

Article

Evaluation of the Kinetic and Thermodynamic Behavior of Tracers for Their Applicability in SWCTT

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Abstract: Determining residual oil saturation by the single-well chemical tracer test (SWCTT) is of key importance for assessing the potential of enhanced oil recovery (EOR) and developing EOR pilot projects. However, the test trials conducted since the first injections of tracer compositions until now have not resulted in a detailed analysis of the selection of candidates for single-well tracers and their limits of applicability in various reservoir conditions. The purpose of this study was to consider the influence of the structure on the kinetic and thermodynamic components of tracers to assess their application's operating intervals. It is shown that the rate of single-phase and two-phase hydrolysis of the primary partitioning tracer makes it possible to predict the shut-in time by calculating when the tracer is injected at the reservoir temperature. The influence of the tracer structure during the extraction process with an increase in the hydrocarbon chain of the ester in a different range of brine salinity and temperature has been studied. As a result, this work provides a method for evaluating the thermodynamic and kinetic behavior of primary tracers to establish minimum and maximum threshold *K*-values at various values of residual oil saturation, temperature, and brine salinity, taking into account the optimal time of the well shut-in to carry out at least 1/2 hydrolysis of esters.

Keywords: single-well tracer test; partition coefficients; high and low salinity; hydrolysis rate



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1. Introduction

Before applying enhanced oil recovery (EOR) methods, it is crucial to evaluate the effectiveness of the technologies used, which is especially important for late-stage fields of development [1]. It requires measuring and comparing residual oil saturation before and after applying technology to EOR. The difference between these values serves as an indicator of the effectiveness of improved oil recovery technologies. In practice, the oil saturation of the reservoir is usually determined from the data of geophysical (penetration depth ~80 cm) well surveys (well logging) and based on core studies [2,3]. Compared to expensive well logging operations or complex core studies, an alternative way to determine the oil saturation used in the field is through single-well tracer studies (having a larger exploration radius ~3–7 m) [4,5]. The single-well chemical tracer test (SWCTT) technology, used to evaluate the efficiency of EOR, makes it possible to measure oil saturation by injecting substances (usual esters) partitioned between phases (oil-water) into the reservoir through a production well, which undergo a hydrolysis reaction to form a secondary tracer (alcohol) and acid during a well shut-in time [2,4–6]. The duration of the well shut-in depends on the reactivity of the primary tracer in reservoir conditions. After the shut-in, the well is returned to production. During reverse production, fluid samples are taken through a wellhead sampler, preserved if necessary, and then analyzed for tracer content. On average, the interval for sampling wellhead production is 10–20 min [7]. The sampling frequency determines the accuracy of data interpretation when calculating the extremum of the tracer production profile.

Since the secondary tracer, alcohol, does not dissolve in oil, it is extracted before the ester, which is predominantly in oil. Based on the difference in the arrival time to

the wellhead between the two tracers and the K -value, the residual oil saturation S_{or} is calculated [5,6]:

$$S_{or} = \frac{\beta}{\beta + K} \quad (1)$$

where K -value is the partitioning coefficient (see experimental section) of primary tracer, S_{or} is the residual oil saturation, and β is the delay coefficient of the secondary tracer, which is determined by Equation (2):

$$\beta = \frac{V_1 - V_2}{V_2} \quad (2)$$

where V_1, V_2 —is the cumulative volume of fluid production containing the maximum value of the primary and secondary tracer concentration.

In recent years, the SWCTT method has become widespread as interest in the quantitative measurement of residual oil saturation has increased. Some experts [4,5] prefer the SWCTT study because of its accuracy and larger study radius. More than 600 tests have been performed to determine the residual oil saturation using the SWCTT method in the USA, Canada, the Middle East, Europe, South America, and the South Asian region [8–11]. The technique has been widely used to assess the effect of polymer, surfactant, and alkaline–surfactant–polymer (ASP) flooding and to study the impact of “Smart Water” flooding [8,12–14].

There are practically no universal substances that would become an effective SWCTT indicator for working in an extensive temperature range. Some recent studies [15] have explored the possibilities of new aromatic esters with good kinetic and thermodynamic properties in field tests. Aliphatic esters do not have such broad properties, due to which it is necessary to select candidates for tracers for specific the reservoir conditions among them.

For each tracer type, there are some criteria by which it can initially determine its suitability for SWCTT technology. To prepare aqueous solutions at the wellhead, esters with a low water solubility index, which should be at least 1% and preferably a high boiling point, are limited [16,17]. When choosing an ester, remember that the secondary tracer formed by it should have a high degree of solubility in water with the value of a measure of hydrophobicity $\log K_{ow}$ (logarithm of the molecular 1-octanol–water partition coefficient at $T = 20\text{ }^\circ\text{C}$) value not exceeding 0.3 (i.e., have a minimum partitioning in the oil phase). Table 1 shows data on the physical and chemical characteristics of esters and alcohols. If, for the secondary tracer, $\log K_{ow}$ is negative or close to 0, then, for the use of several alcohols as partitioning and non-partitioning cover tracers, $\log K_{ow}$ may be higher. Esters such as methyl formate can also be excluded since such an ester has a negative $\log K_{ow} = -0.21$, and it will not be partitioned in the oil.

