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The stability and evolution of oil systems studied *via* advanced methods *in situ*

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The potential of physical methods for *in situ* studies of the phase stability and physicochemical evolution of heavy oils is analyzed. The basic principles of *in situ* application of the methods are outlined; the scope and limitations of each approach are discussed. Particular attention is paid to the visualization of the asphaltene aggregation process using attenuated total reflection Fourier transform IR spectroscopy and magnetic resonance imaging, as well as small-angle X-ray and neutron scattering, electron spin resonance and electron and optical microscopy. These methods provide complementary information on the properties and behaviour of oil disperse systems on various spatial and temporal scales ranging from the rotational mobility of asphaltene molecules and the dynamics of their local environment with a characteristic time of $\sim 10^{-10}$ s and evolution of the size characteristics and shape of asphaltene aggregates to visualization of asphaltene aggregation and formation of precipitates in crude oils and their blends with spatial resolution from a few to thousands of micrometres with a characteristic time from seconds to hundreds of hours. The approaches described can be efficiently applied in a wide range of temperatures and pressures, as well as in the presence of chemicals that affect the stability of heavy oils.
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I. Introduction

In recent years, the modern petroleum industry has faced considerable challenges associated with the need to develop efficient technologies for production and extensive processing of heavy crude oils and their components. The difficulty of using this type of crude hydrocarbons is caused by the high cost of recovery and transportation and by fundamental problems that arise in the processing of heavy crude oils using traditional catalytic processes. A highly intractable problem is the formation of deposits in the process equipment during heavy oil transportation and processing,[1–6] resulting in inefficient heat exchange and considerable loss of energy and feed during the industrial process, which can be as high as several percent of the crude oil equivalent.

Thus, a fundamental condition for the development of effective processes for heavy oil production and processing is understanding of the key factors that determine the aggregative behaviour and stability of oil disperse systems, behaviour and chemical transformations of their components under various external conditions including elevated temperature and pressure and the presence of aromatic or aliphatic compounds, surfactants, alkenes or polymers specially added to suppress precipitation or compounds used to dissolve asphaltene deposits (alcohols, esters, amines, *etc.*) including chlorine and sulfur compounds.[7–10]

Asphaltenes are known to be among the major components of heavy oils, playing the key role in the formation of precipitates.[11,12] Asphaltenes are prone to self-association to form aggregates, which may induce, under certain conditions, their irreversible flocculation and sedimentation.[13] However, despite the great number of publications devoted to determination of the molecular mass, size and shape of asphaltene molecules and the structure and physicochemical properties of asphaltenes, their aggregation mechanism in real crude oils still remains an unsolved issue.[14]

One of the fundamental problems faced by researchers is the structural and molecular variability of asphaltenes, which are defined as the heaviest fractions of crude oil insoluble in normal alkanes (n-pentane, n-heptane and so on).[15] Commonly, asphaltene molecules are considered to have an aromatic polycyclic hydrocarbon core consisting of 5–8 rings with heteroatoms (mainly nitrogen, oxygen and sulfur). The substituents in the rings are mainly alkyl chains with various functional groups containing heteroatoms, sulfide and nitrogen-containing saturated structures,[16] carbonyl, ether and ester groups.[17,18] The attempts to define asphaltenes more strictly encounter difficulties caused by the variability of their molecular structures, associated with both the diversity of chemical reactions involved in the crude oil formation and differences in the reaction conditions (temperature, pressure).[19,20] The large size and the aggregation susceptibility of asphaltene molecules and the presence of functional groups prone to further polymerization to give high-molecular-mass hydrocarbons and coke are responsible for blocking catalyst active sites.[21–23] This serves as a strong impetus for the search for new processes for asphaltene conversion to valuable chemical compounds.[24,25]

A significant factor influencing the asphaltene aggregation and precipitation is their local environment, which determines the nature of intermolecular interactions of asphaltenes with other crude oil components. Apart from the pressure and temperature, the chemical composition of the local environment also plays an important role in asphaltene stabilization.[12,26] For example, the addition of waxes changes the solubility of asphaltenes in crude oil, since wax can affect the interaction between asphaltenes and resins, which are polymeric compounds containing heteroatoms (N, S and O), but comprising less conjugated aromatic rings than asphaltenes; they are also less polar and are soluble in aliphatic solvents.[27] High temperature and pressure can also change the local environment of asphaltene molecules, which leads to an increase or decrease in the solubility in crude oil.[12,28] It is evident that prediction of crude oil stability and solubility of asphaltenes under specified conditions requires the fundamental knowledge of the character of intermolecular interactions between asphaltenes and other heavy oil components present in the local environment; this knowledge can be gained only by means of *in situ* studies of local rheological properties of crude oils and molecular dynamics of asphaltenes under various conditions.

Currently, the structures and properties of heavy crude oils and oil residues[13] are studied by highly informative physicochemical methods including Fourier transform ion cyclotron resonance mass spectrometry (ICR MS),[29] small-angle X-ray (SAXS) and small-angle neutron (SANS) scattering,[30] nuclear magnetic resonance imaging (MRI),[31,32] X-ray absorption near-edge structure (XANES) spectroscopy,[33] magnetic circular dichroism (MCD) spectroscopy,[34,35] attenuated total reflectance Fourier transform infrared (ATR FTIR) spectroscopy,[36] high-Q ultrasonic spectroscopy[37] and some other methods. The description and analysis of the results obtained by each method can cover hundreds of pages; however, one has to admit that the investigations are often encountered with restrictions that preclude unambiguous interpretation of the experimental data and gaining reliable information on the properties and phase composition of crude oils and their behaviour under different external conditions. Actually, the data obtained by even the most advanced physicochemical methods in the *ex situ* mode do not reflect processes that take place in crude oils under real conditions and, hence, they are unable to predict the behaviour of various crude oils and to determine the conditions for their stability and/or formation of oil deposits. As a rule, the listed methods are used to characterize crude oils and their heavy components, for example, to identify the atomic composition of asphaltene molecular fragments from their exact mass, and to gain information about their structure and physicochemical properties. However, it has to be stated that there is still no clear understanding of the causes for the loss of stability and aggregative stability of various heavy oils under particular conditions.[38] Currently, most observations indicate that aromatic compounds[39] and resins[40] can function as stabilizers and solvents for asphaltenes in oil dispersions, while deposition processes are facilitated by high concentrations of asphaltenes and paraffins.[4] However, the asphaltene-to-resin and aromatic-to-aliphatic ratios underlying the known oil stability indices[4,41] still cannot serve as universal indicators determining the stability.

The application of physical methods *in situ* is a milestone on the way to identification of the factors determining the stability of oil disperse systems and elucidation of the mechanisms of aggregation and disaggregation of high-molecular-mass components of heavy oils. It is important to use a set of complementary methods that would cover

various spatial and temporal scales for *in situ* investigations, but not a single, even a unique, method.[42] This would help not only to gain data on the molecular dynamics of asphaltenes and resins and local characteristics of oil disperse systems (viscosity, diffusion and aggregation rate of heavy components), but also to identify the factors determining the stability of oil dispersions and to propose energy-efficient approaches that would ensure higher aggregative stability of heavy oils.

This review represents the first attempt to analyze the currently existing, most efficient investigation methods *in situ* that provide complementary information about the properties and behaviour of oil disperse systems on various spatial and temporal scales, starting from the mobility of single molecules of heavy oil fractions and the dynamics of their local environment with characteristic times of $\sim 10^{-10}$ s and evolution of the aggregate size and shape to 'chemical imaging' of aggregation and formation of deposits in crude oils and their blends at the micro- and macro-levels (from a few to thousands of micrometres) with a characteristic time from several seconds to hundreds of hours. The described approaches can efficiently operate over broad temperature and pressure ranges and upon addition of special chemicals that affect the stability of heavy oils.

II. Chemical imaging of the asphaltene aggregation processes by attenuated total reflectance Fourier transform infrared spectroscopy

Fourier transform IR spectroscopy is widely used for chemical analysis of various hydrocarbon systems, including oil components and oil-derived products.[43] However, the application of FTIR spectroscopy to crude oils is restricted by pronounced infrared absorption of these multicomponent systems, which virtually precludes the *in situ* use of the traditional techniques of transmission FTIR spectroscopy to study the stability and physicochemical evolution of disperse systems in heavy crude oils.

Chemical imaging using attenuated total reflection FTIR spectroscopy is a unique method for studying various pharmaceutical drugs[44] and functional materials — polymers[45] and biomaterials.[46,47] This approach was adapted and successfully applied to characterize the deposits formed in crude oils[36] and to study the crude oil behaviour *in situ*.[48–52] Focal plane array ATR FTIR spectroscopy can be termed as 'chemical photography',[53] which makes it possible to study materials at the microscopic level with a spatial resolution. The array detection of the ATR IR spectra can be applied to studying the chemical properties and evolution of local microscopic sites of samples, in particular, at elevated temperature and pressure, in the *in situ* mode with minimal requirements to sample preparation and sample quantity. This approach opens up unique opportunities for more profound understanding of aggregation of heavy oil components, conditions and mechanisms of deposition and evolution of the deposits, which is necessary for the development of special measures for preventing undesirable loss of stability of hydrocarbon systems.

The simultaneous recording of a set of individual IR spectra corresponding to different local areas of the sample provides fundamentally new information as compared with the averaged chemical composition of the whole sample determined with a single-element detector. An array detector produces a two-dimensional picture (chemical image), in which each point is correlated with the integrated absorbance of a characteristic IR band measured for a local site of the surface. Hence, it is possible to analyze the spatial distribution of chemical components. The application of IR spectroscopy to a local sample site in which the chemical changes of interest take place actually results in increasing sensitivity of the method and decreasing spectral acquisition time. Colour coding is commonly used for effective process-

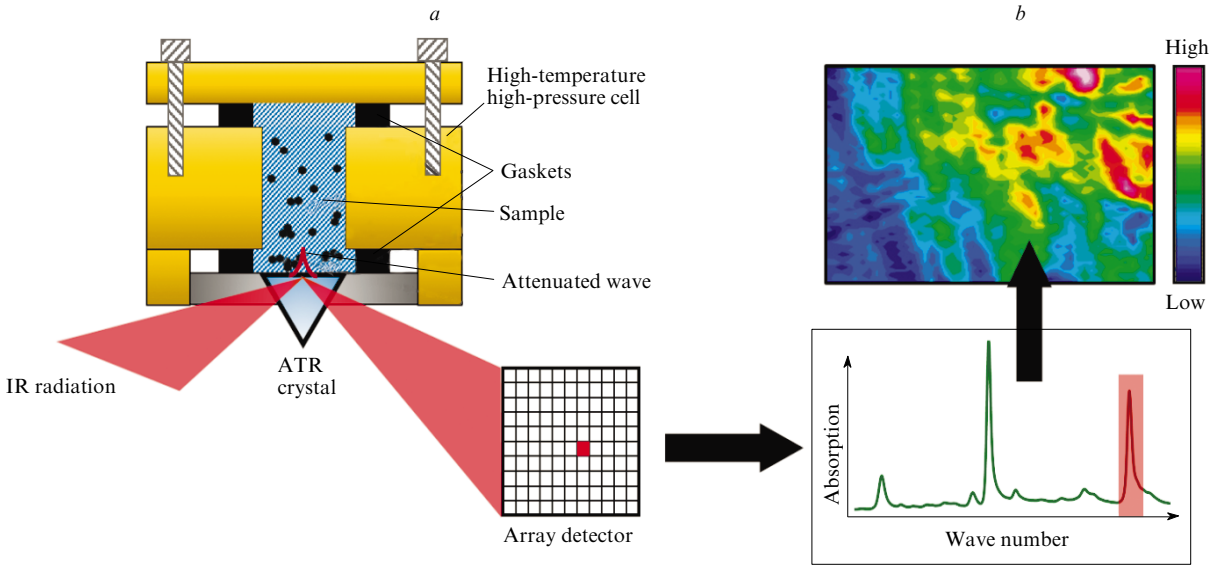


Figure 1. Schematic diagram of the chemical imaging of asphaltene precipitation by ATR FTIR spectroscopy.
(*a*) High-temperature high-pressure cell and array detector; (*b*) IR spectrum corresponding to the area of the sample marked in red and two-dimensional image (chemical image), in which each point is matched by the integrated absorbance of the characteristic IR band. The formed 2D image shows the distribution of the component corresponding to the selected IR band in the sample.

ing of large data arrays and discrimination of the regions with different IR band absorbance (Fig. 1).

Chemical imaging can be used as micro-imaging with a spatial resolution of down to several micrometres by means of an infrared microscope and as macro-imaging, which provides images of a larger area of the sample and can serve for *in situ* studies of fast processes on a real time basis. The combination of these approaches gave the first opportunity to study the formation of deposits in the real equipment used for petroleum refining.[36] Asphaltenes, carbonates, sulfates, sulfoxides, coke and so on were identified in the deposit. The application of IR microscopy was especially useful for the detection of oxalate groups, which could not be identified by macro-imaging. Using chemical imaging technique, Tay[54] developed statistical approaches for the quantitative determination of various characteristics of oil precipitates, including the spatial distribution of chemical components in the sample and characteristic sizes of microscopic areas (agglomerates) with enhanced concentrations of oxalates and sulfates, which were 25 and 30 μm, respectively, for the examined samples.

