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3

Adsorption and Aggregation of Asphaltenes in Petroleum Dispersed Systems

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1. Introduction

In current usage, the word "petroleum" has attained an almost magical meaning due to its importance to several aspects of modern life, influencing economic, policy, social factors. The price of petroleum is an important factor which will affect the character, rate and terms of future societal development.

The task of understanding actual physical and chemical structures in petroleum systems is non-trivial. Petroleum systems are highly complex and contain a potentially rich palette of possible structures and components. In technological processes, petroleum systems typically evolve in open systems of energy flows and matter flows.

2. Crude oil is a nanostructured "soft" system

«Petroleum is a complex mixture of hydrocarbons which is located in the Earth's crust in liquid, gaseous, and solid forms. Natural gas, heavy viscous oil and bitumens are forms of petroleum». This definition provided by a British encyclopedia is somewhat limited. Current scientific knowledge affords a more correct description of petroleum as a system containing numerous hydrocarbon components with different chemical natures. Such a correct definition allows a variety of physical properties and states related to internal structuring.

Classical physics defines three states of matter: solid, liquid, and gas. It provides adequate models of gaseous and solid states. The liquid state is somewhat more difficult to characterize, due to several critical obstacles. In addition, little attention has previously been paid to boundary states (coexistence of any two or even all three states at certain thermodynamic conditions). Different sciencific disciplines created separate terminologies such as metamaterials, which properties derive from artificially created periodic microstructure. Concepts such as multiphase heterogeneous or particularly ordered media or complex materials have appeared. Finally the Nobel winner in physics J.-P. de Gennes (de Gennes, 1992) united all terminologies under a common term «soft materials»

and founded the concept of a new field in condensed matter physics which received the conditional name "Physics of a Soft Matter", covering physics of polymers, liquid crystals, critical phenomena, biological systems and colloids. Properties of Soft Materials (SM) strongly correlate at micro-, meso-, and macro-levels under external influences.

Open systems in technology provide a means for formation of space-time structures. The synergetic approach was developed by a brilliant chemist, Nobel winner I.Prigogine (Prigogine, 1977). The condition of "soft" objects is determined by the inclination of the systems to undergo ordering through the action of intermolecular attractive forces (enthalpy factor) and disordering factor - leading any system to chaos or disintegration (entropy factor). The competition between order and chaos comprises an important condition of "soft" objects.

Various structural elements and the range of intermolecular interactions cause morphological diversity of supermolecular structures at all levels. These processes are called self-assembly or self-organization. These key phenomena serve as the basis for a new physical chemistry approach – the physical chemistry of intermolecular interaction or nanochemistry, which was founded by Nobel winner J.M. Lehn (Lehn, 1987).

Petroleum systems undoubtedly refer to objects of “Soft Matter”. Today, the “Petroleomics concept” (Mullins et al., 2007) follows the slogan “Characterization of all chemical constituents of petroleum, their interactions and their reactivity”. Petroleum component structures and their interaction potentials define the reactivity of petroleum system.

A universal criterion is that petroleum systems are mostly multiphase and heterogeneous with highly developed interfaces. The degree of dispersity is inversely proportional to a characteristic linear scale of inclusions. The degree of dispersity is a kernel of classification of disperse systems and should be accounted for as an additional variable in all equations describing the thermodynamic state of a system. At nano-scale ranges, this fact becomes especially important (Anisimov, 2004).

3. Petroleum dispersed systems

Approaching petroleum systems as homogeneous fluids with averaged characteristics is justifiable for the study of hydrodynamic flow processes in porous media at macroscopic scales. Upon recovery, the viscosity of filtered fluids varies considerably with the presence of additives (polymers, surfactants). In micellar solutions, the surface tension is reduced by several orders of magnitude. Not all methods of recovery are equally successful in various oilfields. Representations of an "average molecule" in petroleum components are incorrect. Phase behavior and dispersion conditions/structure of petroleum systems are determining factors in processing technology at all stages of the petroleum value chain, including recovery, transport, storage, processing and applications. A majority of these processes are accompanied by phase transitions, where the activity of the disperse structures is crucial.

Petroleum systems contain complex matter which is the subject of new field of condensed matter physics. Petroleum systems are typical oleo-dispersed, lyophilic systems, or systems of low polarity dispersive media. The medium is in dynamic balance with elements of a dispersed phase. Traditional tools for studying petroleum systems are limited only by the

definition of fractional, grouping, chemical content, and etc. However, observed behaviour of physical and chemical properties in the molecular or dispersed state can differ significantly even with identical chemical contents. Regulation of micro-structural parameters at production, transportation, refinery and application of oil and oil fractions by practically accessible methods comprises the basis of new effective physical and chemical technologies (Syunyaev et al., 1991). Phase transformations from one physical condition to another are accompanied by nucleation, dispersion and formation of micro-heterogeneous systems. The degree of dispersity is considered a necessary additional parameter of state. This data contains initial information which is crucial for proper selection of new technological strategies (Syunyaev et al., 1991).

Recent exhaustion of easily accessible petroleum and gas resources has resulted in more focused attention directed towards extraction and processing of heavy, high viscosity oils and natural bitumens comprising a significant portion of remaining world energy reserves. These resources exist in highly concentrated dispersed systems with significant contents of resin-asphaltene substances (RAS). These petroleum systems demand investigation of microstructure caused by the presence of RAS. For the proper study of Petroleum Dispersed Systems, it is not sufficient to only determine fractional, group, and chemical compounds, elemental analysis, and etc. Of no less importance is to define the interval of the molecular or dispersed state for the tested system at given external conditions. A uniform integrated approach based on analysis and management of microstructure of petroleum systems opens opportunities to regulate properties of intermediate and final products in all technological sequences in the petroleum industry.

