

Partition Coefficients for Acetic, Propionic, and Butyric Acids in a Crude Oil/Water System

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The effects of pH, temperature, and organic acid concentration on the partition coefficients for short-chain organic acids were measured in a crude oil/water system. Acetic, propionic, and butyric acids, as probable substrates for microbial souring of oil reservoirs, were used in conjunction with two types of crude oil. Temperatures of 35–75 °C, pH values of 4.0–7.0, and acid concentrations of 10–1000 mg/L were studied. Initial naturally occurring levels of organic acids in the crude oils were also determined. pH had by far the largest effect on the partition coefficient for all three organic acids for both types of oil. At conditions normally seen in an oil reservoir (pH 5–7), the great percentage (85+%) of these acids were dissolved in the aqueous phase. The log of the partition coefficient K increased approximately linearly with the number of carbon atoms in the acid. It was seen that organic acids are readily available carbon sources for sulfate-reducing bacteria (SRB) at normal reservoir conditions, and that crude oil may provide a source of organic acids in a low-pH, water-flooded reservoir.

Introduction

Short-chain organic acids such as acetic acid, propionic acid, and butyric acid are favored substrates for metabolism by SRB. In oil reservoirs undergoing secondary recovery (water flooding), the SRB utilize these carbon sources and dissolved sulfate to produce hydrogen sulfide (H₂S) in the phenomenon known as "souring". Since only substrates dissolved in the aqueous phase are thought to be available for bacterial metabolism, it is relevant to the understanding of souring to know how short-chain organic acids partition between the oil and water phases. In a water-flooded oil reservoir, where equilibrium can be expected between the flowing injection water and the oil (which may be stationary in a low-permeability zone), the quantity and type of organic acid available for SRB metabolism in the aqueous phase may be very important information in modeling and controlling souring.

Experimental Section

A three-variable central composite designed experiment was used to determine the effects of pH, temperature, and organic acid concentration on the partition coefficients in a crude oil/water system. Three levels of each variable were used in the design: temperatures of 35, 55, and 75 °C; pH values of 4.0, 5.5, and 7.0; and high, medium, and low levels of acid concentration. The high concentration consisted of 1000 mg/L acetic acid, 500 mg/L propionic acid, and 100 mg/L butyric acid; the medium concentration was 550 mg/L acetic acid, 275 mg/L propionic acid, and 55 mg/L butyric acid; and the low concentration was 100 mg/L acetic acid, 50 mg/L propionic acid, and 10 mg/L butyric acid. These variables and their levels were selected to represent reservoir conditions based on input from oil company personnel sponsoring this research.

Table 1. Composition of the Aqueous Phase Used in the Experiments

distilled water	970 cm ³	NH ₄ Cl	0.3 g
Na ₂ SO ₄	0.8 g	MgCl ₂ ·6H ₂ O	3.0 g
NaCl	20 g	KH ₂ PO ₄	0.2 g
KCl	0.3 g	CaCl ₂ ·2H ₂ O	0.15 g

Table 2. Dionex Ion Chromatograph Analysis Specifications

column size	AS10	regenerant	K ₂ B ₄ O ₇ ·4H ₂ O
pore size	4 mm	regenerant concn	100 mM
detector	conductivity	eluent flow rate	1.0 cm ³ /min
eluent	K ₂ B ₄ O ₇ ·4H ₂ O	suppressor liquid	H ₂ SO ₄
eluent concn	3.5 mM	suppressor concn	25 mM

The measured experimental response was the partition coefficient for each of the three organic acids, as defined in the equation

$$K = \frac{\text{concentration in oil by mass}}{\text{concentration in water by mass}} \quad (1)$$

The acetic acid (Fisher) was ACS reagent-grade with 99.7% minimum purity. Propionic acid and *n*-butyric acid (Sigma) were approximately 99% pure. The aqueous phase used was a solution (no. 1) developed by Widdel and Pfennig for SRB (1), as modified for a high-salinity, low-sulfate environment (Table 1). All chemicals used in this solution were ACS reagent-grade manufactured by Sigma Chemical Co.

