

AJKFLUIDS2019-5305

DRAFT: LARGE SCALE WETTABILITY QUANTIFICATION IN POROUS MEDIA USING TRACERS

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ABSTRACT

Tracers are widely used to study physical phenomena taking place inside the porous medium such as hydrodynamics of the reactor by residence time distribution, and characterizing the oil reservoirs for heterogeneity and residual oil saturation. In this work, we use tracer techniques to characterize oil phase tracers to quantify the wettability of a fluid in a multi-phase flow in a porous medium. The wetting fluid will have more contact area with the sediments. The quantification of contact area of a fluid with sediments during flow will give us insights into the wettability and wettability alteration. A two tracer method is used to quantify the wetted area by one fluid in the porous medium. We first find the adsorption characteristics of the tracers for non-aqueous-phase tracers on the sediments. Subsequently flow experiments are performed to conduct residence time distribution (RTD) analysis using single phase flow. The adsorption characteristics during flow are identified for various flow rates. The difference in RTD curves of the two tracers of a phase is used to estimate the area in contact with the fluids with the sediment surface.

NOMENCLATURE

A Absorbance
 A_w Amount of sediments in contact with the liquid (gm)
 c Concentration of solution (mol/lit)

C_{eq} Concentration at equilibrium (mol/lit)
 C_{exit} Exit tracer concentration (mol/lit)
 C_i Injected tracer concentration in the inlet steam (mol/lit)
 ϵ A constant for a particular substance at a particular wavelength (lit/(mol.cm)), called molar absorptivity
 $F(t)$ Cumulative distribution function
 K_a Adsorption partition coefficient (ml/gm)
 l Optical path length or cuvette length (cm)
 m Amount of dry porous substrate (gm)
 M_i Amount of tracer injected in pulse input stream (mM)
 ϕ Porosity
 Q Volumetric flow rate of liquid solvent (ml/min)
 q No of moles adsorbed/gram (mol/gm)
 ρ_L Density of the flowing fluid (gm/ml)
 τ_{na} Mean residence time of non-adsorbing tracer (min)
 τ_a Mean residence time of adsorbing tracer (min)
 V Bulk volume of the porous substrate (ml)

INTRODUCTION

To increase oil production from porous sediments of the oil reservoirs using tertiary recovery methods, characterization of the porous reservoirs is necessary. Wettability of the sediments is one of the most important property of the reservoirs, which governs the tendency of oil to adhere to the rock surface in presence of another fluid [1–7]. The fluid phases present inside the reservoirs are water, oil and gas. Generally, water is more

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wetting and occupies the smaller pores and grain surface of the larger pores [8]. If the reservoir is water wet, a lot of oil can be recovered before water production starts called water breakthrough [8]. However, if the reservoir is oil wet, water flows more easily through larger pores leading to quick water production and lower oil recovery [2, 7].

Wettability alteration using surfactant is suggested to recover more oil from these oil wet reservoir. In recent years, low-salinity water flooding is used to improve the recovery from oil wet reservoirs [9]. The wettability alteration due to low salinity is hypothesized as the governing phenomenon for increased oil recovery. However, wettability quantification has been difficult at large scale.

Various methods are used to quantify wettability in oil rocks like Contact Angle method, Amott-Harvey Index and USBM methods [5, 6]. Contact Angle method is applied to a small core or a smooth surface only, therefore is not a scalable method for large scale wettability quantification [1, 3, 7]. Amott-Harvey Index method uses resident fluid displacement by spontaneous imbibition and forced imbibition to quantify wettability. This method also is not scalable to reservoir as it is not possible to apply different pressures at the well. USBM method is very similar to Amott-Harvey Index and wettability is quantified by the work done in displacing the fluid at different injection pressures. USBM method is generally used for oil sediments however is applicable to very small rock samples only [1, 5].

Tracers have been widely used for characterizing oil reservoirs for quantifying residual oil or heterogeneity [10–13]. Only a few studies are available which investigate the application of tracer technique for wettability determination [14]. The wetted area by a liquid in a porous medium can be used to quantify the wettability of the liquid. To this end, Schwartz et al. [15] used a dual tracer method to quantify wetted area of a liquid on the catalyst in a gas-liquid trickle bed reactor. However, applicability of this method for a liquid-liquid system in a fine porous medium like oil reservoirs has not been established.