The Integrated Theory of Adsorption and Aggregation Equilibrium (ITAAE) is postulated. Separately, there are few classical theories of adsorption. Theories exist for aggregation of complex molecules, such as surfactants, polymers, dyes, and biomolecules. The evolution of such "soft" systems is defined by the hierarchy of InterMolecular Potentials (IMP). There is no doubt that petroleum macromolecules (asphaltenes, paraffines, adamantanes, tethrameric acids etc.) or structural units (nanoaggregates and nanoclusters) belong to that family. According to approaches of supramolecular chemistry or nanochemistry, a variety of these molecules results in a wide morphological spectrum of supermolecular structures in petroleum at nano and micro-scales. These are heavy petroleum, bitumens, emulsions, pitches, tars, coke, foams and gas hydrates.

ITAAE is necessary to understand situations where the contribution of collective IMP in the bulk phase is comparable with the influence of the interface. This situation occurs in porous media. Petroleum disperse systems (PDS) are multicomponent systems with a hierarchy of intermolecular interactions (IMP). Various selective contributions to IMP determine appropriate terms to establish solubility parameters. This theory is a key to understand structuring of PDS on nano- and microscales. Special attention should be drawn to the new and still not fully understood effect of superficial aggregation when surface forces manage formation of superficial units during and after Langmuire and Brunauer-Emmett-Teller (BET) adsorption. This kinetic effect is closely related to phase stability in open systems.

4. Adsorption of petroleum asphaltenes onto mineral surfaces

Asphaltenes and resins comprise the most polar petroleum macromolecules. The polarity causes the relatively high interfacial activity. Strong asphaltene and resin adsorption

tendencies lead these substances to contribute to several undesirable phenomena in petroleum industry: well bore plugging and pipeline deposition; stabilization of water/oil emulsions; sedimentation and plugging during crude oil storage; adsorption on refining equipment and coke formation. Knowledge of kinetic and thermodynamic adsorption parameters opens a possibility to regulation of capillary number and wettability. Actually it affords a method for physical and chemical engineering of liquid-solid interfaces in the oil industry.

Adsorption is the redistribution of the components of substance between bulk phase and surface layer. Dissolved molecules displace molecules of solvent during the process of adsorption from solution. Different mechanisms of surface layers formation are possible due to different nature of adsorbed components, their concentrations, morphology of adsorbent's surface, its wettability. At low concentrations Henry low is performed. In this case adsorption linearly depends on concentration of dissolved substance. The most physically proved model for monomolecular adsorption is a Langmuir model. BET theory is used in more complicated cases of polymolecular adsorption (Hunter, 2001). Asphaltene adsorption on reservoir's rock surface is of special interest in practice of oil production. Asphaltenes are the most high-molecular polar oil components and they have high surface activity (Sayyouh et al., 1991; Syunyaev&Balabin, 2007). Adsorption precedes asphaltenic, resinous and paraffinic formation of macroscopic deposits on reservoir's pores and on surfaces of production equipment. Early colmatage of reservoir may lead to premature well shutdown (Ekholm et al., 2002). Surface layers of asphaltenes and resins can change rock characteristics. This influences filtrational characteristics of the processes of oil and water migration in porous media (Basniev et al., 1993). Adsorption of these substances determines surface hydrophobization. Some researchers consider that gel-like films form at quartz surface during the adsorption process. These films greatly reduce oil penetrability in porous media (TatNIPI, 1988). Adsorption and following deposit formation are significant problems in refinery (Syunyaev et al., 1991; Speight, 1999). Filtration of fluids is based on Darcy Law:

$$\mathrm{Q} = -\frac{\mathrm{k}}{\eta} \times grad\, P\,,$$

where Q – filtration rate, k - permeability of petroleum collector, η – viscosity of fluid, $grad\, P$ – pressure gradient. Coefficient k is connected with porosity of rock m. In simple case when porous media is as a set of similar channels of diameter D the next equation combines all these parameters

$$\mathrm{D} = 4\sqrt{\frac{2\mathrm{k}}{\mathrm{m}}}$$

As a sequence it follows that adsorption of petroleum macromolecules: asphaltenes, resins and paraffines modifies inner pore surface and sequently influences to permeability **k**. Porous media is classified to next classes (Table 1).

Movement in supercapillary pores is obeyed on macroscopic hydrodynamic laws. On the contrary in micropores fluids are immobile practically. Movement in mesopores is defined by a balance between hydrodynamical and intermolecular forces. Interactions of molecules

with walls of such pores are rather high. The most widespread oil reservoirs are quartz sands and dolomite rocks and clays with bulky block-structured packing.

