

## Organic Molecules as Sorbing Tracers for the Characterization of Fracture Surface Areas in Enhanced Geothermal Systems (EGS)

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### ABSTRACT

The specific fracture surface area to volume ratio  $A/V$  is a crucial parameter for assessing the heat exchange efficiency and, thus, allowing for the success evaluation of hydraulic stimulations in geothermal reservoirs. Unfortunately, this ratio cannot directly be determined with existing techniques. Based on the assumption that  $A/V$  is proportional to the surface area available for sorption, several inorganic cations were recently proposed as sorbing (cation exchanging) tracers to derive  $A/V$  values. However, the main disadvantages of inorganic ions are the limited number of available ion types, their potential geogenic background, and their challenging detection at trace concentrations in the field.

To overcome these limitations and to improve the applicability of sorbing tracers, the spectrum of potentially suitable chemical substances as sorbing tracers is broadened by considering organic molecules. The organic tracers discussed in this work are cationic and fluorescent, therefore, highly water soluble and easy to measure at very low concentrations. Furthermore, different molecular structures can be selected or even individually adapted according to the prevailing reservoir conditions. Additional sorption processes with the reservoir rocks beside cation exchange may also play a role allowing the application of these organic molecules even in highly saline reservoirs. First results from lab column experiments with different organic amines under varying conditions (different salt concentrations) are presented emphasizing the potential of using organic molecules as sorbing tracers in the future.

### 1. INTRODUCTION

Tracer testing using conservative (e.g., Adams et al., 1992; Stefansson 1997; Rose et al., 2001; Sanjuan et al., 2006) or reactive compounds (e.g., Rose et al., 2012; Leecaster et al., 2012; Nottebohm et al., 2012; Schaffer et al., 2013; Rose and Clausen, 2014; Maier et al., 2015a; 2015b) is generally considered as a promising technique to determine reservoir parameters, which are not accessible with conventional methods. However, there is still a lack of “smart” tracers, which are able to measure and/or monitor the surface area responsible for rock-fluid heat and mass exchange (U.S. DOE, 2008). The specific fracture surface area to volume ratio  $A/V$  is a crucial parameter for assessing the heat exchange efficiency and evaluating the success of hydraulic stimulations in Enhanced Geothermal Systems (EGS). However, this parameter cannot directly be measured and, therefore, new in-situ methods are required for its estimation. Since the interface area between the reservoir fluid and the rock material surfaces should be proportional to the area available for sorption (Dean et al., 2015), the injection of sorbing tracers represents a promising technique to deduce a measure for  $A/V$ . Thus, changes of the surface area size in the reservoir might also be detectable by repeated sorbing tracer tests. Sullivan et al. (2003) and Dean et al. (2012; 2015) recently proposed inorganic cations ( $\text{Li}^+$  and  $\text{Cs}^+$ ) as potential sorbing (cation-exchanging) tracers due to their: i) absence in many natural waters, ii) high water solubility, iii) low toxicity, iv) low cost, and v) commercial availability of their salts in large quantities. However, the limited number of available ion types and their complicate analysis in trace concentrations in the field are the main disadvantages of using these ions as sorbing tracers. Furthermore, solely ion exchange interactions, which are very sensitive to the ambient hydrochemical conditions (ionic strength), dominate from all sorption processes.

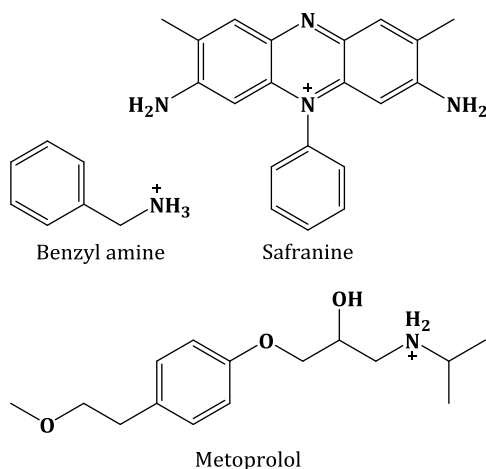
To improve the applicability of sorbing tracers, the spectrum of potentially suitable chemical substances as sorbing tracers is broadened by considering also organic molecules for the characterization of fracture surfaces and the success of fracturing in geothermal systems. The discussed organic molecules are cationic fluorophores and they overcome the potential drawbacks regarding detectability and natural geogenic background concentrations. Furthermore, additional sorptive interactions beside cation exchange with the reservoir rocks may be exploited allowing the application of these organic molecules even in saline reservoirs where ion exchange is suppressed to a low level. The results from initial column experiments with the organic cations benzylamine, metoprolol at 80 °C and different background concentrations of NaCl are presented. Additionally, safranin was included into the investigation, since it is the sole organic compound, which was earlier tested for its potential as sorbing tracer (Rose et al., 2012; Leecaster et al., 2012).