A unique chemical imaging procedure has been used to identify the major components of heavy oils that form precipitates.[48, 49, 52] Thorough analysis of the measured IR spectra demonstrated that, apart from hydrocarbons, oils contain various carbonyl compounds, ethers and esters, sulfoxides, pyrroles and pyridines. Fourier transform IR spectroscopic analysis of asphaltenes precipitated with excess heptane revealed both fused aromatic rings and heteroatomic functional moieties (pyrrole, pyridine, sulfoxide) in their molecules. Using chemical imaging, stabilities of various types of asphaltenes containing particular functional groups have been determined. Specifically, it was shown that aggregation and sedimentation in excess heptane involve, first of all, asphaltenes that contain polycyclic aromatic hydrocarbons and sulfoxides, ethers and esters and then pyridine and pyrrole rings.[49] Asphaltenes with various types of thiophene-containing groups showed the highest stability to aggregation. Comparison of the results has also proved that stability of crude oils is determined by not only the relative contents of aromatic and saturated compounds. All other factors being equal, the key role in the aggregation and sedimentation of asphaltenes can belong to paraffins and naphthenes present in oils.[52]

Later, chemical imaging has been used to address the loss of phase stability arising upon the blending of different types of crude oils under different external conditions.[48] Two heavy crude oils (A, B) and one light crude oil (C) with markedly dissimilar characteristics were chosen, and chemical analysis was carried out for the major components of the precipitates formed in the case of incompatibility of the crude oils blended in pairs at various temperatures (60 and 200 °C). A detailed description of crude oil characteristics has been reported by Gabrienko *et al.*[48] Blending was carried out using the light oil and one of the heavy oils, because in this case, incompatibility and precipitates or deposits could be expected. The stability of blends was monitored by the ATR chemical imaging technique using cells (see Fig. 1) that enabled monitoring the behaviour of crude oil blends directly during heating and, hence, provided unique information about changes in the phase and chemical composition of samples induced by various external impacts (temperature, pressure). The ratio of the mixed crude oils was varied in order to study the effect of the blend composition on the stability. The resulting spectroscopic data were used to establish a correlation between the composition of oil blends and possible precipitation.

It was shown that at a temperature of 60 °C, asphaltenes are the major components of the precipitates formed in crude oil blends.[48] As the temperature increases (200°C), the solubility of asphaltenes in the blends increases. Apart from asphaltenes, salts (in particular, sulfates) are the major components of the deposits. The preliminary crude oil desalting resulted in a considerable decrease in the deposition and precipitation in oil blends at 200 °C (Fig. 2).

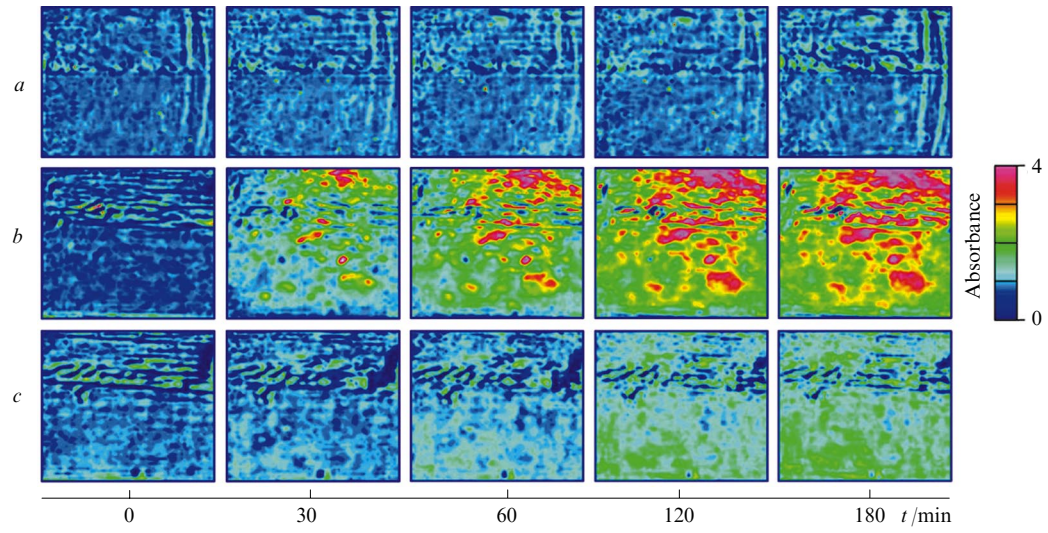


Figure 2. FTIR spectroscopic images of oil blends recorded *in situ* at 200 °C.[48]
Heavy (A) to light (C) crude oil ratio is 1 : 1 (*a*), 1 : 5 (*b*), 1 : 5 (with preliminary treatment to remove salts) (*c*). The images were obtained by plotting the distribution of the integrated absorption of the FTIR bands in the 1000 – 1200 cm^{-1} range at each point of the imaged area of ~610 × 530 μm.

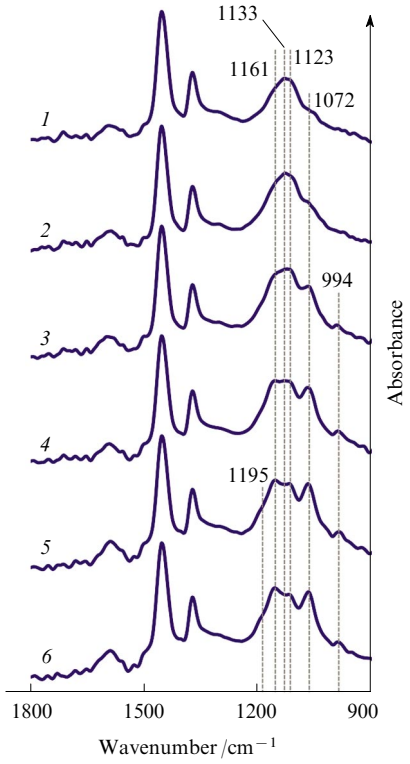


Figure 3. FTIR spectra of the precipitates formed from oil blend with a heavy (A) to light (C) crude oil ratio of 1 : 5 at 200 °C.[48] The spectra show the change in the chemical composition of the precipitate *vs.* time of heating of oil blend: after 30 (*1*), 60 (*2*), 90 (*3*), 120 (*4*), 150 (*5*) and 180 min (*6*).

It was assumed, considering the spectroscopic data,[48] that hydrogen bonds are formed between the sulfoxide groups of sulfates and hydroxyl groups of asphaltene molecules. This means that the mechanism of asphaltene precipitation from oil blends changes with increasing temperature. For example, mixing of crude oils at 60 °C results in asphaltene precipitation *via* destabilization and subsequent aggregation. Meanwhile, inorganic salts (sulfates) represent the major component of the deposits detected at 200 °C; salts can be precipitated together with asphaltenes because of the formation of intermolecular hydrogen bonds between the salt and asphaltene molecules (Fig. 3).

Yet another vivid example of the application of ATR FTIR spectroscopy-based chemical imaging is a study of the behaviour of a crude oil – CO_2 binary system and the effect of CO_2 on the asphaltene aggregation processes.[55] This study is of considerable interest for the disposal of CO_2 and development of CO_2-based effective enhanced oil recovery methods. In particular, there are known methods for increasing oil recovery by 8% – 16% using sub- or supercritical (SC) CO_2 and, hence, addressing simultaneously the acute greenhouse effect problem.[56] The major difficulty of using CO_2 in technologies of this type is aggregation and precipitation of asphaltenes, which may induce the loss of reservoir permeability, well plugging and sharp decrease in the oil recovery.[57] Therefore, it is important to investigate the mechanism of CO_2 interaction with crude oil and analyze the conditions for asphaltene precipitation in the crude oil – CO_2 binary system.

For handling heavy crude oils and oil blends at elevated CO_2 pressures, Kazarian and co-workers [55] manufactured a special cell and developed the experimental strategy (Fig. 4) based on original research and used them to study the interaction of SC CO_2 with various polymers.[58, 59] Using developed method, the behaviour of crude oil and precipitates formed at elevated CO_2 pressures was studied in the *in situ* mode with a spatial resolution; in particular, unique information was obtained about the local changes in the chemical composition of the samples. It should be specially emphasized that this *in situ* investigation of the asphaltene behaviour at elevated CO_2 pressure with chemical analysis of the major components of the precipitates is the first example of research of this type, which became possible owing to the developed spectroscopic imaging technique.

During the experiment, a heavy oil sample was placed into a cell in which the appropriate amount of CO_2 was admitted until the specified pressure (1 – 100 atm) and temperature (50 °C) were reached. Mixing of oil with CO_2 was accomplished under controlled conditions, which made it possible to study *in situ* the stability of asphaltenes occurring directly in the heavy oil. It was found that dissolution of CO_2 in heavy oil at a 50 atm pressure increases the liquid phase volume by $9 \pm 1\%$ with respect to the initial volume. One hour after CO_2 admission into the cell, the formation of a precipitate was detected (Fig. 5). From analysis of the spectral bands at 1140 and 1030 cm^{-1} in the recorded IR spectra, it followed that the interaction

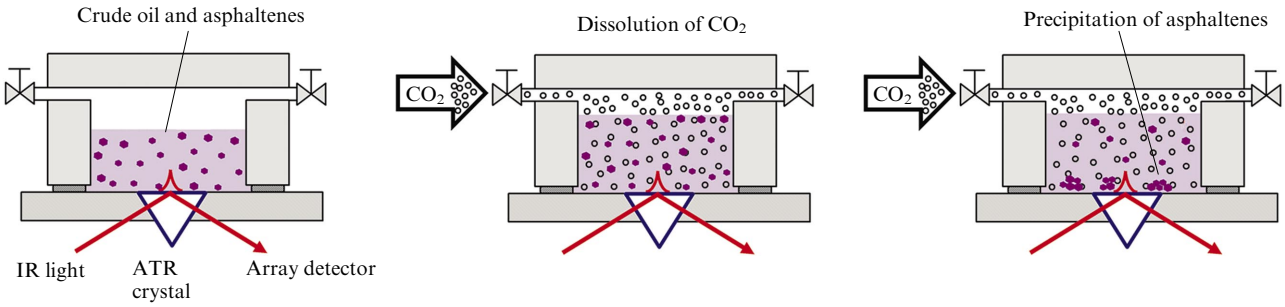


Figure 4. Schematic diagram of *in situ* visualization of the behaviour of heavy oils at elevated CO_2 pressures by ATR FTIR spectroscopy.[55]

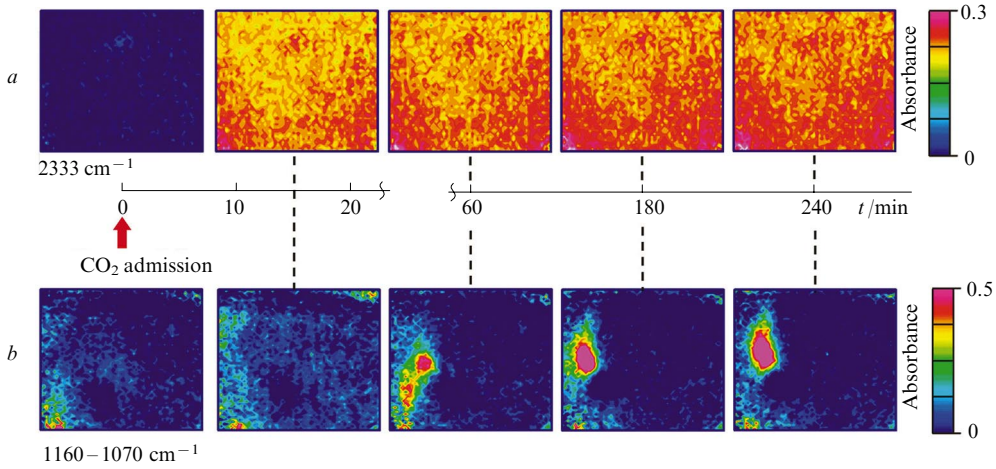


Figure 5. FTIR spectroscopic images of heavy crude oil obtained *in situ* at 25°C and 50 atm of CO_2.[55]
(*a*) Distribution of the absorption (integrated intensity) at the 2333 cm^{-1} band characterizing the distribution of CO_2 over the imaged area of the sample; (*b*) distribution of the absorption (integrated absorbance) at the 1160 – 1070 cm^{-1} band characterizing the distribution of asphaltenes over the imaged area of the sample.

of heavy oil components with CO_2 leads to precipitation of mainly asphaltenes containing C – O – R and S=O groups.

The researchers[55] proposed the mechanism of destabilization of asphaltenes distributed in crude oil upon the interaction with CO_2 at high pressure. It is known that asphaltene molecules are stabilized in crude oil largely *via* interaction with the molecules of resins, which act as peptizing agents. The discovery of specific functional groups (C – O – R, S=O) in the precipitated asphaltenes indicates that they interact with CO_2 to form non-covalent complexes. Thus, it was suggested that CO_2 competes with the resin molecules for asphaltenes. This leads to a decrease in the resin concentration in the local environment (on the surface) of asphaltene molecules and, as a consequence, to the loss of aggregation stability and asphaltene precipitation.[55] The results attest to the efficiency of the proposed approaches and prove the benefits of using advanced spectroscopic methods *in situ* for studying sophisticated systems such as heavy crude oils.

The formation of the deposit detected in the thin layer near the crystal surface by *in situ* ATR FTIR spectroscopy is preceded by processes that take place in the hydrocarbon bulk. Therefore, it seems reasonable to resort to other investigation methods capable of providing *in situ* information about the processes that take place in the bulk. One of the unique methods for investigation of multicomponent oil systems and processes taking place under various external conditions is magnetic resonance imaging.

III. Nuclear magnetic resonance spectroscopy. Magnetic resonance imaging

The extensive range of methods based on the nuclear magnetic resonance effect which are now available for investigations of heavy oils can be classified, somewhat arbitrarily, into three main groups

— NMR spectroscopy techniques, which provide information about chemical compounds present in the sample and their structure at the molecular level;

— measurement of NMR relaxation times and diffusion coefficients providing information about the local dynamics of molecules in the system (including different types of motion in space);

— magnetic resonance imaging, which provides spatially resolved information about a multicomponent system and its evolution; the possibility of assigning the measured characteristics to particular sites of the sample fundamentally distinguishes MRI from all other methods.

