# Partitioning Behavior of Organic Contaminants in Carbon Storage Environments: A Critical Review

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**Abstract.** Carbon capture and storage is a promising strategy for mitigating the $CO_2$ contribution to global climate change. The large scale implementation of the technology mandates better understanding of the risks associated with $CO_2$ injection into geologic formations and the subsequent interactions with groundwater resources. The injected supercritical $CO_2$ (sc-$CO_2$) is a nonpolar solvent that can potentially mobilize organic compounds that exist at residual saturation in the formation. Here, we review the partitioning behavior of selected organic compounds typically found in depleted oil reservoirs in the residual oil–brine–sc-$CO_2$ system under carbon storage conditions. The solubility of pure phase organic compounds in sc-$CO_2$ and partitioning of organic compounds between water and sc-$CO_2$ follow trends predicted based on thermodynamics. Compounds with high volatility and low aqueous solubility have the highest potential to partition to sc-$CO_2$. The partitioning of low volatility compounds to sc-$CO_2$ can be enhanced by co-solvency due to the presence of higher volatility compounds in the sc-$CO_2$. The effect of temperature, pressure, salinity, pH, and dissolution of water molecules into sc-$CO_2$ on the partitioning behavior of organic compounds in the residual oil-brine-sc-$CO_2$ system is discussed. Data gaps and research needs for models to predict the partitioning of organic compounds in brines and from complex mixtures of oils are presented. Models need to be able to

better incorporate the effect of salinity and co-solvency, which will require more experimental data from key classes of organic compounds.

## 1. Introduction

Carbon capture and storage (CCS) is a technology which aims to capture $CO_2$ gas from its point source of emission and deposit it underground with 99% permanence over at least 100 years.[1] Despite the scientific debate[2] about the viability of implementing CCS on the scales necessary for climate change mitigation, it remains one of the most promising mitigation approaches for anthropogenic $CO_2$ emissions and subsequent climate change.[3] Many different types of geologic formations have been proposed as possible end-of-pipe $CO_2$ receptors, and various demonstrations have been implemented in each of them.[4] The most common geologic formations that may be deployed for CCS include saline aquifers, unmineable coal seams, organic-rich shales, basalts and depleted oil and gas reservoirs.[4] Especially in the United States, depleted oil reservoirs are of particular interest because they have been proposed as the first adopters of CCS due to the potential to offset costs of CCS through enhanced oil recovery.[4] Use of depleted oil reservoirs for implementing large-scale CCS projects is also a way to reduce infrastructure costs associated with the injection and pipeline transport of $CO_2$ as an infrastructure of $CO_2$ transporting pipelines is already built close to oilfields undergoing enhanced oil recovery (EOR) using $CO_2$.[5] Depleted oil reservoirs generally also have had more extensive site characterization than brine aquifers and unmineable coal seems[6] and there is considerable experience within the oil and gas industry regarding injection of sc-$CO_2$ for EOR purposes.

Enhanced oil recovery is often performed with sc-$CO_2$ flooding for light and medium oils. When $CO_2$ flooding is practiced for EOR, injected sc-$CO_2$ is typically obtained from natural sources

and is typically recovered for use elsewhere and, therefore it does not constitute CCS.[7] However, once oil production from EOR operations drops, these oilfields can then be used for CCS. The amount of $CO_2$ that can be stored in the oil and gas reservoirs of the United States of America and Canada alone have been estimated to be about 143 gigatons (Gt),which accounts for ~40 years of storage potential; this does not account for unexplored oil and gas reservoirs.[4] Globally, 675 to 900 Gt of $CO_2$ are expected to be stored in depleted oil and gas reservoirs. These numbers would increase up to 25% if undiscovered oil and gas fields are included.[1]

Experience regarding EOR using sc-$CO_2$ flooding can be used to devise a conceptual model for the types of phases present in a CCS scenario using depleted oil fields. Typically, up to 30% to 40% of the oil in a reservoir remains in the formations after primary production and EOR operations.[4, 8] In EOR using sc-$CO_2$, a sc-$CO_2$ flood is injected to increase the bulk volume of the oil and decrease its viscosity which forces oil out of the pores.[4] Upon injection of sc-$CO_2$ for EOR, four phases are present: a) a $CO_2$-rich phase with light hydrocarbons, b) an oil-rich phase with heavier hydrocarbons,[9] c) a $CO_2$-saturated formation water or brine, and d) the formation solids. The solubility of the various organic compounds present in oils, in sc-$CO_2$ and in $CO_2$-saturated brines is not well documented in the scientific literature, but is necessary to assess the potential migration of various organic compounds from the CCS site in sc-$CO_2$ or brines that may migrate from the formation to an overlying aquifer.

The possibility of $CO_2$ leakage from these formations is one of the major concerns emanating from the large-scale deployment of the technology. Failure of the cap rock,[10] well blow-out,[11] poorly plugged wells,[12] and seismic activity[13] are the most likely pathways of $CO_2$ migration to

overlying formations. The migration of $CO_2$ may occur either as sc-$CO_2$ or as $CO_2$-saturated brine. For either case the water resources along the migration pathways may be affected by the presence of naturally occurring organics or trace metal contaminants in the migrating $CO_2$-rich phase.[14, 15]

Depleted oil reservoirs contain a variety of organic compounds, many of which are toxic and carcinogenic (e.g. BTEX and PAHs found in oilfield brines)[16–22] and their respective maximum contaminant levels in drinking water are very low.[23] The solubility of many of the organic compounds typically found in oilfields in the injected sc-$CO_2$ or in $CO_2$-saturated brines under CCS conditions have not been measured. Therefore, their potential for migration from the storage reservoir to overlying waters is difficult to estimate with any certainty. Obtaining knowledge about the partitioning behavior of organic compounds found in oil reservoirs is necessary for first order estimates of migration potential, migration modeling through seals and well bores, and overall predictive integrated risk assessment efforts for carbon storage systems.

The solubility of organic compounds in water is affected by temperature, pressure, and salinity (TPX), which subsequently affects their partitioning between sc-$CO_2$ and brine. The conditions of CCS formations differ vastly by location which highlights the necessity for solubility data for a range of important compound classes over a wide range of pressure, temperature, and salinity conditions.[24] These conditions entail temperatures in the range of 304-433 K, pressures of 73.9-500 bar and total dissolved solids (TDS) between 10,000 and 400,000 mg/L.[25] Under these conditions, water saturated sc-$CO_2$ can exist as a separate phase along with $CO_2$ saturated brine and the residual oil phase.

This study briefly reviews the basic principles affecting the solubility of organic compounds in sc-$CO_2$ and $CO_2$-saturated brine, the existing knowledge of specific classes of organic compounds typically found in oil reservoirs, and available data on their partitioning behavior between oil-brine-sc-$CO_2$ phases under CCS conditions. The objectives of this review are to 1) compile available experimental data on simple sc-$CO_2$-organic and aqueous-sc-$CO_2$ systems, 2) determine discernible trends in the partitioning behavior (i.e. solubility in sc-$CO_2$, and aqueous-sc-$CO_2$ partition coefficients) of selected, individual organic compounds to predict trends expected in a brine-crude oil-sc-$CO_2$ system based on thermodynamic arguments, and 3) identify critical gaps in knowledge and data required to predict partitioning of organic compounds in an oil-brine-SC-$CO_2$ system. Due to dearth of data on the partitioning of individual organic compounds between crude oil mixtures and sc-$CO_2$, the data presented in this study is for pure phase or mixtures with only a select few compounds. The environmental implications of these findings on the potential for organic compound migration to overlying aquifers due to $CO_2$ injection are discussed. Future research directions are proposed which will provide the data required to make better predictions about the potential for organic compounds to affect water quality in overlying aquifers.

## 2. Thermodynamic Principles and Environmental Factors Controlling the Solubility of Organic Compounds in an Oil-Brine-Supercritical $CO_2$ system

Modeling the partitioning behavior of organic compounds in depleted oil reservoirs requires information on the solubility of a variety of organic compounds in sc-$CO_2$, as well as their solubility in brine (water). While the prediction of the solubility of apolar and some polar

organics in water is fairly well-understood, the solubility of these compounds in a system with a supercritical component, at very high TDS, and for a multi-component system such as crude oil, is less well understood. The solubility of a compound in sc-$CO_2$ is determined by its chemical potential, ($\mu_i$), in the sc-$CO_2$ rich phase (eq. 1). The chemical potential of a species is the same in all phases present when at chemical equilibrium.

$$\mu_i = \left[\frac{\partial G}{\partial n_i}\right]_{T,P,n_j} \qquad \text{(eq. 1)}$$

The fugacity of a compound is used as a surrogate for chemical potential. For an isothermal change for component $i$ in any system the relationship between chemical potential and fugacity is given by eq. 2

$$\mu_i - \mu_i^0 = RT \ln \frac{f_i}{f_i^0} \qquad \text{(eq. 2)}$$

where $\mu_i^0$ is the chemical potential of a compound in its standard state, R is the universal gas constant, T is the temperature, $f_i$ is the fugacity of the compound in the system of interest, and $f_i^0$ is the fugacity of the compound in its standard state. The fugacity of a compound *i* is dependent on system pressure, temperature, and importantly, composition of the phases present (eq. 3).[26]

$$d\ln f_i = \left(\frac{\partial \ln f_i}{\partial T}\right)_{P,x} dT + \left(\frac{\partial \ln f_i}{\partial P}\right)_{T,x} dP + \sum_{j=1}^{m-1}\left(\frac{\partial \ln f_i}{\partial x_j}\right)_{T,P,x_k} dx_j \qquad \text{(eq. 3)}$$

$$k = 1,\ldots, j-1, j+1,\ldots, m-1$$

This composition will depend on the components of the oil and/or brine phase in equilibrium with the sc-$CO_2$ phase, which is highly variable across sites.

In the crude oil-brine-sc-$CO_2$ system, the fugacity of an organic compound in the supercritical phase can be estimated in order to predict the solubility of a selected compound in the sc-$CO_2$ phase. Compounds with higher solubility in sc-$CO_2$ would be of greater interest than those of lower solubility in a scenario where the sc-$CO_2$ phase leaked from the storage reservoir. Two types of thermodynamic models (section 2.1) can be used to estimate fugacity and/or solubility of organic compounds: Equations of state (EOS) and quantitative structure property relationships (QSPRs). However, both types of models are currently unable to accurately predict the solubility of the organic compounds in a crude oil-brine-sc-$CO_2$ system, and certain limitations apply to each type of model.

Factors that prevent accurate predictions include the high and variable electrolyte content of the brines and variations in the resulting pH of the brine after sc-$CO_2$ injection (section 2.2). The entrainment of water into sc-$CO_2$ is another factor that may affect the ability of these models to accurately predict the partitioning behavior of organic compounds into sc-$CO_2$ as it has been shown to have effects (see section 7).

### 2.1. Thermodynamic Principles and Modeling of Organic Compound Partitioning into Supercritical $CO_2$

Equilibrium solubility in either sc-$CO_2$ or in $CO_2$-saturated brines can be estimated using established thermodynamic methods including equations of state (EOS) and quantitative structure property relationships (QSPRs). Each of these is briefly described here along with an indication of the data required to develop and calibrate these approaches for $CO_2$ storage conditions.

Several EOS, all of which are empirical, including Redlich-Kwong,[27] Soave modification of Redlich-Kwong equations,[28] Peng-Robinson,[29] Stryjerk-Vera modifications of Peng-Robinson,[30, 31] Patel-Teja,[32] and Adachi and Lu,[33] among others can potentially be used, with varying levels of accuracy, to model the partitioning behavior of organics in the depleted oil reservoirs. These EOS require an application of mixing rules to calculate the solubility of organic compounds in sc-$CO_2$ (see Supporting Information); binary interaction parameters need to be incorporated into EOS to account for the repulsive and attractive terms between the various organic compounds and sc-$CO_2$. Typical mixing rules include the van der Waals mixing rules, Panagiotopoulos and Reid,[34] and Wong-Sandler,[35] among others. Valderrama,[36] in his review on EOS, stated Gibbs free energy models and nonquadratic mixing rules with interaction parameters in the volume constraints give the best results for mixtures containing a supercritical component. However, the use of EOS to model systems with a supercritical component is still lacking; some organic compound solubility in sc-$CO_2$ cannot be accurately modeled by these systems.[36] Additionally, there is greater error when calculating solubility in multicomponent systems. For example, the error in solubility predictions using the Soave-Redlich-Kwong EOS, combined with van der Waals mixing rules, increased from 3% to 15% for single components (anthracene, phenanthrene, and carbazole) to 14% to 50% for a mixture of all three.[37] This is a result of the need for more accuate binary interaction parameters for the system, and is indicative of increased uncertainty for modeling the partitioning of individual organic compounds in complex systems, such as crude oil mixtures, where hundreds of binary interaction parameters are involved.

An alternative to EOS is the development of quantitative structure-property relationships (QSPR). A QSPR tries to account for all of the variables that may affect the state of a compound in a particular phase. Only three reports of QSPRs for organic compounds in sc-$CO_2$ are available,[38–40] but the approach may be promising and appears to be applicable for both polar and apolar compounds. Engelhardt and Jurs[38] introduced a quantitative structure-property relationship (QSPR) to predict the solubility of organic compounds in sc-$CO_2$. Seven solute descriptors were used in the QSPR, which include topological descriptors, electronic descriptors, geometric descriptors, and hybrid descriptors. In the training set, solubility measurements of 52 organic compounds, with a range of polarities and molar volumes, including naphthalene, anthracene, and benzoic acid at 308 K and 140 bar were used to create the QSPR model, and measurements of solubility of 2-aminobenzoic acid, 5-hydroxyindole, dibenzofuran, oleic acid, oxindole (enol), and 1-methylnaphthalene were used to test the model for its predictive capability. The QSPR resulted in errors of less than one log unit for both sets, however its applicability to CCS conditions is limited due to lack of information in the CCS temperature and pressure space. This suggests that a QSPR may be developed to predict the partitioning of a wide range of organic compound classes in sc-$CO_2$ under carbon storage conditions.

Another type of QSPR, termed a Linear Solvation Energy Relationship (LSER), has been used to estimate the partitioning of organic compounds from water to sc-$CO_2$.[39,40] The modeling of organic compound partitioning coefficients using LSERs requires solute descriptors such as hydrogen bonding acidity, basicity, molar volume, among others to predict the partitioning coefficient of organic compounds between water and sc-$CO_2$. These descriptors are widely available in the literature. An LSER developed for solubility of organic compounds in sc-$CO_2$

could predict the solubility of a variety of organic compounds in sc-$CO_2$ within ±0.20 log units, however the LSER was developed for a specific temperature and pressure where the density of sc-$CO_2$ was 0.76 g/cm$^3$. Another LSER was developed that could predict the partitioning of organics between water and sc-$CO_2$ within ±0.30 log units for a range of $CO_2$ densities. This suggests that LSER could be developed for a range of values in the temperature and pressure space, however, they still need to be adjusted to account for salinity and solubility enhancement due to co-solvents (see Sections 4 and 5), which would change the partitioning behavior.

