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DETERMINATION OF DROPLETS SIZE DISTRIBUTION IN OIL-WATER EMULSIONS BY THE METHOD OF NUCLEAR MAGNETIC RESONANCE RELAXOMETRY

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Abstract. Were received the relations for express-control of water concentration and droplets size distribution (DSD) in water-oil emulsions by portable proton magnetic resonance (PMR) relaxometer. Was shown, that method on the base of PMR-relaxometry for DSD determination is fast, high informative and can be used for water in oil emulsions control at the preparation process of water from oil separation.

ОПРЕДЕЛЕНИЕ РАСПРЕДЕЛЕНИЯ РАЗМЕРОВ КАПЕЛЬ В ЭМУЛЬСИЯХ МЕТОДОМ ПРОТОННОЙ МАГНИТНОЙ РЕЗОНАНСНОЙ РЕЛАКСОМЕТРИИ

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Ключевые слова: экспресс-контроль, концентрация воды, распределение капель воды, релаксометрия.

Аннотация. Были получены соотношения для экспресс-контроля концентрации воды и распределения капель воды (РКВ) в водо-нефтяных эмульсиях портативным протонно-магнитным резонансным (ПМР) релаксометром. Было показано, что метод на базе ПМР-релаксометрии быстрый, высокоинформативный и может быть применен для экспресс-контроля водо-нефтяных эмульсий в процессах подготовки нефти путем отделения воды от нефти.

Urgent requirement of oil-industry laboratories and oil preparation technology processes - is the possibility for express-analysis of physical-chemical parameters (PCP) of oil disperse systems, which are important for crude oils preparation. This physical-chemical parameters are: concentrations of water in crude oils and disperse distribution of water droplets in emulsions. Method of pulse nuclear (proton) magnetic resonance relaxometry (PMRR) has great, yet not disclosed opportunities for this express analysis. During fifty years of its development pulse PMRR-method proved its uniqueness as a powerful method equally suitable for refined scientific investigations and for routine analysis and control. It has advantages: possibility for simultaneous measurement of several physical-chemical parameters of matter; independence from the phase inversion in the oil/water emulsions; nondestructive and non contact opportunity of control and automation, short time of measurement.

PMR-relaxation method gives information about relaxation parameters of the proton's $i=3$ phases: spin-lattice T_{1i} and spin-spin T_{2i} relaxation times, characterizing groups of protons with different molecular mobility; populations (or concentrations) of proton phases P_{1i} and P_{2i} (we distinguish three phases); correlation times τ_{Ci} (times of the proton place in the molecular position); pre exponentials τ_{oi} (vibration periods of atoms); correlation times of atom exchanges τ_{Cei} ; activation energies E_{Ai} ; translation D_{tr} and rotation D_{rot} diffusion coefficients;

interproton distances R_{ij} ; temperatures T_{Phi} of the phase transitions; degree of the protons phases ordering, derived from relaxation times ratio $S = T_{1i}/T_{2i}$ and others. This set of PMRR structure-dynamical parameters (SDP) combined with high resolution PMR-spectra with its lines positions and amplitudes, derived from free induction decay (FID) after 90° -pulse, gives almost full picture about molecular dynamics of the studied oils.

Laboratory NMR-relaxometers can not be used for the manual on-line control at technology process line, as well as for pollution of soils and waters determination directly in nature. So we have designed new portable, easily transported relaxometers NMR NP-1 [2, 3] and NMR NP-2 with weight less, then 12 kg, power supplied by accumulator, connected with Notebook (fig.1).



Fig. 1. Portable relaxometer NMR NP-2

It is used for express-analysis of PCP and has no prototypes. In Moscow, Kazan, Perm, Ekaterinburg and other State Universities our NMR Relaxometers are used for scientific researches and educational process. Portable relaxometer can be power supplied from 12 V accumulator or ≈ 220 V, almost need not sample preparation. Time of measurement is less, then 2 minutes. Sensibility is $K = v^2 D^3$ [$\text{MHz}^2 \text{cm}^3$] = 2700-4150 $\text{MHz}^2 \text{cm}^3$, which is near to “Minispec pc120” (Bruker, Germany). Magnetic system is built of rare earth elements alloys NdFeB . Homogeneity of constant field is H_0 is $< 10^{-4} H_0$. Probe coil heterogeneity of H_1 field is less, then 2% in 75% of volume.

