Proceedings World Geothermal Congress 2010
Bali, Indonesia, 25-29 April 2010

Development of Thermosensitive Tracers for Push-Pull Experiments in Geothermal Reservoir Characterization

Martin Nottebohm, Tobias Licha, Iulia Ghergut, Karsten Nödler and Martin Sauter

University of Göttingen, Applied Geology

Goldschmidtstr. 3, D- 37077 Göttingen

martin.nottebohm@geo.uni-goettingen.de

Keywords: Hydrolysis, thermosensitive tracers, push pull experiments, reservoir characterization

ABSTRACT

The aim of the laboratory experiments presented here is to identify molecular structures for thermosensitive tracers which are adequate for the assessment of reservoir temperatures from short-term, single-well, push-pull tracer testing techniques under the typical low temperature conditions of geothermal reservoirs in Northern Europe.

Considering the widespread experience in the application of naphthalene sulfonates as tracers in geothermal reservoirs, this substance class provides well studied base molecules to be modified into thermally sensitive tracers. It is planned to use the hydrolysis reaction from various esters of naphthol sulfonates. In order to find esters with adequate reaction kinetics the mechanism of hydrolysis is studied on 44 phenol acetates and transferred to naphthol sulfonates.

1. INTRODUCTION

In addition to geophysical and seismic experiments, tracer tests with virtually chemically inert tracers have been established as a useful tool for the characterization of geothermal reservoirs (Rose et al. 2001, Sanjuan et al. 2006, Ghergut et al. 2007). These tracers are used for flow path tracking and the investigation of fluid residence times. Several organic compounds have successfully been used for such tests, e.g. naphthalene sufonates, fluoresceine and fluorinated benzoic acids. In the future, short-term push-pull experiments using chemically inert tracers on different test sites in Northern Europe will be extended to simultaneous investigations on the thermal development of the reservoir together with its heat exchange capacities and properties.

Thermosensitive tracers have a high potential for increasing information in the characterization of geothermal reservoirs (DuTeaux and Callahan 1996). They have been used for tracking thermal fronts in such reservoirs and also for calculating thermal drawdowns (Tester et al. 1986, Robinson and Birdsell 1987). Therefore, the hydrolysis reaction was demonstrated to be suitable in addressing the encountered temperature ranges in the reservoirs and time scales of the experiments. Thus this reaction type seems to have the potential of extending its use to the typical features of a push-pull experiment. The features include, a) low temperature ranges, b) the confined duration of the experiments and c) the likely presence of oxygen.

The thermosensitive tracers to be developed will have to address the specific characteristics of Northern European reservoirs and the specific demands of the experimental set up of push-pull experiments. Therefore these tracers should show a comparatively rapid thermal degradation (days) under mild temperatures (approx. 120-140 °C). Their reactivity with oxygen, even under oxygen limiting conditions need to be investigated since the presence of oxygen due to the experimental design of push-pull experiments cannot be ruled out. Furthermore, the tracers must be readily soluble in water and brine.

Different homologues of naphthalene sulfonate isomeres have been successfully used as ionic, highly mobile, highly fluorescing and chemically inert tracers at several geothermal sites (e.g. Ghergut et al. 2007). This opens the possibility of measuring breakthrough curves by direct onsite fluorescence measurements. The possibility of detecting different isomers of those compounds in the laboratory allows the possibility of designing tracers with different reaction kinetics employed simultaneously in one tracer test with increased information. Our aim is to develop thermosensitive tracers based on naphthalene sulfonates by introducing hydroxyl groups into these molecules which are likely to form esters. The hydrolysis of these esters at the relevant temperature and time scales will then be the thermosensitive extension to the naphthalene sulfonate molecular structure and tracer properties. To predict the most successful modification to the molecular structures of naphthalene sulfonates the hydrolysis of phenolacetates is applied as a study object.

Furthermore, the presented paper describes for the first time the stability of naphthalene sulfonates and naphthol sulfonates at elevated temperatures in the presence of oxygen traces.

