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TITLE: A new generation of tracers for the characterization of interfacial areas during supercritical carbon dioxide injections into deep saline aquifers: Kinetic interface-sensitive tracers (KIS tracer)

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A new generation of tracers for the characterization of interfacial areas during supercritical carbon dioxide injections into deep saline aquifers: Kinetic interface-sensitive tracers (KIS tracer)

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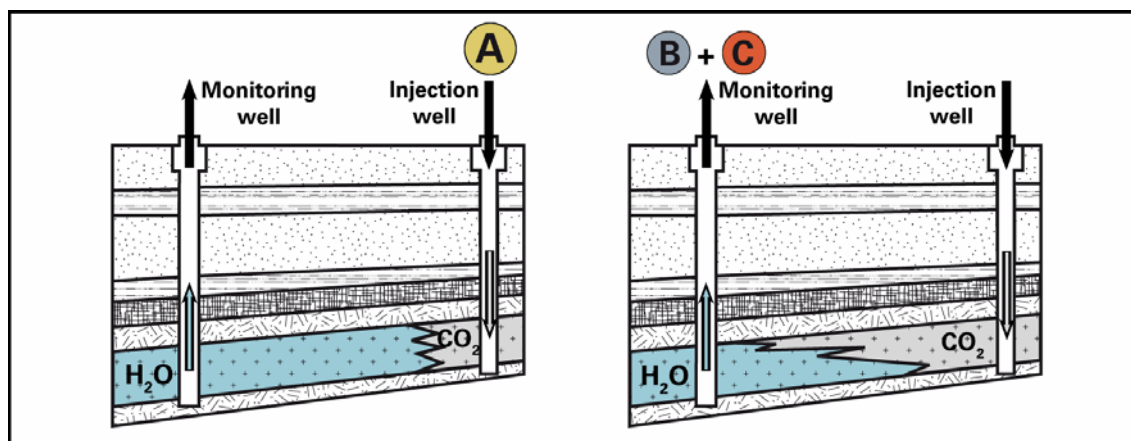
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Abstract

The storage of supercritical carbon dioxide in deep saline aquifers requires new techniques to assess plume spreading, storage efficiencies and operational strategies after and during injections. In this work, a new class of reactive tracers (KIS tracers) planned to be used for the characterization of interfacial areas between supercritical CO₂ and formation brine is presented. The implementation of a time-dependent hydrolysis reaction at the interface enables to investigate the development of the CO₂/brine interface. Besides the basic concept for these novel tracers and the methodology for a suitable target molecular design, the desired tracer properties as well as the exemplary synthesis of first promising compounds are presented here. Additionally, the first experimental results of an analog study in a static two-phase batch system are shown and evaluated with a newly developed macroscopic model. Subsequently, the numerical forward modeling of different functions for the interfacial area change is described. The first results are promising and show the potential for new applications of KIS tracers after further research.

Graphical abstract



Nomenclature

c	concentration of reaction product in water phase
c_0	initial concentration of reaction product in water phase
c_a	tracer concentration in scCO ₂
c_i	tracer concentration at interface
$c_{i,max}$	tracer concentration at saturated interface
k_l	hydrolysis reaction rate constant in water (one-phase system)
k_a	effective hydrolysis reaction rate constant (two-phase system)
m	slope of a line
p	pressure
p_c	pressure at critical point
pH	pH value
pK_a	logarithmic acid dissociation constant
q	specific mass flux across interface
scCO ₂	supercritical carbon dioxide
t	time
A	interfacial area size
A_{eff}	effective interfacial area
A_{scCO_2}	reactive Tracer in scCO ₂ phase (reactant)
B_{H_2O}	reaction product 1 in water phase
C_{H_2O}	reaction product 2 in water phase
D	diffusion coefficient
D_{H_2O}	diffusion coefficient in water
D_{scCO_2}	diffusion coefficient in scCO ₂
D_{OW}	pH-dependent <i>n</i> -octanol/water distribution coefficient
$E_T(30)$	empirical solvent polarity indicator (based on solvatochromism)
K_L	Langmuir sorption coefficient
K_{OW}	<i>n</i> -octanol/water distribution coefficient
NAPL	non-aqueous phase liquid
T	temperature
T_c	temperature at critical point
V	volume of water phase
λ	fluorescence: excitation wavelength → emission wavelength

1 Introduction

The storage of CO₂ into geological formations, such as unmineable coal beds, depleted oil or gas reservoirs, sedimentary basins and deep saline aquifers is recently one of the most promising technologies to mitigate anthropogenic greenhouse gas emissions into the earth's atmosphere (Lackner, 2003; Bachu and Adams, 2003; IPCC, 2005, 2007). Deep saline aquifers are considered as the most potential sequestration sites of CO₂ due to their large storage capacities and wide presence compared with other geological sequestration alternatives (Lackner, 2003; IPCC, 2005). The global storage capacity of these aquifers is estimated to be in the order of up to 10 teratons (IEA, 2001; Bachu and Adams, 2003).

When CO₂ is injected as supercritical fluid (scCO₂) above its critical point ($p_c = 7.39$ MPa, $T_c = 31.1$ °C) it has a lower density than the formation brine. Therefore, it is buoyant with respect to the brine and flows unevenly upwards until it reaches the top of the aquifer, usually represented by overlying and sealing caprocks. At this point the CO₂ is able to continue the migration only in lateral direction. Here, four trapping mechanisms play a major role (IPCC, 2005): (i) structural and stratigraphic trapping: hindrance of vertical CO₂ migration by impermeable caprock (static trapping) or very slow CO₂ migration over long distances in open systems (hydrodynamic trapping); (ii) capillary or residual trapping: retention of CO₂ by capillary forces as immobile phase in the pore space, disconnection from initial plume at the edges; (iii) solubility trapping: dissolution of CO₂ in brine, decreasing solubility with increasing temperature and salinity of brine (20–60 g L⁻¹); (iv) geochemical trapping: reaction of dissolved CO₂ in reservoir leads to formation of HCO₃³⁻/CO₃²⁻ species (ionic trapping) or precipitation of carbonate minerals at rock surfaces (mineral trapping) at higher pH.

Due to the different time scales ($t_{(i)} = t_{(ii)} < t_{(iii)} \ll t_{(iv)}$) dissolution and mineral trapping processes can be neglected during and shortly after the injection (IPCC, 2005; Juanes et al., 2007; Ide et al., 2007). Therefore, several authors assume sharp interfaces for the existing three-phase system scCO₂/brine/rock in their modeling approaches (Juanes et al., 2007; MacMinn and Juanes, 2009; Dentz and Tartakovsky, 2009). This approximation appears to be plausible from the physicochemical point of view, since as a result of the low solubility between the phases a very high concentration gradient exists between them. More concisely, a several angstroms thick interphase is formed due to the diffusion of scCO₂ into the brine phase (Tewes and Boury, 2005).

To assess the fate of CO₂ during and after injection into these aquifers, an understanding of spreading, mixing and plume migration is fundamental. Particularly, knowledge on the size, the amount, and the shape of the injected CO₂ plume is important to provide more information on the trapping effectiveness in the formation.

Dissolution of scCO₂ into the brine is limited by the interfacial area. Thus, numerous subsequent chemical processes (e.g., mineral dissolution, precipitation) are also directly affected. Therefore, the extent of the interfacial area between injected scCO₂ and brine is of great interest. The larger the interface, the larger is the reacted or dissolved mass. In most cases, it is desired to maximize this area to increase the storage effectiveness in terms of long-term trapping. During injections the interfacial area increases with time due to mixing, spreading and dispersive processes (Dentz and Carrera, 2005; Dentz and Tartakovsky, 2009). Therefore, novel tracers, which are able to describe and to characterize the spatial and temporal development of the plume and its interface in the reservoir, are required.

