TEMPERATURE STABILITY OF 1,5-NAPHTHALENE DISULFONATE AT SIMULATED GEOTHERMAL CONDITIONS

Yaroslav G. Dashkevich[1,2], Bruce W. Mountain[1], Terry M. Seward[2], Jeffrey A. Winick[3]

[1]GNS Science, Wairakei Research Centre, Taupo, New Zealand

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

[3]Mighty River Power Limited, Rotorua, New Zealand

E-mail: Y.Dashkevich@gns.cri.nz

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

ABSTRACT

The thermal stability of 1,5-naphthalene disulfonate (1,5-NDS) has been investigated. It was subjected to a number of simulated geothermal environments in batch autoclave reactors. Experimental temperature was changed from 280 to 350℃. Exposure times were 10 and 40 hours. The results show strong dependence on the solution composition (salt concentration, pH and pOH). Comparison with published data shows lower 1,5-NDS stability when in isolation compared with a mixture of several naphthalene sulfonates. For most conditions no dependence on the initial tracer concentration is observed. Two decomposition mechanisms of pseudo-first order are suggested to explain 1,5-NDS behaviour.

1. INTRODUCTION

Chemical tracers are widely used in the geothermal industry to estimate enthalpies, reservoir properties, and the behaviour of re-injected fluid.

Aromatic sulfonates fulfill several requirements making them suitable for injection tests. These include: thermal stability, non-absorptivity, low detection limit, low background concentration, low environmental impact and low cost.

In the last twenty years, a number of studies on their thermal stability have been conducted including unsubstituted and substituted benzene sulfonic acids (Adams et al., 1992), naphthalene mono- (NSA), di- (NDS), and naphthalene trisulfonates (NTS) (Rose et al., 1999; Rose et al., 2001; Mountain and Winick, 2012).

Rose et al. (2001) tested the thermal stability of the naphthalene sulfonates (2-NSA, 1,5-NDS, 2,7-NDS, 1,3,6-NTS). They used a 25 µg/kg mixture in pH-buffered solutions sealed in quartz glass ampoules for seven days. The results showed moderate decomposition of 1,5-NDS and 1,3,6-NTS at temperatures of 310-330℃. No change in concentration of 2-NSA and 2,7-NDS was observed.

Mountain and Winick (2012) investigated the thermal stability of 100 µg/kg tracer mixture (1-NSA, 2-NSA, 1,5-NDS, 1,6-NDS, 2,6-NDS, 2,7-NDS) using a continuous-flow reactor at temperatures 270-390℃ in the presence of greywacke cuttings from a geothermal well. Estimated residence times were from 6 to 60 hours. They showed an increase in the thermal stability in the order 1,5-NDS, 1,6-NDS, 1-NSA, 2,6-NDS/2,7-NDS, and 2-NSA. At 300-340℃, they observed an increase in concentrations of 1-NSA and 2-NSA. At 390℃, all compounds almost completely decomposed.

These experiments provided information on the thermal stability of naphthalene sulfonates; however, they were conducted at diverse conditions, which hinder direct comparison between different experimental studies. For example, Mountain and Winick (2012) observed lower stability of 1,5-NDS while Rose et al. (2001) did not observe an increase in the concentration of the monosulfonates. Also, both studies used a mixture of naphthalene sulfonates that prevents investigation of possible interactions between compounds.

In our experiments we investigated the stability of 1,5-NDS using solutions of different concentrations (100 µg/kg, 1.5 mg/kg, 25 mg/kg) in various matrices, i.e., deionised water (DI), pH 6.5 phosphate buffer, geothermal re-injection brine from the Nga Awa Purua power station (NAP) and a 0.4 mole/kg solution of NaCl (to simulate a concentrated geothermal brine), sealed in quartz glass tubes. The temperature range utilised was 260-350℃ and the experiment durations were 10 and 40 hours.

2. METHOD

Naphthalene mono- and disulfonates were sourced from Mighty River Power and Contact Energy. Solutions of the tracers (1 mg/kg) were analysed separately by HPLC. The purest powders were selected for further study. Almost all powders are impure with small amounts of other tracers present.