In addition, the success of the performed test directly depends on the optimal choice of the tracer composition, which will contribute to the qualitative determination of the parameters required in the calculation of the residual oil saturation of the formation. The reservoir temperature determines the type of partitioning tracer utilized, which is a parameter that affects the degree of hydrolysis of the primary tracer. Formic acid esters hydrolyze 50-times faster than acetic acid esters and can be used at low reservoir temperatures in the range from 21 to 57 $^\circ\text{C}$. Above this temperature, esters of acetic acid should be preferred, as they react more slowly and are mainly used in the temperature range from 54 to 121 $^\circ\text{C}$ [24,25].

It is convenient to use the dynamic value of the 1/2 hydrolysis ($\tau_{1/2}$) to analyze the shut-in time well—the time during which half of the original primary tracer will react (i.e., $H = 50\%$). To enable the detection of tracers (primary and secondary) and the interpretation of the obtained data at the following stages at the wellhead during reverse production of the study, hydrolysis should undergo from 10 to 50% of the primary tracer–ester [4,5,25].

Table 1. Physico-chemical properties of tracer candidates [18–23].

No.	Compound Name	# CAS	Boiling Point, °C	Solubility in Water, g/100 g (20 °C)	log K_{ow}
Primary (partitioning) tracers					
1	Methyl formate	107,313	31.8	30.3	−0.21
2	Ethyl formate	109,944	54.3	9.4	0.23
3	Propyl formate	110,747	81	2.8	0.83
4	Methyl acetate	79,209	57.1	31.9	0.18
5	Ethyl acetate	141,786	77.5	8.6	0.73
6	Propyl acetate	109,604	102	2.4	1.24
7	Isopropyl acetate	108,214	89	4.3	1.02
8	Methyl propionate	554,121	79.8	6.5	0.82
9	Ethyl propionate	105,373	99	2.4	1.43
Secondary and cover tracers					
10	Methanol	67,561	64.7	Total	−0.77
11	Ethanol	64,175	78.5	Total	−0.31
12	n-Propanol	71,238	97	Total	0.34
13	i-Propanol	67,630	82.5	Total	0.05
14	n-Butanol	71,363	117.7	7.7	0.84
15	i-Butanol	78,831	108	8.7	0.76

The primary tracer is hydrolyzed to acid and alcohol exclusively in the aqueous phase, while the rate of the processes occurring is primarily due to formation (reservoir) temperature, and completeness depends on the well shut-in time. The optimal time of the well shut-in (usually 2–15 days [5,26–28]) is determined by the rate of the hydrolysis of the selected tracer at the specified formation temperature.

Thus, in order to establish the boundary conditions for the applicability of the tracer in the field, this paper considers the kinetic and thermodynamic features of primary tracers that can be used in various reservoir conditions. The estimated kinetic parameters were evaluated depending on the temperature and partitioning coefficient in the water–oil phase, and a method for selecting the working interval of the primary tracer was presented for a given residual oil saturation, produced brine salinity, and reservoir temperature, as described in the study results.

2. Experimental Section

2.1. Materials

Ethyl acetate (Sigma Aldrich, Burlington, MA, USA), ethyl formate (Acros organics, Geel, Belgium), and ethyl propionate (Sigma Aldrich, Burlington, MA, USA) with a mass fraction of the main substance >98% were chosen as primary tracers. Oil (dehydrated, without mechanical impurities, density is $825 \text{ kg} \cdot \text{m}^{-3}$) from Western Siberia deposits was used for research. Different electrolytes (sodium chloride, calcium chloride, magnesium chloride, Sigma–Aldrich, 99%) dissolved in distilled water were used to prepare the brine model.

For obtaining graphs, a solution was prepared with a different known concentration of the primary tracer in the brine model range from 0.5 to 2.5% mass. Calibration solutions were designed in the vials with disposable fluoroplastic screw caps. Gas chromatographic analysis was used to determine the concentration. The measurements were performed on an Agilent 7820 A gas chromatograph with a flame ionization detector (FID). The GC oven is equipped with a chromatographic column designed to quantify tracers in the aqueous phase. The compounds were identified by individual quenching of the pure substances.

The OpenLAB CDS ChemStation Edition software version C.01.07 SR3 was used to process the results.

