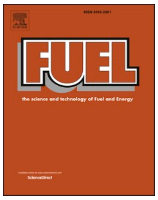
Fuel 300 (2021) 120915

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel



Full Length Article

Variation of the partition coefficient of phase-partitioning compounds between hydrocarbon and aqueous phases: an experimental study

Mario Silva [a,b,c,*], Helge Stray [c], Mahmoud Ould Metidji [a,c], Tor Bjørnstad [a,c]

[a] The National IOR Centre of Norway, University of Stavanger, 4036 Stavanger, Norway
[b] Department of Energy Resources, University of Stavanger, 4036 Stavanger, Norway
[c] Institute for Energy Technology (IFE), Department of Tracer Technology, Instituttveien 18, 2007 Kjeller, Norway

ARTICLE INFO

Keywords:
PITT
Phase-partitioning
Tracers
IOR
Ionic strength
Hydrocarbon
Temperature

ABSTRACT

Many non-ionic chemical compounds will form real solutions in equilibrium between two immiscible phases in contact. The partition coefficient (K) is defined as the quotient between the equilibrium concentration of the substance in the hydrocarbon and the aqueous phase. The reversible partition of a compound between hydrocarbon and aqueous phases is the basis of the partitioning inter-well tracer test (PITT). PITTs are of high interest for the characterization of oil reservoirs, in hydrogeology for assessment of the contamination of soils by non-aqueous phase liquids (NAPLs), and in process technology. The K value of substance is influenced by the actual chemical and physical conditions of the system where it will be used as phase-partitioning tracer. Thus, it is important to evaluate the extent of variation that the K value can exhibit under different relevant conditions.

In the present document, we report the methodology and findings from the experimental determination of the K values of 4-methoxybenzyl alcohol, 3,4-dimethoxybenzyl alcohol, 4-chlorobenzyl alcohol, 2,6-dichlorobenzyl alcohol, pyridine, 2,3-dimethylpyrazine and 2,6-dimethylpyrazine between different hydrocarbon and aqueous phases. These 7 compounds were previously identified as interesting PITT tracer candidates. Individual K-values were determined under different temperatures, compositions of the hydrocarbon phase (synthetic mixtures of toluene, isooctane, and 1-octanol and 5 real crude oils), and different ionic strengths (I) and ionic compositions of the aqueous phase. The reversibility of the partitioning phenomena was also evaluated. The composition of the hydrocarbon phase and the ionic strength of the water phase were found to influence the K values of all seven compounds. Results suggest that the substitution of monovalent ions with divalent ions in the aqueous phase, keeping the ionic strength constant, does not influence the K values. Temperature effects on the K-values are always visible for 3,4-dimethoxybenzyl alcohol, 2,6-dichlorobenzyl alcohol, pyridine, 2,3-dimethylpyrazine and 2,6-dimethylpyrazine. Dependent on the hydrocarbon phase composition, temperature also influences the K-values for 4-methoxybenzyl alcohol and 4-chlorobenzyl alcohol.

1. Introduction

Further exploration of conventional mature water-flooded oil reservoirs is necessary to satisfy the global hydrocarbon demand within the “stated policies” scenario [1]. Thus, improved oil recovery (IOR) projects will take a central part in oil production. These projects are often expensive and require a thorough knowledge about the oil reservoir. One of the most important parameters is the knowledge of the residual oil saturation (S_{OR}) in the flooded volumes between injector/producer well pairs. S_{OR} can be used to identify IOR targets, select IOR methods, and assess IOR operations. Knowledge of S_{OR} can be obtained through the partitioning inter-well tracer test (PITT). The PITT measures S_{OR} (or even remaining oil saturation) in the inter-well region of water-flooded oil reservoirs and is based on the production delay of an oil/water partitioning tracer relatively to a passive water tracer [2]. This delay is caused by the equilibrium distribution of the partitioning tracer between the near-stagnant hydrocarbon phase and the flowing aqueous phase. S_{OR} can be obtained from the time of arrival of the tracers on the producer well (either by direct calculation or incorporation in a reservoir simulator) as follows [3,4]:

$$S_{OR} = \frac{T_R - T_W}{T_R + T_W(K-1)} \tag{1}$$

---

[*] Corresponding author at: Institute for Energy Technology (IFE), Department of Tracer Technology, Instituttveien 18, 2007 Kjeller, Norway
E-mail address: mario.silva@ife.no (M. Silva).

https://doi.org/10.1016/j.fuel.2021.120915
Received 4 January 2021; Received in revised form 16 March 2021; Accepted 19 April 2021

Where T_R is the retention time of the partitioning tracer, T_W the retention time of the passive water tracer, and K the oil/water partition coefficient of the partitioning tracer. Eq. (1) is the result of a mass balance of the transport of the tracers through the porous medium of an oil reservoir, assuming a stagnant hydrocarbon phase and an instantaneous equilibrium distribution of the partitioning tracer between the oil phase and the water phase [5]. K is defined as the quotient between the equilibrium concentration of the tracer in the hydrocarbon-phase and the aqueous-phase:

$$K = \frac{C_{TO}}{C_{TW}} \tag{2}$$

Where (C_{TO}) is the equilibrium concentration of the tracer in the oil/hydrocarbon phase and (C_{TW}) its equilibrium concentration in the aqueous phase, when both phases are in contact.

While T_R and T_W in Eq. (1) are experimental data resulting from the field test, the determination of the K value of a compound is typically performed in laboratory experiments that take into consideration the chemical and physical conditions of the involved organic and aqueous fluids [3,6–9]. Such experiments are “static”, based on the produced fluids, and do not account for the variations that can occur in the field in the flooded regions between injector/producer well-pairs, such as varying temperature, salinity, or composition of the hydrocarbon phase in the path between injector/producer pairs. The partition of a substance between a hydrocarbon phase and an aqueous phase has been shown to be influenced by these parameters [10–12]. For a given system, with fixed conditions, the relationship between the equilibrium concentration of a substance soluble in both of the two immiscible phases in contact is a constant [13]. This means that, under fixed system conditions, K is independent from the initial concentration of the substance in any of the phases. Once the phases become in contact, the concentrations of the substance in both phases will vary until K reaches the value for the conditions of the system. Temperature, composition of the hydrocarbon-phase and concentration of salts in the water cause variation of the K-values, and absence of mutual phase saturation before contact of the phases and uncontrolled experimental conditions leading to results reported before distribution equilibrium is achieved, cause erroneously measured values of K for the actual experimental conditions [14–17]. To ensure accuracy of S_{OR} measurements, it is therefore important to understand how, and on what magnitude, variations in relevant factors of a hydrocarbon/water system affect the K value of substances used as phase-partitioning tracers.

The present work is primarily experimental in nature and intended to evaluate the effects of temperature, hydrocarbon composition, salt content of the aqueous phase and nature of the ions, and pH on the K value of phase-partitioning compounds. The results obtained can be used to correct the values of K used in Eq. (1) for S_{OR} determination based on the data of the field tests. For this purpose, seven molecules (2,3-dimethylpyrazine; 2,6-dimethylpyrazine; pyridine; 4-chlorobenzyl alcohol; 2,6-dichlorobenzyl alcohol; 4-methoxybenzyl alcohol and 3,4-dimethoxybenzyl alcohol) previously identified as promising phase-partitioning tracer candidates [18] were used as partitioning tracers. The experiments performed also evaluated the occurrence of partitioning and its reversibility, to ensure that a surfactant like behaviour was not observed. The K values were determined for systems with a synthetic hydrocarbon mixture as well as with real crude oil, using five different oils from fields in operation on the Norwegian continental shelf.

2. Materials and methods

2.1. Materials

4-Chlorobenzyl alcohol (99%), 2,6-dichlorobenzyl alcohol (99%), 4-methoxybenzyl alcohol (>98%), 3,4-dimethoxybenzyl alcohol (99%), pyridine (≥99%), 2,3-dimethylpyrazine (99%), 2,6-dimethylpyrazine (≥98%), toluene (anhydrous, 99.8%), isooctane (anhydrous, 99.8%) and 1-octanol (anhydrous, > 99%) were obtained from Sigma-Aldrich (Sigma-Aldrich Norway AS, 0252 Oslo). 5 oil samples from 5 oilfields on the Norwegian continental shelf (Heidrun, Norne, Snorre, Ekofisk and Eldfisk) were obtained from the respective operators.

The acronyms for the compounds used in the present study and some of their relevant properties are presented in Table 1.

2.2. Analytical instrumentation

The present study used two different techniques for identification and quantification of the studied compounds. Ultra-performance liquid chromatography (UPLC) coupled with UV detection was primarily used to quantify the tracer compounds in aqueous phases. An UPLC Agilent Technologies 1290 Infinity II (Agilent Technologies, Santa Clara, California, USA) equipped with a Waters “Acquity UPLC BEH” reversed-phase C18 1.7 µm packed column (Waters Corporation, Milford, Massachusetts, USA) was employed. The benzyl alcohols were detected at 222 nm, while the pyrazines and pyridine were detected at 254 nm. Gradient elution was used for efficient separation of the target compounds. The flow of the mobile phase was 0,5 mL/min and it was composed of 3 eluents: 5 mM NH_4HCO_2 (A), methanol (B) and acetonitrile (C). The initial composition of the mobile phase consisted of 98% A, 1% B and 1% C. The fraction of eluent B increased to 20% after 4 min and remained at this value for 1,5 min. C was kept constant at 1%. The fraction of B was then increased to 70% on minute 8 and kept for 0,5 min. The fraction of C was again kept constant at 1%. The mobile phase conditions were restored to the initial ones at minute 9 and maintained for 1 min. The total time of the chromatographic run was 10 min.

Gas-phase chromatography (GC) coupled with mass spectrometry (MS) was used primarily to identify and quantify the compounds in the organic phase. A Thermo Scientific Trace™ 1310 gas chromatograph (Thermo Fischer Scientific, Waltham, MA, USA) equipped with a chromatographic column Restek Rtx®-5MS (30 m X 0.25 mm X 0.25 µm) and coupled with a triple quadrupole mass spectrometer Thermo Scientific TSQ 8000 (Thermo Fischer Scientific, Waltham, MA, USA) was employed. 1 µL of sample with appropriate dilution was injected in split mode (1:20). The temperature of the injector was 250 °C. The carrier gas consisted of helium (99.999%) at 1 mL/min. The initial temperature of the oven was 50 °C and the value was maintained for 3 min. This was followed by a heating ramp of 30 °C /min to 290 °C. Temperature was kept at 290 °C for 8 min. The temperature of the ion transfer line was 290 °C and the ion source was kept at 320 °C. The MS was operated in electron impact (EI) ionization mode (+70 eV).

2.3. Experimental procedure

The details of the experimental procedures to study the influence of each of the tested variables on the K value of studied compounds are presented hereafter. All experiments were based on the so called “shake

Table 1
Some relevant physico-chemical properties and acronyms of the studied compounds.