Tracer analysis was performed using reverse-phase paired-ion chromatography (Shimadzu Prominence HPLC with fluorescence detector, Waters Atlantis T3, 30x2.1 mm, 3 µm particle size column, and ThermoFisher BetaBasic C18, 10x4 mm, 3 µm particle size guard column). The excitation wavelength was 222 nm, emission wavelength was 338 nm. The mobile phase was 5 mM tetrabutyl ammonium phosphate (TBAP) in 27 v. % methanol/water. A solution of 1 M TBAP was purchased from Sigma-Aldrich. Methanol and water were HPLC gradient grade from ThermoFisher Scientific. Flow rate was 1.2 ml/min (with a backpressure of about 3200 psi). The column was kept at 35℃. The injection volume was 50 µL. A 10 point calibration was applied (1 µg/kg to 1 mg/kg). The quantification limit was 0.1 µg/kg for 1,5-NDS and 0.4 µg/kg for 1-NSA.

Deionised water (18.2 mΩ) made by Arium pro UV filter (Sartorius Stedium) and pH-modified (pH 4.2 at 25 ℃) low pressure separator brine from NAP power station located in the Rotokawa geothermal field were used for preparing experimental solutions.

The composition of the four different matrices used were: deionised water, pH 6.5 buffered (0.744 g/l of KH_2PO_4 and 0.424 g/l of Na_2HPO_4) deionised water, NAP brine (Table 1), and 23.4 g/l (0.4 M) solution of NaCl in deionised water. Each matrix was spiked with 1,5-NDS to obtain 25 mg/kg, 1.5 mg/kg, and 100 µg/kg concentrations. Due to the previous field tracer studies, the NAP brine contained several tracers with a maximum concentration 1.5 ppb (2-NSA).

Table 1. Composition of geothermal fluid from NAP used in the experiments. Concentrations in mg/kg. I = ionic strength (mole/l).

Na	618	SiO_2	1089
K	163	B	25
Ca	3.3	Li	7.7
Mg	0.2	Cl	1019
Fe	2.1	SO_4	124
Al	1.3	I	0.04

The experimental solutions were bubbled with nitrogen for 10 minutes in a 50 ml syringe then 1.5 ml aliquots were transferred into open quartz glass tubes (ID 7 mm, OD 9 mm) that were purged with nitrogen. The tubes were then temporarily covered with Parafilm and sealed using an oxygen-acetylene flame leaving about 2 ml of head space. The average time between transfer and sealing was about 20 minutes. Thirty six tubes (three for each concentration/matrix combination) were put into four 120 ml steel autoclaves. The remaining volume was half-filled with water to provide a confining pressure around the glass tubes. The autoclaves were placed into a 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 which they were cooled down to ambient temperature with cold water.

Since no change in concentration (compared with the initial solution) was observed after storing tubes for a week at ambient temperature in a dark room (Table 2), samples of the solutions taken before deoxygenating were used as controls. To keep track of the tubes, each was weighed before putting in the autoclave and then again after the experiment. The usual change in mass was about -3 mg, but when absolute weight change was more than 10 mg it was concluded that these tubes leaked and were discarded.

3. EXPERIMENTAL RESULTS

Figure 1 shows the concentration of naphthalene sulfonates after heating normalised to the total concentration in the control samples. There is no statistically significant correlation between initial concentration and relative amount of disulfonate decomposed, except for solutions made with deionised water. In this case, 1,5-NDS stability decreases with higher initial concentration at most conditions (Fig. 1a, b, d, e, g and j). At temperatures 295-325℃, in unbuffered solutions, it increases with the ionic strength (I) of the solution in most cases (Fig. 1d, e and f). A similar effect for the benzene sulfonic acids was reported by Adams et al. (1992). The benzene sulfonates were stable at temperatures up to 300℃ for 336 hours in geothermal water while they decomposed at the same conditions in distilled water (both solutions were deoxygenated). In buffered solutions, the decay rate is close to that in NaCl solutions, even though the ionic strength is only 0.006 M (Fig. 1a-d). At lower temperatures there is no difference in tracer concentration between NAP brine and NaCl solutions (Fig. 1a-b).

In unbuffered solutions we observed an increase in concentration of 1-NSA, which was present in the initial solution as a minor contaminant. Its stability increases similar to that of 1,5-NDS (Fig. 1). There was almost no 1-NSA remaining in most of the buffered solutions.