### 2. MATERIALS AND METHODS

#### 2.1 Chemicals

Benzylamine (CAS 100-46-9), safranin (CAS 477-73-6), both from Acros Organics, and metoprolol as tartrate salt (CAS 56392-17-7) from Sigma-Aldrich were tested as sorbates (sorbing tracers) in the experiments (Fig. 1). All chemicals were of high purity (>95%) and are readily ionized at the investigated pH due to their high  $\text{p}K_a$  values (benzylamine, metoprolol) or permanent charge (safranin) (Schaffer and Licha, 2014). Phenol (CAS 108-95-2) purchased from Merck Darmstadt was used as reference tracer. The conservative behavior of the reference tracer was proven by comparing the breakthrough curves with deuterium oxide (CAS 7789-20-0) from Sigma-Aldrich. The inorganic chemicals HCl and NaCl used for adjusting the pH and different background concentrations of  $\text{Na}^+$  were

purchased from Merck Darmstadt and Acros Organics, respectively. All solutions were prepared in ultrapure water obtained from a combined water purification system from Millipore.



**Figure 1: Tested organic molecules. The nitrogen moieties are readily protonated at experimental pH and, therefore, only the ionized (cationic) species occurs in solution.**

## 2.2 Reservoir material

Unweathered red Weser sandstone (Bad Karlshafen, Germany) was used as analogue material to imitate typical reservoir rocks of the North German Basin. The rock samples were ground, sieved (<63  $\mu\text{m}$ ), washed and titrated with HCl to pH = 5 prior to the experiments, in order to provide a homogeneous distribution and high surface area. The sandstone consists of quartz (>70%), feldspars, mica, iron oxides and clay minerals (mainly illite, smectite, chlorite).

## 2.3 Column experiments

The column experiments were conducted in a modified HPLC system (Varian/Agilent) equipped with a UV-Vis detector, a fluorescence detector, and a peltier-thermostated column oven ( $T = 80\text{ }^\circ\text{C}$ ). Salt solutions containing the intended concentrations of  $\text{Na}^+$  were adjusted to pH = 5 and used as eluents. Two different  $\text{Na}^+$  (NaCl) background concentrations ( $c = 10$  and  $100\text{ mmol/L}$ ) were applied for evaluating the influence of competing inorganic ions on the retardation (sorption) behavior of the tested molecules. The eluents were pumped with a flow rate of  $0.15\text{ mL/min}$  through a stainless steel column ( $14 \times 2^{\circ}\text{mm}$ ) filled with the powdered sandstone. After an equilibration phase (>3 d), the eluent solutions additionally containing the respective tracers ( $c = 10\text{ }\mu\text{mol/L}$ ) were sequentially injected as tracer pulses. The breakthrough curves were measured at the column outlet (using compound specific wavelengths, see Fig. 2 and Fig. 3). Before the injection of sorbing tracers, the conservative reference tracer was injected in order to determine the hydraulic conditions (pore volume, dispersivity, etc.) of the columns. Sorption leads to a retardation of solutes relative to the water flow and the conservative tracer (Schaffer and Licha, 2015). The extent of interactions can inversely be determined by comparing the breakthrough curves of the sorbing tracer with the breakthrough curves of the conservative tracer. The resulting retardation factor  $R$  of the sorbing tracers is proportional to  $A/V$  (and the fracture-surface/water partitioning coefficient  $K_{fw}$ ) (Wels and Smith, 1994):

