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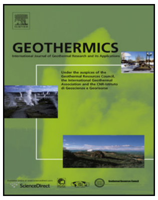

Amides as thermo-sensitive tracers for investigating the thermal state of geothermal reservoirs

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ABSTRACT

The application of thermo-sensitive tracers is a promising technique for evaluating the thermal state of geothermal reservoirs. To extend the compound spectrum for hydrolyzable compounds to reservoir temperatures between 100 and 200 °C carboxamides were studied. The kinetic parameters of 17 self-synthesized amides were determined in hydrothermal batch and autoclave experiments. The influence of the molecular structure and the role of pH/pOH on hydrolysis kinetics were studied. Additionally, the thermal stabilities of the hydrolysis products were evaluated. The results demonstrate the high potential of tracers based on amide hydrolysis for use in medium enthalpy reservoirs.

1. Introduction

Tracer testing is a very powerful tool to probe geothermal reservoirs, since it provides unique data (Chrysikopoulos, 1993) vital for the implementation of sustainable reservoir management and, thus, optimized exploitation strategies (Ungemach et al., 2005). Especially in geothermal systems where cooled fluids are re-injected, the monitoring of the spatial and temporal distribution of cooling is of high interest because the energy extraction is usually higher than the natural heat flow (O'Sullivan et al., 2010). Consequently, the risk of thermal breakthrough is increased (e.g., Malate and O'Sullivan, 1991; Stefansson, 1997).

In recent decades, the idea of tracers having thermo-sensitive properties was introduced as a promising concept for estimating the thermal state (reservoir temperatures) and for tracking the thermal drawdown of geothermal reservoirs (e.g., Robinson et al., 1984; Tester et al., 1986; Robinson and Birdsell, 1987; Plummer et al., 2010; Rose and Clausen, 2014). One currently pursued thermo-sensitive tracer approach is to evaluate the thermal decay of established conservative tracers such as naphthalene sulfonates, Amino G, rhodamine WT, and fluorescein (Adams and Davis, 1991; Rose et al., 1999, 2001; Rose and Clausen, 2014). Very high temperatures, however, are required to achieve a significant decomposition of these organic molecules. As the thermal decay mechanisms are likely to be unspecific, the resulting reaction products are usually unknown. To avoid this loss in potential reservoir information Rose and Clausen (2014) recently started to investigate the thermo-decay mechanisms more specifically.

Another promising approach is the use of compounds containing chemical groups that are susceptible to hydrolysis. Due to the temperature-dependence of this reaction with water, these compounds are also thermo-sensitive. Furthermore, this reaction type has the advantage of involving a single reaction and having well-defined reaction products; secondary reactions can virtually be excluded. Robinson and Tester (1990) studied the hydrolysis reaction kinetics of amides and esters at different temperatures and varying pH, and demonstrated the high potential of these compound classes as thermo-sensitive tracers. The compound selection in their study, however, was limited to the commercial availability of water-soluble substances.

This limitation was resolved in Nottebohm et al. (2012) by incorporating thermo-sensitive functional groups into established tracer molecules (naphthalene sulfonates), while maintaining many of the desired properties of the established tracers such as fluorescence and high water solubility. In their work, additional systematic

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investigations (batch experiments) on the dependence of structural properties on the reaction kinetics of phenolic esters demonstrated the possibility of adapting the tracer kinetics to the prevailing conditions at the tested reservoir (e.g., temperature range, experiment duration). The transferability to dynamic systems and, thus, the full capability of hydrolyzable compounds to act as thermo-sensitive tracer was shown by Maier et al. (2015a,b), who studied the ester phenol acetate in laboratory column experiments under various experimental conditions. The results revealed that these tracers are suitable for the detection of temperatures, cooled fractions, and thermal gradients in porous media. Furthermore, the fundamental theory of Robinson et al. (1984) and Tester et al. (1986) was validated.

Esters, however, show relatively fast reaction kinetics, so their practical application as thermo-sensitive tracers is limited to low fluid temperatures (<100 °C) and/or short residence times as encountered in lab experiments, shallow (low-enthalpy) systems, or exploited (cooled down) reservoirs. In contrast, tracers based on the unspecific thermal decay are much more stable and require high temperatures (>200 °C) in order to achieve sufficiently high reaction rates of the tracer degradation.

In order to fill the remaining "kinetic gap" in thermo-sensitivity (reactivity) between esters and the much slower reacting tracers based on thermal decay (100–200 °C), the reaction kinetics for a wide spectrum of self-synthesized, water-soluble, and fluorescent carboxamides (secondary amides) were investigated in this study by adapting the approach by Nottebohm et al. (2012). Hydrothermal batch and high-pressure autoclave experiments at temperatures ranging between 95 °C to 190 °C were conducted. The role of the molecular structure (e.g., steric effects) as well as the influence of temperature (Arrhenius parameters) and pH/pOH (catalysis) on the amide hydrolysis kinetics were studied. This assists the molecular design of new tracer compounds. To evaluate the practical applicability of the tested compounds, the thermal stabilities of two of the hydrolysis products (aromatic sulfonates) were studied at temperatures up to 350 °C and several transformation products were identified by means of mass spectrometry.