## 2.2. Environmental Factors Affecting Solubility

The high salt content of brines and the pH decrease due to dissolution of $CO_2$ in the brine can affect solubility of organic compounds. The general decrease in aqueous solubility of organic compounds with increasing salt concentration can be estimated empirically with Setchenow constants (eq. 5).

$$\log \frac{\gamma_0}{\gamma} = \log \frac{c_{iw}^{sat}}{c_{iw,salt}^{sat}} = K_i^s [salt]_{tot} \qquad \text{(eq. 5)}$$

In eq. 5, $\gamma_0$ is the activity coefficient of the organic compound in a salt solution, $\gamma$ is the activity coefficient of the organic compound of interest in an infinitely dilute solution, $c_{iw}^{sat}$ is the solubility of the compound in an infinitely dilute solution, and $c_{iw,salt}^{sat}$ is the solubility of the compound in a salt solution, $[salt]_{tot}$ is the total molar salt concentration and $K_i^s$ is the Setchenow constant in units of $M^{-1}$. The values of $K_s$ depend on the ion type and are determined empirically for different classes of organic compounds. Values of $K_s$ exist for apolar organics

and for some monoploar and polar compounds for solutions up to the salinity of seawater.[41] This equation is valid up to approximately 0.7 M ionic strength, after which the effect of the dissolved salts on the molar volume of the solution has to be taken into account.[41] This is likely to be the case for saline geologic formations or depleted oil reservoirs which can have TDS in the 10's of g/L. Pitzer equations are used to determine the activity of organic species in brines, which are valid for high salt concentrations.[42] The Pitzer equations are semi-empirical ion-interaction models, and only applicable to organic electrolytes in solution. However, most compounds dissolved in oil are neutral (i.e. BTEX, PAHs), therefore another model is needed to account for the high levels of TDS in the brine.

Other EOS, such as the others previously discussed, can also be used to model the effect of the salt content on solubility of organic compounds in brine.[43–46] Most of these EOS use experimental data on light hydrocarbons ($C_1 - C_5$) for their correlations.[43–46] These models have been shown to be fairly accurate for the conditions of interest; however error increases as salt concentration and temperature increase.[44]

Small organic acids and some phenols can protonate as the solution pH is decreased and become neutral organic species. These can be major organic constituents in subsurface brines[18] which display a pH dependent aqueous solubility. For simple monoprotic acids the relative concentrations of the undissociated ($[HA]$), and dissociated ($[A^-]$) form of the organic acid can be determined using eq. 6.

$$\log \frac{[A^-]}{[HA]} = pH - pK_{ia} \qquad \text{(eq. 6)}$$

As pH is increased, aqueous solubility of the compound increases as it becomes charged. Most important organic acids with relevance to depleted oil reservoirs have $pK_{ia}$ between 4 and 10.[41] The pH of the brine in depleted oil reservoirs is expected to drop after $CO_2$ injection so the solubility of some organic acids in brine and in sc-$CO_2$ would be expected to decrease, however, this depends on the pKa for those acids and on the change in pH of the reservoir.

Site specific aqueous phase concentrations of organics will therefore likely cover a wide range of aqueous phase concentrations, based on pH and on differences in the composition of the oil phase. Studies of organic compounds in produced water from oil reservoirs show that there indeed is a wide variation of aqueous concentrations of organic compounds.[16–20]

## 3. Measured Solubility of Organic Compounds in Supercritical $CO_2$

### 3.1 Trends in Solubility of Organic Compounds in Supercritical $CO_2$

Supercritical $CO_2$ has been used for decades in the food[47,48] and pharmaceutical industry,[49] in treatment technologies (e.g. soil remediation),[50,51] and energy production (e.g. oil and gas extraction),[37] among other areas, to extract organic compounds into the sc-$CO_2$ phase. The solubility of many types of organics in the binary system of pure solute and sc-$CO_2$ has been measured. This data set, albeit dispersed in the literature can be used to predict the types of compounds that are expected to be mobilized by sc-$CO_2$, even if the mechanisms driving the solubility of these organic compounds are unknown.

The trends of solubility of several organic compound classes of importance in dry sc-$CO_2$ (i.e. in absence of dissolved water in the sc-$CO_2$ phase) follow the respective thermodynamic rules, e.g. apolar and polar organic compounds with high vapor pressure have higher solubility in sc-$CO_2$, and trends expected based on their structures and functional groups (**Table 1**). Small apolar and weakly monopolar compounds, such as hexane and benzene, have relatively high solubility in sc-$CO_2$.[52–55] Small polar compounds, such as acetic acid and phenol, have lower inherent volatility and lower solubility in sc-$CO_2$ compared to small apolar and weakly monopolar compounds.[56–58] As temperature increases, the vapor pressure and the solubility of both apolar and polar compounds in sc-$CO_2$ increase. Larger compounds, typically with a molecular weight greater than 200 g/mol, have lower solubility in sc-$CO_2$ due to their lower inherent volatility whether, apolar, monopolar, or polar. These larger compounds include longer-chained alkanes, larger aromatic acids, long-chained aliphatic acids, large PAHs, and other larger organic compounds. As the length of a carbon chain or number of rings increase in an organic compound, solubility in sc-$CO_2$ tends to decrease.

The position of functional groups appears to affect the solubility of aromatic organic acids, where aromatics with functional groups on the ortho- position have greater solubility in sc-$CO_2$ than their meta- and para- counterparts.[56, 59–67] Pfohl et al.[59] explained the increase in solubility by steric hindrance; the group on the ortho- position acted as a shield to the hydroxyl group, decreasing the compound's ability to form strong intermolecular bonds. This was found to be true especially for cresol, dihydoxybenzene, and hydroxybenzoic acid isomers.

**Table 1.** Measured Solubility of Selected Pure Phase Organic Compounds in sc-$CO_2$

| Organic Compound | Temperature (K) | Vapor Pressure at 298 K (bar) | Pressure (bar) | Solubility (mol/mol) |
|---|---|---|---|---|
| **Alkanes** | | | | |
| **n-Hexane**[53] | 353 | 6.8E-01[41] | 75 | 5.10E-02 |
| | | | 92 | 7.00E-02 |
| | | | 107 | 1.14E-01 |
| **n-Decane**[68] | 344 | 1.7E-03[41] | 90 | 3.2E-03 |
| | | | 105 | 6.0E-03 |
| | | | 126 | 3.4E-02 |
| **n-Hexadecane**[68] | 308 | 1.9E-06[41] | 83 | 2.6E-03 |
| | | | 96 | 7.8E-03 |
| | | | 113 | 8.7E-03 |
| **n-Octadecane**[68] | 310 | 1.7E-07[41] | 100 | 1.10E-03 |
| | | | 140 | 3.90E-03 |
| | | | 180 | 5.80E-03 |
| **BTEX** | | | | |
| **Benzene**[55] | 373 | 1.3E-01[41] | 40 | 5.5E-02 |
| | | | 52 | 4.4E-02 |
| | | | 59 | 4.4E-02 |
| **Toluene**[55] | 373 | 3.7E-02[41] | 38 | 3.8E-02 |
| | | | 46 | 3.3E-02 |
| | | | 55 | 3.1E-02 |
| **Ethylbenzene**[69] | 393 | 1.2E-02[41] | 81 | 2.7E-02 |
| | | | 121 | 3.4E-02 |
| | | | 161 | 7.7E-02 |
| **o-Xylene**[70] | 353 | 8.9E-03[41] | 88 | 3.8E-02 |
| | | | 136 | 6.5E-02 |
| | | | 148 | 1.4E-01 |
| **m-Xylene**[71] | 394 | 1.1E-02[41] | 102 | 2.8E-02 |
| | | | 125 | 3.7E-02 |
| | | | 161 | 7.1E-02 |
| **p-Xylene**[55] | 373 | 1.2E-02[41] | 40 | 2.2E-02 |
| | | | 49 | 2.2E-02 |
| | | | 59 | 2.2E-02 |
| **Aromatic Acids** | | | | |
| **o-Cresol**[59] | 373 | 4.0E-04[41] | 104 | 4.5E-03 |
| | | | 201 | 3.2E-02 |
| | | | 252 | 9.4E-02 |
| **m-Cresol**[59] | 373 | 2.0E-04[41] | 102 | 3.1E-03 |
| | | | 199 | 1.9E-02 |
| | | | 250 | 4.0E-02 |
| **p-Cresol**[59] | 373 | 1.6E-04[41] | 103 | 3.2E-03 |
| | | | 202 | 2.0E-02 |
| | | | 302 | 3.9E-02 |
| **o-Dihydroxybenzene**[60] | 318 | 2.2E-06[41] | 109 | 7.9E-06 |
| | | | 130 | 1.1E-05 |
| | | | 141 | 1.2E-05 |

| | | | | |
|---|---|---|---|---|
| **o-Hydroxybenzoic Acid**[61] | 328 | 2.0E-07[41] | 122 | 1.3E-04 |
| | | | 162 | 4.0E-04 |
| | | | 203 | 6.2E-04 |
| **Benzoic Acid**[72] | 328 | 1.1E-06[41] | 120 | 4.5E-04 |
| | | | 220 | 4.0E-03 |
| | | | 270 | 4.6E-03 |
| **Aliphatic Acids** | | | | |
| **Acetic Acid**[73] | 323 | 2.1E-02[41] | 70 | 1.1E-02 |
| | | | 77 | 1.3E-02 |
| | | | 84 | 1.6E-02 |
| **PAHs** | | | | |
| **Acenaphthene**[74] | 308 | 3.1E-06[41] | 122 | 2.0E-03 |
| | | | 152 | 2.1E-03 |
| | | | 182 | 2.4E-03 |
| **Phenanthrene**[37] | 308 | 2.2E-07[41] | 101 | 5.6E-04 |
| | | | 141 | 9.4E-04 |
| | | | 181 | 1.2E-04 |
| **Anthracene**[37] | 308 | 9.8E-09[41] | 102 | 1.3E-06 |
| | | | 141 | 5.4E-06 |
| | | | 181 | 8.4E-06 |
| **Other Groups** | | | | |
| **Thiophene**[75] | 334 | 5.3E-02[41] | 80 | 2.3E-02 |
| | | | 90 | 3.0E-02 |
| | | | 96 | 4.1E-02 |
| **p-Nitrophenol**[76] | 328 | 5.5E-08[41] | 122 | 1.6E-04 |
| | | | 162 | 3.1E-04 |
| | | | 203 | 4.6E-04 |

The sc-$CO_2$ is a nonpolar solvent with low polarizability and low dielectric constant, which theoretically makes it a good solvent for hydrocarbons. However, the analysis above suggests that sc-$CO_2$ is not a good solvent for larger molecules (e.g. MW >200 g/mol) such as large PAHs.[77] Carbon dioxide is net apolar, but the polar C-O bonds allow it to act as a Lewis acid and Lewis base.[78] In a sc-$CO_2$-water system in a depleted oil reservoir, this allows for sc-$CO_2$ to solvate small polar molecules, but not as strongly as $H_2O$ since the dipole moments between C-O bonds are not as strong as for H-O bonds in water. For the dissolution of large apolar molecules in water there is a diminishing effect of favorable entropy of dissolution, which accounts for lower aqueous solubility.[41] Similar arguments can be applied to sc-$CO_2$ as a solvent. Since both

water and $CO_2$ are more greatly displaced by large molecules, dissolution of larger molecular weight compounds is not a favorable process.

### 3.3 Effects of Temperature and Pressure on Solubility of Organic Compounds in Supercritical Carbon Dioxide

The effect of temperature and pressure on the vapor pressure of an organic compound and therefore on its solubility in sc-$CO_2$ has been well documented in the literature. An isobaric temperature increase results in a decrease in solubility of organic compounds in sc-$CO_2$, until a "crossover pressure", where their solubility in sc-$CO_2$ increases with increased temperature at the same pressure (**Figure 1**).[79] The crossover pressure, however, is characteristic of each solute. This phenomenon has been well documented by Foster, et al.[79] who modeled the crossover pressure in fluid phase equilibrium. They emphasized that the crossover pressure is a function of the organic compound-sc-$CO_2$ system, and the location of this point was in the vicinity of the critical density of the system.[79]

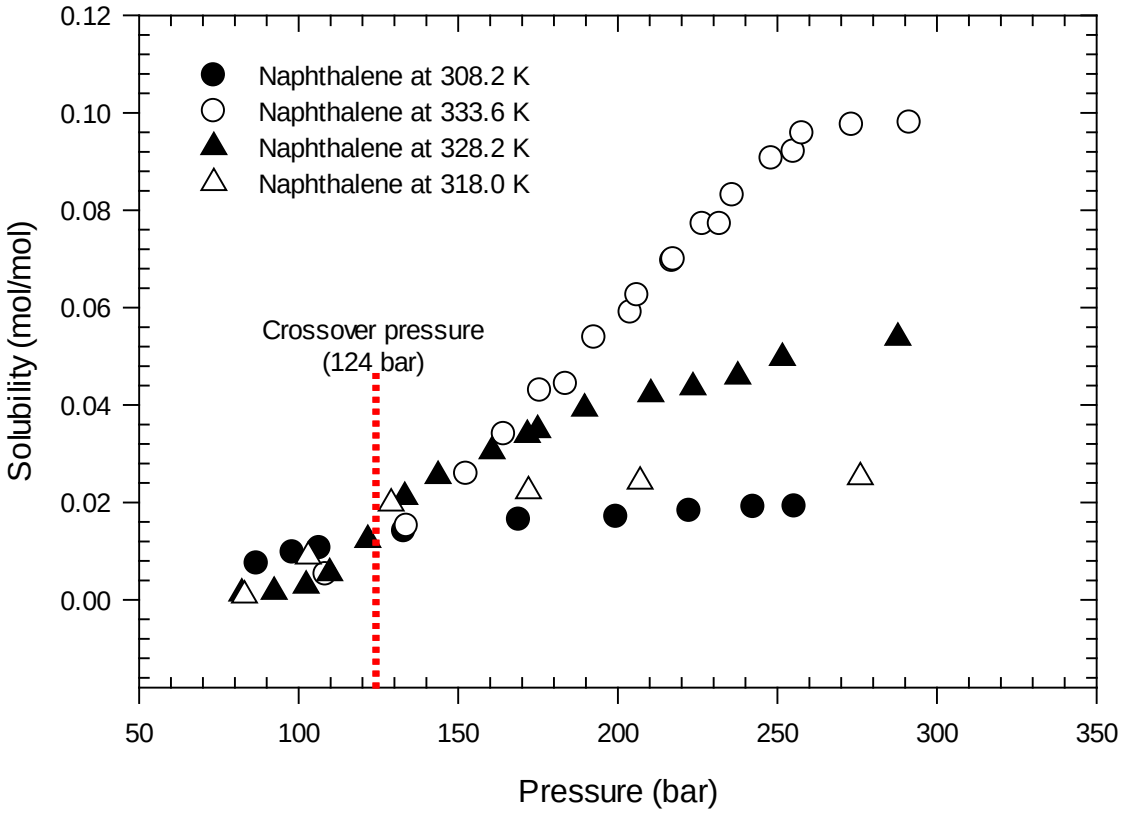


**Figure 1**. The *crossover pressure* of naphthalene.[80, 81]

Isothermal pressure increase results in a decrease in solubility up to the critical point, but then solubility increases steadily after reaching the critical point (**Figure 2**).[52,81] While solubility data for low pressures is not typically applicable to depleted oil reservoirs, it is interesting to note that the minimum solubility occurs at around the critical pressure of $CO_2$; therefore the solubility of organic compounds in sc-$CO_2$ should increase with increasing pressure given that reservoir pressures and temperatures are above the critical point for $CO_2$.