Since the mid-20th century when NMR spectroscopy started to be actively used in chemical research as an analytical method, a tremendous number of papers have appeared covering various aspects of application of this method to crude oils and oil-based organic feedstock.[60 – 69] Primary attention has been devoted to chemical analysis of complex multicomponent hydrocarbon systems, while the issues of stability and phase transformations in oils under some external action have not been addressed. Meanwhile, the study of NMR relaxation processes and measurement of diffusion coefficients have found use, first of all, in petrophysical studies,[70, 71] whereas papers in which these methods have been applied to crude oils and their evolution processes are few. Two major trends can be distinguished: 1) establishing correlations between NMR parameters (relaxation time, diffusion coefficients) and macroscopic properties of oils (viscosity, concentration of heavy fractions and so on); 2) study of asphaltenes and their aggregation in heavy oils and blends. The first subject is addressed by Chen *et al.*[72,] and Korb *et al.*,[73] who studied the distribution of spin – lattice and spin – spin relaxation times (T_1 and T_2, respectively), their mutual correlation and relationship with the diffusion coefficient (D). In particular, it was found that crude oils with high asphaltene and resin contents show considerable dispersion of T_1, whereas the dispersion of T_2 is small and does not depend on the concentration of heavy components.[72]

Study of the aggregation of asphaltenes in dilute solutions and heavy crude oils by measuring the relaxation times and diffusion coefficients gives important information about the local dynamics and structure of aggregates con-

sisting of asphaltenes and resins. For example, measurement of the diffusion coefficients of asphaltene molecules in toluene over a broad concentration range (0.01 mass % – 10 mass %) revealed the formation of intricate structures of different types ('continent' or 'archipelago') and scales (nano, micro and macro size).[74] It was also shown that aggregation is a complex multistage process including definite stages characterized by corresponding parameters and sizes of particle aggregates.[75–77]

The most spectacular results demonstrating the efficiency of nuclear magnetic resonance *in situ* were obtained by MRI. Currently, there are quite a number of papers and reviews addressing various physicochemical applications of this method.[78–83] Meanwhile, detailed analysis of published data demonstrates that the number of papers in which heavy crude oils and phase transformations are studied *in situ* using MRI is moderate as compared with other applications of the method. In our opinion, this situation is paradoxical and deserves special consideration.

One can propose several reasons why magnetic resonance imaging, which is exceptionally popular in many applications, stays in the background as applied to the physicochemical evolution in heavy oils. First of all, this is due to rather low resolution of MRI compared with classic optical and X-ray microscopy. Phase segregation processes in heavy oils, for example, can give rise to stable particle agglomerates measuring tens of micrometres,[84] which still cannot be directly seen in the MRI image. In these cases, methods with a better spatial resolution are indeed more efficient, which has been vividly demonstrated, for example, in the combined use of ATR FTIR and MRI methods.[85] However, if a complex oil-based disperse system loses stability upon some external action, then certain processes could give rise to local areas with properties differing to a sufficient degree to be visualized by MRI, even when there are dispersed phase particles beyond the resolution of the method

Classic examples of the above situation are MRI studies of sedimentation and gelation processes in suspensions and sols.[86–88] In the initial samples where the size of solid particles (*e.g.*, asphaltenes or paraffins) is less than the resolution of the method, the images show no specific details — the system is homogeneous according to MRI (Fig. 6 *a*). However, when these particles precipitate or if gel-like deposits are formed, particles with specific magnetic resonance characteristics are concentrated in particular areas. As the size of these areas becomes greater than the resolution of the method, they start to be observable, with a vague boundary appearing in the MRI images (see Fig. 6 *b*). If during further particle accumulation, the thickness of the transient layer between the areas with different resonance characteristics becomes commensurable with or less than the resolution of the method, a clear boundary appears in the magnetic resonance images (see Fig. 6 *c*). Thus, it becomes possible to follow the evolution of asphaltene and paraffin aggregation and to quantitatively describe the process kinetics.

Other possible reasons for insufficiently wide application of MRI to follow the physicochemical evolution of heavy oils include the relatively high cost of the method and the instrumental limitations for *in situ* experiments. For example, in most of the known studies, the experiments were conducted at −40 to 80 °C, with the sample being at the atmospheric pressure. Also, interpretation of the experimental results may be associated with difficulties if the samples are multicomponent oil disperse systems.

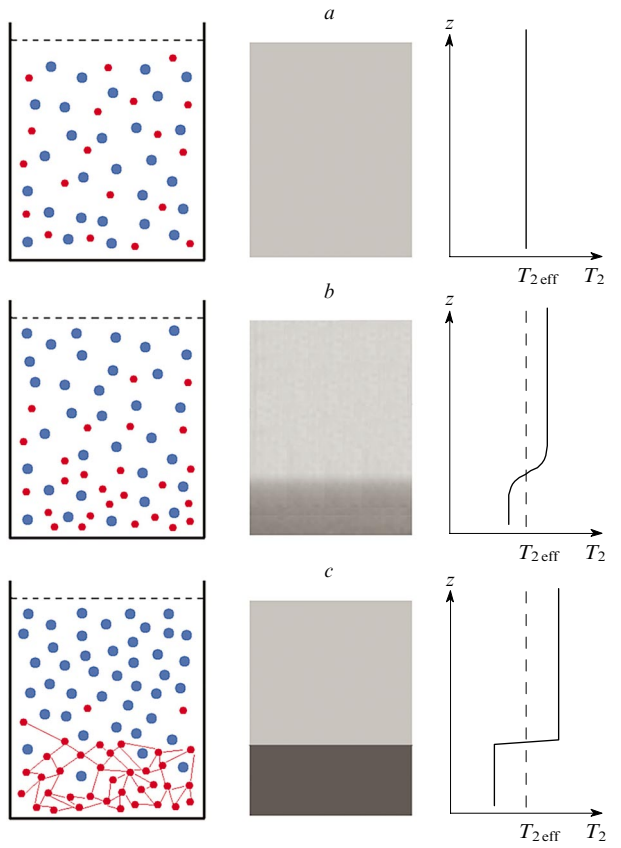


Figure 6. Schematic representation of MRI vizualization of systems with particle size beyond the resolution of the method during particle precipitation.
(*a*–*c*) Different precipitation stages (see the text).

In the absence of convincing examples demonstrating the potential of this method as applied to heavy oils, researchers prefer less expensive and simpler methods whenever possible. In recent years, the situation has fundamentally changed, despite the above problems. Currently, MRI finds increasing use in the studies of phase transformations in heavy oils where it demonstrates high efficiency.

A key feature of MRI determining its high information content is the possibility to adjust parameters of image recording to a particular task. The change in the pulse sequence parameters allows one to vary the measurable range of NMR relaxation times T_1 and T_2 by choosing one in which the relaxation times depend most appreciably on the characteristics of interest.[89] Specifically, if an oil sample contains poorly miscible phases (*e.g.*, water–oil emulsion) or one and the same compound in different physical states (*e.g.*, waxes, which are present in oil both in the dissolved and microcrystalline states), by adjusting the instrumental parameters, one can achieve high-contrast visualization of particular areas with different NMR relaxation times.[90]

Magnetic resonance imaging in the *in situ* mode is efficiently used for visualization and studying the behaviour of interfaces (water–crude oil, crude oil–hydrocarbon gas, crude oil–supercritical CO_2, *etc.*). This allows measuring local physicochemical characteristics of an oil system (vis-

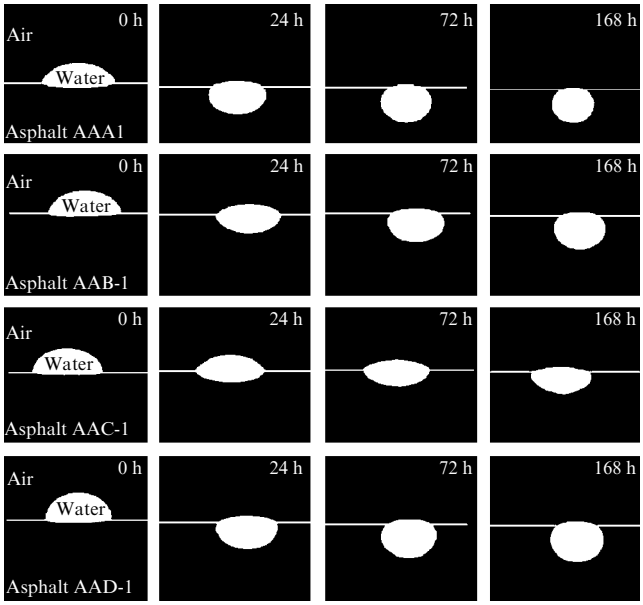


Figure 7. Series of magnetic resonance images of a water drop placed on the surface of various asphalts during sinking.[92]
The images show the designations for asphalt brands and time periods elapsed from placing the drop on the sample surface.

cosity, solubility, rate of diffusion, excess surface energy of small particles of a solid dispersed phase, *etc.*) under specified conditions,[91] including the case where the formation of interfaces is not accompanied by any significant phase or chemical transformations in the oil. An illustrative example is the application of MRI to measure the contact angles and calculate the surface tension at the asphalt – water interface.[92] A stationary hemispherical water drop was placed on the surface of asphalts of various composition and the magnetic resonance images were recorded as the drop slowly sank into the sample (Fig. 7). Owing to considerable difference between the asphalt and water relaxation times, the contact angles at the interface were determined with high accuracy and, hence, the desired physicochemical characteristics for each sample were accurately calculated.

This approach is fairly versatile and provides visualization of the evolution of interfaces in crude oils that occur in porous media under intense external impacts. This is especially significant for the studies of multiphase mass transfer processes that take place during extraction of heavy oils by sub- or supercritical carbon dioxide displacement from the rock. In the former case, displacement occurs without mixing of carbon dioxide with crude oil (immiscible displacement), whereas in the latter case, SC CO_2 and oil are partly mixed as a result of rather fast diffusion of the supercritical fluid (miscible displacement).

Processes of this type were studied in considerable detail by MRI *in situ* using model samples. Zhao *et al.*[93] developed the first cell for MRI probe in which *in situ* measurements could be carried out at temperatures up to 80°C and pressures up to 15 MPa; the cell was packed with sand and the model medium (dodecane displaced by carbon dioxide). This cell was used to measure the fundamental characteristics of the displacement process; in particular, the instability of the displacement front was found to disappear on going to the near miscible displacement (upon CO_2 transition to supercritical state).[93] Later, the effects of pressure and flow rate on the displacement efficiency under near miscible conditions were studied[94,95] and the important role of the mixing region profile geometry and area (volume) for the process kinetics was identified (Fig. 8).

In the above-discussed studies, crude oil or a model system did not undergo significant physicochemical transformations accompanied by a change in the homogeneity of

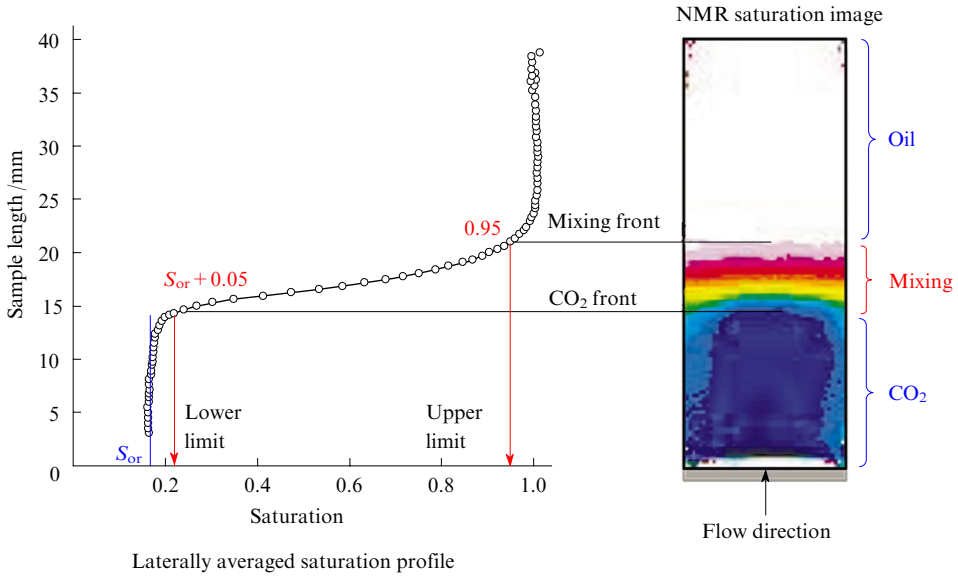


Figure 8. Mixing region of oil (model fluid) and a supercritical CO_2 flow observed by MRI *in situ*.[95]
S_{or} is the residual oil saturation. Blue colour in the image corresponds to the region with low oil content in the saturation profile (high concentration of CO_2) and white colour indicates the region with high content of the displaced oil.

composition (for example, deposition of heavy fractions), despite the fact that heavy oils had high contents of asphaltenes and resins prone to aggregation under certain external action (elevated temperature and pressure, addition of chemicals, *etc.*).[84] The complex multistage aggregation processes of these compounds finally result in the formation of insoluble solid deposits, which differ substantially in magnetic resonance characteristics from the other crude oil components. It is reasonable to expect that MRI, which efficiently visualizes the concentration ranges of chemical compounds with definite spin – spin relaxation times and their boundaries, would be useful for the studies of such processes.

The pioneering work along this line is the MRI study of sedimentation of asphaltenes in asphalts induced by flocculation additives.[96,97] Asphalt samples, either subjected or not to oxidative ageing, were dissolved in toluene and then titrated with isooctane until the asphaltene-containing fractions started to precipitate. The aggregation of asphaltenes in the sample bulk was recorded in magnetic resonance images, which made it possible to determine the critical concentration of the flocculant needed for initiating the asphaltene sedimentation with a rather high accuracy and to elucidate the influence of the concentration of asphaltenes in the initial samples and the degree of oxidative ageing on the precipitation intensity.

The approach described relatively recently was considerably extended by increasing the information content of the procedures, which provide high-quality imaging and quantitative description for the whole evolution, and utilized to investigate heavy crude oils of various compositions and origins.[98] In particular, in relation to the asphaltenes – toluene – heptane ternary system, it was shown that MRI *in situ* can visualize various mechanisms of formation of asphaltene deposits under the action of a flocculant (n-heptane): in the presence of a large excess of the flocculant, a suspension was formed and then transformed into a gel-like precipitate upon sedimentation and particle coarsening (Fig. 9 *a*, the interface drifts downward); if the flocculant concentration is below some limiting value, no formation of suspension in the bulk takes place, but large particle agglomerates slowly precipitate on the bottom. The thickness of the precipitated layer increases with time to reach a limiting value (Fig. 9 *b*, the interface drifts upward).