Asphaltene and resin adsorption was studied by a great number of research groups (Ekholm et al., 2002; TatNIPI, 1988; Balabin&Syunyaev, 2008; Syunyaev et al., 2009; Acevedo et al., 2000; Lopez-Linares et al., 2006; Gonzalez&Middea, 1987; Drummond&Israelachvili, 2004; Toulhoat et al., 1994; Akhlaq et al., 1997; Dudasova et al., 2007; Alboudwarej et al., 2005; Batina et al., 2003; Batina et al., 2005; Castillo et al., 1998; Acevedo et al., 1998; Acevedo et al., 2000; Acevedo et al, 2003; Ekholm et al., 2002; Xie&Karan, 2005; Dudasova et al., 2008; Rudrake et al., 2009; Abdallah&Taylor, 2007; Labrador et al., 2007; Turgman-Cohen et al.; 2009). Adsorption of asphaltenes on solid surfaces has been characterized by several experimental techniques, including measurement of contact angles (Drummond & Israelachvili, 2004; Toulhoat et al., 1994; Akhlaq et al., 1997), UV and NIR spectroscopy (Dudasova et al., 2007; Alboudwarej et al., 2005), atomic force microscopy (Toulhoat et al., 1994; Batina et al., 2003; Batina et al., 2005), Fourier transform infrared microscopy (Batina et al., 2005), photothermal surface deformation (Castillo et al., 1998; Acevedo et al., 1998; Acevedo et al., 2000; Acevedo et al., 2003), quartz microbalance (Ekholm et al., 2002; Xie&Karan, 2005; Dudasova et al., 2008; Rudrake et al., 2009), X-ray photoelectron spectroscopy (Dudasova et al., 2007; Abdallah&Taylor, 2007) and ellipsometry (Labrador et al., 2007; Turgman-Cohen et al., 2009). In this study we studied influence of porosity of the rock on adsorption parameters of the asphaltenes.

Macropores	Supercapillary	D>100 μm	Free motion on hydrodynamic forces	Large and medium size Sands, Carbonates
Mesopores	Capillary	D: 0,1-100 μm	Influence of capillary forces	Cemented Sands, Limestones and Dolomites
	Subcapillary	D: 2nm – 100 nm	No movement. Fluids are fixed by intermolecular forces	Clays, Fine crystalline Limestones and Dolomites
Micropores		D < 2 nm	No movement. Fluids are fixed by intermolecular forces	Clays, Ceolites

Table 1. Classification of Porous materials.

Asphaltenes were extracted from West Syberian crude by standard method described in previous work (Balabin&Syunyaev, 2008). The value 750 g/mol was chosen as average molecular mass of asphaltenes (Mullins et al., 2007). Adsorption of asphaltenes was studied at concentration 1 g/l in benzene (density 0,88 g/cm^3, molar mass 78 g/mol). Four fractions of quartz sand, three fractions of dolomite and two fractions of mica were used as adsorbents. Quartz and dolomite particles are considered to be quasispherical particles. Mica models crumbling rock with plate-like particles. Adsorbents were provided by company "Batolit". Its parameters are shown in Table 2. The particle size distribution was evaluated using optical microscope (OPTITECH SME-F2).

Mineral adsorbents					
Adsorbent	Material Density, d_0, g/cm^3		Powder apparent density, d_p, g/sm^3	Medium size, mcm	Porosity m, 1-d_p/d_0
Dolomite	D-03	3,00	0,65	3	0,75
	D-10	3,00	1,05	10	0,58
	D-30	3,00	1,15	30	0,55
Mica	M-05	2,77	0,35	5	0,84
	M-30	2,77	0,55	30	0,77
Quartz	Q-5	2,65	1,085	5	0,59
	Q-10	2,65	1,085	10	0,59
	Q-100	2,65	1,110	100	0,58
	Q-200	2,65	1,180	200	0,55
Metal adsorbent (steel shot)					
	Density, d_0, g/cm^3		Medium diameter, mm		
DSL – 0,4	7,2		0,5		
DSL – 1,4	7,2		1,4		
DSL – 3,6	7,2		3,6		

Table 2. Adsorbent properties.

Near-InfraRed-spectroscopy (NIR) became more and more popular technique for study of petroleum systems (Balabin&Syunyaev, 2008; Oh&Deo, 2002). NIR device – Near-IR FT Spectrometer InfraLUM FT-10 (LUMEX, Russia) was used for measurements. The spectra have been registered at the temperature from 22 to 25 °C. No cell thermostating was used. Background spectrum was taken before and after each measurement; then, the averaged background spectrum was subtracted from the sample spectrum. This technique allowed obtaining an analytical signal with satisfactory accuracy and precision. The instrument calibration was performed using four pure hydrocarbons (toluene, hexane, benzene, and isooctane). Figure 1 represents the scheme of NIR experiment for adsorption observation.

Kinetic experiments were carried out by continuously measuring the light absorption in a NIR range (8,500-13,000 cm^{-1}) in benzene asphaltenes solution in contact with powders.

Quantity of adsorbed asphaltenes was determined by registration of transmittance spectra of bulk phase above the adsorbent top. Knowing the time dependent bulk concentration of asphaltenes $C(t)$ and the initial concentration we are able to evaluate the adsorbate mass $m(t)$ and the adsorbed mass density $\Gamma(\mathrm{t})$. Fundamental Buger-Lambert-Beer law was used for concentration measurements. Final formula for determination of adsorption (Syunyaev et al., 2009) is presented below.

$$\Gamma(\mathrm{t}) = \frac{\mathrm{m(t)}}{\mathrm{S_{ads}}} = \frac{V_0}{S_{ads}} \cdot C_{SS} = \frac{V_0}{S_{ads}}[C_0 - C_{\mathrm{AS}}(t)] \tag{1}$$

where C_0 is assigned bulk concentration at initial moment of time , $\mathbf{C_{AS}}$ is time –dependent measured concentration, $\mathrm{S_{ads}} = s_{SP} \cdot m_{ads}$ is the total surface area of adsorbent; s_{SP} is the specific surface area of adsorbent (e.g., per gram); m_{ads} is the mass of adsorbent (e.g., in

