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Diffusivity of crude oils contained in macroporous medium: ^{1}H NMR study

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Nomenclature

LO: light oil;
HO: heavy oil;
ω_1: mass fractions of a liquid;
PFG NMR: pulse field gradient nuclear magnetic resonance;
T: temperature;
RF: radiofrequency;
g: intensity of field gradient pulses;
t_d: observation time the diffusion process (diffusion time);
T_1: longitudinal NMR relaxation time;
T_2: transverse NMR relaxation time;
A_0: initial amplitude of the free induction signal after applying the first 90^o – radiofrequency pulse;
DD: diffusion decay of the spin echo amplitude owing to the self-diffusion process;
D: self-diffusion coefficient;
$P(D)$: function of distribution of self-diffusion coefficients;
$<r^2>$: mean-square displacement of diffusing molecules;
d: average particle diameter;
D_n: most probable self-diffusion coefficient in the case of their distributions;
Eq.: equation.
g_0: constant magnetic field gradient
δ: durations of field gradient pulses;
Δ: time between field gradient pulses;
γ: gyromagnetic ratio for proton;
τ: time interval between the first and the second RF pulses;
τ_1: time interval between the second and the third RF pulses;
σ: parameter of the width of the log-normal distribution of D;
Φ: porosity;
ρ_1: density of liquid;
ρ_2: density of sand.

Sample preparation

Fractionated quartz sands with a linear particle diameters d = (0.08 - 0.10) mm, and d = (0.1 - 0.16) mm were prepared by sieving, then the fractions were washed in distilled water and dried at a temperature of T = 100^{o}C for about 10 hours. The required amount of crude oil, taken according to the desired volume fraction of oil in the sample φ_1, was dissolved in toluene. The resulting solution was thoroughly mixed with the corresponding amount of sand. Finally, the toluene was evaporated from the solution to obtain a constant weight of the final sample with a predetermined concentration of oil φ_1. The prepared sample was placed in a glass NMR test tube with an outer diameter of ~ 7 mm and the tube was sealed. The error in estimating the sample concentration does not exceed ~ 1.5%. The interval of φ_1 was 0.08 - 1.00. Samples were equilibrated before measurements during two weeks. Measurements were repeated several times over a period of few months. All the results were reproduced.

Stimulated echo pulse sequence

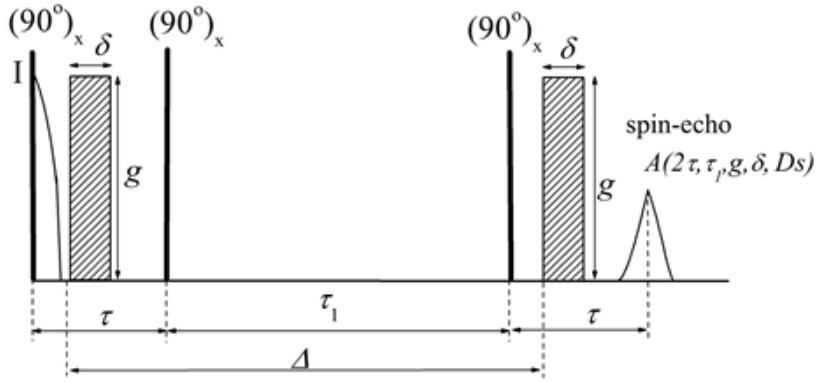

Figure S1 Stimulated spin-echo pulse sequence for self-diffusion measurements.[1,2] In this figure 90° radiofrequency (RF) pulses are shown as solid bars. Gradient pulses with amplitude g and duration δ are shown as hatched rectangles. τ is the time interval between the first and the second RF pulses; τ_1 is the time interval between the second and the third RF pulses; Δ is the time between gradient pulses. The observation time of the diffusion process (diffusion time) is $t_d = (\Delta - \delta/3)$.

