



# Measurement of partition coefficients of phenol and cresols in gas-charged crude oil/water systems

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## Abstract

An instrument has been constructed for monitoring the partition coefficients of phenol and cresols between crude oil and water under sub-surface conditions. The device has the capacity for introducing methane gas into crude oil, thereby allowing measurements under live oil (solution gas-containing) conditions. The partition coefficients of phenol and cresols have been measured in crude oil: water substrates under “live” oil and “dead” oil (without solution gas) conditions over a temperature range 25–150 °C. Over the range investigated it is seen that the introduction of gas (crude oil saturated at 100 bar with methane) into the system resulted in an approximate doubling of partition coefficients compared to the equivalent dead oil: brine systems. The partition coefficient data obtained using the device may be employed in a number of petroleum exploration and production activities such as the determination of residual oil saturation of a water-flooded petroleum reservoir. Partition coefficient measurements may help in predicting toxic organic solute loadings in oilfield discharge waters.

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## 1. Introduction

As many compounds partition effectively between oil and water in petroleum systems (Larter and Aplin, 1995), an understanding of the systematics of this process may aid geochemists in studies not only of petroleum migration (Lucach et al., 2002) but also of production chemistry. The residual oil saturation (ROS) of a petroleum reservoir is the oil saturation remaining after the conclusion of primary depletion or after either gas or water displacement. On the United Kingdom Continental Shelf, water-flooding represents the baseline of any development strategies applied towards improving recovery factors (Jayasekera and Goodyear, 2000). The volume average recovery factor for producing oilfields in the central and northern North Sea was predicted to be 45% (Jayasekera and Goodyear, 2000); this

indicates that large volumes of oil will remain in the reservoir. During a reservoir's lifetime increasing amounts of water are co-produced with the oil, until ultimately only small amounts of oil are co-produced with water. In the late stages of production, injection water may contact unswept portions of the reservoir with oil that has not been produced. An indication that injected water with low organic solute loads may have contacted sizeable oil banks may be assessed by investigating the distributions and levels of water-soluble, but oil-derived compounds, in the produced waters. Partitioning of tracer compounds between residual oil and aqueous brine phases may yield information on the amount of residual oil present in water-flooded reservoirs. The ROS may be determined by single well (Wellington and Richardson, 1994) and inter-well (Tang and Harker, 1991) tracer tests, where the compound or hydrolysis products are distributed between oil and water phases in the reservoir. Several synthetic compounds are available for tracer tests e.g. perfluoromethylcyclopentane (Ljosland et al., 1993) and

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ethyl acetate (Knaepen et al., 1990); however, the methods require costly injection of the solute into the reservoir fluid phases followed by subsequent fluid production, sampling and analysis. Carboxylic acids (e.g. acetic acid), phenols and BTEX (benzene, toluene, ethylbenzene and xylene) are naturally occurring constituents of reservoir fluids which effectively partition between oil and water (Larter and Aplin, 1995) and which could also be used for such applications. Reinsel et al. (1994) measured partition coefficients of acetic, propionic and butyric acids in crude oil water systems. However, due to the very low partition coefficients these acids are difficult to measure routinely in associated oils. The analysis of BTEX compounds, although fairly routine, is susceptible to sampling and sample aging problems due to their high volatility; however, sampling problems appear to be less of an issue with alkyl phenol analysis and post-sample alteration issues can be managed.

Alkyl phenol distributions and concentrations have been determined in crude oils (Ioppolo et al., 1992; Ioppolo-Armanios et al., 1995; Taylor et al., 1997), oil-field formation waters (Macleod et al., 1993; Dale et al., 1995) and oilfield production waters (Tibbetts et al., 1992). Phenols have been used as partition tracers and their partitioning behaviour under sub-surface conditions is better understood than for any other compound class (Bennett and Larter, 1997). The number and position of alkyl groups relative to the active hydroxyl functionality in phenol compounds leads to a wide range of partition behaviour between coexisting oil and water phases. Reservoir water samples are invariably dominated by phenol and the cresols with C<sub>2</sub>–C<sub>3</sub> alkylphenols present in lower relative concentrations. In contrast, related crude oils are relatively enriched in C<sub>2</sub>–C<sub>3</sub> alkylphenols compared to the cresols and phenol (Macleod et al., 1993). As partition coefficients for C<sub>0</sub>–C<sub>3</sub>-alkylphenols range from 1.3 (phenol) to 67 (2,4,6-dimethylphenol) in dead oil/water systems (Taylor et al., 1997), they are ideal tracers for assessing the relative volumes of oil and water in petroleum systems.

In order to achieve successful determination of ROS, the partition coefficient of a given solute must be accurately measured under simulated reservoir conditions. The methods employed for simulating partition processes under reservoir conditions require elaborate instrumentation. Carlisle and Kapoor (1982) constructed a high pressure (up to 5000 psi), high temperature (up to 104 °C) system for rapid determination of partition coefficients of ethyl acetate in crude oil (Gulf Coast)/water systems. Ethyl acetate oil/water partition coefficients increased with increasing temperature and water salinity, while a slight decrease accompanied increasing gas-to-oil ratios (GORs). Knaepen et al. (1990) constructed a flow injection analysis (FIA)-based system for determining partition coefficients of ethyl acetate and pentanol in crude oil (N. Sea) water systems

up to 4930 psi and 150 °C. The apparatus enabled investigation of partition coefficients according to varying tracer type and concentration, crude oil type, pressure, GORs, temperature and water salinity. Bennett and Larter (1997) measured the oil–water partition coefficients of C<sub>0</sub>–C<sub>2</sub> alkyl phenols in dead crude oil–water systems under conditions of high pressure (0–4930 psi), high temperature (up to 150 °C) and varying salinity [0–10% sodium chloride (NaCl)]. Partition coefficients increased with salinity and decreased with temperature, with no change due to pressure variation (25–340 bar).

