



The impact of partition coefficient data on the interpretation of chemical tracer behaviour in carbon geosequestration projects



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ABSTRACT

Partition (or distribution) coefficients determine the relative equilibrium concentrations of chemical constituents (or chemical tracers) in each of the phases of a multi-phase system under dilute conditions. The various fluid phases in a reservoir have differing transport properties (e.g. varying relative permeability) and to correctly interpret the behaviour of injected chemical tracers it is essential that accurate partition coefficients are known. In the context of carbon geosequestration or long-term storage of CO₂, chemical tracers will be predominantly exposed to an environment consisting of supercritical CO₂ and formation water as the main fluid phases. To estimate/simulate the reservoir properties relevant to injected CO₂ tagged with chemical tracers, it is therefore necessary to incorporate high pressure/temperature CO₂/water partition coefficients into any model/simulation. In this paper, we present a method to determine these partition coefficients for gaseous chemical tracers using a variation of the widely used EPICS (or equilibrium partitioning in a closed system) method. With this method, only the concentration in one phase (in this case, CO₂) needs to be measured. We then report these values for a series of representative chemical tracers (i.e. krypton, xenon, sulfur hexafluoride, perdeuterated methane and R134a) at pressure/temperature conditions that have been previously used at the CO₂CRC's Otway CCS demonstration project in Victoria, Australia. These values were generally lower than the corresponding Henry's Law coefficients at comparable temperatures. Experiments also examined the impact of adding CH₄ to the system to mimic feedstock gas at the CO₂CRC Otway project and provide data pertinent to scenarios where CO₂ is injected into depleted CH₄ gas fields. These values are compared with Henry's Law coefficients and another recently published set of high pressure/temperature partition coefficients. With computational simulations, we have shown that these differences are potentially significant and demonstrate their impact in three typical CO₂ geo-sequestration scenarios (i.e. injection into two types of aquifers and injection into a depleted reservoir with a gas cap).

1. Introduction

Chemical tracers are a complimentary method to geophysical and other geochemical techniques for monitoring the subsurface behaviour and properties of injected CO₂ in geosequestration projects (Myers et al., 2013). Unlike these other techniques (e.g. 4D seismic, InSAR), the sensitivity can be improved by simply scaling up the amount of tracer injected. Depending on the background concentrations of the tracers that are being used, this potentially allows for the detection of very low rates of any leaking outside of the intended storage reservoir. Furthermore, for monitoring and verification purposes chemical tracers

provide the unique opportunity to identify the source of CO₂ in a reservoir by co-injecting or “tagging” with different chemical tracers (Wells et al., 2007).

Despite this usefulness, chemical tracers are only an indirect monitoring tool as the CO₂ itself will typically have differing transport properties relative to chemical tracers (with the possible exception of isotopically labeled CO₂). An understanding of the relationship between subsurface behaviour of injected CO₂ and chemical tracers is therefore required before accurate estimates or interpretations can be ascertained about the subsurface transport of CO₂ within the storage reservoir during injection/production or leakage processes. In a reservoir,

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injected chemical tracers can partition between the various fluid phases and possibly even with the reservoir sediment through adsorption processes. Partition coefficients are typically used to quantify the thermodynamic equilibria that arise from these partitioning processes under the assumption of dilute conditions.

Partition coefficients which are a more general form of Henry's Law coefficients (i.e. Henry's Law coefficients are the ratio of the analyte concentration in the aqueous phase to the partial pressure in the gas phase) are predominantly determined in a laboratory by introducing a solute into a multi-phase system at low concentrations and independently measuring the concentrations in each of the phases once equilibrium has been established (Leo et al., 1971). For ideal compounds (i.e. those that do not exhibit strong intermolecular interactions or undergo a chemical reaction within one of the phases) the partition coefficient is simply the ratio of the measured concentrations in each of the phases and the partitioning behaviour can be described as a linear relationship with respect to concentration. As the partition coefficients are a ratio of concentrations, they can be prone to significant experimental errors when the denominator and numerator of this ratio are large. Partition coefficients describe the distribution of the chemical species at very low concentrations and as such describe the behaviour of chemical tracers fairly well because they are typically used only under very dilute conditions. However, experimental determination of various partition coefficients can be difficult for a number of reasons (e.g. technical/analytical quantification challenges, limited solubility) (Timko et al., 2004). In these instances, various correlation or computational models of the partitioning behaviour can be used to estimate partition coefficients (Katritzky et al., 2010).

For organic compounds, a variety of models for correlating octanol/water partition coefficients with compound structure using functional groups (Mannhold and van de Waterbeemd, 2001; Meylan and Howard, 1995) and water solubility with octanol/water partition coefficients have been developed (Banerjee et al., 1980; Kamlet et al., 1986). More recently supercritical CO₂/water partition coefficients were measured for a number of organic compounds and possible correlations/relationships to octanol/water partition coefficients, carbon disulfide/water partition coefficients, water solubility and linear solvation energy have been examined (Timko et al., 2004). However, these models focus on how the structure of organic compounds affect partitioning processes and are not particularly suitable for inert gas tracers.