2 HYDROLYSIS CONSTANTS OF PHENOLIC ESTERS MEASURED BY HS-SPME-GC-MS

Esterification has been established as a powerful derivatization technique for the analysis of phenols in water by GC-MS. This derivatization reaction is especially attractive as it is compatible with solid phase microextraction (SPME) and thus the complete analysis can be fully automated (Buchholz 1994). Considering the large number of analytes, which are possible to detect simultaneously in one sample by this approach under controlled and identical conditions, this method is most suitable to investigate the influence of structural differences in phenolic acetates on their hydrolysis kinetics. Data quality and comparability in the reaction constants between the investigated compounds has been shown to be very accurate by e.g. Bierwagen and Keller (2000). This is the only experimental design in which the sterical inhibiting influences of substituted groups can be investigated together with inductive and mesomeric effects of different substituents on the molecule with a high precision.

Due to their highly ionic character naphthalene sulfonates cannot be detected by gas chromatography. Therefore, phenolic esters are analyzed instead in order to transfer the findings of structural effects influencing the kinetics of hydrolysis to naphthalene sulfonates.

2.1 Experimental Method

The hydrolysis constants for 44 phenolic esters including naphthol at ambient temperature were identified using a HP 6890 GC system with a HP 5972A mass selective detector from Hewlett Packard and a solid phase micro extracting (SPME) system from CTC Analytics.

For the sample preparation 150 mg $NaHCO_3$ were added to 1 ml of a 12.5 µg/l standard mix which included all analytes. Then the phenols were esterified by adding 50 µl of acetic anhydride. At set of samples was prepared initially and then every 12 hours one sample was measured. With this schedule at least 4 data points within 168 hours of preparation for the decrease in concentration were obtained for every compound in the consecutive determination of the hydrolysis constant k.

The investigated character of ester hydrolysis is given by:

$$\text{RCOCOCH3} + \text{H2O} \rightarrow \text{RCOH} + \text{HOCOCH3}$$

The first order rate constant k was calculated by:

$$\ln\left(\frac{c}{c_0}\right) = -k \cdot t$$

Therefore k is linear for plotting c [mol/l] on the y-axis and 1/t [min] on the x-axis. Then k can be calculated from the slope of the linear regression line. An example for the data fit and calculation of k for 4-chloro-3-cresol is given in Figure 1.

The half-life in first order kinetics can be calculated from:

$$t_{1/2} = \frac{\ln 2}{k}$$

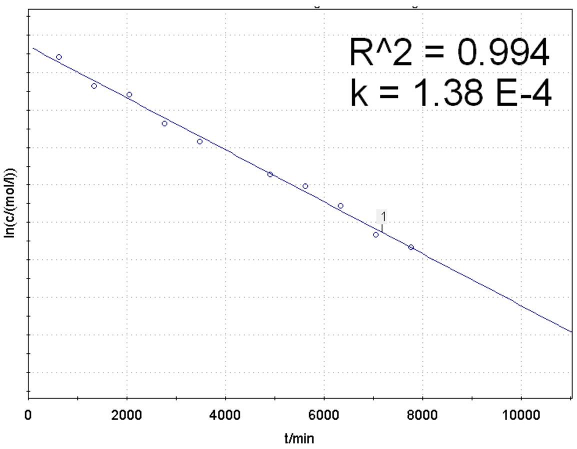


Figure 1: Calculation of the first order rate constant k for 4 chloro 3 cresol

2.2 Results

By plotting the rate constants k for the hydrolysis reactions versus the pKa of the non esterified substances it can easily be demonstrated that the reaction rate increases by up to 4 orders of magnitude with increasing acidity of 3 orders of magnitude for the acid constant pKa. Furthermore this correlation is linear for at least 3 groups of substances (Figure 2). This implies that Hammet´s law is valid for this type of reaction as well as substance class and thus transferable to other compounds. The classification into three groups agrees with the molecular structure of the compounds as each involves substances that have several similarities concerning their chemical structure. In one group a chlorine atom is located next to the hydroxyl group and in the second group two chlorine atoms are located next to the hydroxyl group. As a result the ester is better protected from hydrolysis attack by water molecules and the reaction rate decreases.