Up to now, such time-dependent tracers for reservoir studies are not available. Current studies are limited to equilibrium tracers. On the one hand, volume-sensitive partitioning tracers are used to quantify the amount or the saturation of immiscible hydrophobic phases (e.g., NAPLs or scCO₂) in porous multiphase systems under equilibrium conditions. Frequently used compounds are (Noordman et al., 2000): alcohols (Dwarakanath and Pope, 1998), gases (e.g., SF₆ and Kr; Vulava et al., 2002), fluorinated hydrocarbons (McCallum et al., 2005; Wells et al., 2007) and naturally occurring isotopes (e.g., ²²²Rn; Hunkeler et al., 1997). On the other hand, so-called “interfacial tracers” exist (Saripalli et al., 1998; Setarge et al., 1999; Annable et al., 1998). Anionic surfactants, such as linear alkylbenzenesulfonates (Saripalli et al., 1998; Kim et al., 1999), which adsorb exclusively on the interface between the water and the non-aqueous phase are applied. Hence, these tracers are interface-sensitive. But similarly to conventional partitioning tracers, a thermodynamic equilibrium between water and liquid/liquid-interface is assumed. Therefore, the application is only useful in static time-independent systems. Furthermore, these tracers are dissolved in the water phase and cannot be injected together with the scCO₂ phase.

The work presented provides first insight into the development of novel reactive tracers, termed as kinetic interface-sensitive tracers (KIS tracer). These tracers have the potential to overcome above-mentioned deficits by describing the plume and interface development with time. This is obtained by the implementation of an intended and well

studied hydrolysis reaction of the tracer molecule, which allows an irreversible chemical reaction at the scCO₂/water interface. Due to the reaction kinetics controlling the phase transfer a time-dependent component is integrated. In CO₂ sequestration reservoirs, the tracers may help to provide additional information on the following issues:

- Effect of pressure stimulation on mixing
- Plume spreading, characterization of interfacial area and area change
- Identification of fingering effects
- Estimation of residual scCO₂ saturation
- Assessment of storage capacity and effectiveness
- Optimization of operational strategies, management of injection wells

2 Theory – conceptual model

2.1 Application of KIS tracers during CO₂ injections

Before the CO₂ injection, the KIS tracer (A_{scCO_2}) is dissolved in supercritical or mixed with liquid CO₂. Afterwards, the mixture is injected simultaneously through the injection well into the brine saturated aquifer. The tracer reacts at the brine/scCO₂ interface to highly water soluble reaction products B_{H_2O} and C_{H_2O} . Subsequently, these products are measured in the water phase over time (monitoring well). Due to the spreading of the scCO₂ plume, the interfacial area increases with time (Fig. 1). The larger the interface (reaction surface) between both phases, the higher is the mass of the reaction products in the water phase. The high water solubility leads to negligible back-partitioning of the reaction products into the scCO₂ phase. Because of the implemented interface-sensitive hydrolysis reaction with known kinetic parameters, it is possible to establish a correlation between time, concentration in water phase, and interfacial area size for given reservoir conditions (T , p , pH). For the field evaluation and interpretation of the time-dependent interface development, these correlations may be integrated as specific reaction terms into a flow and transport model of the reservoir.

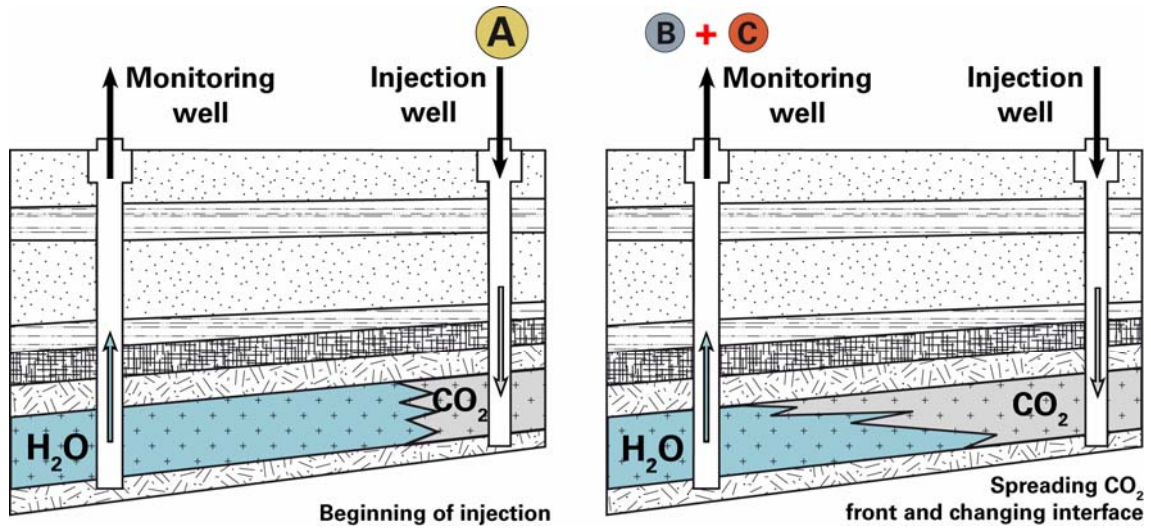


Fig.1 Injection well: Injection and spreading of scCO₂ together with dissolved KIS tracer. Monitoring well: Measurement of KIS tracer reaction products in the brine.

2.2 Underlying processes

The basis of KIS tracers is an interface-sensitive hydrolysis reaction at the scCO₂/brine interface. Here, the tracer substance A_{scCO_2} reacts irreversibly into two reaction products B_{H_2O} and C_{H_2O} in the presence of water (H₂O) at the interface:



The parameter k_1 depends on the physical and chemical conditions (e.g., T and pH) at the point of reaction and expresses the reaction rate constant of the hydrolysis reaction. Due to the presence of two mobile phases, several underlying physicochemical processes influencing the mass transfer from scCO₂ to the brine phase and the reaction speed have to be taken into account as well (Fig. 2):

(i) Dissolution of tracer in scCO₂ and diffusion toward the interface. A_{scCO_2} is dissolved and evenly distributed into the scCO₂ phase. This assumption is reasonable because the diffusion coefficients in scCO₂ are one order of magnitude higher than in water (e.g., for phenol $T = 35\text{--}55\text{ }^\circ\text{C}$: $D_{scCO_2} = 1\text{--}3\text{E}\text{--}08\text{ m}^2\text{ s}^{-1}$ (Lai and Tan, 1995) and $D_{H_2O} = 0.5\text{--}2\text{E}\text{--}09\text{ m}^2\text{ s}^{-1}$ (Niesner and Heintz, 2000)). Thus, a fast transport without limitations (small transport resistance) to the interface is expected.

(ii) Adsorption at the interface. The surface active tracer molecules A_{scCO_2} are assumed to accumulate at the interface (energy minimization) and saturate the interface after an initial time. This adsorption process normally follows a non-permeable mono-layer isotherm type, such as a Langmuir or Frumkin isotherm (Benjamin, 1997). The absolute

amount of adsorbed molecules depends linearly on the interfacial area. Due to an excess of dissolved A_{scCO_2} in the supercritical phase, the interface is assumed to be permanently saturated. Therefore, the concentration of A_{scCO_2} at the interface can be expected to remain constant.

(iii) Reaction at the interface. After adsorption at the interface, A_{scCO_2} reacts in contact with water. The envisaged hydrolysis reaction (see Section 3.1) of an ester with water follows a (pseudo)-first order kinetics (Nottebohm et al., 2012). Due to the constant interface concentration, the reaction kinetics simplifies to (pseudo)-zero order kinetics with linear behavior. Thus, the reaction kinetics is the limiting step for phase transfer across the interface.

(iv) Phase transfer. The highly water soluble reactions products B_{H_2O} and C_{H_2O} are distributed into the brine due to diffusion and thus away from the interface. Therefore, the concentrations of B_{H_2O} and C_{H_2O} increase proportionally to the decrease of A_{scCO_2} and can be measured in the water phase.