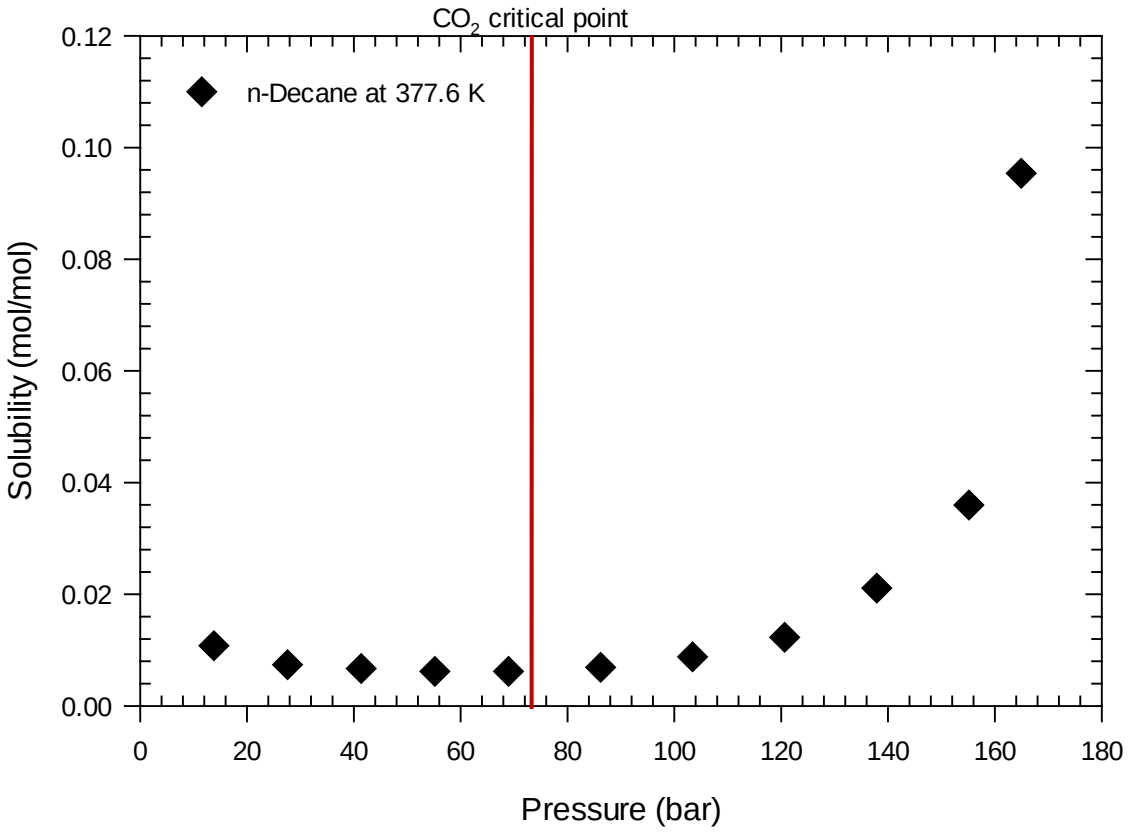


**Figure 2.** Isothermal pressure increase of n-decane at 377.6 K.[82]

## 4. Experimental Data on the Partitioning Behavior of Organic Compounds in a Supercritical $CO_2$-Water-Pure Phase system

### 4.1 Supercritical $CO_2$ – Water – Pure Phase Organic

In a $CO_2$ storage scenario, e.g. a depleted oil reservoir, water is present mostly as brine. In many cases sc-$CO_2$ will be in contact with brine containing dissolved organic compounds, but not necessarily the pure phase organics. Partitioning coefficients (K factors) for some organic compounds between sc-$CO_2$ and water have been reported (**Table 2**). This partitioning

coefficient (a ratio of the solubility of the organic compound in the supercritical phase to the solubility of the organic in the aqueous phase) is often used in risk assessment models for groundwater contamination from leakage of sc-$CO_2$.[14] K factors will depend on pressure as well as on temperature for water-sc-$CO_2$ partitioning, especially near the critical point of $CO_2$ where the density of the gas increases most with changes in pressure. Equations of state need to capture this dynamic behavior of K-factors over the temperature and pressure space relevant to carbon storage. Despite this, reported K-factors (determined experimentally) for partitioning of organics between water and sc-$CO_2$ indicate trends that are consistent with expectations.

**Table 2**. Partitioning coefficients (K) of Selected Organic Compounds in a Pure Phase-Water-sc-$CO_2$ System

| Organic Compound | Temperature (K) | Pressure (bar) | K (mol $CO_2$ per mol $H_2O$) | $K_{aw}$ at 298 K |
|---|---|---|---|---|
| **Alkanes** | | | | |
| **Hexane**[40] | 300 | 80 | 9.0E+03 | 5.5E+01[41] |
| **Cyclohexane**[40] | 300 | 80 | 4.9E+03 | 7.8E+00[41] |
| **BTEX** | | | | |
| **Benzene**[83] | 318 | 80 | 8.6E+02 | 4.5E+00[41] |
| | | 90 | 1.6E+03 | |
| | | 101 | 2.8E+03 | |
| **Aromatic Acids** | | | | |
| **Phenol**[84] | 313 | 81 | 5.6E-01 | 2.6E-05[41] |
| | | 158 | 9.9E-01 | |
| | | 255 | 1.0E+00 | |
| **m-Cresol**[85] | 313 | 97 | 6.0E-01 | 3.8E-05[41] |
| | | 124 | 2.2E+00 | |
| | | 165 | 3.9E+00 | |
| **Benzoic Acid**[84] | 313 | 79 | 6.1E-01 | 1.6E-06[41] |
| | | 150 | 1.4E+00 | |
| | | 251 | 2.0E+00 | |
| **Aliphatic Acids** | | | | |

| | | | | |
|---|---|---|---|---|
| **Acetic Acid**[86] | 313 | 146 | 4.3E-02 | 1.1E-05[41] |
| **PAHs** | | | | |
| **Naphthalene**[83] | 318 | 81 | 1.3E+02 | 1.8E-02[41] |
| | | 90 | 2.1E+02 | |
| | | 100 | 3.5E+02 | |
| **Other Groups** | | | | |
| **2-Nitrophenol**[87] | 333 | 200 | 7.2E+01 | 7.9E-04[41] |
| **4-Nitrophenol**[87] | 333 | 200 | 1.8E-01 | 2.2E-08[41] |

Trends in the partitioning data follow those expected based on the relative solubility of the compounds in each phase (water and sc-$CO_2$). Small apolar compounds, such as benzene and hexane,[40,83,85] have relatively higher partitioning coefficients to sc-$CO_2$, due to their high solubility in sc-$CO_2$ and low solubility in water. Small polar compounds, such as phenol and acetic acid, which have only moderate solubility in sc-$CO_2$, but high aqueous solubility, have low partitioning coefficients.[84–88] Conversely, naphthalene has moderate solubility in sc-$CO_2$, but low aqueous solubility, and thus exhibits a high partitioning coefficient to sc-$CO_2$.[83] Phenol, which exhibits similar behavior in pure phase solubility to sc-$CO_2$ as naphthalene, has a much lower partitioning coefficient from water to sc-$CO_2$ than naphthalene because of its ability to form hydrogen bonds with water.[84,85,87] Experiments investigating the extraction rates of various organic compounds from contaminated water and soil using sc-$CO_2$ have shown similar trends. Organic compounds with the highest K-factors having the highest extraction rates in sc-$CO_2$, and naphthalene extraction efficiency was higher than larger PAHs.[50,51] While the trends in the partitioning data roughly follow the trends predicted from the relative solubility of each compound in each phase, currently K values must be determined experimentally since the impact of other organic phases (co-solvents) or water in sc-$CO_2$ on the activity of each species in sc-$CO_2$ cannot be easily predicted (see sections 5 and 7, respectively).

### 4.2 Effects of Electrolytes and pH on Supercritical $CO_2$ – Water – Oil Partitioning

There are few studies on the effect of electrolytes in the aqueous phase on the partitioning behavior of organic compounds to sc-$CO_2$. Curren and Burk[89] measured the partitioning of pentachlorophenol (not found in depleted oil reservoirs) between water and sc-$CO_2$. With the addition of NaCl they found that the activity of pentachlorophenol in water, and therefore its partitioning into sc-$CO_2$ from the NaCl solution, increased with increasing ionic strength. Their findings are consistent with expectations based on the "salting out" effect, the increase in activity of organic compounds due to the presence of electrolytes. A review of the effect of salts on organic compounds in seawater by Xie, et al.[90] showed that the salting out effect was greater for organics with large molar volumes. For example, at 298 K, the salting out effect for NaCl followed the order: Pyrene > anthracene > naphthalene > benzene which follows their trend in molar volume (Pyrene > anthracene > naphthalene > benzene).

As the pH of the brine phase decreases, which is expected due to the dissolution of injected sc-$CO_2$, organic acids will protonate and partition to sc-$CO_2$ to a greater degree. This is a result of their lower solubility in water and their increased solubility in sc-$CO_2$. Therefore, the K-factors of small organic acids between brine and sc-$CO_2$ will tend to increase with decreasing pH.[89]

## 5. Solubility Enhancement of Organic Compounds in the Presence of Volatile Organic Compounds

Solubility enhancement or co-solvency effect is the enhancement of the solubility or partitioning in sc-$CO_2$ of one organic contaminant due to the presence of another. In equation of state models, these effects can in principle be handled using appropriate mixing rules and binary interaction parameters, however, implementation of these parameters into an EOS for a crude oil system with many components is challenging. In QSPRs the co-solvency effect can potentially be incorporated using an appropriate parameter to capture the effect of single or multiple co-solvents on the sc-$CO_2$ properties.

In the case of depleted oil and gas reservoirs the co-solvency effect may be particularly relevant for understanding the partitioning phenomena to the sc-$CO_2$ phase because of the high concentration and large variety of organics present in each site. Lucien and Foster[91] by reviewing the solubility enhancement presented two theories for why solubility enhancement occurs in multicomponent systems. The first theory, introduced by Kurnik and Reid,[92] suggested that as the upper critical endpoint or critical point of the less volatile compound of the system is approached, solubility is increased. The addition of a co-solvent causes the upper critical endpoint to occur at lower temperatures than for a binary system. The second theory, by Dobbs and Johnston,[93] suggests that the co-solvent behaves as an entrainer, where the compound with lower solubility is enhanced by the presence of the other solute. The physical reasons for the co-solvent effect are not known. The solubility of organic compounds in sc-$CO_2$ increases with increasing concentration of co-solvent in the sc-$CO_2$ phase (relative to the water and/or brine phase)[94] (**Table 3**). Compounds with higher volatility and solubility in sc-$CO_2$ have been shown to enhance the solubility of less volatile compounds (**Table 3**).

**Table 3.** Solubility Enhancement of Organic Compounds with Higher Volatility Co-solvents in sc-$CO_2$.

| Organic Compound | Temperature (K) | Pressure (bar) | Pure Phase Solubility (mol/mol) | Co-solvent(s) | Solubility with Co-solvents (mol/mol) | Solubility Enhancement (%) |
|---|---|---|---|---|---|---|
| **Aromatic Acids** | | | | | | |
| **Benzoic Acid**[94] | 328 | 200 | 3.8E-03 | Benzene (3 mol %) | 9.0E-03 | 136 |
| | | 200 | 3.8E-03 | Benzene (7.6 mol %) | 1.6E-02 | 329 |
| | | 200 | 3.8E-03 | Acetone (3.5 mol %) | 6.4E-03 | 67 |
| | | 200 | 3.8E-03 | Acetone (9.3 mol %) | 1.8E-02 | 365 |
| | | 200 | 3.8E-03 | Cyclohexane (3 mol %) | 5.2E-03 | 35 |
| | | 200 | 3.8E-03 | Cyclohexane (6.5 mol %) | 1.1E-02 | 192 |
| | | 200 | 3.8E-03 | Methylene Chloride (5.4 mol %) | 1.2E-02 | 224 |
| | | 200 | 3.8E-03 | Methylene Chloride (12.7 mol %) | 1.9E-02 | 391 |
| **o-Hydroxybenzoic Acid**[61,64] | 328 | 101 | 3.4E-05 | Acetone (3.5 mol %) | 9.3E-04 | 2635 |
| | | 101 | 3.4E-05 | Methanol (3.5 mol %) | 1.1E-03 | 3135 |
| | | 121 | 1.3E-04 | Acetone (3.5 mol %) | 1.5E-03 | 1054 |
| | | 121 | 1.3E-04 | Methanol (3.5 mol %) | 2.5E-03 | 1823 |
| | | 202 | 6.2E-04 | Acetone (3.5 mol %) | 2.5E-03 | 303 |
| | | 202 | 6.2E-04 | Methanol (3.5 mol %) | 5.1E-03 | 723 |
| **PAHs** | | | | | | |
| **Phenanthrene**[37, 95] | 308.2 | 101 | 5.6E-04 | Naphthalene | 1.0E-03 | 84 |
| | | 141 | 9.4E-04 | Naphthalene | 2.1E-03 | 123 |
| | | 181 | 1.2E-03 | Naphthalene | 1.6E-03 | 26 |
| **Others** | | | | | | |
| **Carbazole**[37] | 308.2 | 161 | 1.8E-05 | Anthracene & Phenanthrene | 2.3E-05 | 29 |
| | | 181 | 2.3E-05 | Anthracene & Phenanthrene | 2.8E-05 | 23 |
| | | 201 | 2.8E-05 | Anthracene & Phenanthrene | 2.9E-05 | 3 |
| **Dibenzothiophene**[96] | 309 | 104 | 4.9E-04 | Naphthalene | 9.9E-04 | 102 |
| | | 139 | 9.7E-04 | Naphthalene | 2.7E-03 | 178 |
| | | 208 | 1.3E-03 | Naphthalene | 4.1E-03 | 215 |

Even though the co-solvency effects can be complex, they are predictable as illustrated with the case of aromatic acids. The solubility of the isomers o-hydroxybenzoic acid and m-hydroxybenzoic acid in sc-$CO_2$ was enhanced by the addition of acetone and methanol, respectively (**Table 3**).[64] Methanol provides higher solubility enhancement for the isomers than

acetone. Both methanol and acetone are more volatile than the isomers, but acetone has a higher vapor pressure. However, since methanol can act as a Lewis acid and base, it can associate with these aromatic acids better than acetone, therefore enhancing the solubility of the isomers.

Aromatic acids have the ability to act as Lewis acids and Lewis bases, and have limited solubility in sc-$CO_2$, and when the aqueous phase is present, their partitioning to sc-$CO_2$ is further limited because they are relatively soluble in water. Roop and Akgerman[97] found that benzene was relatively successful in enhancing the solubility of phenol in sc-$CO_2$. Methanol, however, despite its high volatility and solubility in sc-$CO_2$, decreased the solubility of phenol in sc-$CO_2$ because it increased phenol solubility in water. This occurred also for acetic acid, where the presence of alcohols in the aqueous phase decreased the K-factor of acetic acid.[86]

The solubility of aromatic acids in sc-$CO_2$ can be increased in the presence of co-solvents, with various aromatic acids exhibiting solubility enhancement in the presence of more volatile compounds, which include benzene, acetone, and methanol. In a ternary system with oil-sc-$CO_2$ and water, higher volatility compounds that cannot act as a Lewis acid and Lewis base, such as benzene or hexane, are the best co-solvents. This shows that multi-component mixtures, such as crude oil, will have an effect on the partitioning behavior of organic compounds to sc-$CO_2$.