In this work, we characterize oil phase tracers for quantifying wettability using dual tracer method [15]. In the dual tracer method, one tracer of the oil phase is a passive tracer and the other one is an adsorbing tracer. We estimate the adsorption partition coefficient of tracers for oil phases using batch experiments. We also perform flow experiments using single phase to quantify adsorption coefficient for various flow rates. Using the flow adsorption coefficients we will be able to estimate the mass or the area of the sediments in contact with the liquid.

METHODOLOGY TO QUANTIFY THE WETTED AREA (A_w)

To quantify wetted area using tracer, two tracers are needed for one phase. One tracer should be a non-adsorbing tracer and another one should be an adsorbing tracer.

The first moment of the exit age density of an ideal or non-adsorbing tracer can be estimated by mean residence time (MRT) distribution as given in Eqn. (1);

$$\tau_{na} = \frac{\phi V}{Q} = \left(\frac{Q}{M_t} \right) \int_0^{\infty} t C_{exit}(t) dt, \quad (1)$$

where, ϕ is the porosity, V is the bulk volume of the porous substrate (ml), Q is the fluid flow rate (ml/min), τ_{na} is the mean residence time (MRT) of the non-adsorbing/ideal tracer (min), C_{exit} exit tracer concentration (mol/lit), t is the exit time after injection (min) and M_t is the amount of the tracer injected in pulse input stream (mM). Now if adsorbing tracer is injected in a similar manner and in similar conditions, then the first moment of the exit age density of the tracer is estimated by mean residence time, which is more than the MRT of the non-adsorbing tracer given by,

$$\tau_a = \frac{\phi V}{Q} + \frac{K_a A_w}{Q}, \quad (2)$$

where, τ_a is the mean residence time of the adsorbing/ non-ideal tracer (min), K_a is adsorption partition coefficient (ml/gm) and A_w is the wetted solid mass of the substrate (gm) or it can be written in terms of wetted area of the solid. Delay in the re-

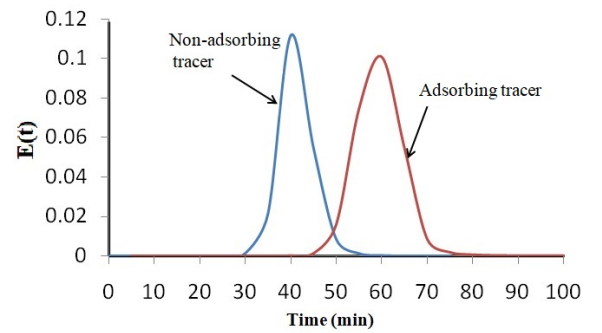


FIGURE 1. DUAL TRACER METHOD, PULSE INPUT, EXIT AGE DENSITY FUNCTION VERSUS TIME PLOT FOR ADSORBING AND NON-ADSORBING TRACER.

sponse curves shown in Fig. 1, can be estimated by the difference in the MRT, equal to $\frac{K_a A_w}{Q}$. To quantify the A_w by the dual

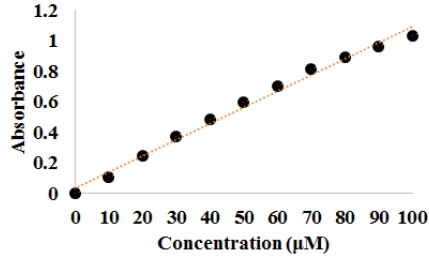


FIGURE 2. CALIBRATION CHART OF IDB AT 233 nm.

tracer method, K_a is needed. K_a can be found using batch experiments, however flow conditions can affect the adsorption of the adsorbing tracer. Therefore, at laboratory scale flow experiments are performed to quantify adsorption coefficients at different flow rates. Below we present batch and flow experiments for organic phase tracers.