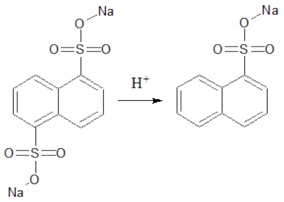
Unlike 1-NSA, there was no increase in 2-NSA or 1,6-NDS concentration, which indicates no isomerisation has occurred.

4. DISCUSSION

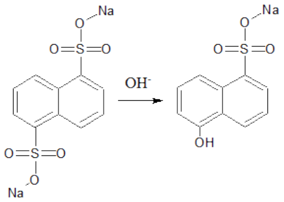
4.1 Reaction mechanism

Naphthalene sulfonates exist in the solution in the ionic form; therefore we can assume that the correlation between salt concentration in the solution and the tracer stability could be a result of the salt effect. Aromatic sulfonic acids have very low pKa values, e.g., for benzene sulfonic acid the pKa is -2.7 (Guthrie, 1977). They should be completely deprotonated at our experimental and typical geothermal conditions. We assume naphthalene sulfonic acids behave in a similar manner.

From the increase in 1-NSA concentration in the unbuffered solutions, we can assume that 1,5-NDS degradation takes place through electrophilic desulfonation:



Given the low concentration of 1-NSA in the buffered solutions, we expect decomposition to take another pathway. As at temperatures near 300℃ those solutions are characterised by low pOH (Fig. 2), it is possible to hypothesise the following reaction pathway:



This reaction is consistent with the observation by Rose and Clausen (2014) of 2-naphthol as a bi-product of 7-amino-1,3-naphthalene disulfonate decomposition.

Table 2. Average 1,5-NDS concentration in the control samples. Total = 2,6-NDS + 2,7-NDS + 1,6-NDS + 1-NSA + 2-NSA.

	Deionised water			Buffered solution			NAP		
	100 µg/kg	1.5 mg/kg	25 mg/kg	100 µg/kg	1.5 mg/kg	25 mg/kg	100 µg/kg	1.5 mg/kg	25 mg/kg
Initial solution									
1,5-NDS	105	1.59	25.7	107	1.57	25.5	105	1.56	25.3
Total	111	1.59	25.8	109	1.56	25.6	115	1.56	25.4
One week in a quartz glass tube at ambient temperature									
1,5-NDS	107	1.57	25.8	106	1.56	25.7	105	1.55	25.6
Total	111	1.60	25.9	110	1.56	25.8	108	1.56	25.7