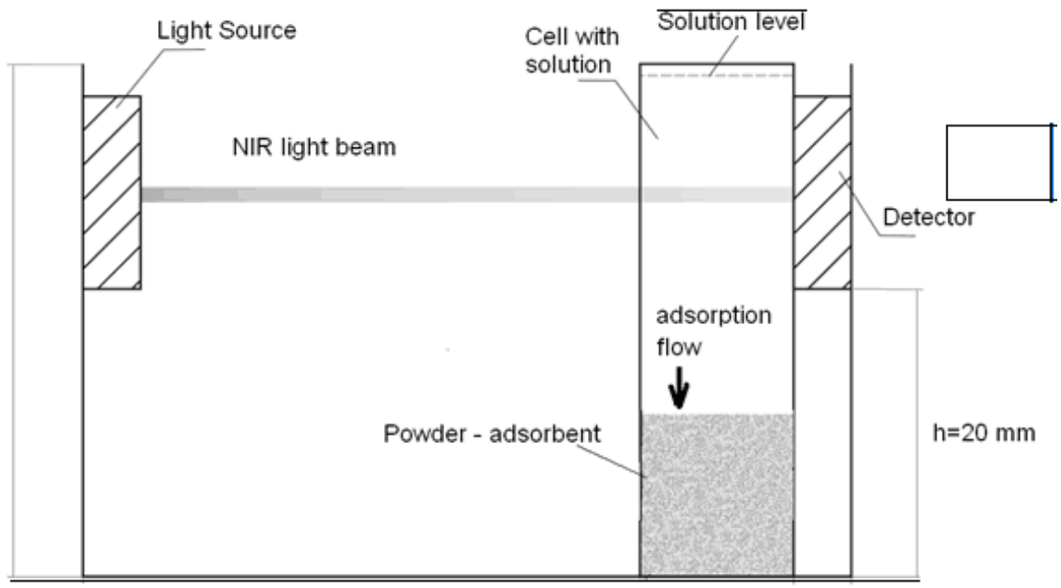


Fig. 1. Experimental setup for measuring adsorption on powders.

grams); V_0 is the volume of solution in the cell (5 ml in our experiments). Accuracy of the $\Gamma(\mathrm{t})$ evaluation depends on the accuracy of $C(t)$ evaluation.

The first order equation of reversible Langmuir adsorption kinetics (Hunter, 2001; Hiemenz&Rajagopalan, 1997) was used for data approximation:

$$\Gamma(\mathrm{t}) = \Gamma_{\max}\frac{KX_0}{KX_0+1}\left[1-\exp(-(k_a+k_d)t\right] = \Gamma_{\max}\cdot \mathrm{a}\cdot\left[1-\exp(-(k_a+k_d)t\right] \quad (2)$$

where $\Gamma_{\max}$ is maximal adsorbed mass density and coefficient a defines relative fraction of adsorbent surface occupied by asphaltene molecules**.** Equation (2) needs asphaltene concentration in mole fractions. The mole fraction for our concentration is placed below

$$C_0 = 0{,}1\ \mathrm{g/l} \quad X_0 = 1{,}18\cdot 10^{-5}$$

In (2) $K=\frac{k_a}{k_d}$ is equilibrium constant of adsorption/desorption at concentration X_0. k_a and k_d are the rate constants of adsorption and desorption, respectively. Next step is to determine the equilibrium adsorption parameter Γ_{eq}, which can be achieved at assigned concentration. $\Gamma_{\max}$ determines maximum possible adsorbent capacity when surface is covered by monomolecular layer.

$$\Gamma_{eq} = a\cdot\Gamma_{\max}$$

Boundary spectra area contains noise. For more accuracy removal of noise area was done. Truncated spectra were integrated for integral transmittance A calculation. Example of asphaltene solution spectra is presented at Figure 2.

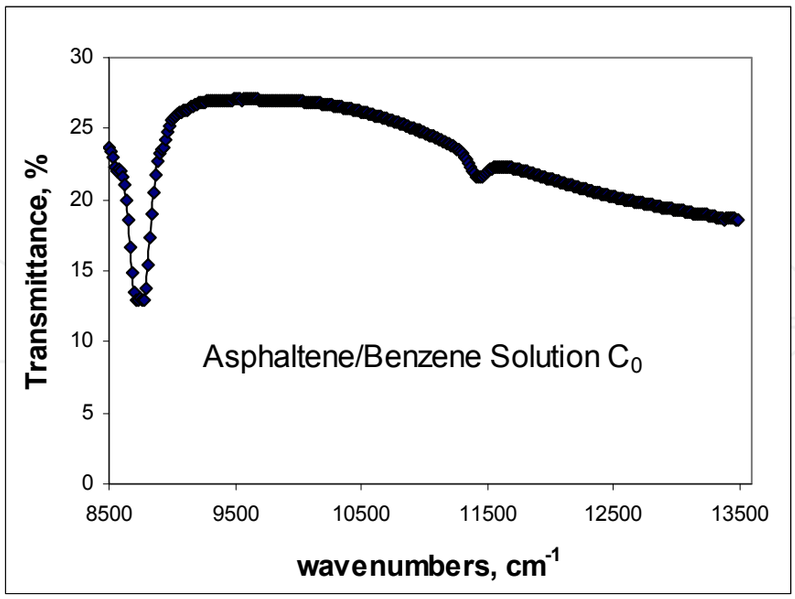


Fig. 2. Transmittance Spectra of Initial Asphaltene solution in Benzene (C_0=1 g/l) in Near Infrared Region.