Due to the limited availability of supercritical CO₂/water partition coefficients, Henry's Law coefficients which are accurate under dilute conditions at low pressures have been used as a proxy for modeling the behaviour of chemical tracers for CCS applications (LaForce et al., 2014; Zhang et al., 2011). Air, however, is a gas and is not a good mimic of the solvent characteristics of condensed phase supercritical CO₂. With this substitution there is the potential that the tracer partitioning processes are not correctly modeled, resulting in inaccurate interpretation of tracer behaviour and determination of reservoir properties. The main experimental difficulty with determining supercritical CO₂/water partition coefficients is that they must be conducted at high pressure/temperature to mimic reservoir conditions; however, this can be typically overcome with appropriate laboratory equipment. The determination of supercritical CO₂/water partition coefficients can be accomplished by measuring the tracer concentrations in both the CO₂ and water phases. However, accurately measuring the concentration of gaseous tracers dissolved in the aqueous phase under equilibrium conditions can be complex at the relevant reservoir pressure/temperature due to the need to de-pressurize the sample and quantitatively extract the sample from the water. For analytical quantification (e.g. gas chromatography), the dissolved gas in the water phase must be extracted using ultrasonic vacuum extraction (Holt et al., 1995). Due to the added complexity of this method and the potential for incomplete extraction, this method might potentially compromise the integrity of the analysis. Recently, however, this approach was successfully undertaken to determine high pressure/temperature CO₂/water partition

coefficients for noble gases (i.e. helium, neon, argon, krypton and xenon) through direct measurements of concentrations in both the CO₂ and water phases (Warr et al., 2015). Careful procedures were implemented to maximize the recovery of dissolved gases from the water phase.

In this study, a variation of the EPICS (or Equilibrium Partitioning In a Closed System) method is used as an alternative to the direct measurement method to overcome the technical difficulties associated with analytical measurement of a dissolved gas in the water phase, by conducting several partitioning experiments with different liquid/gas ratios and only measuring the gaseous solute concentration in the gas phase (Gossett, 1987; Robbins et al., 1993) or the liquid phase in the case of dissolved organic solutes (Lau et al., 2010). A regression type analysis is then used to determine the relevant partition coefficient.

A series of high pressure/temperature laboratory experiments is detailed and implemented here to determine supercritical CO₂/water partition coefficients for various inert gas chemical tracers (i.e. krypton, xenon, sulfur hexafluoride, perdeuterated methane and R134a). Using a similar concept to the EPICS method, a range of CO₂/water volume ratios were used for these experiments and the tracer concentrations were measured only in the CO₂ phase. We have also conducted a series of experiments using a 80 mol% CO₂/20 mol% CH₄ gas mixture to understand what impact methane might have on the chemical tracer partitioning behaviour considering that it is commonly associated with carbon dioxide in natural systems. Methane at approximately 20 mol% was present in the injected CO₂ for the CO₂CRC Otway Stage 1 project into a depleted gas field (Jenkins et al., 2012). These experiments were conducted at two different temperatures (i.e. 59 and 83 °C replicating the Otway Stage 1 and Stage 2B conditions) to develop an understanding of the influence of temperature on the partitioning processes. Simulations of tracer flow in the reservoir are used to provide a basis to compare the impact of using Henry's Law coefficients and the high pressure partition coefficients determined here on the interpretation of field results.

2. Method and materials

2.1. Chemicals

The tracer gas mixture containing Xe, R134a, Kr, and SF₆ is supplied by Coregas (Australia) as a 1.01% xenon, 1.00% R134a, 0.998% krypton and 0.993% sulfur hexafluoride mixture in CO₂. Perdeuterated methane (CD₄) was obtained from Cambridge Isotopes Laboratory (USA) with a quoted isotope purity value of 99.5%. Food grade CO₂ from BOC (Australia) is used for this study and was found to have less than 100 ppb of each of the tracer chemicals as measured by GC–MS; the low levels of these impurities were found to have a negligible effect. To determine the impact of CH₄ on the partitioning behaviour, an 80 mol% CO₂/20 mol% CH₄ gas mixture was obtained from Coregas (Australia).

Calibration of the GC–MS was performed using two certified standard gas mixtures (~1 and ~10 ppm) in helium from Coregas (Australia).

2.2. Equipment and experimental methods

Fig. 1 is a schematic detailing the configuration of the equipment used for the partitioning experiments during equilibration (Fig. 1a) and sampling (Fig. 1b). Water containing no appreciable salt concentration (i.e. de-ionized water) is used for these partitioning experiments enabling direct comparison with literature values for Henry's Law partition coefficients. A 316 stainless steel cylindrical vessel (42.5 cm long × 11.7 cm diameter) with an internal volume of 1.775 L and fitted with a single ¼ inch NPT male fitting at both the top and bottom was used for this study. The vessel is fitted with ball valves (FKB and H83 series from Swagelok) and used in a vertical configuration where denser

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