Compound	M.W. (g mol^{-1})	log P	M.P. (°C)	B.P. (°C)	pKa
Pyridine	79,04	0,65	− 42	115	5,25*
2,3-Dimethylpyrazine	108,07	0,54	− 12	156	1,62*
2,6-Dimethylpyrazine	108,07	0,55	37	154	1,55*
4-Chlorobenzyl alcohol	142,02	0,82	71	232	13,9
2,6-Dichlorobenzyl alcohol	175,98	1,07	98	268	13,5
4-Methoxybenzyl alcohol	138,07	0,71	23	259	13,6
3,4-Dimethoxybenzyl alcohol	168,08	0,62	22	297	13,3

Data Source: NIST chemistry WebBook

* Value for the mono-protonated species.

flask method". This method consists of the mixing of two immiscible phases with the solute candidate tracer dissolved in one of them. After equilibrium has been reached, the concentrations of the solutes were measured in one or both phases. In all experiments the hydrocarbon phase and the aqueous phase to be used in the binary system were mutually saturated with each other before partition experiments with the solutes commenced. Only after this process the compounds under study were added (typically to the aqueous phase) by dilution of aliquots from a mother solution of known concentration. This step consisted of adding small volumes (between 500 μL and 1 mL) of the concentrated solution of the tracers to 500 mL of the aqueous phase previously saturated with the organic phase.

2.3.1. Preliminary partition experiments and influence of pH

Two aqueous solutions were prepared containing the seven studied compounds, each at a concentration of 10 mg L^{-1}, with salinities composed of 2,5% NaCl and 5,0% NaCl (m/V), respectively. 5 aliquots were taken of each of the solutions and their pH was adjusted to 5, 6, 7, 8 and 9, respectively, by adding either HCl or NaOH. A "model oil" synthetic hydrocarbon solution composed of 20% (vol.) toluene, 70% (vol.) *iso*-octane and 10% (vol.) octanol was prepared. Thus, a mixture of hydrocarbons composed of branched alkanes, aromatic, and aliphatic slightly polar components was obtained. The mixture was used in further experiments with varying fractions of *iso*-octane and 1-octanol to evaluate the effects of varying aliphatic composition and polarity of the hydrocarbons on the partitioning of the investigated molecules. An aliquot of 15 mL was taken from each of the aqueous solutions at the different pH values containing the studied compounds and placed in 20 mL vials with aluminium caps with PTFE septum. 5 mL of the model oil were added to each of the vials. The mixture was thoroughly shaken and placed in a thermal cabinet at 25 °C for 24 h. After 24 h, a 2 mL sample was taken from the aqueous phase of each vial using a syringe with a 24 ga needle. The concentration of the tracer compounds was then determined in these samples. All experiments were performed in triplicate. Using a mass balance, the concentration of the compounds in the hydrocarbon phase can be determined:

$$C_{TO} = \frac{(C_{TWi} - C_{TWf})V_W}{V_O} \tag{3}$$

Where C_{To} is the concentration of the tracers in the hydrocarbon phase, C_{TWi} is the concentration of the tracers in the aqueous phase before contact with the hydrocarbon phase, C_{TWf} the concentration of the tracers in the aqueous phase after the equilibrium contact with the hydrocarbon phase, V_W is the volume of aqueous solution and V_O the volume of the model oil used in the experiments.

2.3.2. Influence of hydrocarbon composition, water salinity and temperature on the K values

Solutions of the potential tracer compounds under study were prepared at a concentration of 10 mg L^{-1} in deionized water, 2,5% NaCl, 5,0% NaCl, 7,5% NaCl and 10% NaCl. The pH of these solutions was adjusted to 8,0 ± 0,1 by adding 280 mg L^{-1} of $NaHCO_3$. A model oil composed of 20% toluene (vol.) and varying fractions of octanol (0%−20% vol.) and *iso*-octane (60%−80% vol) was used as the hydrocarbon phase. The purpose of using such mixtures was to evaluate the effect of polarity and "nature" of the organic phase (more aromatic or more aliphatic) on the partitioning of the tested compounds. Series of 15 mL of each of the tracer solutions were placed in 20 mL vials with aluminium caps with PTFE septum together with 5 mL of the various model oil mixtures. These mixtures were shaken and placed in thermal cabinets at 25 °C, 50 °C, 75 °C and 100 °C respectively to evaluate the effect of temperature on the partitioning. After 24 h, samples of the aqueous phases were taken, and the concentration of the tracers determined by UPLC-UV.

In order to verify the reversibility of the partitioning and its independence of initial concentration, series of samples of 2 mL of the model oil solutions containing the chemical compounds from the experiments above were taken and transferred to 10 mL vials with aluminium caps with PTFE septum. 5 mL of the previously prepared solutions of 2,5% NaCl, 5,0% NaCl, 7,5 NaCl and 10% NaCl respectively were mixed with the 2 mL organic phase and the incubation process and analytical process repeated.

Many of the results obtained for 2 compounds (4-chlorobenzyl alcohol and 3,4-dimethoxybenzyl alcohol) required their individual retesting. K values for 4-chlorobenzyl alcohol exhibited sometimes very high values and the opposite was observed for 3,4-dimethoxybenzyl alcohol. In both cases, an accurate determination of the K value could be compromised if experimental adjustments were not done, as variations in the concentrations of these compounds could not be accurately determined. The same procedure described in the present point was employed with different initial concentrations of the two compounds in solution. When required, the initial concentrations of 4-chlorobenzyl alcohol and 3,4-dimethoxybenzyl alcohol were of 200 mg L^{-1} and 1 mg L^{-1}, respectively.

2.3.3. Influence of the presence of divalent ions in the aqueous phase

To examine the effect of replacing monovalent ions with divalent ions at the same ionic strength, the experiments performed as described in 2.3.2 were repeated using a fixed "model oil" mixture composed of 80% (vol) *iso*-octane and 20% (vol) toluene. The aqueous solutions of the partitioning compounds were prepared in a mixed solution of monovalent and divalent ions building up the same ionic strength (I) as the ones using only NaCl. Equation (5) was used to calculate I (expressed in M).

$$I = \frac{1}{2}\sum_{i=1}^{n} C_i Z_i^2 \tag{4}$$

Where C_i is the molar concentration of ion i (M), Z_i is the charge number of that same ion and n is the number of different ions.

The amount of NaCl present in each solution was reduce to 1/4 relatively to those described in chapter 2.3.2, and Na_2SO_4, $CaCl_2$ and $MgCl_2$ were added in sufficient amounts to reach the same values of I. Table 2 presents the amounts of each salt used and I of each solution.

2.3.4. Partition to real crude oils

The procedure described in 2.3.2 was employed using the real (stock tank) oils in replacement of the synthetic hydrocarbon mixture. Again, whenever necessary, individual tests involving different initial concentrations of 4-chlorobenzyl alcohol and 3,4-dimethoxybenzyl alcohol were performed to achieve accurate determination of the K values. All experiments were performed with 3 real replicates.

3. Results and discussion

3.1. Preliminary partition experiments and dissolution in both phases

In all preliminary experiments (described in 2.3.1) a decrease in concentration of the studied compounds in the aqueous phase was observed after equilibrium contact with the model oil. It is important to assess if the decrease of concentration is due to the establishment of a real solution in the hydrocarbon phase. A "surfactant-like" behaviour, where the compounds concentrate at the interface between phases, would also lead to a lower concentration of the compounds in the aqueous phase. This type of behaviour is unwanted. Thus, samples of the hydrocarbon phase after contact with the tracer solution were taken and analysed by GC-MS (EI mode). This mode of operation allows to obtain qualitative information about the detected peaks. Results show that the studied compounds are detected in the hydrocarbon phase. A match of the mass spectrum of 95% or greater with the library of the mass spectrometer ("NIST MS search" version 2.0) was obtained for every

Table 2
Salt, respective amount present, and I of the aqueous solutions of the studied compounds.

C. NaCl (g/L)	C. NaCl (M)	C. Na_2SO_4 (g/L)	C. Na_2SO_4 (M)	C. $CaCl_2$ (g/L)	C. $CaCl_2$ (M)	C. $MgCl_2$ (g/L)	C. $MgCl_2$ (M)	I (M)
25 *	0,43	0	0	0	0	0	0	0,43
50 *	0,86	0	0	0	0	0	0	0,86
75 *	1,28	0	0	0	0	0	0	1,28
100 *	1,71	0	0	0	0	0	0	1,71
6,25	0,11	2,0	0,014	5,1	0,046	4,4	0,046	0,43
12,5	0,22	2,0	0,014	11,1	0,10	9,5	0,10	0,86
18,75	0,32	2,0	0,014	17,0	0,15	14,6	0,15	1,28
25	0,43	2,0	0,014	23,0	0,21	19,7	0,21	1,71

*Experiments described in 2.3.2. are present in this table to show the value of I.

compound (see Fig. 1 in "supplementary materials). It is therefore safe to argue that the benzyl alcohols, pyrazines, and pyridine in the present study form a real solution in both phases and that a real partition phenomenon was observed. The study then proceeded to evaluate the influence of pH on the K value of the compounds.

3.2. *Influence of pH on the K values*

Possible modifications of the chemical structure of the compounds induced by changing acidity can affect their partitioning behaviour. Five pH values between 5 and 9 were used to evaluate the K-value of the potential tracer compounds in contact with a synthetic hydrocarbon mixture (as described in section 2.3.1). Fig. 2 presents the K values of the