Kinetic dependences of integral spectra were received for all samples of powders. All spectra were treated identically. Data processing steps for different samples are presented in Figures 3 and 4. All spectra were normalized to values at start time-point.

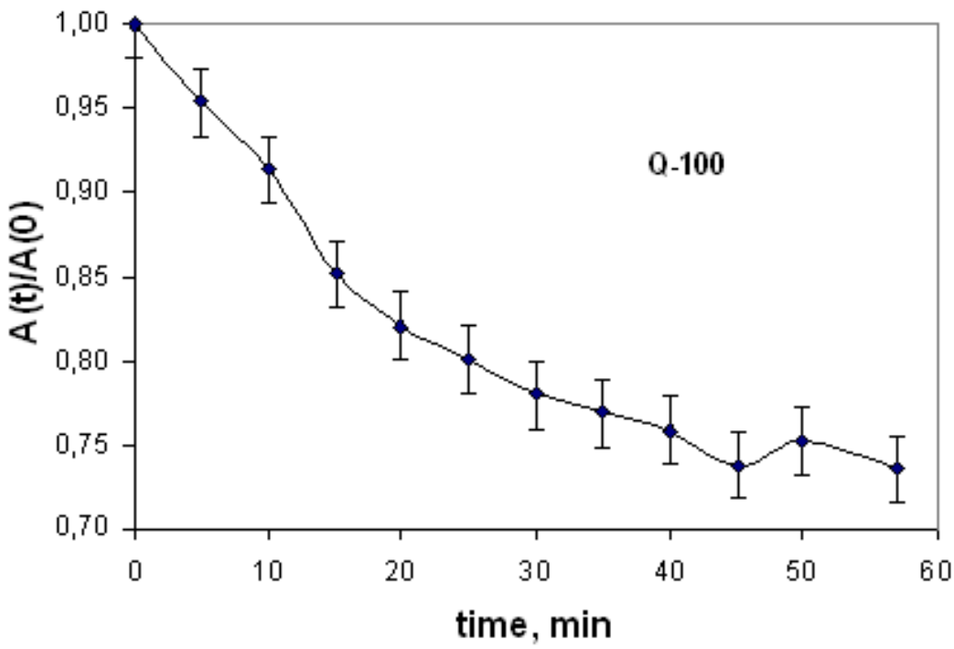


Fig. 3. Time change of integral transmittance of asphaltene solution (normalized to a value in initial time point). Sample Q-100.

Figure 3 represents example of normalized solution bulk concentration C_{AS} spectra for Q-100 quartz sand fraction. Figure 4 and Figure 5 show next steps of dependencies interpretation for adsorption kinetics analysis. Actually it demonstrates surface concentration C_{SS} changes by example of dolomite D-10 powder.

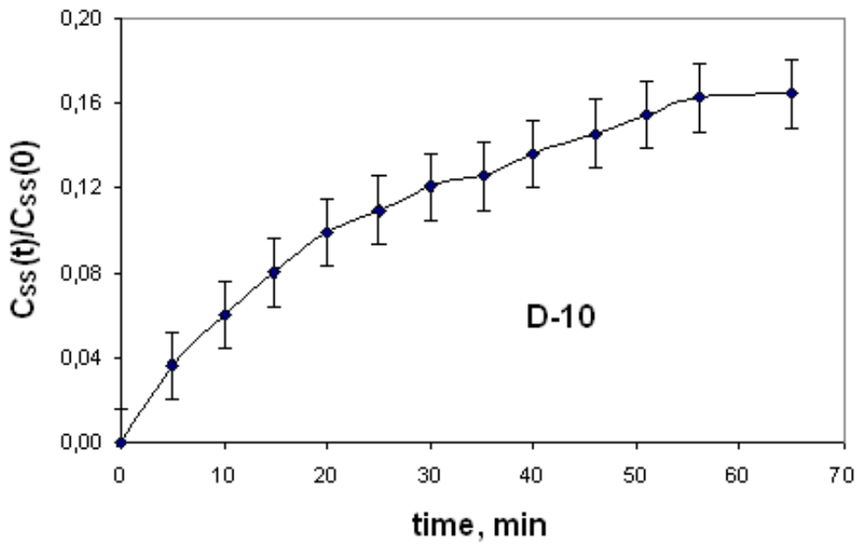


Fig. 4. Kinetics of change of surface concentration (normalized to a value in initial time point). Sample D-10.

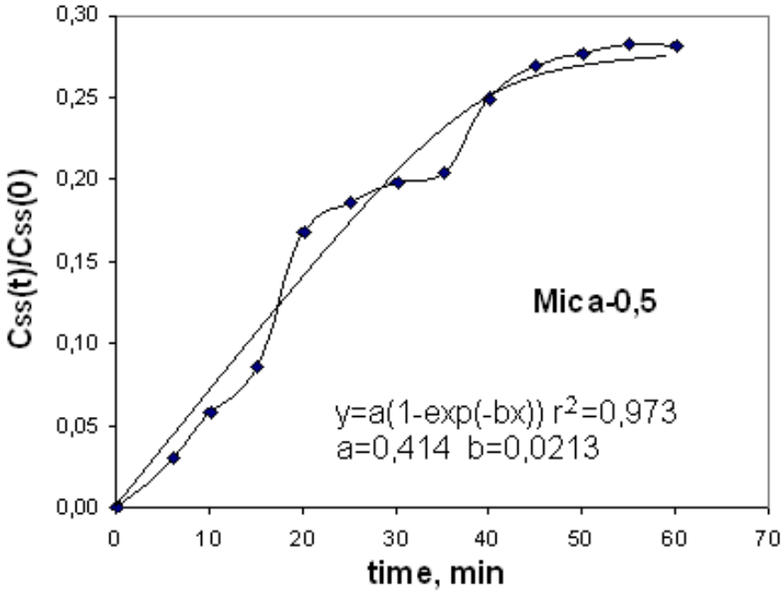


Fig. 5. Fitting of kinetic curve of surface concentration. Adsorption is proportional to concentration (normalized to a value in initial time point). Sample M-05.