The trends of physicochemical evolution of asphaltene-containing model systems proved to be similar to the corresponding processes observed by MRI in the samples of heavy crude oils. Gabrienko *et al.*[85] have shown that switching between the mechanisms of formation of asphaltene deposits depends on the flocculant concentration and on the initial content of asphaltenes in oil. It was also shown that under the action of the flocculant, asphaltene molecules with oxygen- and/or nitrogen-containing functional groups are the first to lose the aggregative stability, whereas the other types of asphaltenes can remain stable. As a result, samples with high contents of asphaltenes and resins possess an abnormal threshold for the formation of gel-like deposits, *i.e.*, the formation of a suspension in the bulk requires a greater amount of the flocculant.

The developed approaches for *in situ* studying the phase inhomogeneity of oil systems, the evolution of the size and boundaries of regions present in the oil bulk by MRI are fairly versatile and are applicable to a broad range of problems. A serious challenge in the production, transportation and refining of heavy and waxy crude oils is to ensure the oil flow during any operation (flow assurance problem). Crude oils with high contents of solid C_{18+} n-paraffins show a pronounced tendency for forming solid deposits on the inner walls of pipelines and tanks when the oil temperature decreases down to the environmental temperature.[99–105] This results in a sharp increase in the hydraulic resistance and retardation of the flow rate down

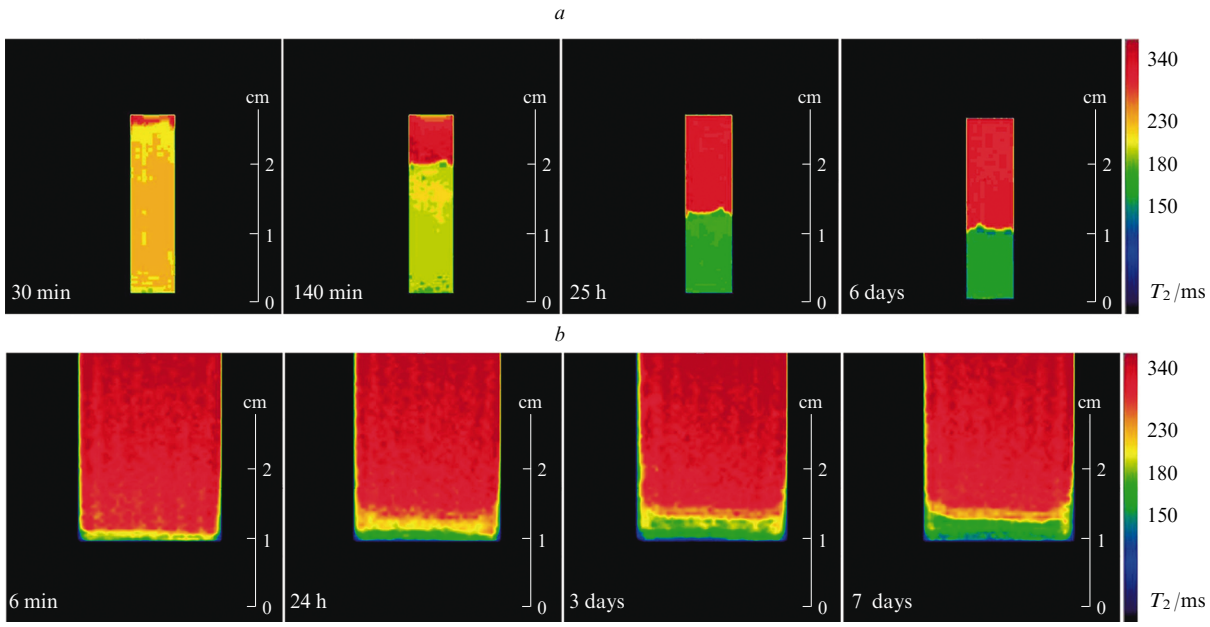


Figure 9. Time variation of the asphaltene solution in toluene upon the addition of n-heptane.[98]
Flocculant : solution ratio (v/v): 2 : 1 (*a*), 1 : 1 (*b*). Time that passed after the flocculant addition is indicated near the images.

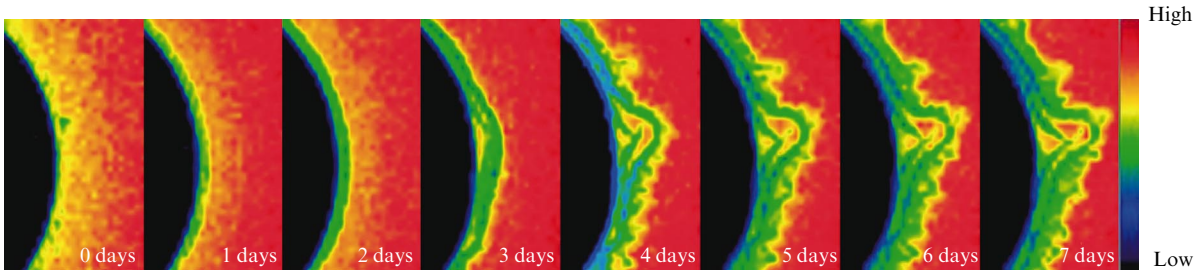


Figure 10. Series of magnetic resonance images showing origin, growth and formation of multilayer structure of wax deposits in a heavy oil sample under the action of temperature gradient.[113]

to complete flow arrest, which is associated with enormous economic losses. Therefore, particular attention of researchers is devoted to the mechanism of phase segregation and formation of deposits at various stages of extraction and transportation of this type of oil.[106, 107]

A pioneering study dealing with the use of MRI for studying the behaviour of waxy crude oil in the initial stage of recovery (extraction from the reservoir rock) was devoted to the foamy behaviour upon decrease in the external pressure.[108] An oil sample was mixed with methane at a pressure of 13.1 MPa and a temperature of 60 °C in a special cell; after that, pressure was reduced step-by-step to 1.4 MPa with simultaneous *in situ* recording of magnetic resonance images. As a result, phase segregation of oil in the mixture bulk was visualized. The formation of gas channels on passing the bubble point was detected for the first time (the channels were clearly visualized at a pressure of 3.4 MPa and lower) and a stepwise change in the system viscosity upon sharp pressure change was observed.[108] It is of interest that at pressures above the bubble point, a stepwise pressure decrease results first in a sharp viscosity increase, which is followed by smooth viscosity decline. At pressures below the bubble point, pressure decrease leads, conversely, first to a sharp viscosity drop, which is followed by a smooth viscosity increase.

A number of publications[109 – 111] are devoted to MRI investigation of the formation of gas (air) voids in waxy crude oils during pipeline transportation at cold weather. For modelling processes that take place in real pipelines, the authors devised a special flow loop for the transfer of crude oil cooled to a temperature corresponding to natural environmental conditions within the MRI probe. During the study, they visualized the formation of gas voids both in the oil gel bulk and in the near-wall regions. The volume fraction of the voids in the sample can reach 7% – 12% for the highest cooling rates (1.01 °C min^{-1}).[109 – 111] When the cooling rate is < 0.65 °C min^{-1}, voids are mainly formed near the pipeline wall.

The formation of gas voids is far from being the only source of hampered transportation of waxy oil at low temperature. As the oil temperature decreases below the cloud point (the temperature at which the waxes dissolved in crude oil start to crystallize and precipitate[99, 112]), heavy oil no longer flows as a single phase, which is accompanied by the appearance of concentration and temperature gradients in the pipeline and formation of solid deposits in the pipeline's inner walls. Morozov *et al.*[113] were the first to use MRI to study these processes *in situ*. They designed a special cell, which can create and maintain a specified temperature gradient in a waxy crude oil sample and record simultaneously magnetic resonance images to visualize the concentration and temperature profiles within the sample and monitor the deposition on a real time basis.

After the method was tested on model systems, an *in situ* study of crude oil samples with a high wax content was carried out and the origin, development and aging of multilayer wax deposits were visualized. In particular, it was found that at relatively high temperatures of the cold surface inside the cell, an incipient wax gel is formed by the molecular diffusion mechanism and ages uniformly throughout the thickness, which gives rise to a thin solid inner layer and a loose branched structure of the outer layer.[113] Conversely, reduced temperatures of the cold inner surface (40 °C) compared with the outer surface (80 °C) and, as a result, high temperature gradients promote the formation of a thick deposit, which ages non-uniformly and is thus separated into two layers as a result of counter diffusion of wax molecules and retarded formation of the branched outer layer (Fig. 10).[113]

This approach proved to be efficient for *in situ* studies of the physicochemical evolution in waxy crude oils under temperature gradient conditions. It is important to note that, apart from the temperature conditions, efficient oil transportation depends considerably on the flow rate and shear stress in the multicomponent oil dispersion. Magnetic resonance imaging has been used for a long time to study fluid flow processes (measurement of flow rates, rheological parameters and so on).[114, 115] Therefore, application of this method to studying both heavy and waxy crude oils seems reasonable. As an example, worthy of note is the paper of Mendes *et al.*,[116] who studied the rheology and flow of heavy crude oils and model systems by MRI. They used the classic Couette cell geometry: the test samples were placed between two coaxial cylinders, one (outer) being rotated and the other (inner) remaining immobile. Magnetic resonance imaging during cell operation allowed the authors to measure the local flow velocity field for the fluid and calculate the desired rheological parameters as functions of the temperature history of the fluid and fluid flow conditions during cooling. In particular, thixotropic behaviour of the fluid and reversible structural changes of the flow were found for shear rates lower than the limiting value and, correspondingly, irreversible changes were detected for higher shear rates.[116]

The examples of MRI applications to the physicochemical evolution of oil disperse systems upon external action presented in this Section demonstrate the efficiency of this method for *in situ* studies. The possibility of spatial location

with a resolution from hundreds of micrometres to several centimetres provides researchers with the unique opportunity to study the phase stability and physicochemical processes in oils throughout the sample bulk on different temporal scales, starting with processes that take place in the first tens of seconds or several minutes and up to slow processes, the characteristic times of which may be several days.

IV. Small-angle X-ray and neutron scattering

Unfortunately, the above-described methods for investigation of heavy oils are unsuitable for monitoring the processes that occur in an oil disperse system on a few nanometre scale. In this respect, small-angle X-ray and neutron scattering open up the unique opportunity to study aggregation of asphaltenes at the supramolecular level, considering rather large size of asphaltene molecules and aggregates, which range, according to different data, from a few to a few tens of nanometres.[117]

Historically, SAXS and SANS have been long and efficiently used to analyze the structure and size characteristics of asphaltenes *ex situ*.[118, 119] The small-angle scattering technique implies detection of small scattering angles (up to 5 degrees) for a collimated X-ray beam that has passed through the sample layer. Despite different natures of the radiation used (neutrons or X-rays), the key principles and approaches to data processing are largely similar for SAXS and SANS. As a rule, SAXS and SANS data are presented as dependences of the scattered intensity (I) on the parameter q, which is equal to $4\pi\sin\theta/\lambda$, where 2θ is the scattering angle, λ is the radiation wavelength. The scattered intensity $I(q)$ decreases with increasing q. Small-angle curves for great q values ($q \gg 0.1$ Å^{-1}) are usually extrapolated by the function $I(q) \sim q^{-x}$, where x provides qualitative information about the particle shape. In particular, the value $x = 1$ corresponds to very oblong (1D) particles, $x = 2$ means planar (2D) particles, and $x = 4$ is indicative of compact (3D) particles.

In real multicomponent disperse systems, the x values are, most often, intermediate, which markedly complicates the analysis of scattering curves and hampers unambiguous interpretation of the results. In this case, qualitative estimate of the particle shape can be based on the radius of gyration — a key characteristics depending on both the particle size and particle shape. Components of the anisotropic tensor of the radius of gyration can be found by analyzing SAXS curves in special coordinates.[120] The effective radius of gyration of the particle (R_G) and the radii of gyration of the cross-section ($R_{G\,cross}$) and thickness ($R_{G\,thick}$) for a disc-shaped particle can be derived from the slope of SAXS curves in the coordinates $\{\ln[I(q)], q^2\}$, $\{\ln[I(q)q], q^2\}$ and $\{\ln[I(q)q^2]\ q^2\}$, respectively. For example, in the case of continuous spherical particles, $R_G^2 = (3/5)R^2$, where R is the radius of the sphere.

This is exemplified in Fig. 11, which shows the SAXS curves for heavy oil in the coordinates $\{\ln[I(q)], q^2\}$, $\{\ln[I(q)q], q^2\}$ and $\{\ln(I(q)q^2), q^2\}$.[121] The possibility of rectification of the scattering curves in the coordinates $\{\ln[I(q)q], q^2\}$ indicates that the particle shape can be described quite adequately by an oblong rotational ellipsoid. In this case, the radius of gyration of the cross-section ($R_{G\,cross}$) is relevant, whereas the $R_{G\,thick}$ value makes sense and is used, as a rule, for disc-like particles. More detailed description of the methods and approaches used for qualitative and quantitative analysis of SAXS curves and data processing details can be found in several publications [117, 120, 122] devoted, in particular, to the application of this method for *ex situ* characterization of asphaltenes.[123 – 127]

Asphaltene molecules are known to be prone to aggregation by so-called π – π-stacking mechanism (Yen model),[128, 129] which gives rise to nanometre-sized aggregates that can be present in crude oil or certain organic solvents. The SAXS and SANS methods are used, most often, to study solutions of asphaltenes that have been isolated from oil and purified from resins.[130 – 134] There are a few publications dealing with *in situ* SAXS studies of the structure and size characteristics of asphaltenes directly in crude oil [135 – 137] because of the difficulty of adapting the method for conducting the experiments at elevated temperature and pressure and ambiguous interpretation of the results obtained for a complex multicomponent system.

