

EARTH SCIENCE AND RESOURCE ENGINEERING  
[www.csiro.au](http://www.csiro.au)



# Chemical Tracer Partition Coefficients for CCS

Matthew Myers, Cameron White, Bobby Pejdic, Linda Stalker and Andrew Ross

March 22, 2013

CSIRO Report # EP133018

ANLEC R&D Project 3-1110-0125 Fundamentals of tracer applications for CO<sub>2</sub> Storage

## Copyright and disclaimer

© 2013 CSIRO To the extent permitted by law, all rights are reserved and no part of this publication covered by copyright may be reproduced or copied in any form or by any means except with the written permission of CSIRO.

## Important disclaimer

CSIRO advises that the information contained in this publication comprises general statements based on scientific research. The reader is advised and needs to be aware that such information may be incomplete or unable to be used in any specific situation. No reliance or actions must therefore be made on that information without seeking prior expert professional, scientific and technical advice. To the extent permitted by law, CSIRO (including its employees and consultants) excludes all liability to any person for any consequences, including but not limited to all losses, damages, costs, expenses and any other compensation, arising directly or indirectly from using this publication (in part or in whole) and any information or material contained in it.



# Contents

Acknowledgments .....	6
Executive Summary .....	7
<b>Part I Chemical Tracers and Partition Coefficients</b>	<b>8</b>
1 Chemical Tracers in CCS Projects .....	9
1.1 Introduction .....	9
1.2 Tracers Relevant to the CO <sub>2</sub> CRC Otway Project and Frio Brine Projects .....	9
2 Partition Coefficients and Review of the Literature.....	12
2.1 Currently Known Information on the Partitioning Behaviour of Inert Gas Tracers.....	14
2.2 Currently Known Information on the Partitioning Behaviour of Reactive Ester Tracers.....	15
3 Conclusions .....	17
4 References.....	18
<b>Part II Partition Coefficients: Thermodynamics and Experimental Methods</b>	<b>20</b>
1 Experimental Methods for Determining Tracer Partition Coefficients.....	21
1.1 Thermodynamics .....	21
1.2 High-pressure/temperature experimental apparatus and sampling protocols .....	22
1.3 Direct measurement of concentrations in two separate phases .....	22
1.4 Measurement of concentration in one phase, varying volume ratio of two phases with total amount of solute kept constant .....	23
1.5 Measurement of concentration in one phase, varying volume ratio of two phases while the initial concentration of solute in one of the phases is kept constant .....	25
2 Scope of experimental projects determining tracer partition coefficients .....	27
3 Conclusions .....	28
4 References.....	29
<b>Part III Reactive Ester Tracer Partition Coefficients</b>	<b>30</b>
1 Experimental Methods and Theory .....	31
1.1 Chemicals .....	31
1.2 Apparatus and Experimental Methodology.....	31
1.3 Preparation of Tracer Samples for GCMS Analysis .....	32
1.4 GCMS Analysis of Parent Ester Tracers.....	33
2 Results and Discussion .....	34
3 Conclusion.....	42

## Figures

Figure 1 An example of the different liquid to headspace ratios used to determine H for a given tracer. Total volumes of each sample bottle are constant as well as the amount of tracer added.....	24
Figure 2 A representation of the sample bottle setup for liquid tracers, the concentration of tracer in the liquid phase is the same in all bottles but the amount of moles varies.....	26
Figure 3 Schematic of tracer setup including pumps, recirculation capacity and sampling ports.....	32
Figure 4 van't Hoff plot for propylene glycol diacetate.....	38
Figure 5 van't Hoff plot for triacetin.....	38
Figure 6 van't Hoff plot for tripropionin.....	39
Figure 7 van't Hoff plot for propylene glycol monoacetate isomer 1.....	39
Figure 8 van't Hoff plot for propylene glycol monoacetate isomer 2.....	40
Figure 9 van't Hoff plot for dipropionin isomer 1.....	40
Figure 10 van't Hoff plot for dipropionin isomer 2.....	41
Figure 11 Plot of enthalpy data vs. number of carbons for parent ester tracers.....	42

## Tables

Table 1 Tracers Implemented at CCS Projects.....	10
Table 2 List of Known Supercritical CO <sub>2</sub> /Water Mole-Fraction Based Partition Coefficients in the Literature (from Timko et al. 2004 and references therein)*.....	13
Table 3 Temperature Dependence of Henry's Coefficients for Inert Gas Tracers. Data amalgamated from (Mroczek, 1997, Wilhelm et al., 1977 and Gomes and Grolier, 2001. ....	14
Table 4 Supercritical CO <sub>2</sub> /water Partition Coefficients for Reactive Ester Tracers at 62 °C.....	15
Table 5 Socpe of Tracer Partition Coefficient Studies.....	27
Table 6 Dimensionless partition coefficient data for reactive parent ester tracers and their daughter hydrolysis products at varying temperatures.....	34
Table 7 The calculated enthalpies of selected tracers.....	41

## Acknowledgments

The authors wish to acknowledge the financial assistance provided through Australian National Low Emissions Coal Research and Development (ANLEC R&D), financial assistance from CSIRO Petroleum and Geothermal Portfolio and data provided by the CO2CRC. ANLEC R&D is supported by the Australian Coal Association Low Emissions Technology Limited and the Australian Government through the Clean Energy Initiative.

## Executive Summary

The primary aims of this project are to establish general methodologies for determining supercritical carbon dioxide/water partition coefficients for chemical tracers and to determine these in a series of laboratory experiments for a variety of chemical tracers relevant to CCS. There is a general lack of information on these partition coefficients and that often octanol/water and/or air/water partition coefficients are used as substitutes in simulations of tracer behaviour. However, supercritical carbon dioxide/water coefficients are necessary for both planning tracer field trials and accurately interpreting tracer behaviour. In the context of a monitoring and verification program for a CO<sub>2</sub> storage project, an accurate interpretation of tracer results is critical for determining whether leaking from the storage reservoir is occurring thus demonstrating a potential containment breach. To demonstrate the rationale for this project a review of known partition coefficients for chemicals of relevance to CCS as tracers is given. This review confirms that there is a general lack of data on supercritical carbon dioxide/water partition coefficients. The chemical thermodynamics governing the partitioning process is discussed and the general theory and experimental protocol for determining supercritical carbon dioxide/water partition coefficients is given. The specific methodologies implemented in this project for determining these coefficients for reactive ester tracers (propylene glycol diacetate, triacetin and tripropionin) and inert gas tracers (xenon, krypton, R134a, sulphur hexafluoride and perdeuterated methane) is given alongside a comprehensive table of partition coefficients at various temperatures for these tracers. We have shown that temperature dependence of the partition coefficient correlates well with a van't Hoff type relationship (i.e.  $\ln K$  vs.  $1/T$ ). These correlations provide considerable insight into the thermodynamics associated with the partitioning process and will enable the accurate simulation of these chemical tracers at any temperature within the studied range of temperatures.

# Part I Chemical Tracers and Partition Coefficients



# 1 Chemical Tracers in CCS Projects

## 1.1 Introduction

It is important to review the current literature to obtain any relevant information that may have been published on tracer compound partition coefficients between supercritical (and other forms of) CO<sub>2</sub> and water (with or without added minerals). It has been noted by various researchers examining the potential use of tracer compounds in carbon storage projects that quantified partition coefficients are greatly lacking in the literature (Myers et al., 2012a). As such, the Commonwealth Scientific Industrial Research Organisation (CSIRO) has invested in new equipment designed to make these measurements for various tracer applications. This project aims to measure partition coefficients for tracers that have already been deployed at various carbon storage sites. For example, the CO2CRC granted the project access to use the tracer data set generated at the CO2CRC Otway Stage 1 and Stage 2B projects in Victoria. With quantified partition coefficients, it will be possible to provide better constrained interpretations of observed tracer data and contribute towards reducing uncertainty in model forecasting. The following is a short summary of particular chemical tracers applied to various recent CCS projects globally with the goal of identifying a set of tracers that will be characterised as a part of this study. This will serve to validate the usefulness of the results that will be generated by the laboratory experiments that comprise the main research component of this project. Furthermore, this study will focus exclusively on chemical tracers that are added to the formation during injection and will not examine naturally occurring tracers (i.e. chemical species already previously present in the formation mobilized as a result of CO<sub>2</sub> injection).

Predicting and understanding the behaviour of CO<sub>2</sub> is challenging due to its complex phase behaviour (i.e. CO<sub>2</sub> can exist in the subsurface as a liquid, gas, supercritical fluid or a solute in water depending on the physical/chemical conditions) and the wide range of possible trapping mechanisms (i.e. residual, solubility, structural and mineral). Commonly proposed storage scenarios involve pumping CO<sub>2</sub> into reservoir rock formations at depths greater than 800 metres, where the pressure/temperature typically exceeds the critical point of carbon dioxide (7.38 MPa, 31.1°C). Chemical tracers represent a complimentary reservoir characterisation and monitoring tool to alternative approaches such as geophysical measurements (e.g. time lapse seismic) and have been used extensively worldwide at carbon capture and storage (CCS) sites. The majority of tracer applications within CCS are related to either understanding the subsurface movement of carbon dioxide (Boreham et al., 2011; Freifeld et al., 2005; Underschultz et al., 2011; Vandeweyer et al., 2011), quantifying the trapping capacity (Zhang et al., 2011) or determining containment and leakage rates for monitoring and verification programs (Strazisar et al., 2009; Wells et al., 2010; Wells et al., 2007). Chemical stability, cost effectiveness, ease of detection, toxicity, injection/sampling protocols and subsurface behaviour, together dictate the choice of tracer for a particular application or scenario.

## 1.2 Tracers Relevant to the CO2CRC Otway Project and Frio Brine Projects

Perdeuterated methane (CD<sub>4</sub>), krypton (Kr) and sulphur hexafluoride (SF<sub>6</sub>) were used as tracer gases for the CO2CRC Otway Stage 1 Project (Boreham et al., 2011). The breakthrough of the injected CO<sub>2</sub> plume was identified by the presence of the tracer compounds, an increase in CO<sub>2</sub> concentration over background

levels and a change in the  $\delta^{13}\text{C}$  of the measured  $\text{CO}_2$ . From the available publications on this project, reservoir simulation of tracer behaviour within the relevant geological formations is currently lacking (Boreham et al., 2011; Jenkins et al., 2012; Underschultz et al., 2011). Although, some activity has been directed at reservoir simulation of the results, a full synthesis has not yet been published. This can be partially attributed to a distinct lack of fundamental information on tracer behaviour (derived from laboratory based experiments) with which to develop accurate models. Also in this case, the effect of methane (both within the storage reservoir and as component of the injected gas which contains approximately 20% methane) on tracer behaviour adds additional complexity to the system and its effect is largely unknown. In this case, these uncertainties in the physical properties of the tracer compounds translate into uncertainty in the interpretation of the final observations.