5. Kinetic parameters of adsorption

Combined usage of Langmuir adsorption kinetics equation (2) and equation (1) allows us to calculate characteristics of adsorption-desorption process of asphaltenes onto surface of searched surfaces: relative fraction of occupied surface by molecules (a), the maximal adsorbed mass density (Γ_{max}), the equilibrium constant of adsorption (K), the rate constants of adsorption (k_A) and desorption (k_D). These parameters are resulted in Table 3.

Sample	a	$\mathbf{k_a+k_d}$, min^{-1}	$K = \frac{k_A}{k_D}$	k_D, min^{-1}	k_A, min^{-1}	ΔG, kJ/mol
Q-5	0,23	0,04	2 570	0,000017	0,044	19,1
Q-10	0,29	0,03	3 423	0,000009	0,032	19,8
Q-100	0,29	0,04	3 490	0,000013	0,044	19,9
Q-200	0,27	0,03	3 098	0,000008	0,026	19,6
Mica-05	0,41	0,02	5 978	0,000004	0,021	21,2
Mica-30	0,28	0,04	3 210	0,000012	0,038	19,7
D-03	0,17	0,03	1 745	0,000019	0,034	18,2
D-10	0,18	0,04	1 795	0,000022	0,040	18,2
D-30	0,19	0,05	1 985	0,000025	0,050	18,5

Table 3. Kinetic and thermodynamic parameters of asphaltene adsorption onto rock sands.

The rate of asphaltene adsorption is greater than desorption rate for studied concentration. Gibbs adsorption energy values define character of adsorption as physical, not chemical. Rate of asphaltene adsorption is less then resins (in two orders) reported earlier (Balabin&Syunyaev, 2008). Parameters of resin adsorption from benzene solutions on quartz are submitted in Table 4.

Sample	$k_A + k_D$, min^{-1}	$K = \frac{k_A}{k_D}$	k_D, min^{-1}	k_A, min^{-1}	ΔG, kJ/mol
Resin	0.180	6.0	0.0259	0.15	4.4

Table 4. Adsorption parameters of resins on quartz sand.

The adsorption of asphaltenes is practically irreversible. Significantly larger masses and molecule sizes of asphaltenes appear to be the reason. Diffusion of such molecules to solid surface is embarrassing. The mechanism of diffusion limited adsorption is realized (Syunyaev et al., 2009; Diamant & Andelman, 1996). Gibbs energy values are more or less the same for surfaces of all investigated materials: quartz, dolomite, and mica. It is known that quartz and dolomite are the main components of oil reservoir framework rocks. The porosity has no influence on kinetic parameters of adsorption. Asphaltenes adsorption at the surfaces of quartz and dolomite is the most active.

As a whole, the designed values of asphaltene adsorption parameters on metal surfaces are close to values obtained for mineral powders. Parameters of adsorption-desorption processes on metal surface are listed in Table 5.

Sample	a	$k_A + k_D$, min^{-1}	$K = \frac{k_A}{k_D}$	k_D, min^{-1}	k_A, min^{-1}	ΔG, kJ/mol
DSL-0,5	0.039	0.00022	2.88E+04	7.64E-09	2.20E-04	25
DSL-1,4	0.0756	0.00052	9.34E+03	5.52E-09	5.16E-04	27.9
DSL-3,6	0.044	0.00192	7.53E+05	2.55E-09	1.92E-03	32.9

Table 5. Parameters of asphaltene adsorption on metal surfaces.

According to designed Gibbs adsorption energies minerals can be distributed in the following order: mica > quartz > dolomite for fine-grained mineral powders, mica = dolomite > quartz for coarse-grained mineral powders. Among investigated mineral adsorbents, mica is the most active in relation to asphaltenes.

In our experiments adsorption leads to reduction of bulk asphaltene concentration. Inside porous media asphaltene molecules occupy accessible sites on surface. Mineral adsorbents model the porous media of a petroleum collector. Structural parameters were appreciated using model of "nonideal soil" when the porous media is described as the spatial volume consisting of constant radius spheres package. The alternative description of the porous media as «an ideal ground», represent system of incorporating cylindrical capillaries with the characteristic length close to radius of a grain. Calculated values of the specific area of the adsorbents according to model of "nonideal soil" are presented in Table 6. After estimation of the specific area the maximal capacity of Langmuire asphaltene monolayer was calculated from common relation for molar volume ***(V_m)***

$$V_M = \frac{M}{N_A \rho},$$

where M - molecular mass (750 g/mol), N_A - Avogadro constant (mol^{-1}), ρ-asphaltene density (ρ = 1.1 g/cm^3). As the cross section of a "spherical" asphaltene molecule makes 1, 2 nm^2 so surface capacity of adsorbed layer makes 1 mg/m^2.