While using the SAXS and SANS methods to study the asphaltene aggregation, one should pay attention to the asphaltene concentration in the crude oil samples. Indeed, in the case of high concentration of nano-sized particles, X-rays are multiply scattered giving rise to interference effects, which may lead to faulty interpretation of the results. A consequence of this effect is, for example, a considerable change in the shape of the SAXS curve for samples with asphaltene concentrations of > 20 mass %, which may result in underestimation of the particle size.[122, 138] Meanwhile, strictly speaking, unambiguous

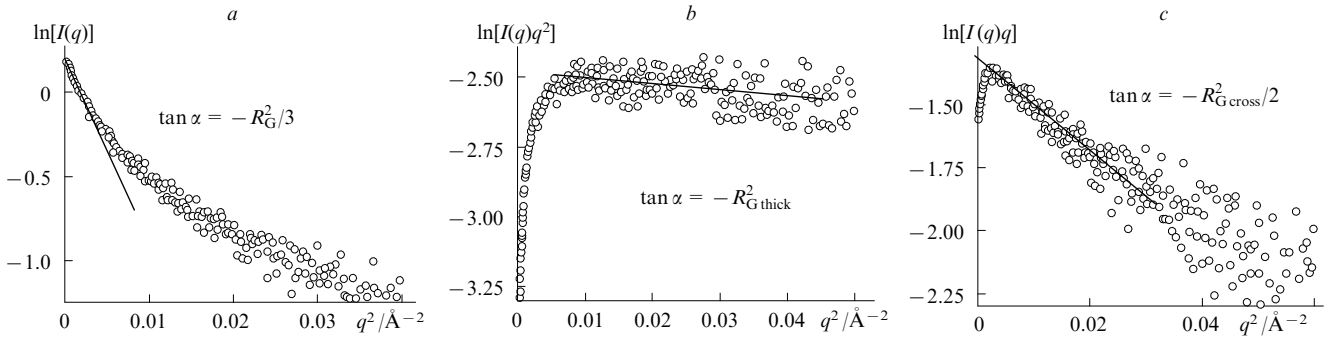


Figure 11. SAXS curve for a heavy oil sample in the coordinates $\{\ln[I(q)], q^2\}$ (*a*), $\{\ln[I(q)q^2], q^2\}$ (*b*), $\{\ln[I(q)q], q^2\}$ (*c*).[121]

determination of the sizes of single asphaltene particles is possible only for true solutions, which are formed for asphaltenes, according to published data, only at low concentrations (< 0.01 mass % – 0.02 mass %).[84, 128] As the concentration is increased to 0.1 mass % – 0.5 mass %, asphaltene aggregates are already formed, with their size increasing with increasing asphaltene concentration.[14, 84]

The size of asphaltene aggregates depends on quite a few parameters (hydrocarbon type and chemical composition of crude oil, temperature, pressure, added solvents) and, according to SAXS, varies most often from 2 to 50 nm.[117] The asphaltene aggregates can be of different shape, for example, oblong rotational ellipsoids[126, 127] or planar discs,[138 – 140] or they can have fractal structure in the case of large particles > 30 nm.[30, 132, 132] As an example, Table 1 summarizes the size characteristics of asphaltenes occurring in crude oils of different origin, derived from analysis of SAXS curves *in situ*, together with the main physicochemical properties of samples.[136] It can be seen that the characteristic radii of gyration of asphaltene particles differ considerably for different samples and vary from 2.61 to 3.15 nm for R_G and from 0.9 to 1.34 nm for $R_{G\,cross}$. The SAXS curves for these crude oils at large q values are rather well approximated by the function $I(q) \sim q^{-x}$ for $x = 2.8$, 2.7 and 3.0 for samples A1, A2 and A3, respectively. The results attest to a considerable shape anisotropy of asphaltene particles, which can be described as oblong ellipsoids.[120, 121]

Table 1. Main physicochemical properties of crude oil samples and the corresponding size characteristics of asphaltenes derived from analysis of *in situ* SAXS curves.[42, 136]

Crude oil sample	A1	A2	A3
Density /g cm^{-3}	0.957	0.971	0.867
Asphaltenes (mass %)	6.7	8.2	2.6
Resins (mass %)	35.1	19.1	8.8
S (mass %)	4.7	2.0	1.1
H : C	1.73	1.77	1.59
R_G /nm	2.68 ± 0.05	2.61 ± 0.05	3.15 ± 0.05
$R_{G\,cross}$ /nm	0.95 ± 0.08	0.90 ± 0.08	1.34 ± 0.06

Small-angle X-ray scattering *in situ* was used to qualitatively investigate the cause of different size of asphaltene aggregates formed in crude oil samples; this was shown to depend not only on the different molecular structures of asphaltenes themselves, but also on different compositions of the surrounding lighter components, in particular, resins and aromatic compounds, which serve as stabilizers and solvents for asphaltenes in oil dispersions.[39, 40] The higher the content of aromatic compounds and resins in oils, the smaller the size of asphaltene particles. In turn, aliphatic compounds present in oils have a destabilizing action on asphaltenes, resulting in aggregation and possible precipitation.[15, 30, 104]

The complexity of a multicomponent system such as heavy oil often does not allow one to separate the factors affecting the stability (peptization) of asphaltene particles. On the one hand, according to numerous published data, the resins are considered to play the crucial role in asphaltene stabilization in oils.[39, 40, 141, 142] It is believed that the relatively high resin : asphaltene ratio ensures the stability of crude oil virtually irrespective of the content of aromatic hydrocarbons. On the other hand, the stability of asphaltenes is often estimated by an index that is defined as the ratio of the overall content of asphaltenes and saturates to the overall content of resins and aromatics in the oil sample,[4] or by other similar parameters[41] that do take into account the contents of aromatics.

Despite the large body of data on the influence of aromatics and saturates on asphaltene disaggregation – aggregation processes, the number of systematic studies addressing the effect of organic compounds of other types on these processes is quite moderate. For example, effective use of sulfur- and chlorine-containing organic compounds for dissolution of asphaltene deposits has been mentioned.[143, 144] However, these compounds have not found wide use in oil production as they are highly toxic and incompatible with further oil refining processes. Data on the use of alcohols, esters, amines, alkenes and other compounds[145 – 150] as components of solvents for asphaltene-containing deposits are also available. Most often, solvent mixtures are selected empirically, and their efficiency depends appreciably on the nature of asphaltene deposit.

It has been shown[121] that SAXS, including the *in situ* mode, is suitable for systematic research into the effects of a broad range of organic compounds on the aggregation of asphaltenes. Several tens of organic compounds of various natures, which led to different extents of peptization of aggregates, have been studied. All of the tested chemicals can be conventionally divided into three groups. The first group that promotes aggregation includes cyclohexane, methanol, formic acid, heptane, acetonitrile, decane, hexan-1-ol, oct-1-ene, furfural and especially tetra-n-butylammonium fluoride (TBAF); the second group comprises compounds that favour disaggregation of asphaltenes: decalin, DMF, DMSO, nitrobenzene, aniline, cyclohexanol, monoethanolamine, triethanolamine, 1-methylnaphthalene and dichloroethane. Finally, acetone, glycerol, ethyl acetate, dioxane, benzyl alcohol, oleic acid, limonene, pinene, cycloheptatriene, nitromethane and some other compounds have virtually no effect on the radius of gyration derived from analysis of small-angle X-ray scattering curves.

Thus, it was demonstrated that the polarity of organic compounds is not a parameter unambiguously determining their influence on the aggregation and disaggregation of asphaltenes. For example, cyclohexane and decalin, which both formally belong to naphthenes, have opposite effects. The added hexan-1-ol or cyclohexanol also induces opposite aggregation effects. It was also shown that the presence of double bonds in the molecules of organic agents added virtually does not contribute to asphaltene disaggregation; meanwhile, terpene derivatives have been proposed earlier for the dissolution of asphaltene deposits.[148 – 150]

It has been shown by SAXS that small polar molecules affect the aggregation of asphaltenes in different ways. Indeed, methanol, acetonitrile and formic acid induce aggregation of asphaltene particles, whereas ethanolamines, dichloroethane, dimethylformamide and dimethyl sulfoxide induce, conversely, disaggregation of asphaltene particles. The addition of furfural or TBAF leads to considerable enlargement of aggregates. In the case of furfural, partial condensation of furfural with asphaltene molecules appa-

rently takes place, inducing the formation of larger aggregates. In the case of TBAF, the loss of aggregative stability of asphaltene colloids in solution is possible.[121] The addition of nitrobenzene leads to a considerable disaggregation effect. Meanwhile, nitromethane has virtually no effect on the asphaltene particle size, which is indicative of the lack of direct reactions between the nitro group and the polar groups of asphaltenes. The performed systematic research revealed the relationship between the effective size of the observable aggregates and their Hansen solubility parameter[151] and the solubility of asphaltenes in certain organic compounds.[152 – 154]

As noted in previous Sections, despite the extensive possibilities for visualization of mass transfer processes, local structural changes and composition of crude oils by MRI and for chemical imaging of the precipitates formed upon the loss of stability of oil dispersions by ATR FTIR spectroscopy *in situ*, the spatial resolution of the methods, which is limited to tens or hundreds of micrometres, precludes investigation of the initial stages of asphaltene aggregation taking place in the oil bulk on a nanometre scale. Meanwhile, exactly the initial stages of aggregation processes, which depend on the oil composition and the nature of local intermolecular interactions, dictate the evolution scenario and characteristic time of aggregation and the morphology and size of the final asphaltene-containing particles.

The SAXS technique is suitable for studying the initial stages of asphaltene aggregation in various systems upon the change in external conditions (temperature, pressure) or upon the addition of a coagulating agent and the kinetics of size evolution of the aggregates on the spatial scale from a few to a few tens of nanometres.

As an example, Figure 12 shows the kinetics of size evolution of the aggregates that are formed upon the addition of n-heptane to various crude oils.[42] It can be seen that the most pronounced change in the size of asphaltene-containing particles occurs over the first several minutes after addition of the coagulating agent. The scale of these changes can considerably vary depending on the type of oil, ranging from a few to hundred percent. Subsequently, fitting of the aggregate size takes place, which is probably associated with the spatial homogenization of the composition and relaxation of the multicomponent system to a thermodynamically more favourable state. In this connection, attention is drawn by the behaviour of one of the crude oils (see Fig. 12 *d*), in which a noticeable growth of asphaltene aggregates still occurs even after 36 h.

The temperature and pressure in the system are the key factors that often govern the asphaltene aggregation and the efficiency of modern oil extraction techniques. Crude oil, which initially resides in the reservoir rock at high temperature and pressure, can additionally stabilize asphaltenes. The sharp decrease in the temperature and pressure as crude oil is produced may result in the loss of stability and formation of deposits in the oil pumps and valves, which considerably inhibits the oil production process.[6, 155]

Quite a few publications deal with SAXS and SANS studies *in situ* of the effect of temperature on the asphaltene aggregation in model systems. In particular, it has been shown by SANS that even minor heating (from 25 to 80 °C) of a solution of asphaltenes in the model system (toluene – heptane) leads to a substantial decrease in the asphaltene aggregate size, if the initial size exceeds ~10 nm.[142] Meanwhile, for smaller aggregates (< 5 nm), a similar temperature change has a weak peptizing action.

Eyssautier *et al.*[156] used SAXS to elucidate the temperature effect on the structural properties of asphaltenes in vacuum residues. The measurements were carried out in the temperature range from 80 to 240 °C. According to SAXS

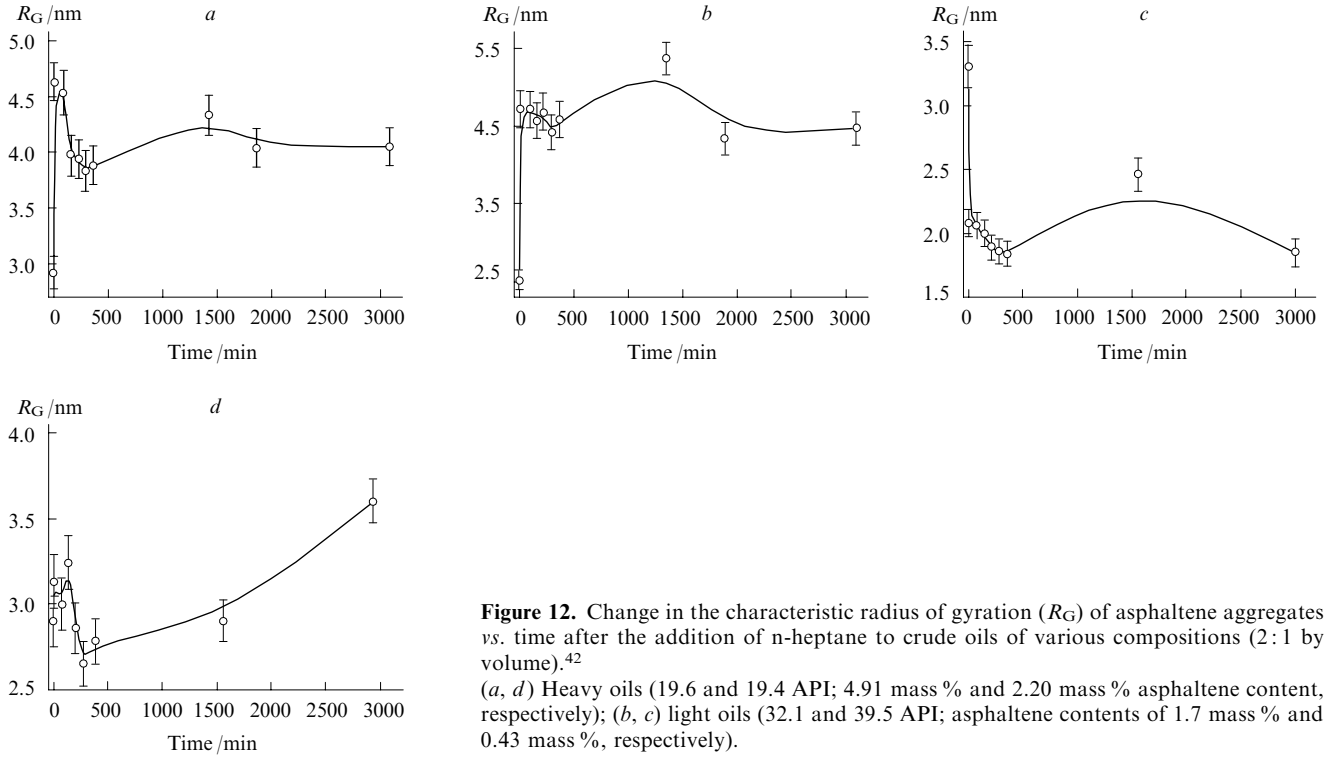


Figure 12. Change in the characteristic radius of gyration (R_G) of asphaltene aggregates *vs.* time after the addition of n-heptane to crude oils of various compositions (2 : 1 by volume).[42]
(*a*, *d*) Heavy oils (19.6 and 19.4 API; 4.91 mass % and 2.20 mass % asphaltene content, respectively); (*b*, *c*) light oils (32.1 and 39.5 API; asphaltene contents of 1.7 mass % and 0.43 mass %, respectively).

data, heating of the system entails a smooth decrease in the size of asphaltene aggregates (R_G) from 4.1 to 3.3 nm, with particle shape remaining essentially the same. Thiyagarajan *et al.*[157] employed small-angle neutron scattering to investigate the evolution of the morphology and size characteristics of asphaltenes dissolved in 1-methylnaphthalene at temperatures up to 400 °C. It was shown that at elevated temperatures, particle size decreases and the shape considerably changes, namely, the particles become less anisotropic. However, in similar solutions of crude oil-based asphaltenes of a different origin, the use of SANS at elevated temperature made it possible to observe the formation of fractal aggregates, the fractal structure being retained up to 350 °C.[158]

To summarize the brief survey of applications of small-angle scattering techniques, we would like to note that the multicomponent nature of disperse systems of heavy crude oils and the presence of particles of different size and shape makes analysis and interpretation of the results fairly challenging. Therefore, asphaltene size and shape and evolution of these characteristics under definite external conditions can be unambiguously determined by SAXS and SANS only upon comparison with the results obtained by other methods (scanning or transmission electron microscopy, scanning tunnelling microscopy, IR spectroscopy and so on).