2.2. Experimental Apparatus

A piston-cylinder (Amcore, Tyumen, Russia) with a volume of 50 mL was used to determine the tracer's K -value and degree of hydrolysis (Figure 1). These measurements of K -value were made under static conditions. A brine model of different concentrations was prepared by dissolving the salt in distilled water. Next, 24 mL of brine model, 24 mL of oil, and 0.5 mL of tracer were injected into the piston cylinder. Such volumes were chosen to maximize the filling of the piston cylinder and reduce the gas cap during sampling. The high-pressure piston pump created pressure in the cylinder up to 7 MPa. Samples were placed in an oven. The temperature was set at an accuracy of ± 1 °C and kept for the time required for primary tracer separation in the organic and water phases and for the hydrolysis reaction to proceed (24 h). After the expiration of time, samples of the liquid phase through the backpressure regulator were taken through the cooling line into vials with disposable screw caps made of fluoroplastic ($T = -5$ °C). After sampling, samples were analyzed on a gas chromatograph to quantify the tracer content in the aqueous phase.

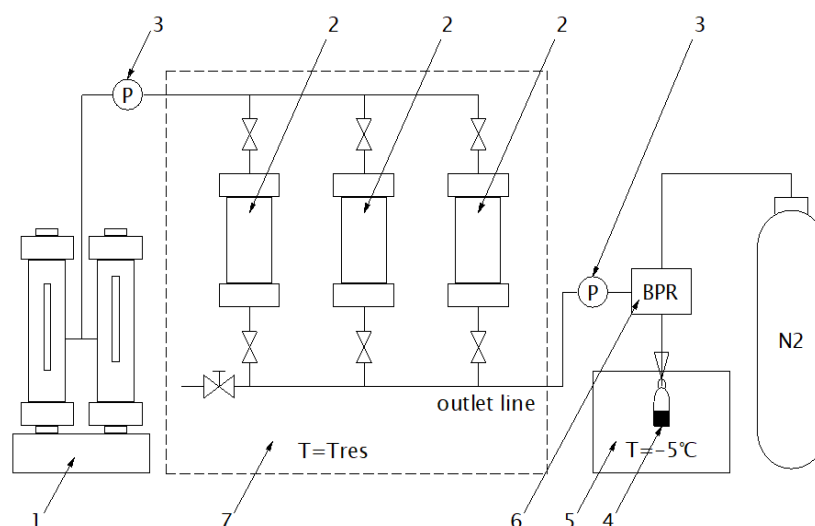


Figure 1. Scheme of equipment for tracer testing under reservoir conditions in water-organic phases. 1. High-pressure plunger pump; 2. Piston cylinder (3 pcs.) for tracer solution in oil/water phases; 3. Pressure sensors; 4. Vial for effluent collection; 5. Cryostat (thermostat); 6. Backpressure regulator; 7. Thermo-regulated oven (heating up to reservoir temperature— T_{res}).

2.3. K -Value and Degree of Hydrolysis Calculation

The equation for calculating the K -value [29] for the water phase after equilibrium for a closed system with equal volumes of water and oil phases ($V_w = V_o$) can be represented by:

$$K = \frac{C_e^{o,t}}{C_e^{w,t}} = \frac{n_e^{o,t}}{n_e^{w,t}} = \frac{m_e^{o,t}}{m_e^{w,t}} \quad (3)$$

where $C_e^{o,t}$ —concentration of ester in the oil phase at the current moment in time; $C_e^{w,t}$ —concentration of ester in the aqueous phase at the current moment in time; $n_e^{o,t}$ —the amount of ester substance in the oil phase at the current moment in time; $n_e^{w,t}$ —the amount of ester substance in the aqueous phase at the current moment in time; $m_e^{o,t}$ —the mass of ester in the oil phase at the current moment in time; $m_e^{w,t}$ —the mass of ester in the aqueous phase at the current moment in time.

Taking into account the weight loss of ester for hydrolysis and transition to the oil phase, K -value can be represented through the concentrations of tracers in the water phase as follows:

$$K = \frac{m_e^{w,i} - \omega_e^{w,t} \times m_w - \omega_{alc}^{w,t} \times m_w \times \left(\frac{M_e}{M_{alc}}\right)}{\omega_e^{w,t} \times m_w} \quad (4)$$

where $m_e^{w,i}$ —the mass of ester in the aqueous phase at the initial moment; m_w —the mass of the aqueous phase; $\omega_e^{w,t}$ —a mass fraction of ester in the aqueous phase at the current moment in time; $\omega_{alc}^{w,t}$ —a mass fraction of alcohol in the aqueous phase at the current moment in time; M_e —the molar mass of ester; M_{alc} —the molar mass of alcohol.