The aim of this paper is to describe a technique for measuring partition coefficients (partition coefficient of a solute between oil and water =  $P_{ow}$ ) of phenol and cresols, between crude oil and water under simulated conditions of reservoir pressure and temperature with organic solutes at natural concentrations. The instrumentation has been equipped with a hydro-pneumatic accumulator (abbreviated to accumulator), allowing measurement of  $P_{ow}$  in crude oil/water systems using “live” oils with solution gas present. The application of such partition coefficient data to reservoir engineering and production problems is also suggested.

## 2. Methods

### 2.1. Experimental set up

The instrument configuration and operating conditions for measuring partition coefficients under “dead” oil/water conditions were described previously (Bennett and Larter, 1997). Components of the FIA-based partition device, including the apparatus for gas addition are shown schematically in Fig. 1. The partition system is entirely contained within a fume hood and consists of four components:

(1) Gas addition—the accumulator (stainless steel vessel) is divided into two compartments by a neoprene separator. The upper compartment is connected to a nitrogen gas line while the lower compartment is connected to an oil pump and a methane gas line. The accumulator was configured with a series of switching valves to allow oil and gas into the lower compartment of the accumulator. The live oil is formed in the accumulator by firstly pumping oil (ca. 0.4 l) into the accumulator and then pressurising with methane gas up to 100 bar (1500 psi), allowing time for dissolution of the methane into the oil phase. A pressure of 1500 psi is a typical saturation pressure for many marine oils and, while wet gas components were not added, the system does allow a qualitative assessment of the impact of gas content on oil–water partition coefficients. During experiment runs when live oil was released into the

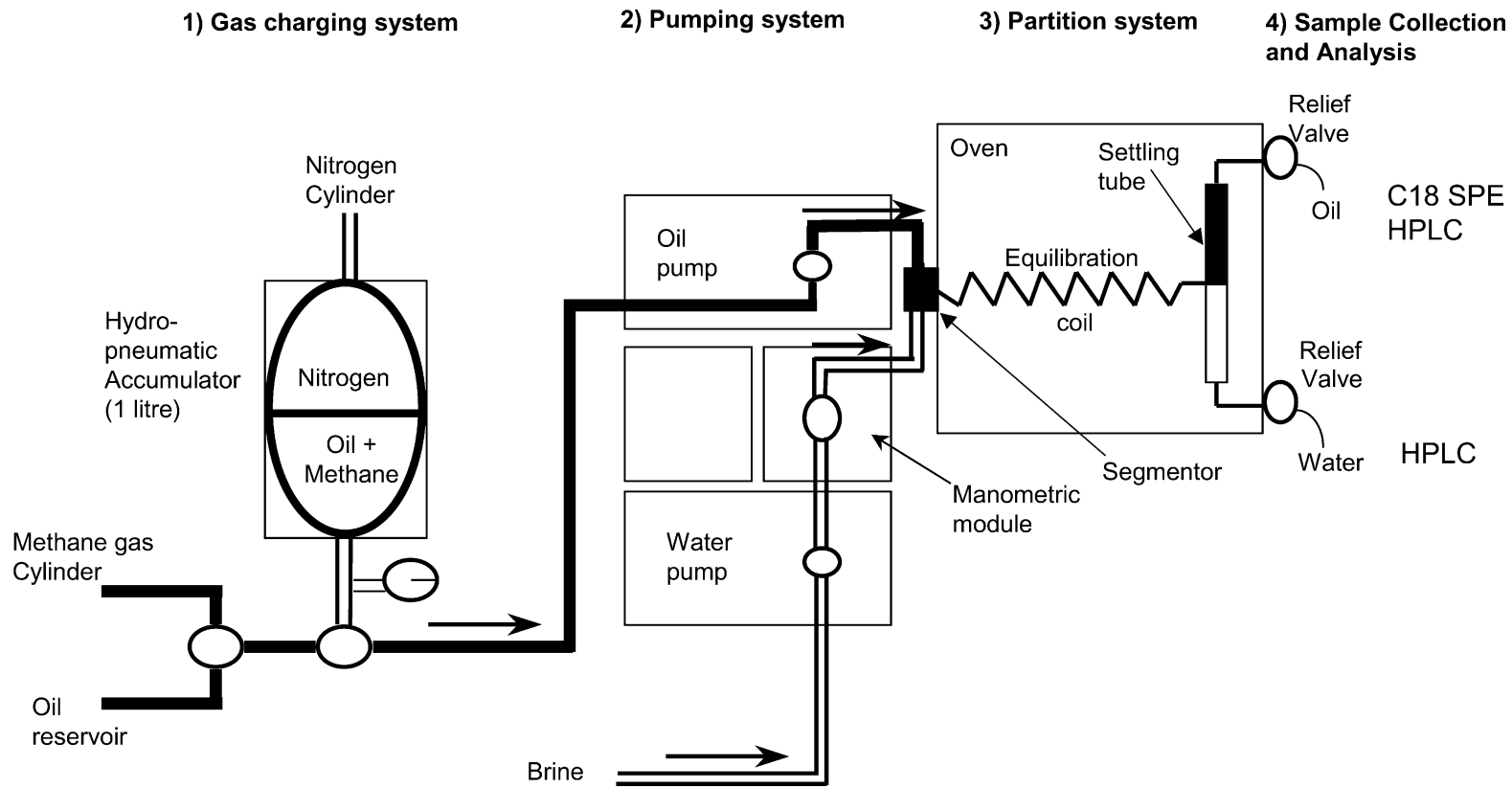


Fig. 1. Schematic representation of partition device equipped with a hydro pneumatic accumulator for gas addition.

pump system, constant pressure was maintained in the accumulator by allowing nitrogen gas to bleed into the upper compartment via a pressure regulator.