In addition to the interface-sensitive part of mass transfer across the interface, partitioning between both phases also has to be taken into account. Despite the low polarity and water solubility of A_{scCO_2} small amounts of A_{scCO_2} may partition into the brine phase. The resulting reaction in the water phase follows first order kinetics and would lead to an exponential increase of B_{H_2O} and/or C_{H_2O} in the water phase. Hence, the superposition of interface reaction and partitioning results in a non-linear function. *Vice versa*, a low back-partitioning of the polar and highly water soluble reaction products B_{H_2O} and C_{H_2O} into the $scCO_2$ phase may also occur. Because of the increasing complexity, it is desirable to be able to neglect or to minimize partitioning effects within the data evaluation. To estimate and compare the tendency for partitioning between both phases at reservoir conditions the *n*-octanol/water distribution coefficient K_{OW} was used as a model parameter due to similar solvent hydrophobicities of *n*-octanol and $scCO_2$ ($\log K_{OW(scCO_2)} = 2.85$ (50 °C, 143 bar; Nakaya et al., 2001), $\log K_{OW(n-octanol)} = 2.88$ (25 °C, 1 bar; SciFinder, 2012). Furthermore, Timko et al. (2004) showed for non-acidic compounds, such as the KIS tracers, that the $\log K_{OW}$ is correlated to the $scCO_2$ /water partitioning behavior.

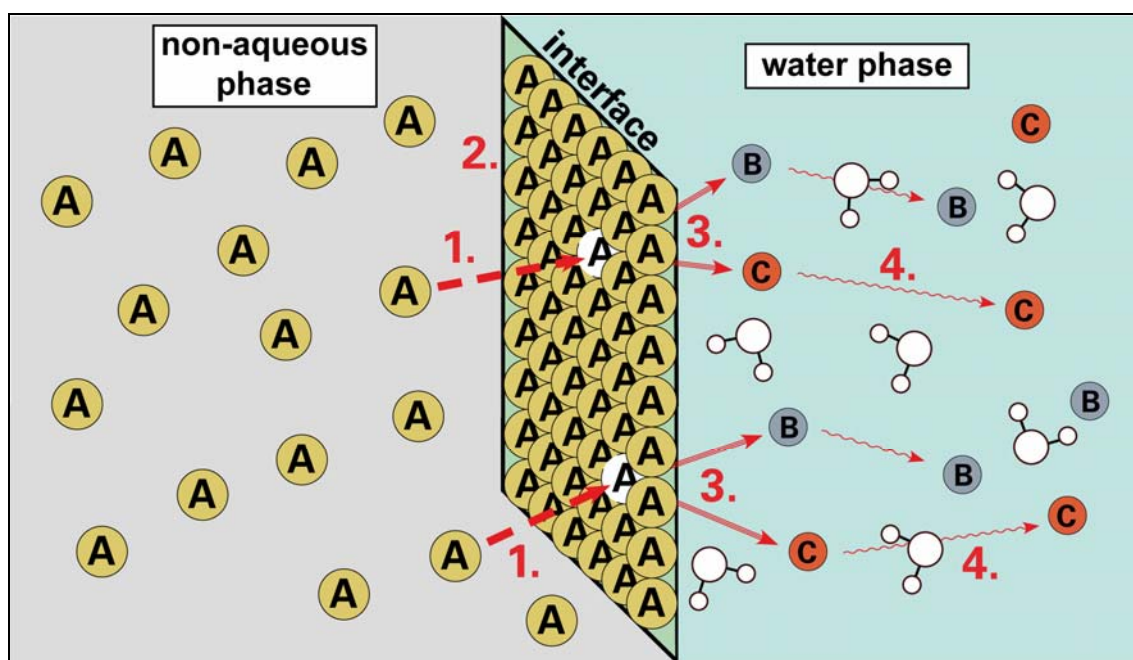


Fig. 2 Schematic representation of all involved processes at the scCO₂/water interface during KIS tracer application.

3 KIS tracer design

Molecular target design has been established as a methodology for producing molecules with desired properties or effects especially in the field of pharmaceutical, biochemical (Kuntz et al., 1994) and material sciences (Kang and Zhang, 2000). Due to the exploitation and combination of well studied structural elements and molecular properties (e.g., functional groups, substructures, and homologs) novel tailor-made compounds with controlled structures and properties are conceivable and can be synthesized for a magnitude of applications. During the molecular design quantitative structure-property relationships (QSPR) can be used as a tool for predicting molecule properties for the molecule selection/modification and to transfer their chemical behavior to unknown systems. In this work for instance, the relation of the molecule structure to the $\log K_{OW}$ value was used to estimate the water/scCO₂ partitioning behavior of the synthesized esters (see Section 3.2).

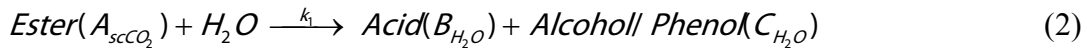
Up to now, the molecular design of tracer substances for environmental studies has not yet been considered. This also applies to challenging tracer tests in CO₂. Published tracer tests are limited to classical hydrogeological and thus commercially available tracer compounds. For example, Freifeld et al. (2005) and McCallum et al. (2005) applied several perfluorocarbons and noble gases (Kr, SF₆) for the determination of CO₂ travel times and the CO₂ saturation within the formation. Identical compounds were

used from Wells et al. (2007) and Hortle et al. (2011) to detect CO₂ leakage. For the same purpose, Bachelor et al. (2008) proposed the spiking of injected CO₂ with radioactive isotopes (¹⁴C and ²²²Rn).

Due to the limitations of conventional tracers, the general applicability of molecular design for geoscientific problems is shown here with KIS tracers as an example, especially developed for CO₂ injections into deep saline aquifers.

3.1 Tracer requirements

A prior consideration of the KIS tracer requirements is essential for a successful target design of potential tracer substances. For describing interfacial areas between scCO₂ and brine a defined reaction of the tracer with water is required. Splitting reactions with water as nucleophilic reagent belong to hydrolysis reactions as a subgroup of solvolysis. Hydrolysable substances are alcoholic and phenolic esters, acid chlorides, acid amides, and nitriles. Due to the comparably easy synthesis, different phenol esters were suggested and used in this work. The simplified hydrolysis reaction scheme is the following:



The esters are dissolved in scCO₂ (A_{scCO_2}) and should show minimal partitioning into the polar water phase. Since scCO₂ is an excellent solvent for non-polar compounds (Luque de Castro and Tena, 1996), the applied esters should also have non-polar substructures (e.g., linear *n*-alkyl chains, aromatic rings) with corresponding high log K_{OW} values.

In contrast, at least one of the hydrolysis reaction products has to be highly polar, water soluble and mobile in order to determine it in the water phase. For this purpose, the formed acids can be exploited (B_{H_2O}). Their ability of deprotonation is very convenient, since anions are formed depending on pH. Thus, especially the esters of strong organic acids with very low logarithmic acid dissociation constants pK_a seem to be the most promising compounds.

The requirements for the second reaction product (C_{H_2O}) are not so strict. The formed alcohols or phenols can be polar or even non-polar. If the product is medium polar with suitable distribution coefficients between the brine and scCO₂ phase, it may even be used as additional partitioning tracer. However, the major task of the alcohol or phenol,

respectively, is the adjustment of the KIS tracer properties during the molecular design. Beside the modification of the tracer polarity, the alcohols or phenols used for esterification have a large influence on the hydrolysis reaction rate constant k_l . This rate constant can be modified and adapted to reservoir conditions (T , pH) as well as for experimental durations. Steric hindrance, mesomeric and inductive effects are only some reasons for different hydrolysis kinetics and can be considered during synthesis (Nottebohm et al., 2012).

Regarding the practicability for field applications, the concentrations of reaction products should preferably be measured with standard equipment in a high temporal resolution, a high selectivity, and with a low detection limit. Therefore, the synthesis of the target compounds was focused on compounds with fluorescence properties.