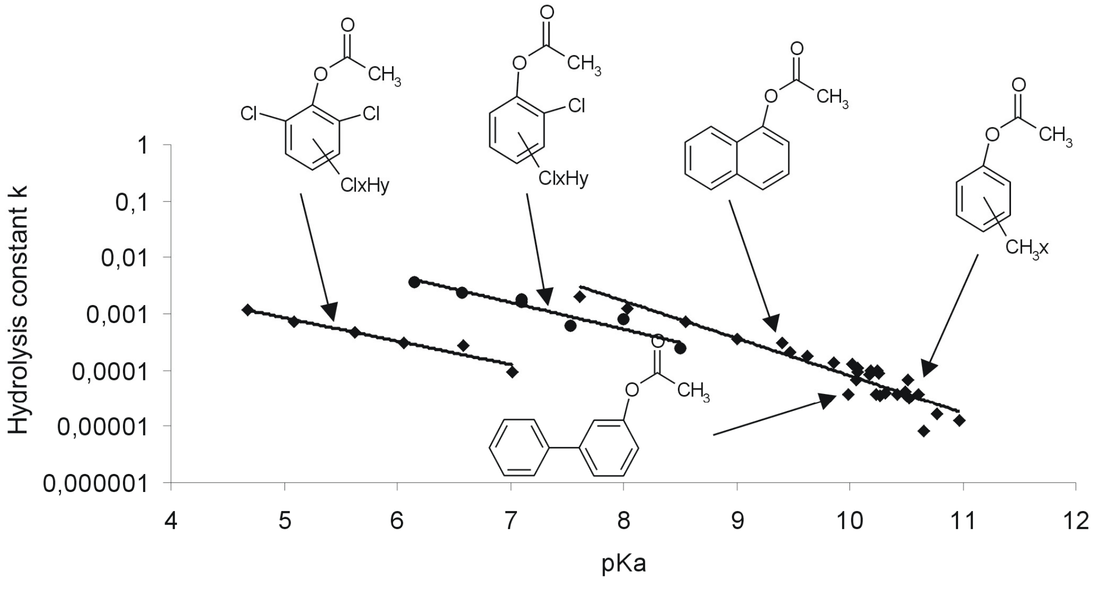


Figure 2: Hydrolysis constant k at ambient temperature versus pKa

Also mesomeric (M) and inductive (I) effects from different substituents affects the hydrolysis reaction rate. If the substituents are not in a direct neighbour position to the hydroxyl group their sterical hindrance effect can be neglected and the effect on hydrolysis kinetics is solely assigned to the substituents electron density influence on the aromatic ring(s). This effect can best be studied by comparing the reaction rates of respective phenolics (i.e 3.5 DMP vs. 3.5 DCP) in table 1. Functional groups which posses a positive inductive effect (+I) lead to a decreased reaction rate (e.g. alkyl groups) and functional groups with a negative inductive effect (-I) increase reaction rates (e.g. Cl). By increasing the number of substituents this effect is intensified. Following this context, most of the trimethyl phenols are significantly more stable than cresols and the chloro phenols with a single chlorine group are more stable than their higher chlorinated analogues.

It must be concluded, that for substituents with a negative inductive effect (-I) the steric hindrance effect as a counter effect on the hydrolysis reaction rate is significant. For substituents with a positive inductive (+I) effect on the aromatic ring system the addition of steric hindrance can be neglected, as long as the alkyl groups are small (up to C3).

Following QSAR strategies (Hansch et al. 1995) these mechanisms controlling the hydrolysis kinetics maybe transferred to more complex phenolic compounds. This can be seen on naphthol and 2 hydroxy biphenyl which plot on the same regression line as phenol (Figure 2). As such, it can be predicted how the acetate esters of naphthol sulfonates would behave. First of all, the sulfonic group with its pronounced negative inductive effect (-I) combined with its negative mesomeric effect (-M) will decrease the electron density in the aromatic system and thus make the hydroxyl group more acidic and the respective esters less stable. This higher acidity of the hydroxyl group compared to naphthol is supported by the experimental data from Zollinger and Büchler (1950) who present lower pKa values for sulfonated naphthols compared to naphthol. As a consequence, the hydroxyl group and the sulfonic group must not be on the same aromatic ring in order to keep the accelerating effect of the sulfonic group on the hydrolysis as low as possible. Furthermore, the number of sulfonic groups should be as low as possible. However, it should be at least one sulfonic group since the overall aqueous solubility is controlled by the sulfonic group.