Using the pressure/volume/temperature software PVT-SIM, the methane content of the oil at 1500 psi saturation pressure was calculated as equivalent to 35 mol% methane. Determination of the swelling factor (and density) for the live oil vs the original dead oil composition at 160 °C indicated up to 10% difference. Therefore, differences in partition coefficients of phenol and cresols greater than 10% would be considered as arising from the behaviour of phenol and cresols under the conditions of the live oil and dead oil: brine systems.

(2) Pumping system—The pumping system was based on high performance liquid chromatography (HPLC) equipment and consists of a Gilson master (305) pump with a titanium pump head capable of handling water of varying salinity and a slave (306) pump with a stainless steel head capable of pumping oil. The HPLC pumps and partition system were primed to a pressure of 2000 psi, i.e. greater than that in the accumulator. The “live” oil was bled from the accumulator into the HPLC pump and then discharged via the HPLC pump, at a flow rate equal to the rate of brine introduction ( $0.25 \text{ ml min}^{-1}$ ), into the partition system (Fig. 1). Pressure was monitored by a Gilson (805) manometric module and within the partition system pressure was maintained by relief valves, affording a working pressure range from 25 to 4930 psi (0–340 bar). The partition experiments were conducted at a constant pressure of 2000 psi, well above the oil saturation pressure so that only a single under-saturated oil phase is present.

(3) Partition system—crude oil and waters are brought into contact at the “T-piece” (segmentor, Fig. 1) where segmentation occurs. Individual segments of oil and water are propelled (flow rate,  $0.5 \text{ ml min}^{-1}$ ) along an open tubular stainless steel coil (equilibration coil:  $3 \text{ m} \times 0.5 \text{ mm}$ ). Equilibration of solutes between oil and water segments is promoted by the generation of strong internal mixing within individual oil and water segments. The equilibration system is contained within an HPLC oven (Applied chromatography systems LC 750) with accurate temperature monitoring ( $\pm 1 \text{ }^\circ\text{C}$ ) by a chrome-alumel thermocouple (Kent Instruments). After equilibration in the equilibration coil, oil and water are separated according to density difference in a settling tube (Fig. 1), at which point the separated phases flow through the relief valves. Prior to using the instrument it is useful to assess the separation characteristics of oil and water through simple “shake and separate” experiments at room temperature and pressure.

A series of partition experiments was conducted to observe the oil–water separation properties in the presence of gas. Miller oil and waters showed excellent separation properties under dead oil: water experiment conditions. However, in the presence of gas under low

salinity (5% NaCl) conditions it was found that stable emulsions formed when oil and water were brought into contact. The emulsion adversely affected fluid emergence via the relief valves and consequently pressure stability in the system. It is important to avoid emulsion formation or vigorous mixing of the two phases since, upon emergence from the relief valves, the oil and water would re-partition under ambient conditions, which would therefore lead to erroneous partition coefficients with respect to instrument conditions. The instrument conditions were revised until phase separation occurred, allowing collection of separated oil and water phases. Phase separation occurred when salinity was increased and equilibration experiments were conducted with Miller oil and water containing 15% NaCl under varying temperatures (25–150 °C) and with or without methane gas.

(4) Sample collection—fluids are sampled upon emergence from the upper exit relief valve (oil) and lower exit relief valve (water). Following fluid emergence during “bleed” (valve opening) and re-seat (valve closure), a slight pressure drop (ca. 20 psi) is experienced in the interval, which has a negligible effect on the actual pressure setting indicated by the manometric module ( $\sim 1\%$  change). During live oil experiments, gas evaporates from the liquid (most noticeable from the oil) phase upon passing through the relief valve; this was allowed to bleed off into the fume hood. The fluid samples are collected into 1 ml glass vials and are filled to exclude air headspace. Water samples are submitted immediately for analysis, whereas oil samples require a preparative step using  $\text{C}_{18}$  non end-capped solid phase extraction ( $\text{C}_{18}$  NEC SPE) to isolate a phenol enriched fraction prior to analysis by reversed phase-high performance liquid chromatography combined with electrochemical detection (RP-HPLC-ED).

## 2.2. Sample processing

The analytical methods for determining alkyl phenol concentrations in oil and water samples were described by Bennett et al. (1996). Briefly, for oil samples  $\text{C}_{18}$  NEC SPE was employed to isolate an alkyl phenol-enriched fraction. The  $\text{C}_{18}$  bonded silica sorbent was conditioned using 3 ml of *n*-hexane under gravity flow. The remaining solvent was removed by gentle air flush. Approximately 0.5 ml of oil was loaded directly on to the top of the SPE column followed by 4.5 ml of *n*-hexane to recover a hydrocarbon fraction. The alkyl-phenol-enriched fraction is eluted with 5 ml of methanol/water (1:1) and is diluted to 10 ml, with methanol/water. The water samples required no preparation and the phenols were analysed directly by RP-HPLC-ED. Due to the speed of sample processing, data were generated mainly on water samples.

### 2.3. RP-HPLC–ED analysis

A Hewlett-Packard HP1050 HPLC system was used for the analysis of the alkyl phenols. The column was a Hamilton PRP-1 (150 × 4.1 mm i.d.) with particle diameter 10 μm. Samples were injected on to the column in 20 μl injection volumes using an autosampler. HPLC conditions were adopted from Nieminen and Heikkilä (1986). The mobile phase comprised 17% acetonitrile and 83% aqueous 0.1 M sodium acetate adjusted to pH 11.5–11.6 with 1 M NaOH. Flow rate was 2 ml/min. Alkyl phenols were detected using an Antec Decade Electrochemical Detector (Presearch UK). The detector cell was equipped with a glassy carbon electrode and a silver/silver chloride reference electrode. The applied potential used for alkyl phenol analysis was +0.6 Volts.