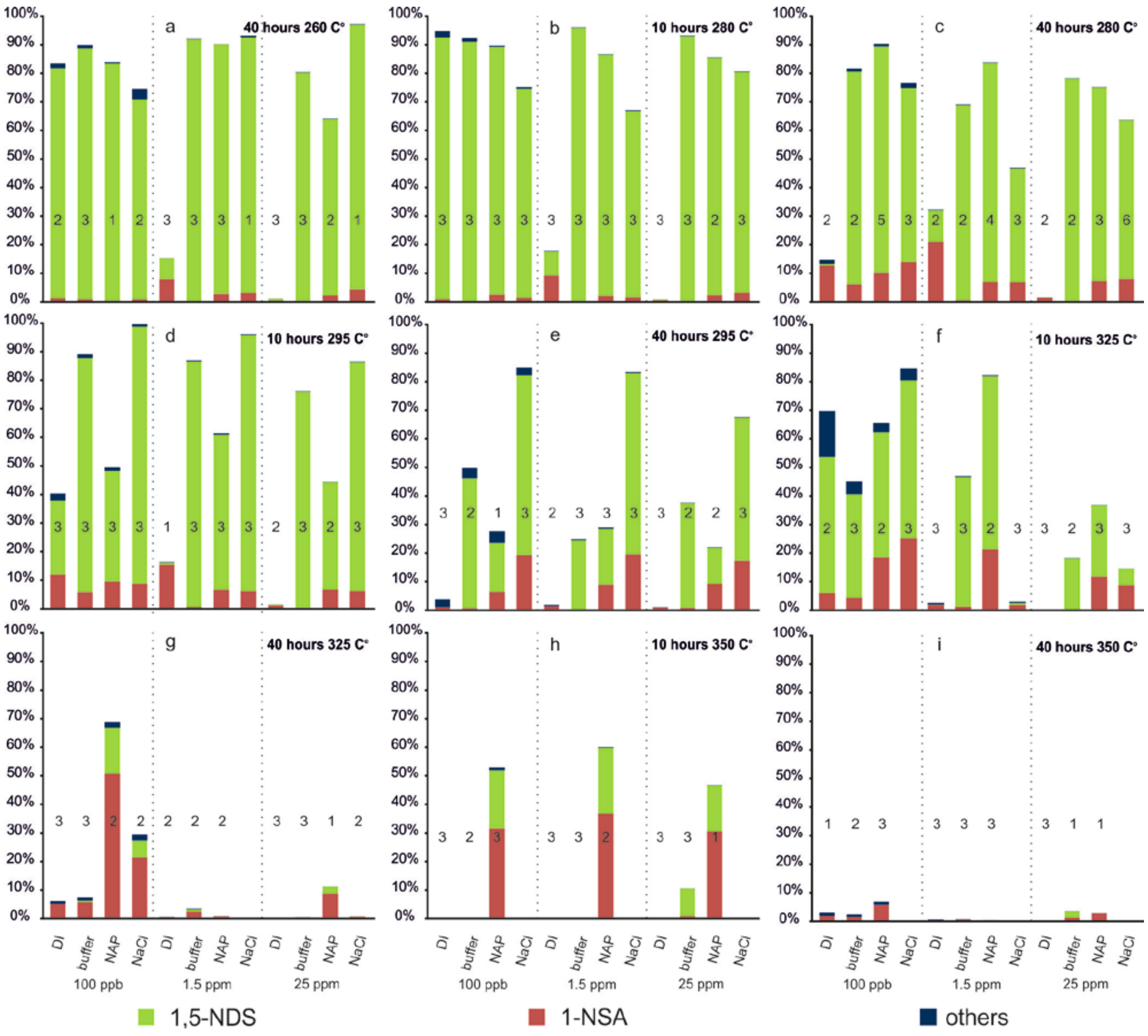


Figure 1. Concentrations of 1,5-NDS and 1-NSA after exposure to temperatures from 260 to 350 ℃ for 10 and 40 hours. Results are normalised by total initial concentration. Other includes 2,6-NDS, 2,7-NDS, 1,6-NDS, 2-NSA. DI = deionized water, buffer = 6.5 pH phosphate buffer, NAP = geothermal water, NaCl = 0.4 M solution of NaCl. Numbers on bars = number of replicates.

4.2 Decay kinetics

Rose et al. (2001) suggested a first order decay rate for 1,5-NDS of the form:

$$-dC_n / dt = k_n \cdot C_n$$

$$\ln\left(\frac{C_n}{C_0}\right) = -k_n \cdot t$$

Using Arrhenius equation:

$$k_n = A_0 \exp(-\frac{E_a}{RT})$$

it is possible to estimate the activation energy (E_a) and pre-exponential factor (A_0) (Table 3).

The activation energies in unbuffered solutions from our experiments range from 72 – 133 kJ while in buffered solutions they are 150 – 167 kJ. This indicates that there are differences in the reaction mechanism between unbuffered and buffered solutions.

Similar activation energies (slopes of the lines in Fig. 3) for NAP and NaCl matrices support the hypothesis that, in the unbuffered solutions, decomposition takes place according to a similar mechanism. The observed positive correlation between stability and salinity is due to lower activity of dissociated naphthalene sulfonates in a solution with higher ionic strength. Negatively charged sulfonates are surrounded by positively charged cations shielding them from interaction with H^+. That would result in decrease of the pre-exponential factor (A_0), without affecting the activation energy.

High scatter of the results for samples in deionised water (Fig. 3, DI) could be due to oxygen contamination of one batch of experiments. Additionally, the low concentration of tracer in deionised water experiments means that variations caused by the presence of oxygen would have a more pronounced effect.

The measured decomposition rate with 1,5-NDS in solution alone was higher than in the mixture of several naphthalene sulfonates (Fig. 3), possibly because of the increased concentration of the reaction products.