Based on the results from the phenolic acetates, considerations for an appropriate thermally reacting tracer set with adequate reaction times are justified. In the experiments of Robinson and Tester (1990) it was found that the reaction rates of hydrolysis reactions increase by a factor of approximately 20 if the temperature increases by 100 K. In Figure 2 can be seen that in this case the half-lives ($t_{1/2}$) for most of the substances are not yet sufficient for the favored timescales of even short-term tracer tests. Furthermore, it has to be considered that the addition of sulfonic groups will lead to a lower pKa of the hydroxyl group according to its -I effect and thus accelerate the hydrolysis reaction compared to the data from naphthol. There are now two possibilities for molecule modifications which will lead to a decrease in the reaction rate of hydrolysis. The first option will be the addition of functional groups with a positive inductive effect (+I) to the molecule. The second option will be esterification with other acids than acetic acid. It is known that acids with longer or branched alkyl chains can have a sterical hindrance to the ester group, thus leading to slower reaction rates (Organikum, 2004).

Table 1. Hydrolysis constants and half-lives at ambient temperature and estimated half-lives for 120°C for 43 phenols and naphthol. Abbreviations: DMP: Dimethyl phenol, TMP: Trimethyl phenol, EP: Ethyl phenol, PP: Propyl phenol, Kre:Cresol, CP: Chloro phenol, DCP: Dichloro phenol, TrCP: Trichloro phenol, TeCP: Tetrachloro phenol, PCP: Pentachlor phenol, pKa values were calculated using SciFinder Scholar™.

compound	pKa	hydrolysis constant k [min^-1]	t/2 [h]	t/2 [h] estmated for 120°C
2.6DMP	10,66	8,10E-06	1426,2	71,3
2.4.6TMP	10,97	1,24E-05	931,6	46,6
2.3.6TMP	10,77	1,69E-05	683,6	34,2
2.3.5TMP	10,53	3,09E-05	373,9	18,7
2EP	10,27	3,45E-05	334,9	16,7
2PhenylP	9,99	3,64E-05	317,4	15,9
2nPP	10,49	3,65E-05	316,5	15,8
3.4DMP	10,23	3,69E-05	313,1	15,7
2.4DMP	10,61	3,70E-05	312,2	15,6
2.5DMP	10,42	3,74E-05	308,9	15,4
o-Kre	10,31	3,86E-05	299,3	15,0
2iPP	10,49	4,07E-05	283,8	14,2
3.4.5TMP	10,51	6,56E-05	176,1	8,8
3EP	10,06	6,75E-05	171,1	8,6
3.5DMP	10,18	8,47E-05	136,4	6,8
p-Kre	10,26	8,91E-05	129,7	6,5
3nPP	10,07	9,45E-05	122,2	6,1
4iPP	10,19	9,83E-05	117,5	5,9
4EP	10,25	9,86E-05	117,2	5,9
m-Kre	10,07	1,07E-04	108,2	5,4
3iPP	10,02	1,31E-04	88,5	4,4
4Cl-3-Kre	9,63	1,38E-04	83,7	4,2
Phenol	9,86	1,39E-04	82,9	4,1
4CP	9,47	2,12E-04	54,6	2,7
Naphthol	9,40	2,98E-04	38,8	1,9
3CP	9,00	3,64E-04	31,8	1,6
3,4DCP	8,55	7,38E-04	15,7	0,8
3,5DCP	8,04	1,27E-03	9,1	0,5
3,4,5TrCP	7,61	2,00E-03	5,8	0,3
2CP	8,50	2,43E-04	47,5	2,4
2,3DCP	7,53	6,30E-04	18,3	0,9
2,4/2,5DCP	8,00	8,06E-04	14,3	0,7
2,3,4 TrCP	7,10	1,63E-03	7,1	0,4
2,4,5TrCP	7,10	1,80E-03	6,4	0,3
2,3,5TrCP	6,57	2,33E-03	5,0	0,2
2,3,4,5 TeCP	6,15	3,74E-03	3,1	0,2
2,6DCP	7,02	9,47E-05	122,0	6,1
2,4,6TrCP	6,59	2,74E-04	42,1	2,1
2,3,6TrCP	6,06	2,99E-04	38,7	1,9
2,3,4,6TeCP	5,63	4,62E-04	25,0	1,3
2,3,5,6 TeCP	5,09	7,26E-04	15,9	0,8
PCP	4,68	1,18E-03	9,8	0,5

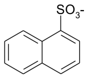
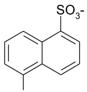
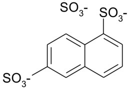
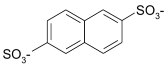
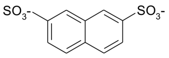
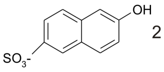
3. THERMAL STABILITY OF NAPHTHOL/ NAPHTHALENE SULFONATES IN THE PRESENCE OF OXYGEN TRACES