For the Frio Brine Projects in Texas, various perfluorocarbons,  $\text{SF}_6$ , Kr and  $\text{CD}_4$  were injected as tracers to detect  $\text{CO}_2$  breakthrough in an interwell (injector/producer) configuration (Hovorka et al., 2006). For similar reasons as with the CO2CRC Otway Project, a detailed reservoir simulation of tracer behaviour has not been published. Although tracer injections were useful in the case of both the Otway and Frio Brine projects for limited/qualitative interpretations (i.e. determining breakthrough of injected  $\text{CO}_2$ ), for other purposes such as monitoring for leaks into the atmosphere, knowledge of the partitioning behaviour between water and  $\text{CO}_2$  under a variety of geological conditions is instrumental. As such an understanding of tracer behaviour in  $\text{CO}_2/\text{CH}_4$  and water would not only be very helpful for modelling tracer behaviour for the Otway and Frio Brine field trials, it would also provide critical information for interpreting tracer behaviour in future projects. Furthermore, tracer partition coefficient often determines the suitability of a tracer for a particular application (e.g. for estimating sweep volumes, non-partitioning tracers are appropriate whereas partitioning/reactive tracers are not).

Table 1 summarises the application of particular chemical tracers at various CCS sites around the world including at the Otway and Frio Brine sites. Not surprisingly, inert tracers which include perfluorocarbons (e.g. perfluorocyclohexane, perfluoromethylcyclopentane), krypton, xenon, sulphur hexafluoride, R134a and deuterated methane are the dominant choices due to their limited interaction with the reservoir rocks and formation water. Tracers with reactive functional groups are much less common.

**Table 1 Tracers Implemented at CCS Projects**

Tracers (*tracers chosen for characterisation as part of this ANLEC project)	CCS site / Application
Sulphur hexafluoride*, perdeuterated methane* and krypton*	Otway Stage 1 / understanding the migration of a $\text{CO}_2/\text{CH}_4$ mixture between a producer 300 metres up-dip from an injector and the influence of a natural gas-water contact on mixing (Boreham et al., 2011; Underschultz et al., 2011)
Sulphur hexafluoride *, krypton*, perfluorocarbons (perfluoromethylcyclohexane, perfluorotrimethylcyclohexane, perfluoromethylcyclopentane, perfluorodimethylcyclohexane) perdeuterated methane*	Frio Brine I / understanding the migration of carbon dioxide between a producer 30 metres up-dip from an injector (Freifeld et al., 2005)  Frio Brine II / $\text{CD}_4$ and other tracers were tested to understand evolution of a $\text{CO}_2$ plume in an interwell configuration.
Perfluorocarbons (perfluorodicyclohexane, perfluorotricyclohexane and	West Pearl Queen / surface gas samples are taken to assess formation-to-surface $\text{CO}_2$ leakage

---

perfluorodimethylcyclobutane)	rates (Wells et al., 2007)
Krypton* and xenon*	Otway Stage 2B / in a single-well “push-pull” test to determine residual CO <sub>2</sub> saturation (Zhang et al., 2011)
Perfluoromethylcyclopentane and perfluorodimethylcyclohexane	K12B/to understand the migration of CO <sub>2</sub> between wells in a compartmentalized field
Reactive esters (propylene glycol diacetate, triacetin and tripropionin) and their hydrolysis products*	Otway Stage 2B / in a single-well “push-pull” test to determine residual CO <sub>2</sub> saturation

---

## 2 Partition Coefficients and Review of the Literature

Partition coefficients describe the equilibrium behaviour of a given chemical species between two immiscible phases (e.g. oil/water and air/water). For sufficiently dilute solution conditions (i.e. the concentration of the chemical species in each phase is much lower than the solubility limit), it is defined as the ratio of the chemical concentrations in each of the two phases (Srebrenik and Cohen, 1976). As tracers are typically utilized at low concentrations (i.e. ppm or lower concentration), partition coefficients are essential for accurately characterizing their behaviour in multi-phase systems. Both theory and practice have demonstrated that partition coefficients often exhibit Arrhenius type temperature dependence (i.e.  $\log K$  vs.  $1/T$  where  $T$  is the thermodynamic temperature and  $K$  is the partition coefficient) (Bahadur et al., 1997; Moreira et al., 1993).

Octanol-water partition coefficients have been used extensively in understanding and predicting the bioaccumulation and environmental fate of organic species (Cronin et al., 2003). Henry's Law coefficients (otherwise known as air/water partition coefficients) have been used to understand the interaction of atmospheric chemicals with bodies of water (Rathbun, 2000).

For CCS projects, the two most dominant phases within the formation are typically supercritical  $\text{CO}_2$  and water. However, there is currently limited fundamental information on the supercritical  $\text{CO}_2$ /water partitioning behaviour for organic compounds (see Table 2 for a list of reported values) (Timko et al., 2004). Notably, there is no existing supercritical  $\text{CO}_2$ /water partition coefficient data for any inert gases used in the referenced CCS tracer test applications. Furthermore, there are currently no reports of any of the compounds in Table 2 (where the partition coefficients have been measured for supercritical  $\text{CO}_2$ /water partitioning) being used as tracers for either CCS or oil and gas projects. Rather, other partition coefficients (namely air/water [Henry's] and octanol/water) are often used as parameters in modelling tracer behaviour. In particular, the EOS7C module in the TOUGH2 dynamic reservoir simulation software has a parameter for the inverse Henry's coefficients which is used to describe tracer partitioning behaviour between  $\text{CO}_2$  and water (Oldenburg et al., 2004). Octanol and air have very different chemical properties than supercritical carbon dioxide and as such these alternative parameters may not be representative or indicative of actual subsurface behaviour (Zhang et al., 2011).

The overall aim of this project is to address this knowledge gap through a variety of laboratory based experiments with the goal of determining the partitioning behaviour for a variety of chemical tracers under a range of physical conditions. This will result in more accurate modelling and interpretation of tracer data leading to reduced risk and uncertainty for site characterisation, insurance/permitting, well drilling/operation and monitoring/verification assessments. Generally this lack of fundamental information on tracer behaviour has resulted on a reliance on other types of partition coefficient (as described above) potentially resulting in inaccuracies or flaws in the interpretation of chemical tracer data.

Clearly there is a need to determine the partition coefficients of tracers in regards to their partitioning behaviour between supercritical  $\text{CO}_2$  and  $\text{H}_2\text{O}$  or formation fluids for CCS projects. An estimation technique has been achieved (Fredenslund et al., 1975; Magnussen et al., 1981) for determining octanol/water partition coefficients uses structure activity relationships (SARs), which involves assigning a "contribution value" to chemical bonds and functional groups present in a molecule and summing these to obtain a partition. Although SARs has been used extensively, there is uncertainty in whether these estimates are sufficiently accurate for certain applications (Renner, 2002). Timko et al. (2004) measured the supercritical  $\text{CO}_2$ /water partition coefficients for a variety of organic compounds (e.g. aldehydes, ketones, esters, halides, phenols, alkanes and aromatic hydrocarbons) and showed that there is no adequate correlation with octanol/water partition coefficients, where the values are known for a much larger number of compounds (Haynes, 2011; Timko et al., 2004). They also looked at correlations with solubility parameters

(e.g. Hansen solubility indices) and other solvent/water partition coefficients (e.g. carbon disulfide/water) and found that none of these methods were sufficient for prediction. Currently, the limited data of partition coefficients precludes the development of even a rudimentary SARs type method for predicting supercritical CO<sub>2</sub>/water partition coefficients. Consequently, in order to accurately model subsurface partitioning behaviour, an appropriate experimental protocol must be designed and conducted to actually determine the supercritical CO<sub>2</sub>/water partition coefficients for relevant tracers.

**Table 2 List of Known Supercritical CO<sub>2</sub>/Water Mole-Fraction Based Partition Coefficients in the Literature (from Timko et al. 2004 and references therein)\***

Compound	Partition Coefficient	Compound	Partition Coefficient
Acetophenone	48.5 ± 4.6	Propiophenone	121 ± 13
Benzaldehyde	39.1 ± 3.7	Propylbenzoate	1050 ± 220
Bromobenzene	1090 ± 100	Tetrahydrofuran	8.5 ± 1.0
3-buten-2-one	7.8 ± 1	Toluene*	1200 ± 250.5
Chlorobenzene	1140 ± 110	Acetylacetone	3
Cyclohexane	4900 ± 600	Aniline	2.1
Cyclohexene	1900 ± 300	Benzene	2756
Cyclopentene	1400 ± 180	Benzoic acid	1.3
Ethylbenzoate	550 ± 100	Benzyl alcohol	1.9
Fluorobenzene	770 ± 150	Caffeine	0.15
Hexane	9000 ± 3000	2-chlorophenol	14
2-methoxyacetophenone	47.3 ± 4	4-chlorophenol	3
3-methoxyacetophenone	84.0 ± 7	Cyclohexanone	41
Methylbenzoate	205 ± 21	1,2-dichloromethane	154
Naphthalene	347	2,4-dichlorophenol	70
2-nitrophenol	80	2,4-dichlorophenoxyacetic acid	0.1
4-nitrophenol	0.2	2,4-dimethylphenol	10.7
Parathion	18.3	Hexafluoroacetylacetone	0.7
Pentachlorophenol	80	2-hexanone	118
Phenol	1	3-methyl-4-chlorophenol	6
Salicylic acid	0.3	2-methyl-4,6-dinitrophenol	55
1,1,2,2-tetrachloroethane	84	2-methyl-5-hexyloxymethyl-8-	500
2,3,4,5-tetrachlorophenol	15	3-methylphenol	4
1,1,2-trichloroethane	28	Vanillin	1.5
2,4,6-trichlorophenol	150		

\* Errors associated with partition coefficients have been added to the table where available. Partition coefficients were determined at 300 K at a variety of densities (or pressures). Mole-based partition coefficients are used as they are invariant with respect to density.

## 2.1 Currently Known Information on the Partitioning Behaviour of Inert Gas Tracers

Unfortunately, as mentioned earlier, there is a complete lack of data available for the supercritical CO<sub>2</sub>/water partition coefficients for inert gas tracers. Consequently Henry's Law coefficients have been used instead of supercritical CO<sub>2</sub>/water partition coefficients as input parameters in reservoir simulations to characterise the subsurface partitioning behaviour of krypton and xenon (Zhang et al., 2011). Henry's Law coefficients have been determined for sulphur hexafluoride from 25 °C to 230 °C (Mroczek, 1997), krypton from 0 °C to 75 °C (Wilhelm et al., 1977), xenon from 0 °C to 75 °C (Wilhelm et al., 1977), R134a from 0 °C to 60 °C (Zheng et al., 1997) and perdeuterated methane from 12 °C to 42 °C (Gomes and Grolier, 2001) (see Table 3). These studies show that for these compounds, as expected, there is generally Arrhenius type temperature dependence. Furthermore, octanol-water partition coefficients have been determined for a very large number of non-gaseous chemical compounds (Haynes, 2011). A search of the literature has revealed that information on the octanol/water partitioning behaviour of many relevant fluorinated organic compounds (e.g. R134a and most perfluorocarbons) is also not currently available presumably due to their low solubility. It seems then that there is a distinct lack of data regarding the octanol/water partitioning behaviour of inert tracers as well. Given that the behaviour of tracer compounds from both of these classes will need to be interpreted for a number of geosequestration projects and are an important indicator of the effectiveness of a site for CO<sub>2</sub> storage, it is critical that the behaviour of these tracers in the conditions present in typical underground storage reservoirs is understood. Obtaining the partitioning behaviour over relevant geological pressures and temperature regimes for supercritical CO<sub>2</sub>/water interfaces is therefore an important step in developing this understanding.