The aggregation of asphaltenes at the molecular level is determined by intermolecular interactions and local environment of asphaltene molecules. In this respect, a unique investigation method for asphaltene evolution at the atomic and molecular level, which supplements the results of other methods, is electron spin resonance spectroscopy, as well as a wide range of accompanying methods that have been markedly advanced in recent years.

V. Electron spin resonance

Electron spin resonance spectroscopy is an efficient method for *in situ* studying the structures of paramagnetic particles and dynamics of their local environment in various media,[159, 160] in particular, at elevated temperatures and pressures.[161] Quantitative analysis of the resonance line shape and the degree of averaging of hyperfine and spin – orbit coupling anisotropy provides information about the rotational dynamics and mobility of radicals, paramagnetic ions, molecules and associates,[162] changes in their local concentrations in the system, including in the sub- and supercritical state,[163, 164] interparticle interactions[165] and so on.

A highly important advantage of the resonance method when applied to studies of heavy oil stability, in particular, aggregation of asphaltenes, is the possibility of *in situ* application without special sample preparation and virtually without any noticeable invasion into the system, because the resonance energy quantum is small. This feature is often utilized to *in situ* study the mechanisms of catalytic transformations of various components of hydrocarbon feedstock by ESR, which allows one to trace the changes in the state of catalysts,[166, 167] their active sites[168] and to detect intermediates directly during the reaction.[169]

A condition for applicability of ESR is the presence of free radicals in the system, that is, molecules or ions with non-zero electron spin density; often spin probes or labels specially introduced in the system serve as such species.[170] The application of the resonance method to study crude oils is traditionally associated with recording of intense signals of two types. In heavy fractions of crude oil, an intense ESR spectrum of vanadyl VO^{2+} complexes (vanadium oxo cation in the oxidation state +4), which act as natural spin probes, is most often recorded.[171] In addition, the spectra of crude oils often exhibit a singlet, which is assigned to unpaired electrons of the carbon π-systems.[172, 173]

The theory of ESR spectra of the VO^{2+} ions is set forth in detail in classic publications.[174, 175] The vanadyl ions are characterized by long spin – lattice relaxation time, which results in narrow resonance lines in the spectrum even at elevated temperatures. This allows the ESR spectroscopy of the VO^{2+} ions to be used in the *in situ* mode to study crude oils.

Vanadyl complexes have a moderate *g*-factor anisotropy [the $(g_\perp - g_{||})$ difference is in the 0.015 – 0.04 range]. The hyperfine coupling (HFC) tensor between the unpaired d^1 electron and the ^{51}V nucleus with the spin 7/2 (99.75% abundance) in vanadyl porphyrin complexes has a rather large anisotropy: the $|A_{||}|$ value is usually in the range of 400 – 550 MHz, while $|A_\perp|$ is 120 – 200 MHz. Therefore, it is, in principle, possible to gain information about the rotational dynamics of the particles that incorporate the vanadyl complex (*e.g.*, asphaltenes and their aggregates), as a result of partial averaging of anisotropic interactions in the system.

The isotropic ESR spectrum of a relatively rapidly rotating vanadyl complex is known to consist of eight equidistant lines, the positions of which are determined by *g*-tensor and HFC tensor parameters. Back in 1965, it was noted that the isotropic HFC constant of the vanadyl complex can characterize the VO^{2+} ligand environment in the equatorial plane; in particular, the g_{iso} and A_{iso} values depend on the composition of the local environment.[176] Subsequently, the relationship was established between the binding energies of these ligands to VO^{2+} and HFC parameters.[171] Increase in the ligand field strength in the equatorial plane is accompanied by a decrease in A_{iso} and an increase in g_{iso}; the ligand field is mainly determined by the chemical nature of the ligand.

Analysis of the ESR parameters for various vanadyl complexes has shown that each VO^{2+} equatorial environment (S_4, N_4, N_2O_2, O_4) is correlated with definite g_{iso} and A_{iso} values.[171, 177] This correlation diagram was later corrected and supplemented by the values corresponding to O_2S_2,[177, 178, 179] N_2S_2 and NS_3 [179] environments. The A_{iso} values for various complexes vary in the range of $(90 - 110) \times 10^{-4}$ cm^{-1} ($\Delta A_{iso} = 20 \times 10^{-4}$ cm^{-1}), while g_{iso} is in the range of 1.967 – 1.982 ($\Delta g_{iso} = 0.015$). The resulting huge array of data led researchers to the idea to use the discovered correlations for identification of vanadyl complexes in the samples of both crude oils [177, 180 – 182] and various oil components: asphaltenes,[171, 179, 180] asphalts,[180] oil distillation residues,[180, 183] polar and non-polar fractions,[177, 184] as well as chemically treated crude oils and asphaltenes.[180, 181] For most of samples, the g_{iso} and A_{iso} values were close to the characteristic values of vanadyl porphyrin complexes. Also, the obtained data attest to the possible presence of other types of vanadyl complexes with coordination environments such as N_3S,[180, 183, 184] N_3O,[180, 182] N_2O_2,[177] N_2OS,[182] N_2S_2,[184] NOS_2,[182 – 184] NS_3,[184] O_2S_2,[179, 182] S_4.[177, 179, 184]

This approach based on the analysis of only isotropic HFC constants and *g*-factors of vanadyl complexes has not been extensively developed, probably, because of considerable overlap of the g_{iso} (A_{iso}) correlation diagrams for different complexes,[175, 179, 185, 186] especially if the complexes containing phenolate and α-hydroxyl ligands are included.[175, 185] The described method also does not take into account the effects of solvent and local molecular environment; meanwhile, it has been shown, for example, for $VO(acac)_2$ (acac is acetylacetonate) that the scatter of the A_{iso} and g_{iso} values for different solvents can reach $\sim 6 \times 10^{-4}$ cm^{-1} and 0.002, respectively.[171, 187]

The last-mentioned problem is significant for the studies of multicomponent oil systems in which, for example, hydrogen bonding is possible between the vanadyl oxygen and a proton of the solvent molecule,[187] as well as additional coordination of the solvent molecular groups having basic properties to the free axial position of a complex.[171] It can be expected that for complexes without steric restrictions to the access of the solvent molecule to VO^{2+}, the local environment would considerably influence the ESR spectral parameters of the complexes. Furthermore, in a real system, the A_{iso} and g_{iso} values can be affected by the dielectric permittivity of the solvent[188] and temperature.[177, 189] Finally, the accurate determination of g_{iso} and A_{iso} in multicomponent oil samples may be hampered by the presence of an anisotropic contribution of slowly rotating components.

More recently, a similar correlation diagram was also constructed for anisotropic components of the HFC and *g* tensors in frozen solutions.[175, 185] This diagram was found to have an even higher information content, because $g_{||}$ depends directly on the ligand field in the equatorial plane; the range of possible values for $g_{||}$ and $A_{||}$ is approximately twice as great as the range of g_{iso} and A_{iso} values. The subsequent analysis of the ESR spectral parameters of various vanadyl complexes that may be encountered in crude oils has shown that, instead of the $g_{||}$ ($A_{||}$) correlation diagram, which comprises points with different combinations of four atoms of the local equatorial environment, it is more correct to use single $A_{||,i}$ values for ligands of various types (i) in the equatorial plane of the complex.[175, 185, 190, 191] The $A_{||}$ value is additive in its nature and is determined to a good accuracy (usually at least $\pm 2 \times 10^{-4}$ cm^{-1}) from the expression $A_{||} = \Sigma A_{||,i}$, where $A_{||,i}$ is the contribution of a particular equatorial ligand. A review[191] summarizes the published data and presents the $A_{||,i}$ values for ligands of approximately twenty different types. These values can be used for *in situ* qualitative determination of VO^{2+} coordination in complexes of unknown structure in crude oils.

Currently, no integration or analysis of resonance characteristics of vanadyl complexes present in various crude oil samples can be found in public access publications. Nevertheless, $A_{||}$ values for various oils are, most often, in the $(158 \pm 2) \times 10^{-4}$ cm^{-1} range,[179, 192] and even with a smaller scatter, they are close to the corresponding values for pure porphyrin complexes with different ligand environments.[193] This leads to a conclusion that vanadyl predominantly occurs in oils as porphyrin complexes.[179, 194, 195] However, it cannot be ruled out that in some cases, one nitrogen atom of the ligand environment of V^{4+} can be replaced by sulfur or oxygen. Thus, progress in the application of ESR for identification and analysis of vanadyl complexes in oils requires more detailed and systematic examination of the recorded spectra and accurate simulation of the spectra taking into account the variance of the spin Hamiltonian parameters.

One more approach, which proved to be more efficient, to the application of ESR to investigations of the properties and stability of heavy crude oils is quantitative analysis of integral intensities of the isotropic and anisotropic spectra under various external conditions (elevated temperature and pressure, presence of a coagulating agent, *etc.*). As noted above, high-viscosity crude oils give rise, under normal conditions, to anisotropic spectra of vanadyl complexes present in heavy components of crude oils.

An increase in the rate of rotational reorientation of particles, *e.g.*, asphaltenes containing paramagnetic moieties of vanadyl porphyrin complexes, would lead to averaging of the anisotropy of interaction between the unpaired electron spin and the ^{51}V nuclear spin equal to 7/2 and to transformation of the anisotropic ('frozen') spectrum to an isotropic one. Since the rotation rate of particles depends considerably on their size, this opens up a possibility of separating contributions of asphaltenes of different size to the ESR spectrum. In this case, VO^{2+}-containing moieties serve as natural spin probes for monitoring the dynamics and the local environment of heavy components of oils at the molecular level and aggregation processes under various conditions, including elevated temperatures and pressures.

In the case of rather fast rotation of vanadyl complexes with a characteristic reorientation time $\tau_{rot} \sim < 0.2$ ns, the line width of a 'nearly isotropic' spectrum is often analyzed using the Kivelson equation

$$\Delta H_{pp}(m_I) = A + B m_I + C m_I^2 \quad (1)$$

where m_I is the nuclear spin projection, and the coefficients B and C are proportional to τ_{rot}. This dependence of the line width of hyperfine structure (HFS) is attributable to incomplete averaging of the *g* and HFC anisotropy and to the dependence of the longitudinal and transverse relaxation times on m_I. This equation was discussed for the first time by McConnell;[196] later the proposed approach was developed in the theoretical studies[197–199] and confirmed experimentally for various vanadyl complexes in various solvents.[200, 201]

In several studies published in the 1970s, the temperature dependences $\tau_{rot}(T)$ derived by means of the Kivelson equation were used to classify heavy oils and resins in terms of their ability to form carbon deposits of various types on heating to 350–450 °C.[202, 203] It was shown that in the case of high mobility of vanadyl components of heavy oils, needle-like deposits with fibrous texture are formed, while low mobility is correlated with the formation of compact graphite particles with a mosaic structure.[203] The measurement of the time dependence of τ_{rot} at fixed temperatures also made it possible to determine the activation energy for the initial stage of formation of carbon deposits to be ~ 163 kJ mol^{-1} (Ref. 204). It is noteworthy that the deposits have anisotropic structure — their molecular planes are mainly arranged parallel to the external magnetic field due to the anisotropy of magnetic susceptibility of the deposit, which was detected by analysis of the angular dependence of the anisotropic ESR spectra of the samples after they have been cooled in $\sim 0.2-1$ T magnetic fields.[202]

In essence, the list of publications in which the Kivelson equation was used to study the dynamics of vanadyl compounds in oils is limited to the publications mentioned above. Apparently, the reason is that the major part of vanadyl complexes are contained in aggregates with >2 nm size. In this case, τ_{rot} is >0.2 ns even for dilute solutions at high temperatures close to the solvent boiling point and the Kivelson formula is inapplicable. Yet another, perhaps more important, reason is that the Kivelson equation and the approach based on measuring the line width for the 'nearly isotropic' spectrum are inapplicable to analysis of the size distribution of vanadyl-containing species in crude oils.

The characteristic reorientation time τ_{rot} can be estimated independently using the Stokes – Einstein – Debye equation

$$\tau_{rot} = \frac{\pi D^3}{6}\frac{\eta(T)}{k_B T} \quad (2)$$

where η is the solution viscosity, D is the hydrodynamic diameter of the molecule and k_B is the Boltzmann constant. As the temperature increases, the line width and amplitude are averaged because of fast thermal rotation. For $T \sim 300 - 400$ K and viscosities characteristic of common solvents ($\eta \sim 0.3$ cP), by combined use of Stokes – Einstein – Debye and Kivelson equations, one can determine the hydrodynamic diameter of the complex in solution if it does not exceed ~ 2 nm.