3.2 Tracer design / synthesis

As a consequence of the prior emphasized requirements, the esterification of naphthalenesulfonic acids is most promising. Because of $pK_a < 1$, these acids are deprotonated at even very low pH levels and therefore, very water soluble permanent anions are formed. Thus, no significant retardation can be expected for organic acids at $pH > pK_a + 2$ (Schaffer et al., 2012). This also applies for naphthalenesulfonates, which are established conservative, non-sorptive tracers for geothermal applications, very stable at high temperatures and anaerobic conditions (Rose et al., 2001; Rose et al., 2002; Nottebohm et al., 2010). Furthermore, a back-partitioning of the anions into the scCO₂ phase can be excluded. For reservoirs, which are already contaminated with these compounds different constitutional isomers can be prepared to make the identification of the tracer unique. Furthermore, naphthalenesulfonates are highly fluorescent with a detection limit in the low $\mu\text{g L}^{-1}$ range. Pre-concentration and subsequent chromatographic separation lowers the detection limit by around one order of magnitude and enables the determination of different isomers even in highly saline matrices (Nottebohm and Licha, 2012).

Additional analytical problems might occur in sequestration reservoirs that contain significant residuals of hydrophobic aromatic compounds (e.g., depleted petroleum reservoirs), such as polycyclic aromatic hydrocarbons, since the dissolution of these substances in scCO₂ can be expected during the injection. The leached compounds accumulate at the scCO₂/brine interface and might cause fluorescence interferences with

the tracer reaction products. Thus, online measurements would be no longer possible and chromatographic systems have to be used again for sample clean-up and compound separation prior to fluorescence analysis.

If mononaphthalenesulfonic acids are applied, the esterification of the sulfo group leads to non-polar esters. In dependence of the deployed alcohol or phenol the ester properties can further be modified. For example, the esterification with linear aliphatic alcohols leads to non-polar but also non-fluorescent esters whereby the measurement of these compounds is more complicated. For this reason, aromatic alcohols (phenols, naphthols) can be used for the esterification of the naphthalenesulfonic acids (Fig. 3). The resulting fluorescent esters are hydrophobic ($\log K_{OW} > 4$).

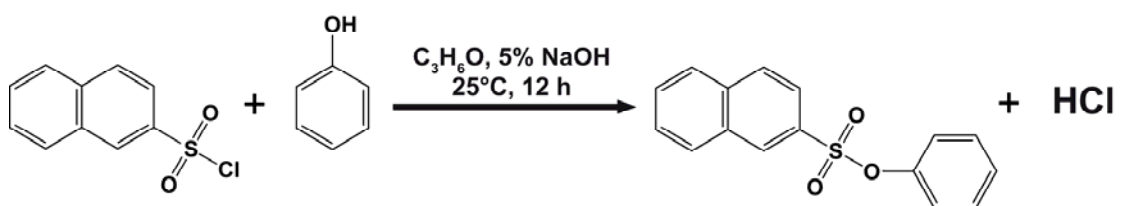


Fig. 3 Synthesis of phenyl naphthalene-2-sulfonate from naphthalene-2-sulfonyl chloride and phenol.

For the modification of the hydrophobic properties, different esters were synthesized by esterification of naphthalene-2-sulfonic acid (2-NSA) with different methyl substituted phenols. The more non-polar the employed phenol, the more non-polar is the resulting ester (Table 1). The esterification of chlorophenols therefore leads to more hydrophobic esters. However, the higher toxicity of these compounds should be also taken into account when used in field studies.

The ester compounds were synthesized on the basis of naphthalene-2-sulfonyl chloride and the respective phenol under alkaline catalyzed conditions (Fig. 3) in a slightly modified procedure according to Vennila et al. (2008). Instead of 4 mL acetone 6 mL were used. The identity and purity of the esters were confirmed by ¹H-Nuclear Magnetic Resonance (¹H-NMR) spectroscopy. The purity was >95%. The hydrolysis reaction results in 2-NSA and the respective phenol homologues (Table 1). The reaction scheme and the fluorescent properties for the phenyl ester are shown in Figure 4.

Table 1 Properties of synthesized KIS tracer compounds, phenyl acetate and their respective reaction products.

Ester (Abbreviation)	→	Acid	+	Alcohol / Phenol
Phenyl naphthalene-2-sulfonate (2-NSAPh) CAS 62141-80-4	$\log K_{OW}^*$ 4.29	Naphthalene-2-sulfonic acid (2-NSA) $\log K_{OW}^* = 0.63$ $pK_a^* = 0.27$ $\log D_{OW} (pH > 5)^* = -2.87$		Phenol $\log K_{OW}^*$ 1.54
<i>p</i> -tolyl naphthalene-2-sulfonate (2-NSA-4-Ph) CAS 108980-59-2	4.48			4-methylphenol (<i>p</i> -cresol) 2.07
3,5-dimethylphenyl naphthalene-2-sulfonate (2-NSA-3,5-Ph) CAS 889803-73-0	5.13			3,5-dimethylphenol (3,5-xylenol) 2.55
Phenyl acetate (PhAc) CAS 122-79-2	1.65	Acetic acid		Phenol 1.54

* SciFinder predicted values, calculated using Advanced Chemistry Development (ACD/Labs) Software (1994–2012).

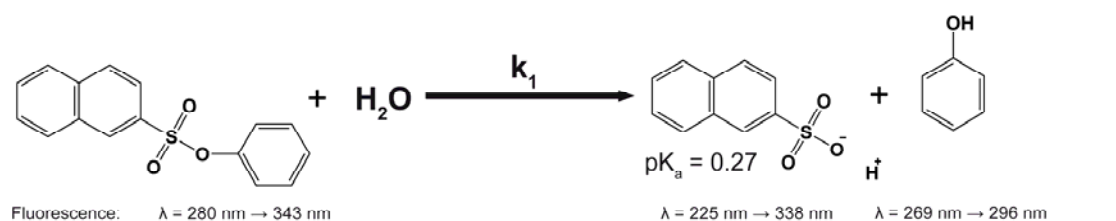


Fig. 4 Hydrolysis reaction of phenyl naphthalene-2-sulfonate with water and the fluorescent properties of the reagent and the reaction products.

4 Experiments and modeling

4.1 Lab experiments

4.1.1 Analog approach

Due to the necessity of high pressure cells to generate scCO₂ for identifying and quantifying the expected involved processes the new tracers cannot be tested easily under reservoir conditions. Available pressure cells and scCO₂ reactors are limited in size and in their setup variability. Furthermore, direct online measurements in the water phase cannot easily be employed and a sampling over time is not possible due to small

cell volumes of only a few milliliters. Therefore, the use of pressure cells seems to be feasible only for a limited number of fundamental static batch experiments, such as the determination of solubilities, partitioning coefficients, further thermodynamic equilibrium parameters, and the inertness of the tracer in mixture with other compounds.

In order to overcome these limitations, to investigate and to interpret the tracer behavior in defined systems at larger scale, the scCO₂ was replaced with another solvent. Particularly, organic solvents, which are immiscible with water, are expected to show a similar behavior and allow the process identification and separation at the interface on a larger scale without special equipment. For this purpose, different non-polar solvents were selected and tested with respect to density, polarity, inertness, and solubility in water.

The alkane *n*-octane has proven most suitable as scCO₂ analog. Table 2 compares some selected properties of scCO₂ at reservoir conditions with *n*-octane at atmospheric conditions. Density of scCO₂ depends strongly on temperature. In contrast, the density of *n*-octane is almost constant but lies in the same range. The solubility of scCO₂ in water under equilibrium conditions is higher than that of *n*-octane. Due to the timescale of scCO₂ dissolution (non-equilibrium), the salinity of the brine, and the presence of further dissolved gases (e.g., methane) a significantly lower water solubility can be assumed (IPCC, 2005). Therefore, *n*-octane develops analogously to scCO₂ a sharp interface to the water phase (see Section 1). For the comparison of the solvent polarity, which influences the tracer solubility and the partitioning between both phases, two different parameters were selected. On the one hand the log K_{OW} value, which depends for scCO₂ strongly on the pressure (Nakaya et al., 2001), and on the other hand the $E_T(30)$ value as empirical solvent polarity indicator (Reichardt, 1994) were used. As desired, these values lie for *n*-octane in the same range as for scCO₂. Additional advantages of *n*-octane are the low cost as well as the comparable low toxicity and vapor pressure. Therefore, the handling is uncomplicated and the compound can be used in larger amounts. All obtained values for kinetic rate constants, interface adsorption parameters, mass fluxes and mass transfer coefficients in the *n*-octane/water system can be transferred and adapted later to scCO₂ based on calibrated process models.