The last contribution to the numerator $\omega_{alc}^{w,t} \times m_w \times \left(\frac{M_e}{M_{alc}}\right)$ the mass of ester consumed for the hydrolysis reaction. For the case of a slow hydrolysis reaction rate (i.e., the hydrolysis reaction is much slower than the partitioning tracer) and for tracers used in PITT technology (which lacks hydrolysis), this contribution is zero. The ratio of the weight of the ester consumed for hydrolysis to the initial weight of the ester is the degree of hydrolysis H :

$$H = \frac{\omega_{alc}^{w,t} \times m_w \times \left(\frac{M_e}{M_{alc}}\right)}{m_e^{w,i}} \quad (5)$$

3. Results and Discussion

To estimate the 1/2 hydrolysis of the primary tracer, consider the case of hydrolysis in a single-phase system (i.e., K -value = 0). It should be noted that the degree of hydrolysis in the reaction study in single-phase (water) and two-phase (water/oil) systems are different. This is explained by the progress of two competing processes (interfacial partitioning of the ester and its hydrolysis reaction in the aqueous phase). Table 2 shows the literature data on the rate constants and the energy of activation of the neutral hydrolysis reaction of the primary tracers.

Table 2. The rate constant (k_N , days⁻¹), 1/2 hydrolysis ($\tau_{1/2}$, days), and activation energy (E_A , kJ·mol⁻¹) for neutral ester hydrolysis.

Ester	T , °C	k_N	$\tau_{1/2}$	E_A	Reference
Ethyl formate	25 °C	0.4	1.6	93	[30]
Methyl acetate	25 °C	1.5×10^{-4}	4600	-	[31]
Ethyl acetate	25 °C	5.4×10^{-5}	12,777	120	[24]
Ethyl propionate	96 °C	-	4.9	-	[6]
Methyl benzoate	175 °C	0.31	2.2	59	[32]
Ethyl benzoate	100 °C	8.6×10^{-3}	80	-	[33]

The reaction rate constants at other temperatures for the hydrolysis of some esters can be recalculated using the Arrhenius equation (Equation (6)):

$$\ln \frac{k_{T2}}{k_{T1}} = \frac{E_A}{R} \cdot \left(\frac{T_2 - T_1}{T_1 \cdot T_2} \right) \quad (6)$$

where k_{T2} and k_{T1} —hydrolysis rate constants at two different temperatures (days⁻¹); E_A —activation energy (kJ/mol); R —universal gas constant (J/mol·K).

From the calculated data obtained for the rate constant at different temperatures, we estimated the 1/2 hydrolysis for the esters shown in Figure 2. It is shown that a significant increase in hydrolysis time (well shut-in time) is caused by the replacement of the functional group from H- to CH₃- in the acid-moiety ester. Data from the literature on the reaction rate of neutral hydrolysis for esters with a chain longer than CH₂-CH₃- in acid-moiety are

limited. However, as can be seen from the kinetics of formate and acetate, an increase in the length of the hydrocarbon radical acid-moiety esters in the hydrolysis rate leads to an increase in the 1/2 hydrolysis (Figure 2, right offset). To a lesser extent, the hydrolysis time changes as the hydrocarbon substituent increases in alcohol moiety. Accordingly, varying the acid and alcohol moiety structure in the ester is key in selecting the partitioning tracer candidate for reservoirs with different reservoir temperatures.