BATCH EXPERIMENTS FOR ADSORPTION COEFFICIENT OF ORGANIC TRACERS

n-dodecane (DD) is chosen as oil phase, proxy for reservoir oil. Silica gel particles of sizes 60 – 120 mesh (120 – 250 μm), surface area 350 – 450 m^2/gm are used as proxy sediments. Hukan et al. [16] have used p-dibromobenzene (DBB) and Iodobenzene (IDB) as tracers for organic phase to measure liquid carry over from scrubbers. Both tracers are easily detectable in laboratory, are commercially available and are not found initially in the reservoirs [16]. We use p-dibromobenzene and Iodobenzene as are possible adsorbing and non-adsorbing tracers for oil reservoir. UV-vis spectrophotometer is used to measure tracer concentrations in the oil phase. UV-Vis spectrophotometer works on Beer Lambert's law, which is given in Eqn. (3);

$$A = \log_{10} \frac{I_o}{I} = \epsilon c l \quad (3)$$

where, A denotes the absorbance, l is the optical path length or cuvette length (cm), c is the concentration of solution (mol/lit) and ϵ is a constant called molar absorptivity or molar extinction coefficient. From Eqn. (3) we observe that absorbance is proportional to concentration of the sample. UV-vis spectrophotometer scans are done in wavelength ranging of 200 – 350 nm for oil phase tracers. Figures 2 and 3 show the calibration chart of absorbance versus concentration for IDB at 233 nm wavelength and for DBB at 230 nm, respectively obtained for concentrations ranging from 10 μM to 100 μM . A day wise variation was seen in the slope of the calibration curve which may be due to

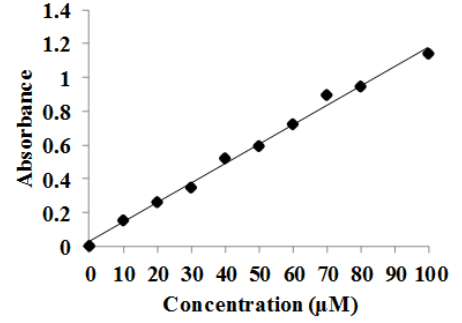


FIGURE 3. CALIBRATION CURVE OF DBB AT 230 nm.

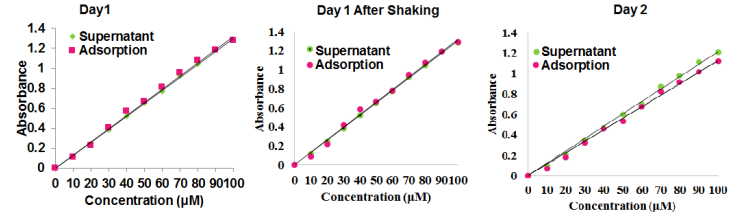


FIGURE 4. ADSORPTION ISOTHERMS FOR (IDB).

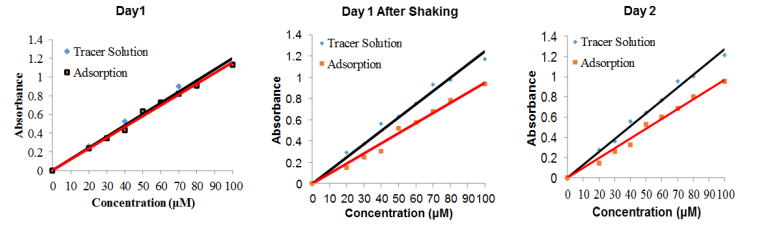


FIGURE 5. ADSORPTION STUDY OF (DBB) ON SILICA SUBSTRATE.

the oxidation of dodecane in presence of air or due to solvent evaporation. Dodecane reacts with air and forms dodecanone or dodecanol [17]. The sequence of reaction that take place in n-dodecane when it comes in contact with air have been studied by Crecente et al. [17]. Therefore during adsorption experiments, while taking UV spectra, we used a same age reference of DD to obtain a single calibration curve as shown in Figs. 2 and 3.

For batch experiments of adsorption, concentration of IDB and DBB ranging from 10 μM to 100 μM are contacted with silica gel and the sample is shaken. Adsorption experiments are carried out at room temperature [16]. Three solid to liquid ratios are used for the estimation of adsorption partition coefficient (K_a) i.e., for 1 gm of silica gel particles 10, 12 and 14 ml of tracer solutions are used.