The relatively immobile vanadyl complexes give rise to the well-known anisotropic spectrum, which is the sum of characteristic anisotropic spectra for various m_I values. The transition from the isotropic to anisotropic spectrum occurs at molecular rotation times $\tau_{rot} \sim 1/\Delta\omega = 1/(2\pi|A_\perp - A_{||}|) \sim 0.5$ ns ($\Delta\omega$ is the difference between the resonance frequencies of ESR transitions for perpendicular and parallel orientations of the molecule relative to a constant external field) in the range $0.2 \text{ ns} \sim < \tau_{rot} \sim < 50$ ns. In this case, neither anisotropic nor 'nearly isotropic' spectrum, nor even their superposition with different weights is able to satisfactorily describe the ESR line shape. In this range, so-called slow rotation of the vanadyl complex takes place, and the ESR spectrum is transformed from one (anisotropic or isotropic) to the other form in a non-trivial way.[205]

Until recently, the authors used simplified semiquantitative methods for analysis of the slow rotation ESR spectra of crude oils, based on determination of the relative intensities of single non-overlapping resonance lines, which can be assigned to either anisotropic or isotropic spectrum,[180, 206 – 208] and the distance between the peaks of the components corresponding to either $m_I = 1/2$(iso) and $m_I = 3/2$(iso) of the isotropic spectrum or to $m_I = 1/2$(perp) and $m_I = 3/2$(perp) of the anisotropic spectrum for the perpendicular arrangement of the complex relative to the external magnetic field.[209] In particular, the temperature dependence of the peak intensity ratio of the HFS components for $m_I = 1/2$(iso) and 3/2(perp) was used to determine the effective association energy of vanadyl complexes with asphaltenes.[180, 206, 207] It should be noted that this approach is not quite correct, because it does not take into account the change in the viscosity of the medium with temperature, which can independently lead to gradual transformation of the anisotropic spectrum into isotropic one.

Trukhan[210] proposed a rather simple semiquantitative method for analysis of the ESR spectra of heavy components of crude oils based on determination of the contributions of the anisotropic and isotropic spectra to the total integrated intensity of the observed spectrum. Analysis of the temperature dependences of the integrated intensities of the isotropic and anisotropic ESR components for asphaltenes dissolved in benzene made it possible to evaluate the size distribution of asphaltenes with small hydrodynamic radii. In particular, the percentage of mobile asphaltenes dispersed in benzene was found to decrease with temperature rise from ~ 260 to 330 °C, which is associated with a noticeable decrease in the dissolving capacity of benzene on going to the supercritical state ($T_c = 289$ °C).[210]

The ESR spectral pattern of single vanadyl complexes in the slow rotation regime has been calculated to a certain accuracy long time ago[211 – 213] using the Liouville stochastic quantum equations.[214] Within this approach, researchers were able to describe the experimental ESR spectra of $VO(acac)_2$ in toluene at $\tau_{rot} = 0.4$ and 4 ns,[211] 0.3 and 1.5 ns,[213] $VO(acac_2pn)$ in toluene [$acac_2pn$ is 1,2-propylenediiminobis(acetylacetone)] (0.02 – 50 ns), $VO(NCS)_4^{2+}$ in ethyl acetate (0.3, 0.7 and 3 ns),[213] polymer gel cross-linked with vanadyl ions (8 – 100 ns)[215] and so on. Also, the ESR spectra for the system $VO(acac)_2$ – nematic liquid crystals (0.3 – 6 nm)[212] and vanadyl-labelled polar heads of cell membranes lipids[216] were simulated taking account of the dependence of reorientation time on the rotation direction and partial spatial ordering. An advanced calculation procedure was used to simulate the ESR spectra of vanadyl-labelled dendrimers at τ_{rot} in the range of 0.2 – 60 ns.[217] Unfortunately, the described approaches do not allow the use of thoroughly developed magnetic resonance theory for accurate simulation of the ESR spectral patterns of crude oils and their heavy components. The major complications faced by researchers in this case were related to the multicomponent nature of the system and the necessity to take into account the contributions of vanadyl-containing molecules and aggregates of various sizes and natures to the experimental spectrum and to the inevitable demand for increasing the accuracy of simulation of the experimental spectra, which is crucial for gaining quantitative information about the dynamics of paramagnetic particles in the viscous medium.

It was not until recently that progress has been made in the interpretation and simulation of the slow rotation ESR spectra of crude oils. It was shown that accurate simulation of the ESR spectral pattern of oil disperse systems, in which most of vanadyl-containing molecules and aggregates occur in the slow rotation regime, can serve for determining their size distribution.[218] The correctness of the approach was demonstrated by simulation of the ESR spectra of a heavy oil and two its complementary fractions, heptane-soluble and -insoluble ones, for which the parameters of vanadyl particle size distribution functions were considerably different. Using this method, the size distribution function for vanadyl-containing groups in various oil components was derived *in situ* for the first time. In a simulation of the experimental spectra recorded over the whole temperature range in which the transition between the anisotropic and isotropic ESR spectra takes place, the distribution function was found to shift towards smaller sizes and to narrow down by approximately 1 nm with temperature increasing from 200 to 350 K (Fig. 13). Thus, it was shown that the

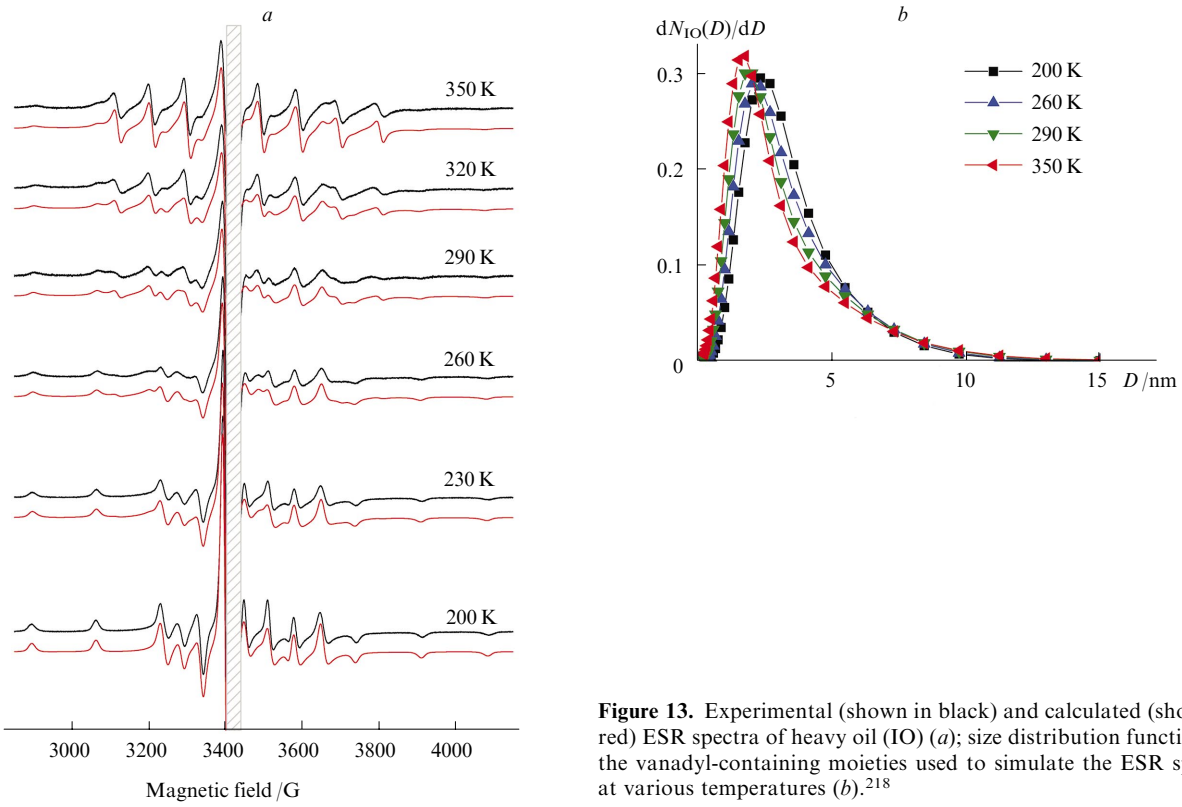


Figure 13. Experimental (shown in black) and calculated (shown in red) ESR spectra of heavy oil (IO) (*a*); size distribution functions of the vanadyl-containing moieties used to simulate the ESR spectra at various temperatures (*b*).[218]

proposed approach and method for analysis of the ESR spectra of oils and their heavy fractions is a unique tool for *in situ* investigation of mobility and elucidation of the vanadyl particle size distribution.[218]

It is noteworthy that at present, available computational packages (*e*,*g*., MATLAB tool kit: EasySpin of version 2.5 and above) can be used for simulating the ESR spectra in the slow rotation regime;[219] this ensures a good fit between the experimental and calculated spectra at characteristic times $\tau_{rot} > 0.2$ ns.

The possibility of simulating the ESR spectra of vanadyl complexes over a broad range of τ_{rot} values opens up great prospects for application of electron spin resonance spectroscopy *in situ* to study the dynamics of vanadyl-containing oil particles at elevated temperature. For example, the simulation of the temperature dependences of the ESR spectra of atmospheric residues of crude oils demonstrated that the temperature rise from 250 to 350 °C leads to narrowing down of the size distribution function of asphaltenes by approximately 20% – 30%.[220] At 420 °C, phase separation takes place in the system: approximately half of vanadyl-containing particles lose mobility, being concentrated in carbon deposits, while the other half retains high mobility characterized by $\tau_{rot} < 0.2$ ns.

Further development of methods for analysis of the ESR spectra of multicomponent oil disperse systems is impossible without determination and inclusion of spin Hamiltonian for all vanadyl-containing components. The variance of *g* and HFC tensor components,[221] line widths [222] determined by the types of complexes that are present in oil, the difference between their local environments and the non-Brownian type of diffusion of heavy molecules and fragments containing vanadyl ions [213] may lead to ambiguous interpretation of the results obtained within the proposed approaches. In the vast majority of studies, analysis of the spectra was reduced to determination of the average values for spin Hamiltonian, although high-precision analysis of, for example, line widths in the ESR spectra of heavy oils even at low temperature could, in principle, provide information about the structure of vanadyl complexes and their interaction with the local environment, which is important for interpreting the spectra at higher temperatures and pressures.

An efficient tool for gaining information about the interactions of a paramagnetic particle with the environment is to analyze spin relaxation processes. The spin – lattice (T_1) and spin – spin (T_2) relaxation rates and kinetics of spin echo decay depend appreciably on the local environment of the paramagnetic centre. Details of spin relaxation of free radicals and vanadyl-containing asphaltenes in oils have been studied.[223] Despite the obvious difficulty of describing the relaxation processes in multicomponent systems, the discovered characteristic differences between T_1 and T_2 for different samples account for the proneness of free radicals and vanadyl complexes to form stable associates. This conclusion was confirmed more convincingly by Mamin *et al.*,[224] who used high magnetic fields (3.4 T, W range) to separately measure the relaxation times T_1 and T_2 of free radicals and vanadyl complexes in various asphaltene samples. Analysis of the spin echo decay kinetics with separation of the contributions of the spin dipole – dipole coupling and spectral diffusion has shown that a considerable part of free radicals and vanadyl complexes are spaced by distances not more than several nanometres. The results of these works indicate that the intermolecular interactions between vanadyl complexes and free radicals are likely to promote asphaltene aggregation.

VI. Other methods for studying heavy crude oils *in situ*

Among the *in situ* investigation methods that proved to be efficient and provide useful information about the stability and physicochemical evolution of oil disperse systems, mention should be made of optical, electron and tunnelling microscopy and methods based on light scattering.

VI.1. Dynamic light scattering

Dynamic light scattering is often used to study the phase stability of heavy oils and asphaltene aggregation processes. The data obtained by this method comply with and complement the results of small-angle X-ray and neutron scattering. In particular, it has been shown[225] that the hydrodynamic radii of asphaltene aggregates according to dynamic light scattering are in the range from 5 to 10 nm, whereas the radius of gyration determined by SAXS and SANS is 3.7 and 7.7 nm.

Dynamic light scattering is actively used to study model systems, in particular, the aggregation kinetics of asphaltenes dissolved in toluene upon the addition of heptane.[84, 226–228] The aggregation of asphaltenes in a toluene – heptane system can follow two different mechanisms: diffusion-limited aggregation in which every collision of colloid particles results in coarsening and reaction-limited aggregation in which the particle coarsening occurs upon a much greater number of collisions between asphaltenes in a colloid solution, *i.e.*, the probability of particle aggregation upon collisions is much lower than 1.[229, 230] As a result, the asphaltene aggregation rate increases with increasing heptane concentration (Fig. 14). The heptane titration of dilute solutions of asphaltenes can be used to determine the threshold amount of the coagulating agent that induces the aggregation of asphaltenes with a higher accuracy than the standard method based on the measurement of absorbance of the solution.[230]

Dynamic light scattering has also served for demonstrating that an increase in the resin concentration increases the stability of asphaltenes,[230] which results in a higher amount of heptane needed to destroy the aggregation equilibrium of the initially stabilized asphaltenes and is manifested as increasing characteristic time of aggregation. Similar *in situ* approaches have been used to study the effect of depressant additives on the aggregation of asphaltenes in the toluene – heptane system[10] and the dispersing effect of sonication, which decreased the size of asphaltene aggregates in a model system from 600 to 200 nm.[230]

Despite the simplicity and obvious advantages, dynamic light scattering has a number of significant drawbacks, which limit its applicability to *in situ* studies of crude oils. In particular, a crucial condition for the application of this method is high dilution of the initial oil components and study of actually model systems, for example, asphaltene solutions (0.01 mass % – 0.1 mass %) in toluene; meanwhile, other oil components can substantially affect the stability of asphaltenes in oils. This restricts the use of the obtained results for understanding the processes taking place in real crude oils.