In order to use the hydrolysis of the earlier described esters based on naphthalene sulfonates in push-pull experiments quantitatively as tracers, the thermal stability of the emerging naphthol sulfonates must be known. Additionally, thermally stable naphthalene sulfonates described earlier are also investigated as reference substances. The thermal stability of 1.5-naphthalene disulfonate and 1.3.6-naphthalene trisulfonate has been described by Rose et al. (2001). He found that these compounds are stable up to 300°C in an anoxic environment. Our own push-pull experiments, however, show a lower recovery of this compound class relative to ^3H_2O which maybe addressed to the presence of oxygen traces originating from the experimental design of these field experiments.

3.1 Thermal Batch Experiments with Individual Compounds

For the thermal stability tests, 2-naphthol-6-sulfonate and five naphthalene sulfonates were investigated in individual heated batch experiments: 1- naphthalene monosulfonate (1NMS), 1.5-naphthalene disulfonate (1.5NDS), 1.6-naphthalene disulfonate (1.6NDS), 2.6-naphthalene disulfonate (2.6NDS) and 2.7-naphthalene disulfonate (2.7NDS). The reagents were selected based on their commercial availability. Naphthalene trisulfonates were not tested since only a composite of different isomers was available. Sulfonates were received from TCI-Europe in their highest available purity. The determination of the excitation and emission maxima and the determination of the respective concentrations in the batch experiments were performed using a Cary-Eclipse fluorimeter from Varian. A list of the test substances with their structural formula together with their respective fluorescence properties is given in Table 2.

Table 2. Compounds analyzed for thermal decay with the chemical structure compound name and excitation and emission maximum.

chemical structure	compound name	excitation-/ emission maximum
	1 Naphtalene sulfonate	222/330
	1.5 Naphthalene disulfonate	223/332
	1.6 Naphthalene disulfonate	229/340
	2.6 Naphthalene disulfonate	231/330
	2.7 Naphthalene disulfonate	230/341
	2 Hydroxy 6 Naphthalene sulfonate	230/430

For the heated batch experiments the substances were dissolved in ultrapure water (18 mohm) and then diluted to 5 mg/l. Ultrapure water was received from a Mili-Q Gradient A10 system from Millipore. No buffers were added to later avoid problems in the identification of degradation products by ESI-LC-MS. Earlier tests with an identical set up and the addition of buffers (carbonate, phosphate) showed no significant differences in the results. Individual reference solutions were kept in order to be able to quantify the fluorescence loss relative to them later on.

All experiments were conducted with 4 replicates individually for each test substance, each with a total volume of 20 ml of the respective solution in 40 ml hostaflon TFM vessels from CEM. No attempts were made to reduce the oxygen in the vessels. The vessels were put into a GC-oven from Chrompack and heated up within 60 min to the target temperature and kept at this temperature for a significant time steps (days) before being removed.

At the end of the heating batch experiment the oven was cooled down within 30 min to room temperature. The samples were immediately taken from the vessels and according to the linear working range of the fluorimeter diluted with ultrapure water. The loss due to heat treatment by the batch experiments was quantified relative to the fluorescence intensities of reference solutions.

It was found that the semi-quantitative loss in fluorescence intensity at 150°C for a 24 hour heat treatment is as follows: naphthol sulfonates > naphthalene sulfonates > naphthalene disulfonates. This effect increases significantly for temperatures above 130°C. It could be confirmed by batch experiments that naphthalene disulfonates are more stable than their monosulfonated analogues which diminished to 95% within 165h. However, naphthalene sulfonates also showed a significant loss in fluorescence intensities from 35% (2.6 NDS) to 58% (1.6 NDS). The results are shown in Figure 3.

Because of the strong discrepancy between these results and the fact that some of these compounds have been stable in geothermal reservoirs over months (e.g. Sanjuan et al. 2006) the samples were analyzed by LC-MS techniques to identify the type of relevant reaction and to exclude possible quenching effects in the fluorescence measurements. Since breakdown products of naphthalene (di)sulfonates have earlier been investigated with different intensions and are therefore known (Gosetti et al. 2005), initially more attention was drawn to the investigation of the processes leading to the fluorescence decay of the naphthalene sulfonates.