**Table 3 Temperature Dependence of Henry's Coefficients for Inert Gas Tracers. Data amalgamated from (Mroczek, 1997, Wilhelm et al., 1977 and Gomes and Grolier, 2001.**

Compound	Temperature (°C)	Henry's coefficient (MPa)
Krypton	0	663
	20	1150
	40	1850
	60	2830
	75	3760
Xenon	0	1250
	20	2010
	40	3040
	60	4380
	75	5600
R134a	5	155
	35	454
	65	823
CD <sub>4</sub>	11.7	0.0640
	25	0.0424
	35	0.0733
	44.5	0.0528
	51.2	0.0874
SF <sub>6</sub>	25	22900
	50	34900
	75	42200

100	43500
125	40100
150	33900
175	27200
200	20700
225	15500
230	14600

## 2.2 Currently Known Information on the Partitioning Behaviour of Reactive Ester Tracers

For several years, we have been developing a class of reactive ester tracers capable of quantifying the residual carbon dioxide saturation in a formation and have determined the supercritical CO<sub>2</sub>/water partitions coefficients for propylene glycol diacetate, triacetin, tripropionin and their hydrolysis products (Myers et al., 2012b). The partition coefficients were determined at the reservoir temperature and pressure intended for the CO<sub>2</sub>CRC Otway Stage 2B “Residual Saturation and Dissolution Test” (Table 4), where they have been recently utilised in the field as part of a larger test sequence (Paterson et al., 2010; Zhang et al., 2011). However, to extend the utility of these tracers to other field trails, further tests need to be performed over a larger range of geologically appropriate pressures and temperatures.

**Table 4 Supercritical CO<sub>2</sub>/water Partition Coefficients for Reactive Ester Tracers at 62 °C**

Compound	Partition coefficient based on mole fraction of solute in solvent, $k_i^x$	Partition coefficient based on concentration at 15 MPa, $k_i$
Propylene glycol diacetate	54.5 ± 5.3	8.77 ± 0.86
Propylene glycol monoacetate 1	1.04 ± 0.12	0.167 ± 0.019
Propylene glycol monoacetate 2	9.79 ± 2.22	1.57 ± 0.36
Triacetin	27.7 ± 5.6	4.46 ± 0.90
Diacetin 1	0.837 ± 0.214	0.135 ± 0.034
Diacetin 2	0.769 ± 0.107	0.124 ± 0.017
Monoacetin 1	0.876 ± 0.272	0.141 ± .044
Monoacetin 2	0.163 ± 0.057	0.0263 ± 0.0093
Tripropionin	313 ± 58	50.3 ± 9.3
Dipropionin 1	5.09 ± 0.85	0.820 ± 0.137
Dipropionin 2	4.83 ± 1.06	0.778 ± 0.170
Monopropionin 1	8.72 ± 1.64	1.40 ± 0.26
Monopropionin 2	0.349 ± 0.089	0.0562 ± 0.0143
Acetic acid	0.914 ± 0.256	0.147 ± 0.041
Propionic acid	1.50 ± 0.60	0.241 ± 0.097
Glycerol	a	a
Propylene glycol	a	a

<sup>a</sup> Glycerol and propylene glycol were not detected in the supercritical carbon dioxide phase. This is presumably due to their low solubility in supercritical carbon dioxide



### 3 Conclusions

In order to successfully determine the partitioning behaviour of chemical species in the subsurface environment, the methodology used for determining partition coefficients for tracers must be accurate and robust (Renner, 2002). In the next part, the thermodynamics of the partitioning process will be discussed and several methodologies for determining the supercritical CO<sub>2</sub>/water partition coefficients will be presented (Ramachandran et al., 1996; Robbins et al., 1993).

## 4 References

- Bahadur, N.P., Shiu, W.-Y., Boocock, D.G.B. and Mackay, D., 1997. Temperature Dependence of Octanol–Water Partition Coefficient for Selected Chlorobenzenes. *Journal of Chemical & Engineering Data*, 42(4): 685-688.
- Boreham, C. et al., 2011. Monitoring of Co<sub>2</sub> Storage in a Depleted Natural Gas Reservoir: Gas Geochemistry from the Co<sub>2</sub>crc Otway Project, Australia. *International Journal of Greenhouse Gas Control*, 5(4): 1039-1054.
- Cronin, M.T.D. et al., 2003. Use of Qsars in International Decision-Making Frameworks to Predict Ecologic Effects and Environmental Fate of Chemical Substances. *Environmental Health Perspectives*, 111(10): 1376-1390.
- Fredenslund, A., Jones, R.L. and Prausnitz, J.M., 1975. Group-Contribution Estimation of Activity-Coefficients in Nonideal Liquid-Mixtures. *Aiche Journal*, 21(6): 1086-1099.
- Freifeld, B.M. et al., 2005. The U-Tube: A Novel System for Acquiring Borehole Fluid Samples from a Deep Geologic Co<sub>2</sub> Sequestration Experiment. *Journal of Geophysical Research-Solid Earth*, 110(B10).
- Gomes, M.F.C. and Grolier, J.P., 2001. Determination of Henry's Law Constants for Aqueous Solutions of Tetradeuteriomethane between 285 and 325 K and Calculation of the H/D Isotope Effect. *Physical Chemistry Chemical Physics*, 3(6): 1047-1052.
- Haynes, W.M. (Editor), 2011. *Crc Handbook of Chemistry and Physics*. CRC Press/Taylor and Francis, Boca Raton, FL.
- Hovorka, S.D. et al., 2006. Measuring Permanence of Co<sub>2</sub> Storage in Saline Formations: The Frio Experiment. *Environmental Geosciences*, 13(2): 105-121.
- Jenkins, C.R. et al., 2012. Safe Storage and Effective Monitoring of Co<sub>2</sub> in Depleted Gas Fields. *Proceedings of the National Academy of Sciences*, 109(2): E35-E41.
- Magnussen, T., Rasmussen, P. and Fredenslund, A., 1981. Unifac Parameter Table for Prediction of Liquid-Liquid Equilibria. *Industrial & Engineering Chemistry Process Design and Development*, 20(2): 331-339.
- Moreira, L.A., Oliveira, F.A.R., Silva, T.R. and Oliveira, J.C., 1993. Development of a Non-Isothermal Method for Determination of Diffusional Parameters. *International Journal of Food Science & Technology*, 28(6): 575-586.
- Mroczek, E.K., 1997. Henry's Law Constants and Distribution Coefficients of Sulfur Hexafluoride in Water from 25 °C to 230 °C. *Journal of Chemical & Engineering Data*, 42(1): 116-119.
- Myers, M., Stalker, L., Pejčić, B. and Ross, A., 2012a. Tracers - Past, Present and Future Application in Co<sub>2</sub> Geosequestration. *Applied Geochemistry*: in press.
- Myers, M., Stalker, L., Ross, A., Dyt, C. and Ho, K.-B., 2012b. Method for the Determination of Residual Carbon Dioxide Saturation Using Reactive Ester Tracers. *Applied Geochemistry*: in press.
- Oldenburg, C.M., Moridis, G.J., Spycher, N.F. and Pruess, K., 2004. *Eos7c Version 1.0: Tough2 Module for Carbon Dioxide or Nitrogen in Natural Gas (Methane) Reservoirs*, Lawrence Berkeley National Laboratory, Berkeley, CA
- Paterson, L. et al., 2010. The Co<sub>2</sub>crc Otway Stage 2b Residual Saturation and Dissolution Test.
- Ramachandran, B.R., Allen, J.M. and Halpern, A.M., 1996. The Importance of Weighted Regression Analysis in the Determination of Henry's Law Constants by Static Headspace Gas Chromatography. *Analytical Chemistry*, 68(2): 281-286.
- Rathbun, R.E., 2000. Transport, Behavior, and Fate of Volatile Organic Compounds in Streams. *Critical Reviews in Environmental Science and Technology*, 30(2): 129-295.
- Renner, R., 2002. The Kow Controversy. *Environmental Science & Technology*, 36(21): 410A-413A.
- Robbins, G.A., Wang, S. and Stuart, J.D., 1993. Using the Static Headspace Method to Determine Henry's Law Constants. *Analytical Chemistry*, 65(21): 3113-3118.
- Srebrenik, S. and Cohen, S., 1976. Theoretical Derivation of Partition Coefficient from Solubility Parameters. *The Journal of Physical Chemistry*, 80(9): 996-999.

- Strazisar, B.R., Wells, A.W., Diehl, J.R., Hammack, R.W. and Veloski, G.A., 2009. Near-Surface Monitoring for the Zert Shallow Co(2) Injection Project. *International Journal of Greenhouse Gas Control*, 3(6): 736-744.
- Timko, M.T., Nicholson, B.F., Steinfeld, J.I., Smith, K.A. and 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.
- Underschultz, J. et al., 2011. Co2 Storage in a Depleted Gas Field: An Overview of the Co2crc Otway Project and Initial Results. *International Journal of Greenhouse Gas Control*, 5(4): 922-932.
- Vandeweyer, V. et al., 2011. Monitoring the Co2 Injection Site: K12-B. *Energy Procedia*, 4(0): 5471-5478.
- Wells, A., Strazisar, B., Diehl, J.R. and Veloski, G., 2010. Atmospheric Tracer Monitoring and Surface Plume Development at the Zert Pilot Test in Bozeman, Montana, USA. *Environmental Earth Sciences*, 60(2): 299-305.
- Wells, A.W. et al., 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.
- Wilhelm, E., Battino, R. and Wilcock, R.J., 1977. Low-Pressure Solubility of Gases in Liquid Water. *Chemical Reviews*, 77(2): 219-262.
- Zhang, Y. et al., 2011. Single-Well Experimental Design for Studying Residual Trapping of Supercritical Carbon Dioxide. *International Journal of Greenhouse Gas Control*, 5(1): 88-98.
- Zheng, D.-Q., Guo, T.-M. and Knapp, H., 1997. Experimental and Modeling Studies on the Solubility of Co2, Chc1f2, Chf3, C2h2f4 and C2h4f2 in Water and Aqueous Nacl Solutions under Low Pressures. *Fluid Phase Equilibria*, 129(1-2): 197-209.

# **Part II** Partition Coefficients: Thermodynamics and Experimental Methods

# 1 Experimental Methods for Determining Tracer Partition Coefficients

Phase partitioning is a fundamental tracer property dictating subsurface behaviour. As such, tracer partition (or distribution) coefficients are required to correctly interpret tracer field results and for accurate reservoir simulations. Currently, there is lack of information on tracer partition coefficients between supercritical CO<sub>2</sub> and water. Due to this, in reservoir simulations of tracer behaviour, air/water (Henry's coefficients) or octanol/water partition coefficients are frequently substituted potentially leading to invalid predictions and large errors in estimates of reservoir properties. This project aims to address this lack of data through a program of laboratory experiments with the primary aim of determining these partition coefficients for a number of chemical tracers.

This part primarily consists of:

- A discussion of the thermodynamics related to distribution (or partition) coefficients
- A technical description of the general experimental methods that can be used to determine supercritical CO<sub>2</sub>/water partition coefficients
- A summary of the tracer distribution coefficients that will be determined as part of this project

## 1.1 Thermodynamics

Distribution (or partition) coefficients are concerned with the equilibria of chemical species between two or more phases. For systems where there are no external force fields or internal barriers, this is formally defined as equivalency of the pressure (P), temperature (T) and chemical potential ( $\mu$ ) across the phases. Given pressure and temperature equivalency between phases, the partitioning behaviour of chemical species between phases is associated with the chemical potentials.