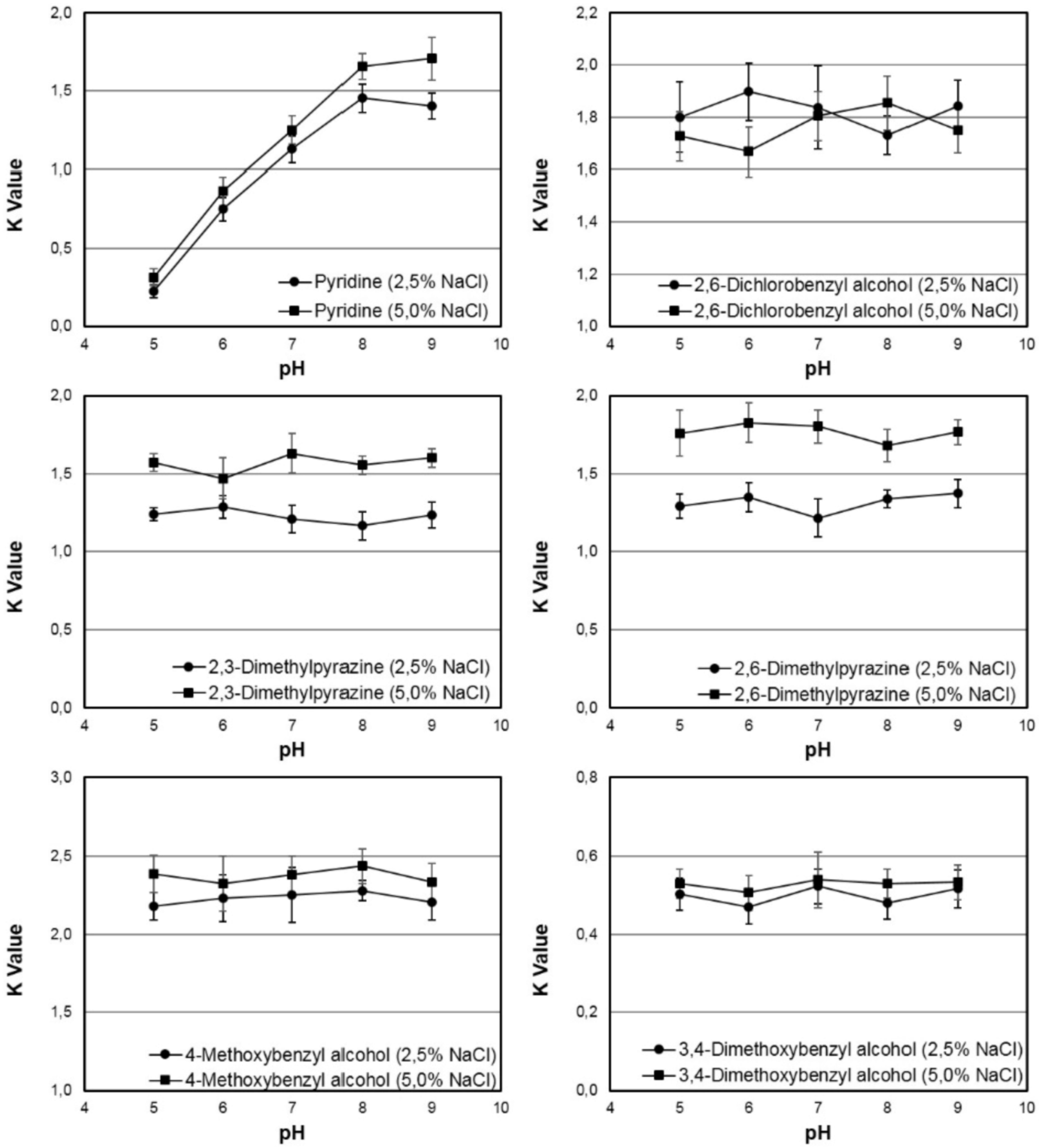


Fig. 1. K values of the partitioning compounds as function of pH at two different salinities in contact with a model oil constituted by 20% (vol.) toluene, 70% (vol.) *iso*-octane and 10% (vol.) octanol at 25 °C. For pyridine, the distribution coefficient is depicted.

tested compounds ± σ (N = 3) as function of the pH of the aqueous phase. The data about pH conditions available in the literature [19] suggests that the range of pH tested is representative for most produced waters from oilfields. The primary goal of the present study was to characterize the partition behaviour of the compounds it focusses on aiming for their use as oil/water partitioning tracers for inter-well tests in oil reservoirs. Furthermore, the range of pH studied also provides relevant information for different disciplines where the partition behaviour of the molecules in the present study plays an important role.

The results depicted in Fig. 1 show that only the partitioning of pyridine is affected by pH. The variations observed for the other compounds can be attributed to the uncertainty (when precision data is considered) in the experimental testing and analysis. The pKa-value of the protonated form of pyridine (pyridinium) is 5,25 (see Table 1). This means that pyridinium will be the predominant species of pyridine in aqueous solution when the pH value is $< 5{,}25$. As the value of pH increases, an equilibrium between the protonated and the unprotonated forms of pyridine is established. In fact, whenever the pH conditions of the system are such that the formation of pyridinium is significant, the observed distribution value is not K, but rather the distribution ratio D. D differs from K due to the fact that it accounts for all dissolved species originated by the same compound dissolved in both phases [20].

$$D = \frac{C_{T(ni)O} + C_{T(i)O}}{C_{T(ni)W} + C_{T(i)W}} \tag{5}$$

Where $C_{T(ni)O}$ is the concentration of non-ionic species of the compound in the hydrocarbon phase, $C_{T(i)O}$ the concentration of the ionic species of the compound in the hydrocarbon, $C_{T(ni)W}$ the concentration of the non-ionic species of the compound in the water phase and $C_{T(i)W}$ the concentration of the ionic species of the compound in the water phase.

Ions are not soluble in a pure hydrocarbon phase. The acid dissociation constant (K_a) for pyridinium (the protonated form of pyridine) is defined as:

$$K_a = \frac{[PYR][H^+]}{[PYRH^+]} \tag{6}$$

Eq. (6) can be rearranged and rewritten as:

$$\frac{[PYR]}{[PYRH^+]} = 10^{(pH-pKa)} \tag{7}$$

When the pH of the aqueous phase is close to the pKa value of pyridinium (5,25), substantial amounts of this substance will be present. D remains valid, however, only pyridine in its neutral form will be able to dissolve in the hydrocarbon phase. At higher pH values, the concentration of pyridinium is orders of magnitudes smaller than pyridine. Thus, acid-base equilibrium can be neglected, and the partitioning behaviour of this tracer candidates becomes like all others. The partition values for pyridine at pH 8 and 9 show no trend and the variations observed become also explainable by the precision data. To ensure no influence of pH in the K values, the rest of the present study was performed with aqueous solutions at pH 8,0.

3.3. *K Values as function of hydrocarbon composition, salinity and temperature, and reversibility of the partitioning*

The results obtained at the experimental conditions described in 2.3.2 are presented in Figs. 2–8. To facilitate the reading of the figures, all K values obtained in the experiments performed with an aqueous phase containing 2,5% and 7,5% NaCl are not depicted here in the main text. These results can, however, be found in the "supplementary material" file to this article.

The results show that the K value of compounds is generally influenced by all the parameters studied here (oil composition, temperature, and salinity). Higher values of salinity of the aqueous phase, higher temperature of the system, and increasing fraction of octanol in the hydrocarbon mixture, all cause higher partition to the hydrocarbon phase. Some exceptions are observed: temperature in the cases of 4-chlorobenzyl alcohol and 4-methoxybenzyl alcohol, and salinity in the case of 2,6-dichlorobenzyl alcohol.

Temperature drives the increase of partitioning as a result of four primary effects: i) all the compounds in the present study can form hydrogen bonds with water. Hydrogen bonds are strong electrostatic interactions that require higher amounts of energy than dipole interactions to be broken. Increasing temperatures means more energy available in the system to disturb hydrogen bonds. ii) Raoult's law

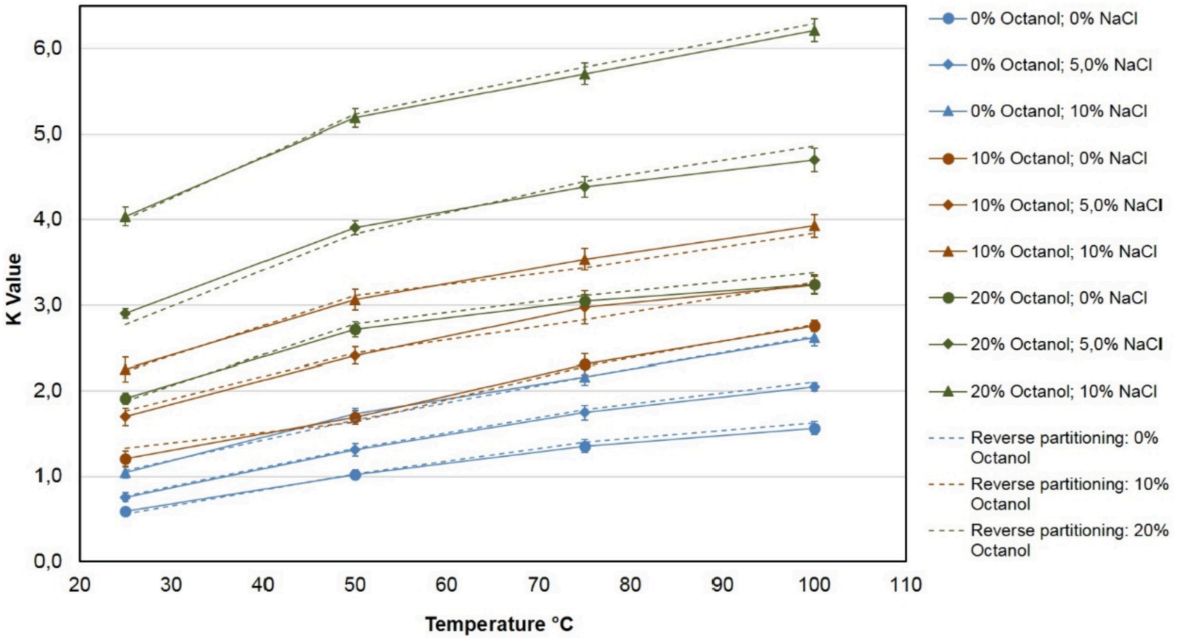


Fig. 2. K values of pyridine ± σ (N = 3) as function of temperature, composition of the hydrocarbon phase and salinity (the compound is initially dissolved in the aqueous phase). The dashed lines represent the K-values obtained under the same experimental conditions when the compound is initially dissolved in the hydrocarbon phase.

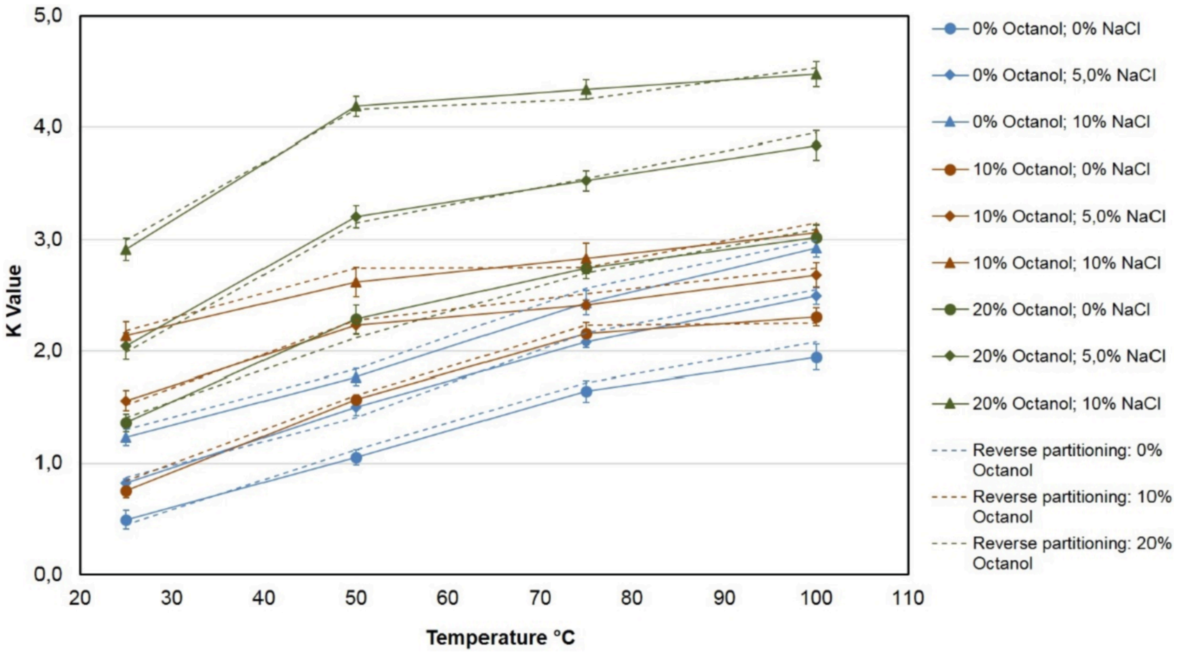


Fig. 3. K values of 2,3-dimethylpyrazine ± σ (N = 3) as function of temperature, composition of the hydrocarbon phase and salinity (the compound is initially dissolved in the aqueous phase). The dashed lines represent the K values obtained under the same experimental conditions when the compound is initially dissolved in the hydrocarbon phase.