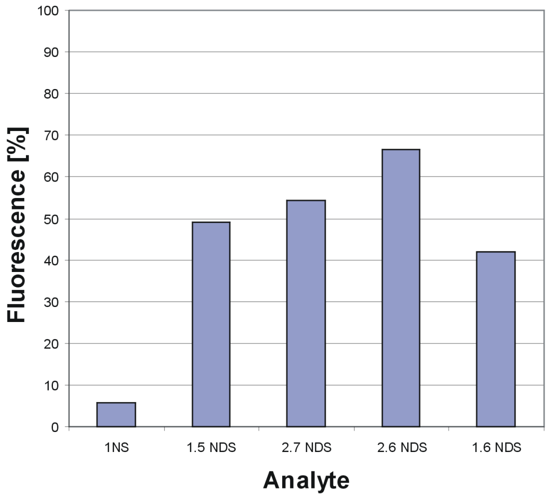


Figure 3: Decrease in fluorescence of naphthalene sulfonate after 165h at 150°C

3.2 Investigation of the Reaction Products by LC-MS

LC-MS methods are a powerful tool for a) the identification of known substances in unknown matrices and b) giving some indications of the possible structure of unknown substances by the investigation of the specific masses and product-ions. Therefore this technique can be used to investigate whether a possible decrease in fluorescence of the sample is caused by quenching effects of the matrix or can be assigned to the decay of the substance. Furthermore, it is possible to identify potential reaction products. Should only one stable reaction product be formed, then this could be used later instead of the sulfonates as a target substance to quantify the hydrolysis and thus the thermal drawdown of the geothermal reservoir. Should more than one reaction product be identified, their identification will yield more information on the character of the decay reaction. This is especially helpful if for example additives need to be identified to prevent the reaction in the field during push-pull experiments. It may also help to reconsider the experimental design of push-pull tests if the cause of the decay is known.

The reaction products were analyzed using a Varian ProStar System with a 1200 Quadrupole MS. The mobile phase consists of: eluent A: 1mM acetic acid, 1mM tributylamine as ion pairing agent with 5% methanol (pH 4.5) and eluent B as 100% methanol. In order to elute all the analytes from the column (Phenomenex C18(2), 150x3 mm, 3 µm particle size) within an acceptable runtime a gradient was applied from 30 to 70% B in 25 min. For the identification of the specific mass to charge ratio (m/z) of the reaction products, the samples were scanned from 90 to 400 amu using negative electrospray ionisation (ESI) as ionization technique. Additionally neutral loss experiments were performed to support the functional group specific identification. To determine the relative distribution pattern of breakdown products for the individual sulfonates with time, the samples were analyzed by ESI-LC-MS with the earlier identified masses (m/z: 245, 229, 213, 255, 351, 335, 217, 216, 143 and 137 amu) in selected ion monitoring (SIM) mode.

A total ion chromatogram (TIC) for 1-NMS before and after a stability test with 66 h runtime is given in Figure 4. It is clearly shown that the decrease in the fluorescence signal is not caused by quenching effects since the results from LC-MS measurements are in good agreement with results obtained by direct fluorescence. Furthermore, it shows different reaction products, instead of a single stable one. A list of the investigated reaction products is given in Figure 5.

Nearly all reaction products show an increasing signal (concentration) with reaction time. The differences of the peak areas in between the different isomers correlate with the results in the decrease of fluorescence. Additionally, the good comparison for the obtained concentration of the sulfonates by LC-MS with fluorescence measurements allows the conclusion that the obtained breakdown products cannot be analyzed by fluorescence spectroscopy, and thus do not falsify fluorescence data.

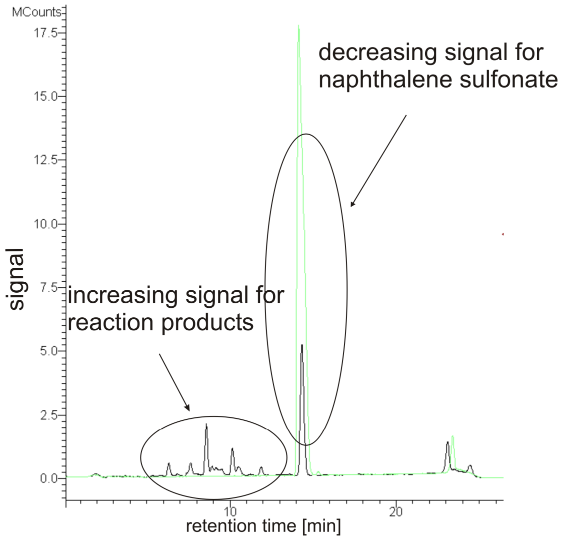


Figure 4: TIC-Spectrum of 1-NMS before (green line) and after the stability test (black line)