The experimental procedure involved measuring 20 cm³ of the aqueous phase, adding the proper amount of organic acids via a stock solution containing all three acids, and then adjusting the pH to the desired level (± 0.1 pH unit) with 0.1 M NaOH. This pH-adjusted aqueous phase was then added to a 50 cm³ narrow-necked reaction vessel which contained 20 cm³ of crude oil. The vessels were then stoppered, sealed, and autoclaved for 20 min at 121 °C to sterilize the contents and eliminate the possibility of microbial activity consuming the organic acids. The vessels were incubated at the chosen temperature, and the oil and water phases were sampled after allowing vessels to equilibrate without mixing for approximately seven days. In preliminary experiments, it was shown that equilibrium was reached within two days. Three

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Table 3. Liquid Chromatography Fractionation Data (mass %)

oil	aliphatic	aromatic	C ₅ soluble ^a	C ₅ insoluble ^b
ARCO	32.5	66.6		
INEL	62.68	22.53	6.38	6.40

^a Non-pentane-precipitable resins. ^b Pentane-precipitable asphaltics.

Table 4. Elemental Analysis Data (Mass %)

oil	carbon	hydrogen	nitrogen	sulfur
ARCO	85.0	9.2	0.25	1.73
INEL	82.37	11.60	0.35	3.24

Table 5. Initial Acid Levels of ARCO and INEL Crude Oils

oil source	ARCO	INEL
acetic acid concn (mg/L)	3	1
propionic acid concn (mg/L)	<1	<1
butyric acid concn (mg/L)	<1	<1

Table 6. Statistical *p* Values for Combined Experimental Data from ARCO and INEL Crude Oils

	<i>R</i> ²	<i>p</i> value ^a		
		temperature	pH	concentration
acetic acid	0.8281	0.3921	0.0001	0.0042
propionic acid	0.9726	0.0163	0.0001	0.9986
butyric acid	0.9745	0.0541	0.001	0.8160

^a A *p* value ≤ 0.05 means that a change in the variable over the experimental range has a significant effect on the measured response (in this case, *K*, the partition coefficient) at a 95% confidence level.

Table 7. Partition Coefficients (*K*) for ARCO Oil

vessel no.	pH	<i>t</i> /°C	concn	<i>K</i> (but)	<i>K</i> (prop)	<i>K</i> (Ac)
1	4	35	low	0.243	0.047	0.011
2	7	35	low	0.000	0.000	0.007
3	4	75	low	0.484	0.095	0.036
4	7	75	low	0.091	0.019	0.015
5	4	35	high	0.345	0.075	0.015
6	7	35	high	0.005	0.001	0.001
7	4	75	high	0.316	0.075	0.016
8	7	75	high	0.019	0.003	0.002
9	4	55	middle	0.344	0.078	0.019
10	7	55	middle	0.011	0.002	0.001
11	5.5	35	middle	0.075	0.008	0.018
12	5.5	75	middle	0.084	0.010	0.009
13	5.5	55	low	0.144	0.022	0.008
14	5.5	55	high	0.057	0.011	0.002
15	5.5	55	high	0.068	0.017	0.004
16	5.5	55	middle			
17	5.5	55	middle	0.060	0.012	0.005
18	5.5	55	middle	0.043	0.008	0.002

incubators were used in this procedure so the entire experiment could be run at one time.

Aqueous-phase organic acid concentrations were determined by inverting the vessel, withdrawing 0.5 cm³ (duplicate samples), and diluting 1:10 with ultrapure water. A Dionex Al-450 ion chromatograph, which separates peaks for each of the short-chain organic acids, was used to determine the concentrations (Table 2). The minimum level of detection and the instrument error have both been determined to be approximately 1 mg/L.