A typical RP-HPLC–ED run sequence consisted of alternating a standard mixture (concentrations made to levels found in samples, ca. 1 ppm) with two samples. The concentrations of phenol and cresols in oil and water samples are reported in ppm (mg l<sup>-1</sup>).

The reproducibility for measuring alkyl phenol concentrations in crude oils and waters by RP-HPLC–ED analysis and data generated by the partition system were given previously (Bennett et al., 1996; Bennett and Later, 1997). In this study, the measurements from an equilibration experiment with Miller oil and brine under live oil conditions at 150 °C were repeated and good reproducibility of phenol and cresol concentrations (Table 2) and subsequent  $P_{ow}$  values was obtained (Table 3).

## 3. Results and discussion

### 3.1. Partition coefficient calculations

The partition coefficient is represented by the concentration of substrate in oil ( $C_o$ ) relative to its concentration in water ( $C_w$ ) at equilibrium and may be calculated from Eqs. (1) and (2):

$$P_{ow} = C_o/C_w \quad (1)$$

Table 1

System conditions employed and concentrations (ppm) of phenol and cresols in the original Miller oil (determined in triplicate, standard deviation and relative percentage standard deviation shown in parentheses) and oil samples (15% NaCl) following equilibration (1:1, vol:vol) with live (saturated at 100 bar, 25 °C with 100% methane gas) and dead Miller crude oil, relative to temperature (°C)

Samples	Conditions		Concentrations				Ratios	
	Pressure (psi)	Temperature (°C)	Phenol	<i>m</i> -cresol	<i>p</i> -cresol	<i>o</i> -cresol	Phenol	<i>o</i>
							<i>cresols</i>	<i>m + p</i>
Miller oil			2.92 (0.09, 3.12)	2.00 (0.04, 2.02)	2.36 (0.04, 1.57)	8.88 (0.17, 1.93)	0.22	2.04
Live oil (a)	2000	150	1.91	1.64	1.95	7.99	0.16	2.23
Live oil (b)	2000	150	1.92	1.61	1.85	8.48	0.16	2.45
Dead oil	375	150	1.54	1.68	2.05	7.47	0.14	2.00

Repeated experiment identified as samples Live oil (a) and (b).

Table 2

System conditions employed and concentrations (ppm) of phenol and cresols in water samples (15% NaCl) following equilibration (1:1, vol:vol) with live (saturated at 100 bar, 25 °C with 100% methane gas) and dead Miller crude oil, relative to temperature (°C)

System	Conditions		Concentrations				Ratios	
	Pressure (psi)	Temperature (°C)	Phenol	<i>m</i> -cresol	<i>p</i> -cresol	<i>o</i> -cresol	Phenol	<i>o</i>
							<i>cresols</i>	<i>m + p</i>
100 bar methane	2000	25	0.32	0.08	0.07	0.16	1.03	1.07
100 bar methane	2000	90	0.69	0.19	0.20	0.33	0.96	0.85
100 bar methane (a)	2000	150	0.93	0.37	0.35	0.79	0.61	1.10
100 bar methane (b)	2000	150	0.95	0.36	0.32	0.73	0.67	1.07
No solution gas	375	25	0.56	0.16	0.17	0.41	0.76	1.24
No solution gas	375	90	1.14	0.37	0.38	0.82	0.73	1.09
No solution gas	375	150	1.39	0.50	0.50	1.07	0.67	1.07
Formation water			3.88	1.12	0.73	2.24	0.95	1.21

Data for a North Sea Formation water are included for comparative purposes. Repeated experiment identified as system 100 bar methane (a) and (b).

Table 3

Partition coefficient data for phenol and cresols following equilibration (1:1, vol:vol, 2000 psi) with live (saturated at 100 bar, 25 °C with 100% methane gas) and dead Miller crude oil, relative to temperature (°C)

System	Conditions		$P_{ow}$			
	Pressure (psi)	Temperature (°C)	Phenol	<i>m</i> -cresol	<i>p</i> -cresol	<i>o</i> -cresol
100 bar methane	2000	25	8.14	24.00	32.71	54.50
100 bar methane	2000	90	3.22	9.53	10.80	25.91
100 bar methane(a)	2000	150	2.15	4.41	5.74	10.24
100 bar methane(b)	2000	150	2.07	4.56	6.38	11.16
No solution gas	375	25	4.20	11.50	12.88	20.66
No solution gas	375	90	1.56	4.41	5.21	9.83
No solution gas	375	150	1.08	2.64	3.37	6.93

$$P = V_w/V_o \cdot (C_{oi}/C_w) - 1 \quad (2)$$

where  $V_w$  and  $V_o$  represent the volume of water and oil, respectively, and  $C_{oi}$  represents the initial concentration of alkyl phenols in the crude oil.

Since measurements were carried out with an equal volume of oil and water (vol: vol, 1:1) and the initial concentrations ( $C_{oi}$ ) of phenol and cresols in the starting oil (Miller oil) sample were determined accurately (in triplicate, Table 1), then partition coefficients may be measured using the following equation:

$$P_{ow} = (C_{oi}/C_w) - 1 \quad (3)$$

### 3.2. Partition coefficient measurements under live and dead crude oil: water conditions

In our previous study (Bennett and Larter, 1997), only “dead” (containing no solution gas) crude oil/water systems were considered. Typically, under reservoir conditions petroleum contains solution gases, predominantly methane. Because methane is generally the main constituent of the gases the influence of dissolved methane on the  $P_{ow}$  values of phenol and cresol in the oil–water systems was investigated.