$$R = 1 + \frac{A}{V} \cdot K_{fw} \quad (1)$$

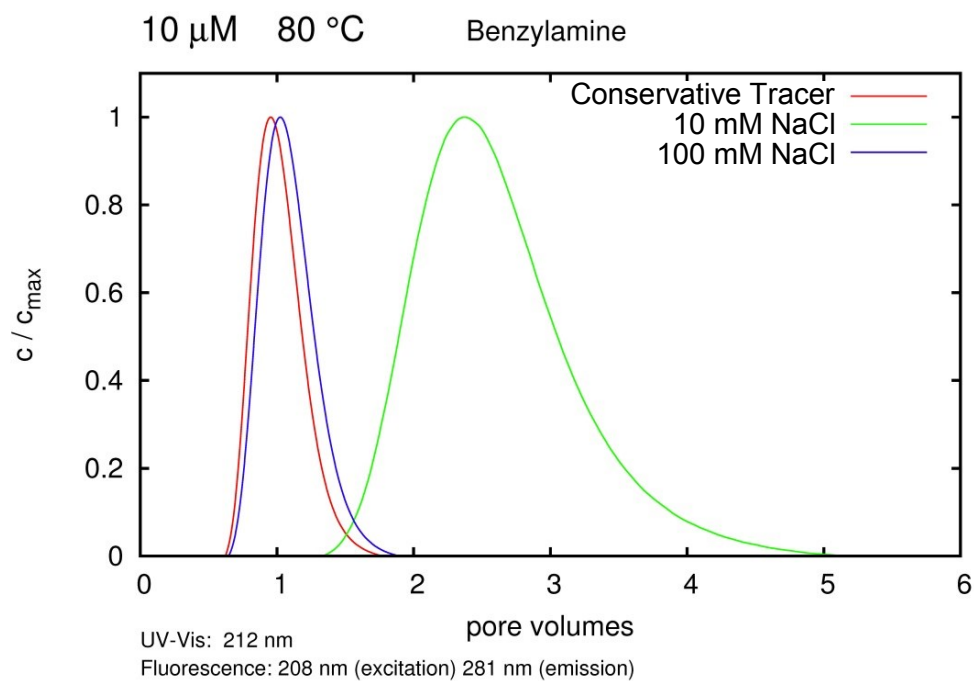
and, thus, a direct relative measure for  $A/V$ .  $R$  was determined by calculating the ideal breakthrough time (geometric center, first moment of area) of the observed tracer breakthrough curve and subsequent normalization to the conservative reference tracer ( $R = 1$ ). If  $K_{fw}$  is known (e.g., from lab experiments), it is even possible to derive absolute values for  $A/V$ .

## 3. RESULTS AND DISCUSSION

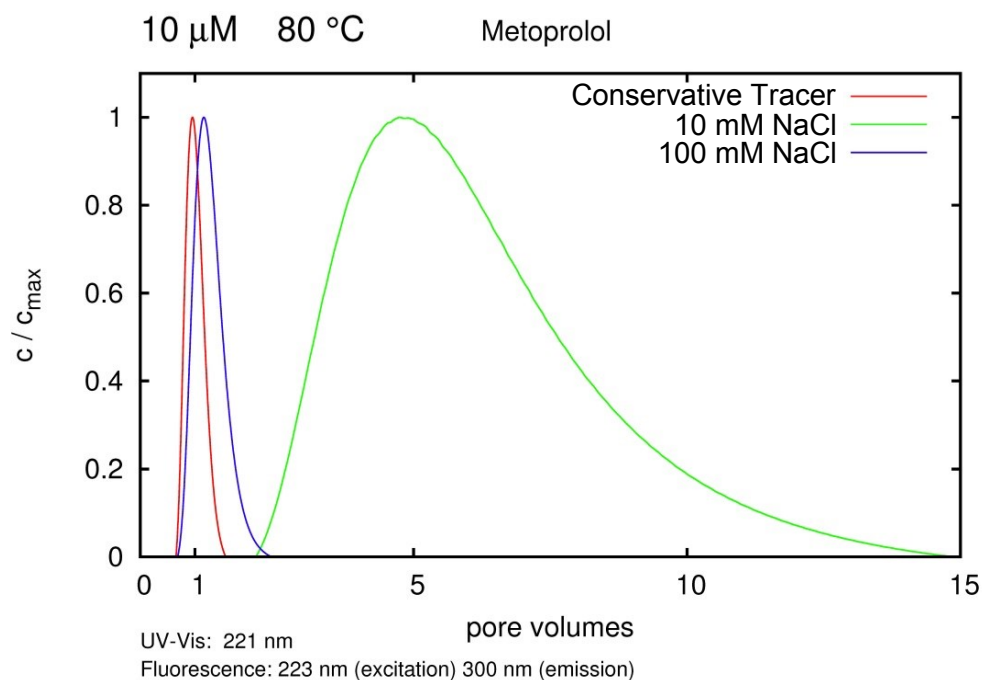
The first tested potential sorbing tracer compound benzylamine showed a considerable retardation (Fig. 2) of  $R = 2.54$  for the lower NaCl concentration of  $10\text{ mmol/L}$  ( $0.58\text{ g/L}$ ). For the ten times higher salt concentration ( $5.8\text{ g/L NaCl}$ ), a significantly lower retardation was observed ( $R = 1.08$ ). Assuming  $A/V = \text{const.}$ ,  $K_{fw}$  is reduced by a factor of around 19. This reduced sorption can be attributed to the increased competition between the cationic amine and the inorganic  $\text{Na}^+$  cation for the exchange sites of the sorbent (Schaffer et al., 2012a and 2012b; Niedbala et al., 2013). Consequently, lower or even no retardations are expected at higher salt concentrations. Thus, the successful application of benzylamine as sorbing tracer is unlikely in very saline reservoirs.

