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

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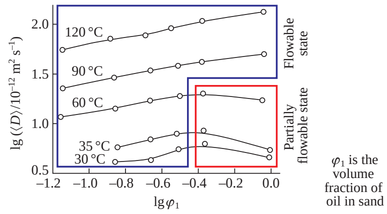
Diffusivity of crude oils confined in pores of sand decreased with raising the fraction of oil at ordinary temperatures. This behaviour is suggested to be caused by adsorption of the high-molecular fractions of oils at the solid–liquid interface.



Extraction of crude oils from natural reservoirs is currently one of the most relevant challenges for oil companies.[1,2] Crude oils are quite complex in their compositions because they contain thousands of chemical species.[3,4] This leads to a wide range of formed structures, phases and molecular assembles.[3,5,6] Heavy oils are usually very viscous and cannot be easily extracted at normal temperature and pressure because of high content of resins and asphaltenes, which may form nano-aggregates and plug pores of reservoirs.[3–5,7] To effectively extract oils from rocks, information about the state of the oil in oil-saturated collectors is needed.[8,9] NMR diffusometry is one of the most robust due to its high permittivity, non-destructivity, wide ranges of diffusion time and molecular displacements, relatively easier methods of samples preparations.[3–6,8–13] Successful applications of NMR diffusometry were reported for consolidated sedimentary rocks[14–16] and unconsolidated sediments.[17] We studied diffusivity of two types of crude oils, light (low viscosity, LO) and heavy (high viscosity, HO) oils,[†] confined in the model of macroporous collector, sands with two grain sizes.

Some characteristics of the oils are given in Table 1. Characteristics of the translational mobility, such as the shape of the diffusion decay of the spin-echo signal, as well as self-diffusion coefficients (D) were determined by Pulsed Field Gradient ^{1}H NMR (PFG NMR).[11,18,‡]

Table 1 Some characteristics of light (LO) and heavy (HO) crude oils.

Oil	Density/ g cm^{-3}	Dynamic viscosity/mPa s	Content of resins and asphaltenes (wt%)
LO	0.875	2.1	~2–3
HO	0.960	275	~30

In the case of isotropic and unrestricted diffusion, the intensity of the stimulated spin echo amplitude, A, is:[11,18]

$$A = \left(\frac{A_0}{2}\right)\exp\left(-\frac{2\tau}{T_2} - \frac{\tau_1}{T_1}\right)\exp(-\gamma^2\delta^2 g^2 D t_\mathrm{d}), \quad (1)$$

where A_0 is the initial amplitude of the free induction signal, T_1 and T_2 are the longitudinal and transverse relaxation times, respectively, τ is the time interval between the first and the second radio frequency (RF) pulses, τ_1 is the time interval between the second and the third RF pulses, γ is the gyromagnetic ratio for protons, g and δ are amplitude and duration of gradient pulses, t_d is the diffusion time. In our work, the decay of the spin-echo amplitude owing to the self-diffusion process (diffusion decay, DD) was recorded at the fixed values of δ and t_d while g was varied. Therefore, the time interval between RF pulses remains constant and the contribution of the relaxation decay term of equation (1) can be excluded from consideration when processing the experimental curves. PFG NMR parameters were calibrated using distilled water at 30 °C. The value of t_d was within the range of 5–100 ms. Temperature of the sample was controlled by a sensor placed in the stream of air.

In all these cases, DDs of the studied systems were complicated (Figure 1). Analysis showed that they cannot be described as a sum of two or three contributions of a type of (1). Therefore, we applied a function with continuous distribution of diffusion coefficients:

$$\frac{A(g^2)}{A(0)} = \int_0^\infty P(D)\exp(-\gamma^2\delta^2 t_\mathrm{d} D g^2)\,\mathrm{d}D, \quad (2)$$

where $P(D)$ is the distribution of the resonance nuclei in a sample with a value for D in the interval from D to $D + \mathrm{d}D$. First, a normal

[†] Crude oils extracted from Mordovo-Karmalskoe oil field (Tatarstan, Russia) were used. Densities were determined by an aerometric method, while coefficients of dynamic viscosity were determined using rotation viscometer Alpha (Fungilab). All measurements were performed at 20 °C and pressure 105 Pa. Fractionated quartz sands with a particle diameters d = 0.08–0.10 and 0.1–0.16 mm were used. Details of the sample preparation are described in Online Supplementary Materials.