Miller crude oil is a typical non-degraded North Sea oil (Smalley and Warren, 1994), generated from Upper Jurassic, Kimmeridge Clay Formation source rocks at around 0.8% vitrinite reflectance (Chen, 1995). The alkyl phenol distribution in a polar non-hydrocarbon isolate recovered by  $C_{18}$  NEC SPE of the original Miller crude oil is shown in Fig. 2a. The oil distribution is dominated by phenol and cresols, and contains appreciable quantities of  $C_2$  alkyl phenols.

Fig. 2b and d show the RP-HPLC–ED chromatograms for phenol and cresols in oil and water (15% NaCl) samples after equilibration (ca. 30 min) with equal volumes of live Miller oil at 25 °C and 2000 psi. A clear enhancement of phenol versus cresols relative to the abundances in the original oil sample is seen in the chromatogram (cf. Fig. 2a and d) and is confirmed by

the ratio of phenol relative to cresols (Tables 1 and 2). The RP-HPLC–ED chromatogram of the equilibrated water shows the  $C_2$  alkyl phenols as trace constituents, requiring expansion of the plot response over the  $C_2$  alkyl phenols elution interval to observe their distributions (Fig. 2d). The cresols are also present at low levels due to their low water solubility under the salinity conditions employed. Compared to the original oil, the partitioned water samples show enhancement of *p*-cresol and *m*-cresol relative to *o*-cresol, indicated by the ratio  $o\text{-cresol}/p\text{-cresol} + m\text{-cresol}$  [abbreviated to  $o/(m+p)$ ; Tables 1 and 2]. The close proximity of the methyl group (hindered hydroxyl group) to the active hydroxyl functionality in *o*-cresol may decrease hydrogen bonding interactions with water, limiting the solubility of *o*-cresol in water. Fig. 2c and e show the RP-HPLC–ED chromatogram for phenol and cresols in oil and water (15% NaCl) samples following equilibration (ca. 30 min) experiments at 150 °C and 2000 psi. Interestingly, from comparison of the levels of cresols in water samples (Fig. 2d and e), it is seen that the increase in temperature enhances cresol extraction into the water phase (Table 2). There is a contribution from an unknown contaminant component (Fig. 2e) which appears in the water samples following the higher temperature experiments; however, this does not affect the quantification of phenol and cresols. Fig. 2f shows the RP-HPLC–ED distributions of phenol and cresols in a natural formation water sample obtained from a North Sea reservoir (no water sample was available from the Miller field). The enhancement in phenol relative to cresols and reduction in the  $o/(m+p)$  components to the oil sample (Table 2) is consistent with an origin from partition equilibration which may have occurred during oil production in the drill stem or in the oil–water separator. The distribution of phenol and cresols in waters from the oil–water equilibration experiments shown in Fig. 2d and e is remarkably similar to those encountered in natural formation waters.

The concentrations of phenol and cresols in water samples following equilibration with live oil and dead

oil are listed in Table 1 and are shown relative to temperature in Fig. 3a–d. Compared to the water samples from dead oil conditions, the presence of methane results in up to 50% reduction in levels of phenol and cresols in the water phase. Also apparent in Fig. 3a–d are the successively higher concentrations of phenol and cresols extracted into the water phase with increasing temperature, following the same trends described previously for phenol and cresols in dead oil:brine systems (Bennett and Larter, 1997).

The partition coefficient data for phenol and cresols measured using live oil and dead oil:brine systems under varying temperature conditions are listed in Table 3 and are presented graphically in Fig. 4a–d. Over the temperature range investigated, it is seen that the introduction of gas into the system results in an approximate doubling of partition coefficients over equivalent dead oil:brine systems. The results follow trends similar to those described by Knaepen et al. (1990) for the behaviour of partition coefficients of pentan-1-ol and ethyl