## 6. Compilation of Data

A compilation of data for the solubility of organic compounds in sc-$CO_2$, typically found in oil reservoirs, is provided in Table 4. The temperature, pressure, and mole fraction solubility or partitioning coefficient range are presented. This compilation of data can be used by researchers

who need solubility data for organic compounds in sc-$CO_2$, or by CCS researchers and policy makers for inputs into CCS models. This list also highlights the gaps in data that are necessary to understand the full partitioning behavior of organic compounds in sc-$CO_2$, in particular the lack of co-solvency data for larger, less volatile compounds (such as PAHs, larger alkanes and cycloalkanes) in the presence of volatile organic compounds, such as BTEX or short-chained alkanes.

**Table 4.** Experimental Supercritical $CO_2$ Solubility Data of Organic Compounds Found in Oil Reservoirs.

| Organic Compound | Temperature Range (K) | Pressure Range (bar) | Mole Fraction Solubility Range | Organic Compound | Temperature Range (K) | Pressure Range (bar) | Mole Fraction Solubility Range |
|---|---|---|---|---|---|---|---|
| **Alkanes – In order of carbon chain length** | | | | | | | |
| n-Pentane[98] | 278 – 378 | 1 – 96 | 1.0E-02 – 7.4E-01 | n-Hexadecane[99] | 393 | 100 – 1000 | 9.0E-03 – 3.1E-01 |
| n-Hexane[52] | 298 – 313 | 4 – 77 | 1.3E-02 – 7.5E-02 | n-Hexadecane[68] | 308 | 83 - 124 | 2.6E-03 – 9.9E-03 |
| n-Hexane[53] | 313 – 393 | 7 – 115 | 1.5E-02 – 4.9E-01 | n-Octadecane[68] | 310 – 353 | 100 – 200 | 1E-04 – 8.6E-03 |
| n-Hexane[40] | 300 | 80 | 9.0E+03* | n-Tetracosane[100] | 308 – 318 | 50 – 209 | 3.9E-04 – 7.7E-03 |
| n-Heptane[101] | 310 – 478 | 1.8 – 134 | 5.0E-03 – 8.9E-01 | n-Tetracosane[102] | 310 | 88 – 261 | 5.4E-04 – 1.1E-03 |
| iso-Octane[103] | 323 – 348 | 20 – 28 | 1.1E-02 – 3.1E-02 | n-Pentacosane[102] | 308 | 104 – 202 | 2.2E-04 – 6.0E-04 |
| n-Octane[104] | 313 – 348 | 15 – 114 | 4.0E-03 – 4.2E-02 | n-Octacosane[105] | 308 – 325 | 82 – 327 | 1.1E-04 – 1.1E-03 |
| 2,3-Dimethylhexane[72] | 318 – 328 | 120 – 240 | 4.8E-04 – 7.1E-03 | n-Octacosane[106] | 308 – 318 | 80 – 250 | 1.2E-05 – 3.9E-04 |
| n-Nonane[107] | 343 | 37 – 118 | 4.0E-03 – 3.3E-03 | n-Octacosane[100] | 308 – 328 | 50 – 209 | 3.8E-04 – 1.6E-03 |
| n-Nonane[108] | 315 – 418 | 20 – 168 | 1.3E-03 – 1.1E-01 | n-Octacosane[102] | 308 | 100 – 340 | 3.9E-05 – 8.6E-05 |
| n-Decane[103] | 323 – 348 | 20 – 30 | 7.0E-04 – 2.3E-03 | n-Nonacosane[102] | 308 | 126 – 215 | 3.1E-05 – 6.6E-05 |
| n-Decane[82] | 277 - 511 | 3 - 188 | 1.0E-04 – 3.5E-01 | n-Triacontane[106] | 308 – 318 | 90 – 250 | 5.1E-06 – 3.0E-04 |
| n-Decane[109] | 344 – 378 | 63 – 165 | 5.0E-03 – 8.4E-02 | n-Dotriacontane[99] | 393 | 100 – 1000 | 3.0E-03 – 3.7E-01 |
| n-Decane[110] | 344 – 378 | 40 – 155 | 1.0E-03 – 3.6E-02 | n-Dotriacontane[100] | 308 – 338 | 46 – 206 | 2.5E-04 – 1.2E-03 |
| n-Decane[107] | 344 | 43 – 119 | 2.0E-03 – 1.6E-02 | n-Hexatriacontane[100] | 308 – 338 | 30 – 207 | 2.5E-04 – 1.0E-03 |
| n-Decane[68] | 344 | 89 – 128 | 3.2E-03 – 6.5E-02 | Cyclohexane[111] | 366 – 410 | 1 – 145 | 4.9E-02 – 2.3E-01 |
| n-Undecane[108] | 315 – 418 | 20 – 200 | 5.0E-04 – 9.4E-02 | Cyclohexane[40] | 300 | 80 | 4.9E+03* |
| n-Dodecane[112] | 318 – 418 | 16 – 204 | 1.0E-03 – 5.7E-02 | | | | |
| **BTEX** | | | | | | | |
| Benzene[52] | 298 – 313 | 8 – 76 | 4.1E-03 – 2.5E-02 | Toluene[83] | 318 | 79 – 108 | 1.1E+03 – 5.1E+03* |
| Benzene[54] | 313 | 7 – 77 | 9.0E-03 – 3.3E-02 | Toluene (+ Benzene, Naphthalene, and Parathion Co-solvents)[83] | 318 – 330 | 79 – 110 | 6.5E+02 – 5.2E+03* |
| Benzene[55] | 313 – 393 | 4 – 63 | 1.1E-02 – 4.5E-01 | Toluene[40] | 300 | 80 | 1.2E+03* |
| Benzene[83] | 318 | 79 – 110 | 8.5E+02 – 2.8E+03* | Ethylbenzene[69] | 313 - 393 | 56 – 161 | 3.7E-03 – 7.7E-02 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Benzene (+ Toluene, Naphthalene, and Parathion Co-solvents)[83] | 318 – 330 | 80 – 110 | 4.4E+02 – 3.7E+03* | Ethylbenzene[113] | 308 – 328 | 13 – 84 | 1.6E-03 – 6.6E-03 |
| Benzene[85] | 313 – 323 | 96 – 165 | 9.8E+02 – 4.9E+03* | o-Xylene[70] | 313 – 353 | 7.9 – 149 | 2.4E-02 – 1.5E-01 |
| Benzene(+ m-Cresol, p-Chlorophenol, and Benzene Co-solvents)[114] | 313 – 323 | 96 – 152 | 9.6E+02 – 4.2E+03* | m-Xylene[115] | 462 – 582 | 20 – 52 | 1.1E-01 – 8.2E-01 |
| Toluene[103] | 323 – 348 | 20 – 28 | 7.6E-03 – 2.1E-02 | m-Xylene[70] | 313 – 353 | 7 – 104 | 3.2E-02 - 4.4E-02 |
| Toluene[116] | 311 – 477 | 3 – 153 | 3.0E-03 – 7.3E-01 | p-Xylene[55] | 353 – 393 | 4 - 62 | 1.1E-02 – 1.8E-01 |
| Toluene[115] | 393 – 543 | 9 – 52 | 5.2E-02 – 7.5E-01 | p-Xylene[70] | 313 – 353 | 6 – 124 | 2.5E-02 – 1.7E-01 |
| Toluene[55] | 353 – 393 | 5 – 65 | 2.0E-02 – 2.5E-01 | | | | |

## PAHs and Substituted PAHs and Benzenes – In Alphabetical Order

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Acenaphthene[74] | 308 – 348 | 121 – 354 | 1.3E-03 – 1.4E-02 | Naphthalene (+Phenol Co-solvent)[95] | 308 – 318 | 54 – 280 | 2.3E-04 – 5.3E-02 |
| Acenaphthene (+Fluoranthene and Triphenylene Co-solvents)[117] | 308 – 338 | 121 – 355 | 1.5E-03 – 9.9E-03 | Naphthalene (+Biphenyl Co-solvent)[95] | 308 – 318 | 54 – 280 | 1.4E-04 – 2.5E-02 |
| Anthracene[118] | 303 – 343 | 104 – 415 | 3.5E-06 – 3.5E-04 | Naphthalene[96] | 309 - 328 | 75 – 275 | 8.0E-04 – 5.5E-02 |
| Anthracene[93] | 308 | 120 – 350 | 5.0E-05 – 8.0E-05 | Naphthalene (+ Dibenzothiophene Co-solvent)[96] | 309.15 | 75 – 275 | 1.9E-02 – 4.7E-02 |
| Anthracene (+Methanol Co-solvent)[93] | 308 | 120 – 350 | 6.9E-05 – 1.04-04 | Naphthalene[83] | 318 | 81 – 100 | 1.3E+02 – 3.5E+02 |
| Anthracene[119] | 308 – 318 | 104 – 276 | 8.9E-06 – 1.1E-04 | Naphthalene (+Benzene, Toluene, and Parathion Co-solvent)[83] | 318 – 330 | 81 – 120 | 6.5E+01 – 1.1E+03 |
| Anthracene (+Phenanthrene Co-solvent)[119] | 308 – 318 | 104 – 276 | 3.2E-05 – 1.2E-04 | Naphthalene[120] | 308 | 140 – 244 | 1.6E-02 – 1.9E-02 |
| Anthracene[60] | 323 | 92 – 293 | 3.1E-06 – 1.5E-04 | Naphthalene (+n-Pentane Co-solvent)[120] | 308 – 328 | 96 – 244 | 2.3E-02 – 1.1E-01 |
| Anthracene[37] | 308 | 102 – 181 | 1.3E-05 – 8.4E-05 | Naphthalene (+2,6-Dimethylnaphthalene Co-solvent)[120] | 303 – 317 | 244 – 314 | 1.2E-02 – 5.3E-02 |
| Anthracene (+Carbazole and Phenanthrene Co-solvents)[37] | 308 | 102 – 181 | 3.6E-05 – 1.2E-04 | Naphthalene[121] | 308 – 338 | 74 – 280 | 4.0E-04 – 1.6E-01 |
| Benzo(ghi)perylene[77] | 313 – 523 | 100 – 450 | ND – 4.6E-04 | Naphthalene (+Biphenyl Co-solvent)[121] | 308 | 77 – 280 | 1.4E-03 – 4.0E-02 |
| Biphenyl[80] | 309 – 330 | 105 – 489 | 4.5E-03 – 1.8E-01 | Naphthalene[37] | 308 | 98 – 200 | 9.3E-03 – 1.8E-02 |
| Biphenyl (+Naphthalene Co-solvent)[95] | 308 – 318 | 57 – 277 | 3.0E-05 – 2.3E-02 | 1-Methylnaphthalene[121] | 308 – 328 | 77 – 280 | 1.6E-03 – 5.9E-02 |
| Biphenyl[121] | 308 – 328 | 77 – 280 | 8.0E-04 – 4.0E-02 | 1-Methylnaphthalene (+2-Methylnaphthalene Co-solvent)[121] | 308 | 77.2 – 246 | 1.0E-03 – 2.4E-02 |
| Biphenyl (+Naphthalene Co-solvent)[121] | 308 | 77 – 280 | 9.0E-04 – 3.1E-02 | 2-Methylnaphthalene[121] | 308 – 328 | 77 – 280 | 1.7E-03 – 7.9E-02 |
| Chrysene[122] | 308 | 84 – 251 | 7.3E-07 – 8.8E-06 | 2-Methylnaphthalene (+1-Methylnaphthalene Co- | 308 | 77 – 246 | 7.0E-04 – 2.7E-02 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | | solvent)[121] | | | |
| Chrysene[77] | 313 – 523 | 313 – 523 | ND – 3.6E-03 | Perylene[77] | 313 – 523 | 100 – 450 | ND – 7.0E-04 |
| 2,3-Dimethylnaphthalene[123] | 308 – 328 | 90 – 276 | 3.4E-04 – 9.0E-03 | Phenanthrene[123] | 318 – 338 | 120 – 280 | 3.3E-04 – 3.8E-03 |
| 2,3-Dimethylnaphthalene (+Phenanthrene Co-solvent)[92] | 308 – 318 | 120 – 280 | 2.5E-03 – 7.0E-03 | Phenanthrene[118] | 303.2 – 343 | 80 – 415 | 2.3E-05 – 4.1E-03 |
| 2,3-Dimethylnaphthalene (+2,6-Dimethylnaphthalene Co-solvent)[92] | 308 – 318 | 120 – 280 | 3.7E-03 – 1.0E-02 | Phenanthrene (+Naphthalene Co-solvent)[92] | 308 | 120 – 280 | 1.7E-03 – 3.2E-03 |
| 2,3-Dimethylnaphthalene[124] | 308 – 323 | 101 – 144 | 3.1E-05 – 6.0E-04 | Phenanthrene (+Benzoic Acid Co-solvent)[92] | 308 | 120 – 280 | 1.0E-03 – 2.1E-03 |
| 2,6-Dimethylnaphthalene[123] | 308 – 328 | 97 – 276 | 3.1E-04 – 9.2E-03 | Phenanthrene (+2,3-Dimethylnaphthalene Co-solvent)[92] | 308 - 318 | 120 – 280 | 5.3E-04 – 2.3E-03 |
| 2,6 –Dimethylnaphthalene (+Phenanthrene Co-solvent)[92] | 308 | 120 – 280 | 2.9E-03 – 4.3E-03 | Phenanthrene (+2,6-Dimethylnaphthalene Co-solvent)[92] | 308 | 120 – 280 | 1.1E-03 – 2.1E-03 |
| 2,6-Dimethylnaphthalene (+2,3-Dimethylnaphthalene Co-solvent)[92] | 308 – 318 | 120 – 280 | 3.0E-03 – 8.1E-03 | Phenanthrene (+Benzene Co-solvent)[94] | 328 | 111 – 305 | 1.5E-03 – 8.6E-03 |
| 2,6-Dimethylnaphthalene[124] | 308 – 323 | 101 – 144 | 1.6E-05 – 1.8E-04 | Phenanthrene (+Acetone Co-solvent)[94] | 328 | 200.5 | 3.6E-03 – 6.7E-03 |
| 2,6-Dimethylnaphthalene(+Naphthalene Co-solvent)[120] | 303 – 317 | 244 – 314 | 4.1E-03 – 1.70E-02 | Phenanthrene (+Cyclohexane Co-solvent)[94] | 328 | 202 | 3.5E-03 – 5.9E-03 |
| 2,6 –Dimethylnaphthalene[125] | 308 – 328 | 80 – 150 | 5.1E-04 – 3.1E-03 | Phenanthrene (+Methylene Chloride Co-solvent)[94] | 328 | 202 | 5.3E-03 – 1.2E-02 |
| 2,6 –Dimethylnaphthalene(+2,7 – Dimethylnaphthalene Co-solvent)[125] | 308 – 318 | 90 – 250 | 4.8E-04 – 7.3E-03 | Phenanthrene (+ Naphthalene Co-solvent)[95] | 308 – 318 | 86 – 280 | 4.8E-05 – 2.7E-03 |
| 2,7 –Dimethylnaphthalene[125] | 308 – 328 | 80 – 250 | 7.5E-04 – 1.2E-02 | Phenanthrene (+ Anthracene Co-solvent)[119] | 308 – 318 | 103 – 242 | 2.4E-04 – 2.3E-03 |
| 2,7 –Dimethylnaphthalene (+2,6 – Dimethylnaphthalene Co-solvent)[125] | 308 – 318 | 90 – 250 | 6.8E-04 – 1.1E-02 | Phenanthrene[122] | 318 – 328 | 101 – 175 | 1.8E-04 – 1.5E-03 |
| Ethenylbenzene[69] | 313 – 393 | 60 – 161 | 2.9E-03 – 5.5E-02 | Phenanthrene[72] | 318 - 328 | 120 – 270 | 4.0E-04 – 2.3E-03 |
| Fluoranthene[122] | 308 – 328 | 86 – 247 | 9.1E-06 – 9.3E-04 | Phenanthrene[37] | 308 | 101 -181 | 5.6E-04 – 1.2E-03 |
| Fluoranthene[74] | 308 – 348 | 121 – 355 | 1.0E-04 – 1.5E-03 | Phenanthrene (+Anthracene and Carbazole Co-solvents)[37] | 308 | 101 -181 | 7.8E-04 – 1.4E-03 |
| Fluoranthene (+Acenaphthene and Triphenylene Co-solvents)[117] | 308 – 338 | 121 – 355 | 5.2E-05 – 1.6E-03 | Pyrene[118] | 308 – 343 | 83 – 483 | 2.7E-06 – 9.4E-04 |
| Fluorene[118] | 303 – 343 | 69 – 484 | 1.1E-05 – 9.2E-03 | Pyrene[77] | 313 – 523 | 100 - 450 | ND – 4.7E-03 |
| Isopropylbenzene[69] | 313 – 393 | 56 – 183 | 1.8E-03 – 9.9E-02 | 1,2,4-Trimethylbenzene[69] | 313 - 393 | 60 – 161 | 2.0E-03 – 3.9E-02 |
| Naphthalene[80] | 308 – 338 | 81 – 291 | 1.3E-03 – 9.8E-02 | 1,3,5-Trimethylbenzene[69] | 313 – 393 | 60 – 181 | 1.5E-03 – 9.0E-02 |
| Naphthalene (+Phenanthrene Co-solvent)[92] | 308 | 120 – 280 | 1.5E-02 – 2.1E-02 | Triphenylene[122] | 308 – 328 | 85 – 251 | 1.0E-06 – 4.2E-05 |
| Naphthalene (+2,3-Dimethylnaphthalene Co-solvent)[92] | 308 | 120 – 280 | 1.9E-02 – 2.6E-02 | Triphenylene[74] | 308 – 348 | 121 – 355 | 2.0E-06 – 9.5E-05 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Naphthalene (+Benzoic Acid Co-solvent)[92] | 308 – 318 | 120 – 280 | 1.8E-02 – 3.7E-02 | Triphenylene (+Acenaphthene and Fluoranthene Co-solvents)[117] | 308 – 338 | 121 – 355 | 2.0E-06 – 1.2E-04 |
| Naphthalene (+Phenanthrene Co-solvent)[95] | 308 – 318 | 77 – 280 | 1.1E-03 – 1.9E-02 | | | | |