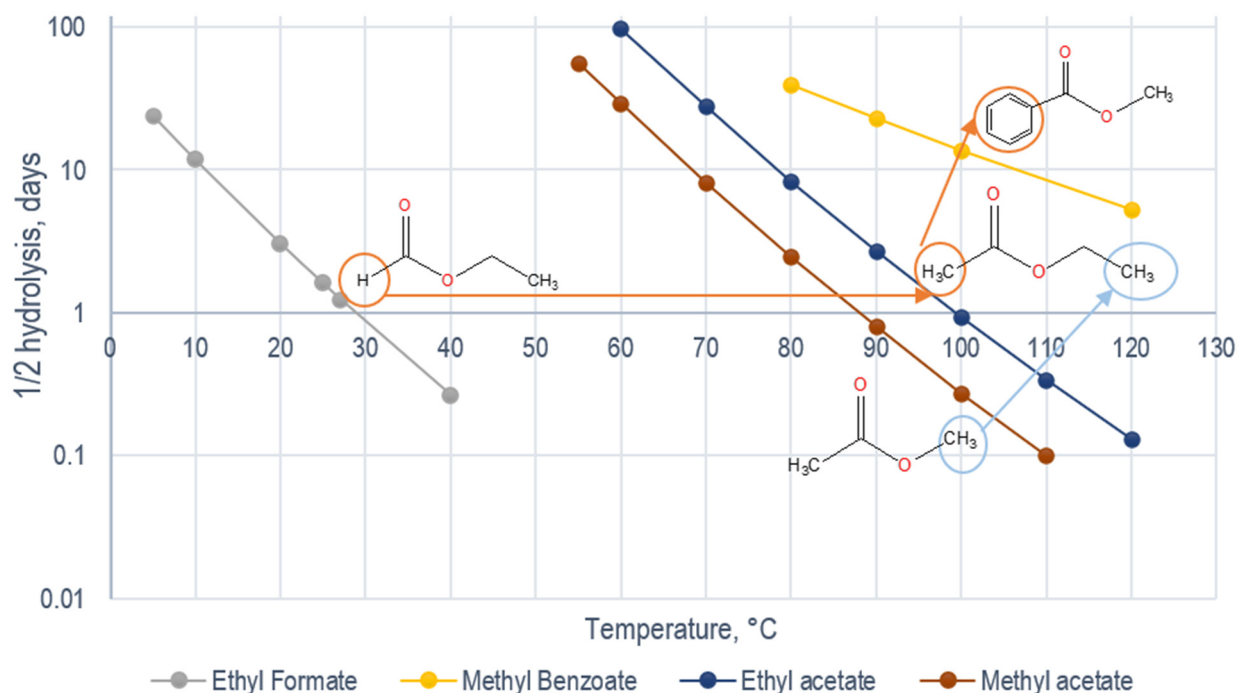


Figure 2. One-half hydrolysis (neutral) of esters at various temperatures (log scale).

However, it should be remembered that, after the injection of ester in the aqueous phase into the formation together with the hydrolysis reaction, an extraction process takes place, i.e., the partitioning of ester between two immiscible phases (water, oil). The kinetics of ester hydrolysis in a two-phase system is considered similarly according to the pseudo-first order reaction with the rate constant $k_{(2phase)}$, which is $1 + \beta$ ($\beta = K \cdot (S_{or}/1 - S_{or})$) times less than the reaction rate constant in a single-phase system $k_{(1phase)}$ [34]:

$$\frac{k_{(1phase)}}{k_{(2phase)}} = 1 + K \cdot (S_{or}/1 - S_{or}) \quad (7)$$

Thus, it follows from Equation (7) that, for the shut-in time (t_s , the 1/2 hydrolysis is used), a given K -value can be calculated after converting the reaction rate constant over the half-life from the ratio:

$$t_s = \frac{\ln 2}{k_{(1phase)}} \cdot \left(1 + K \cdot \left(\frac{S_{or}}{1 - S_{or}} \right) \right) \quad (8)$$

Analyzing the change in the 1/2 hydrolysis of the esters with different reaction rates, in Figure 3, the satisfying area of the applicability of an individual tracer can always be distinguished depending on the temperature of the reservoir at a minimum and maximum K -value. Figure 3 illustrates the effect of the K -value on the hydrolysis time, and the value of the 1/2 hydrolysis time that is required to achieve the same chosen temperature, albeit with a different K -value (depending on the type of oil, the K -value may vary). The example of the tracers of ethyl formate and ethyl acetate, using Equation (8), shows how the reaction time changes with an increase in the K -value (Figure 3); here, the value of the residual oil saturation of 0.5 was used, and the value of $1 + \beta$ in this case was equal to $1 + K$. Red dots

in Figure 3 indicate the intervals for using these tracers if the well shut-in time does not exceed fifteen days (blue shade, Figure 3).

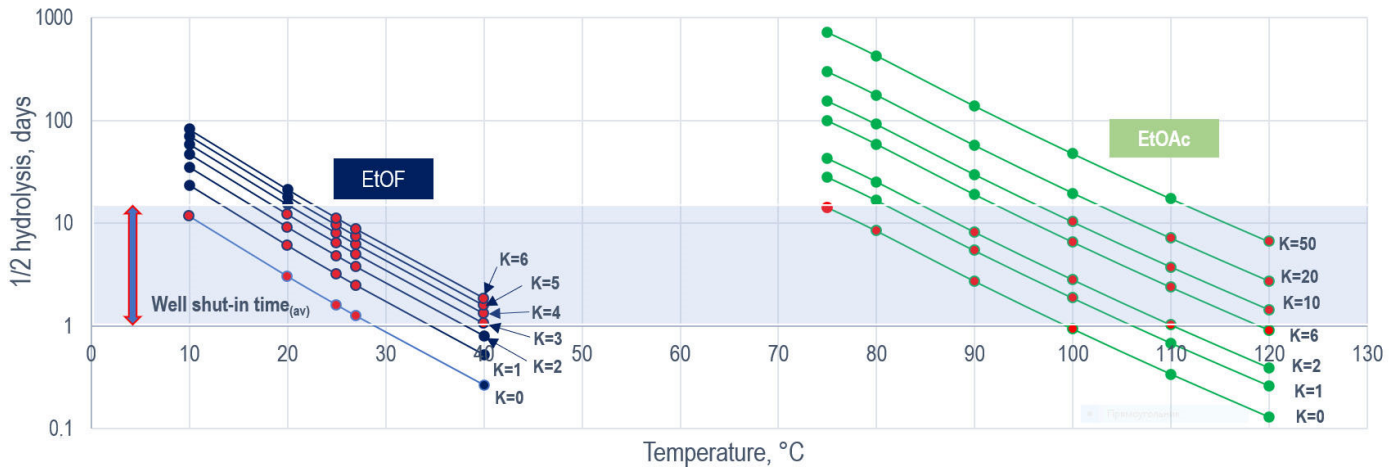


Figure 3. One-half hydrolysis (neutral) of ethyl formate and ethyl acetate in the temperature range at various K -value and $S_{or} = 0.5$ (log scale).