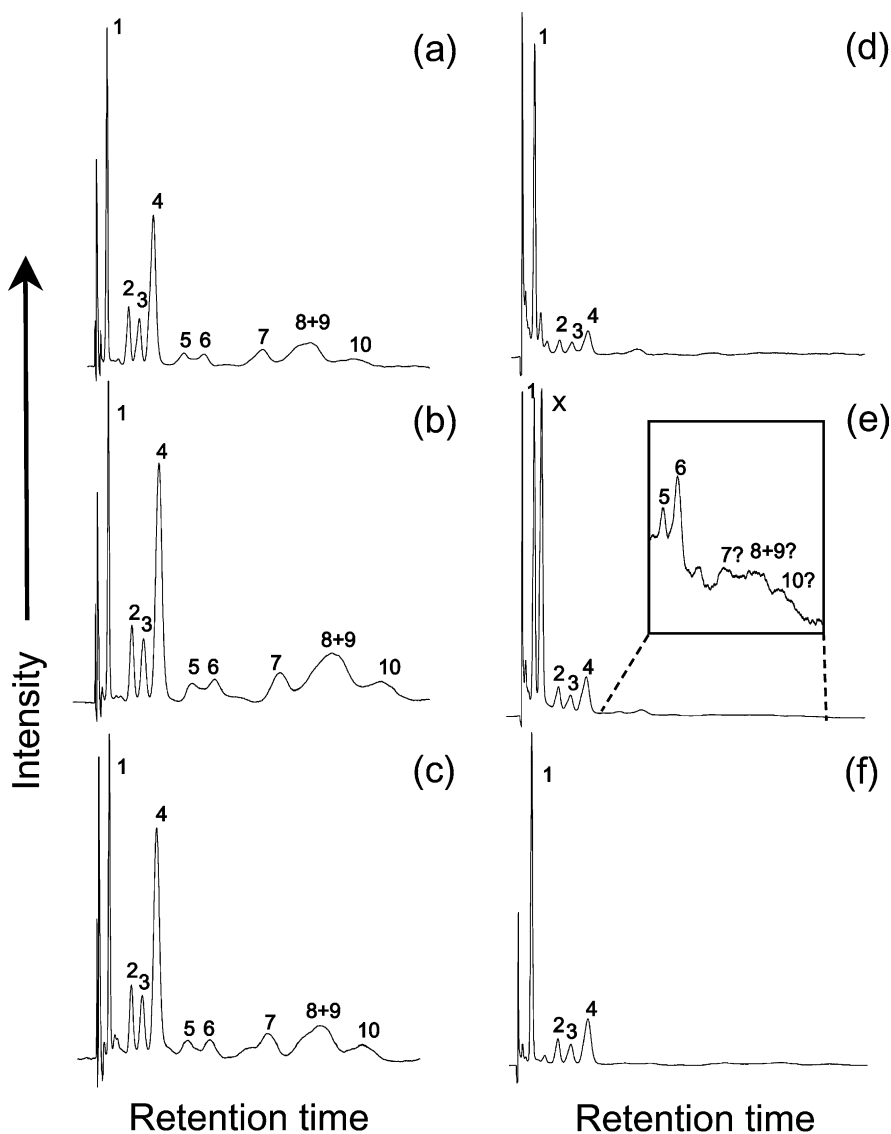


Fig. 2. RP-HPLC-ED chromatograms for phenol and cresol distributions in  $C_{18}$  NEC SPE isolates of (a) Miller oil and following equilibration (1:1, vol:vol) of Miller oil with water (15% NaCl) at 150 °C (b) dead oil and (c) live oil conditions and water samples resulting from the corresponding (d) dead oil (25 bar) and (e) live oil (2000 psi) conditions (inset: vertical scale exaggerated ca. 20 times to show  $C_2$  alkyl phenol elution interval) and (f) a North Sea reservoir production water sample. Key: 1 = phenol, 2 = *m*-cresol, 3 = *p*-cresol, 4 = *o*-cresol, 5 = 3,5-dimethylphenol (DMP) + 4-ethylphenol, 6 = 3,4-DMP + 3-ethylphenol, 7 = 2,5-DMP, 8 = 2,3-DMP + 2-ethylphenol, 9 = 2,4-DMP, 10 = 2,6-DMP, X = unknown.



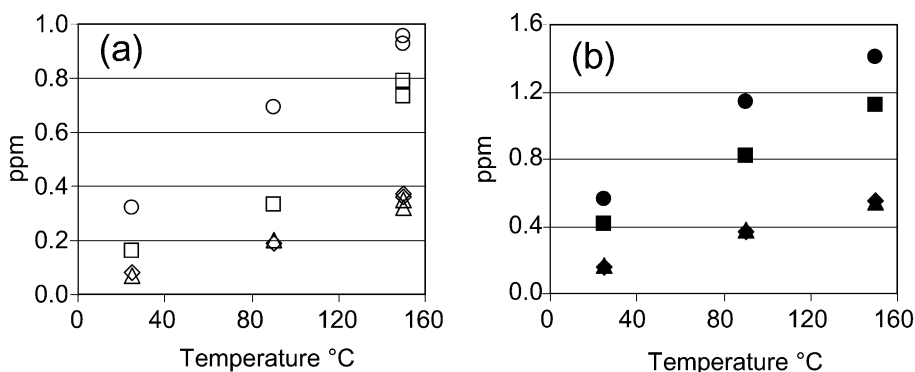


Fig. 3. Concentrations of phenol (squares), *m*-cresol (diamonds), *p*-cresol (triangles) *o*-cresol (circles) in water (15% NaCl) samples following equilibration (1:1, vol:vol) with (a) “live” oil and (b) dead oil at 2000 psi under varying temperature conditions.

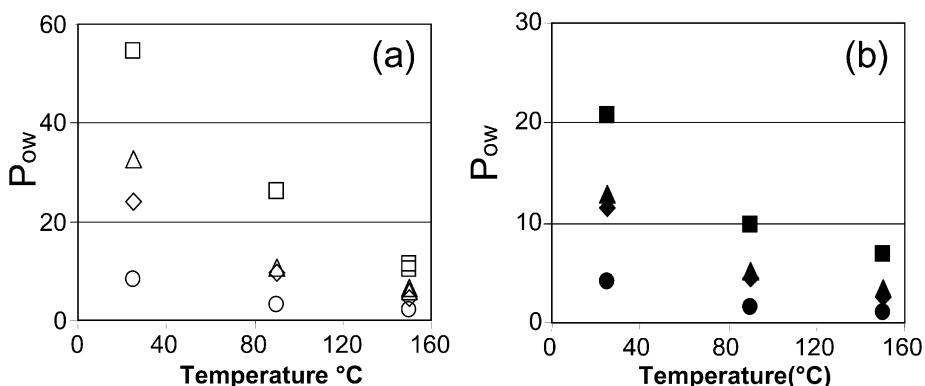


Fig. 4. Partition coefficients ( $P_{ow}$ ) of phenol (squares), *m*-cresol (diamonds), *p*-cresol (triangles) *o*-cresol (circles) in water (15% NaCl) samples following equilibration (1:1, vol: vol) with (a) “live” oil and (b) dead oil at 2000 psi under varying temperature conditions.

acetate between live and dead crude oil:water systems. Knaepen et al. (1990) showed a strong influence of solution-gas (GOR) content on partition coefficients, reporting an increase (up to 50%) in the partition coefficient of ethyl acetate in live oil: brine systems, compared to experiments carried out using dead crude oil: brine systems. In contrast, Carlisle and Kapoor (1982) reported a slight decrease in ethyl acetate partition coefficients with increasing GOR.