## Aliphatic Acids – In Order of Chain Length

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Acetic Acid[73] | 313 – 323 | 73 – 139 | 9.0E-03 – 1.6E-02 | Propionic Acid(+ Water Co-solvent)[88] | 313 | 20 – 200 | 1.0E-03 – 4.5E-01 |
| Acetic Acid(+ Water Co-solvent)[88] | 313 – 333 | 20 – 200 | 2.0E-03 – 4.1E-01 | n-Butyric Acid(+Water Co-solvent)[88] | 313 | 20 – 200 | 2.3E-01 – 6.4E-01 |
| Acetic Acid[86] | 287 – 313 | 145 | 3.4E-02 - 4.3E-02* | | | | |

## Aromatic Acids – In Alphabetical Order

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Benzoic Acid (+Phenanthrene Co-solvent)[92] | 308 | 118 – 280 | 1.8E-03 – 3.7E-03 | m-Hydroxybenzoic Acid (+ o-Hydroxybenzoic Acid Co-solvent)[66] | 318 | 101 – 203 | 9.7E-07 – 7.9E-06 |
| Benzoic Acid (+Naphthalene Co-solvent)[92] | 308 – 318 | 118 – 280 | 2.9E-03 – 1.3E-02 | m-Hydroxybenzoic Acid (+ o-Hydroxybenzoic Acid and p-Hydroxybenzoic Acid Co-solvents)[66] | 318 | 101 – 203 | 1.0E-06 – 8.0E-06 |
| Benzoic Acid (+Benzene Co-solvent)[94] | 328 | 200 | 7.0E-03 – 1.6E-02 | p-Hydroxybenzoic Acid[63] | 373 | 200 – 400 | 1.3E-05 – 7.5E-05 |
| Benzoic Acid (+Acetone Co-solvent)[94] | 328 | 202 | 6.4E-03 – 1.8E-02 | p-Hydroxybenzoic Acid[65] | 328 | 101 – 203 | 1.4E-07 – 3.7E-06 |
| Benzoic Acid (+Cyclohexane Co-solvent)[94] | 328 | 202 | 5.2E-03 – 1.1E-02 | p-Hydroxybenzoic Acid(+ o-Hydroxybenzoic Acid Co-solvent)[65] | 318 – 328 | 101 – 203 | 2.1E-07 – 9.9E-06 |
| Benzoic Acid (+Methylene Chloride Co-solvent)[94] | 328 | 202 | 1.2E-02 – 1.9E-02 | p-Hydroxybenzoic Acid (+m-Hydroxybenzoic Acid Co-solvent)[66] | 318 – 328 | 101 – 203 | 1.7E-07 – 3.5E-06 |
| Benzoic Acid (+Methanol Co-solvent)[93] | 318 - 328 | 120 - 200 | 5.8E-03 – 1.4E-02 | p-Hydroxybenzoic Acid (+m-Hydroxybenzoic Acid and o-Hydroxybenzoic Acid Co-solvents)[66] | 318 | 101 – 203 | 7.9E-07 – 7.2E-06 |
| Benzoic Acid[84] | 313 – 333 | 79 – 297 | 1.6E-04 – 4.5E-04 | Phenol[57] | 309 - 333 | 79 – 250 | 3.5E-03 – 4.7E-02 |
| Benzoic Acid[84] | 313 – 333 | 79 – 297 | 4.0E-01 – 2.1E+00* | Phenol (+ Naphthalene Co-solvent)[95] | 308 – 318 | 54 – 278 | 2.9E-04 – 5.6E-02 |
| Benzoic Acid[72] | 318 - 328 | 120 – 270 | 4.5E-04 – 4.6E-03 | Phenol[85] | 313 – 323 | 96 - 173 | 3.4E-01 – 1.7E+00* |
| Benzoic Acid[123] | 318 – 338 | 120 – 280 | 3.2E-04 – 9.8E-03 | Phenol (+ m-Cresol, p-Chlorophenol, and Benzne Co-solvents)[114] | 313 – 323 | 96 – 152 | 3.2E-01 – 1.5E+00* |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| o-Cresol[59] | 373 | 100 – 310 | 4.5E-03 – 1.3E-01 | Phenol[84] | 313 – 333 | 80 – 300 | 4.1E-04 - 1.5E-03 |
| m-Cresol[85] | 313 – 323 | 96 – 166 | 6.0E-01 – 6.0E+00* | Phenol[84] | 313 – 333 | 80 – 300 | 2.2E-01 – 1.4E+00* |
| m-Cresol (+ Phenol, p-Chlorophenol, and Benzene Co-solvents)[114] | 313 – 323 | 96 – 152 | 6.3E-01 – 4.9E+00 | Phenol[59] | 373 | 100 – 300 | 5.6E-03 – 8.4E-02 |
| m-Cresol[59] | 373 | 100 – 300 | 3.1E-03 – 7.7E-02 | Phenol[58] | 333 – 363 | 100 – 350 | 1.1E-03 – 9.1E-02 |
| p-Cresol[59] | 373 | 100 – 300 | 3.2E-03 – 7.2E-02 | Phenol[87] | 313 – 363 | 150 – 300 | 5.3E-01 – 1.7E+00* |
| o-Hydroxybenzoic Acid[63] | 373 | 200 – 400 | 2.1E-03 – 7.0E-03 | Pyrocatechol (o-dihydroxybenzene)[63] | 328 | 310 | 1.8E-03 |
| o-Hydroxybenzoic Acid[61] | 308 – 328 | 80 – 205 | 7.0E-06 – 6.2E-04 | Pyrocatechol (o-dihydroxybenzene)[62] | 308 – 338 | 121 – 404 | 6.6E-04 – 3.9E-03 |
| o-Hydroxybenzoic Acid (+Acetone Co-solvent)[64] | 318 – 328 | 90 – 200 | 6.8E-04 – 2.5E-03 | Pyrocatechol (o-dihydroxybenzene)[58] | 333 – 363 | 100 – 350 | 1.2E-04 – 4.6E-04 |
| o-Hydroxybenzoic Acid (+Methanol Co-solvent)[64] | 318 – 328 | 90 – 200 | 1.1E-03 – 5.1E-03 | Resorcinol (m-dihydroxybenzene)[63] | 328 | 310 | 4.9E-04 |
| o-Hydroxybenzoic Acid[65] | 328 | 101 – 203 | 3.2E-05 – 5.6E-04 | Resorcinol (m-dihydroxybenzene)[62] | 308 – 338 | 121 – 404 | 1.1E-04 – 9.7E-04 |
| o-Hydroxybenzoic Acid(+ p-Hydroxybenzoic Acid Co-solvent)[65] | 318 – 328 | 101 – 203 | 3.1E-05 – 5.5E-04 | Hydroquinone (p-dihydroxybenzene)[63] | 328 | 310 | 2.1E-05 |
| o-Hydroxybenzoic Acid(+ m-Hydroxybenzoic Acid Co-solvent)[66] | 318 | 101 – 203 | 7.9E-05 – 4.4E-04 | Hydroquinone (p-dihydroxybenzene)[60] | 308 – 318 | 83 - 313 | 2.0E-05 – 1.5E-05 |
| o-Hydroxybenzoic Acid(+ m-Hydroxybenzoic Acid and p-Hydroxybenzoic Acid Co-solvents)[66] | 318 | 101 – 203 | 8.0E-05 – 4.6E-04 | Hydroquinone (p-dihydroxybenzene)[62] | 308 – 338 | 121 – 404 | 6.6E-04 – 3.9E-03 |
| o-Hydroxybenzoic Acid[87] | 313 – 363 | 150 – 300 | 4.0E-02 – 4.1E-01* | Hydroquinone (p-dihydroxybenzene)[67] | 333 - 363 | 100 – 350 | 7.0E-06 – 5.6E-05 |
| m-Hydroxybenzoic Acid[63] | 373 | 200 – 400 | 2.7E-05 – 1.1E-04 | Hydroquinone (p-dihydroxybenzene) (+ p-quinone Co-solvent)[67] | 333 - 363 | 100 – 350 | 1.0E-05 – 5.2E-04 |
| m-Hydroxybenzoic Acid (+Acetone Co-solvent)[64] | 318 – 328 | 90 – 200 | 1.5E-05 – 5.5E-05 | | | | |
| m-Hydroxybenzoic Acid (+Methanol Co-solvent)[64] | 318 – 328 | 90 – 200 | 1.6E-05 – 4.6E-05 | | | | |
| m-Hydroxybenzoic Acid[66] | 318 – 328 | 101 – 203 | 1.9E-07 – 4.8E-06 | | | | |
| m-Hydroxybenzoic Acid (+ p-Hydroxybenzoic Acid Co-solvent)[66] | 318 – 328 | 101 – 203 | 2.2E-07 – 4.6E-06 | | | | |

## Sulfur and Nitrogen Substituted Compounds – In Alphabetical Order

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Benzothiophene[112] | 373 | 13 – 148 | 6.0E-03 – 8.5E-02 | m-Nitrophenol[76] | 308 – 348 | 121 – 486 | 1.3E-04 – 4.5E-03 |
| Carbazole[37] | 308 | 103 – 201 | 1.4E-05 – 2.8E-05 | p-Nitrophenol[76] | 308 – 348 | 121 – 486 | 9.8E-05 – 2.0E-03 |
| Carbazole (+Anthracene and Phenanthrene Co-solvent)[37] | 308 | 103 – 201 | 1.2E-05 – 2.9E-05 | o-Nitrophenol[87] | 333 – 353 | 200 | 1.6E-01 – 1.8E-01* |
| Dibenzothiophene[96] | 309 – 338 | 75 – 275 | 1.9E-05 – 3.2E-03 | Picric Acid[76] | 308 – 348 | 121 – 486 | 2.2E-05 – 2.7E-03 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Dibenzothiophene(+Naphthalene Co-solvent)[96] | 309 | 75 – 275 | 9.9E-04 – 5.6E-03 | Thiophene[75] | 314 – 383 | 20 – 144 | 1.1E-02 – 1.5E-01 |
| m-Dinitrobenzene[126] | 308 – 328 | 95 – 145 | 1.9E-04 – 5.5E-03 | Thiophene (+ 1-Propanol Co-solvent)[75] | 314 – 383 | 20 – 144 | 8.4E-03 – 8.5E-02 |
| 2,4-Dinitrophenol[76] | 308 – 348 | 121 – 486 | 3.9E-04 – 1.4E-02 | Thiophene (+n-Pentane Co-solvent)[127] | 314 – 383 | 20 – 144 | 6.6E-03 – 5.2E-02 |
| 2,5-Dinitrophenol[76] | 308 – 348 | 121 – 486 | 3.2E-04 – 9.4E-03 | Thiophene (+n-Octane Co-solvent)[127] | 314 – 383 | 20 – 144 | 5.0E-03 – 2.7E-02 |
| o-Nitrophenol[87] | 333 – 353 | 200 | 3.0E+01 – 7.2E+01* | | | | |

*Partitioning coefficient from water to sc-$CO_2$
ND – Not detectable

## 7. Water Solubility in Supercritical $CO_2$

Water will dissolve into the sc-$CO_2$ phase and may affect the equilibrium partitioning of organic compounds into sc-$CO_2$ because the addition of a polar fluid into the net nonpolar $CO_2$ will alter its solvent properties. However, investigations on the effect of entrained water in the sc-$CO_2$ phase on the solubility of organic compounds in that phase are scarce. Water content in the sc-$CO_2$ phase was measured to be between 0.04 and 6 mol%, with the average value at 3.6 mol% (measured at 423.2 K).[128] Models have indicated that in sc-$CO_2$, molecules of carbon dioxide orient themselves in a T-shape, which is different than the slipped parallel orientation of $CO_2$ molecules in the gas phase.[129] The weak hydrogen bonding between the $CO_2$ and $H_2O$ molecules has little effect on the $CO_2$-$CO_2$ interactions, the distance between molecules, and the types of orientations. Water cluster formation occurs in sc-$CO_2$, because of the hydrogen bonding between the water molecules, but these bonds are weaker in the supercritical state. At high water concentrations, known phase separations occur, as the dissolution of water clusters in sc-$CO_2$ is entropically unfavorable.[129]

The presence of water clusters in sc-$CO_2$ may therefore enhance the solubility of soluble compounds such as organic acids, but may decrease the solubility of hydrophobic hydrocarbons. For example, the food industry uses sc-$CO_2$ and water to extract caffeine from coffee beans; in fact saturating the beans with water and humidifying the sc-$CO_2$ is a necessary step in extracting the caffeine from the bean.[47,48] The presence of water increases the solubility of caffeine, a monopolar compound, in wet sc-$CO_2$, suggesting that water-saturated sc-$CO_2$ will increase the partitioning of more polar compounds. The extraction of naphthalene from soil by sc-$CO_2$ was

measured with the water content of soil from 0 to 20 wt%.[50] At lower water contents (under 10%), the water was found not to have an effect on the partitioning of naphthalene from the soil to sc-$CO_2$ (the partitioning coefficient of naphthalene from the soil-sc-$CO_2$ system was at 1.5 g in soil/g in sc-$CO_2$ at 0% water content), however at a water content of 20%, the partitioning coefficient dropped by a factor of 100 to 0.15 g/g at 315.2 K and 100 bar;[50] suggesting wet sc-$CO_2$ will decrease the partitioning of nonpolar organic compounds. However, the decrease in partitioning to the sc-$CO_2$ at higher water content could have been a result of the water layer on the soil preventing contact of sc-$CO_2$ with the hydrophilic soil surfaces. Curren and Burk[89] measured the partitioning coefficient of pentachlorophenol from water to both wet and dry sc-$CO_2$. In contrast to naphthalene extraction from soils, these results showed only a small decrease in solubility of naphthalene due to the presence of low amounts of water (0.1 to 0.3 vol %); indicating that water in the sc-$CO_2$ phase did not have a significant effect on the partitioning behavior of pentachlorophenol from water to sc-$CO_2$. This experimental data suggests that the influence of water entrained in sc-$CO_2$ is an important variable to consider in the partitioning experiments, especially in the presence of formation solids, and must be considered in models (either EOS models or QSPR) developed to predict the solubility of compounds in sc-$CO_2$.