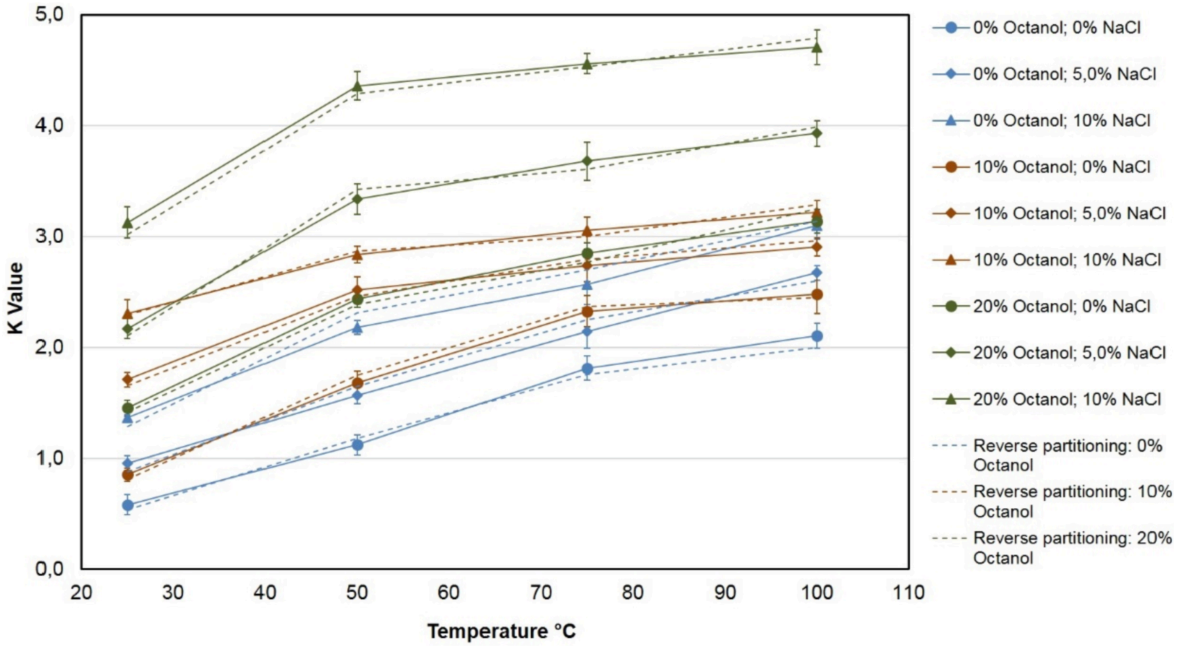


Fig. 4. K values of 2,6-dimethylpyrazine ± σ (N = 3) as function of temperature, composition of the hydrocarbon phase and salinity (the compound is initially dissolved in the aqueous phase). The dashed lines represent the K values obtained under the same experimental conditions when the compound is initially dissolved in the hydrocarbon phase.

demonstrates that the distribution of the compounds between both phases depends on their vapor pressure [21,22], and the vapor pressure of the dissolved non-ionic compounds increases with temperature. Alcohols and amines, with similar chemical structures to the molecules investigated in the present work, have been reported to exhibit strong negative deviations to Raoult's law [23]. These inaccurate predications can, however, be corrected by introducing compound-specific parameters to account for deviations from ideal behaviour in Raoult's law equations [24] and describe accurately the increase of vapor pressure as function of temperature. iii) Temperature is a measure of the velocity of the particles. Higher temperatures will increase the mobility of the molecules in solution, effect that facilitates their diffusion to the hydrocarbon phase. iv) The dielectric constant of polar compounds (such as water) varies significantly (decreases) with increasing temperatures [25]. This effect is negligible in predominantly non-polar compounds (such as hydrocarbons). The dielectric constant (is a measure of the ability of a chemical species to reduce the electric field between charges [26], to "insulate" them from each other. This requires the existence of

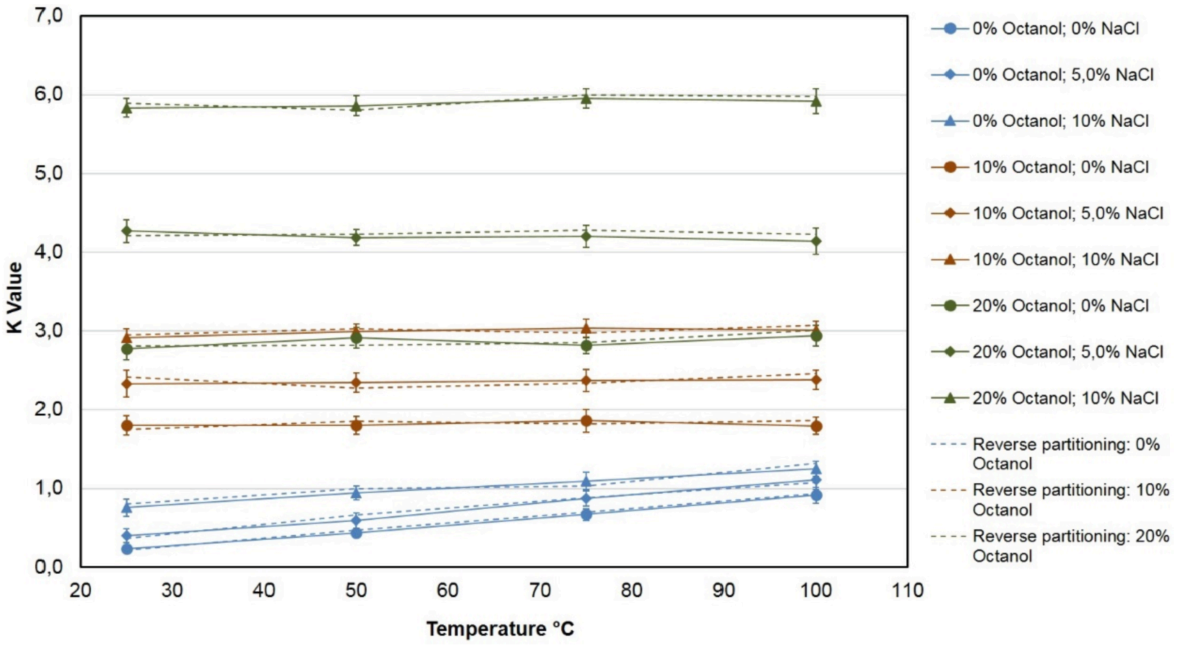


Fig. 5. K values of 4-methoxybenzyl alcohol ± σ (N = 3) as function of temperature, composition of the hydrocarbon phase and salinity (the compound is initially dissolved in the aqueous phase). The dashed lines represent the K values obtained under the same experimental conditions when the compound is initially dissolved in the hydrocarbon phase.

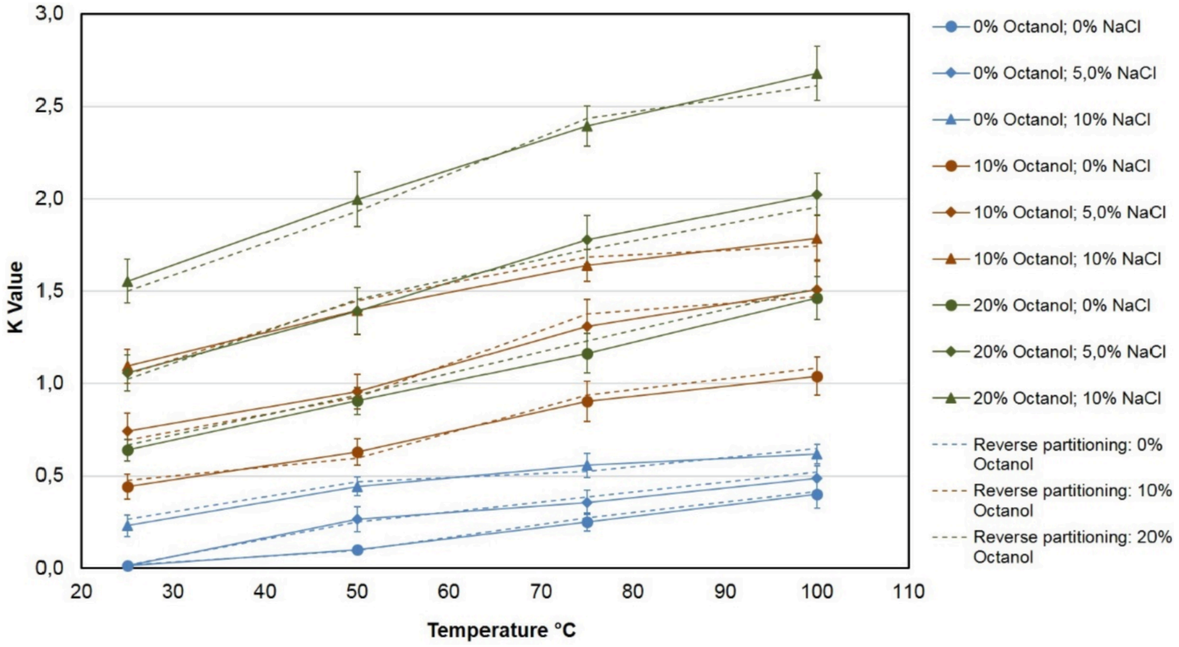


Fig. 6. K values of 3,4-dimethoxybenzyl alcohol ± σ (N = 3) as function of temperature, composition of the hydrocarbon phase and salinity (the compound is initially dissolved in the aqueous phase). The dashed lines represent the K values obtained under the same experimental conditions when the compound is initially dissolved in the hydrocarbon phase.

electrostatic interactions between the substance and the ions. The dielectric constant is therefore an indirect measure of the polarity (charge distribution in the structure) of a chemical species [27].

Consequently, increasing temperatures cause the dipole interactions between water and the compounds in solution to decrease in number and intensity. The reduction of this type of interactions reduces the "forces" keeping tracers in the aqueous phase. Results suggest that the global temperature effect on the K-values of 4-methoxybenzyl alcohol and 4-chlorobenzyl alcohol (Figs. 6 and 8) is observed only in the experiments with non-ionic aqueous phase. The extent of the influence of temperature on the partitioning is dependent on the characteristics of the molecules. The most likely scenario is that the temperature effect is very small compared to the variation of K caused, for example, by salinity. Thus, the increase of K induced by temperature on 4-methoxybenzyl alcohol and 4-chlorobenzyl alcohol is "masked" by the effect of the other parameters and appears only visible in the experiments where these compounds are dissolved in deionized water.