Meaning of this parameter is boundary criterion of concentration changes in a bulk phase (C_0=0.1g/l) and in a space between grains of the porous media. Calculated masses of adsorbed asphaltenes and the appreciated pore volumes allow assuming concentration of the asphaltene solution inside porous space (Table 6). Langmuire model yields diminished values of adsorbed mass. It may be a sequence of well-known effect of concentration polarization (Bacchin et al., 2002) when in the domain near membranes concentration exceeds medium bulk concentration. On internal structure the membranes are similar to porous media. Average calculated concentrations exceeding bulk are presented in Table 6.

Mica is chosen as the substrate in further investigations of asphaltene deposits morphology by atomic force microscopy (AFM). Preliminary data shows that the mechanism of monomolecular adsorption is not realized. The kinetic models can be based on BET theoretical approach (Hunter, 2001; Hiemenz&Rajagopalan, 1997) which describes polymolecular adsorption.

Regular deviations from exponential curve form are observed in all obtained dependencies (Figure 5). These deviations are small and are inside the limits of experimental errors. But these deviations have regular character and are observed earlier also for resins (Balabin

Sample	Γ_{eq}, mg	Adsorbent specific area, m^2/g	Γ_{max}, mg (calculated Langmuire monolayer capacity)	Average asphaltene concentration in pores , g/l
M-05	4.07	0.22	0.87	0.32
M-30	1.41	0.04	0.14	0.22
D-03	1.89	0.33	1.33	0.12
D-30	1.2	0.03	0.13	0.50
Q-10	2.81	0.11	0.45	1.08
Q-200	0.38	0.01	0.02	0.19

Table 6. Average concentration of asphaltene solution in pores of mineral model adsorbents.

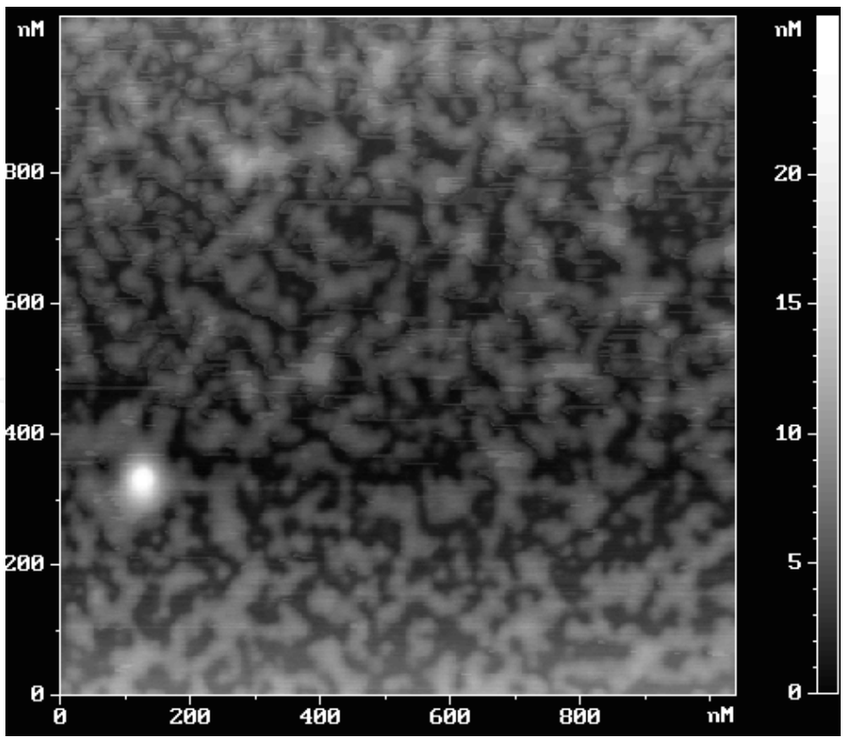


Fig. 5. AFM scans of adsorbed asphaltenes at mica surface.

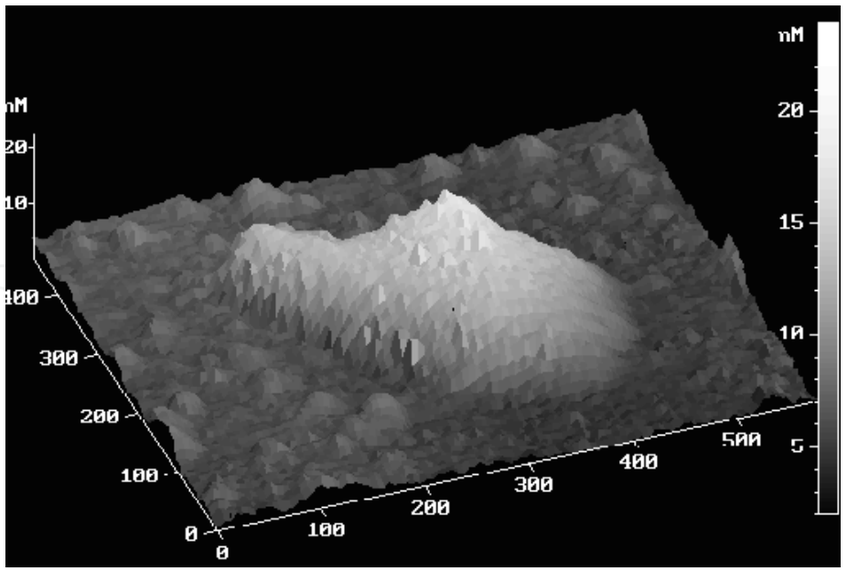


Fig. 6. Polymolecular multilayered adsorption of asphaltenes at mica surface.