[‡] All measurements were performed on a homemade NMR spectrometer (^{1}H resonance frequency of 64 MHz and a maximum magnetic pulse gradient value of 40 T m^{-1}) at the Department of Physics of Almetyevsk State Oil Institute. The stimulated echo pulse sequence was applied (Figure S1, Online Supplementary Materials).[18]

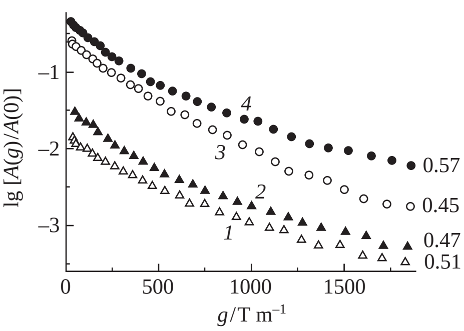


Figure 1 DDs in the LO–sand systems for the volume fractions of oil (*1*) φ_1 = 1.0 and (*2*) φ_1 = 0.44, obtained at T = 120 °C, and in the HO–sand systems when (*3*) φ_1 = 1.0 and (*4*) φ_1 = 0.44, obtained at T = 30 °C. Curves are shifted with respect to the *Y*-axis for convenience. The values of parameter $\ln^2\sigma$ related to the log-normal distribution of D are given near the curves.

distribution for $P(D)$ was applied but it was not fitting well to the experimental. However, the logarithmic normal distribution function for $P(D)$

$$P(D) = \frac{1}{\sqrt{2\pi \ln^2\sigma}} \exp\left[-\frac{\ln^2(D/D_n)}{2\ln^2\sigma}\right] \quad (3)$$

gave better fitting and was used for further analyses.[9,10] Here, D_n (or $\langle D\rangle$) 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 DD from the exponential form of equation (1). Thus, the average values of diffusion coefficients

$$\langle D\rangle = -\lim_{g\to 0}\left\{\frac{1}{\gamma^2\delta^2 t_d}\frac{\partial[\ln A(g^2)]}{\partial g^2}\right\} \quad (4)$$

and $\ln^2\sigma$ were used to quantitative characterize the process of diffusion. The process of diffusion may be quite complicated in such confinement as sand; therefore, it seems strange for the first sight that two parameters are enough to describe it. However, it can be understand by taking into account that the molecular exchange between pores are typically average apparent parameters of diffusion to some extent.[9,11]

Figures 2 and 3 illustrate the concentration φ_1 dependences of the average D measured in systems LO–sand and HO–sand, respectively, over a temperature range of 30–120 °C. For the LO, we observed a ‘distinctive’ shape of the curves, $\langle D\rangle = f(\varphi_1)$, indicating a certain diminishing of translational molecular mobility of the fluid when the proportion of oil particles is decreased in a sample (Figure 2). Similar trends were observed in HO–sand systems, but only at sufficiently high temperatures, $T \geqslant 90$ °C (Figure 3, curves *4* and *5*). It is notable that the dependences of the average D on the liquid content in HO–sand samples at low temperatures (when $T \leqslant 60$ °C) had a fundamentally different form than the shape of the ‘typical’ curves $\langle D\rangle = f(\varphi_1)$. Particularly, there is a maximum of $\langle D\rangle$ at $\varphi_1 \sim 0.44$ (Figure 3, curves *1*–*3*). No changes in the form of the recorded DDs at different t_d (5–100 ms) were observed. More details about this phenomenon can be found in Online Supplementary Materials.