The strong influence of dissolved gas exerted on the  $P_{ow}$  values was explained in terms of strong swelling and accompanying changes in polarity of the organic phase. However, following methane addition to oil one would expect the polarity of the crude oil to decrease. Bennett and Larter (1997) showed for a suite of oils that increasing the non-hydrocarbon content of crude oils (determined by Iatroscan as the sum of % resin and % asphaltene) resulted in increasing values of  $P_{ow}$ . The effect was thought to be due simply to a solubility parameter effect whereby increasing the polarity of an oil increases phenol solubility in it. Therefore, an increase of  $P_{ow}$  values following a decrease in polarity of the organic phase due to methane addition suggests the

effect seen in our experiments is due to other factors. Comparison of swelling factors calculated on live and dead oil equivalents at 160 °C using PVT-SIM program suggests swelling of the oil phase could only account for small differences (<10%) in partition coefficient. A doubling of the partition coefficient from dead oil compared to equivalent live oil: brine conditions suggests other factors contribute to the observations.

The phenol partition coefficients decrease with increasing temperature (cf. Taylor et al., 1997; Bennett and Larter, 1997), in contrast to the partition behaviour of ethyl acetate and pentanol (Knaepen et al., 1990; Carlisle and Kapoor, 1982). In view of the contrasting behaviour of  $P_{ow}$  for alkyl phenols and ethyl acetate in oil/water systems as a function of temperature, caution needs to be exercised when extrapolating partition coefficient data measured under ambient conditions with shake-flask methods to high temperature conditions. Leo et al. (1971) reviewed partition coefficient data from numerous solvent-solute systems, concluding that partition coefficients may either increase or decrease with increasing temperature. In summary, direct measurement of  $P_{ow}$  under simulated sub-surface conditions in



the laboratory provides the best practical means of describing the effect of temperature. The partition device described here facilitates rapid production of such data sets and provides a better data set than those extrapolated from simplified experiments.

### 3.3. Potential applications of partition coefficient data

#### 3.3.1. Determination of residual oil saturation in water flooded oilfields

Huseby et al. (2003) performed an experimental as well as a theoretical and numerical modelling study on the transport of organic oil components from immobile and by-passed oil. Diffusion is the most important process controlling the transport of water soluble compounds from within large oil bodies to moving waters, with partitioning accounting for their mobilisation into the moving injection-production water streams. Water contacting the oil body would remove compounds by partitioning, while continued replenishment of compounds to the oil–water contact from within the oil body would occur at a slow rate via diffusion. The levels of water soluble compounds in the injection-production streams and rate of decline of the solutes in produced waters during production may provide an indication of the size of the contacted oil body that can be simulated using such diffusion/partition processes. In the case of small oil volumes remaining in place, the levels of water soluble compounds in the production stream would decrease rapidly since they would be depleted rapidly with continued water production. Where mobile water streams contact a large oil bank, the production of water soluble compounds would probably occur over longer periods of time. Phenols are ideal candidate compounds for investigating the nature of sub-surface oil–water interactions in this way since they partition readily between oil and water and occur as natural constituents of reservoir fluid phases.

#### 3.3.2. Production water discharge loads

Alkyl phenols are monitored pollutants in produced fluids from petroleum reservoirs (Jacobs et al., 1992; Tibbetts et al., 1992). The presence of solution gas, temperature and salinity strongly influence alkyl phenol  $P_{ow}$ , affecting the distribution of phenol and cresol (and other solutes) between oil and water phases. Regulation of phenol concentrations by management of separator conditions may achieve lower solute discharge levels in production water and thus decrease waste water disposal costs and environmental impacts. Similarly, as waters of different composition are produced through time from a field due to the effects of dilution of formation waters by injected water, a knowledge of oil–water partition properties of phenols can help in the prediction of potential discharge loads through time and thus facilitate cost effective facility design and construction.

If we consider the partition coefficient data measured for the Miller crude oil:brine systems, we are able to modify the toxic solute (phenols) loadings in the separator waters. The lowest phenol and cresol levels were encountered in waters partitioned with Miller oil at 25 °C and with solution gas present (Fig. 3a). The highest phenol and cresol levels were found in waters partitioned with Miller oil at 150 °C and with no solution gas present (Fig. 3b). Therefore, separator conditions at 25 °C and in the presence of solution gas results in the lowest solute loading in partitioned waters which may be considered for discharge into the environment.

## 4. Conclusions

Partition coefficient measurements under live oil:brine conditions proved to be challenging due to emulsion formation under some oil–water conditions. A preliminary investigation by adding dead oil and water in a container and shaking to observe separation characteristics will save wasted time performing high pressure studies. Once the system is optimised, partition coefficients of alkyl phenols can be measured rapidly (ca. 1 h) and reproducibly under simulated reservoir conditions of temperature and under pressure in the presence of methane or wet gases.

Partition coefficients of phenol and cresols increase with solution gas content and in saline conditions, but decrease with increasing temperature, allowing assessment of distributions in both sub-surface oil–water systems and in line production facilities.

Natural oilfield waters contain appreciable quantities of phenol and thus cresols and may be exploited in reservoir exploration and production activities. These include determination of residual oil saturation of water-flooded reservoirs and assessment of production water discharge loads. The partition coefficient data also provide a means of managing phenol and cresol distributions between oil and water. Retention of phenol and cresols in the oil phase is favoured for allowing safe discharge of production waters into the environment.

