Experimental Measurement of BTEX and Alkylated Phenol Multi-phase Partitioning Behaviour under Petroleum Reservoir and Submarine Oil Spill Conditions

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Summary

We describe two novel flow-injection analysis devices used to determine the chemical partitioning behaviour of low molecular weight petroleum species within oil/natural gas/brine multi-phase systems at high pressure and temperature. Each device is operated in a laboratory setting and can emulate chemical partitioning between crude oil (live or dead) and brine across a broad range of temperature and pressure conditions. The utility of each device for a variety of partitioning studies is demonstrated using experimental data collected under petroleum reservoir and submarine oil spill conditions.

Introduction

Chemical partitioning describes the distribution of a compound within a multi-phase system as a function of its differential interaction with each individual phase. This is quantified in two-phase systems using the partition coefficient (P) which typically describes the ratio of a chemical's concentration in both the organic and aqueous phases. The magnitude of P reflects the thermodynamics of the reaction, the physico-chemical properties of the analyte and the bulk properties of each individual phase within the system. This behaviour is widely exploited in controlled environments throughout the manufacturing, industrial and scientific sectors. However, similar phase partitioning also occurs in dynamic systems present in our surrounding environment. For example, chemical partitioning of phenols and carbazoles occurs between oil, water and solid phase sorbents during oil migration between a source kitchen and a reservoir. It also occurs at the oil/water interface within a reservoir and when oil is spilled at depth into submarine environments. Volatile, hydrophilic solutes, such as phenols, also partition within oil/water/steam systems artificially generated during thermally-assisted bitumen recovery processes such as SAGD. Traditional partitioning measurement techniques (e.g. shake flask and HPLC approaches), find limited application in studies of this nature as they are often unable to acheive the extremes of pressure, temperature and live fluids required. We have addressed this issue by building two devices that can emulate the partitioning behaviour of low molecular weight crude oil components in oil/natural gas/brine systems over a very broad range of pressure (1-379 Bar) and temperature (4-200 ^{o}C) conditions in a laboratory setting.

Methods

The generic construction and operation of such a device has been described in detail in the literature (Bennett & Larter, 1997; Bennett *et al.* 2003) and the current variant is shown in Figure 1. Briefly, live or dead crude oil is transferred from a storage reservoir to a mixing region where it encounters some volume of brine. 'Slugs' of oil and brine are transferred sequentially from the mixing region into an isobaric/isothermal region of the instrument where they equilibrate with one another at their interfacial surfaces. Each 'slug' is then collected in a settling tube where phase separation occurs. Water and oil are independently decanted from the system and P values assigned based upon their relative BTEX,

phenol and alkylated phenol content. Analyte concentrations are determined using a combination of headspace and liquid phase sampling techniques along with SPE and GC/MS.
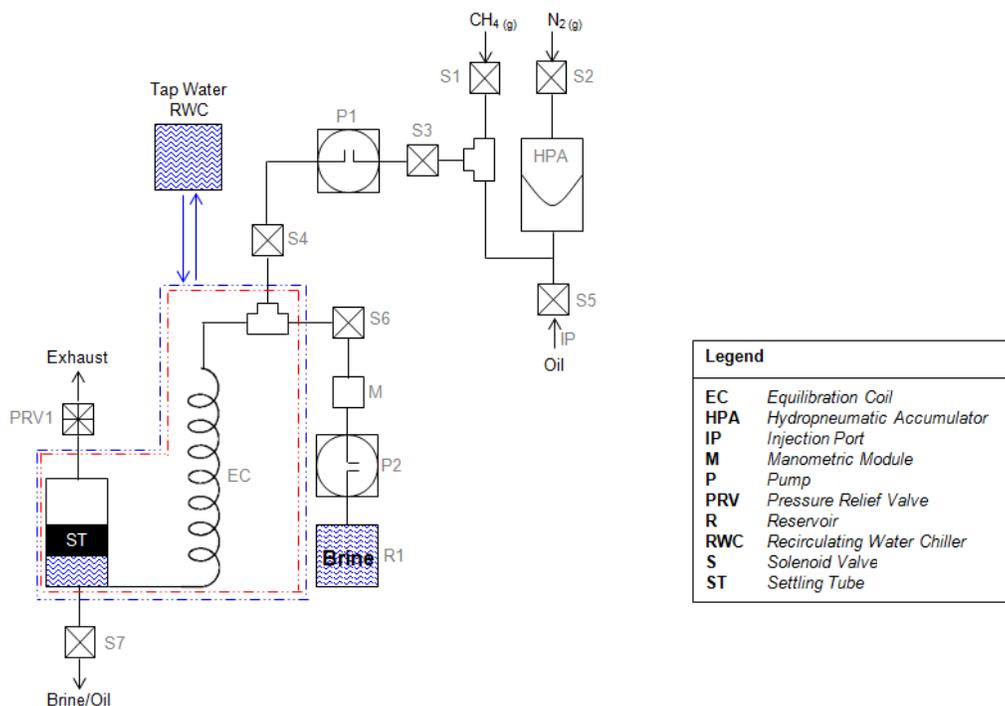

Figure 1: Schematic diagram of one variant of the partition coefficient device at the University of Calgary.