Were studied water-in-oil emulsions samples with 23.8 and 50.6 % relative water content in oils of Romashkinskoye (Republic of Tatarstan, Russia) deposit. Oil №1 has the density $\rho = 908 \text{ kg/m}^3$, viscosity $\eta_{20} = 33.8 \text{ cP}$, concentrations of asphaltenes (A) = 8.3 %, resins (R) = 25.8 %, sulfur (S) = 3.08 %. Oil №2 has $\rho = 987 \text{ kg/m}^3$, $\eta_{20} = 39,5 \text{ cP}$, $\text{Asph} = 10.3 \%$, $\text{Res} = 26.8 \%$, $S = 5.5 \%$. Also oils

with $\rho = 873-879 \text{ kg/m}^3$ and concentrations of salts $C = 0.05\text{M}\div 1\text{M}$ (2.6-53 g/l) were used. These oils and water concentrations were chosen because emulsions from dense oils with high A and R (which are the native surface active substances), have the highest aggregative stability and difficult for separation. Emulsions were prepared on a propeller mixer with the rotation rate of $1500\pm 500 \text{ rpm}$ and time of mixing of $10\pm 5 \text{ min}$. Stratum water used for samples had 3 g/l of salts (73 % of NaCl, 20 % of CaCl_2 , 7 % of MgCl_2).

For T_{1i} and P_{1i} determination spin-echo recovery pulse sequence $90^\circ-\tau-90^\circ-\tau_0-180^\circ$ was used with the measurement parameters: delay time $T = 9 \text{ sec}$, number of 180° pulses $N = 100$, step of sequence $\tau - 3 \text{ ms}$, number of accumulations $n = 3$. To determine T_{2i} and P_{2i} , the pulse sequence of Carr-Purcell-Meiboom-Gill [1] $\{90^\circ-\tau-(180^\circ-2\tau)_N-T\}_n$ was used with parameters: delay time $T = 9 \text{ s}$, number of 180° pulses $N = 900$, interval between 180° pulses $\tau = 200 \mu\text{s}$, number of accumulations $n = 10$.

Water concentration determination by PMR- relaxation method is performed by measuring of spin-spin relaxation times T_{2B} , T_{2H} и T_2^* of pure water, pure oil and their mixture using equation by CPMG sequence [1]:

$$W_{\text{PMR}} = T_{2B} (T_2^* - T_{2H}) 100\% / T_2^* (T_{2B} - T_{2H}). \quad (1)$$

Number of 180° -pulses N in was chosen from equation:

$$N = k3\rho_o - k4, \quad (2)$$

where ρ_o – density of oil in kg/m^3 , $k3 = 0,34$, $k4 = 284$. At low water concentrations W_{PMR} is determined using equation:

$$W_{\text{PMR}} = (T_{2OB}T_{2OH} - T_2^*T_{2OB} - W^*T_{2OH}T_2^*) / T_2^*(T_{2OB} - T_{2OH}) 100\%, \quad (3)$$

where W_{PMR}^* – part of water, added to the emulsion sample.

Dependence of W_{NMR} from T_2^* (s) for oils of densities $\rho = 865-908 \text{ kg/m}^3$ and PDVSA (Venezuela) and Zuzeev (Romashkino deposit) with different number of CPMG 180° pulses in steady state is presented at fig. 2.