One more drawback of the method is a moderate resolution, which is restricted to tenths of micrometre in the case of complex polydisperse systems. In the studies devoted to asphaltene aggregation kinetics, the minimum particle sizes determined by dynamic light scattering were

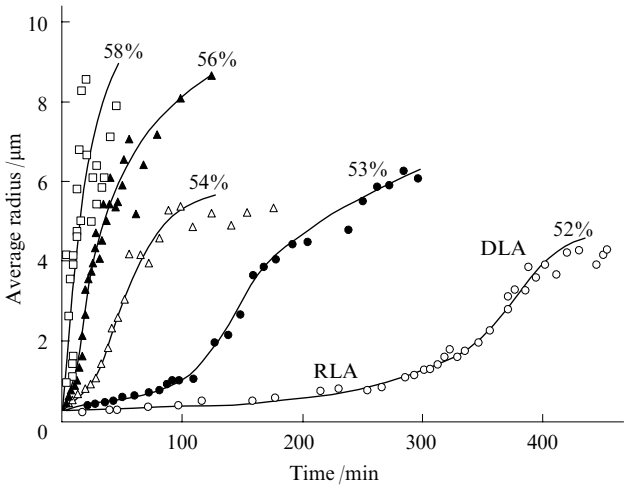


Figure 14. Kinetics of aggregation of asphaltenes dissolved in toluene (10 g litre^{-1}) depending on the addition of particular amounts of n-heptane (indicated in the Figure).[229]
The diffusion-limited aggregation (DLA) and reaction-limited aggregation (RLA) modes are indicated for one curve.

100 – 200 nm;[10, 84, 226–230] therefore, the initial stages of asphaltene aggregation, which largely determine the process mechanism and further evolution of asphaltene-containing particles, remain obscure. Presumably, further progress in the application of light scattering methods to study the asphaltene stability and aggregation would be associated with the development of methods for quantitative analysis of the Brownian paths of the particles (nanoparticle tracking analysis). This would considerably improve the spatial resolution (down to 20 – 30 nm) and provide important information about the dynamics of asphaltenes and aggregates.[231]

VI.2. Optical, electron and tunnelling microscopy

A variety of microscopy techniques are widely used to analyze the stability of oils and aggregation of heavy oil fractions. Despite relatively low resolution and often low contrast, optical microscopy is suitable for the monitoring of asphaltene aggregation *in situ* over broad temperature and pressure ranges.[155, 232–236] For example, it was shown (Fig. 15) that decreasing pressure of crude oil down to a certain threshold value results in a stepwise increase in the size of asphaltene particles from 5 – 10 to 50 – 60 μm. In some cases, a temperature rise accompanied by a pressure decrease leads to a decrease in the oil viscosity and loss of dynamic equilibrium of the system, which may result in aggregation and precipitation of asphaltenes.[232, 233] Depending on the type of oil, a pressure decrease may induce the formation of aggregates of different fractality; according to optical microscopy and dynamic light scattering data, the variation of temperature with decreasing pressure influences the mechanism of asphaltene aggregation.[232]

It is known that introduction of depressant additives into crude oil leads to stabilization of asphaltene particles, the size of which depends on the pressure in the system. Using optical microscopy, it is possible to rather easily select the optimal additive and the desired concentration, which ensures the stability of a certain oil at a particular pressure in the system.[232] While applying optical micro-

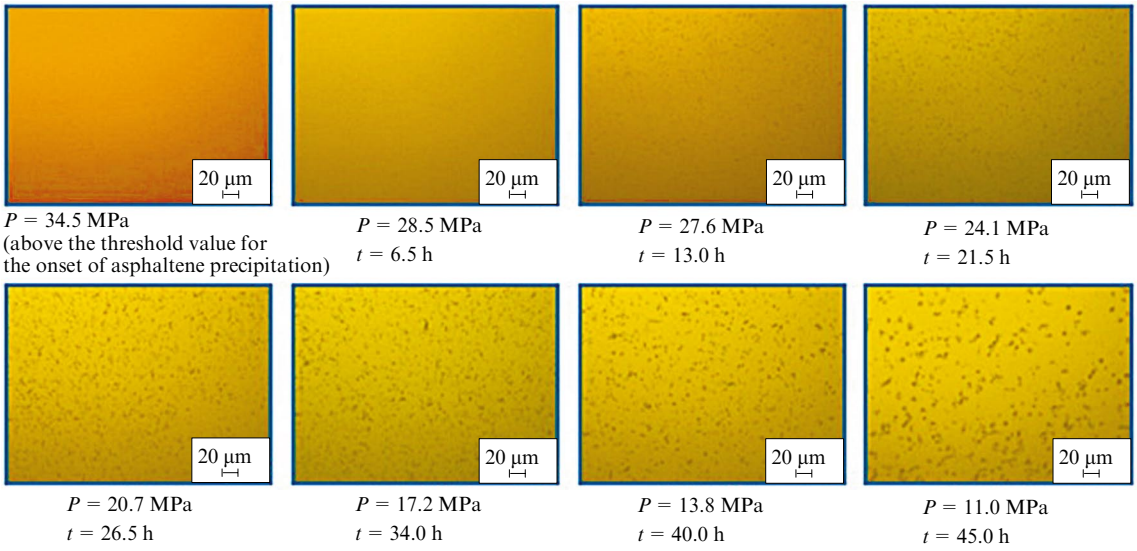


Figure 15. Precipitation of asphaltenes in oil upon pressure decrease (optical microscopy data).[232]

scopy, one should pay special attention to sample preparation. In particular, for the study of crude oils, it is important to maintain the stability of the hydrocarbon fluid recovered from a well, so that samples have appropriate chemical, hydrocarbon type and phase compositions.

The application of electron microscopy markedly improves the resolution and the information content compared with the optical microscopy. However, the use of electron microscopy to study oil systems is often restricted by technological difficulties arising in application of this method *in situ*. However, due to the high importance of the problems under discussion, an increasing number of papers describe studies of asphaltene aggregation by transmission electron microscopy with special 'high pressure' cells.[237] In this case, by 'high pressure' is meant the $10^4 - 10^5$ Pa pressure range, which is much (by 2 – 3 orders of magnitude) inferior to the capability of optical microscopy.[238]

Researchers from Manchester University reported[237] the first electron microscopic images of asphaltenes in heavy crude oil samples after the addition of heptane obtained *in situ* directly in the microscope cell. The authors observed the aggregation of asphaltenes of 10 – 20 nm size, giving rise to larger agglomerates with characteristic size of 100 – 200 nm (Fig. 16). While analyzing the results, the authors concluded that the size of primary asphaltene particles present in the initial stages of aggregation, which they could not detect experimentally, was apparently < 10 nm.

Scanning tunnelling microscopy is suitable for detection of asphaltenes with a higher resolution if they have been deposited as a thin film ($\sim < 10$ nm) on a substrate. Larichev *et al.*[121] compared the data on asphaltene shape and size characteristics obtained by small-angle X-ray scattering and scanning tunnelling microscopy (STM). Good agreement between the data allowed the researchers

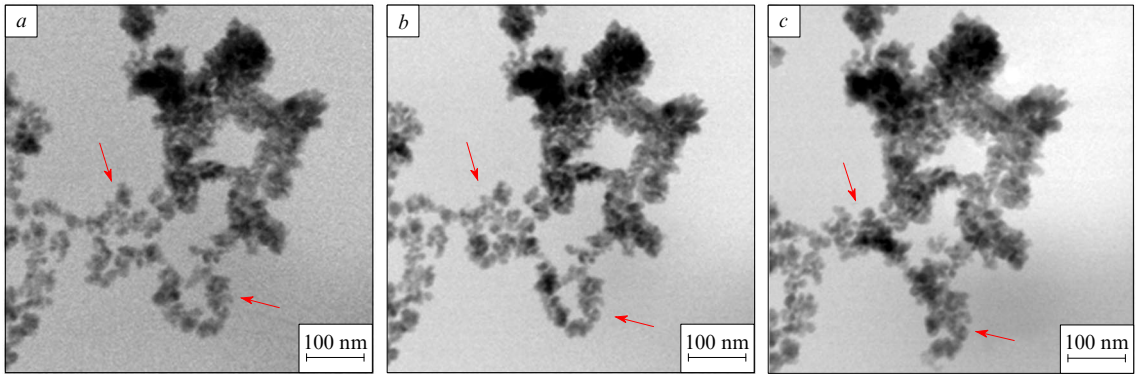


Figure 16. Aggregation of asphaltenes observed *in situ* using bright-field scanning transmission electron microscopy.[237]
(*a*) Oil + heptane emulsion after 4 h; (*b*, *c*) after 1 and 3 min of exposure to electron beam. The arrows point to ~10 nm asphaltene particles.

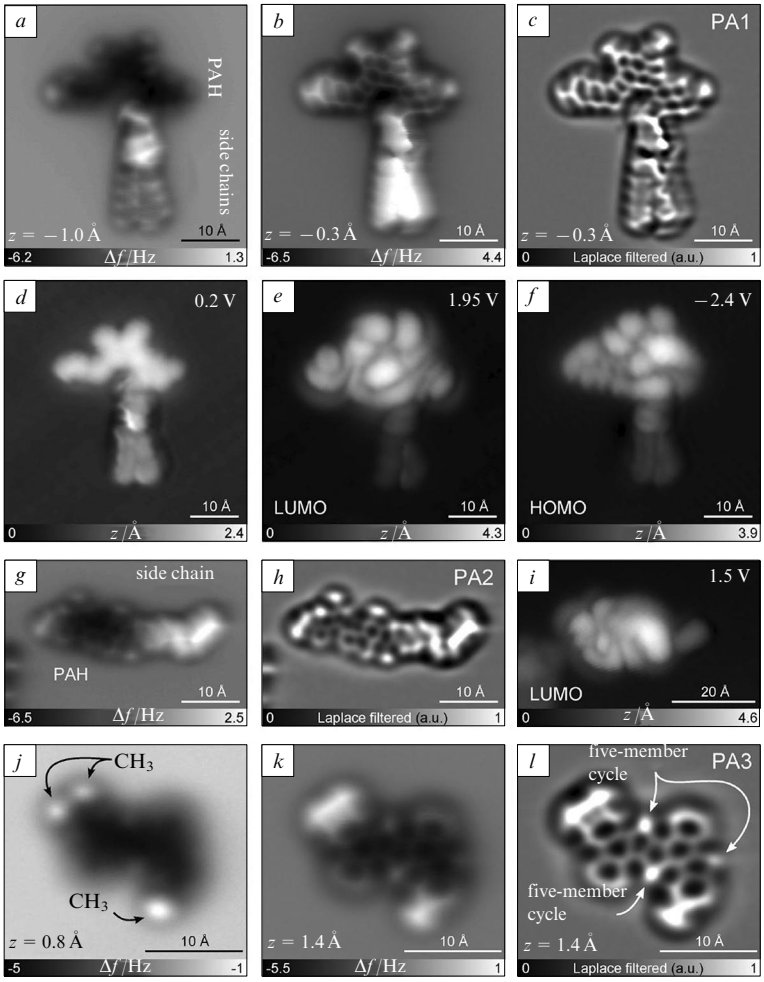


Figure 17. AFM (*a*–c, *g*, *h*, *j*–*l*) and STM (*d*–*f*, *i*) images of three single asphaltene molecules: PA1 (*a*–*f*), PA2 (*g*–*i*) and PA3 (*j*–*l*) isolated from crude oils on a NaCl(2 monolayer)/Cu(111) substrate.[239]
PAH are polycyclic aromatic hydrocarbons, Laplace filtered means that the image has been treated with the Laplace discrete operator, LUMO is the lowest unoccupied molecular orbital, HOMO is the highest occupied molecular orbital.

to use SAXS to study the aggregation of asphaltenes upon the addition of various organic chemicals to the system.

The molecular structure of asphaltenes was visualized for the first time with atomic resolution using a combination of atomic force microscopy (AFM) and scanning tunnelling microscopy after asphaltenes were thermally evaporated under ultra-high vacuum and deposited on a cooled substrate (Fig. 17).[239] The structures of the polycyclic aromatic hydrocarbons that form asphaltenes of various types was unambiguously described in detail. It should be understood that asphaltenes present directly in crude oil may have a different structure. In particular, during sample preparation by evaporation of heavy asphaltene molecules in vacuum, elimination of aliphatic substituents and partial thermal destruction of asphaltenes are possible, and the formation of additional rings is also possible. This may lead, for example, to overestimation of the proportion of asphaltene molecules with the 'continent' type structure (one large aromatic moiety composed of 8 – 14 fused aromatic rings with different aliphatic substituents) as more stable to this type of treatment compared with the molecules with 'archipelago' type structure (several smaller moieties composed of 2 – 4 fused aromatic rings connected by aliphatic chains).[84]

Although in this case, AFM and STM techniques visualized only isolated molecules, the results provide answers to many disputable questions about the structure and molecular architecture of single asphaltenes and give grounds for understanding of the thermodynamics of aggregation and intermolecular interactions of asphaltenes with their local environment. In particular, the obtained information is already actively used for molecular dynamics modelling of the aggregate formation.[240, 241]

VII. Conclusion

In conclusion, we would like to note that in recent years, a quantum leap has been observed in the use of physical methods for detailed investigation of the phase stability and physicochemical evolution of crude oils *in situ*. Heavy oil is one of the most complex multicomponent dispersions, which includes a multitude of organic and inorganic com-

pounds, heteroatoms, metals, heavy components, polymers and so on. Currently, oil producers all over the world distinguish about 2000 sorts of crude oils with different properties, hydrocarbon type and chemical composition. As a result of this diversity of oils and the multicomponent nature of the feedstock, several percent of each crude oil barrel (in caloric equivalent) is spent for the provision of production, transportation and refining. The greater part of losses is associated with the uncontrolled loss of oil stability during recovery, blending, transportation and refining. The understanding of the key factors and trends determining the aggregative properties and stability of oil disperse systems and the behaviour and chemical transformations of their major components under various external conditions, in particular, at elevated temperature and pressure is a topical issue for oil producing and oil refining industries, which are, unfortunately, often distanced from each other.

A fundamental condition for successful solution of problems in this field is, in our opinion, using a set of advanced complementary methods that would provide *in situ* information about the system on various spatial and temporal scales, rather than a single, even unique, method. It is noteworthy that while studying the phase stability and physicochemical evolution of oil disperse systems at elevated temperatures and pressures, one should bear in mind that under certain conditions, irreversible chemical transformations can take place in the complex multicomponent system, resulting in a change in the hydrocarbon type and chemical composition of oils and in the local environment of heavy components of oils, which may considerably affect the phase stability of the system and markedly complicate the observable patterns.

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