It was found that many compounds identified in the heated batch experiments have the same m/z ratio and similar retention times as detected by Storm (2002) although he investigated the reaction products of the oxidative destruction of 1.5 NDS (masses 245, 229, 255 and 213) by ozonization at ambient temperature. Salicylic acid (m/z 137) could be identified using the pure substance as a reference standard. For the compound with the m/z ratio 216 no possible reaction product structure can yet be suggested from SIM. A list of the suggested structures in agreement to Storm (2002) is given in Figure 6.

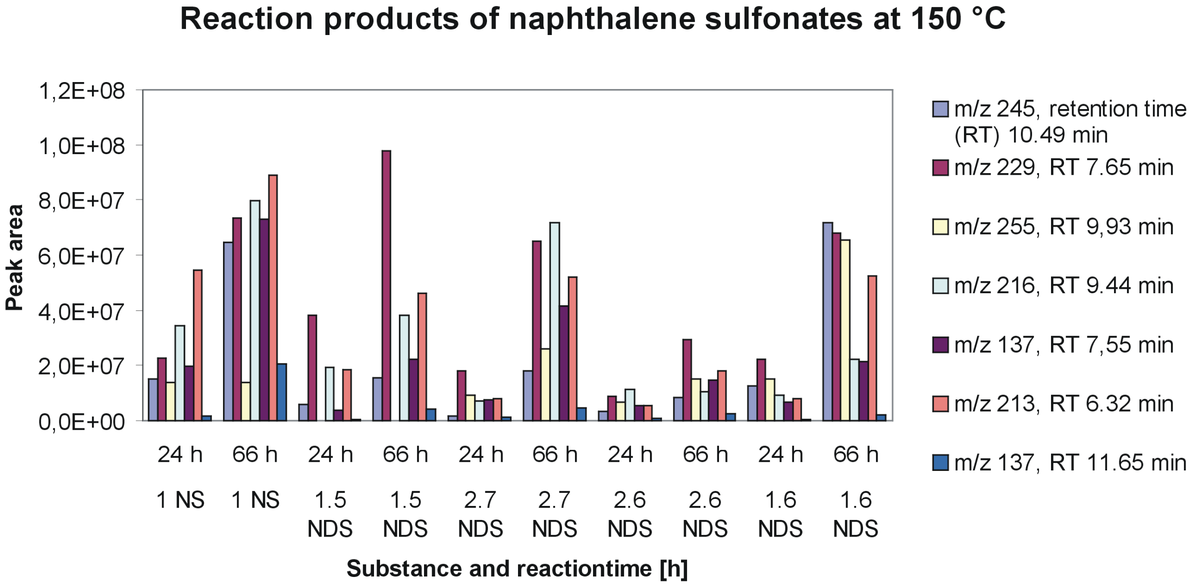


Figure 5: Investigated reaction products of different naphthalene sulfonates after 24 h and 66 h reaction time at 150°C

The structures of the reaction products strongly imply that the reaction is initiated by the presence of oxygen at elevated temperatures. However, to estimate the exact mechanism and cause of the reaction more efforts in the precise structural analysis will be undertaken and it has to be clarified which products are compound specific, i.e. final products, and which ones are intermediates of this reaction.

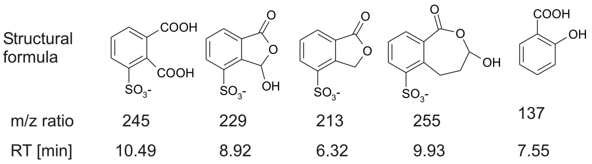


Figure 6: Proposed and identified reaction products of the thermal degeneration of naphthalene sulfonates

CONCLUSIONS

The hydrolysis of organic esters can offer an appropriate reaction sensitive to the thermal variability in geothermal reservoirs. The strong influence of the reaction product acidity on the reaction kinetics makes it possible to cover a broad range of different temperatures in the reservoir and different tracer test times. The linear relation in this context allows the prediction of reaction rates if the hydrolysis constants of similar substances are known. Furthermore, it is possible to control the kinetics of this reaction by the influence of the substituent’s steric, inductive and mesomeric effects.

