Proceedings World Geothermal Congress 2020+1
Reykjavik, Iceland, April - October 2021

Experimental Determination of Rate Constants for the Breakdown of the Organic Tracers 2-NSA, 2,6-NDS, 2,7-NDS, 1,5-NDS and 1,6-NDS Under Geothermal Conditions

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

ABSTRACT

Naphthalene sulfonates are widely used in the geothermal industry as tracers. Experimental results show, however, that these compounds do have their temperature limits. Knowledge of the rate of thermal breakdown is essential to ensure successful tracer tests. In addition, information on 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 geothermal environments.

The experiments were conducted to measure the rate of the thermal breakdown reactions. Five polyaromatic (di)sulfonates: 1,5-naphthalene disulfonate (1,5-NDS), 1,6-naphthalene disulfonate (1,6-NDS), 2,6-naphthalene disulfonate (2,6-NDS), 2,7-naphthalene disulfonate (2,7-NDS) and 2-naphthalene sulfonate (2-NSA) were studied. Aqueous solutions containing NDS/NSA were sealed inside glass ampoules using an oxy-acetylene torch and placed in cold-seal pressure vessels. These were exposed to between 200°C and 330°C for different times from 20 hours to 3 months. The experimental solution consisted 0.05M NaCl at neutral pH. The various naphthalene sulfonates were analysed by high performance liquid chromatography (HPLC) using fluorescence detection.

The rate constants were estimated by least squares fitting of the results. These show that NDS breakdown rates are temperature dependent. Stability increased as follow: 1,5-NDS<1,6-NDS<2,6-NDS/2,7NDS <2-NSA. Additionally, 2-NSA and 1-NSA were detected as breakdown products of naphthalene disulfonates. 2-NSA and 1-NSA were not stable at 300˚C.

1. INTRODUCTION

The efficiency of geothermal energy production is improved by evaluating geothermal reservoir properties resulting 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 must 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 the limits of their thermal stability is needed.

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

The thermal stability of aromatic compounds used for geothermal tracers has been the subject of research during the last two decades. These previous studies included 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 reactors to investigate 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. The concentrations of both 2-NSA and 2,7-NDS remained apparently unchanged at 330°C after one week.

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 geothermal 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 in 2-NSA up to 380 ºC. At 390ºC, all tracers were thermally unstable.

The influence of the reservoir pH 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.

In the current study, the stabilities of 1,5-NDS, 1,6-NDS, 2,6-NDS and 2,7-NDS were investigated at constant tracer concentration using 0.05M NaCl solution of neutral pH. The aim is to determine the rate constants for the thermal breakdown of the naphthalene disulfonates and to investigate possible isomerization processes.

2. METHOD

Several series of experiments were conducted to determine the stability of naphthalene sulfonates at elevated temperatures. All of experiments were designed to obtain kinetic data for the for five polyaromatic sulfonates: 1,5-NDS, 1,6-NDS, 2,6-NDS, 2,7-NDS and 2-NSA. 1-NSA was not present in the starting solution.

Six series of quartz glass tubes were prepared for reaction at different experimental temperatures (200°C, 225°C, 250°C, 270°C, 300°C and 330°C). Each series consisted of six to eight subsets subjected to different exposure times (20 hours to ~3 months). Six replicates for each temperature were prepared such that one set comprised 36 to 48 tubes. All experiments had the same initial composition. Each tube contained a starting solution of de-oxygenated NaCl solution with naphthalene (di)sulfonates: 1,5-NDS, 1,6-NDS, 2,6-NDS, 2,7-NDS and 2-NSA (Table 1.). The tubes were evacuated and sealed using an oxygen-acetylene torch. The tubes were enclosed in standard cold-seal pressure vessels and placed in an oven at the appropriate temperature.

Table 1: Composition of experimental solutions.