Generally, for a particular species  $i$  in phase  $j$ , the chemical potential is given by

$$\mu_i^j = \underline{\mu}_i^j + RT \ln a_i^j$$

where  $\underline{\mu}$  is the chemical potential at a reference state,  $R$  is the gas constant and  $a$  is the activity. For the case of one component in two phases and equal temperature and pressure for the two phases, the equilibrium conditions reduces to

$$\underline{\mu}^1 + RT \ln a^1 = \underline{\mu}^2 + RT \ln a^2.$$

The activity is defined as

$$a^j = x^j \gamma^j$$

where  $x$  is the mole fraction and  $\gamma$  is the activity coefficient in each of the two phases. At dilute conditions (i.e. concentrations typically present for tracers and well below the solubility) the activity coefficient becomes constant and can be incorporated into the chemical potential (i.e.  $\mu$ ). The equilibrium condition becomes

$$\underline{\mu}^1 + RT \ln x^1 = \underline{\mu}^2 + RT \ln x^2.$$

Rearranging this gives the distribution coefficient as

$$K = \frac{x^2}{x^1} = e^{\frac{\mu^1 - \mu^2}{RT}}$$

with its temperature dependency (commonly known by the Arrhenius equation). There are several different ways of representing the distribution coefficient (e.g. the TOUGH2 reservoir simulator uses inverse Henry's coefficient with units of  $\text{Pa}^{-1}$ , Eclipse and UTCHEM uses the dimensionless ratio of tracer concentration in two phases). For simplicity, this project will focus on the dimensionless distribution coefficient (i.e. ratio of the equilibrium concentrations in each of the phases), which can be easily converted to other forms through unit conversions and is the basis for thermodynamic equilibrium condition given above.

## 1.2 High-pressure/temperature experimental apparatus and sampling protocols

Recently, we reported a detailed description of the experimental apparatus to determine distribution coefficients for reactive ester tracers between supercritical carbon dioxide and water (Myers et al., 2012). In summary, a high pressure/temperature rated container is filled with carbon dioxide and water. Liquid  $\text{CO}_2$  is injected into the container using a high pressure syringe pump and the temperature and pressure are adjusted by varying the amount of carbon dioxide/water and the container temperature. The sample volume between two 3-way valves is used to obtain samples (after the sample loop fluid equilibrates with bulk fluid) of the gas phase and the water phase. In the case of non-volatile tracers (e.g. reactive ester tracers), these samples are slowly released into a volume of solvent in a glass vial. For this project, we have made several modifications and improvements to this initial design. Firstly, a high pressure piston-type circulation pump has been added to decrease equilibration time and reduce sampling variation. This allows us to increase experimental throughput, sampling reliability and reduce equilibration related issues with the increased hydrolysis rate of the reactive ester tracers at higher temperature (e.g. above  $80\text{ }^\circ\text{C}$ ). A sampling system for obtaining high pressure gas samples of volatile tracers (i.e. xenon) in carbon dioxide has been developed. A series of diaphragm valves rated for vacuum to high pressure are used to evacuate the sampling line and a high pressure/low volume sample vessel. After evacuation, the gas sample at container pressure is expanded using the three-way valves into the small volume sample vessel for subsequent gas chromatographic analysis.

An extensive search of the literature has identified three methods to determine the distribution coefficients:

1. Direct measurement of concentrations in a closed pressurised vessel of both the supercritical  $\text{CO}_2$  and water phases (Timko et al., 2004).
2. Measurement in a closed pressurised vessel of only one phase (e.g. only  $\text{CO}_2$ ) and varying the ratios of the phase volumes while keeping the amount of the partitioning chemical species constant in the vessel (Gossett, 1987; Hansen et al., 1993; Ramachandran et al., 1996).
3. Measurement in a closed pressurised vessel of only one phase (e.g. only  $\text{CO}_2$ ) and varying the ratios of the phase volumes while keeping the initial concentration in one of the phases (e.g. water) constant in the vessel (Robbins et al., 1993).

## 1.3 Direct measurement of concentrations in two separate phases

Conceptually this is the easiest method for determining partition coefficients and requires only one experiment; however, in practice it may be very difficult to attain an accurate determination of the partition coefficient. This method requires independently determining the concentration of a chemical species in both the supercritical carbon dioxide phase and the water phase and the partition coefficient is simply the ratio of these concentrations. Gas chromatography/mass spectroscopy (GCMS) is typically the most general and accurate way to determine these concentrations. Despite being convenient, there are a number of issues related to using water samples in a GCMS, namely the large expansion volume of water during injection and column/detector intolerance for water. Complete extraction of polar compounds into an organic phase more suitable for GCMS can be very difficult. Furthermore, extraction into a gas phase

using purging techniques is often incomplete for organic compounds with limited volatility and dissolved gases have a strong tendency to remain in water. The efficiency of extraction techniques from water is often difficult to predict precluding the accurate determination of dissolved gas concentration in the water phase.

This method has been used to determine the supercritical water/carbon dioxide partition coefficients for a variety of organic compounds (Timko et al., 2004). For collecting gas phase samples, carbon dioxide is slowly bubbled through chilled acetone for efficient collection of volatile compounds. The water samples were diluted into acetone before injection into a GCMS; in this case, water is diverted from the detector before the analyte elution from the column. Using this technique, Timko et al. reports errors for the solute concentrations in both phases using GCMS are 5 to 15 % resulting in 10 to 30 % errors for the partition coefficient. We have used this method with several modifications recently to determine the partition coefficients for reactive ester tracers (Myers et al., 2012).

The advantages and disadvantages to this method are summarized below:

---

**Advantages:**

Only a single experiment needs to be conducted

Only method applicable to reactive tracers

Method is not sensitive to the relative ratios of water and supercritical CO<sub>2</sub>

**Disadvantages:**

Large error due to difficulty in determining concentrations in water phase

Not suitable for gaseous or non-volatile tracers

Reliable sampling from both water and gas phases can be problematic

---

This is the method that will be used in this project to determine the distribution coefficients for the reactive ester tracers (i.e. propylene glycol diacetate, triacetin and tripropionin) and their related hydrolysis products. To implement this method, 1 g of each of the reactive tracers will be dissolved in 1 L giving a concentration of 1 g/L. This solution will be injected into the container where an appropriate amount of CO<sub>2</sub> will be added with the high pressure syringe pump. After heating to the appropriate temperature, the pressure will stabilize when equilibrium is achieved. To ensure uniform mixing, the circulation pump (rate of 8 mL/min) will be operated for approximately 8 hours at the beginning of the experiment and for 8 hours prior to each set of samples obtained.

## 1.4 Measurement of concentration in one phase, varying volume ratio of two phases with total amount of solute kept constant

This method involves a series of separate measurements of tracer concentrations in one phase while varying the volume ratio of the two phases and keeping the total amount of solute constant (see Figure 1 for an example of an experimental design for this method) (Gossett, 1987). Using this procedure, it is necessary to only measure the tracer concentration in the supercritical CO<sub>2</sub> phase; as such, errors associated with measuring gas/volatiles concentrations in water are eliminated. For the series of experiments, the number of moles of solute is kept constant and is partitioned between two phases giving the mass balance relationship

$$n = n_1 + n_2$$

where  $n$  is the total number of moles of solute and  $n_1$  and  $n_2$  are the number of moles in each of the two phases. Thermodynamic equilibrium is assumed for each of the measurements giving

$$K = \frac{c_1}{c_2}$$

where  $K$  is the dimensionless distribution coefficient and  $c_1$  and  $c_2$  are the solute concentrations in each of the two phases. The mass balance then becomes

$$n = KV_1c_2 + V_2c_2$$

where  $V_1$  and  $V_2$  are the volumes of each the two phases. With the total volume

$$V = V_1 + V_2,$$

this becomes

$$n = K(V - V_2)c_2 + V_2c_2.$$

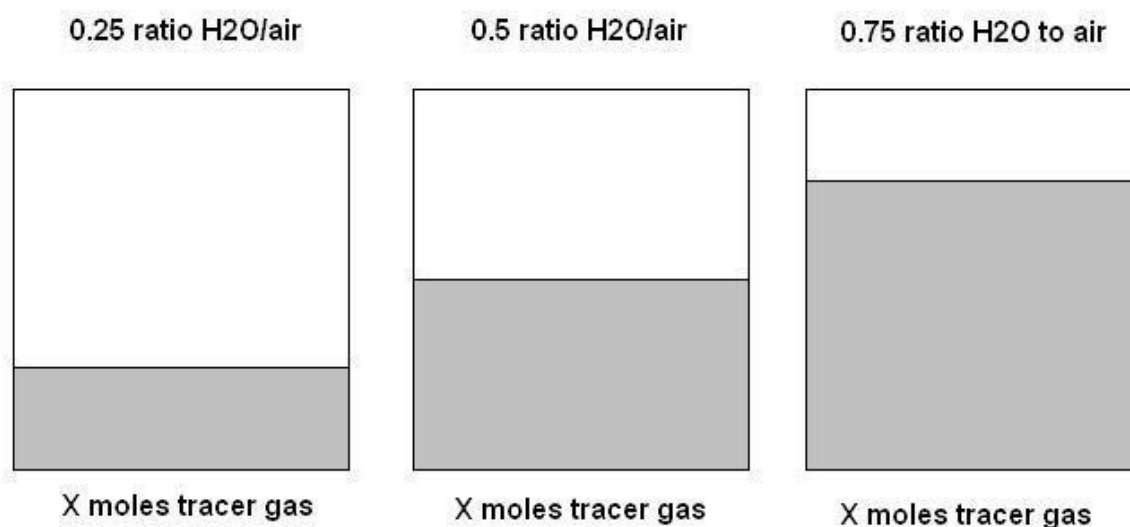
Rearrangement of this gives

$$\frac{1}{c_2V_2} = \frac{K}{n} \left( \frac{V}{V_2} \right) + \frac{1-K}{n}.$$

The distribution coefficient  $K$  is determined by plotting the experimental data ( $c_2$  is derived from GC analysis of the corresponding sample) from each of the measurements in the form  $1/c_2V_2$  versus  $V/V_2$ . A linear regression is performed on this data and the ratio  $A$  of the y-intercept and the slope is determined. The estimated distribution coefficient determined using this method is given by

$$K = \frac{1}{1+A}.$$

**Figure 1** An example of the different liquid to headspace ratios used to determine  $H$  for a given tracer. Total volumes of each sample bottle are constant as well as the amount of tracer added.



Ramachadran et al. (1996) has shown using computer simulations that for the linear regression analysis detailed above to determine the distribution coefficient it is necessary to statistically weight the obtained data to obtain consistent results with minimal errors. This is due to the reciprocal nature of the plots generated for the linear regression. We assume that there is little error in the measurement of the water and  $\text{CO}_2$  volumes and the measurement error is associated with the measurement of the concentration. In short, using the analysis above concentration measurements with the smallest error will have the largest errors in the linear regression analysis. This will cause inaccurate determinations of the distribution coefficient. To correct for this, each data point included in the linear regression should have a weighting of  $(c_2V_2)^2$ .