The K value of a compound is a measure of its relative solubility

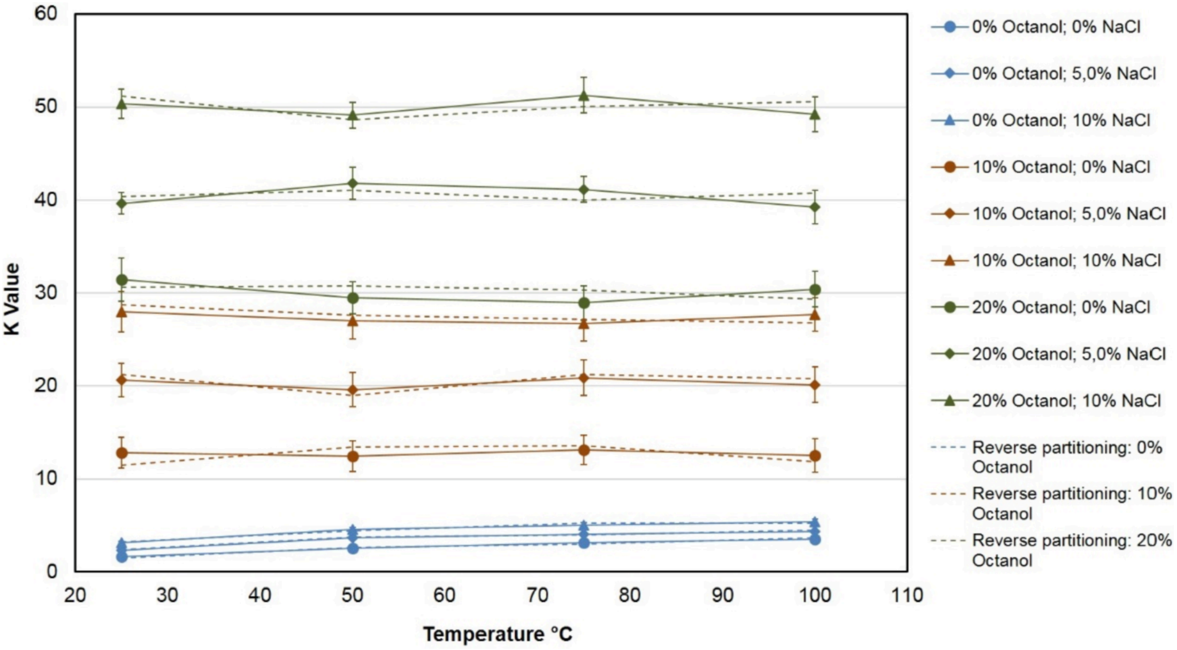


Fig. 7. K values of 4-chlorobenzyl alcohol ± σ (N = 3) as function of temperature, composition of the hydrocarbon phase and salinity (the compound is initially dissolved in the aqueous phase). The dashed lines represent the K values obtained under the same experimental conditions when the compound is initially dissolved in the hydrocarbon phase.

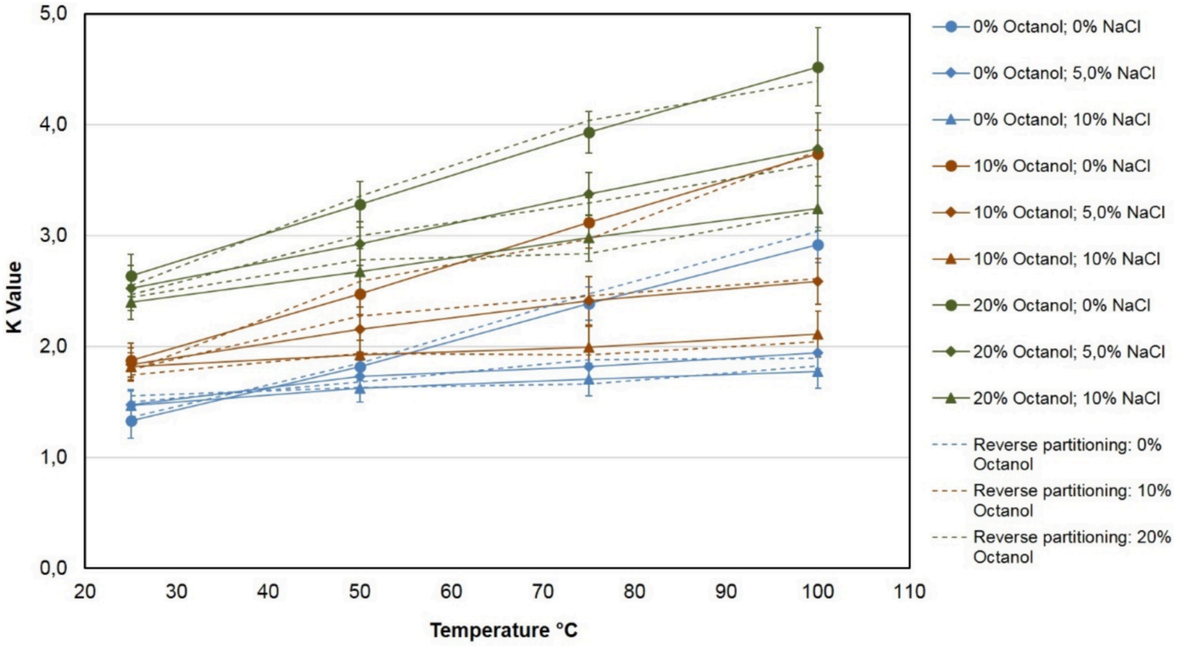


Fig. 8. K values of 2,6-dichlorobenzyl alcohol ± σ (N = 3) as function of temperature, composition of the hydrocarbon phase and salinity (the compound is initially dissolved in the aqueous phase). The dashed lines represent the K values obtained under the same experimental conditions when the compound is initially dissolved in the hydrocarbon phase.

between a hydrocarbon and an aqueous phase. Compounds which partition between such two phases are not ionized in any of the solutions. Non-ionized organic compounds are dissolved in water due to polar dipole interactions and/or the establishment of hydrogen bridges. The strength and number of available dipole and hydrogen bridges is reduced by the presence of ions in the water. This is a well-known phenomenon that generally reduces the solubility of non-ionic organic compounds in water [28,29]. The reduction of solubility of organic compounds in water caused by increasing salinity of the solution is commonly called "salting-out effect". The salting-out effect is widely explored, for example, as a sample preparation technique in analytical chemistry, particularly when liquid–liquid extraction of analytes is performed [30,31]. Increasing the amount of Na^+ and Cl^- ions in the aqueous phase reduces the solubility of molecules. Thus, more molecules will partition to the hydrocarbon phase and the K value will increase. The solubility of organic compounds in water has been correlated to the activity of the ions in solution by a proportional constant factor [28]. Results in Figs. 2–7 suggest that such a correlation is not valid when the partition phenomena is observed. The K values of the potential tracer compounds under study always increase with increasing salinity. However, the results suggest that the magnitude of the variation is also dependent on the composition of the hydrocarbon phase.

2,6-dichlorobenzyl alcohol (Fig. 8) shows a variation of K value inversely proportional to the concentration of ions in solution (K decreases with increasing salinity). No study about the solubility or partition of any benzyl alcohol as function of salinity is, to the best of our knowledge, published. While the solubility in water of non-ionic molecules generally decreases with increasing salinity, exceptions have been reported. For example, a "salting-in" effect has been described in cyclic organic compounds with chlorate and amino groups [28], and abnormal behaviour reported for benzene, naphthalene and biphenyl [32], and 1,2-benzantracene and benzo[a]pyrene [33]. A possible explanation for the "salting-in" effect observed for 2,6-dichlorobenzyl alcohol is the formation of a coordinated sphere of ions around the molecule due to its dipolar nature. 2,6-Dichlorobenzyl alcohol has 1 chlorine atom on each of the carbons bounded to the carbon with the methanolic group. Both the chlorine atoms and the oxygen are highly electronegative and consequently a negative dipole is induced on that side of the molecule and a positive dipole on the opposite end. Cations will tend to aggregate on the negative dipole side while anions will surround the molecule on the positive dipole side. Additionally, the π electrons in the benzene ring are mobile and will tend to concentrate close to the electronegative elements. This effect might even be more pronounced as the concentration of positive ions increases around the negative dipole, further enhancing the molecule's polar nature, and consequently increasing its solubility in water. This would explain not only the decrease of K value with increased salinity, but also higher values of K as function of temperature for the same salinity, as higher temperature mean more movement, thus less stable electrostatic interactions. The same type of phenomena observed for the partitioning of 2,6-dichlorobenzyl alcohol (Fig. 8) has been reported in liquid–liquid extraction operations, as for example in the works by Makoś et al. [34,35]. While studying the extraction of aromatic and aliphatic organic acids from water, the authors verified that the yield of the process would decrease with increasing NaCl concentrations for some of their target compounds. They offer a possible explanation for this phenomenon: as the concentration of NaCl increases, so do the viscosity and density of the solutions, leading to the formation of less efficient micro-emulsions where the mass transfer occurs in the interface between the phases. This is another possible explanation for the effect observed on 2,6-dichlorobenzyl alcohol.

Variations on the composition of the hydrocarbon-phase also have a significant impact on the K value of the compounds. Increasing fractions of 1-octanol generate higher K values. Hydrocarbons are generally classified as non-polar compounds, however the relative polarities between different hydrocarbons can vary significantly. Cyclic molecules, branching of the structure and increasing unsaturation are known to increase the relative polarity of this class of organic compounds [36]. This will naturally affect the extent of the lipophilic interaction which drives the partition process. Introducing a linear saturated compound into the mixture such as 1-octanol increases the influence of lipophilic interactions, such as Van der Waals forces. Furthermore, the presence of an OH group in the linear structure induces a permanent dipole on the molecule and makes hydrogen bridges possible [37,38]. Results show clearly higher K values with the increase of the octanol faction in the hydrocarbon phase. This is most likely due to two effects caused by the factors aforementioned: i) the establishment of hydrogen bridges between the OH group and the molecules (all tracers studied can establish hydrogen bridges with the solvents); ii) a "surfactant" like alignment of the tracer molecules, that increases the strength of the lipophilic forces driving then into the hydrocarbon phase.

The results of the experiments where the partition of the tracers occurs from the hydrocarbon to the aqueous phase (dashed lines in Figs. 2–8) show good agreement with the results of the partition from the aqueous phase to the hydrocarbon phase. All the differences between the obtained K values can be explained by the precision of the experimental methodology. Thus, it is safe to argue that the partitioning of the studied candidate tracer compounds between a hydrocarbon phase and an aqueous phase is constant and reversible for fixed conditions of temperature, salinity and hydrocarbon composition, vary with experimental conditions and is independent of the initial concentrations of the potential tracer compounds.

3.4. K Value as function of the presence of divalent ions in the aqueous phase

NaCl is the major salt making-up brines in oilfields. However, common oilfield brine concentrations and compositions vary considerably. Other major components may be the following divalent ions: Ca^{2+}, Mg^{2+}, Fe^{2+}, Ba^{2+}, CO_3^{2-} and SO_4^{2-} [19]. It is therefore important to evaluate whether the electrostatic interactions in the aqueous phase which influence the K value of the tracers are significantly changed by introducing multivalent keeping the ionic strength constant. Fig. 9 presents the K values obtained in the experiments described in section 2.3.3 compared to the K values in experiments with the I of the aqueous phase made-up of NaCl exclusively. The hydrocarbon phase was composed of 80% (vol) *iso*-octane and 20% (vol) toluene in this case. All K values obtained for every tested compound are presented.

Results suggest that the partitioning of the tracer candidates between phases is not dependent on the valency of the ions. No significant difference is encountered between the K values obtained in the experiments where the I of the water is made-up of divalent or exclusively monovalent ions. The ionic strength of the aqueous phase appears to be the relevant parameter.