Na^+	Cl^-	NaCl	$pH_{25°C}$	1,5-NDS	2-NSA	1-NSA	2,6-NDS	2,7-NDS	1,6-NDS
mg l^{-1}		*mol l^{-1}*		*mol l^{-1}*					
1203	1757	0.05	~7.0	7.28E-08	1.19E-07	n.d.	8.40E-08	6.85E-08	7.89E-08

n.d. = below detection limit, i.e 1.40E-10 mol l^{-1} for the NDS and 1.93E-09 mol l^{-1} for NSA

2.1 Analytical methods

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

2.2 Determination of the rate constants

The measured log molal concentrations after different heating times were used to obtain the rate constant k (Table 2.). The data were fitted using GraphPad Prism 7.03 software which employs a linear least squares procedure. The rate constants were utilized in Arrhenius plots of ln k versus inverse temperature (Figure 1.) and the activation energy and pre-exponential factor determined from theses plots are listed in Table 3.

Observations more than three standard deviations from mean were considered outliers and the Extreme Studentized Deviate test was applied (Ekezie and Ogu, 2013). When the P-value for each datum point was calculated to be lower than 0.05, the null hypothesis was rejected.

2.3 Speciation of solutions and calculation of pH

Calculation of the pH, degree of NaCl hydrolysis, and NaCl ion pairing at the experimental temperature and pressure was necessary to determine as these effects the composition of the experimental solutions at temperature. The concentrations of OH^-, H^+, Na^+, Cl^-, HCl^o and $NaOH^o$ were evaluated by considering the equilibrium relationships amongst the relevant species:

$$H_2O = H^+ + OH^- \tag{1}$$

$$Na^+ + H_2O = NaOH^{º} + H^+ \tag{2}$$

$$Cl^- + H_2O = HCl^{\circ} + OH^- \tag{3}$$

$$Na^+ + Cl^- = NaCl^{\circ} \tag{4}$$

The charge balance equation can be written:

$$m_{Na^+} + m_{H^+} = m_{Cl^-} + m_{OH^-} \tag{5}$$

Additionally, the Na and Cl species are constrained by the following two mass balance equations:

$$m_{Na_{total}} = m_{NaCl^{\circ}} + m_{Na^+} + m_{NaOH^{\circ}} \tag{6}$$

$$m_{Cl_{total}} = m_{NaCl^{\circ}} + m_{Cl^-} + m_{HCl^{\circ}} \tag{7}$$

The equilibrium constants at elevated temperatures for NaOH were taken from Ho et al. (2000), for HCl from Ho et al. (2001), for NaCl from Ho et al. (1994), and finally for the water dissociation from Bandura and Lvov (2006). The Debye-Hückel equation (Helgeson, 1969) was used to calculate the individual ion activity coefficients, γ_i, for the charged species,

$$-log\gamma_i = \frac{Az_i^2\sqrt{I}}{1+B\mathring{a}_i\sqrt{I}} + \dot{B} \cdot I \tag{9}$$

where z is the charge of the species; A and B are constants whose values depend on the dielectric constant of the solvent and the temperature; å is the effective diameter of the species in the solution in Å (Kielland, 1937) and I is the ionic strength of the solution, in molal units given by:

$$I = \frac{1}{2}\sum m_i \cdot z_i^2 \tag{10}$$

where m is a molality of each species in the solution.

To calculate species distribution at temperature, a non-linear system of equations was solved numerically using the multiroot function according to Albarede (1995) within RStudio software linked to EqSolvR library (Mroczek and Mroczek, 2017). The pH values calculated at temperature are distinguished here by “t” subscripts (i.e. pH_t).

3. RESULTS AND DISCUSSION

During the experiments, 2-NSA behaved conservatively, while the other tracers (1,5-NDS, 1,6-NDS, 2,6-NDS and 2,7-NDS) showed evidence of thermal decay. 1-NDS was observed as a breakdown product of NDS decomposition, as previously observed by Dashkevich et al. (2015).

The measured rate constants are listed in Table 2. They show an increase in stability of the naphthalene sulfonic acids according to 1,5-NDS<1,6-NDS<2,6-NDS/2,7NDS<2-NSA. 2,6-NDS and 2,7-NDS were stable at 200°C, and possibly at 225°C, where k is close to zero for both 2,6-NDS and 2,7-NDS (0.001 ± 0.001 day^{-1} and 0.002 ± 0.002 day^{-1}, respectively). For all four NDS, their stability decreases with increase in temperature.