Characterization of diffusion process in confinement

The self-diffusion process, which is characterized by non-single-exponential diffusion decays, can be described by an effective or average value of the self-diffusion coefficient $<D>$:[3,4]

$$< D >= \int_0^\infty P(D) D dD \qquad \text{(S1)}$$

Then the experimental value of $<D>$ is determined from the initial slope of the curve $A(g^2)$ as:

$$< D >= -\lim(g \to 0) \left\{ \frac{1}{\gamma^2 \delta^2 t_d} \cdot \frac{\partial [\ln A(g^2)]}{\partial g^2} \right\} \qquad \text{(S2)}$$

In many cases the function $P(D)$ can be approximated by a log-normal distribution function of D:[3]

$$P(D) = \frac{1}{\sqrt{2\pi \cdot \ln^2 \sigma}} \cdot \exp\left[- \frac{\ln^2\left(\frac{D}{D_n}\right)}{2 \ln^2 \sigma} \right] \qquad \text{(S3)}$$

Where D_n is the most probable value of D and $\ln^2\sigma$ is the width of the log-normal distribution of D, which characterizes the deviation of the diffusion decay from the exponential form of Eq.(1). Parameters D_n and $\ln^2\sigma$ of Eq.(S3) were chosen by fitting the expression (S1) to the obtained DDs. The description of the diffusion decay using (S1) and (S3) is carried out only in order to emphasize the complexity of their form, as well as to quantify the degree of deviation of the experimentally measured DD from the exponential form. Thus, the quantitative parameters characterizing diffusion are the average D, ($<D>$ or D_n), and the width of distribution function, $\ln^2(\sigma)$.

Independence of DDs on diffusion time

Non-exponential diffusion decays can be occurred for a number of reasons. Oil components differ in molecular weight, molecular structure and, therefore, physical properties of pure components of oil, such as density, viscosity and diffusivity are different. In a mixture (crude oil) presence of different molecular components, each of which is defined by its D ranging in some interval of $D + dD$ should lead to a complex, multi-exponential form of DD (Fig. 1). Additionally, the formed micelles,[5] and asphaltene aggregates[6,7] may complicate form of DD even more.

To explain the independence of D on diffusion time t_d we should to compare the values $(<r^2>)^{0.5}$ and l, where $(<r^2>)^{0.5}$ is the obtained experimental root mean square displacement (RMD) of diffusing molecules and l is the linear size of the available space for this run in the studied samples. Given that the porosity, Φ, of the used sand reaches ~ 0.45[8] and the content of the liquid, φ_1, in all studied systems is less than the value of Φ, we can say that the oil does not completely occupy the pore space of the sample. Then it is possible to assume that the liquid

envelops each grain of sand by some layer the thickness of which is *h*, that in our case can be considered as available for the diffusive motion part of the space, i.e., $h \sim l$. When $(<r^2>)^{0.5} < h$, self-diffusion is not limited and the measured *D* value should not depend on t_d. When $(<r^2>)^{0.5} > h$, the liquid molecules begin to "feel" the hard obstacles, and the measured *D* should decrease.[1]

Assume that:

- every grain of sand is a sphere with radius $r_0 = d/2$;
- the grains do not touch each other;
- the condition for volume additivity of sand and fluid is met when they are mixed; then we can write:

$$h = \frac{1}{3} \cdot \frac{\rho_2}{\rho_1} \cdot \frac{\omega_1}{1-\omega_1} \cdot r_0 \qquad \text{(S4)}$$

In equation (S4) the mass fraction (ω_1) and volume fraction (φ_1) of the liquid in the sample are related as:

$$\omega_1 = \frac{\varphi_1}{\frac{\rho_2}{\rho_1} - \varphi_1\left(\frac{\rho_2}{\rho_1} - 1\right)} \qquad \text{(S5)}$$

Where $\rho_2 \sim 2.65 \cdot 10^3$ kg/m^3 is the sand density[9] and ρ_1 is the density of the liquid. The value of ρ_1 for used oils varied within the range of $(0.92 - 0.98) \cdot 10^3$ kg/m^3, so in the transition from mass fraction (ω_1) to volume fraction (φ_1) and back, we used the average value $\rho_1 \sim 0.95 \cdot 10^3$ kg/m^3. In turn, the values of the RMD $(<r^2>)^{0.5}$ can be estimated by Einstein's equation:[1]

$$< r^2 >= 6 < D > \cdot t_d \qquad \text{(S6)}$$

Estimates for the values *h* and $(<r^2>)^{0.5}$ by using Eq. (S4) and (S6) for samples with $\varphi_1 = 0.17$ and 0.35 are given in Table S1 and they indicate that the values of $(<r^2>)^{0.5}$ in all cases are less or even significantly less than the value of *h*. Perhaps these results can explain the independence of the measured self-diffusion coefficients on the diffusion time when its value is

varied in the range of t_d = 5 - 100 ms. This is understandable because the value of h in this case may be considered as the distance between the barriers for diffusing molecules.