## 8. Implications of Organic Partitioning in Supercritical $CO_2$ and Future Research

This review provides a comprehensive list of the solubility of organic compounds in sc-$CO_2$ and ranges of measured partition coefficients between sc-$CO_2$ and water for selected environmentally important compounds. Discernible trends in the partitioning behavior of selected organic compounds commonly found in oil reservoirs have been discussed. For risk assessment purposes,

these trends can provide some insights into which classes of compounds have the highest potential for migration in the event that sc-$CO_2$ or brine are mobilized away from a carbon storage site. Combined with existing toxicity data, this can be used for risk-ranking purposes and indicate which compounds should be studied in detail. For detailed risk characterization, models will be used to quantify the mass of organic contaminants that can be transported away from carbon storage sites. These models will require measured or estimated values of partition coefficients for a large range of organic compounds between a crude oil mixture, brine, and sc-$CO_2$. However, there are significant gaps in available solubility and partitioning data, especially for important compounds like PAHs. There is a lack of experimental data on how the solubility of organic compounds is affected by other components in a crude oil mixture. There is also little experimental data available on the partitioning coefficients between sc-$CO_2$ and brine. Partitioning coefficients of representative compounds, over a range of crude oil compositions and salinities, are needed to determine the partitioning behavior of organic compounds from crude oil to sc-$CO_2$ and brine to sc-$CO_2$, respectively.

There are at least two viable modeling approaches to estimate the partition coefficients. One is to develop an EOS for the numerous compounds of interest present at carbon storage sites. The second approach is to develop QSPR relationships for the various classes of compounds present at carbon storage sites. To develop these models, both will require a significant amount of partitioning data for organic compounds between sc-$CO_2$, crude oil, and brine to calibrate them (e.g. binary interaction parameters in multicomponent systems are needed for EOS and empirical constants are needed for QSPRs). This partitioning data under the pressures and temperatures relevant to storage conditions are still under development. While EOS are most often used to

model sc-$CO_2$-organic compound equilibria, they are computationally difficult (i.e. solved by iteration) and require the use of binary interaction parameters that must incorporated into mixing rules that account for altered solubilities due to relevant intermolecular interactions. QSPRs, the alternative, are computationally much easier, but a better understanding of the properties controlling solubility for a range of compound classes (e.g. alkanes and cycloalkanes, BTEX, organic acids, PAHs, and organosulfurs, etc.) in a multicomponent system is needed for these models to be accurate enough to be used in CCS models.

Two important factors controlling the solubility of organics in sc-$CO_2$ are co-solvency and the high salt concentration of brines. Neither of these factors is adequately handled in EOS or QSPR methods. The large number of compounds in crude oil and the relatively high solubility of each will undoubtedly lead to co-solvency effects. The solubility of many organic compounds has been enhanced by over 100% due to the presence of other organic compounds. The ability of different organic compounds (e.g. organic acids vs. small volatile apolar hydrocarbons) to increase the solubility of larger organic compounds like PAHs is poorly understood and currently not predictable. These co-solvency effects need to be described in a solute descriptor term in a QSPR, or through the use of appropriate binary interaction parameters in EOS models, so that they can be implemented in risk assessment models.

An undeveloped alternative, in regards to supercritical fluids, is to treat the co-solvency effect similarly to how completely water-miscible solvents affect the solubility of compounds with relatively low aqueous solubility.

The co-solvency effect in water assumes a log-linear relationship between the activity coefficient of a given organic compound in water and the volume fraction of the co-solvent.[41] Typically, in the aqueous phase, cosolvents are completely miscible with water ($\gamma_{iw} \approx 1$), and the cosolvency effect can be described by

$$\log \gamma_{il}(f_v) = \log \gamma_{il}(f_v^1) - \sigma_i^c(f_v) \qquad \text{(eq. 7)}$$

Where $\gamma_{il}(f_v)$ is the activity coefficient of the organic compound in the solvent-cosolvent system, $\gamma_{il}(f_v^1)$ is the activity coefficient of the organic compound in the pure solvent, $f_v$ is the volume fraction of the solvent, and $\sigma_i^c$ is the slope, or cosolvency power of the solvent for the solute, which is given by:

$$\sigma_i^c = \frac{\log \gamma_{iw} - \log \gamma_{il}(f_v)}{(f_v)} \qquad \text{(eq. 8)}$$

Where $\gamma_{iw}$ is the activity coefficient of the organic compound in pure water.

A similar process may be able to be applied to a crude oil-sc-$CO_2$ mixture. Although there are hundreds of compounds found in crude oil and the exact composition of every oil reservoir may not be known, cycloalkanes, alkanes, and aromatics are generally accepted to be the largest groups of organic compounds found in oil.[22] If the co-solvency effects of these groups of compounds could be generalized in a way to quantify their effects on less soluble compounds, this could be a more efficient way to accurately determine the solubilities of important (i.e. toxic and/or carcinogenic) organic compounds in a crude oil mixture.

Methods are available to account for effect of high salt concentration in brine on the solubility of organic compounds (e.g. Pitzer equations for charged species and other EOS). However, these equations require the use of binary interaction parameters, and have less accuracy for higher salt

concentrations, temperatures, and different mixtures of electrolytes. Pitzer equations are more applicable to polar ionic compounds, and other EOS have not explored the effect of brines on larger hydrocarbons (>$C_5$).

There are several additional considerations in the determination of the partition coefficients including the effect of pH, the presence of water dissolved in the sc-$CO_2$, and factors influencing the density of sc-$CO_2$. Carbon dioxide dissolved in brine will alter the pH, which can alter the partitioning behavior of organic acids from brine to sc-$CO_2$. Experimental data will be needed to determine the magnitude of pH effects. Water present in sc-$CO_2$ may affect the solubility of both apolar and polar compounds. The solubility of water in $CO_2$ as a function of temperature and pressure must be determined. The density of the $CO_2$, especially near the critical point, greatly affects the solubility of organic compounds in that phase. If the dissolution of various components from crude oil sufficiently alter the density of the sc-$CO_2$ in the range of temperatures and pressures at carbon storage sites, this could alter solubility of other compounds significantly. If any of these processes are shown to significantly affect the partitioning behavior of the various organic compounds, they will have to be incorporated into an EOS or a QSPR to provide better predictions of the partitioning.

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## ASSOCIATED CONTENT

### Supporting Information

The file contains the calculation of the solubility of an organic compound in sc-$CO_2$ using Peng-Robinson equation of state and associated equations (e.g. van der Waals mixing rules) to demonstrate how to obtain the solubility.

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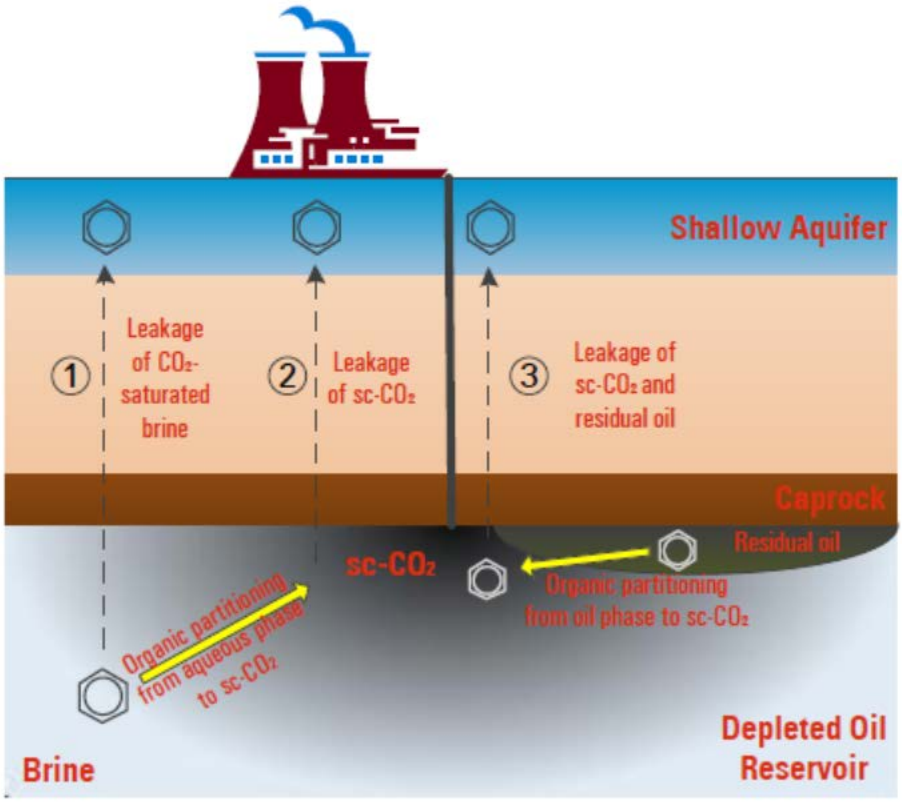


**References**

(1) *IPCC Special Report Carbon Dioxide Capture and Storage.* International Panel on Climate Change, Geneva, Switzerland, 2005; http://www.ipcc.ch/pdf/specialreports/srccs/srccs_technicalsummary.pdf.

(2) Haszeldine, R. S. Carbon capture and storage: how green can black be? *Science (New York, N.Y.)* **2009**, *325* (5948), 1647–52; DOI10.1126/science.1172246

(3) Benson, S. M.; Cole, D. R. $CO_2$ sequestration in deep sedimentary formations. *Elements* **2008**, *4* (5), 325–331; DOI 10.2113/gselements.4.5.325.

(4) *Carbon Sequestration Atlas of the United States and Canada*; National Energy Technology Laboratory; Department of Energy: Pittsburgh, PA, 2010. http://www.netl.doe.gov/technologies/carbon_seq/refshelf/atlasIII/2010atlasIII.pdf

(5) Klusman, R. W. A geochemical perspective and assessment of leakage potential for a mature carbon dioxide–enhanced oil recovery project and as a prototype for carbon dioxide sequestration; Rangely field, Colorado. *AAPG Bulletin* **2003**, *87* (9), 1485–1507; DOI 10.1306/0440302032.

(6) *Report of the Interagency Task Force of Carbon Capture and Storage*; Environmental Protection Agency and Department of Energy: Washington, D.C., 2010; http://www.epa.gov/climatechange/downloads/CCS-Task-Force-Report-2010.pdf.

(7) *$CO_2$-driven Enhanced Oil Recovery as a Stepping Stone to What?*; Highlights of PNNL-195577; Pacific Northwest National Laboratory: Richland, Washington, 2010; http://www.pnl.gov/main/publications/external/techncal_reports/PNNL-19557.pdf

(8) Fayers, J. F.; Hawes, R. I.; Mathews, J. D. Some aspects of the potential application of surfactants or CO2 as EOR processes in North Sea reservoirs. *Journal of Petroleum Technology* **1981**, *33* (9), 1617–1627; DOI 10.2118/9976-PA.

(9) Blunt, M.; Fayers, F. J.; Orr, F. M. Carbon dioxide in enhanced oil recovery. *Energ. Convers. Manage* **1993**, *34* (9-11), 1197–1204; DOI 10.1016/0196-8904.

(10) Shukla, R.; Ranjith, P.; Haque, A.; Choi, X. A review of studies on $CO_2$ sequestration and caprock integrity. *Fuel* **2010**, *89* (10), 2651–2664; DOI 10.1016/j.fuel.2010.05.012.

(11) Duncan, I. J.; Nicot, J.-P.; Choi, J.-W. Risk assessment for future $CO_2$ sequestration projects based $CO_2$ enhanced oil recovery in the U.S. *Energy Procedia* **2009**, *1* (1), 2037–2042; DOI 10.1016/j.egypro.2009.01.265.

(12) Lewicki, J.; Birkholzer, J.; Tsang, C.-F. Natural and industrial analogues for leakage of $CO_2$ from storage reservoirs: identification of features, events, and processes and lessons learned. *Environ. Geol.*, **2007**, *52* (3), 457–467; DOI 10.1007/s00254-006-0479-7.

(13) Tsang, C.-F.; Benson, S.; Kobelski, B.; Smith, R. Scientific considerations related to regulation development for $CO_2$ sequestration in brine formations. *Environ. Geol.*, **2002**, *42* (2-3), 275–281; DOI 10.1007/s00254-001-0497-4.

(14) *Modeling Studies on the Transport of Benzene and $H_2S$ in $CO_2$-Water Systems*; Highlights of LBNL-4339; Lawrence Berkeley National Laboratory: Berkeley, California, 2011; http://escholarship.org/uc/item/121205mq.

(15) Kharaka, Y.; Thordsen, J.; Kakouros, E.; Ambats, G.; Herkelrath, W.; Beers, S.; Birkholzer, J.; Apps, J.; Spycher, N.; Zheng, L.; Trautz, R.; Rauch, H.; Gullickson, K. Changes in the chemistry of shallow groundwater related to the 2008 injection of $CO_2$ at the ZERT field site, Bozeman, Montana. *Environ. Earth Sci.* **2010**, *60* (2), 273–284; DOI 10.1007/s12665-009-0401-1.

(16) Utvik, T. I. R. Chemical characterisation of produced water from four offshore oil production platforms in the North Sea. *Chemosphere* **1999**, *39* (15), 2593–2606; DOI 10.1016/S0045-6535.

(17) Witter, A. E.; Jones, A. D. Chemical characterization of organic constituents from sulfide-rich produced water using gas chromatography/mass spectrometry. *Environ.Toxicol. Chem.***1999**, *18* (9), 1920–1926; DOI 10.1002/etc.5620180908.

(18) Kharaka, Y. K.; Hanor, J. S. 5.16 - Deep Fluids in the Continents: I. Sedimentary Basins. In *Treatise on Geochemistry*; Holland, E.-C. H. D.; Turekian, K. K., Eds.; Pergamon: Oxford, 2003; pp. 1–48.

(19) McAuliffe, C. Determination of dissolved hydrocarbons in subsurface brines. *Chemical Geology* **1969**, *4* (1-2), 225–233; DOI 10.1016/0009-2541.

(20) Zarrella, W. M.; Mousseau, R. J.; Coggeshall, N. D.; Norris, M. S.; Schrayer, G. J. Analysis and significance of hydrocarbons in subsurface brines. *Geochim.Cosmochim.Acta* **1967**, *31* (7), 1155–1166; DOI 10.1016/S0016-703.