3.5. K Values obtained with 5 crude oils from the Norwegian continental shelf

The same partition experiments as performed with synthetic hydrocarbon mixtures were carried out using crude oils from the Norwegian oil fields Heidrun, Norne, Snorre, Ekofisk and Eldfisk. These are all fields still in production on the Norwegian continental shelf. Figs. 10–16 present the K values obtained for each of the tracers and oils as function of the ionic strength of the water at two different temperatures (50 °C and 100 °C). Experiments were also performed at 25 °C and 75 °C, but the results are not presented here, again to facilitate the reading of the figures. The full portfolio of results are available in the table format in the "supplementary materials" file to the present document.

In real field experiments with PITTs, the optimum K-value to maximize the probability of success of the test vary with expected S_{OR} in the flooded volume between well pairs and with inter-well distance.

Although these limits are somewhat flexible, as they are related to the velocity of the tracers while traveling through the inter-well region and the S_{OR} present, they must be considered in the planning of a PITT. If the K value of the partitioning tracer is too low, there is the possibility that its production curve will overlap with the ones from the co-injected passive water tracers. This means that the difference in the arrival times of both tracer types is so small that it cannot be accurately determined. This will make the determination of S_{OR} impossible using Eq. (3). On the other hand, if K is too high, the time of arrival of the partitioning tracer (s) can be so long that it makes the interpretation of the test very difficult (or impossible). A PITT typically takes some months to conclude. Thus, prolonging it by a poor selection of the tracers used should be avoided. This can result in very flat production curves which significantly increase the difficulty of interpretation of the test because it is difficult (or impossible) to determine the first moment (as a reasonable measure of the arrival time) of the production curve. K values in the range 2–5 are, in average, well suited for a phase-partitioning tracer to be used in a given reservoir [8,39]. Thus, the goal of these experiments was to evaluate the range of conditions in which the compounds in the present study could be used in the field.

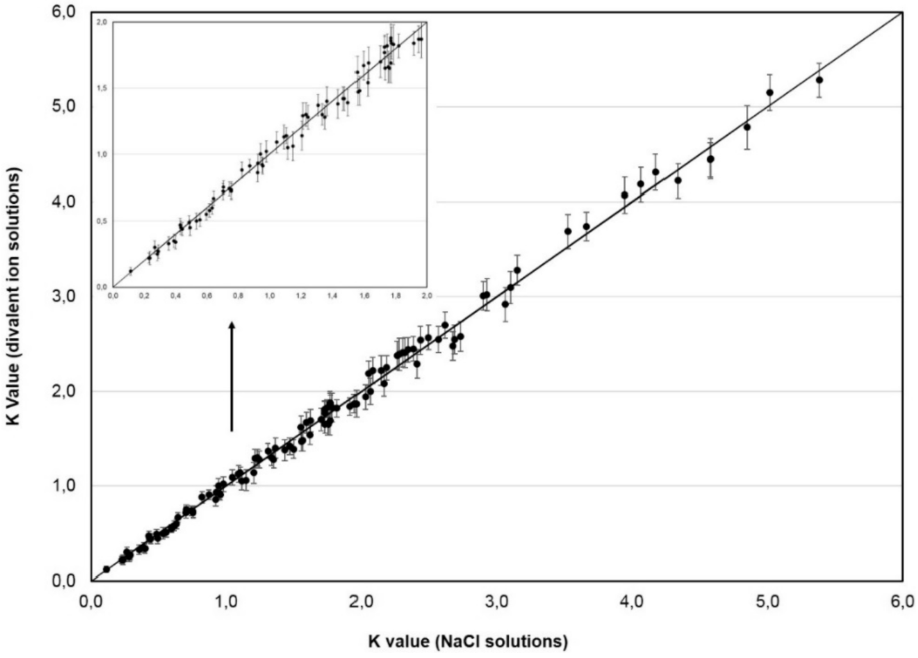


Fig. 9. K values ± σ (N = 3) of the tested compounds in experiments with an aqueous phase containing divalent ions vs the K values in experiments with an aqueous phase containing only NaCl. Hydrocarbon phase composed of 80% (vol) *iso*-octane and 20% (vol) toluene. Each point obtained from the same compound at the same conditions of temperature and I of the aqueous phase.

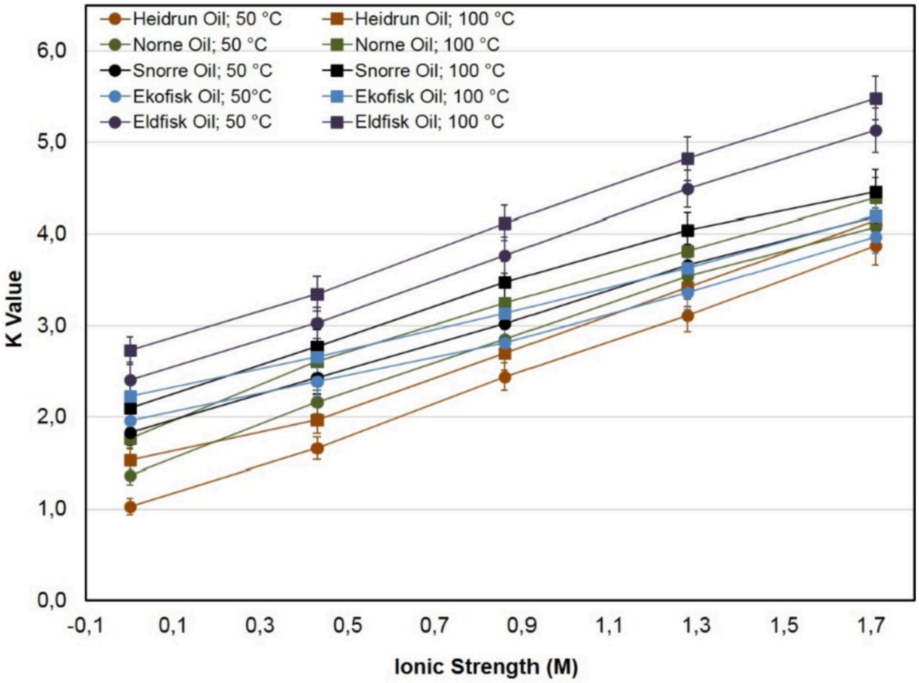


Fig. 10. K value of pyridine to 5 different crude oils as function of the ionic strength of the aqueous phase at 50 °C and 100 °C.

The results from the partitioning experiments with real oils also show the influence of temperature, salinity, and composition of the hydrocarbon phase in the K values of the tracer candidates. Furthermore, the trends produced by salinity and temperature are the same as in the experiments with the model oils. This suggests that the influence of these two parameters, although “buffered” by the hydrocarbon phase, is intimately dependent on the chemical properties of the molecules.

The range of variation of the K values of pyridine is similar to that observed in the experiments with model oil. Most of the K values obtained are well within the desired range. This suggests that pyridine would perform well as a phase-partitioning tracer for PITTs. 2,3-dimethylpyrazine and 2,6-dimethylpyrazine exhibit very similar K values for the same systems. This was also observed in the experiments with the synthetic hydrocarbon mixture. The similarity between these molecules (positional isomers) explains the small difference in K values, as the physico-chemical properties of both molecules are very similar. Generally, 2,3-dimethylpyrazine and 2,6-dimethylpyrazine also exhibit K values to the stock tank oil samples that suggest that these are promising

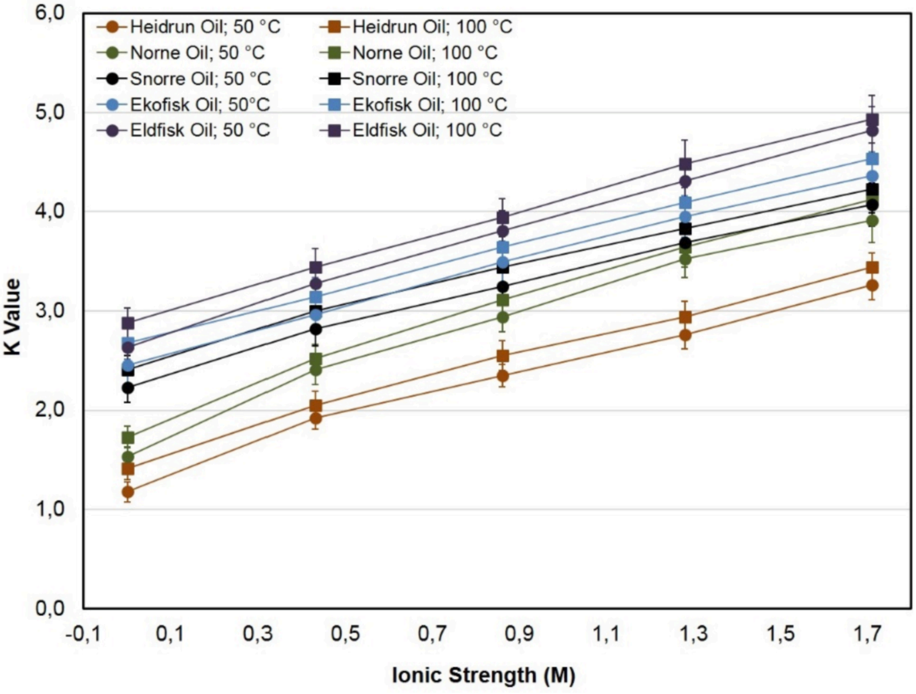


Fig. 11. K value of 2,3-dimethylpyrazine to 5 different crude oils as function of the ionic strength of the aqueous phase at 50 °C and 100 °C.

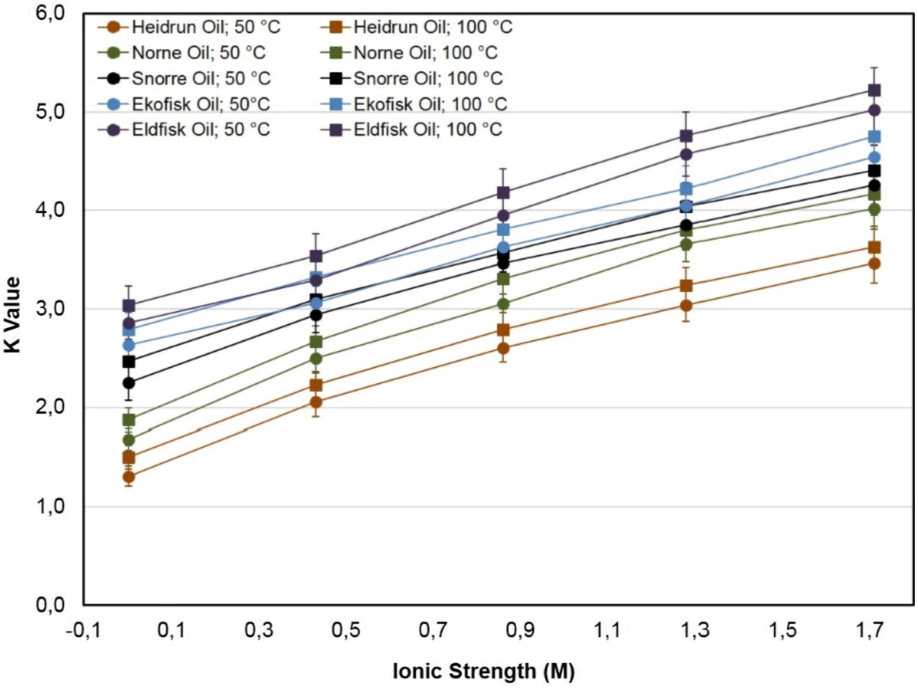


Fig. 12. K value of 2,6-dimethylpyrazine to 5 different crude oils as function of the ionic strength of the aqueous phase at 50 °C and 100 °C.

compounds for use as PITT tracers.