Generally higher retardations were observed for the pharmaceutical beta-blocker metoprolol (Fig. 3). The retardation varies between  $R = 6.23$  in a  $10\text{ mmol/L}$  and  $R = 1.25$  in a  $100\text{ mmol/L NaCl}$  solution. Equal to benzylamine,  $K_{fw}$  is reduced by a similar factor (around 21) implying a certain predictability of competitive effects as also proposed by Niedbala et al. (2013) and Kutzner et al. (2014). The more complex molecular structure (e.g., oxygen-containing ether or hydroxyl groups, secondary amine) may explain the higher absolute

retardation of metoprolol compared to benzylamine. This may be explained by additional sorptive interactions beside ion exchange, such as hydrogen bonding, that are able to contribute to the overall sorption of this organic cation (Kutzner et al., 2014).

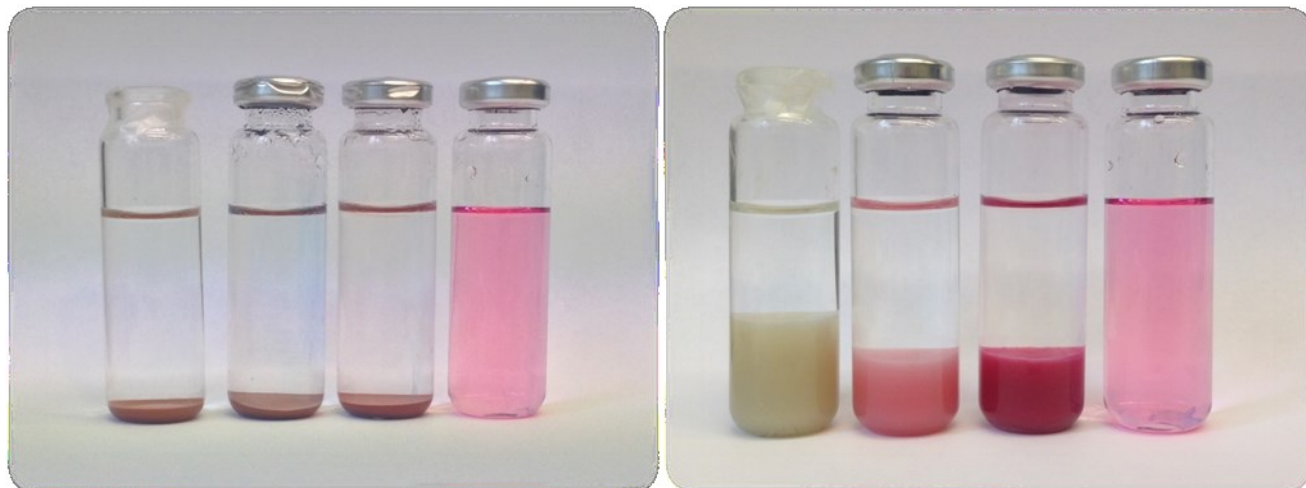


**Figure 2:** Normalized breakthrough curves of benzylamine for two different background concentrations of NaCl (green, blue) relative to the conservative reference tracer phenol (red) at pH = 5 and 80  $^{\circ}$ C. The recording frequency of the fluorescence detector was 4 Hz.