Table 2 Comparison of physical and chemical properties between scCO₂ with *n*-octane as analog compound.

Parameter	scCO ₂	<i>n</i> -octane
Density [g cm ⁻³]	0.52 (150 bar, 65 °C) ^a	0.67 (1 bar, 65 °C) ^b
	0.75 (150 bar, 40 °C) ^a	0.69 (1 bar, 40 °C) ^b
$E_T(30)$ [kcal mol ⁻¹]	28.5 (150 bar, 40 °C) ^c	31.1 (1 bar, 25 °C) ^d
log K_{OW} [-]	3.14 (150 bar, 50 °C) ^e	4.78 (1 bar, 25 °C) ^b
	4.87 (180 bar, 50 °C) ^e	
Solubility [mg L ⁻¹]	20–60 E+03 ^f	1.3 ^b

^a Calculated after Stryjek and Vera (1986) (www.criticalprocesses.com).

^b SciFinder predicted values, calculated using Advanced Chemistry Development (ACD/Labs) Software (1994–2012).

^c Eberhardt et al. (1997).

^d Reichardt (1994).

^e Nakaya et al. (2001).

^f IPCC (2005).

As an analog for the aqueous brine phase (buffer) solutions with different pH values can be used. This allows investigating the effects of different hydrolysis rate constants due to their direct relation to the pH value. The hydrolysis rate changes by about one order of magnitude per one pH unit increase (Nottebohm et al., 2012).

4.1.2 Experimental setup

For identifying, verifying, and separating the processes relevant for the developed novel KIS tracer application, major effort was made to simplify the experimental setup. The reason is that a profound knowledge of processes controlling the tracer interface sensitivity is fundamental to all consecutive investigations and the process modeling. Thus, an undisturbed (closed) system with fixed boundary conditions (constant interfacial area size, phase volume ratio, T , pH) and high temporal resolution measurements are necessary.

For this reason, static batch experiments were conducted directly in sealed small-volume fluorescence spectroscopy cuvettes ($V = 4$ mL). This approach has the advantage that the concentrations of the reaction products and the possibly partitioned tracer can be measured in short time intervals without mass loss and without disturbing the closed system by sampling. Furthermore, it is possible to adjust certain temperatures and stirring rates in the cells to avoid unwanted temperature changes and diffusive effects.

After providing 3 mL deionized or buffered and degassed water in the cuvette, 1 mL of *n*-octane containing the dissolved (KIS) tracer (2-NSAPh or PhAc) was carefully added above the water phase. The interfacial area was constant ($A = 1 \text{ cm}^2$). Consecutively, the concentration increase of the respective reaction products (2-NSA or phenol) in the water phase was recorded every minute for several thousand minutes by using fluorescence spectroscopy.

The resulting concentration curves of the measured compounds were used to determine the mass flux across the interface and to calibrate the numerical model that was developed in parallel to the experiments.

4.2 Numerical modeling

To understand the relationship between interface development and resulting concentration curves of the reaction products in the water phase, a numerical modeling approach using the finite element method was implemented. The problem can be described as a heterogeneous reaction of the KIS tracer at the scCO₂/water interface. The KIS tracer in the scCO₂ migrates to the interface and reacts here with the water in a hydrolysis reaction. In this study, a macroscopic model with averaged quantities was developed.

4.2.1 Model description

The comprehensive problem consists of the two different immiscible phases (scCO₂ or analog solvent and water) and of the allocation of the KIS tracer with its reaction products. Since the reaction at the interface is the limiting step in the mass transfer across the interface and due to high diffusion rates and the excess of tracer in the scCO₂ phase, the interface is permanently saturated. Here, a Langmuir (Langmuir, 1918) isotherm is assumed for the adsorption process onto the interface:

$$c_i = \frac{K_L \cdot c_{i,max} \cdot c_a}{1 + K_L \cdot c_a} \quad (3)$$

K_L is the Langmuir sorption coefficient. For high tracer concentrations c_a in the scCO₂ phase the interface concentration c_i is approximately equal to the maximum concentration of the saturated interface $c_{i,max}$. The assumption includes that the hydrolysis at the interface and the migration of the reaction products into the water

phase take place within one time step. It is additionally assumed that the reacted small fraction of tracer Δc_i at the interface is instantaneously replaced from the scCO₂ bulk due to large diffusion coefficients. Consequently, due to the interface limited transfer the KIS tracer decay in the non-aqueous phase follows the linear zero order reaction kinetics of the hydrolysis reaction. The effective reaction rate constant k_a of the limiting step can be expressed as a specific constant mass flux q of the reaction products into the water phase:

$$q = k_a = \frac{\Delta c_i}{\Delta t} \quad (4)$$

This allows the reduction of the numerical model to a single-phase problem. The model geometry follows the cuvette used in the lab experiment (see Section 4.1.2) with a base area $A = 1 \text{ cm}^2$. The height depends on the volume and therefore the filling level of water. The upper model boundary is equal to the interfacial area. The constant q of tracer products into the water phase, which is represented by the model domain, is defined as boundary condition. All other boundaries are no-flow boundaries (Fig. 5).

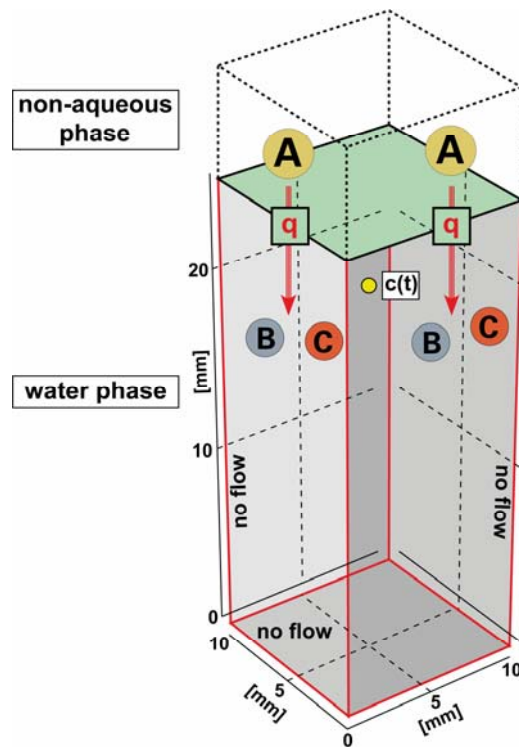


Fig. 5 Sketch of the numerical model domain: The yellow dot at 20 mm height represents the observation point where the fluorescence signal is measured. Red boundaries are no flow boundaries. On the upper green boundary the flux q is defined, where the reaction products flow into the water.

For the ionic tracer reaction product 2-NSA no back-partitioning into the scCO₂ phase is assumed. Hence, the concentration curve is only allowed to rise or to level at a constant value. The distribution of the product across the water volume is described through a diffusion process:

$$\frac{\partial c}{\partial t} = -D \frac{\partial^2 c}{\partial x^2} \quad (5)$$

Therefore, a steady-state concentration increase establishes in the model region (observation point) for a given constant interfacial area size.