The oil-phase organic acid concentration was determined by withdrawing 5 cm³ of oil after laying the reaction vessel on its side to allow access to the oil phase. A 10 cm³ sample of 0.1 M Na₂CO₃ was then added to extract the acids from the oil. It was shown in separate experiments that 0.1 M Na₂CO₃ used in the following method extracted 79% of the acetic acid, 94% of the propionic acid, and 92% of the butyric acid compared to a water control. Except for acetic acid, it is believed that these extractions are within the experimental

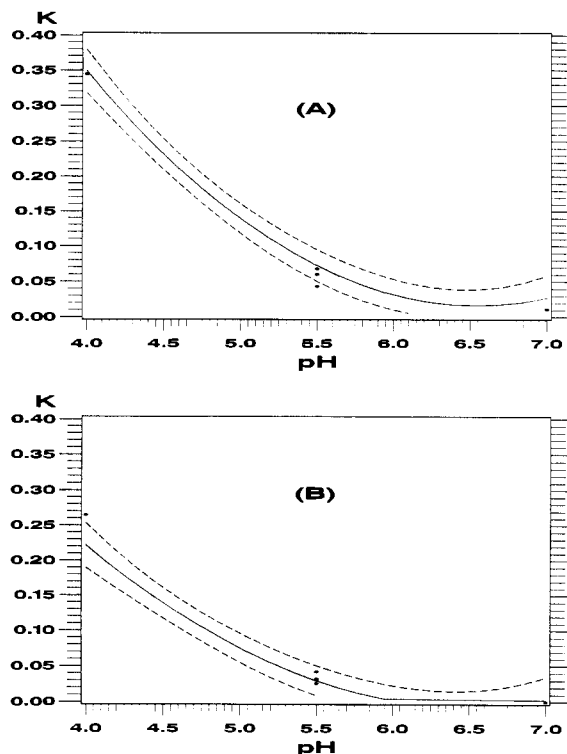


Figure 1. Partition coefficient *K* for butyric acid vs pH, at middle temperature and middle concentration levels: (A) ARCO oil, (B) INEL oil. Data points (●) are shown along with the statistically predicted curve (—) and 95% confidence intervals (---). Shown are the data points corresponding to the middle levels of temperature and concentration. The predicted values and prediction intervals, however, are based on data from the entire design.

Table 8. Partition Coefficients (*K*) for INEL Oil

vessel no.	pH	<i>t</i> /°C	concn	<i>K</i> (but)	<i>K</i> (prop)	<i>K</i> (Ac)
1	4	35	low	0.241	0.056	0.020
2	7	35	low	0.000	0.000	0.007
3	4	75	low	0.137	0.031	0.011
4	7	75	low	0.000	0.015	0.010
5	4	35	high	0.218	0.051	0.011
6	7	35	high	0.000	0.001	0.001
7	4	75	high	0.236	0.057	0.014
8	7	75	high	0.000	0.001	0.001
9	4	55	middle	0.265		
10	7	55	middle	0.000	0.001	0.003
11	5.5	35	middle	0.029	0.007	0.002
12	5.5	75	middle	0.027	0.007	0.002
13	5.5	55	low	0.000	0.009	0.008
14	5.5	55	high	0.042	0.010	0.003
15	5.5	55	high	0.026	0.008	0.003
16	5.5	55	middle	0.042	0.013	0.006
17	5.5	55	middle	0.032	0.007	0.002
18	5.5	55	middle	0.031	0.007	0.002

error possible with this method so no correction factors were used. If not all the organic acids were extracted from the oil during these experiments, the partition coefficients would be slightly higher than their reported values.

The sample was shaken for 2 h at 160 oscillations/min to allow intimate mixing of the oil and the extraction agent and then was centrifuged for 15 min at 20 000 rpm on a Sorvall RC5C centrifuge. The sample was shaken slightly to break the emulsion and poured into a separatory funnel, and the aqueous phase now containing the acids was withdrawn from the bottom of the funnel. This sample, already diluted 1:2 by the addition of 10 cm³ of the extraction agent, was filtered and run in duplicate on the Dionex ion chromatograph.