Table 2. Rate constants (day^{-1}) for the decomposition of 2-NSA, 2,6-NDS, 2,7-NDS and 1,6-NDS at different temperatures

Temperature/°C	$pH_{25°C}$	pH_t	2,6-NDS	2,7-NDS	1,6-NDS	1,5-NDS
				1st order reaction rate constant k/day^{-1}		
200	~7.0	5.6	<0.001	<0.001	0.002 ± 0.000	0.003 ± 0.001
225	“	5.6	0.001 ± 0.001	0.002 ± 0.002	0.012 ± 0.000	0.013 ± 0.002
250	“	5.6	0.005 ± 0.001	0.005 ± 0.002	0.017 ± 0.000	0.066 ± 0.002
270	“	5.6	0.021 ± 0.007	0.015 ± 0.001	0.085 ± 0.004	0.166 ± 0.007
300	“	5.7	0.049 ± 0.008	0.039 ± 0.002	0.245 ± 0.015	0.839 ± 0.044
330	“	5.7	0.120 ± 0.019	0.118 ± 0.021	0.806 ± 0.125	2.554 ± 0.076

Table 3. Arrhenius constants for the decomposition of 1,5-naphthalene disulfonate in Nga Awa Purua power station brine.

solution	T/ °C	experiment duration	$pH_{25°C}$	ionic strength/M	A_0/day^{-1}	Ea/KJ/mol	R^2	$T_{1/2}$/day at 300°C
1,5-NDS	200-330	Up to 3 months	~7.0	0.05	3.68e10	117	0.99	1
1,6-NDS	200-330	Up to 3 months	“	0.05	9.58e08	105	0.98	3
2,6-NDS	225-330	Up to 3 months	“	0.05	7.44e09	123	0.97	14
2,7-NDS	225-330	Up to 3 months	“	0.05	6.48e08	112	0.99	16

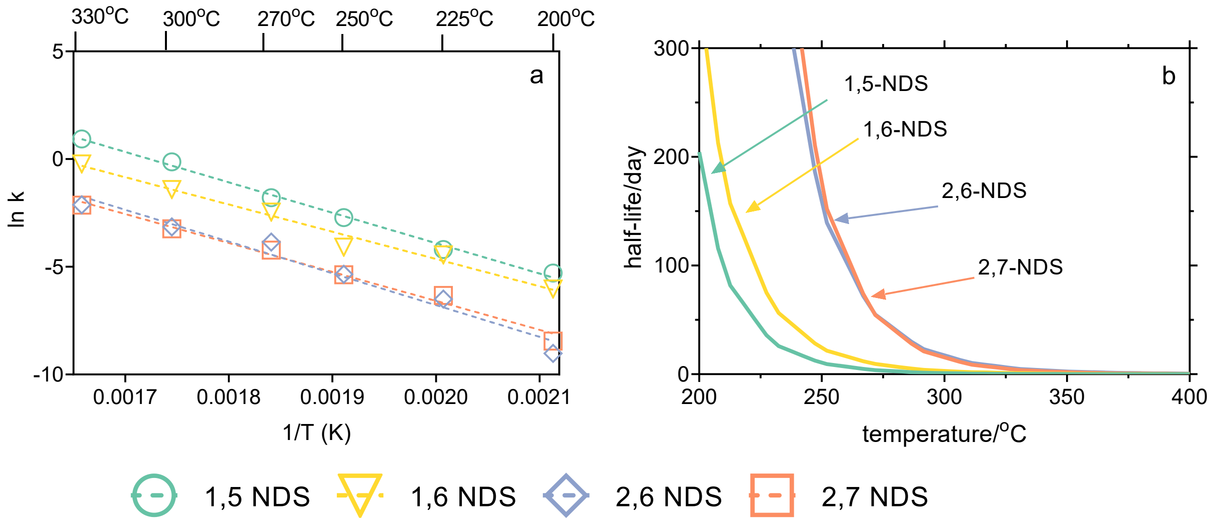


Figure 1: (a) Arrhenius plots of ln(k) vs. inverse temperature between 200°C and 330°C for 1,5-NDS, 1,6-NDS, 2,6-NDS and 2,7-NDS. (b) Plots of half-life vs. temperature based upon the Arrhenius decay data. 2-NSA was not plotted as it was stable at all experimental temperatures.