4.2.2 Relation between concentration curve and interfacial area size

As stated above, the concentration of KIS tracer reaction product depends only on the interface size and time. The zero order kinetics of the hydrolysis reaction results for a constant interfacial area in a linear concentration curve $c(t)$:

$$c(t) = c_0 + q \frac{A}{V} t \quad (6)$$

Where A is the interfacial area, V the volume and c_0 the initial concentration in the water phase. From linear regression analysis the mass transfer rate q can be determined with:

$$q = m \frac{V}{A} \quad (7)$$

Here, m is the slope of the concentration curve. For the case of a time-dependent variable interfacial area $A(t)$ a decomposition ansatz is applied:

$$A(t) = f_A(t) \cdot A_{max} \quad (8)$$

A dimensionless time-dependent function $f_A(t)$ is used to scale a constant maximum area A_{max} . The function $f_A(t)$ must be equal to one when A_{max} establishes and has some additional properties:

$$f_A(t) \in [0, 1] \quad \text{and} \quad \exists \hat{t} \in [0, t_{max}] \quad \text{with} \quad f_A(\hat{t}) = 1 \quad (9)$$

The application of the ansatz in Eq. (8) in Eq. (6) leads to:

$$\frac{dc}{dt} = \frac{A_{max}}{V} q \cdot f_A(t) \quad \text{and} \quad (10)$$

$$c(t) = c_0 + \frac{A_{max}}{V} q \cdot \int f_A(t) dt \quad (11)$$

For the determination of A_{max} a case-by-case analysis of $c(t)$ has to be carried out:

$$i) \quad \exists \dot{c}(\hat{t})=0 \quad \Rightarrow \quad f(\hat{t})=1 \quad \text{if} \quad c(\hat{t}) = \max\{\dot{c}(\hat{t})\} \quad (12)$$

$$ii) \quad \exists ! \dot{c}(\hat{t})=0 \quad \Rightarrow \quad f(\hat{t})=1 \quad \wedge \quad A(\hat{t}) = A_{max} \quad (13)$$

$$iii) \quad \neg \exists \dot{c}(\hat{t})=0 \quad \Rightarrow \quad f(t_{max})=1 \quad \vee \quad f(0)=1 \quad \text{with} \\ A(T) = A_{max} \quad \vee \quad A(0) = A_{max} \quad (14)$$

Hence, A_{max} can be calculated with:

$$A_{max} = \frac{(c(\hat{t}) - c_0) \cdot V}{q} \cdot \frac{1}{\int_0^{\hat{t}} f_A(t) dt} \quad (15)$$

At this point it can clearly be seen that the time-dependent function $f_A(t)$ and consequently A_{max} are highly dependent on the sampling rate and detection limit of the reaction products.

4.3 First results from static batch experiments

Initially, the lab experiments were conducted with phenyl acetate (PhAc) as well as with the potential KIS tracer compound phenyl naphthalene-2-sulfonate (2-NSAPh) (Table 1). PhAc is the phenyl ester of acetic acid. Due to the significantly lower $\log K_{OW}$, the KIS tracer can be compared with a more hydrophilic compound as a reference. Thus, it is more likely that PhAc shows a stronger partitioning into the water phase than the more hydrophobic 2-NSAPh. The resulting concentration curves of the respective hydrolysis reaction products phenol (reactant: PhAc) and naphthalene-2-sulfonate (reactant: 2-NSAPh) are shown in Figure 6.

As expected, the desired hydrolysis reactions went on and both products could be measured online in the water phase by fluorescence spectroscopy. But obviously, both compounds developed a completely different curve shape. As mentioned above, a considerable partitioning additional to the interface sensitive part of mass transfer across the interface leads to an exponential increase of the phenol concentration curve for PhAc. Therefore, the interface sensitivity is lost and the compound is not suitable as KIS tracer. In contrast, 2-NSA showed a very promising curve shape. After an initial startup phase of around 2,000 min, a steady state condition established in the concentration change and the concentration increase became linear. The start-up phase

might be caused by the initial saturation of the interface, partitioning of ester impurities (2-NSA) and the final establishment of constant diffusion gradients. Furthermore, the linear slope of the concentration curve seems to confirm the expected reduction of first order to zero order kinetics and indicates a negligible partitioning of the ester between both phases.

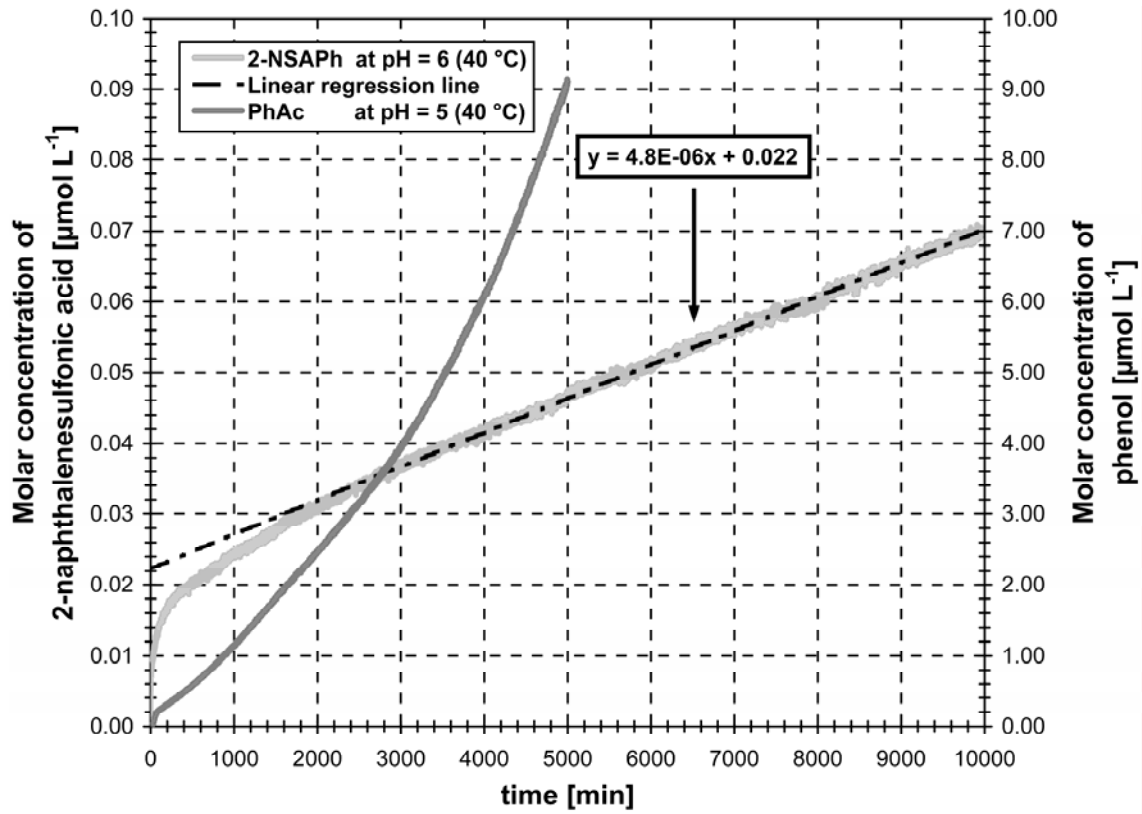


Fig. 6 Comparison of measured concentration curves for the hydrolysis reaction products of phenyl acetate (PhAc) and phenyl naphthalene-2-sulfonate (2-NSAPh).

For the evaluation of the interface sensitivity, a linear regression analysis was carried out for the values $t > 2,000$ min (Fig. 6, $R^2 = 0.99$). By applying the obtained slope $m = 4.8E-06 \mu\text{mol L}^{-1} \text{min}^{-1}$, and the given values $A = 1 \text{ cm}^2$, $V = 3 \text{ mL}$ for the cuvette in Eq. (7), q was calculated with $2.4E-06 \mu\text{mol m}^{-2} \text{s}^{-1}$. The fitted m depends directly on k_l of the hydrolysis reaction and is only valid for the given conditions. Conceivable changes in T , pH and the molecule structure would lead to different k_l and thus to different m and q , respectively (see Sections 3.1 and 4.1.1). During CO_2 injections, the pH is lower in the vicinity of the $\text{scCO}_2/\text{water}$ interface than for the experiments conducted in this study. Therefore, k_l and q are also expected to be lower under field conditions.

The numerical model was calibrated using the observed m from the static batch experiment and a constant interfacial area of $A = 1 \text{ cm}^2$ (Fig. 7). Additionally, three

different classical test functions $A(t)$ with properties according to Eq. (8) were applied and the resulting concentration curves were modeled to gain further insight into the behavior of KIS tracers. The concentrations are proportional to the integrated $A(t)$ which represents an effective area A_{eff} :

$$c(t) \propto \int_0^t A(t) dt = A_{eff} \quad (4.1)$$

Furthermore, the model allows the distinction between different functions for $A(t)$ even when A_{eff} and thus also the total amount of reacted tracer is equal (Fig. 7). Hence, A_{eff} is one of the main target parameters for proving the effectiveness of scCO₂ injections.