Compound	Pressure (Bar)	Temperature Range (^{o}C)	Function	R
o-Cresol	25	25-125 (25°C Increments)	P = (-0.03448.T)+8.596	-0.996 (N=5)
o-Cresol	200	25-125 (25°C Increments)	P = (-0.03248.T)+8.270	-0.997 (N=5)
o-Cresol	340	25-125 (25°C Increments)	P = (-0.03192.T)+8.028	-0.998 (N=5)
Phenol	25	25-125 (25°C Increments)	P = (-0.00676.T)+1.959	-0.993 (N=5)
Phenol	200	25-125 (25°C Increments)	P = (-0.00712.T)+2.066	-0.988 (N=5)
Phenol	340	25-125 (25°C Increments)	P = (-0.00640.T)+1.846	-0.993 (N=5)

Table 1: Linear fits to partition coefficient (P) values determined for o-Cresol & Phenol in a North.Sea oil/water system obtained using the first iteration of the partition device. Data was recorded over the 25-125 ^{o}C temperature (T) range in 25°C increments at three different pressures (25, 200 & 340 Bar). Negative R values highlight the inverse relationship between P and T. The independence of pressure and the mathematical form of each function demonstrate the insensitivity of P to changes in pressure for systems with no free gas phase (after Bennett & Larter 1997).

Compound	Water Salinity Range (g/L)	Function	R
m-Cresol	0-100 (20 g/L Increments)	P = (0.01689.S)+2.427	0.988 (N=5)
o-Cresol	0-100 (20 g/L Increments)	P = (0.02916.S)+3.755	0.993 (N=5)
p-Cresol	0-100 (20 g/L Increments)	P = (0.01781.S)+2.654	0.997 (N=5)

Table 2: Linear fits to partition coefficient (P) values determined for Cresol isomers in a North Sea oil/brine system using the first iteration of the partition device. Data was recorded at 25 ^{o}C and 25 Bar pressure over the 0-100 g/L salinity (S) range in 20 g/L increments. Positive R values highlight the proportional relationship between P and salinity (Bennett & Larter, 1997).

Oil	NSO Content (%)	P (*p*-Cresol)
North Sea Oil 1	19.2	2.2
North Sea Oil 2	36.0	5.2
Californian Oil 1	58.4	9.8
Californian Oil 2	65.6	16.4

Table 3: P values determined for *p*-Cresol in four different oils as a function of NSO content (Bennett & Larter 1997).

Example 1: Multi-phase Partitioning under Petroleum Reservoir Conditions

The first device, built at Newcastle University, U.K., could be operated over a broad range of temperature (ambient-150 ^{0}C) and pressure (1-340 Bar) conditions and was used primarily for the investigation of chemical partitioning under reservoir conditions (Bennett & Larter, 1997; Bennett *et al.* 2003). Data was collected for a range of C_0-C_3 alkylphenols and experimental P values were found to be inversely proportional to temperature, relatively insensitive to pressure and proportional to both salinity (0-100 g/L) and the bulk NSO content for 'dead' crude oils (Bennett & Larter, 1997; Tables.1-3). The generation of 'live' oil (saturated with CH_4 at 100 Bar pressure) led to an approximate two-fold increase in measured P values, but, also increased the probability of emulsion formation for some of the oils investigated (Bennett *et al.* 2003).

Example 2: Multi-phase Partitioning under Submarine Oil Spill Conditions

A more sophisticated version of the partition coefficient device (Fig. 1) is currently under construction at the University of Calgary as part of the C-IMAGE project (http://cimage.rc.usf.edu). This work aims to determine the partitioning behaviour of low molecular weight crude oil components immediately after their release into a low temperature, high pressure deep marine environment. Experimental output from this instrument will inform numerical models that can simulate the environmental distribution and fate of toxic species present within the crude oil and also guide the placement of remediative actions should a submarine oil spill occur. Analytical challenges will be described and early data collected using this device will be presented.

Conclusions

Two novel flow-injection analysis devices have been built that allow the experimental determination of chemical partitioning behaviour over a broad range of temperature (4-200 ^{o}C) and pressure (1-370 Bar) conditions in a laboratory setting. The first instrument was used to investigate the partitioning behaviour of C_0-C_3 alkylphenols and to provide insights into the influence of migration and reservoir storage on petroleum geochemistry. P was found to be inversely proportional to temperature, rather independent of pressure and proportional to both salinity and NSO content (Bennett & Larter, 1997). The addition of CH_4 to crude oil, at a saturating pressure of 100 Bar, led to an approximate two-fold increase in recorded P values for the analytes investigated (Bennett *et al.* 2003). Early data collected using an updated version of the partition coefficient device is presented. This instrument will be used to investigate the partitioning behaviour of BTEX and C_0-C_3 alkylphenols under conditions that simulate the release of crude oil into deep high pressure submarine environments.

Acknowledgements

References

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