2-NSA is the most stable naphthalene sulfonate among the polyaromatic (di)sulfonates. Its higher stability is explained by two unequal bonding positions, α or β (1 or 2) of electrophilic substitution (Figure 2). Substitution into the α position is favoured kinetically over substitution at the β position, however, the β carbon is thermodynamically more stable (Cerfontain and Telder 2010). Thus, 2-NSA is the most stable molecule over the experiments. Moreover, 2-NSA concentration increased over time, and the increase was promoted by increases in temperature (Figure 3.). However, it is not possible to determine which of naphthalene disulfonate isomers contributed the most in 2-NSA formation. 1,6-NDS, 2,6-NDS and 2,7-NDS disproportionated significantly at t ≥250°C, while at the same time, 2-NSA concentration increased. It is concluded that 2-NSA must constitute one of the breakdown products.

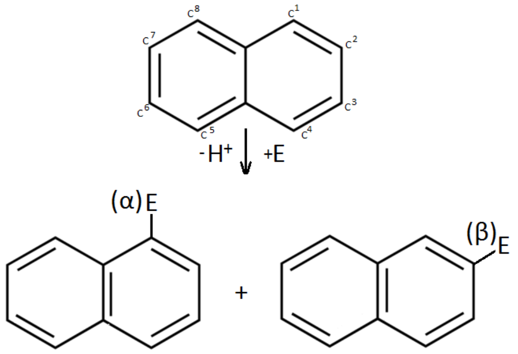


Figure 2: Electrophilic aromatic substitution in the naphthalene. E- electrophile α - position 1, β- position 2.

At 300°C, rapid increase in the concentration of 2-NSA over first two weeks (Figure 3.) was only temporary and reflected faster breakdown of naphthalene disulfonates. After two weeks, the 2-NSA concentration began to gradually decrease over time.

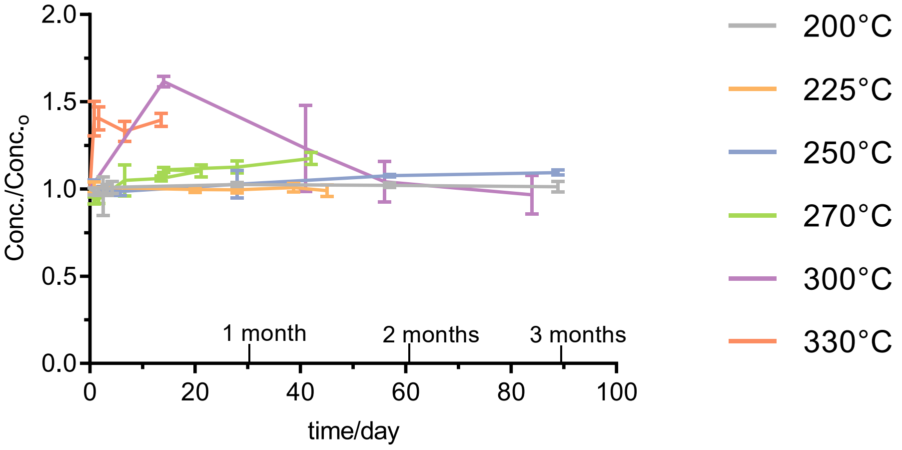


Figure 3: 2-NSA concentrations normalised to 2-NSA concentration at time 0 h for different temperatures between 200°C and 330°C. 1σ uncertainties are shown.

The isomer, 1-NSA, has also been observed as a decomposition product of NDS thermal decomposition (Mountain and Winick, 2012). In the current study, 1-NSA was detected at 225˚C M and above (Figure 4.) with its concentration increasing with increasing temperature. At 300˚C, 1-NSA exhibited a rapid increase in concentration is observed a decrease after four days. At 330˚C, 1-NSA was stable up to 5 days.