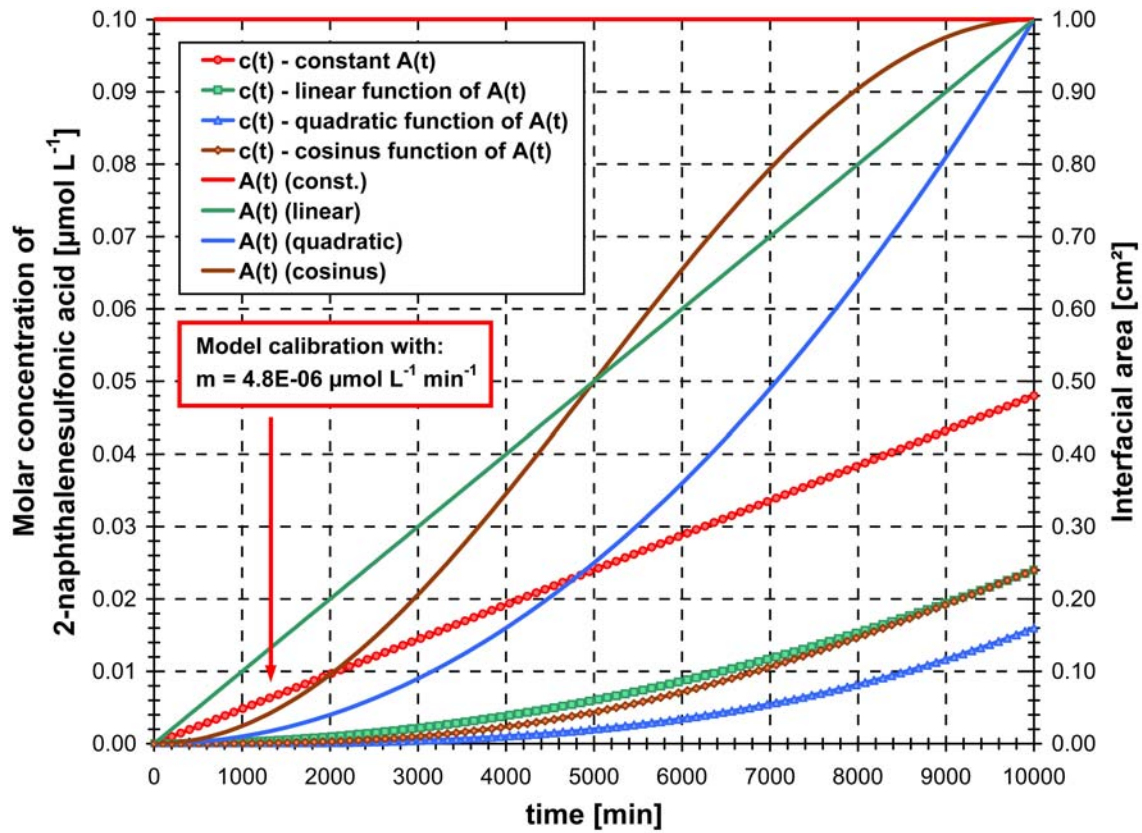


Fig. 7 Comparison of different modeled scenarios: Concentration curves are modeled based on different functions for $A(t)$. For the model calibration (red line) the constant A from the experiment was used.

5. Summary and conclusions

The interfacial area between scCO₂ and brine is an important parameter for the evaluation of CO₂ storage in deep saline aquifers, since numerous relevant trapping mechanisms and physicochemical processes are directly dependent on this reactive interface. Up to now, these interfacial areas and their development during injection cannot be studied directly. In this work, a methodology for the design of kinetic-

interface sensitive tracers (KIS tracers) was presented. These tracers are believed to have the potential to close the existing gaps for field experimental interpretation by implementing an interface-sensitive reaction. Here, the idea and the theoretical concept for these novel tracers were presented. After defining the tracer requirements and showing possibilities for a tailor-made molecular design, several compounds were successfully synthesized. An analog approach was proposed for testing the tracer behavior by replacing the non-aqueous scCO₂ phase with organic solvents. Additionally, a relationship between measured concentration curves and interfacial area was derived and a first model for the tracer evaluation in static batch systems was presented.

The results show, that molecular target design is a suitable method to develop these kinds of new tracers. As expected, the tested esters 2-NSAPh and PhAc confirmed the combination of mass transfer across the interface and hydrolysis reaction. The respective reaction products 2-NSA and phenol were detected in the water phase by fluorescence spectroscopy. However, in contrast to the newly synthesized potential KIS tracer compound 2-NSAPh, which demonstrated the expected linear increase of the reaction product 2-NSA in the water phase and thus interface sensitivity, PhAc showed no interface sensitivity due to a too strong partitioning behavior. The linear concentration increase of 2-NSA is very promising and supports the theoretically derived zero order reaction kinetics at the interface. Thus, a constant mass flux across the interface could be determined. Based on this flux, the new macroscopic numerical model was calibrated and different scenarios were calculated. The model demonstrated the interface sensitivity of KIS tracers and showed the possibility for evaluating the from lab experiments obtained concentration curves. In contrast to conventional equilibrium tracers (partitioning or interfacial tracers), KIS tracers are injected together with the non-aqueous phase and their reaction kinetics (non-equilibrium) is exploited to gain information on the temporal interface or plume development.

Future works will include additional process studies and modeling to describe the relevant processes, dependencies and mechanisms. Furthermore, the experiments will be extended to dynamic systems with a variable interface as well as repeated with additional compounds with regard to their possible application as KIS tracer. The influence of a third phase (rock material) on the tracer behavior will also be investigated.

In parallel, the existing model will be extended and adapted according to the experimental progress. Hence, it is planned to use the model as forecast tool for more complex dynamic systems. Finally, when all relevant physicochemical processes are completely understood, it should be possible to implement the model in a reservoir simulator.

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References

- Annable, M.D., Jawitz, J.W., Rao, P.S.C., Dai, D.P., Kim, H., Wood, A.L., 1998. Field evaluation of interfacial and partitioning tracers for characterization of effective NAPL-water contact areas. *Ground Water* 36 (3), 495–502.
- Bachelor, P.P., McIntyre, J.I., Amonette, J.E., Hayes, J.C., Milbrath, B.D., Saripalli, P., 2008. Potential method for measurement of CO₂ leakage from underground sequestration fields using radioactive tracers. *Journal of Radioanalytical and Nuclear Chemistry* 277 (1), 85–89.
- Bachu, S., Adams, J.J., 2003. Sequestration of CO₂ in geological media in response to climate change: capacity of deep saline aquifers to sequester CO₂ in solution. *Energy Conversion and Management* 44 (20), 3151–3175.
- Benjamin, I., 1997. Molecular structure and dynamics at liquid-liquid interfaces. *Annual Review of Physical Chemistry* 1997 (48), 407–451.
- Dentz, M., Carrera, J., 2005. Effective solute transport in temporally fluctuating flow through heterogeneous media. *Water Resources Research* 41 (8), 1–20.
- Dentz, M., Tartakovsky, D.M., 2009. Abrupt-interface solution for carbon dioxide injection into porous media. *Transport in Porous Media* 79 (1), 15–27.
- Dwarakanath V., Pope, G.A., 1998. New approach for estimating alcohol partition coefficients between nonaqueous phase liquids and water. *Environmental Science and Technology* 32 (11), 1662–1666.
- Eberhardt, R., Löbbecke, S., Neidhart, B., Reichardt, C., 1997. Determination of $E_T(30)$ values of supercritical carbon dioxide at various pressures and temperatures. *Liebigs Annalen* 1997 (6), 1195–1199.
- Freifeld, B.M., Trautz, R.C., Kharaka, Y.K., Phelps, T.J., Myer, L.R., Hovorka, S.D., Collins, D.J., 2005. The U-tube: A novel system for acquiring borehole fluid samples from a deep geologic CO₂ sequestration experiment. *Journal of Geophysical Research B: Solid Earth* 110, B10203.
- Hortle, A., de Caritat, P., Stalvies, C., Jenkins, C., 2011. Groundwater monitoring at the Otway Project site, Australia. *Energy Procedia* 4, 5495–5503.