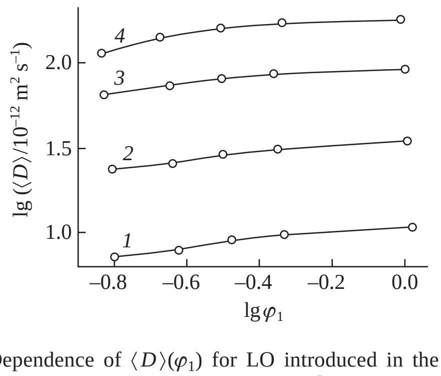


Figure 2 Dependence of $\langle D\rangle(\varphi_1)$ for LO introduced in the sand with d = 0.10–0.16 mm at T = (*1*) 30, (*2*) 60, (*3*) 90 and (*4*) 120 °C.

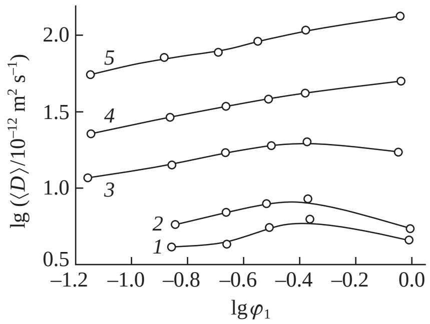


Figure 3 Dependence of $\langle D\rangle(\varphi_1)$ for HO introduced in the sand with d = = 0.08–0.10 mm at T = (*1*) 30, (*2*) 35, (*3*) 60, (*4*) 90 and (*5*) 120 °C.

The reduction of the molecular mobility of the liquid at the decreased liquid fraction can be explained by the increase in the proportion of obstacles. This type of curve $\langle D\rangle = f(\varphi_1)$ is characteristic of self-diffusion in systems with non-associated low molecular weight liquids,[10,19] where the proportion of liquid molecules adsorbed on the surface of the solid phase is negligible.[19] Such curves can be represented analytically by an empirical expression:

$$D \sim \varphi_1^{\chi}, \quad (5)$$

where χ is a constant that depends on the nature of the fluid and substrate. The translational molecular mobility in accordance with (5) should be reduced by increasing the share of obstacles in the system that leads to the ‘ordinary’ form of the curves $\langle D\rangle = f(\varphi_1)$. From a physical point of view, this might be due to: the force interaction between the molecules of liquid and the surface, or steric constraints to liquid molecular motion imposed by these particles.

It should be noted that at high temperatures, $T \sim 120$ °C, in all cases there was a trend toward more intensive lowering of the measured D with decreasing φ_1 (Figure 2, curve *4* and Figure 3, curve *5*). This is due to the fact that a molecule greatly increases its run[11]

$$(\langle r^2\rangle)^{0.5} = 6Dt_d \quad (6)$$

and begins to ‘feel’ the obstacle with higher T. Then, the slope of dependence, $\langle D\rangle = f(\varphi_1)$, is determined not only by the force of interaction of the liquid with the surface of the sand grains,[20] but also by the factor of steric constraints imposed by these particles for molecular motion of the fluid.

In fact, the estimation of the mean square path for diffusing molecules was done using the expression (6) and the value of $\langle D\rangle \sim 10^{-10}$ m^2 s^{-1} (this is the order of D at the highest temperature $T \sim 120$ °C), which for our samples showed that at t_d = 2 ms and t_d = 100 ms the value of $(\langle r^2\rangle)^{0.5}$ is about 1.1 and 7.7 μm, respectively [*cf.* the value of $h \sim 3.1$ and 9 μm (Table S1)]. Thus, the effect of steric restrictions on the movement of molecules at higher temperature measurement is obvious.

For the anomaly in the dependences $\langle D\rangle = f(\varphi_1)$, observed in the HO–sand systems at low temperatures ($T \leqslant 60$ °C) (Figure 3, curves *1*–*3*), the possible mechanism is a quantitative change in the ratio of liquid phase components. It is known that the components with higher adsorption activities are resin-asphaltene fractions (mainly due to the presence of the heteroatoms N, O, S).[21,22] These higher molecular weight fractions are characterized by the lowest values of D. It could be assumed that they would be primarily adsorbed on the surface of the sand. This assumption is in agreement with the pore plugging effect, which is typical of

Table 2 The values of average diffusion coefficient $\langle D\rangle$, the lowest values of the self-diffusion coefficient D' corresponding to the most gently sloping component of the DD in the HO–sand system at $T = 30\,°C$. P' is the relative number of molecules diffusing with D'.