The advantages and disadvantages to this method are summarized below:

---

**Advantages:**



Use of multiple experimental runs with appropriate statistical weightings in a linear regression analysis can potentially lead to low errors in the estimation of the distribution coefficient

Only concentration in the gas phase need to be determined

**Disadvantages:**

This method is only applicable for inert (volatile or non-volatile) tracers

This method requires that the same amount of tracer is added for each measurement

The volume ratios of water and supercritical CO<sub>2</sub> need to be quantified for each measurement

This is the method that will be used in this project to determine the distribution coefficients for the inert gas tracer (i.e. krypton, xenon, perdeuterated methane, sulphur hexafluoride and R134a). To implement this method, a quantified amount of water is added to the container. Supercritical carbon dioxide is then added using the high pressure syringe pump and the container is heated to the desired temperature. The tracers are added using a series of sample loops (formed from adjoining two 3-way valves) in line with the circulation pump. To ensure uniform mixing and phase equilibration, the circulation pump (rate of 8 mL/min) is run for approximately 8 hours prior to sampling of the supercritical CO<sub>2</sub> phase into the high pressure sample containers.

## 1.5 Measurement of concentration in one phase, varying volume ratio of two phases while the initial concentration of solute in one of the phases is kept constant

This method involves a series of separate measurements of tracer concentrations in one phase while varying the volume ratio of the two phases and keeping the initial concentration in one of the phases constant (see Figure 2 for an example of an experimental design for this method) (Robbins et al., 1993). The concentration in this phase is a constant  $c$  and this phase has a volume  $V_2$ . The number of moles of solute in the container is given by

$$n = n_1 + n_2$$

where  $n_1$  and  $n_2$  are the number of moles in each of the two phases. As before, the thermodynamic equilibrium is assumed for each of the measurements giving

$$K = \frac{c_1}{c_2}$$

where  $K$  is the dimensionless distribution coefficient and  $c_1$  and  $c_2$  are the solute concentrations in each of the two phases. The mass balance then becomes

$$n = V_1 c_1 + \frac{V_2 c_1}{K}$$

where  $V_1$  and  $V_2$  are the volumes of each the two phases. With the total volume

$$V = V_1 + V_2,$$

this becomes

$$n = V_1 c_1 + \frac{(V - V_1) c_1}{K}.$$

Dividing by  $V_2$  (or  $V - V_1$ ) gives

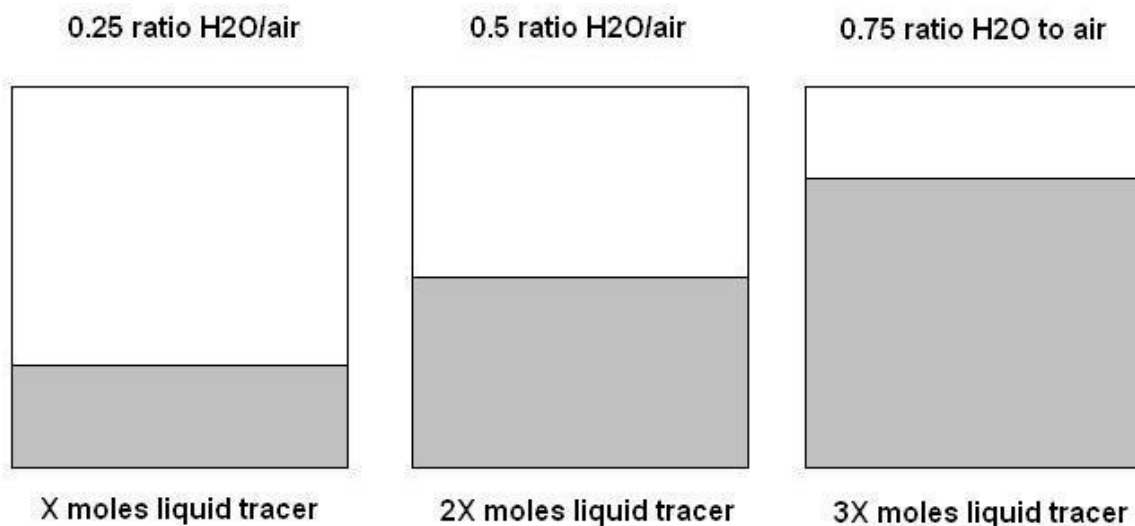
$$c = \frac{V_1 c_1}{V_2} + \frac{c_1}{K}.$$

This can be rearranged to give

$$\frac{1}{c_1} = \frac{1}{c} \left( \frac{V_1}{V_2} \right) + \frac{1}{Kc}$$

The distribution coefficient  $K$  is determined by plotting the experimental data from each of the measurements in the form  $1/c_1$  versus  $V_1/V_2$ . A linear regression is performed on this data and the distribution coefficient is the ratio of slope and the y-intercept. Based on the work of Ramachandran et al. (1996), the experimental data included in this linear regression should have a weighting of  $c_1^2$ .

**Figure 2** A representation of the sample bottle setup for liquid tracers, the concentration of tracer in the liquid phase is the same in all bottles but the amount of moles varies.



The advantages and disadvantages to this method are summarized below:

**Advantages:**

Use of multiple experimental runs with appropriate statistical weightings in a linear regression analysis can potentially lead to low errors in the estimation of the distribution coefficient

Only concentration in one of the phases need to be determined

**Disadvantages:**

This method is only applicable for inert (volatile or non-volatile) tracers

The volume ratios of water and supercritical CO<sub>2</sub> need to be quantified for each measurement

This method is ideal for non-volatile liquid inert tracers that readily dissolve in water and can be analysed with GC measurements from the water phase eliminating the complications associated with sampling from the supercritical CO<sub>2</sub> phase.

## 2 Scope of experimental projects determining tracer partition coefficients

Sulphur hexafluoride ( $\text{SF}_6$ ), perdeuterated methane ( $\text{CD}_4$ ) and R134a (or 1,1,2,2-tetrafluoroethane) were implemented as tracers at the Otway pilot site where  $\text{CO}_2$  was injected into a depleted natural gas reservoir (Boreham et al., 2011; Underschultz et al., 2011). These tracers were used in an interwell configuration and confirmed the arrival of  $\text{CO}_2$  at the observation well. Krypton, xenon and the reactive ester tracers were used at the CO2CRC's Otway Stage 2B Residual Saturation test in single-well "push-pull" tests (Myers et al., 2012; Zhang et al., 2011).

**Table 5 Scope of Tracer Partition Coefficient Studies**

Tracers	Gas Composition	Temperature	Method of Measurement
Reactive esters (propylene glycol diacetate, triacetin and tripropionin)	100% $\text{CO}_2$	50, 70, 85, 100 and 120°C	Direct measurement of tracer concentration in both phases
Reactive esters	80% $\text{CO}_2$ /20% $\text{CH}_4$	50, 70, 85, 100 and 120°C	Direct measurement of tracer concentration in both phases
Xe, Kr, $\text{SF}_6$ , $\text{CD}_4$ and R134a	100% $\text{CO}_2$	59, 83, 100°C	Measurement of concentration in one phase, varying volume ratio of two phases with total amount of solute kept constant
Xe, Kr, $\text{SF}_6$ , $\text{CD}_4$ and R134a	80% $\text{CO}_2$ /20% $\text{CH}_4$	59, 83, 100°C	Measurement of concentration in one phase, varying volume ratio of two phases with total amount of solute kept constant

### 3 Conclusions

In order to successfully determine the partitioning behaviour of chemical species in the subsurface environment, the methodology used for determining distribution coefficients for tracers must be accurate and robust (Renner, 2002). As a result, we are currently testing and optimizing several new methodologies for determining the supercritical CO<sub>2</sub>/water distribution coefficients (Ramachandran et al., 1996; Robbins et al., 1993). Our preliminary data shows that the CO<sub>2</sub>/water distribution coefficient for the reactive esters and their hydrolysis products can be seen to decrease with increasing temperature. This indicates that a greater proportion of the tracer is remaining in the water phase as temperature escalates. With additional data at 70, 100 and 120 °C it will be possible to model the temperature dependence of the distribution coefficients for each tracer and establish a relationship. In the next part, we will report on the procedures used to determine supercritical CO<sub>2</sub>/water partition coefficients for the reactive ester tracers. Furthermore, the partition coefficients themselves will be reported as well as the thermodynamic analysis of this data.

## 4 References

- Boreham, C., Underschultz, J., Stalker, L., Kirste, D., Freifeld, B., Jenkins, C., Ennis-King, J., 2011. Monitoring of CO<sub>2</sub> storage in a depleted natural gas reservoir: Gas geochemistry from the CO<sub>2</sub>CRC Otway Project, Australia. *International Journal of Greenhouse Gas Control* 5, 1039-1054.
- Gossett, J.M., 1987. Measurement of Henry's law constants for C1 and C2 chlorinated hydrocarbons. *Environmental Science & Technology* 21, 202-208.
- Hansen, K.C., Zhou, Z., Yaws, C.L., Aminabhavi, T.M., 1993. Determination of Henry's law constants of organics in dilute aqueous solutions. *Journal of Chemical & Engineering Data* 38, 546-550.
- Myers, M., Stalker, L., Ross, A., Dyt, C., Ho, K.-B., 2012. Method for the determination of residual carbon dioxide saturation using reactive ester tracers. *Applied Geochemistry* 27, 2148-2156.
- Ramachandran, B.R., Allen, J.M., Halpern, A.M., 1996. The Importance of Weighted Regression Analysis in the Determination of Henry's Law Constants by Static Headspace Gas Chromatography. *Analytical Chemistry* 68, 281-286.
- Renner, R., 2002. The KOW Controversy. *Environmental Science & Technology* 36, 410A-413A.
- Robbins, G.A., Wang, S., Stuart, J.D., 1993. Using the static headspace method to determine Henry's law constants. *Analytical Chemistry* 65, 3113-3118.
- 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. *J. Chem. Eng. Data* 49, 768-778.
- Underschultz, J., Boreham, C., Dance, T., Stalker, L., Freifeld, B., Kirste, D., Ennis-King, J., 2011. CO<sub>2</sub> storage in a depleted gas field: An overview of the CO<sub>2</sub>CRC Otway Project and initial results. *International Journal of Greenhouse Gas Control* 5, 922-932.
- Zhang, Y., Freifeld, B., Finsterle, S., Leahy, M., Ennis-King, J., Paterson, L., Dance, T., 2011. Single-well experimental design for studying residual trapping of supercritical carbon dioxide. *International Journal of Greenhouse Gas Control* 5, 88-98.

# **Part III** Reactive Ester Tracer Partition Coefficients

# 1 Experimental Methods and Theory

## 1.1 Chemicals

Triacetin (glyceryl triacetate, Aldrich, W200700, >98.5%, food grade), tripropionin (glyceryl tripropionate, Aldrich, W328618, food grade) and propylene glycol diacetate (Aldrich, 528072, >99.7%) were used as received for this study. Distilled water and 99.99% grade CO<sub>2</sub> (BOC) were used.