In this case, the non-catalytic hydrolysis of esters ($pH \sim 7$) in the temperature range at various K -values was evaluated. The effect of pH of a particular reservoir can affect the reduction in the hydrolysis shut-in time. Under reservoir conditions, the pH is difficult to control, and one reason for this is that the product of the hydrolysis reaction is acid. Thus, by establishing the hydrolysis kinetics of the primary tracer in a system of produced brine with known mineral composition and oil, it is possible to estimate as closely as possible the limits of use of such in a real single-well test.

When entering a porous medium containing residual oil, the primary tracer will pass from the mobile aqueous phase, from which it was initially injected, to an immobile oil phase until phase equilibrium is reached, as shown in Figure 4. Its total concentration in the aqueous solution decreases in proportion to the amount of residual oil. In this case, the interphase equilibrium of the primary tracer (ester) is determined by its K -value. The circulation sign in this figure explains that, since the partition coefficient must be a constant value, in order to maintain this constancy of K , the ester balances between two phases (water and oil), replenishing the lost ester during hydrolysis.

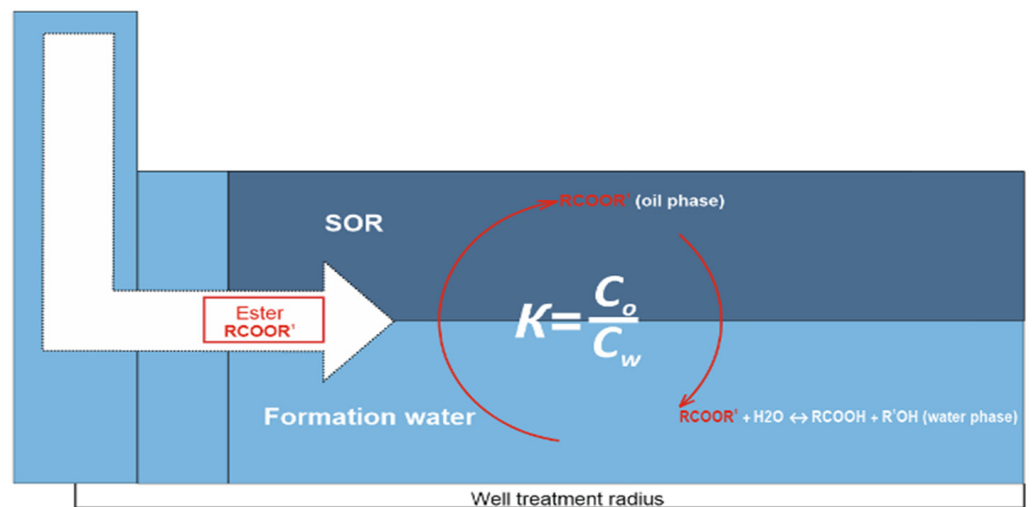


Figure 4. Schematic representation of the reactive-extraction process of primary tracer.

A too-small K -value results in insufficient separation between the tracer's production curves, increasing the error in the determination of S_{or} or even making it impossible. On the other hand, when the K -value is too high, the delay unnecessarily prolongs the test, leading to increased tailing of primary and sharp secondary tracer production history. The optimal range of K -values for a specific field depends on the anticipated oil saturation and has been proposed by Deans [17]:

$$\frac{0.5(1 - S_{or})}{S_{or}} \leq K \leq \frac{1.5(1 - S_{or})}{S_{or}} \quad (9)$$

Deans' coefficients ($\beta = 0.5$; $\beta = 1.5$) represent the optimal range of the delay coefficient of the secondary tracer β showing the K -value range taking into account the S_{or} of the formation. If residual oil saturation varies from 0.2 to 0.5, for example, the K -value used in SWCTT should be within the range of 0.5–6 based on Equation (9). If the residual oil saturation is expected to be high, a tracer with a low K -value can be selected, and the test can be terminated earlier. If the residual oil saturation is low, a common K -value tracer will not exhibit sufficient retardation for a unique estimate of residual oil [35]. However, this interval will be longer for the high salinity/high temperature (HS/HT) reservoir conditions, and the K -value can range from 6 to 50 [25]. For the high-temperature (HT) reservoir, due to the high hydrolysis rate constant, it is desirable to reduce the residence time of the primary tracer in the water phase when closing the well, which is achieved by increasing its concentration in the oil phase. It is worth noting that high K -values will simultaneously lead to an increase in retention time and, as a result, to the flattening of the primary tracer production history, which requires the injection of an additional tracer as a cover tracer (partitioning or/and non-partitioning). The main element in this case is associated with a change in the structure of esters used as primary tracers in SWCTT, in which not only a change in the rate of hydrolysis occurs, but also a change in the hydrophobic properties of the ether. For this, the work studied the effect of low and high temperatures in a different salinity range on the K -value of esters with a different hydrocarbon chain (ethyl formate \rightarrow ethyl acetate \rightarrow ethyl propionate) in a two-phase water–oil system.