Considering this in the next step the hydrolysis kinetics of selected naphthol sulfonic esters with varying pKa of the hydroxyl group and different chain length of the ester group will be investigated.

It has been found that naphthalene sulfonates are sensitive to oxygen at typical temperatures of geothermal reservoirs. Therefore it has to be decided if this could be a relevant process within the reservoirs investigated by push-pull experiments. Samples from these experiments will in future be scanned for the identified typical breakdown products of the naphthalene sulfonates by LC-MS.

Considering the presented experiments and the positive experience from several tracer tests in the past, different isomers of naphthol sulfonate esters promise to be practical thermosensitive tracers in the characterization of deep geothermal reservoirs in Northern Europe by short-term push-pull experiments.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of this work by the German Federal Ministry of Environment (BMU, 0327579).

REFERENCES

Bierwagen, B. and Keller, A. A.: Measurement of Henry´s Law Constant for Methyl Tert-Buthyl Ether Using Solid-Phase Microextraction, (2001), *Environmental Toxicology and Chemistry*, 20, nr. 8, pp. 1625-1629

Buchholz, K., Pawliszyn, J.: Optimization of Solid Phase Microextraction (SPME) in Water and Air for Phenol Analysis, (1994), *Analysis Anal. Chem*., 66, 160-167

DuTeaux, R., Callahan, T.J.: Comparing reactive and non reactive tracers to measure changes in liquid dominated, fractured geothermal reservoirs: *Geothermal Resources Transactions*, 20, (1996), 447-451

Ghergut, I., Sauter, M., Behrens, H., Licha, T., McDermott, C.I., Herfort, M., Rose, P., Zimmermann, G., Orzol, J., Jung, R., Huenges, E., Kolditz, O., Lodemann, M., Fischer, S., Wittig, U., Güthoff, F., Kühn, M.: Tracer Tests Evaluating Hydraulic Stimulation at Deep Geothermal Reservoirs in Germany, *Proceedings*, 31th Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, CA (2007).

Gosetti, F., Gianotti, V. Ravera, M., Genarro, M.C.: HPLC-MS to Investigate the Oxidative Destruction Pathway of Aromatic Sulfonate Wastes, *Journal of Environmental Quality*, 34, (2005), 2328-2333

Hansch, C., Leo, A., and Hoekman, D.: Exploring QSAR - Hydrophobic, Electronic, and Steric Constants. (1995) *American Chemical Society*, Washington, D.C.

Organicum, 22th ed., Wiley-VCH, (2004)

Robinson, B. A., Tester, J. W.: Kinetics of Alkaline Hydrolysis of Organic Esters and Amides in Neutrally-Buffered Solution, *International Journal of Kintics*, 22,(1990), 431-448

Robinson, B. A., Birdsell, S. A.: Tracking Thermal Fronts with Temperaturesensitive, Chemically Reactive Tracers, *Fifth Geothermal Program Review*, (1987), Washington, DC

Rose, P., Benoit, W. R., Kilbourn, P. M.: The application of polyaromatc sulfonates as tracers in geothermal reservoirs, *Geothermics*, 30, (2001), 617-640.

Sanjuan, B., Pinault, J.-L., Rose, P., Gérard, A., Brach, M., Braibant, G., Couzet, C., Foucher, J.-C., Gautier, A., Touzelet, S.: Tracer Testing of the Geothermal Heat Exchanger at Soultz-sous-Forêts (France) between 2000 and 2005, *Geothermics*, 35, (2006), 622-653.

Storm, T.: Aromatische Sulfonate: Untersuchungen zum Stoffverhalten in Industrieabwasser und aquatischer Umwelt mit HPLC-MS, Dr. Thesis, TU Berlin (2002)

Tester, J. W., Robinson, B. A., Ferguson, J. H.: Inert and Reacting Tracers for Reservoir Sizing in Fractured, Hot Dry Rock Systems, *Proceedings*, 11th Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, CA (1986).

Zollinger, H. and Büchler, W.: Einfluss der Sulfongruppen auf den Dissoziationsgrad der Hydroxyle in Naphtholsulfonsäuren, *Helv. Chim. Acta*, (1950), 33, 2002-2010.