## 1.2 Apparatus and Experimental Methodology

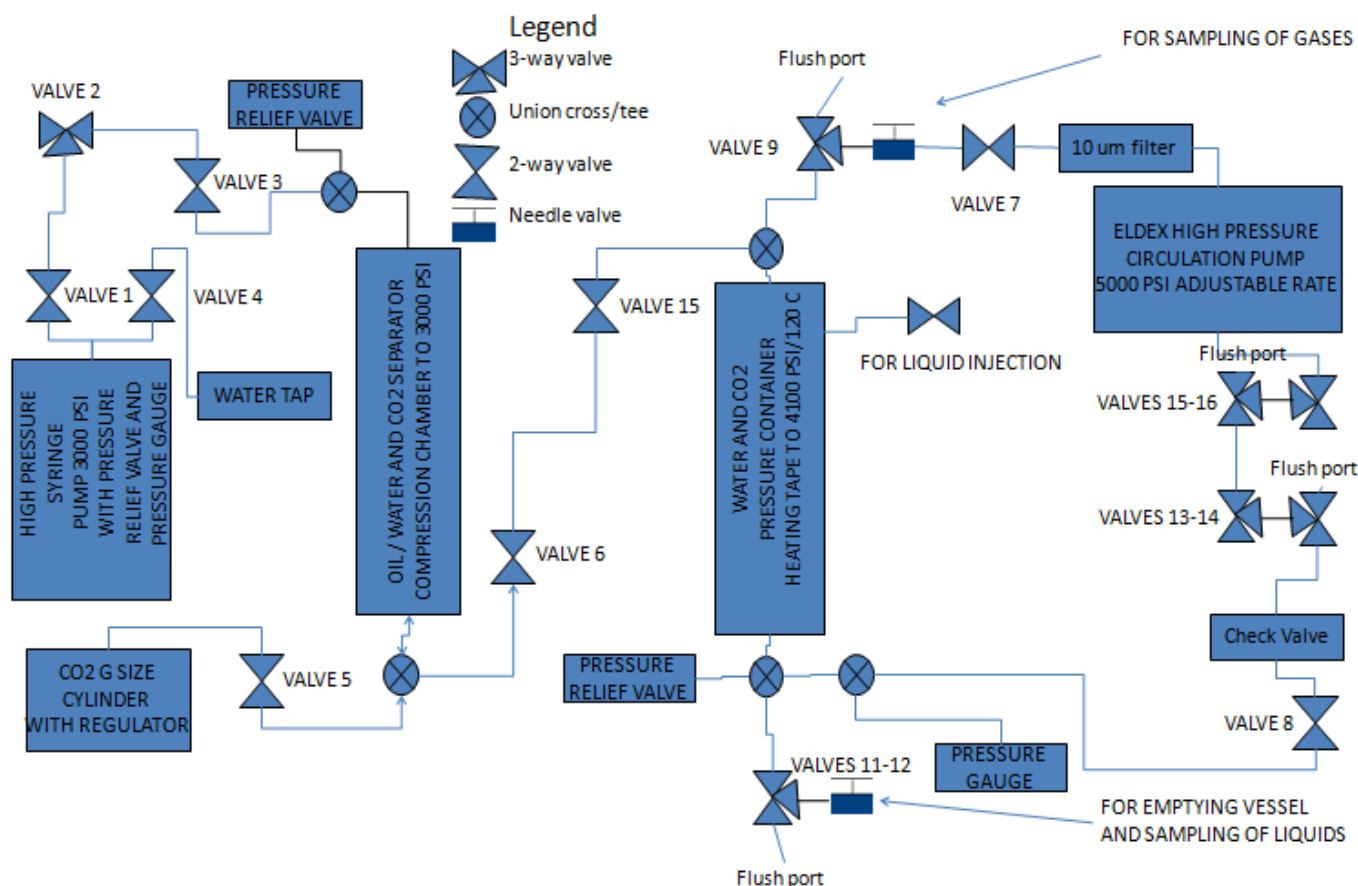
A stainless steel (grade 316) container was designed to allow the experimental fluids to hydrolyse and partition at reservoir conditions (i.e. at elevated pressure and temperature). The container has a volume of 2.0 L with ¼" NPT female threading on both the top and base. Another similar container with a volume of 1 L has a separator installed and acts as a piston with a compression capacity of 930 mL. Using a high pressure syringe-type pump (with water as the compression fluid) and heating tape (with a PID type controller), pressure and temperature were maintained between 14 and 24 MPa (2050–3480 psi) and between 50 and 120°C, respectively (see Figure 1). Both containers were equipped with H83 and FKB series Swagelok valves (rated to at least 27.5 MPa or 4000 psi at 120 °C).

For these studies, the system was filled with 1.5 L of distilled water and 1g (±0.05) g each of propylene glycol diacetate, triacetin and tripropionin. The container was pressurised with CO<sub>2</sub> (99.99% grade) to approximately 5 MPa (i.e. outlet pressure from a G-size gas cylinder), raised to the desired temperature with the heating tape and then further compressed to approximately 20 MPa by the piston pump before isolating the container using a valve. The supercritical CO<sub>2</sub>/water fluid mixture was then recirculated overnight where it equilibrated. After the required temperature and pressure was attained the fluids were allowed to equilibrate and partially hydrolyse over a period of 2 to 20 days, which was dependant on the temperature conditions used. During this time, fluid samples were periodically acquired and analysed in pairs, one from the supercritical CO<sub>2</sub> phase (obtained from the top of the container) and one from the water phase (obtained from the base of the container).

The water sample was obtained by opening a valve attached to the bottom of the container and a second immediately adjacent needle valve, allowing the void volume (which was measured independently) between the two valves to fill up in the manner of a sample loop. After 1 hour (to allow for any equilibration) the first valve was closed and the water collected into a vial by opening the second valve. The sample loop was then flushed with chilled water to remove any residual sample into the vial. After sample collection, the sample loop was cleaned with acetone and then dried thoroughly with compressed air.

The sample from the supercritical CO<sub>2</sub> phase was collected in a similar manner. A valve attached to the top of the container was opened where the fluid was again allowed to equilibrate in the volume between the two valves, then the first valve was closed again isolating the sample loop. To control the release of high pressure gas into a sample vial, a needle valve was used in combination with a ball valve to bubble the gas slowly through 10 mL of chilled water. The sample loop was then flushed with chilled water to remove any residual sample into the vial and then cleaned using the same protocol as the liquid sample. After collection, both samples were frozen before subsequent GCMS analysis.

Figure 3 Schematic of tracer setup including pumps, recirculation capacity and sampling ports



### 1.3 Preparation of Tracer Samples for GCMS Analysis

Two different GCMS columns and methods (detailed below) were used: the first aimed to accurately quantify the concentrations of the parent ester tracers (i.e. propylene glycol diacetate, triacetin and tripropionin) and the second aimed to quantify the concentrations of the different isomers of the hydrolysis alcohol products generated from the parent parent ester tracers (i.e. propylene glycol monoacetate diacetin, dipropionin). Prior to analysis, the samples were thawed to room temperature overnight and vigorously stirred prior to analysis. For the analysis of the parent parent ester tracers, some samples were diluted at either 5:1, 10:1 or 20:1 ratios prior to injection. For the analysis of the hydrolysis products, the samples were injected undiluted.



Concentrations of standards used in constructing the calibration curves ranged from 2 µg/mL to 70 µg/mL. Compounds were identified by library matches and calibration standard peak areas were established using the automatic integration function followed by manual baseline adjustment when required. Repeated (7 times) analysis of the same tracer sample gave a residual standard deviation of less than 8% in all cases.

## 1.4 GCMS Analysis of Parent Ester Tracers

Analysis was performed in split mode (split ratio 15:1) with an Agilent 6890 GC / Agilent 5973 inert MSD fitted with a RESTEK Stabilwax-DA column (30 m x 0.25 mm i.d., 0.25 µm film thickness). The carrier gas was helium with a constant column flow rate of 1.3 mL/min. Injection temperature was 250 °C and injection volume was 1 µL. The initial oven temperature was 70 °C which was ramped at 10 °C/min to 170 °C. The oven temperature was then held at 170 °C for 3 minutes before being ramped to 208 °C at 20 °C/min and held at that temperature for a further 3 minutes. The total run time was 17.9 minutes. The MSD conditions were typically: ionisation energy ~70eV, source temperature 230 °C and electron multiplier voltage ~ 1700V.

### **GCMS Analysis of Daughter Alcohol Tracers Generated by Hydrolysis of the Parent Ester Tracers**

Analysis was performed in split mode (split ratio 2:1) with an Agilent 6890 GC / Agilent 5973 inert MSD fitted with a RESTEK Rtx-Bac1 column (30 m x 0.32 mm i.d., 1.8 µm film thickness). The carrier gas was helium with a constant column flow rate of 1.3 mL/min. Injection temperature was 250 °C and injection volume was 1 µL. The initial oven temperature was 70 °C which was ramped at 10 °C/min to 240 °C. The oven temperature was then held at 240 °C for 5 minutes. The total run time was 22.0 minutes. The MSD conditions were typically: ionisation energy ~70eV, source temperature 230 °C and electron multiplier voltage ~ 1700V.

### **Calculating Partition Coefficients**

The method of determining the dimensionless partition coefficients for these parent esters involves the direct measurement of the chemical concentration in both the liquid and gaseous samples. The partition coefficient  $K_{c/w}^x$  is defined as the ratio of the mole fractions in the supercritical carbon dioxide phase and the water phase and is calculated using

$$K_{c/w}^x = \frac{\frac{C_i^{CO_2}}{\rho_{CO_2}} MW_{CO_2}}{\frac{C_i^{H_2O}}{\rho_{H_2O}} MW_{H_2O}}$$

where  $K_{c/w}^x$  is the mole fraction basis dimensionless partition coefficient,  $C_i^{CO_2}$  and  $C_i^{H_2O}$  are the concentrations measured by GCMS in the supercritical carbon dioxide and water phases,  $\rho_{CO_2}$  and  $\rho_{H_2O}$  are the densities of the supercritical carbon dioxide and water phases (determined using the online calculator at <http://webbook.nist.gov/chemistry/fluid>) and  $MW_{CO_2}$  and  $MW_{H_2O}$  are the molecular weights of water and carbon dioxide. Utilizing this formula for a number of repeat experiments, the average partition coefficient and a standard error can be obtained for a variety of temperatures conditions.

## 2 Results and Discussion

As mentioned earlier, for the reactive esters, samples from both the water and supercritical CO<sub>2</sub> phase were taken in order to determine the amounts of tracer in each phase. GC analysis was then performed on each sample and after calculation of data to obtain the partition coefficients (Equations 1-3) the results for each tracer could be collated (Table 4).

$$\text{Distribution coefficient} = \frac{\text{Concentration in supercritical CO}_2}{\text{Concentration in H}_2\text{O}}$$

Where:

Concentration in supercritical CO<sub>2</sub> = concentration of tracer determined by GC / mass of CO<sub>2</sub> sampled

Concentration in H<sub>2</sub>O = concentration of tracer determined by GC / mass of H<sub>2</sub>O sampled

Consequently, this above equation can also be written as;

$$\text{Distribution coefficient} = \frac{\frac{[\text{tracer in CO}_2](\text{g/cm}^3)}{\text{density CO}_2(\text{g/cm}^3)}}{\frac{[\text{tracer in H}_2\text{O}](\text{g/cm}^3)}{\text{density H}_2\text{O}(\text{g/cm}^3)}}$$

The concentration of the tracers were determined from GCMS analysis while the density of the CO<sub>2</sub> and H<sub>2</sub>O phases were calculated from literature tables utilizing the known temperature and pressure at the time of sampling. As most literature sources give the dimensionless distribution coefficient on a mole fraction basis, the density of CO<sub>2</sub> and H<sub>2</sub>O need to be divided by their respective molecular weights.

$$\text{Partition coefficient} = \frac{\frac{[\text{tracer in CO}_2](\text{g/cm}^3)}{\text{density CO}_2(\text{g/cm}^3)}}{\frac{[\text{tracer in H}_2\text{O}](\text{g/cm}^3)}{\text{density H}_2\text{O}(\text{g/cm}^3)}} \times \frac{\text{MW CO}_2}{\text{MW H}_2\text{O}}$$

For each tracer three separate samples were taken at time intervals spaced to ensure that a significant amount of hydrolysis had taken place. This allowed the partition coefficients to be calculated for the breakdown products of the tracers as well as the parent compounds at several stages along the hydrolysis chain to improve accuracy and robustness of the experiments. The total hydrolysis time was heavily dependent on the temperature, ranging from several weeks at 50°C to several days at 120°C.