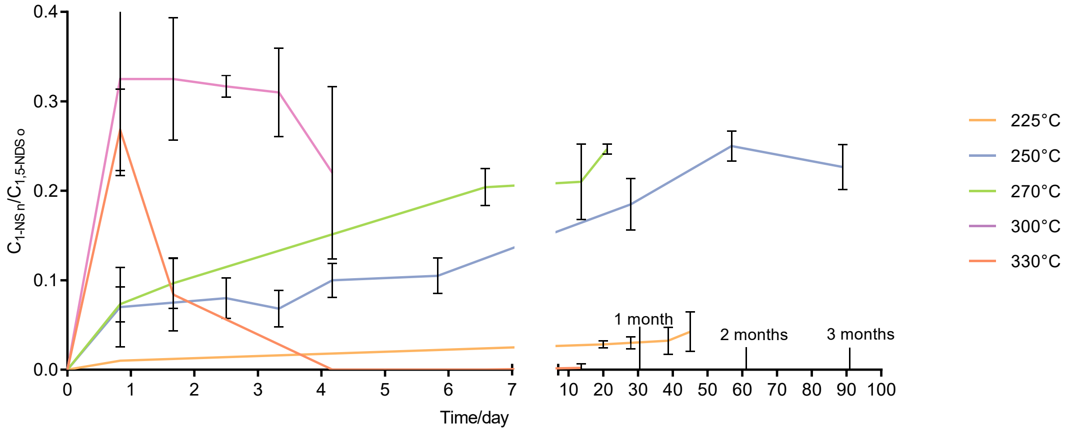
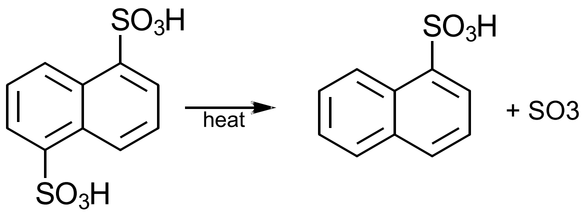


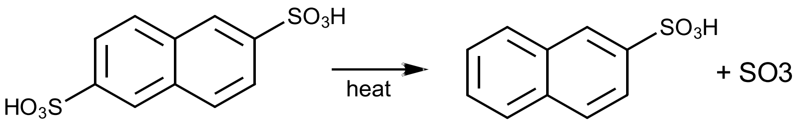
Figure 4: 1-NSA concentrations normalised to 1,5-NDS concentration at time 0 h for different temperatures between 200°C and 330°C. Graph includes standard deviation bars.

The experiments show that the breakdown of NDS produces 1-NSA and 2-NSA (Figure 3. and 4.). The rate of the reaction producing 1-NSA is dependent on the NDS breakdown rate. Loss of one $-SO_3$ group from, for example 1,5-NDS naphthalene results in the creation of 1-NSA:



(11)

while 2,6-NDS decomposition would occur as:



(12)

producing 2-NSA. This results in increases in 1-NSA and 2-NSA concentrations over time between 225°C and 330°C.

4. CONCLUSIONS

A series of experiments has been undertaken to investigate the thermal stability of 2-NSA, 1,6-NDS, 2,6-NDS and 2,7-NDS. They measured the thermal stability of the polyaromatic (di)sulfonates at pH_t= 5.7, at 200°C, 225°C, 250°C, 270°C, 300°C and 330°C in a NaCl 0.05M solution. The exposure time range between 20 hours and 3 months.

The results show the following:

- 2-NSA and 1-NSA are breakdown products of NDS,
- 2-NSA is the most stable of the naphthalene (di)sulfonates isomers,
- Stability increases according to 1,5-NDS<1,6-NDS<2,6-NDS/2,7NDS <2-NSA
- 1,5-NDS, 1,6-NDS, 2,6-NDS and 2,7-NDS stabilities decrease with increasing temperature;
- 2-NSA is stable at 250°C, pH = 5.6, I = 0.05 M for at least three months;
- 2-NSA breakdowns at $T \geq 300^{\circ}C$.

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., & Ahn, J.-H. Thermal stabilities of aromatic acids as geothermal tracers. Geothermics, 21(3), 323–339. (1992).