**Figure 3:** Normalized breakthrough curves of metoprolol for two different background concentrations of NaCl (green, blue) relative to the conservative reference tracer phenol (red) at pH = 5 and 80  $^{\circ}$ C. The recording frequency of the fluorescence detector was 4 Hz.

No breakthrough curves were obtained for the phenazine dye safranin. This is in contrast to the results from Leecaster et al. (2012) and Rose et al. (2012) who used rhyolitic tuff and sand as column filling in their experiments. After the injection, however, a considerable decrease in pumping pressure was observed. Further injections of higher concentrations even led to lower back pressures. This may be an indicator for the occurrence of irreversible sorption processes, e.g., caused by an intercalation of the quaternary ammonium compound into the layers of 2:1 clay minerals (formation of organoclays, Mallakpour et al., 2013). Additionally conducted batch tests revealed a very efficient discoloration of the safranin solutions (7  $\mu\text{M}$  and 133  $\mu\text{M}$ ) in conjunction with a violet coloring of the powdered sandstone (Fig. 4, left photo). Similar and even clearer effects were observed in batch experiments with the pure 2:1 smectite mineral montmorillonite (Fig. 4, right photo). Interestingly, the clay volume decreases tremendously when safranin is added to the solution. This volume reduction explains the decrease in pumping pressure and is a further evidence for the intercalation of safranin into the interlayers and, thus, the irreversible collapse of the clay minerals. Redox effects are very unlikely due to observed coloring and the exposure under atmospheric (aerobic) conditions. Eventually, it can be concluded that the use of quaternary ammonium compounds like safranin is not recommend as sorbing tracers when clay minerals (especially expansive 2:1 phyllosilicates) are present in the reservoir.



**Figure 4: Batch experiments of safranin at 80 °C in a 100 mM NaCl solution using powdered sandstone (left) and Wyoming Na-montmorillonite reference clay (right) as sorbents. The vials on the left in both pictures contain the respective sorbent without safranin and the vials on the right in both pictures contain the reference solution of safranin ( $c = 7 \mu\text{mol/L}$ ) without sorbent. The two vials in the middle contain the respective sorbent with two different concentrations of safranin.**

#### 4. CONCLUSIONS AND OUTLOOK

In order to test the potential of organic cations as sorbing tracers in geothermal systems, the sorption affinity of three selected organic cations with strongly differing molecular structures (a primary amine, a secondary amine with oxygen moieties, and a quaternary ammonium compound), was exemplarily investigated by conducting column experiments with a natural reservoir rock material.

Despite the irreversible sorption of the quaternary ammonium compound safranin, the results of the two other amines are promising due to their moderate sorption of the tested molecules even at relatively high background concentrations of salt. This implies a high potential of cationic organic compounds to act as sorbing tracer. On the one hand, a high sorption is desired in order to derive reliable values for  $A/V$ . On the other hand, however, too high sorption affinities require longer experimental durations and result in lower breakthrough concentrations, which complicate the analysis and/or require larger amounts of injected tracer. Consequently, the main challenge of applying sorbing tracers lies in finding the balance between sufficient high sorption coefficients (retardation factors) for the individual reservoir conditions and the technical as well as economical limitations regarding measurement and cost. In this context, it is advantageous that the structural differences of the organic cations lead to different sorption affinities in the experiments, which may allow a conscious selection and modification of suitable molecules for different boundary conditions. For doing so, more systematic investigations with the objective of identifying relevant molecular substructures are required in order to provide a sufficient data base of potential sorbing tracers. In parallel to the identification of structural elements in the molecules, experiments at higher temperatures and the investigation of the thermal stability of each potential sorbing tracer compound are very important. Here, the inclusion of “sorbing” and removal of “anionic” functional groups into/from established geothermal tracer molecules (molecular target design) may be a promising approach. Eventually, the results are a first stepping stone in order to develop a new in-situ method for detecting and monitoring the impact/success of reservoir stimulation activities, such hydraulic fracturing.

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