In Table 1 below, we summarize the partition coefficient data that has been acquired to date. In instances where we have not reported a value this is due to very low concentrations measured in either the supercritical carbon dioxide phase and/or the water phase. Further experiments are currently underway to adjust hydrolysis conditions to maximize tracer concentrations.

**Table 6 Dimensionless partition coefficient data for reactive parent ester tracers and their daughter hydrolysis products at varying temperatures**

Tracer	Temperature °C	Average partition coefficient	Std Error
--------	-------------------	----------------------------------	-----------

<b>Propylene glycol</b>	50	-	-
	70	0.64	0.15
	85	1.02	0.35
	100	0.96	0.16
	120	1.21	0.015
<b>Glycerol</b>	50	-	-
	70	-	-
	85	-	-
	100	0.71	0.21
	120	1.04	0.21
<b>Propylene glycol diacetate</b>	62	54.5	0.05
	70	18.1	0.10
	90	8.5	0.17
	100	5.8	0.13
	110	3.3	0.18
<b>Triacetin</b>	62	27.7	0.10
	70	8.2	0.07
	85	3.4	0.03
	110	1.1	0.03
	120	0.7	0.05
<b>Tripropionin</b>	62	313	0.09
	70	121	0.10
	85	29.1	0.15
	90	9.3	0.13
	110	7.2	0.17
<b>Propylene glycol monoacetate 1</b>	50	0.89	0.058
	70	1.02	0.13
	85	1.45	0.20
	100	1.18	0.14
	120	1.80	0.19
<b>Propylene glycol monoacetate 2</b>	50	0.74	0.082
	70	0.85	0.13
	85	1.34	0.17

	100	1.02	0.17
	120	1.64	0.19
<b>Monoacetin 1</b>	50	-	-
	70	0.56	0.32
	85	1.73	0.17
	100	0.38	0.099
	120	0.32	0.11
<b>Monoacetin 2</b>	50	-	-
	70	-	-
	85	-	-
	100	-	-
	120	-	-
<b>Diacetin 1</b>	50	0.61	0.033
	70	0.63	0.11
	85	1.12	0.19
	100	0.45	0.21
	120	0.55	0.14
<b>Diacetin 2</b>	50	0.59	0.026
	70	0.87	0.16
	85	1.02	0.13
	100	0.47	0.13
	120	0.68	0.16
<b>Monopropionin 1</b>	50	-	-
	70	0.60	0.21
	85	-	-
	100	0.48	0.012
	120	0.48	0.073
<b>Monopropionin 2</b>	50	-	-
	70	-	-
	85	-	-
	100	-	-
	120	-	-
<b>Dipropionin 1</b>	50	1.33	0.18
	70	1.78	0.052
	85	2.78	0.59

	100	0.90	0.14
	120	0.85	0.11
<b>Dipropionin 2</b>	50	1.61	0.21
	70	1.87	0.028
	85	2.76	0.41
	100	0.93	0.093
	120	0.86	0.24
<b>Acetic acid</b>	50	0.84	0.10
	70	1.74	0.25
	85	3.03	0.21
	100	3.95	0.16
	120	2.60	0.075
<b>Propionic acid</b>	50	1.08	0.36
	70	1.12	0.56
	85	2.50	0.26
	100	3.40	0.25
	120	1.88	0.072

In Figures 2 to 8, we have plotted the natural logarithm of the partition coefficient versus the reciprocal absolute temperature for a number of different chemical tracers. The data generated in these plots is fitted to the van't Hoff equation using a linear regression:

$$\ln K_{c/w}^x = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$$

where  $\Delta H$  and  $\Delta S$  are the enthalpy and entropy changes, respectively, associated with the partitioning process. This allows us to both estimate the enthalpy change and develop a correlation for predicting partition coefficients values over a range of temperatures. The results of the linear regressions of these plots are summarized in Table 2 below.