Table S1

The values of the RMD runs $(\langle r^2 \rangle)^{0.5}$ *for light oil – sand samples at T ≤60°C;* $\langle D \rangle \sim 10^{-11}$ m^2/s.

φ_1	$2 \cdot r_0$ (mm)	h (μm)	$\langle D \rangle \sim 10^{-11}$ m^2/s	
			$(\langle r^2 \rangle)^{0.5}$ t_d = 2 ms	$(\langle r^2 \rangle)^{0.5}$ t_d = 100 ms
0.17	0.1	3.1	0.35 μm	2.4 μm
0.35	-"-	9.0	-"-	-"-

Apparent activation energies of diffusion

Dissimilarity in the form of curves $\langle D \rangle = f(\varphi_1)$ for the studied systems LO - sand and HO – sand (Fig. 2,3) must lead to apparent differences in some values of molecular parameter such as the activation energy of self-diffusion, E_D. Note that the parameter E_D characterizes only those molecules that give contribution in the spin-echo of the diffusion NMR experiment. It is known[10] that this parameter can be determined experimentally by plotting dependences of D on temperature. The temperature dependences of the measured average D, constructed in coordinates $\ln\langle D \rangle$ - $[-(1/T)]$ in the studied interval T = (30 - 120)°C were almost linear. This allowed us to use the Arrhenius type equation:

$$< D >= D_0 \cdot \exp\left(\frac{-E_D}{RT}\right) \qquad \text{(S7)}$$

to determine the values of the activation energy E_D for the studied samples (Table S2). We can see from this table that the parameter E_D has a value up to ~ 39 kJ/mol for pure heavy oil. It is interesting that the activation energy value decreases stepwise to a value of ~ 30 kJ/mol after the introduction of this oil in the porous medium. However, for heavy oil samples - sand in the range of φ_1= 0.15 - 0.44, the activation energy remains almost unchanged, remaining in the range of 27.2 - 31.9 kJ/mol.

Table S2

The values of the apparent activation energy of self-diffusion E_D in oil - sand systems

E_D, kJ/mol					
System	φ_1				
	1.00	0.44	0.33	0.24	0.15
HO – sand	38.7	31.9	28.6	27.2	30.1
LO – sand	31.0	33.2	31.6	33.2	31.0

As for light oil, the value of E_D does not change essentially, even if this oil is introduced into the porous medium. The value of E_D in this case, throughout the range of φ_1, including the value for pure oil, is equal to ~ 32 kJ/mol (Table S1).

If we consider that the activation energy of self-diffusion usually varies simultaneously with the size of the molecule,[11] the observed results can be explained as follows. To study self-diffusion by NMR in a multicomponent system such as, for example, oil, it is necessary to take into account the fact that the contribution of the spin-echo signal to the diffusion decay affects all the molecules that give contribution in the spin-echo of the diffusion experiment, including heavy molecules of resin-asphaltene fractions. The adsorbed molecules exit the diffusion experiment because they have extremely low rotational mobility, consequently their T_2 are short. For this reason, these molecules do not contribute to the total diffusion decays. As a result, the translational molecular mobility in the non-adsorbed portion of the oil must increase, and the effective activation energy, E_D, is somewhat reduced. This effect is most clearly manifested in the heavy oil – sand system, where there is a large proportion of the resin-asphaltene component. Therefore, for this system, we have seen a significant decrease in the E_D values (see Table S2, the second line from the bottom). With regard to the light oil, its content of heavy resin-asphaltene components is very small.[12,13] Hence, the effect of the decreased value of E_D cannot be detected after introducing this oil into the porous medium. The quantity of E_D remained

largely unchanged for any φ_1, including $\varphi_1 = 1.0$ for system light oil – sand (see Table S2, the first line from the bottom).

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