Figures 4 and 5 show the adsorption of IDB and DBB over silica sediment, respectively. Where, Day1 represents

TABLE 1. BATCH ADSORPTION EXPERIMENTALLY MEASURED K_a VALUES FOR (IDB) AND (DBB).

Sample, (gm/ml)	IDB, $K_a(\text{ml/gm}, 1/\text{gm})$	DBB, $K_a(\text{ml/gm}, 1/\text{gm})$
1/10	0.01, 0.001	2.7, 0.27
1/12	0.02, 0.001	3.3, 0.28
1/14	0.01, 0.001	4.2, 0.30

no change in IDB and DBB concentration in contact with silica substrate before shaking, but after shaking we observe change in concentration for DBB only. In Day2 the change in concentration of DBB is maintained, indicating DBB adsorption on silica gel. The amount of tracer adsorbed per unit mass of silica (q_e) is calculated by using Eqn. (4).

$$q_e = \frac{V(C_{in} - C_{eq})}{m} \quad (4)$$

where, V is the liquid volume of the sample (ml), m is the mass of the silica gel particles (gm), C_{in} and C_{eq} are the initial (known) and equilibrium concentration of tracer in the solution (μM).

The adsorption partition coefficient (K_a) of the tracer is measured by the slope of the adsorption isotherm, which relates the adsorbed tracer on the silica gel surface to the concentration of the tracer in the solution at equilibrium. Equation (5) is used to calculate the K_a (ml/gm).

$$K_a = \frac{q_e}{C_{eq}} \quad (5)$$

K_a measured for IDB and DBB presented in Tab. 1. We present K_a in ml/gm for different liquid-solids ratios from Eqn. (5) as well as adsorption per ml of the tracer solution in 1/gm, respectively. We observe that, the adsorption coefficients of DBB are approximately 0.28/gm and IDB does not adsorb on silica gel.

FLOW EXPERIMENT FOR ADSORPTION COEFFICIENT OF ORGANIC TRACERS

The schematic of the apparatus used to perform the flow experiments with step tracer input is shown in Fig. 6. Flow experiments are performed at normal temperature and pressure in a horizontal cylindrical acrylic tube (2.5 cm diameter. and 14

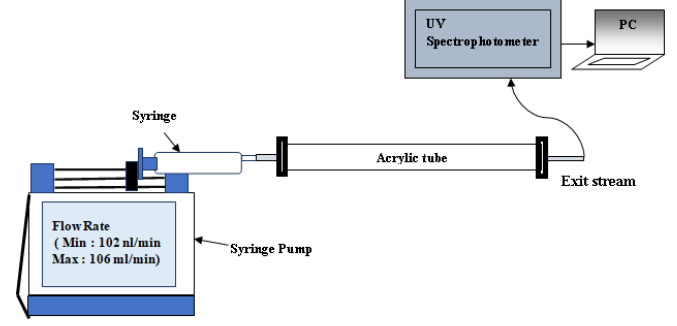


FIGURE 6. SCHEMATIC OF FLOW EXPERIMENTAL SETUP.

cm in length). The acrylic cylindrical tube is completely packed with dry porous silica gel particles. Pure dodecane is injected with a constant flow rate from the inlet of the tube. Continuous flow is maintained by a syringe pump. The fluid flow of the solvents is maintained until the ageing of silica-gel with DD in the porous pack, which is detected by same UV spectra of the two consecutive outlet samples. A 100 ml solution of 1000 μM tracer concentration is prepared in a beaker and filled in the syringe (60 ml). At time $t = 0$, we switch the pure DD with the tracer sample solution (1000 μM tracer solution) and start to collect the exit stream at a constant time interval. The exit tracer concentration is measured by UV- vis spectrophotometer. The ratio of the exit tracer concentration to the injected tracer concentration is used to calculate the residence time density of the trace as given in Eqn. (6):

$$F(t) = \frac{C_{exit}}{C_T} \quad (6)$$

The ratio gives the cumulative residence time density function called $F(t)$, which can be used to calculate the MRT, given by:

$$\tau = \int_0^{\infty} [1 - F(t)] dt \quad (7)$$

The porosity of the silica bed is measured 65–70%. UV- Vis spectrum of exit IDB concentrations is shown in Fig. 7(a) and $F(t)$ curve is shown in Fig. 7(b), obtained at 1.5 ml/min flow rate. Similarly, UV- Vis spectrum of exit DBB concentrations is shown in Fig. 8(a) and $F(t)$ curve, obtained at 1.5 ml/min flow rate is shown in Fig. 8(b). The theoretical or ideal mean residence time is calculated by using Eqn. (1). Figure 6 shows the MRTs using Eqn. (1) and using Eqn. (6) for experimentally found $F(t)$ curves for IDB and DBB respectively, at different flow rates. We obtain an excellent match of theoretical MRT with IDB MRT. We also observed the higher MRT values of DBB. This is due to

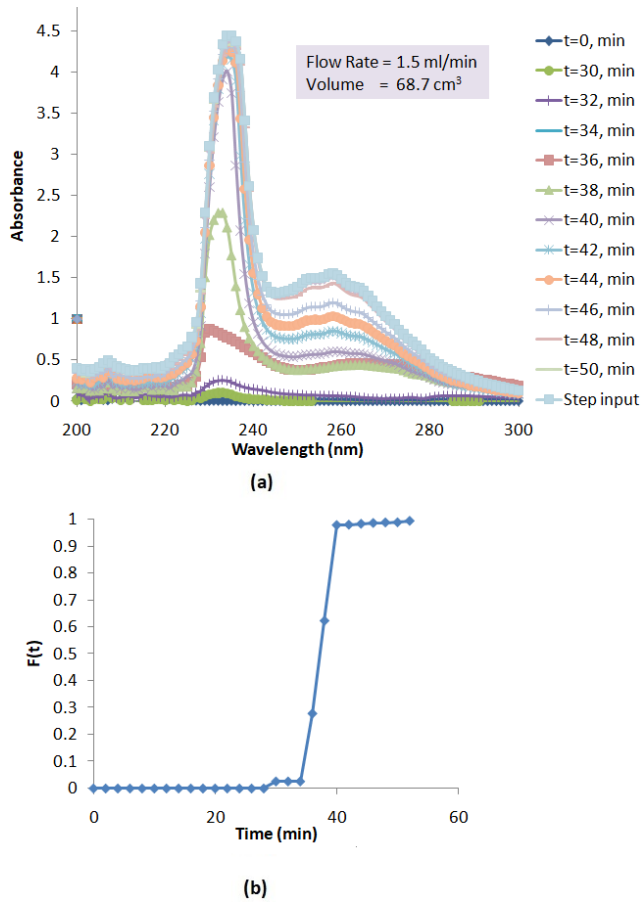


FIGURE 7. FLOW EXPERIMENTAL RESULT FOR (IDB).

adsorption of DBB on silica gel particles.

If we use known mass of the silica gel in the flow experiment, then from Eqn. (1) and (2) we get K_a values as presented in Tab. 2. Flow experiments give pseudo steady state value of K_a (ml/gm), which increases with increasing flow rates as shown in Fig. 9(a). K_a increases with increasing flow rates because, the injected tracer is more when high flow rate is used due to step input. Figure 9(a) shows dependence of K_a on flow rate. Similar linear dependence is also seen in batch experiments with respect to the volume of the solution in contact with silica gel as shown in Fig. 9(b). Therefore, the linear curve shown in Fig. 9(a) can be used to estimate K_a for flow experiments.

CONCLUSIONS

In summary, batch experiments and flow experiments for finding adsorption coefficients of organic phase tracers DBB and IDB are conducted. IDB is found to be a non-adsorbing and DBB is an adsorbing oil phase tracer. We obtain linear variation in K_a (ml/gm) for single phase flow at different flow rates.