Table 3. Arrhenius constants for the decomposition of 1,5-naphthalene disulfonate at a temperature range of 260-350℃. R^2 - coefficient of determination.

	k		
solution	A_0, day^{-1}	E_a, kJ	R^2
DI, 10 h	2.1e7	72	0.11
DI, 40 h	9.6e12	133	0.35
buffer, 10 h	1.1e15	167	0.94
buffer, 40 h	4.1e13	150	0.93
NAP, 10 h	1.3e7	77	0.69
NAP, 40 h	2.3e11	125	0.78
NaCl, 10 h	7.2e11	130	0.49
NaCl, 40 h	4.4e11	129	0.78
Rose et al., 1999, 168 h	8.6e20	259	
Rose et al., 2001, 168 h	3.5e16	205	0.94
Mountain and Winick, 2012	2.8e17	199	0.99

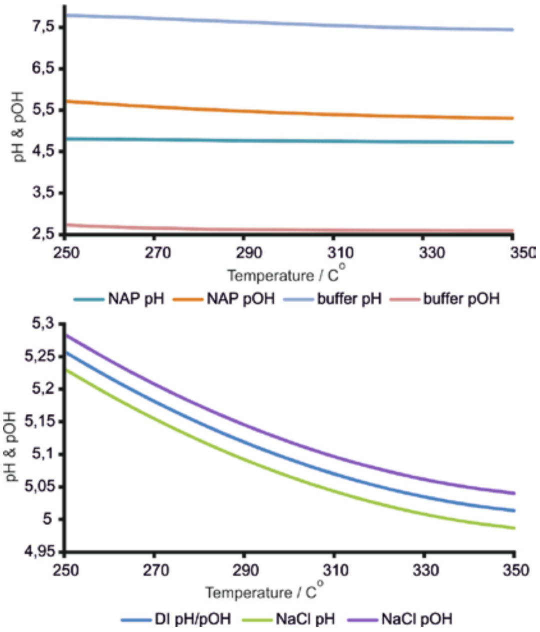


Figure 2. Estimated pH and pOH in the experimental solutions. NAP brine modelled by 13 µM H_2SO_4 (pH 4.6 at 25 ℃); K_w after Bandura and Lvov (2006); pK_a for sulphuric and phosphoric acids after Bethke (2008). These are extrapolated by 4th order polynomial equation if not available for the given temperature. The activity coefficients are calculated after Kielland (1937) (extrapolated by fitting logarithmical equation).

5. CONCLUSIONS

A laboratory study of 1,5-naphthalene disulfonate stability at different concentrations (100 mg/kg, 1.5 mg/kg, 25 mg/kg) in various matrices (deionized water - DI, 6.5 pH phosphate buffer, geothermal water - NAP, 0.4 M solution of NaCl) has been conducted. The temperature range was 260-350℃ and exposure times were 10 and 40 hours.

The results show the following:

1) Except for the solutions using deionised water there is no correlation between decay rate and initial tracer concentration;
2) 1,5-NDS thermal stability depends on the composition of the solution;
3) The decomposition products and, therefore, the reaction mechanism depend on pH and pOH;
4) 1-NSA is one of the products of 1,5-NDS decomposition;
5) No measurable concentration of isomerisation products was observed;
6) The measured decomposition rate of 1,5-NDS, when in solution alone, was higher than in the mixture of several naphthalene sulfonates.

Based on the results, we can expect a complex dependence of tracer stability on reservoir fluid composition (it should decay more slowly in more saline waters) and the composition of the injected tracer mixture. Further investigations of the thermal stability of the naphthalene sulfonates at different conditions are required in order to understand the mechanism of their decomposition.