2. Amide hydrolysis – reaction mechanism, kinetics, and thermo-sensitivity

The hydrolysis of carboxamides is an irreversible splitting reaction with water, yielding carboxylic acids and amines as reaction products. Hydrolysis reactions are generally acid- or base-catalyzed, whereby the base catalyzed type is more relevant in natural systems (Larson and Weber, 1994). Here, a negatively charged transition complex is initially formed due to the nucleophilic attack of a hydroxide ion (OH^-) on the carbonyl group (Fig. 1). For the secondary amides tested in this study, the complex subsequently decomposes to the carboxylic acid R_1—COOH and the primary amine R_2-NH_2 as the leaving group. According to literature, the basic hydrolysis of amides follows an S_N2 reaction (nucleophilic substitution) through a $B_{AC}2$-type (acyl cleavage) mechanism (Larson and Weber, 1994; Carlson et al., 2006; Bruckner and Harmata, 2010). The formation of the transition complex in the bimolecular reaction with OH^- is the rate-limiting step and causes the dependence of hydrolysis reactions on pH/pOH. It is also evident that steric effects (e.g., hindrance of the OH^- attack by shielding the carbonyl group with selected organic side chains R_1 and R_2) may be exploited to influence the reaction kinetics in an intended way (Robinson and Tester, 1990; Nottebohm et al., 2012).

The reaction formally follows third-order kinetics because it depends on the concentration of the reactant [*Amide*], the concentration of water $[H_2O]$, and on the concentration of the catalyst $[OH^-]$:

$$-\frac{d[Amide]}{dt} = -k \cdot [Amide] \cdot [H_2O] \cdot [OH^-] \quad (1)$$

where k is the reaction rate coefficient. However, due to the excess of water, which is simultaneously the solvent and the reaction partner (solvolysis), and the catalyst, which is not consumed during reaction, $[H_2O]$ and $[OH^-]$ remain virtually constant (pOH = const.) during the reaction. Consequently, the reaction velocity depends only on [*Amide*] and can be expressed with a (pseudo-)first-order rate law:

$$-\frac{d[Amide]}{dt} = -k_h \cdot [Amide] \quad (2)$$

where k_h is the effective hydrolysis rate constant. For the half-life, $t_{1/2} = \ln 2/k_h$ applies. The defined hydrolysis products and known stoichiometry also allow for tracking of the reaction kinetics by measuring the concentration of one of the reaction products (here the fluorescent and water-soluble amine):

$$\frac{d[H_2N - R_2 - SO_3{}^-]}{dt} = k_h \cdot [H_2N - R_2 - SO_3{}^-] \quad (3)$$

This is an important advantage for tracer detection, as the concentration increases over time (positive sign) and counteracts dilution of the tracer during transport (e.g., due to dispersive processes, lateral inflow).

The thermo-sensitivity of amide hydrolysis reactions originates from the temperature dependence of k_h. According to Arrhenius' law, the equivalent temperature T_{eq} of the reservoir can be determined from k_h for a constant pOH and known Arrhenius parameters with (Maier et al., 2015b):

$$T_{eq} = -\ln\frac{A}{k_h} \cdot \frac{E_a}{R} \quad (4)$$

where A is the pre-exponential factor, E_a the activation energy, R the gas constant.

3. Materials and methods

3.1. Amides and chemicals

Based on the acylation of primary amines, 17 different secondary amides were synthesized using a modified Schotten-Baumann method (Idzik et al., 2014). All investigated amides (S1–S17) and their respective hydrolysis products (H1–H3) are shown in Table 1. The focus of the amide synthesis was to obtain structurally different compounds that are readily water-soluble and have different fluorescence properties than their hydrolysis products. A high solubility and non-sorbing behavior were realized by introducing an anionic sulfonic group ($pK_a < 1$) to the molecules (Schaffer and Licha, 2014). The optical properties are required to easily follow the reaction progress in field experiments without substantial analytical efforts and were ensured by incorporating aromatic substructures based on established tracer molecules for R_2.

For calibrating the fluorescence spectrometer, the hydrolysis products H1 = sulfanilic acid (4-aminobenzenesulfonic acid, formed from amides S1–S8) and H2 = 4-amino-3-methyl-benzenesulfonic acid (formed from amides S9–S11) were purchased from Sigma-Aldrich, H3 = 4-aminonaphthalene-1-sulfonic acid (formed from amides S12–S17) as sodium salt was purchased from Merck Schuchardt OHG. The buffer salts, di-sodium hydrogen phosphate dihydrate (analytical reagent grade) and potassium dihydrogen phosphate (analytical reagent grade), were received from Fisher Scientific. Ultrapure water for the preparation of all solutions was obtained from a combined water purification system consisting of