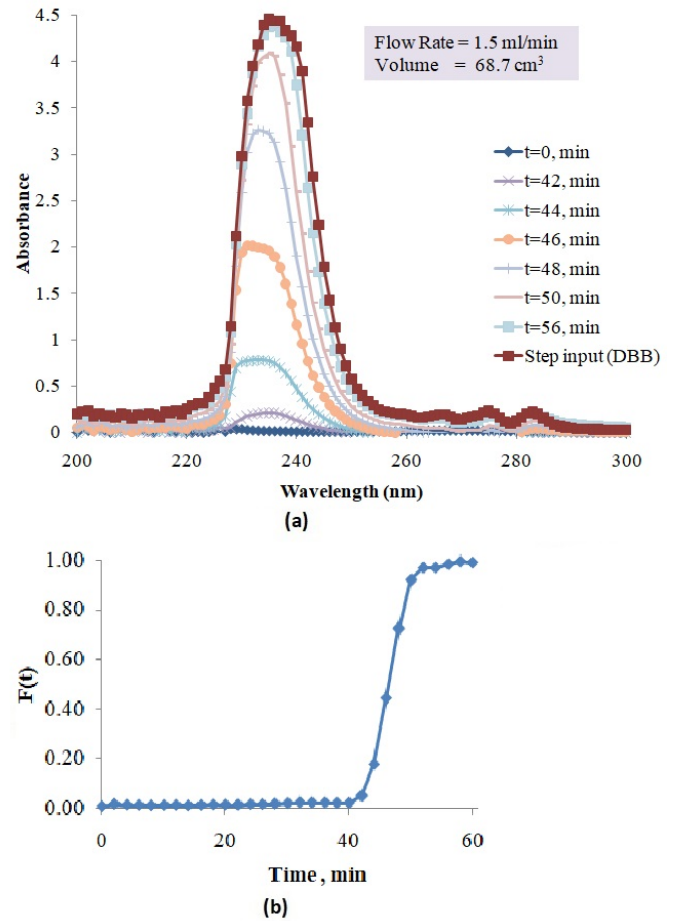


FIGURE 8. FLOW EXPERIMENT RESULT FOR (DBB).

We will use this estimated K_a (ml/gm) to find the sediment area wetted by a fluid during multiphase flow in the porous medium.

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TABLE 2. K_a VALUES OBTAINED FROM FLOW EXPERIMENTS.

$Q, \frac{ml}{min}$	IDB (MRT)	DBB (MRT)	$K_a, \frac{ml}{gm}$	$A_w, (gm)$
2.00	23	33	0.46	44
1.50	32	43	0.39	43
1.00	50	62	0.29	42
0.50	104	117	0.16	40
0.25	194	208	0.08	43

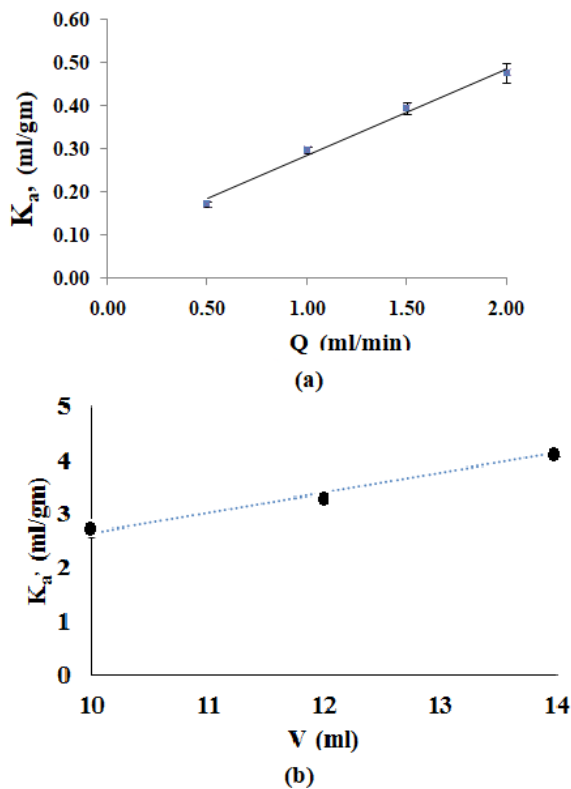


FIGURE 9. ESTIMATED K_a FOR (DBB) FROM (a) FLOW AND (b) BATCH EXPERIMENTS.

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