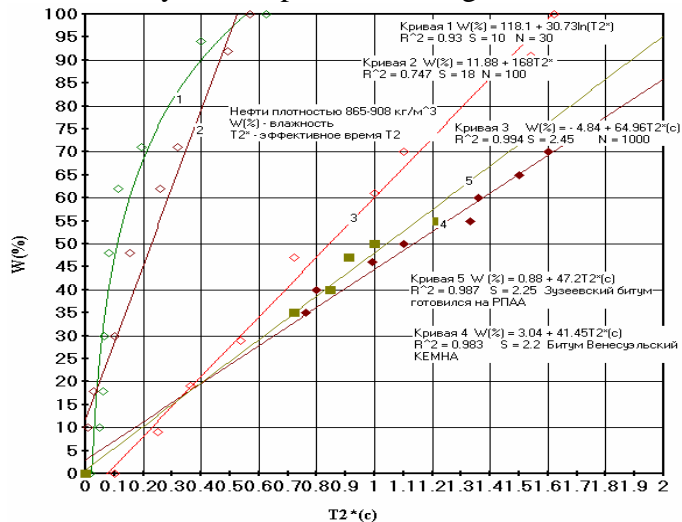


Fig. 2. Dependence of W_{NMR} from T_2^* (s) Curves in oils: 1, 2, 3 – for $N = 30, 100$ and 1000 ; 4 – of PDVSA oil emulsions (Venezuela); 5 – of Zuzeev oil emulsions (Romashkino)

For Zuzeev oil emulsions (Romashkino deposit, Republic of Tatarstan) dependence can be described by the equation:

$$W_{PMR}(\%) = 0.88 + 41.5T_2 (c). \tag{4}$$

For droplets size distribution (DSD) determination exist the following methods: (i) microscopic analysis and (ii) hyper sound spectrometry need transparency or dilution. But they are not operative, low precise and need transparent samples without any impurities and gas bubbles.

PMRR is an alternative method for the DSD determination, which can be used in nontransparent oil-water emulsions with inorganic impurities and gas bubbles. NMRR measurements in relatively large samples (20 cm³) masses ensure good representation. The limitation of the method is the effect of the self-diffusion coefficients *D*, which is prevented using CPMG sequence [1].

DSD curves as dependences of relative number $N_i/\sum N_i$ of droplets with definite diameter D_i from droplets diameters are presented at Fig. 3 (where N_i is the number of droplets with the diameter D_i) using the microscopic data obtained using microscope MC-300 (Austria) with a MD-300 webcam (ArcSoftWebCam software), magnify 640x.

But microscopic method of the DSD determination is not operative. That's why, we used PMR–relaxation method for determination of correlations between D_{AV} , D_{MAX} , $R_{3/2} = D_{3/2}/2$ and relaxation times T_{1A} of water protons in droplets and data obtained earlier for oils with intermediate density $\rho = 870\text{-}910 \text{ kg/m}^3$, which are presented at Table 1. The relations of D_{AV} from T_{1A} (18 experimental points) with correlation coefficients $R^2 = 0.95$ for D_{AV} (eq.(5)) is presented at fig.4.

The integral DSD parameters: average diameters $D_{av} = \sum N_i D_i / \sum N_i$ and Slauter (volume/square) diameters $R_{3/2} = (\sum N_i D_i^3 / \sum N_i D_i^2) / 2$ were calculated and D_{maxI} and D_{maxII} diameters corresponding to two maximums of the DSD curves were determined from the curves. The data for small (SD) and large (LD) diameters are presented in Table, where they are compared with PMRR-data, obtained from equation eq.(5).

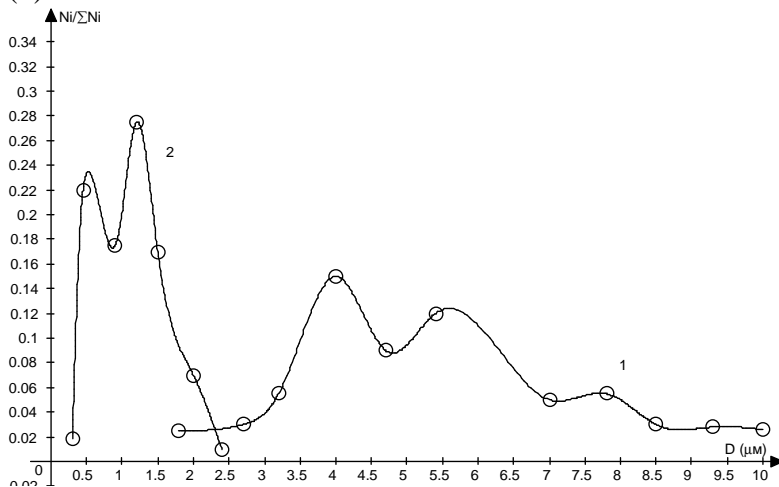


Fig. 3. DSD for 28,3% emulsions, prepared at 1000 rpm (curve 1) and 1500 rpm (curve 2)