The partitioning of 4-methoxybenzyl alcohol to the tested stock tank oils is again independent of temperature (Fig. 13). This was also observed in the experiments with the model oil mixture of hydrocarbons whenever 1-octanol was one of the constituents. The K values of 4-methoxybenzyl alcohol vary little as function of salinity for each type of oil tested and are systematically below 2 for Heidrun and Norne oils. As a result of the low K values observed, the use of 4-methoxybenzyl alcohol as a PITT tracer is more appropriate in fields with long distances between injection/producer pairs or when high values of S_{OR} are expected. Results show that 3,4-dimethoxybenzyl alcohol (Fig. 14) is the most hydrophilic of all the tested compounds. Most of the K values with real stock tank oils are below 2. This also makes the field use of 3,4-dimethoxybenzyl alcohol more appropriate for large distances or higher oil saturations between well pairs. The partitioning of 4-chlorobenzyl alcohol to crude oils agrees with the ones obtained with the model oils when it comes to the influence of temperature. The K values of this compound is independent of temperature. 4-chlorobenzyl alcohol

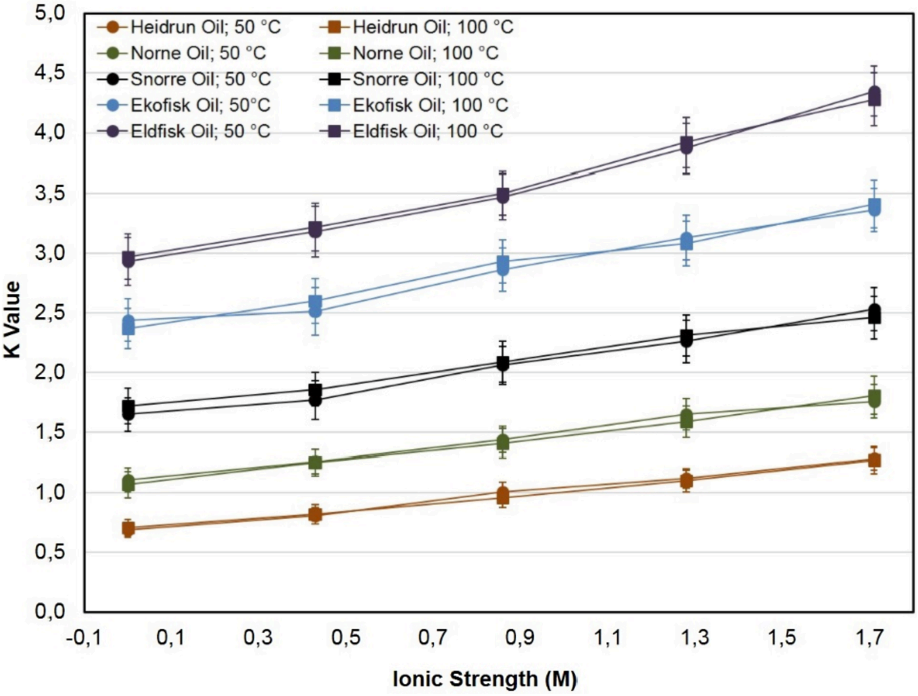


Fig 13. K value of 4-methoxybenzyl alcohol to 5 different crude oils as function of the ionic strength of the aqueous phase at 50 °C and 100 °C.

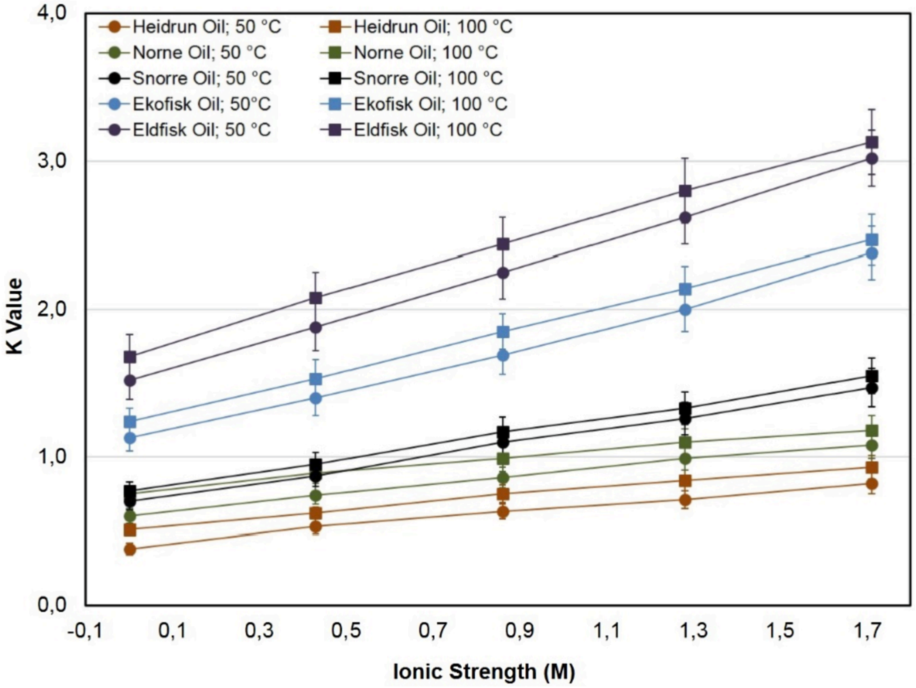


Fig. 14. K value of 3,4-dimethoxybenzyl alcohol to 5 different crude oils as function of the ionic strength of the aqueous phase at 50 °C and 100 °C.

exhibits the higher K values (Fig. 15) to the tested oils. In addition, it shows a higher variation of K as function of salinity (ionic strength) of the aqueous phase. It is the most lipophilic molecule tested and its use as PITT tracer seems more appropriate for short distances between injection and production well pairs or in situations with expected low S_{OR} in the reservoir. The K values of 2,6-dichlorobenzyl alcohol (Fig. 16) vary with the inverse of the ionic strength. Like in the experiments with the model oil mixtures, the K value of this compound decreases as function of I of the aqueous phase for all the oil types tested. Nevertheless, the range of K values obtained suggests that 2,6-dichlorobenzyl alcohol is a tracer with a wide range of applications. The decrease of K as function of the salinity of the water might make this compound particularly interesting for very high salinity reservoirs, where the K values of other phase-partitioning tracers might increase to such values that the test simply becomes too time consuming.

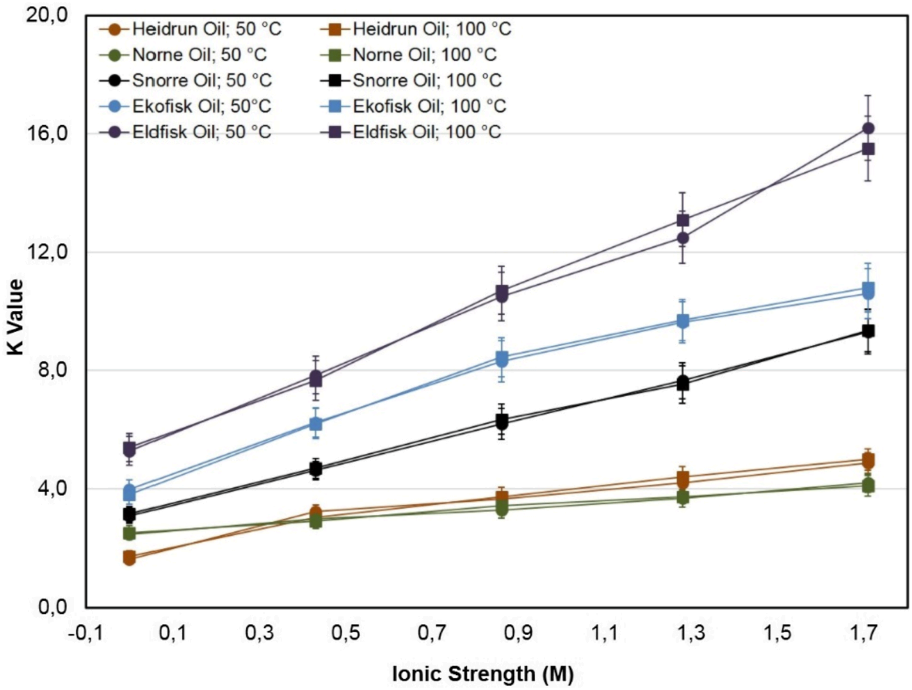


Fig. 15. K value of 4-chlorobenzyl alcohol to 5 different crude oils as function of the ionic strength of the aqueous phase at 50 °C and 100 °C.

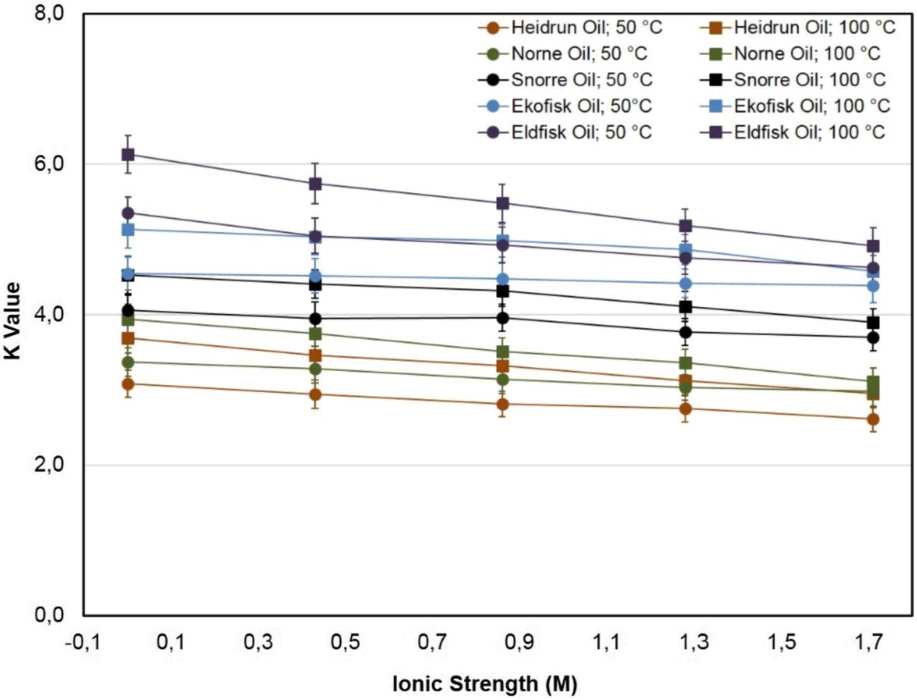


Fig. 16. K value of 2,6-dichlorobenzyl alcohol to 5 different crude oils as function of the ionic strength of the aqueous phase at 50 °C and 100 °C.