- Hunkeler, D., Hoehn, E., Höhener, P., Zeyer, J., 1997. ^{222}Rn as a partitioning tracer to detect diesel fuel contamination in aquifers: Laboratory Study and Field Observations. *Environmental Science and Technology* 31 (11), 3180–3187.
- Ide, S.T., Jessen, K., Orr, F.M., 2007. Storage of CO_2 in saline aquifers: Effects of gravity, viscous, and capillary forces on amount and timing of trapping. *International Journal of Greenhouse Gas Control* 1 (4), 481–491.
- IEA Greenhouse Gas R&D Programme: Davison, J., Freund, P., Smith, A. (Eds.), 2001. Putting carbon back into the ground, http://www.ieaghg.org/docs/general_publications/putcback.pdf. Accessed 10th October 2011.
- IPCC: Metz, B., Davidson, O.R., de Coninck, H. C., Loos, M., Meyer, L.A. (Eds.), 2005. IPCC special report on carbon dioxide capture and storage, Cambridge University Press, Cambridge and New York.
- IPCC: Metz, B., Davidson, O.R., Bosch, P.R., Dave, R., Meyer, L.A. (Eds.), 2007. Summary for policymakers. In: *Climate change 2007: Mitigation*, Cambridge University Press, Cambridge and New York.
- Juanes, R., MacMinn, C.W., Szulczewski, M.L., 2010. The footprint of the CO_2 plume during carbon dioxide storage in saline aquifers: storage efficiency for capillary trapping at the basin scale. *Transport in Porous Media* 82 (1), 19–30.
- Kang, E.T., Zhang, Y., 2000. Surface modification of fluoropolymers via molecular design. *Advanced Materials* 12 (20), 1481–1494.
- Kim, H., Suresh, P., Rao, P.S.C., Annable, M.D., 1999. Consistency of the interfacial tracer technique: experimental evaluation. *Journal of Contaminant Hydrology* 40 (1), 79–94.
- Kuntz, I.D., Meng, E.C., Shoichet, B.K., 1994. Structure-based molecular design. *Accounts of Chemical Research* 27 (5), 117–123.
- Lackner, K.S., 2003. A guide to CO_2 sequestration. *Science* 300 (5626), 1677–1678.
- Lai, C.-C., Tan, C.-S., 1995. Measurement of molecular diffusion coefficients in supercritical carbon dioxide using a coated capillary column. *Industrial and Engineering Chemistry Research* 34 (2), 674–680.
- Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica, and platinum. *Journal of the American Chemical Society* 40 (9), 1361–1403.
- Luque de Castro, M.D., Tena, M.T., 1996. Strategies for supercritical fluid extraction of polar and ionic compounds. *TrAC Trends in Analytical Chemistry* 15 (1), 32–37.
- McCallum, S.D., Riestenberg, D.E., Cole, D.R., Freifeld, B.M., Trautz, R.C., Hovorka, S.D., Phelps, T.J., 2005. Monitoring geologically sequestered CO_2 during the Frio Brine pilot test using perfluorocarbon tracers. In: *Proceedings of the 4th Annual Conference on Carbon Capture and Sequestration*, Alexandria, USA.
- MacMinn, C.W., Juanes, R., 2009. Post-injection spreading and trapping of CO_2 in saline aquifers: impact of the plume shape at the end of injection. *Computational Geosciences* 13 (4), 483–491.
- Nakaya, H., Miyawaki, O., Nakamura, K., 2001. Determination of log P for pressurized carbon dioxide and its characterization as a medium for enzyme reaction. *Enzyme and Microbial Technology* 28 (2–3), 176–182.
- Niesner, R., Heintz, A., 2000. Diffusion coefficients of aromatics in aqueous solution. *Journal of Chemical and Engineering Data* 45 (6), 1121–1124.

- Noordman, W.H., de Boer, G.J., Wietzes, P., Volkering, F., Janssen, D.B., 2000. Assessment of the use of partitioning and interfacial tracers to determine the content and mass removal rates of nonaqueous phase liquids. *Environmental Science and Technology* 34 (20), 4301–4306.
- Nottebohm, M., Licha, T., Ghergut, I., Nödler, K., Sauter, M., 2010. Development of thermosensitive tracers for push-pull experiments in geothermal reservoir characterization. In: *Proceedings of the World Geothermal Congress*, Bali, Indonesia.
- Nottebohm, M., Licha, T., Sauter, M., 2012. Tracer design for tracking thermal fronts in geothermal reservoirs. *Geothermics* 43, 37–44.
- Nottebohm, M., Licha, T., 2012. Detection of naphthalene sulfonates from highly saline brines with high-performance liquid chromatography in conjunction with fluorescence detection and solid-phase extraction. *Journal of Chromatographic Science* 50 (6), 477–481.
- Reichardt, C., 1994. Solvatochromic dyes as solvent polarity indicators. *Chemical Reviews* 94 (8), 2319–2358.
- Rose, P.E., Benoit, W.R., Kilbourn, P.M., 2001. The application of the polyaromatic sulfonates as tracers in geothermal reservoirs. *Geothermics* 30 (6), 617–640.
- Rose, P.E., Johnson, S.D., Kilbourn, P.M., Kasteler, C., 2002. Tracer testing at Dixie Valley, Nevada using 1-naphthalene sulfonate and 2,6-naphthalene disulfonate. In: *Proceedings of the 27th Workshop on Geothermal Reservoir Engineering*, Stanford, USA, SGP-TR-171.
- Saripalli, K.P., Rao, P.S.C., Annable, M.D., 1998. Determination of specific NAPL-water interfacial areas of residual NAPLs in porous media using the interfacial tracers technique. *Journal of Contaminant Hydrology* 30 (3–4), 375–391.
- Schaffer, M., Boxberger, N., Börnick, H., Licha, T., Worch, E., 2012. Sorption influenced transport of ionizable pharmaceuticals onto a natural sandy aquifer sediment at different pH. *Chemosphere* 87 (5), 513–520.
- Setarge, B., Danzer, J., Klein, R., Grathwohl, P., 1999. Partitioning and interfacial tracers to characterize non-aqueous phase liquids (NAPLs) in natural aquifer material. *Physical Chemistry of the Earth, Part B: Hydrology, Oceans and Atmosphere* 24 (6), 501–510.
- Stryjek, R., Vera, J.H., 1986. PRSV: An improved Peng-Robinson equation of state for pure compounds and mixtures. *The Canadian Journal of Chemical Engineering* 64 (2), 323–333.
- Timko, M.T., Nicholson, B.F., Steinfeld, J.I., Smith, K.A., Tester, J.W., 2004. Partition coefficients of organic solutes between supercritical carbon dioxide and water: experimental measurements and empirical correlations. *Journal of Chemical and Engineering Data* 49 (4), 768–778.
- Tewes, F., Boury, F., 2005. Formation and rheological properties of the supercritical CO₂-water pure interface. *The Journal of Physical Chemistry B* 109 (9), 3990–3997.
- Vennila, J.P., Kavitha, H.P., Thiruvadigal, D.J., Manivannan, V., 2008. Phenyl naphthalene-2-sulfonate. *Acta Crystallographica Section E* 64, o2304.
- Vulava, V.M., Perry, E.B., Romanek, C.S., Seaman, J.C., 2002. Dissolved gases as partitioning tracers for determination of hydrogeological parameters. *Environmental Science and Technology* 36 (2), 254–262.
- Wells, A., Diehl, J., Bromhal, G., Strazisar, B., Wilson, T., White, C., 2007. The use of tracers to assess leakage from the sequestration of CO₂ in a depleted oil reservoir, New Mexico, USA. *Applied Geochemistry* 22 (5), 996–1016.