For HT reservoirs, ethyl propionate can be assumed as the preferred tracer for SWCTT due to the slow rate of hydrolysis wherein it cannot be used at moderate to low reservoir temperatures. Nevertheless, the extraction tests in the water–oil system of ethyl propionate showed equally high K -values at temperatures of 60 and 90 °C in brines with investigated salinities. Therefore, the use of ethyl propionate for field tests in the HT of reservoir condition will be inefficient and will lead to a significant increase in retention time and, as a result, to the flattening of the primary tracer produced profile and accordingly the loss of the reliability of the test results. Concurrently, for ethyl acetate having less hydrophobic properties, the obtained K -value in the water–oil system has values from 4.5 up to 17 in the range of salinity from 0 to 200 g/L at 110 °C. The K -value for HT reservoirs over a wide range of salinity confirms the applicability of EtOAc with the possible use of a cover tracer to determine retention time for a reasonable shut-in time.

For an ester with a moderate rate of hydrolysis as ethyl formate, a maximum experimental K -value in the range of 4–5 at HS/LT conditions (Table 3) was found. A slight change in K -value (3.4 and 4.5) for ethyl formate at a temperature rise from 25 to 45 °C in HS region (200 g/L) suggests that it is not possible to achieve a greater partition in the oil phase. It follows from this that the injection of ethyl formate in determining the residual oil saturation is effective in reservoirs with low and high salinity with a temperature limit of 20–45 °C. At higher temperatures, 1/2 hydrolysis of ethyl formate is already below 1 day (Figure 3) and will not become higher if the K -value remains at 5. Thus, the growth of the tracer carbon skeleton in a two-phase system leads to an increase in the constant of the hydrolysis reaction rate and simultaneous growth of the K -value (decrease in affinity for the water phase), showing the boundary conditions for the use of the primary tracer for different reservoirs conditions.

An accurate K -value for certain oil type, water salinity, and reservoir temperature will always take precedence in understanding the tracer's potential for use in SWCTT. Combining the K -values obtained for ethyl formate and ethyl acetate (Table 3) with the kinetic parameters, the intervals of the partitioning coefficient of these tracers were calculated using Equation (8) when used in formations with different temperatures and oil saturation. For ethyl propionate, it was difficult to obtain similar data due to the scarcity of kinetic parameters for the hydrolysis of this ester reported in the literature. The found intervals (Figure 5, marked in color) indicate the minimum and maximum K -value thresholds at which the hydrolysis rate at a given temperature corresponds to the well shut-in time from 1 to 15 days for technological exposure at various residual oil saturation, given that the hydrolysis of the ester will leak by at least 50%.