4. Conclusions

The partition coefficients between water and oil of pyridine, 2,3-dimethylpyrazine, 2,6-dimethylpyrazine, 4-methoxybenzyl alcohol, 3,4-dimethoxybenzyl alcohol, 4-chlorobenzyl alcohol and 2,6-dichlorobenzyl alcohol were determined as function of the hydrocarbon phase composition, temperature of the system and the pH, salinity (ionic strength) and ionic composition of the aqueous phase. K values were also determined with 5 different real black (stock tank) oils from different reservoirs at the Norwegian continental shelf.

All the tested compounds were found to form real solutions in the hydrocarbon phase. The phase partitioning of all the compounds was found to be constant and reversible for system with fixed properties of temperature, salinity of the aqueous phase and hydrocarbon composition. The presence of aliphatic organic molecules containing hydrophilic groups (OH) was found to increase the partitioning of every compound to the hydrocarbon phase. This effect is less pronounced for 3,4-dimethoxybenzyl and more pronounced for 4-chlorobenzyl alcohol.

Increasing temperatures also increase the K values of the molecules, except in the cases of 4-chlorobenzyl alcohol and 4-methoxybenzyl alcohol. In the case of these compounds, the temperature effect is only visible when the hydrocarbon phase is primarily constituted by aromatic organics. Results show that pH only influences the partitioning of pyridine to the hydrocarbon phase. This is the result of the basic properties of this compound that cause it to remain ionized at the lower pH values. If used together with pH insensitive tracers, pyridine might be used to retrieve real pH data from systems where it is used as tracer. Increasing the ionic strength of the aqueous phase reduces the water solubility of all the tested molecules, increasing their partition to the hydrocarbon phase, except for 2,6-dichlorobenzyl alcohol. The K value of this compound is reduced by increasing salinity in the range of ionic strength tested. The presence of divalent ions composing the aqueous phase was found to have no visible effect on the partitioning of the compounds. The ionic strength of the solution appears as the predominant parameter driving the partitioning. Pyridine, 2,3-dimethylpyrazine, 2,6-dimethylpyrazine and 2,6-dichlorobenzyl alcohol exhibit K values, as function of the tested parameters, within ranges that suggest they are appropriate for use as PITT tracers in most oilfields. The range of K values to real oils obtained for 4-methoxybenzyl alcohol and 3,4-dimethoxybenzyl alcohol indicates that these compounds are more appropriate for PITT on large distances between well-pairs or in volumes with expected high S_{OR} values. The use of 4-chlorobenzyl alcohol as PITT tracer is more appropriate for short distances between well-pairs or expected low values of S_{OR} in the flow paths.

CRediT authorship contribution statement

Mario Silva: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft, Visualization, Validation, Writing - review & editing. **Helge Stray:** Methodology, Investigation, Validation. **Mahmoud Ould Metidji:** Visualization, Validation, Writing - review & editing. **Tor Bjørnstad:** Validation, Writing - review & editing, Resources, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors acknowledge the Research Council of Norway and the industry partners, ConocoPhillips Skandinavia AS, Aker BP ASA, Vår Energi AS, Equinor ASA, Neptune Energy Norge AS, Lundin Norway AS, Halliburton AS, Schlumberger Norge AS, Wintershall Norge AS, and DEA Norge AS, of The National IOR Centre of Norway for support.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2021.120915.

References

[1] IEA. World Energy Outlook 2019. Paris: IEA; 2019.
[2] Silva M, Stray H, Bjørnstad T. Stability assessment of PITT tracer candidate compounds – the case of pyrazines. J Petrol Sci Eng 2019;182:106269.
[3] Cooke CEJ. Method of determining fluid saturations in reservoirs (US Patent 3,590,923). US Patent 3,590,923. USA: Esso Production Research Company; 1971.
[4] Tang JS. Interwell tracer tests to determine residual oil saturation to waterflood at Judy Creek Bhl'a'pool. PETSOC-91-04-01 1992;31(08):12.
[5] Deans HA. Using chemical tracers to measure fractional flow and saturation in-situ. In: SPE symposium on improved methods of oil recovery. Tulsa, Oklahoma: Society of Petroleum Engineers; 1978:10.
[6] Tang JS. Partitioning tracers and in-situ fluid saturation measurements. SPE-22344-PA 1995;10(01):33–9.
[7] Sanni M, Al-Abbad M, Kokal S, Dugstad Ø, Hartvig S, Huseby O. Pushing the envelope of residual oil measurement: a field case study of a new class of inter-well chemical tracers. J Petrol Sci Eng 2018;163:538–45.
[8] Viig SO, Juilla H, Renouf P, Kleven R, Krognes B, Dugstad O, et al. Application of a new class of chemical tracers to measure oil saturation in partitioning interwell tracer tests. In: SPE international symposium on oilfield chemistry. The Woodlands, Texas, USA: Society of Petroleum Engineers; 2013.
[9] Wood KN, Tang S, Luckasavitch RJ. Interwell residual oil saturation at leduc miscible pilot. In: SPE annual technical conference and exhibition. New Orleans, Louisiana: Society of Petroleum Engineers; 1990.
[10] Ratnakar RR, Dindoruk B, Wilson L. Experimental investigation of DME–water–crude oil phase behavior and PVT modeling for the application of DME-enhanced waterflooding. Fuel 2016;182:188–97.
[11] Zhang G, Yu J. Effect of commonly used EOR polymers on low concentration surfactant phase behaviors. Fuel 2021;286:119465.
[12] Moradi M, Topchiy E, Lehmann TE, Alvarado V. Impact of ionic strength on partitioning of naphthenic acids in water–crude oil systems – determination through high-field NMR spectroscopy. Fuel 2013;112:236–48.
[13] Leo A, Hansch C, Elkins D. Partition coefficients and their uses. Chem Rev 1971;71(6):525–616.
[14] Dearden JC, Bresnen GM. The measurement of partition coefficients. Quant Struct-Act Relat 1988;7(3):133–44.
[15] Ramachandran SD, Sweezey MJ, Hodson PV, Boudreau M, Courtenay SC, Lee K, et al. Influence of salinity and fish species on PAH uptake from dispersed crude oil. Mar Pollut Bull 2006;52(10):1182–9.
[16] Salager J-L, Marquez N, Graciaa A, Lachaise J. Partitioning of ethoxylated octylphenol surfactants in microemulsion−oil−water systems: influence of temperature and relation between partitioning coefficient and physicochemical formulation. Langmuir 2000;16(13):5534–9.
[17] Stephan C, Dicko M, Stringari P, Coquelet C. Liquid-liquid equilibria of water + solutes (acetic acid/ acetol/furfural/guaiacol/methanol/phenol/propanal) + solvents (isopropyl acetate/toluene) ternary systems for pyrolysis oil fractionation. Fluid Phase Equilib 2018;468:49–57.
[18] Silva M, Bjørnstad T. Determination of phase-partitioning tracer candidates in production waters from oilfields based on solid-phase microextraction followed by gas chromatography-tandem mass spectrometry. J Chromatogr A 2020;1629:461508.
[19] Fakhru'l-Razi A, Pendashteh A, Abdullah LC, Biak DRA, Madaeni SS, Abidin ZZ. Review of technologies for oil and gas produced water treatment. J Hazard Mater 2009;170(2):530–51.
[20] Sangster J. Octanol-water partition coefficients of simple organic compounds. J Phys Chem Ref Data 1989;18(3):1111–229.
[21] Cline PV, Delfino JJ, Rao PSC. Partitioning of aromatic constituents into water from gasoline and other complex solvent mixtures. Environ Sci Technol 1991;25(5):914–20.
[22] Chen CS, Lai Y-W, Tien C-J. Partitioning of aromatic and oxygenated constituents into water from regular and ethanol-blended gasolines. Environ Pollut 2008;156(3):988–96.
[23] González JA, de la Fuentá IG, Cobos JC. Thermodynamics of mixtures with strongly negative deviations from Raoult's Law: Part 4. Application of the DISQUAC model to mixtures of 1-alkanols with primary or secondary linear amines. Comparison with Dortmund UNIFAC and ERAS results. Fluid Phase Equilib 2000;168(1):31–58.
[24] Endo S, Schmidt TC. Prediction of partitioning between complex organic mixtures and water: application of polyparameter linear free energy relationships. Environ Sci Technol 2006;40(2):536–45.
[25] Hawthorne SB, Yang Y, Miller DJ. Extraction of organic pollutants from environmental solids with sub- and supercritical water. Anal Chem 1994;66(18):2912–20.
[26] Pinkert A, Marsh KN, Pang S, Staiger MP. Ionic liquids and their interaction with cellulose. Chem Rev 2009;109(12):6712–28.
[27] Griffiths TR, Pugh DC. Correlations among solvent polarity scales, dielectric constant and dipole moment, and a means to reliable predictions of polarity scale values from cu. Coord Chem Rev 1979;29(2):129–211.
[28] Xie W-H, Shiu W-Y, Mackay D. A review of the effect of salts on the solubility of organic compounds in seawater. Mar Environ Res 1997;44(4):429–44.
[29] Benbouzid H, Le Floch S, Stephan L, Olier R, Privat M. Combined effects of salinity and temperature on the solubility of organic compounds. J Chem Thermodyn 2012;48:54–64.
[30] Tang YQ, Weng N. Salting-out assisted liquid–liquid extraction for bioanalysis. Bioanalysis 2013;5(12):1583–98.
[31] Anthemidis AN, Ioannou K-IG. Recent developments in homogeneous and dispersive liquid–liquid extraction for inorganic elements determination. A review. Talanta 2009;80(2):413–21.
[32] Janado M, Yano Y, Doi Y, Sakamoto H. Peculiar effects of alkali thiocyanates on the activity coefficients of aromatic hydrocarbons in water. J Solution Chem 1983;12(10):741–54.
[33] Whitehouse BG. Observation of abnormal solubility behavior of aromatic hydrocarbons in seawater. Mar Chem 1985;17(4):277–84.
[34] Makoś P, Fernandes A, Przyjazny A, Boczkaj G. Sample preparation procedure using extraction and derivatization of carboxylic acids from aqueous samples by means of deep eutectic solvents for gas chromatographic-mass spectrometric analysis. J Chromatogr A 2018;1555:10–9.

[35] Makoś P, Przyjazny A, Boczkaj G. Hydrophobic deep eutectic solvents as "green" extraction media for polycyclic aromatic hydrocarbons in aqueous samples. J Chromatogr A 2018;1570:28–37.

[36] McAuliffe C. Solubility in water of paraffin, cycloparaffin, olefin, acetylene, cycloolefin, and aromatic hydrocarbons. J Phys Chem 1966;70(4):1267–75.

[37] Xing B, McGill WB, Dudas MJ. Cross-correlation of polarity curves to predict partition coefficients of nonionic organic contaminants. Environ Sci Technol 1994;28(11):1929–33.

[38] Sprakel LMJ, Schuur B. Solvent developments for liquid-liquid extraction of carboxylic acids in perspective. Sep Purif Technol 2019;211:935–57.

[39] Silva M, Stray H, Bjørnstad T. Studies on new chemical tracers for determination of residual oil saturation in the inter-well region. In: SPE Oklahoma city oil and gas symposium. Oklahoma City, Oklahoma, USA: Society of Petroleum Engineers; 2017.