Two different experiments were performed using the three-variable central composite design. The first experiment used

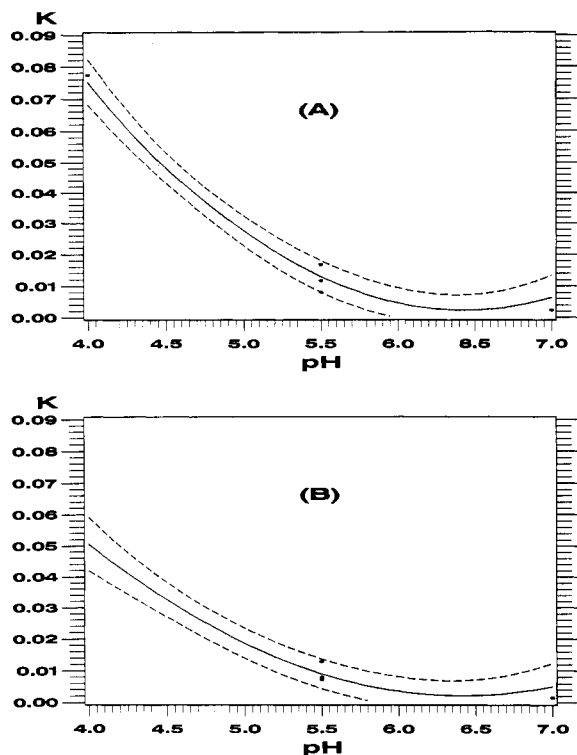


Figure 2. Partition coefficient K for propionic acid vs pH, at middle temperature and middle concentration levels: (A) ARCO oil, (B) INEL oil. Data points (●) are shown along with the statistically predicted curve (—) and 95% confidence intervals (---). Shown are the data points corresponding to the middle levels of temperature and concentration. The predicted values and prediction intervals, however, are based on data from the entire design.

crude oil supplied by ARCO from the Kuparuk field on Alaska's North Slope. The second experiment used crude oil supplied by the Idaho National Engineering Laboratory (INEL) from the Schuricht field in Wyoming. The ARCO oil was sour (high H_2S content) from a field which had undergone water flooding, while the INEL oil was sweet (low H_2S content) from a field with no water flooding. Both oils were tested for their initial level of short-chain fatty acids using the same extraction technique used for the oil phase in the incubated vessels. Liquid chromatography fractionation and elemental analysis data for both oils are shown in Tables 3 and 4, respectively.

Results and Discussion

The oils used in the two experiments each had very low initial levels of short-chain organic acids (Table 5). It was expected that the "sweet" oil which came from a non-water-flooded field (INEL) would have significantly higher acid concentrations than the ARCO oil because of less SRB activity, but this was not the case.

The data from both central composite designed experiments (using the two types of crude oil) fit the same general linear model very well (Table 6). Variables which were significant at a 95% confidence level were pH and concentration for acetic acid, pH and temperature for propionic acid, and pH for butyric acid. As shown by the very low p values, pH was by far the most significant variable affecting the partition coefficient for all three short-chain organic acids. Data from both experiments are shown in Tables 7 and 8.

Since temperature and organic acid concentrations had only minor effects on partition coefficients, only data showing