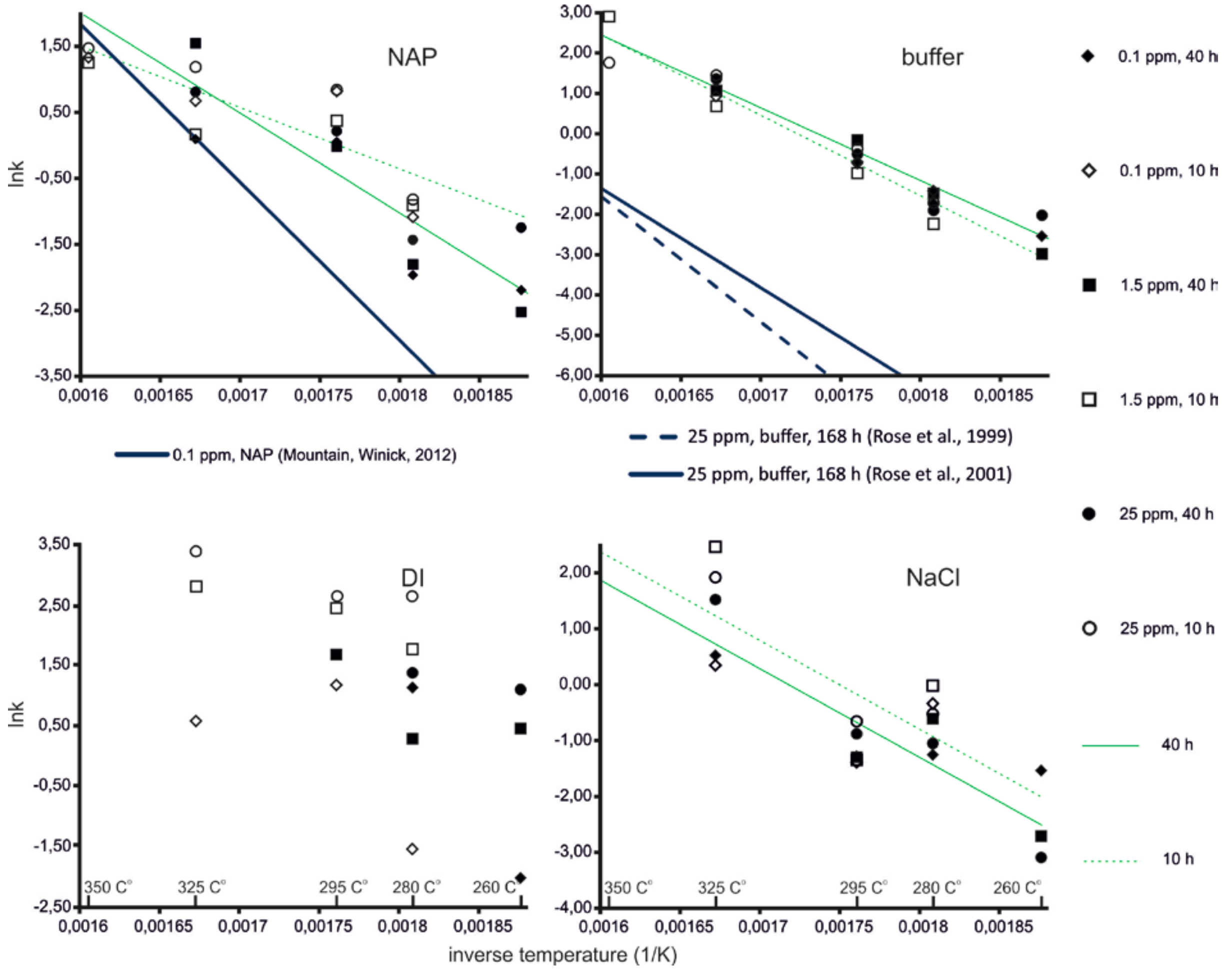


Figure 3. Arrhenius plots of ln k vs. inverse temperature between 260 and 350 ℃ for 1,5-naphthalene disulfonate in different solutions: NAP - geothermal water, buffer - pH 6.5 phosphate buffer, DI - deionized water, NaCl - 0.4 M NaCl. No corrections have been made for pH and pOH.

ACKNOWLEDGEMENTS

The authors would like to thank Mighty River Power, Tauhara North No. 2 Trust, Rotokawa Joint Venture, and the GNS DCF core-funded Geothermal Resources of New Zealand programme for supporting this work.

REFERENCES

Adams A.C., Moore, J.N., Fabry, L.G., Ahn, J.H: Thermal stabilities of aromatic acids as geothermal tracers. *Geothermics* 21, 323 – 330 (1992).

Bandura, Andrei V., Serguei N. Lvov.: The ionization constant of water over wide ranges of temperature and density. *Journal of Physical and Chemical Reference Data* 35.1, 15-30 (2006).

Bethke, C.M: Geochemical and Biogeochemical Reaction Modelling. 2nd Edition, Cambridge University Press, 543 p. (2008).

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 of 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), 2342-2354 (1978).

Kielland, Jacob: Individual activity coefficients of ions in aqueous solutions. *Journal of the American Chemical Society* 59.9, 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).

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).