Figure 4 van't Hoff plot for propylene glycol diacetate

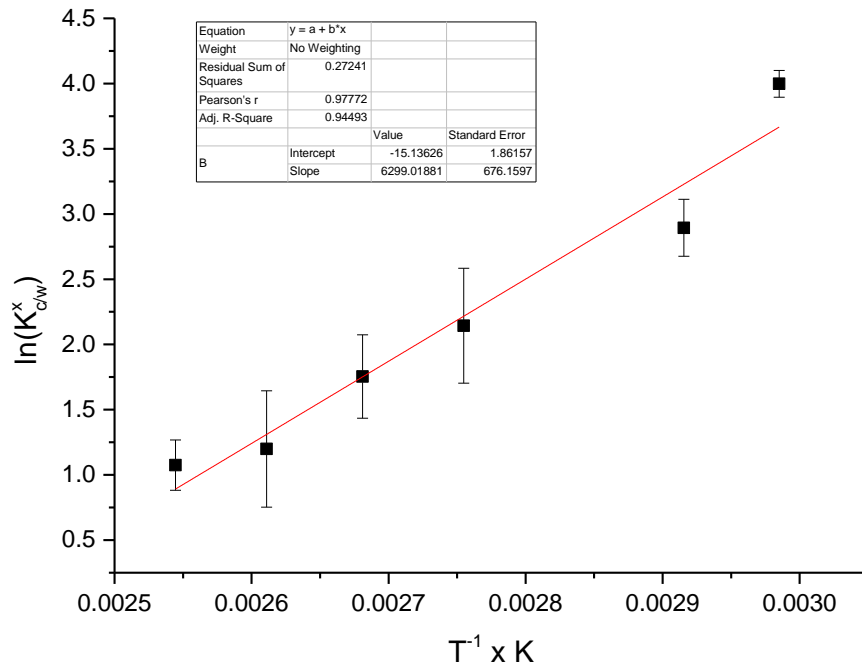


Figure 5 van't Hoff plot for triacetin

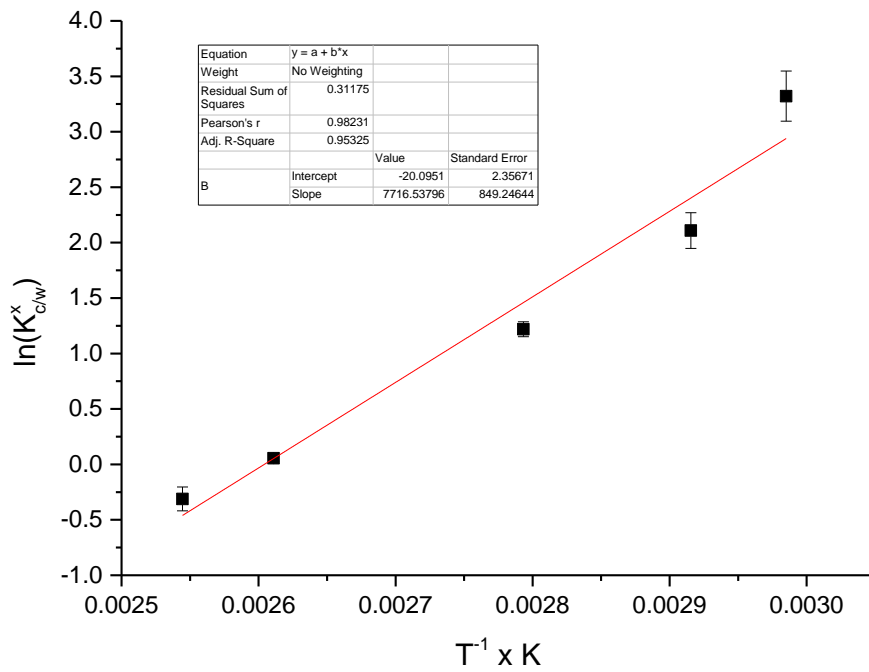


Figure 6 van't Hoff plot for tripropionin

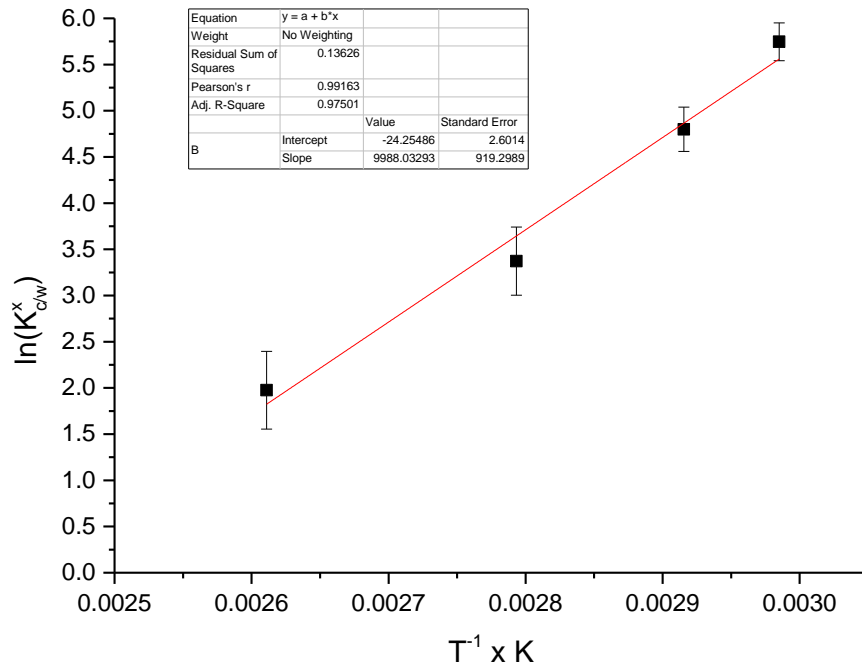


Figure 7 van't Hoff plot for propylene glycol monoacetate isomer 1

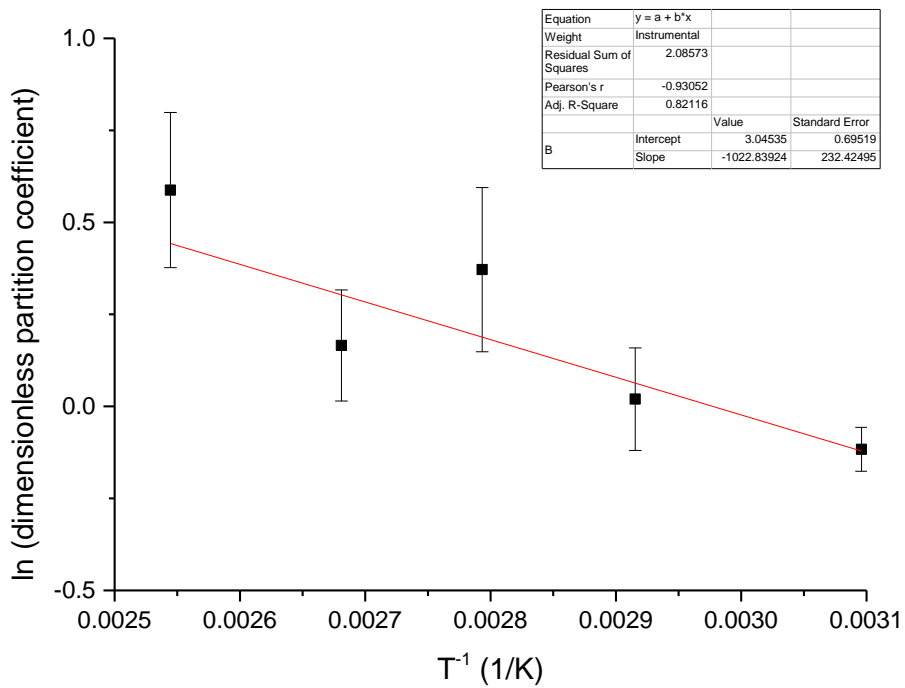


Figure 8 van't Hoff plot for propylene glycol monoacetate isomer 2

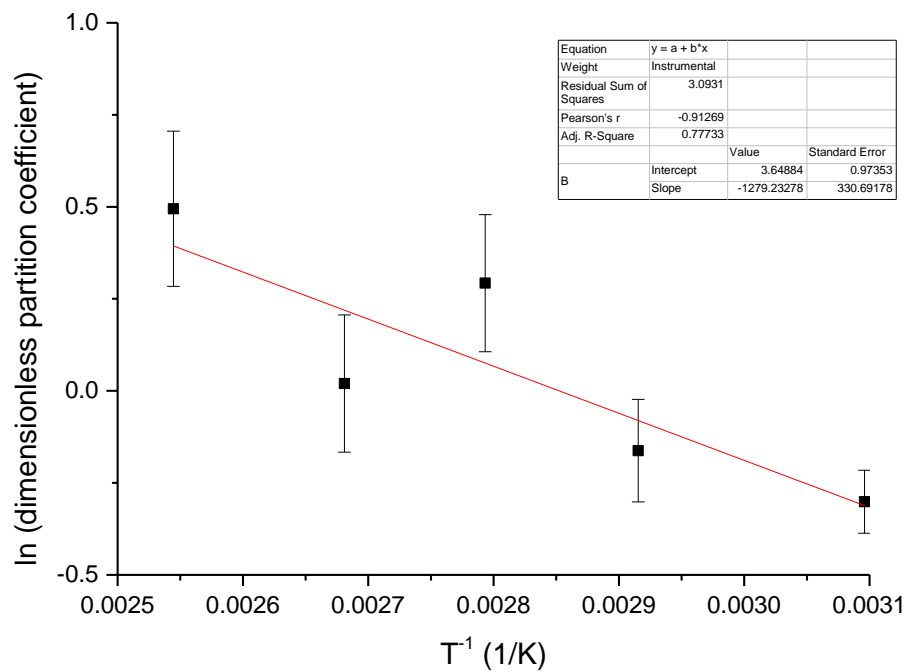


Figure 9 van't Hoff plot for dipropionin isomer 1

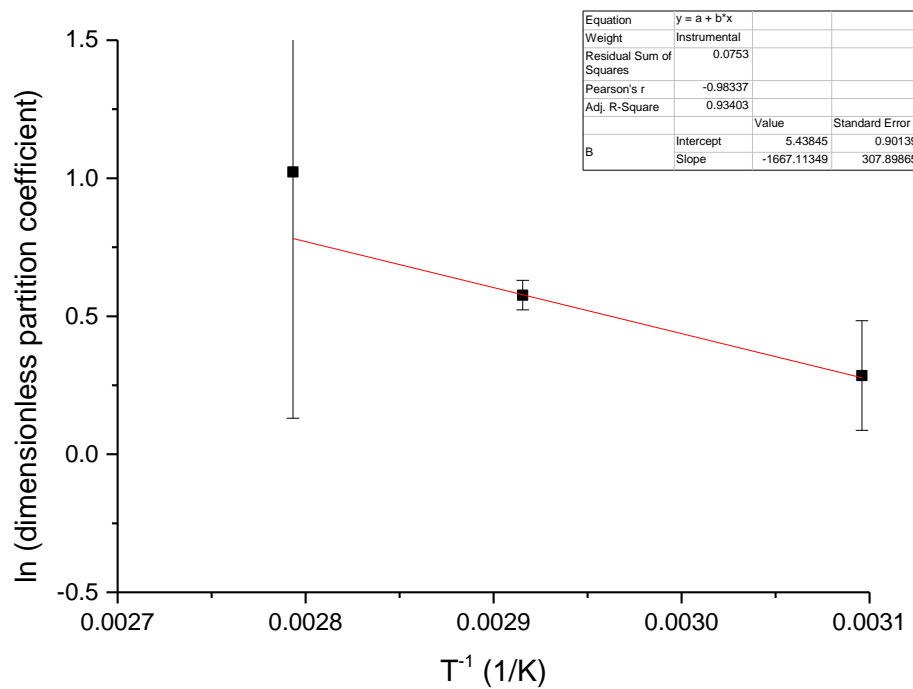




Figure 10 van't Hoff plot for dipropionin isomer 2

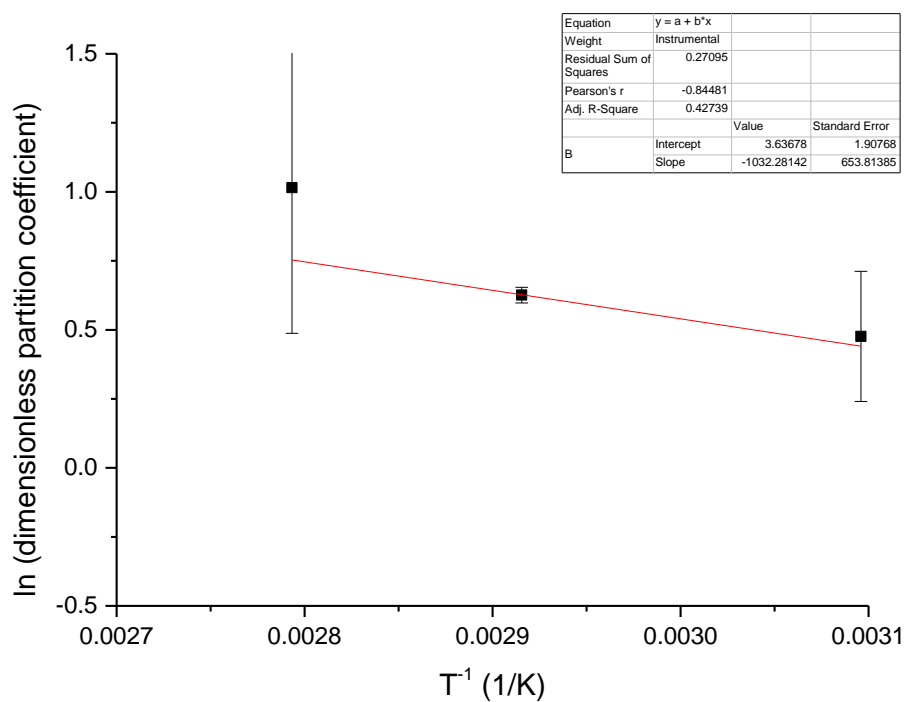


Table 7 The calculated enthalpies of selected tracers

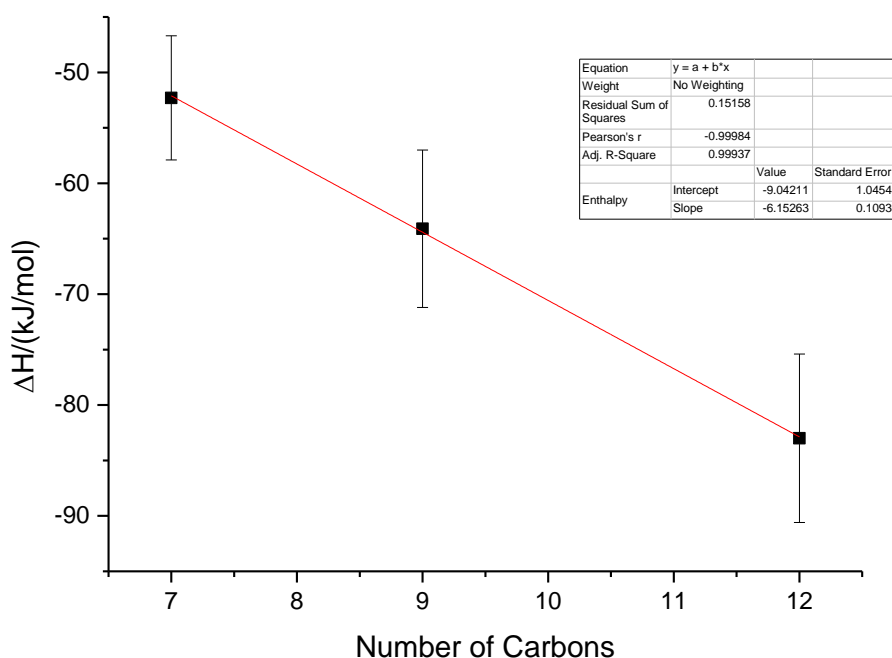
Tracer	$\Delta H$ (kJ/mol)	Error
PGDA	- 52.3	5.6
Triacetin	- 64.1	7.1
Tripropionin	- 83.0	7.6
PGMA isomer 1	8.5	1.9
PGMA isomer 2	10.6	2.7
Dipropionin isomer 1	13.9	2.6
Dipropionin isomer 2	8.6	5.4

### 3 Conclusion

We have successfully determined partition coefficients for the parent ester compounds and their hydrolysis products under a range of temperature conditions. Furthermore, we have shown for several of these tracers that the temperature dependence of the partition coefficients follows a van't Hoff type equation.

Using the parent ester tracer data from Table 2, we have plotted enthalpy vs. number of carbons. There is a linear relationship between the number of carbon atoms and the enthalpy. This type of correlation is consistent with other work for octanol-water partition coefficients and can be useful for making estimating the thermodynamic properties and partition coefficients of similar parent ester compounds.

Figure 11 Plot of enthalpy data vs. number of carbons for parent ester tracers



#### CONTACT US

**t** 1300 363 400  
+61 3 9545 2176  
**e** [enquiries@csiro.au](mailto:enquiries@csiro.au)  
**w** [www.csiro.au](http://www.csiro.au)

#### FOR FURTHER INFORMATION

**Earth Science and Resource Engineering**  
Matthew Myers  
**t** +61 8 6436 8708  
**e** [matt.myers@csiro.au](mailto:matt.myers@csiro.au)

#### YOUR CSIRO

Australia is founding its future on science and innovation. Its national science agency, CSIRO, is a powerhouse of ideas, technologies and skills for building prosperity, growth, health and sustainability. It serves governments, industries, business and communities across the nation.