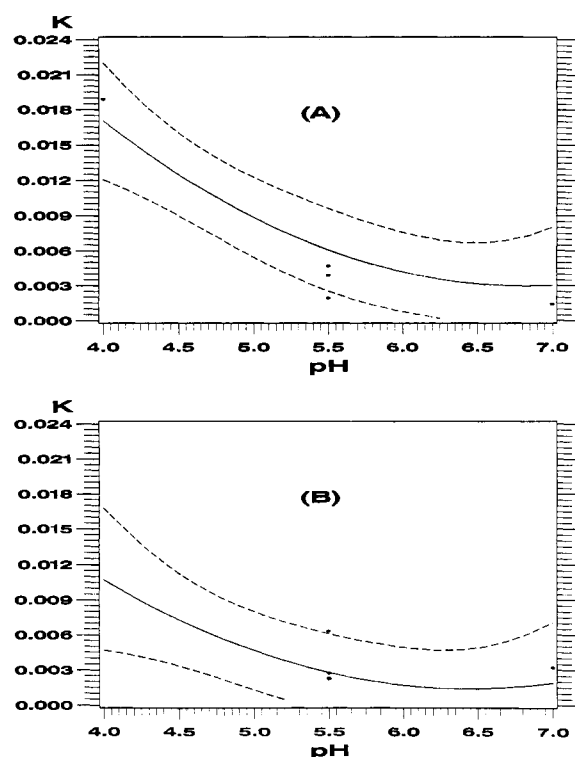


Figure 3. Partition coefficient K for acetic acid vs pH, at middle temperature and middle concentration levels: (A) ARCO oil, (B) INEL oil. Data points (●) are shown along with the statistically predicted curve (—) and 95% confidence intervals (---). Shown are the data points corresponding to the middle levels of temperature and concentration. The predicted values and prediction intervals, however, are based on data from the entire design.

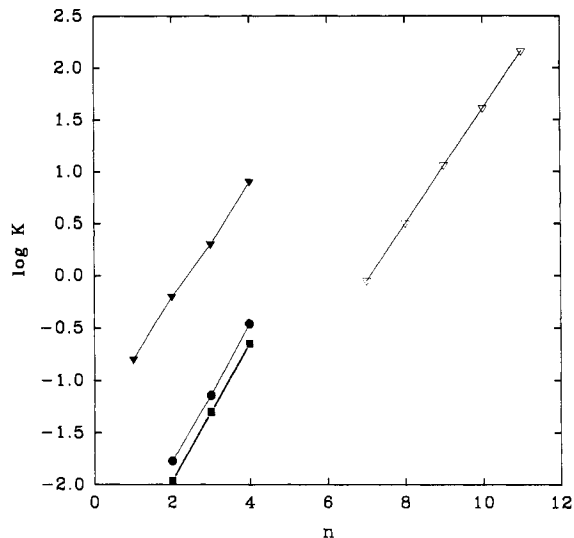


Figure 4. Partition coefficients for ARCO oil and INEL oil compared to relevant literature data: log of the partition coefficient K vs the number of carbon atoms in the organic acid (n). Shown are octanol/water (▼), oxy oil (▽), ARCO oil at pH 4, 55 °C, and the middle concentration level (■), and INEL oil at pH 4, 55 °C, and the middle concentration level (●).

the effect of pH are presented (Figures 1–3). It is evident that the variables in the experiment (pH, temperature, and organic acid concentration) have the same effect on the two types of oil. The main difference is that the ARCO oil had slightly higher partition coefficients for most of the experimental conditions. Figure 4 shows the experimental data

compared to the most comparable data which could be found in the literature (2, 3). A linear relationship between $\log K$ and the number of carbon atoms in the acid is seen in each case.

Conclusions

Temperature and acid concentration have only small effects on the partition coefficients for acetic, propionic, and butyric acids, while pH has by far the largest effect. At conditions normally expected in an oil reservoir (pH 5–7), the large majority of the acids (85+ %) will be dissolved in the aqueous phase. The log of the partition coefficient K increases approximately linearly with the number of carbon atoms in the acid. These results are true for both types of crude oil tested. Since the large majority of organic acids are dissolved in the aqueous phase at normal pH, these carbon sources are readily available for metabolism by sulfate-reducing bacteria. If reservoir conditions exist at below pH 5, however, a significant quantity of organic acids is dissolved in the oil

and could thus replenish depleted organic acids in the aqueous phase if a concentration equilibrium is maintained between the two phases.

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