(21) Lin, C. Y.; Tjeerdema, R. S. Crude Oil, Oil, Gasoline and Petrol. In *Encyclopedia of Ecology*; Jorgensen, E.-C. S. E.; Fath, B., Eds.; Academic Press: Oxford, 2008; pp. 797–805.

(22) Aitani, A. M. Oil Refining and Products. In *Encyclopedia of Energy*; Cleveland, E.-C. C. J., Ed.; Elsevier: New York, 2004; pp. 715–729.

(23) *National Primary Drinking Water Standards*. 40 CFR 141, 2012 http://water.epa.gov/drink/contaminants/index.cfm

(24) Lemieux, J.-M. Review: The potential impact of underground geological storage of carbon dioxide in deep saline aquifers on shallow groundwater resources. *Hydrogeology Journal* **2011**, *19*, 757–778; DOI 10.1007/s10040-011-0715-4.

(25) U.S. Department of Energy, National Energy Technology Laboratory, *U.S. Brine Wells Database*, DOE/NETL-2003/119, **2003**.

(26) Prausnitz, J. M.; Lichtenthaler, R. N.; Gomes de Azevedo, E. *Molecular Thermodynamics of Fluid Phase Equilibr.*; 3rd ed.; Prentice Hall International Series: Englewood Cliffs, NJ, 1998.

(27) Redlich, O.; Kwong, J. N. S. On the thermodynamics of solutions. V. An equation of state. Fugacities of gaseous solutions. *Chem. Rev.*, **1949**, *44* (1), 233–244; DOI 10.1021/cr60137a013.

(28) Soave, G. Equilibrium constants from a modified Redlich-Kwong equation of state. *Chem. Eng. Sci.* **1972**, *27* (6), 1197–1203; DOI 10.1016/0009-2509.

(29) Peng, D.-Y.; Robinson, D. B. A new two-constant equation of state. *Ind. Eng. Chem. Fund.*, **1976**, *15* (1), 59–64; DOI 10.1021/i160057a011.

(30) Stryjek, R.; Vera, J. H. PRSV: An improved Peng—Robinson equation of state for pure compounds and mixtures. *Can. J. of Chem. Eng.*, **1986**, *64* (2), 323–333; DOI 10.1002/cjce.5450640224.

(31) Stryjek, R.; Vera, J. H. PRSV — An improved Peng-Robinson equation of state with new mixing rules for strongly nonideal mixtures. *Can. J. of Chem. Eng.*, **1986**, *64* (2), 334–340; DOI 10.1002/cjce.5450640225.

(32) Patel, N. C.; Teja, A. S. A new cubic equation of state for fluids and fluid mixtures. *Chem. Eng. Sci.*, **1982**, *37* (3), 463–473; DOI 10.1016/0009-2509.

(33) Adachi, Y.; Lu, B. C.-Y. Simplest equation of state for vapor-liquid equilibrium calculation: A modification of the van der waals equation. *AIChE Journal* **1984**, *30* (6), 991–993; DOI 10.1002/aic.690300619.

(34) Panagiotopoulos, A. Z.; Reid, R. C. New mixing rule for cubic equations of state for highly Polar, asymmetric systems. In *Equations of State*; pp. 571–582; DOI 10.1021/bk-1986-0300.ch028.

(35) Wong, D. S. H.; Sandler, S. I. A theoretically correct mixing rule for cubic equations of state. *AIChE Journal* **1992**, *38* (5), 671–680; DOI 10.1002/aic.690380505

(36) Valderrama, J. O. The state of the cubic equations of state. *Ind. Eng. Chem. Res.*, **2003**, *42* (8), 1603–1618; DOI 10.1021/ie020447b.

(37) Goodarznia, I.; Esmaeilzadeh, F. Solubility of an anthracene, phenanthrene, and carbazole mixture in supercritical carbon dioxide. *J. Chem. Eng. Data.*, **2002**, *47* (2), 333–338; DOI 10.1021/je010093f.

(38) Engelhardt, H. L.; Jurs, P. C. Prediction of supercritical carbon dioxide solubility of organic compounds from molecular structure. *J. Chem. Inf. and Comp. Sci.*, **1997**, *37* (3), 478–484; DOI 10.1021/ci960085g.

(39) Lagalante, A. F.; Bruno, T. J. Modeling the water−supercritical $CO_2$ partition coefficients of organic solutes using a linear solvation energy relationship. *The J. Phys. Chem. B.* **1998**, *102* (6), 907–909; DOI 10.1021/jp973047o.

(40) Timko, M. T.; Nicholson, B. F.; Steinfeld, J. I.; Smith, K. A.; Tester, J. W. Partition coefficients of organic solutes between supercritical carbon dioxide and water: experimental measurements and empirical correlations. *J. Chem. Eng. Data.*, **2004**, *49* (4), 768–778; DOI 10.1021/je0301971.

(41) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*; 2nd ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 2003.

(42) Chen, C.-C.; Britt, H. I.; Boston, J. F.; Evans, L. B. Extension and application of the pitzer equation for vapor-liquid equilibrium of aqueous electrolyte systems with molecular solutes. *AIChE Journal* **1979**, *25* (5), 820–831; DOI 10.1002/aic.690250510.

(43) Søreide, I.; Whitson, C. H. Peng-Robinson predictions for hydrocarbons, $CO_2$, $N_2$, and $H_2$ S with pure water and NaCI brine. *Fluid Phase Equilibr.* **1992**, *77* (5), 217–240; DOI 10.1016/0378-3812(92)85105-H.

(44) Li, Y.-K.; Nghiem, L. X. Phase equilibria of oil, gas and water/brine mixtures from a cubic equation of state and henry's law. *Can. J. of Chem. Eng.*, **1986**, *64* (3), 486–496; DOI 10.1002/cjce.5450640319.

(45) Aasberg-Petersen, K.; Stenby, E.; Fredenslund, A. Prediction of high-pressure gas solubilities in aqueous mixtures of electrolytes. *Ind. Eng. Chem. Res.*, **1991**, *30* (8), 2180–2185; DOI 10.1021/ie00057a019.

(46) Dhima, A.; de Hemptinne, J.-C.; Jose, J. Solubility of hydrocarbons and $CO_2$ mixtures in water under high pressure. *Ind. Eng. Chem. Res.*, **1999**, *38* (8), 3144–3161; DOI 10.1021/ie980768g.

(47) Peker, H.; Srinivasan, M. P.; Smith, J. M.; McCoy, B. J. Caffeine extraction rates from coffee beans with supercritical carbon dioxide. *AIChE Journal* **1992**, *38* (5), 761–770; DOI 10.1002/aic.690380513.

(48) Machmudah, S.; Kitada, K.; Sasaki, M.; Goto, M.; Munemasa, J.; Yamagata, M. Simultaneous Extraction and Separation Process for Coffee Beans with Supercritical $CO_2$ and Water. *Ind. Eng. Chem. Res.*, **2011**, *50* (4), 2227–2235; DOI 10.1021/ie101252w.

(49) Ting, S. S. T.; Tomasko, D. L.; Foster, N. R.; Macnaughton, S. J. Solubility of naproxen in supercritical carbon dioxide with and without cosolvents. *Ind. Eng. Chem. Res.*, **1993**, *32* (7), 1471–1481; DOI 10.1012/ie00019a022.

(50) Smyth, T. J.; Zytner, R. G.; Stiver, W. H. Influence of water on the supercritical fluid extraction of naphthalene from soil. *J. of Hazard. Mater.* **1999**, *67* (2), 183–196; DOI 10.1016/S0304-3894.

(51) Hawthorne, S. B.; Langenfeld, J. J.; Miller, D. J.; Burford, M. D. Comparison of supercritical $CHCIF_2$, $N_2O$, and $CO_2$ for the extraction of polychlorinated biphenyls and

polycyclic aromatic hydrocarbons. *Anal. Chem.* **2001** *64* (14), 1614–1622; DOI 10.1021/ac00038a020.

(52) Ohgaki, K.; Katayama, T. Isothermal vapor-liquid equilibrium data for binary systems containing carbon dioxide at high pressures: methanol-carbon dioxide, n-hexane-carbon dioxide, and benzene-carbon dioxide systems. *J. Chem. Eng. Data.,* **1976**, *21 (1),* 53–55; DOI 10.1021/je60068a015.

(53) Li, Y.-H.; Dillard, K. H.; Robinson, R. L. Vapor-liquid phase equilibrium for carbon dioxide-n-hexane at 40, 80, and 120 °C. *J. Chem. Eng. Data.,* **1981**, *26* (1), 53–55; DOI 10.1021/je00023a018.

(54) Gupta, M. K.; Li, Y. H.; Hulsey, B. J.; Robinson, R. L. Phase equilibrium for carbon dioxide-benzene at 313.2, 353.2, and 393.2 K. *J. Chem. Eng. Data.,* **1982**, *27* (1), 55–57; DOI 10.1021/je00027a017.

(55) Kim, C.-H.; Vimalchand, P.; Donohue, M. D. Vapor-liquid equilibria for binary mixtures of carbon dioxide with benzene, toluene and p-xylene. *Fluid Phase Equilibr.* **1986**, *31* (3), 299–311; DOI 10.1016/0378-3812.

(56) Dandge, D. K.; Heller, J. P.; Wilson, K. V. Structure solubility correlations: organic compounds and dense carbon dioxide binary systems. *Ind. Eng. Chem. Prod. RD.* **1985**, *24* (1), 162–166; DOI 10.1021/i300017a030.

(57) Van Leer, R. A.; Paulaitis, M. E. Solubilities of phenol and chlorinated phenols in supercritical carbon dioxide. *J. Chem. Eng. Data.,* **1980**, *25* (3), 257–259; DOI 10.1021je60086a020.

(58) García-González, J.; Molina, M. J.; Rodríguez, F.; Mirada, F. Solubilities of phenol and pyrocatechol in supercritical carbon dioxide. *J. Chem. Eng. Data.*, **2001**, *46*, 918–921; DOI DOI 10.1021/je0003795.

(59) Pfohl, O.; Avramova, P.; Brunner, G. Two- and three-phase equilibria in systems containing benzene derivatives, carbon dioxide, and water at 373.15 K and 10–30 MPa. *Fluid Phase Equilibr.* **1997**, *141* (1-2), 179–206; DOI 10.1016/S0378-3812.

(60) Coutsikos, P.; Magoulas, K.; Tassios, D. Solubilities of phenols in supercritical carbon dioxide. *J. Chem. Eng. Data.,* **1995**, *40* (4), 953–958; DOI 10.1021/je00020a049.

(61) Gurdial, G. S.; Foster, N. R. Solubility of o-hydroxybenzoic acid in supercritical carbon dioxide. *Ind. Eng. Chem. Res.,* **1991**, *30* (3), 575–580; DOI 10.1021/ie00051a020.

(62) Yamini, Y.; Fat'hi, M. R.; Alizadeh, N.; Shamsipur, M. Solubility of dihydroxybenzene isomers in supercritical carbon dioxide. *Fluid Phase Equilibr.* **1998**, *152* (2), 299–305; DOI 10.1016/S0378-3812.

(63) Krukonis, V. J.; Kurnik, R. T. Solubility of solid aromatic isomers in carbon dioxide. *J. Chem. Eng. Data.*, **1985**, *30* (3), 247–249; DOI 10.1021/je00031a002.

(64) Gurdial, G. S.; Macnaughton, S. J.; Tomasko, D. L.; Foster, N. R.; Ting, S. S. T. Influence of chemical modifiers on the solubility of o- and m-hydroxybenzoic acid in supercritical carbon dioxide. *Ind. Eng. Chem. Res.*, **1993**, *32* (7), 1488–1497; DOI 10.1021/ie00019a024.

(65) Lucien, F. P.; Foster, N. R. Influence of matrix composition on the solubility of hydroxybenzoic acid isomers in supercritical carbon dioxide. *Ind. Eng. Chem. Res.*, **1996**, *35* (12), 4686–4699; DOI 10.1021/ie950649q.

(66) Lucien, F. P.; Foster, N. R. Solubilities of mixed hydroxybenzoic acid isomers in supercritical carbon dioxide. *J. Chem. Eng. Data.*, **1998**, *43* (5), 726–731; DOI 10.1021/je980026u

(67) García-González, J.; Molina, M. J.; Rodríguez, F.; Mirada, F. Solubilities of hydroquinone and p-quinone in supercritical carbon dioxide. *Fluid Phase Equilibr.* **2002**, *200* (1), 31–39; DOI 10.1016/S0378-3812.

(68) Eustaquio-Rincón, R.; Trejo, A. Solubility of n-octadecane in supercritical carbon dioxide at 310, 313, 333, and 353 K, in the range 10–20 MPa. *Fluid Phase Equilibr.* **2001**, *185* (1-2), 231–239; DOI 10.1016/S0378-3812(01)00473-3

(69) Bamberger, A.; Schmelzer, J.; Walther, D.; Maurer, G. High-pressure vapour-liquid equilibria in binary mixtures of carbon dioxide and benzene compounds: experimental data for mixtures with ethylbenzene, isopropylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, ethenylbenzene and isopropenylbenzene, a. *Fluid Phase Equilibr.* **1994**, *97*, 167–189; DOI 10.1016/0378-3812(94)85014-3.

(70) Knez, Ž.; Škerget, M.; Ilič, L.; Lütge, C. Vapor–liquid equilibrium of binary $CO_2$–organic solvent systems (ethanol, tetrahydrofuran, ortho-xylene, meta-xylene, para-xylene). *The J. Supercrit. Fluid.* **2008**, *43* (3), 383–389; DOI 10.1016/j.supflu.2007.07.020.

(71) Ng, H. J.; Huang, S. S. S.; Robinson, D. B. Equilibrium phase properties of selected m-xylene binary systems. m-xylene-methane and m-xylene carbon dioxide. *J. Chem. Eng. Data.*, **1982**, *27* (2), 119–122; DOI 10.1021/je00028a004.

(72) Lee, L.; Huang, J.; Zhu, O. Solubilities of solid benzoic acid, phenanthrene, and 2,3-dimethylhexane in supercritical carbon dioxide. *J. Chem. Eng. Data.*, **2001**, *46* (5), 1156–1159; DOI 10.1021/je0100140.

(73) Briones, J. A.; Mullins, J. C.; Thies, M. C.; Kim, B.-U. Ternary phase equilibria for acetic acid-water mixtures with supercritical carbon dioxide. *Fluid Phase Equilibr.* **1987**, *36* (2), 235–246; DOI 10.1016/0378-3812.

(74) Yamini, Y.; Bahramifar, N. Solubility of polycyclic aromatic hydrocarbons in supercritical carbon dioxide. *J. Chem. Eng. Data.*, **2000**, *45* (1), 53–56; DOI 10.1021/je990129.

(75) Elizalde-Solis, O.; Galicia-Luna, L. A. Solubility of thiophene in carbon dioxide and carbon dioxide+1-propanol mixtures at temperatures from 313 to 363 K. *Fluid Phase Equilibr.* **2005**, *230* (1-2), 51–57; DOI 10.1016/j.fluid.2004.11.018.

(76) Shamsipur, M.; Fat'hi, M. R.; Yamini, Y.; Ghiasvand, A. R. Solubility determination of nitrophenol derivatives in supercritical carbon dioxide. *The J. Supercrit. Fluid.* **2002**, *23* (3), 225–231; DOI 10.1016/S0896-844.

