D. and Siega, F.: The Geochemical Response of the Rotokawa Reservoir to the First Five Years of Nga Awa Purua Production, *Proceedings*, 41st Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, CA. (2016).