& Syunyaev, 2008). Concentration oscillations in water solutions of dye were also observed by laser refractometry. It is possible to suppose that adsorption is kinetically limited by diffusion. The mechanism of diffusion relaxation suggested by I. Akhatov is realized (Akhatov, 1988, as cited in Syunyaev at al., 2009). The classic Fick's law can be generalized by introduction of additional relaxation item

$$\tau \frac{\partial \mathrm{j}}{\partial \mathrm{t}} + j = -D \frac{\partial C}{\partial x},$$

where j is diffusion flow, D is the coefficient of translational diffusion, C is concentration of substance, τ is the characteristic time of relaxation.

The equation is transformed to equation in partial derivatives of second order.

$$\tau \frac{\partial^2 c}{\partial t^2} + \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}.$$

Solution for equation appears to be superposition of two concentration time-dependent functions. One of these functions is the derivation for damped oscillations equation.

For porous media neighboring with bulk phase and at condition when adsorption time is much less than diffusion time

$$\tau_{\mathrm{ads}} << \tau_{dif},$$

mechanism of 'adsorption pump" is actualized. While filling porous media by solution the adsorption process occurs faster. This results in decreasing of bulk equilibrium concentration inside porous media. As diffusion process goes more slowly, discontinuous jump of concentrations on border with porous media is appeared. So the region with decreased concentration in border with bulk phase arises. As a consequence the diffusion

flow emerges in this border. Than concentration jump spreads to bulk phase with gradually decreasing amplitude due to diffusive spreading (Figure 7). This is damping concentration wave in bulk phase, which we observe in experiment (Figure. 4).

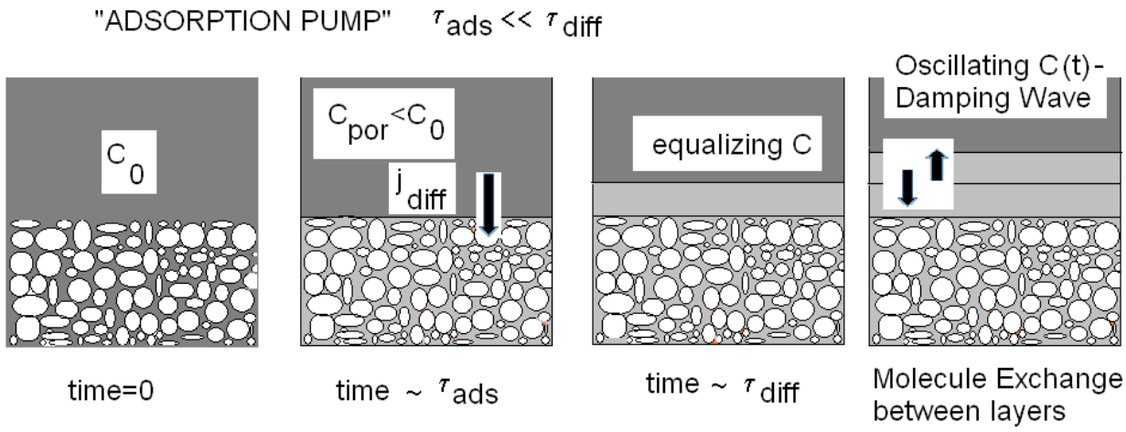


Fig. 7. "Adsorption Pump". Comments are in the text.

6. Conclusion

Asphaltene adsorption at the surface of mineral powders which are a framework of oil reservoir was studied by Near Infrared (NIR) spectroscopy. Experimental procedure of surface asphaltenes concentration measurement is proposed. Adsorption parameters are evaluated in a Langmuir approximation of monomolecular layer occupation. Adsorption characteristics are important for permeability coefficient estimation in Darcy law. That is necessary for further development of filtration theory. Increasing of asphaltene concentration in intergrain space of porous media in comparison with bulk concentration is similar to concentration polarization in membrane technology. The mechanism of initiation of concentration waves in bulk phase neighboring with porous media is offered. Integrated investigation of polymolecular multilayered adsorption using abilities of AFM-analysis is required in future.

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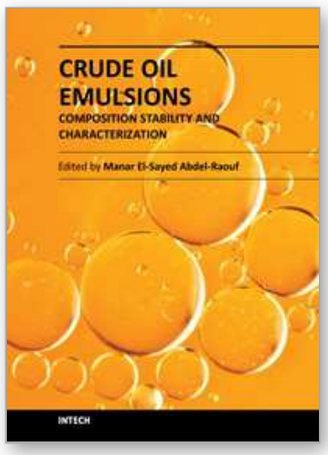
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Petroleum "black gold" is the most important nonrenewable source of energy. It is a complex mixture of different phases and components. Refining it provides a vast number of organic compounds, all of them of which are used to produce petroleum based products for numerous applications, from industry to medicine, from clothing to food industries. We can find petroleum based products all around us. This book deals with some important topics related to petroleum such as its chemical composition and stability. It is well-known that the chemical composition of crude oil differs according to the site of production, and its grade varies from waxy to asphaltenic crude. Both of them are refined to produce different products. The stability of crude oil on aging and transportation is governed by several factors and these factors are included within this book. Some new technologies for petroleum characterization are also introduced. This book is aimed at researchers, chemical engineers and people working within the petroleum industry.

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