(77) Miller, D. J.; Hawthorne, S. B.; Clifford, A. A.; Zhu, S. Solubility of polycyclic aromatic hydrocarbons in supercritical carbon dioxide from 313 K to 523 K and pressures from 100 bar to 450 bar. *J. Chem. Eng. Data.*, **1996**, *41* (4), 779–786; DOI 10.1021/je960022u.

(78) Raveendran, P.; Ikushima, Y.; Wallen, S. L. Polar attributes of supercritical carbon dioxide. *Accounts of Chem. Res.* **2005**, *38* (6), 478–485; DOI 10.1021/ar040082m.

(79) Foster, N. R.; Gurdial, G. S.; Yun, J. S. L.; Liong, K. K.; Tilly, K. D.; Ting, S. S. T.; Singh, H.; Lee, J. H. Significance of the crossover pressure in solid-supercritical fluid phase equilibria. *Ind. Eng. Chem. Res.*, **1991**, *30* (8), 1955–1964; DOI 10.1021/ie00056a044.

(80) McHugh, M.; Paulaitis, M. E. Solid solubilities of naphthalene and biphenyl in supercritical carbon dioxide. *J. Chem. Eng. Data.*, **1980**, *25* (4), 326–329; DOI 10.1021/je60087a018.

(81) Chang, H.; Morrell, D. G. Solubilities of methoxy-1-tetralone and methyl nitrobenzoate isomers and their mixtures in supercritical carbon dioxide. *J. Chem. Eng. Data.*, **1985**, *30* (1), 74–78; DOI 10.1021/je00039a025.

(82) Reamer, H. H.; Sage, B. H. Phase equilibria in hydrocarbon Systems. Volumetric and phase behavior of the n-decane-$CO_2$ system. *J. Chem. Eng. Data.*, **1963**, *8* (4), 508–513; DOI 10.1021/je60019a010.

(83) Yeo, S.-D.; Akgerman, A. Supercritical extraction of organic mixtures from aqueous solutions. *AIChE Journal* **1990**, *36* (11), 1743–1747; DOI 10.1002/aic.690361116.

(84) Brudi, K.; Dahmen, N.; Schmieder, H. Partition coefficients of organic substances in two-phase mixtures of water and carbon dioxide at pressures of 8 to 30 MPa and temperatures of 313 to 333 K. *The J. Supercrit. Fluid.* **1996**, *9* (3), 146–151; DOI 10.1016/S0896/8446.

(85) Ghonasgi, D.; Gupta, S.; Dooley, K. M.; Knopf, F. C. Supercritical $CO_2$ extraction of organic contaminants from aqueous streams. *AIChE Journal* **1991**, *37* (6), 944–950; DOI 10.1002/aic.690370617.

(86) Dooley, K. M.; Cain, A. W.; Knopf, F. C. Supercritical fluid extraction of acetic acid, alcohols and other amphiphiles from acid-water mixtures. *The J. Supercrit. Fluid.* **1997**, *11* (1-2), 81–89; DOI 10.1016/S0896-8446.

(87) Karásek, P.; Pól, J.; Planeta, J.; Roth, M.; Vejrosta, J.; Wičar, S. Partition coefficients of environmentally important phenols in a supercritical carbon dioxide−water system from cocurrent extraction without analysis of the compressible phase. *Anal. Chem.* **2002**, *74* (16), 4294–4299; DOI 10.1021/ac035599v.

(88) Panagiotopoulos, A. Z.; Willson, R. C.; Reid, R. C. Phase equilibria in ternary systems with carbon dioxide, water and carboxylic acids at elevated pressures. *J. Chem. Eng. Data.*, **1988**, *33* (3), 321–327; DOI 10.1021/je00053a028.

(89) Curren, M. S. S.; Burk, R. C. Partitioning of acidic solutes between water and supercritical carbon dioxide. Effect of pH and ionic strength. *J. Chem. Eng. Data.*, **2000**, *45* (5), 746–750; DOI 10.1021/je000008o.

(90) Xie, W.-H.; Shiu, W.-Y.; Mackay, D. A review of the effect of salts on the solubility of organic compounds in seawater. *Mar. Env. Res.* **1997**, *44* (4), 429–444; DOI 10.1016/S0141-1136.

(91) Lucien, F. P.; Foster, N. R. Solubilities of solid mixtures in supercritical carbon dioxide: a review. *The J. Supercrit. Fluid.* **2000**, *17* (2), 111–134; DOI 10.1016/S0896-8446.

(92) Kurnik, R. T.; Reid, R. C. Solubility of solid mixtures in supercritical fluids. *Fluid Phase Equilibr.* **1982**, *8* (1), 93–105; DOI 10.1016/0378-3812.

(93) Dobbs, J. M.; Johnston, K. P. Selectivities in pure and mixed supercritical fluid solvents. *Ind. Eng. Chem. Res.*, **1987**, *26* (7), 1476–1482; DOI 10.1012/ie00067a035.

(94) Schmitt, W. J.; Reid, R. C. The use of entrainers in modifying the solubility of phenanthrene and benzoic acid in supercritical carbon dioxide and ethane. *Fluid Phase Equilibr.* **1986**, *32* (1), 77–99; DOI 10.1016/0378-3812(86)87007-8.

(95) Gopal, J. S.; Holder, G. D.; Kosal, E. Solubility of solid and liquid mixtures in supercritical carbon dioxide. *Ind. Eng. Chem. Proc. D.D.* **1985**, *24* (2), 697–701; DOI 10.1021/i200030a029.

(96) Mitra, S.; Chen, J. W.; Viswanath, D. S. Solubility and partial molar volumes of heavy aromatic hydrocarbons in super critical carbon dioxide. *J. Chem. Eng. Data.*, **1988**, *33* (2), 35–37; DOI 10.1021/je00051a012.

(97) Roop, R. K.; Akgerman, A. Entrainer effect for supercritical extraction of phenol from water. *Ind. Eng. Chem. Res.*, **1989**, *28* (10), 1542–1546; DOI 10.1021/ie00094a018.

(98) Besserer, G. J.; Robinson, D. B. Equilibrium-phase properties of n-pentane-carbon dioxide system. *J. Chem. Eng. Data.*, **1973**, *18* (4), 416–419; DOI 10.1021/je60059a020.

(99) Spee, M.; Schneider, G. M. Fluid phase equilibrium studies on binary and ternary mixtures of carbon dioxide with hexadecane, 1-dodecanol, 1,8-octanediol and dotriacontane at 393.2 K and at pressures up to 100 MPa. *Fluid Phase Equilibr.* **1991**, *65*, 263–274; DOI 10.1016/0378-3812.

(100) Yau, J. S.; Tsai, F. N. Solubilities of heavy n-paraffins in subcritical and supercritical carbon dioxide. *J. Chem. Eng. Data.,* **1993**, *38* (2), 171–174; DOI 10.1021/je00010a001.

(101) Kalra, H.; Kubota, H.; Robinson, D. B.; Ng, H.-J. Equilibrium phase properties of the carbon dioxide-n-heptane system. *J. Chem. Eng. Data.*, **1978**, *23* (4), 317–321; DOI 10.1021/je60079a016.

(102) Smith, V. S.; Campbell, P. O.; Vandana, V.; Teja, A. S. Solubilities of long-chain hydrocarbons in carbon dioxide. *Int. J.Thermophy.,* **1996**, *17* (1), 23–33; DOI 10.1007/BF01448206

(103) Prausnitz, J. M.; Benson, P. R. Solubility of liquids in compressed hydrogen, nitrogen, and carbon dioxide. *AIChE Journal* **1959**, *5* (2), 161–164; DOI 10.1002/aic.690050208.

(104) Weng, W. L.; Lee, M. J. Vapor-liquid equilibrium of the octane/carbon dioxide, octane/ethane, and octane/ethylene systems. *J. Chem. Eng. Data.*, **1992**, *37* (2), 213–215; DOI 10.1021/je00006a020.

(105) McHugh, M. A.; Seckner, A. J.; Yogan, T. J. High-pressure phase behavior of binary mixtures of octacosane and carbon dioxide. *Ind. Eng. Chem. Fund.,* **1984**, *23* (4), 493–499; DOI 10.1021/i100016a020.

(106) Reverchon, E.; Russo, P.; Stassi, A. Solubilities of solid octacosane and triacontane in supercritical carbon dioxide. *J. Chem. Eng. Data.,* **1993**, *38* (3), 458–460; DOI 10.1021/je00011a034.

(107) Jennings, D. W.; Schucker, R. C. Comparison of high-pressure vapor−liquid equilibria of mixtures of $CO_2$ or propane with nonane and $C_9$ alkylbenzenes. *J. Chem. Eng. Data.,* **1996**, *41* (4), 831–838; DOI 10.1021/je960033n.

(108) Camacho-Camacho, L. E.; Galicia-Luna, L. A.; Elizalde-Solis, O.; Martínez-Ramírez, Z. New isothermal vapor–liquid equilibria for the $CO_2$+n-nonane, and $CO_2$+n-undecane systems. *Fluid Phase Equilibr.* **2007**, *259* (1), 45–50; DOI 10.1016/j.fluid.2007.04.022.

(109) Nagarajan, N.; Robinson, R. L. Equilibrium phase compositions, phase densities, and interfacial tensions for carbon dioxide + hydrocarbon systems. 2. Carbon dioxide + n-decane. *J. Chem. Eng. Data.,* **1986**, *31* (2), 168–171; DOI 10.1021/je00044a012.

(110) Chou, G. F.; Forbert, R. R.; Prausnitz, J. M. High-pressure vapor-liquid equilibria for carbon dioxide/n-decane, carbon dioxide/tetralin, and carbon dioxide/n-decane/tetralin at 71.1 and 104.4 °C. *J. Chem. Eng. Data.*, **1990**, *35* (11), 26–29; DOI 10.1021/je200586g.

(111) Shibata, S. K.; Sandler, S. I. High pressure vapor-liquid equilibria of mixtures of nitrogen, carbon dioxide, and cyclohexane. *J. Chem. Eng. Data.*, **1989**, *34* (4), 419–424; DOI 10.1021/je00058a014.

(112) Camacho-Camacho, L. E.; Galicia-Luna, L. A.; Elizalde-Solis, O. Vapor–liquid equilibria of binary and ternary systems containing carbon dioxide, alkane, and benzothiophene. *J. Chem. Eng. Data.*, **2011**, *56* (11), 4109–4115; DOI 10.1021/je200586g.

(113) Tan, C. S.; Yarn, S. J.; Hsu, J. H. Vapor-liquid equilibria for the systems carbon dioxide-ethylbenzene and carbon dioxide-styrene. *J. Chem. Eng. Data.*, **1991**, *36* (1), 23–25; DOI 10.1021/je00001a007

(114) Gupta, S.; Ghonasgi, D.; Dooley, K. M.; Knopf, F. C. Supercritical carbon dioxide extraction of a phenolic mixture from an aqueous waste stream. *The J. Supercrit. Fluid.* **1991**, *4* (3), 181–185; DOI 10.1016/0896-8446.

(115) Sebastian, H. M.; Simnick, J. J.; Lin, H.-M.; Chao, K.-C. Gas-liquid equilibrium in mixtures of carbon dioxide + toluene and carbon dioxide + m-xylene. *J. Chem. Eng. Data.*, **1980**, *25* (3), 246–248; DOI 10.1021/je60086a018.

(116) Ng, H.-J.; Robinson, D. B. Equilibrium-phase properties of the toluene-carbon dioxide system. *J. Chem. Eng. Data.*, **1978**, *23* (4), 325–327; DOI 10.1021/je60079a020.

(117) Yamini, Y.; Bahramifar, N. Solubilities of mixed acenaphthene, fluoranthene, and triphenylene in supercritical carbon dioxide and the separation of binary solid mixtures of polycyclic aromatic hydrocarbons. *J. Chem. Eng. Data.*, **2000**, *45* (6), 1129–1132; DOI 10.1021/je000100k.

(118) Johnston, K. P.; Ziger, D. H.; Eckert, C. A. Solubilities of hydrocarbon solids in supercritical fluids. The augmented van der Waals treatment. *Ind. Eng. Chem. Fund.*, **1982**, *21* (3), 191–197; DOI 10.1021/i100007a001.

(119) Kosal, E.; Holder, G. D. Solubility of anthracene and phenanthrene mixtures in supercritical carbon dioxide. *J. Chem. Eng. Data.*, **1987**, *32* (2), 148–150; DOI 10.1021/je00048a005.

(120) Lemert, R. M.; Johnston, K. P. Solubilities and selectivities in supercritical fluid mixtures near critical end points. *Fluid Phase Equilibr.* **1990**, *59* (1), 31–55; DOI 10.1016/0378-3812

(121) Chung, S. T.; Shing, K. S. Multiphase behavior of binary and ternary systems of heavy aromatic hydrocarbons with supercritical carbon dioxide: Part I. Experimental results. *Fluid Phase Equilibr.* **1992**, *81* (9-11), 321–341; DOI 10.1016/0196-8904.

(122) Barna, L.; Blanchard, J.-M.; Rauzy, E.; Berro, C. Solubility of flouranthene, chrysene, and triphenylene in supercritical carbon dioxide. *J. Chem. Eng. Data.,* **1996**, *41* (6), 1466–1469; DOI 10.1021/je960189n.

(123) Kurnik, R. T.; Holla, S. J.; Reid, R. C. Solubility of solids in supercritical carbon dioxide and ethylene. *J. Chem. Eng. Data.,* **1981**, *26* (1), 47–51; DOI 10.1021/je00023a016.

(124) Johnston, K. P.; Barry, S. E.; Read, N. K.; Holcomb, T. R. Separation of isomers using retrograde crystallization from supercritical fluids. *Ind. Eng. Chem. Res.*, **1987**, *26* (11), 2372–2377; DOI 10.1021/ie00071a033.

(125) Iwai, Y.; Mori, Y.; Hosotani, N.; Higashi, H.; Furuya, T.; Arai, Y.; Yamamoto, K.; Mito, Y. Solubilities of 2,6- and 2,7-dimethylnaphthalenes in supercritical carbon dioxide. *J. Chem. Eng. Data.*, **1993**, *38* (4), 509–511; DOI 10.1021/je00012a006.

(126) Reddy, S. N.; Madras, G. Solubilities of benzene derivatives in supercritical carbon dioxide. *J. Chem. Eng. Data.*, **2011**, *56* (4), 1695–1699; DOI 10.1021/je100863p.

(127) Elizalde-Solis, O.; Galicia-Luna, L. A. Solubility of thiophene + pentane and thiophene + octane binary mixtures in supercritical carbon dioxide at temperatures from 333 to 383 K. *Ind. Eng. Chem. Res.,* **2005**, *44* (15), 5757–5760; DOI 10.1021/ie048780y.

(128) Berkesi, M.; Hidas, K.; Guzmics, T.; Dubessy, J.; Bodnar, R. J.; Szabo, C.; Vajna, B.; Tsunogae, T. Detection of small amounts of $H_2O$ in $CO_2$-rich fluid inclusions using Raman spectroscopy. *J. Raman Spectrosc.* **2009**, *40* (11), 1461–1463; DOI 10.1002/jrs.2440.

(129) Glezakou, V.-A.; Rousseau, R.; Dang, L. X.; McGrail, B. P. Structure, dynamics and vibrational spectrum of supercritical $CO_2$/$H_2O$ mixtures from ab initio molecular dynamics as a function of water cluster formation. *Physical chemistry chemical physics : PCCP* **2010**, *12* (31), 8759–71; DOI 10.1039/b923306g.