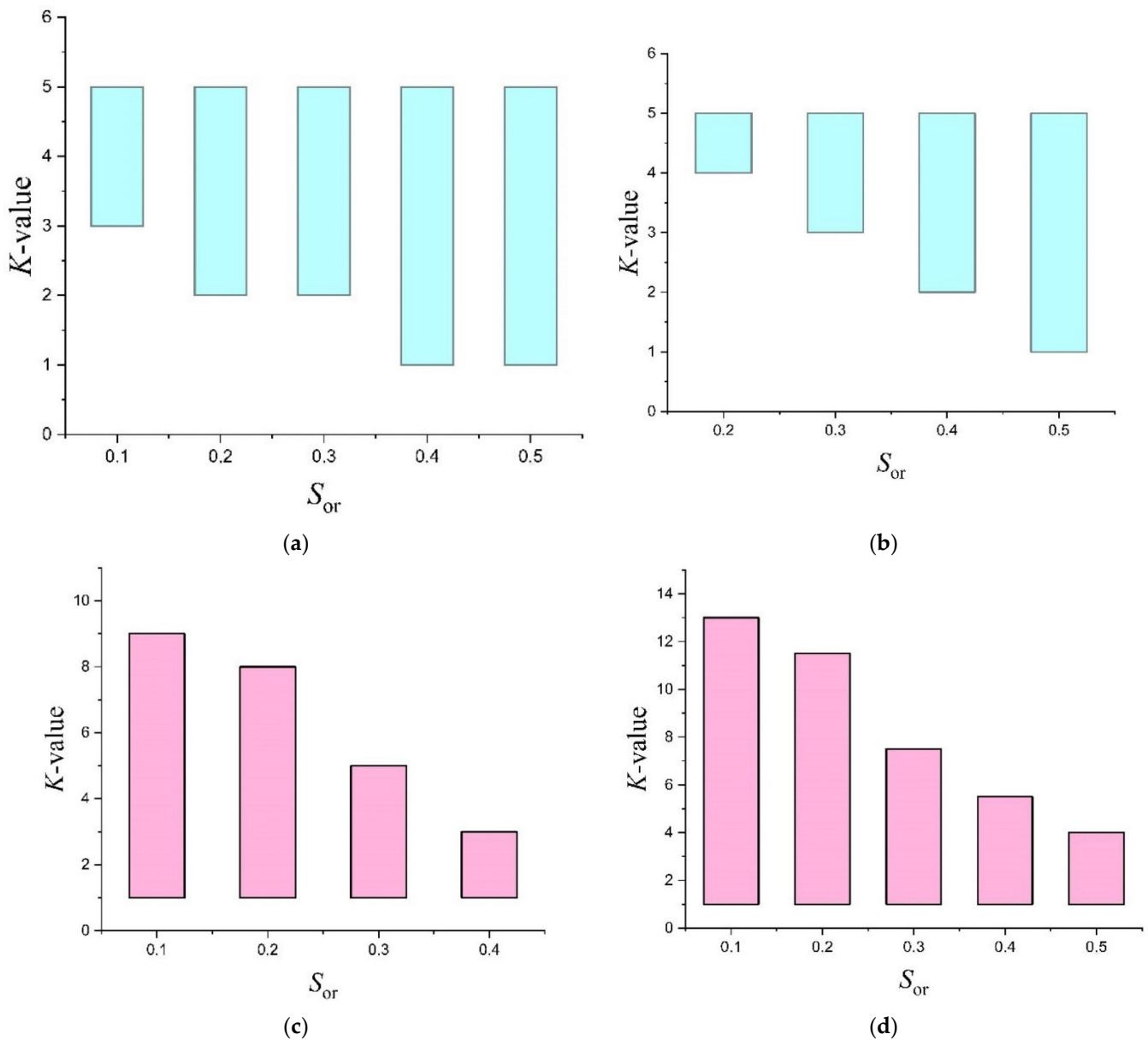


Figure 5. Range of K -values at different values of residual oil saturation S_{or} and formation water salinity, leading to the optimal well shut-in time for ethyl formate: (a) $T = 35\text{ }^{\circ}\text{C}$; (b) $T = 45\text{ }^{\circ}\text{C}$ and ethyl acetate: (c) $T = 70\text{ }^{\circ}\text{C}$; (d) $T = 90\text{ }^{\circ}\text{C}$.

Table 3. Partition coefficients (K -value) of ethyl formate, ethyl acetate, and ethyl propionate in a two-phase oil–water system (1:1) at various temperatures (T , °C) and water salinity (S , g/L).

Tracer	T	K-Value			
		$S = 0$	$S = 100$	$S = 150$	$S = 200$
Ethyl Formate	25	1	1.9	2.6	3.4
	40	1.3	2.2	3	3.6
	45	2.2	3	3.7	4.5
Ethyl Acetate	70	4	6.5	9.1	10.4
	90	4.2	8	11	13.8
	110	4.5	10.2	14.8	17
Ethyl Propionate	60	16.5	27	34	-
	90	20	29	37	-

4. Conclusions

This article focuses on the main criteria for using tracer compositions in SWCTT technology. For this, the initial requirements for primary tracers were analyzed, which should be taken into account when implementing injection in the field. Interpretation of data on the kinetics of hydrolysis of the partitioning tracer indicates the structural effect of the acid and alcohol parts of the ester with a change in its energy properties, which mainly determine the reaction rate in reservoir conditions. The existing relationship between the 1/2 hydrolysis of single-phase (water) and two-phase (oil) hydrolysis of the primary tracer at various K -values is shown, which makes it possible to calculate the optimal shut-in time.

The effect of salinity and temperature on the K -value of aliphatic esters of ethyl formate, ethyl acetate, and ethyl propionate has been studied. It has been shown that an increase in the hydrocarbon radical in the acid part of the ester dramatically changes the extraction process from the aqueous phase into the oil phase and affects the reactivity of the primary tracer in the aqueous phase, which, together, must be taken into account to optimize the composition of the tracer in certain reservoir conditions for the implementation of SWCTT projects. A method for the analytical solution of the choice of optimal primary tracers with an assessment of the boundary conditions for their applicability has been developed. This shows the required minimum and maximum threshold values of K -value at various values of S_{or} , temperature, and brine salinity, taking into account the optimal well shut-in time.

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Abbreviations

k_N	Neutral hydrolysis rate constant
$k_{(1\text{phase})}$	Single-phase hydrolysis rate constant
$k_{(2\text{phase})}$	Two-phase hydrolysis rate constant
K	Partitioning coefficient
V_o	Oil volume
V_w	Water volume
$\tau_{1/2}$	Reaction half-life (1/2 hydrolysis)
t_s	Shut-in time
$\log K_{ow}$	Octanol/water partition coefficient
S	Salinity
EtOF	Ethyl formate
EtOAc	Ethyl acetate
EtOPr	Ethyl propionate
MeOAc	Methyl acetate
LSW	Low salinity water
HSW	High salinity water
LT	Low temperature
HT	High temperature

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