Tab. 1. Integral diameters and DSD-parameters determination errors for 28,3% emulsions, prepared at different mixer propeller rates and compared with PMRR-data

28,3% emulsion, received at mixer rates:		Microscopic analysis				NMRR			
		D_{AV} μm	D_{MAX1} μm	D_{MAX2} μm	$R_{3/2}$ μm	D_{AV} μm	D_{MAX1} μm	D_{MAX2} μm	$R_{3/2}$ μm
SD-emulsion, 1500 rpm		1,9	0,6	1,3	2,6	1,6	0,9	2,3	1,9
LD-emulsion, 1000 rpm		6,2	3,9	5,5	7,0	6,7	1,9	3,5	7,3
Intermethodic error $IMRE = D \cdot 100\% / D_D$	SD-emulsion	1,0	1,0	1,0	2,3	-	-	-	-
	LD-emulsion	1,7	6,7	6,7	1,0	-	-	-	-

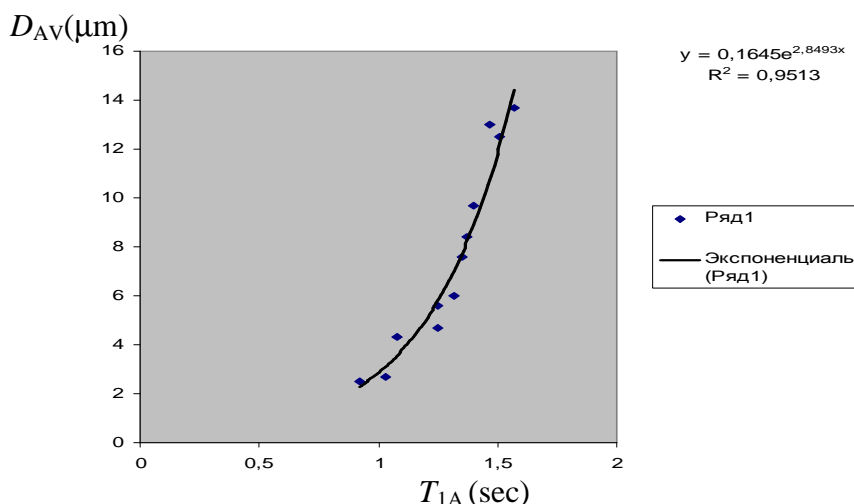


Fig. 4. Relation between $D_{CA}(\mu\text{m})$ and $T_{1A}(\text{sec})$

$$D_{CA}(\mu\text{m}) = 0.164 \exp(2.84 \cdot T_{1A}(\text{sec})). \quad (5)$$

It is in good agreement with the results of the work [4], authors of which found, that for water protons in the pores, relaxation rate $(T_{1,2})^{-1}$ is function of diameter

$$T_{1,2}^{-1} = T_{1,2B}^{-1} + [D_p / 2\alpha \rho_{1,2} + D_p^2 / 4\beta D]^{-1}. \quad (6)$$

where $T_{1,2B}^{-1}$ – relaxativity (relaxation rate) in bulk water, α - form factor, $\rho_{1,2}$ – rate of surface relaxation, β - include the shape factor and other parameters.

Other integral parameters of DSD: D_{max} and $r_{3/2} = D_{3/2} / 2$ with correlation coefficients $R^2 = 0,95$ can be determined from equations:

$$D_{maxI} = 0,32 \cdot \exp(1,37 \cdot T_{1A}); \quad r_{3/2} = 2,40 \cdot (T_{1A})^{4,27}. \quad (7)$$

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