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## References

- Bennett, B., Bowler, B.F.J., Larter, S.R., 1996. Rapid methods for the determination of C<sub>0</sub>–C<sub>3</sub> alkylphenols in crude oils and waters. *Analytical Chemistry* 68, 3697–3702.
- Bennett, B., Larter, S.R., 1997. Partition behaviour of alkylphenols in crude oil/brine systems under subsurface conditions. *Geochimica et Cosmochimica Acta* 61, 4393–4402.
- Carlisle, C.T., Kapoor, S., 1982. Development of a Rapid and Accurate Method for Determining Partition Coefficients of Chemical Tracers Between Oils and Brines (for single-well tracer tests). Report DE-AC19-79BC10100, US DOE, Washington, DC, December 1982.
- Chen, M., 1995. Response of Pyrrolic and Phenolic Compounds to Petroleum Migration and In-Reservoir Processes. PhD Thesis, University of Newcastle upon Tyne.
- Dale, J.D., Larter, S.R., Aplin, A.C., Macleod, G.M., 1995. The organic geochemistry of North Sea oil field production waters. *Organic geochemistry: developments and applications to energy, climate, environment and human history*. In: Grimalt, J.O., Dorronsoro, C. (Eds.), 17th International Meeting on Organic Geochemistry. pp. 396–398.
- Huseby, O., Haugan, A., Sagen, J., Muller, J., Bennett, B., Larter, S., Kikkinides, E.S., Stubos, A.K., Yousefian, F., Thovert, J.-F., Adler, P.M., 2003. Transport of organic components from immobile and bypassed oil in porous media. *Applied Chemical Engineering* 49, 1085–1094.
- Ioppolo, M., Alexander, R., Kagi, R.I., 1992. Identification and analysis of C<sub>0</sub>–C<sub>3</sub> phenols in some Australian crude oils. *Organic Geochemistry* 18, 603–609.
- Ioppolo-Armanios, M., Alexander, R., Kagi, R.I., 1995. Geosynthesis of organic compounds: I. Alkylphenols. *Geochimica et Cosmochimica Acta* 59, 3017–3027.
- Jacobs, R.P.W.M., Grant, R.O.H., Kwant, J., Marquenie, J.M., Mentzer, E., 1992. In: Ray, J.P., Engelhardt, F.R. (Eds.), *Produced Water (Technologies/Environmental Issues and Solutions)*. Environmental Science Research, Vol. 46. Plenum Press, New York, pp. 13–22.
- Jayasekera, A.J., Goodyear, S.G., 2000. The development of heavy oil fields in the United Kingdom Continental Shelf: past, present, and future. *Society of Petroleum Engineers Reservoir Evaluation and Engineering* 3, 371–379.
- Knaepen, W.A.I., Tijssen, R., van den Bergen, E.A., 1990. Experimental aspects of partitioning tracer tests for residual oil saturation with FIA-based laboratory equipment. *Society of Petroleum Engineers Reservoir Engineering* 5, 239–244.
- Larter, S.R., Aplin, A.C., 1995. Reservoir geochemistry: methods, applications and opportunities. In: Cubitt, J.M., England, W.A. (Eds.), *The Geochemistry of Reservoirs*. Geological Society Special Publication No. 86, pp. 5–32.
- Leo, A., Hansch, C., Elkins, D., 1971. Partition coefficients and their uses. *Chemical Reviews* 71, 525–616.
- Ljosland, E., Bjornstad, T., Dugstad, O., Hundere, I., 1993. Perfluorocarbon tracer studies at the Gullfaks field in the North Sea. *Journal of Petroleum Science and Engineering* 10, 27–38.
- Lucach, S.O., Bowler, B.F.J., Frewin, N., Larter, S.R., 2002. Variation in alkylphenol distributions in a homogeneous oil suite from the Dhahaban petroleum system of Oman. *Organic Geochemistry* 33, 581–594.
- Macleod, G., Taylor, P.N., Larter, S.R., Aplin, A.C., 1993. Dissolved organics in formation waters: insights into water-oil-rock ratios in petroleum systems. In: Parnell, J. et al. (Eds.), *Geofluids 93*. Geological Society Special Publication, pp. 18–20.
- Nieminen, E., Heikkila, P., 1986. Simultaneous determination of phenol, cresols and xylenols in workplace air, using a polystyrene–divinylbenzene column and electrochemical detection. *Journal of Chromatography* 360, 271–278.
- Reinsel, M.A., Borkowski, J.J., Sears, J.T., 1994. Partition coefficients for acetic, propionic, and butyric acids in a crude oil/water system. *Journal of Chemical Engineering Data* 39, 513–516.
- Smalley, P.C., Warren, E.A., 1994. The Miller Field. In: Warren, E.A., Smalley, P.C. (Eds.), *North Sea Formation Water Atlas*. Geological Society Memoir No. 15, p. 52.
- Tang, J.S., Harker, B., 1991. Interwell tracer test to determine residual oil saturation in a gas-saturated reservoir. 2. Field applications. *Journal of Canadian Petroleum Technology* 30, 34–42.
- Taylor, P.N., Larter, S.R., Jones, D.M., Dale, J.D., Horstad, I., 1997. The effect of oil-water-rock partitioning on the occurrence of alkylphenols in petroleum systems. *Geochimica et Cosmochimica Acta* 61, 1899–1910.
- Tibbetts, P.J.C., Buchanan, G., Gavel, L.J., Large, R., 1992. In: Ray, J.P., Engelhardt, F.R. (Eds.), *Produced Water (Technologies/Environmental Issues and Solutions)*. Environmental Science Research, Vol. 46. Plenum Press, New York, pp. 97–112.
- Wellington, S.L., Richardson, E.A., 1994. Simultaneous use of ester and CO<sub>2</sub> single-well tracers. *Society of Petroleum Engineers Reservoir Evaluation and Engineering* 9, 240–246.