Addison, S., Winick, J. A., Mountain, B. W., & Siega, F. L., Rotokawa Reservoir Tracer Test History. In New Zealand Geothermal Workshop 2015 Proceedings. (2015a).

Addison, S., Winick, J. A., Sewell, S., Buscarlet, E., Hernandez, D., & Siega, F. L. Geochemical Response of the Rotokawa Reservoir to the First 5 Years of Nga Awa Purua. In Proceedings 37th New Zealand Geothermal Workshop. (2015b).

Albarède, F., Introduction to geochemical modelling. 318 – 340. (1995)

Bandura A. V., Lvov S. N., The ionization constant of water over wide ranges of temperature and density. Journal of Physical and Chemical Reference Data, 35, 1, 15 – 30. (2006)

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

Cerfontain H., Telder. A., Aromatic Sulfonation. Part XVI: Sulfonation of naphthalene and its monosulfonic acids in concentrated aqueous sulfuric acid. Recueil Des Travaux Chimiques Des Pays-Bas, 86(5), (2010).

Dashkevich, Y.G., Mountain, B.W., Seward, T.M., Winick, J.A. Temperature stability of 1,5-naphthalene disulfonate at simulated geothermal conditions. New Zealand Geothermal Workshop, 2-6. (2014).

Dashkevich, Y.G., Mountain, B.W., Winick, J.A. Temperature stability of naphthalene sulfonic and naphthalene disulfonic acids at geothermal conditions. World Geothermal Congress Melbourne, 3–7. (2015).

Ekezie, D.D., Ogu, A.I.: Statistical analysis/methods of detecting outliers in a univariate data in a regression analysis model. International Journal of Education and Research 1(5), 1-24. (2013).

Helgeson, H. C., Thermodynamics of hydrothermal systems at elevated temperatures and pressures. American Journal of Science 267, pp. 729-804. (1969)

Ho, P. C., Palmer, D. A., and Gruszkiewicz, M.S., Conductivity measurements of dilute aqueous HCl solutions to high temperatures and pressures using a flow-through cell. Journal of Physical Chemistry B, 105, pp. 1260-1266. (2001)

Ho, P.C., Palmer, D.A., Wood, R.H.,Conductivity measurements of dilute aqueous LiOH, NaOH, and KOH solutions to high temperatures and pressures using a flow-through cell. Journal of Physcial Chemistry B, 104, 12084-12089. (2000)

Ho, P.C., Palmer, D.A., Mesmer, R.E., Electrical conductivity measurements of aqueous sodium chloride solutions to 600°C and 300 MPa. Journal of Solution Chemistry 23, 997-1018. (1994)

Kielland J., Individual activity coefficients of ions in aqueous solutions. Journal of the American Chemical Society. 59, 1675-1678. (1937)

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

Mroczek S., Mroczek E., 2017. EqSolvR: Chemical Equilibrium Solver. R package version 1.1.0. https://github.com/shearwavesplitter/EqSolvR.

Nottebohm, M., Licha, T., Ghergut, I., Nödler K., Sauter, M.: Development of thermosensitive tracers for push-pull experiments in geothermal reservoir characterization. Proc. World Geothermal Congress, Bali, Indonesia, 25-29 April, (2010).

Sajkowski, L., Mountain, B.W., Seward T. M.,: The pH dependent thermal stability of the naphthalene sulfonic acids 1,5-NDS and 2-NSA. Proc. 42nd Workshop on Geothermal Reservoir Engineering Stanford University, Stanford, California, February 13-15, SGP-TR-212. (2017).

Sajkowski, L., Mountain, B.W., Seward T. M.,: The pH dependent thermal stability of the organic tracers 1,5-NDS and 2-NSA. Proc. 28th New Zealand Geothermal Workshop, Auckland, New Zealand 23-25 November (2016).

Rose, P.E., Benoit, D., Kilbourn, P.: The application of the polyaromatic sulfonates as tracers in geothermal reservoirs. Geothermics 30, 617 – 640. (2001).

Rose, P. E., Goranson, C., Salls, D., Kilbourn, P.: Tracer testing at Steamboat Hills, Nevada, using fluorescein and 1,5-naphthalene disulfonate. Proc. 24th Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, CA. (1999).