φ_1	$\langle D\rangle$/m^2 s^{-1}	D'/m^2 s^{-1}	P'	$\ln^2\sigma$
1.00	4.2×10^{-12}	6.5×10^{-13}	0.1	0.57
0.44	5.7×10^{-12}	10.0×10^{-13}	0.1	0.45

asphaltenes.[4,23] As a result, the composition of the liquid phase will be depleted of the high-molecular-weight fractions, and the molecular mobility in the non-adsorbed portion of fluid, consequently, will increase. This effect should clearly appear at the lowest temperatures,[24] and for the oil with larger proportion of resin-asphaltene fractions, *i.e*., for the systems HO–sand.[21,25] This was observed in our experiments in HO–sand samples (Figure 3, curves *1*–*3*). Sand grain that has absorbed high molecular weight fractions of oil apparently may be considered as a single unit. Then the behavior of dependences $\langle D\rangle = f(\varphi_1)$ in area $\varphi_1 \leqslant 0.44$ will probably satisfy the relation (6). Additional validation of the assumption of selective adsorption of macromolecular fractions is evidenced by a decrease in the parameter $\ln^2\sigma$ at lower temperatures for HO confined in the sand. Indeed, the decrease of $\ln^2\sigma$ indicates a narrowing of the spectrum of the apparent D. Consequently, with an increase in the average $\langle D\rangle$ in the experiment with the system of HO–sand, an increase must be expected in the lowest values of the self-diffusion coefficient D' from the overall spectrum of D. This conclusion is confirmed by the results given in Table 2: at $\varphi = 0.44$ the values of $\langle D\rangle$ and D' are higher than these at $\varphi_1 = 1.00$.

So, we can assume that for the samples with HO, the dependences $\langle D\rangle = f(\varphi_1)$ have the usual form only at sufficiently high temperatures. In our case, the values of these temperatures exceed 90 °C (Figure 3, curves *4* and *5*). Therefore, the value of $T = 90\,°C$ may serve as a kind of critical parameter $T \geqslant T^*$ with regard to the system under study. When $T \geqslant T^*$, heavy oil behaves like a typical liquid, and when $T \leqslant T^*$, the adsorption properties of the highest molecular weight components of this oil appear more obvious.

Thus, the high-viscosity 'immobile' component of oil at low $T \leqslant T^*$ acquires the properties of a conventional liquid only at sufficiently large $T \geqslant T^*$, namely, at a sufficiently high value of the thermal energy of the molecular motion $U \geqslant kT^*$ (k is the Boltzmann constant). The obtained value of $T^* \sim 90\,°C$ for the HO samples is almost the same as that of the upper limit, T_{up}, of the softening temperature range, ΔT_{soft}, of resinous oil components[25] which are abundant in heavy oil. If the bottom limit of the softening temperature range is T_{bot}, then usually ΔT_{soft} is 35–90 °C.[26] When $T \geqslant T^* = T_{up}$, resins behave like typical fluid, therefore the HO at these temperatures has the same properties as a LO. Dissimilarity in the form of curves $\langle D\rangle = f(\varphi_1)$ for the studied systems LO–sand and HO–sand leads also to apparent differences in activation energies diffusion, E_D (see Online Supplementary Materials).

In conclusion, the performed studies provide evidence of the difference in molecular states of light and heavy oil, confined in sand. A proportion of larger molecules (included mainly in the resin-asphaltene fractions) at ordinary temperatures is stationary, adsorbed on the surface of sand. We have discovered the critical temperature T^* of ~ 90 °C, above which almost all the components of the studied oil are capable to move in a typical fluid state.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.03.039.

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