CONDENSED-MATTER SPECTROSCOPY

Magneto-optical Activity of Crude Oil and Its Heavy Fractions

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Abstract—We have experimentally studied optical and magneto-optical spectra of solutions of crude oils of different origin and their heavy fractions in the visible spectral range. Magnetic circular dichroism of oil in the wavelength range ~550 nm has been revealed. We show that the shape of the spectra of this dichroism depends on the origin of crude oil, with the magnetic dichroism magnitude being proportional to the concentration of the oil in the solution. A comparison of the data of magneto-optical spectroscopy with electron paramagnetic resonance spectra and chemical composition of samples has allowed us to conclude that the observed magneto-optical activity is determined by the occurrence of VO^{2+} complexes in the oil samples. The revealed magneto-optical activity of crude oil can form the basis of a unique method of analysis of the composition and properties of oils of different origin and heavy fractions thereof.

INTRODUCTION

Electron spin resonance (ESR) and optical absorption spectroscopy methods have been widely used to reveal particular features of the molecular structure of oil and its high-molecular components, primarily resins and asphaltenes. The ESR method makes it possible to study the state of paramagnetic ions, in particular, V^{4+} ions, which, as a rule, are contained in oil as porphyrin complexes of vanadyl VO^{2+} [1, 2]. In the ground state, the V^{4+} ion has the $3d^1$ configuration with the spin 1/2. A strong covalent bond, which is determined by a short V−O distance, leads to an axial distortion of the nearest environment of the vanadium ion and, as a consequence, to a strong dependence of optical and magnetic resonance spectra on the properties of the compound that contains VO^{2+} complexes. This particular feature allowed researchers to successfully use the ESR method and the optical absorption spectroscopy for obtaining information on the local symmetry, degree of covalence, structure of electron levels, presence of defects in the matrix, etc., in compounds that contain vanadyl complexes (e.g., [3−5]).

In studies of the properties of oils and their heavy fractions, special attention is paid to the investigation of their IR spectra [6], which contain a large number of characteristic narrow peaks that make interpretation of molecular structures easier [6]. In most cases, the visible and UV spectra are described by rather smooth curves [3], which do not contain characteristic peaks and, therefore, are considered to be less informative. However, the absence itself of characteristic features in these spectra is directly related to the properties of heavy oil fractions. A specific brownish color of resins and asphaltenes is one of their characteristic features [7, 8] and is determined by the occurrence of broad electronic absorption bands in the visible and UV ranges. The absorption spectra in these ranges have been studied in [9−11], in which the use of low-concentration oil solutions made it possible to reveal a number of resonant bands in the UV and visible spectral ranges. These works demonstrated the potential of the UV and visible spectroscopy for studying samples of crude oil.

Methods of polarization spectroscopy that study natural optical activity and magneto-optical effects could significantly complement the absorption spectroscopy. In both situations, the main effect under study is circular dichroism, more specifically, natural circular dichroism and magnetic circular dichroism. The natural optical activity of oil is mainly related to carbon atoms that occupy asymmetric positions, i.e., are related to four different atoms or radicals. The optical activity is very sensitive to any changes in the structure of the substance and to intermolecular interaction; therefore, it can yield valuable information on the nature of substituents in molecules (both organic and complex inorganic compounds) and on their conformations, internal rotation, etc. The magneto-optical activity is related to the occurrence of complexes of
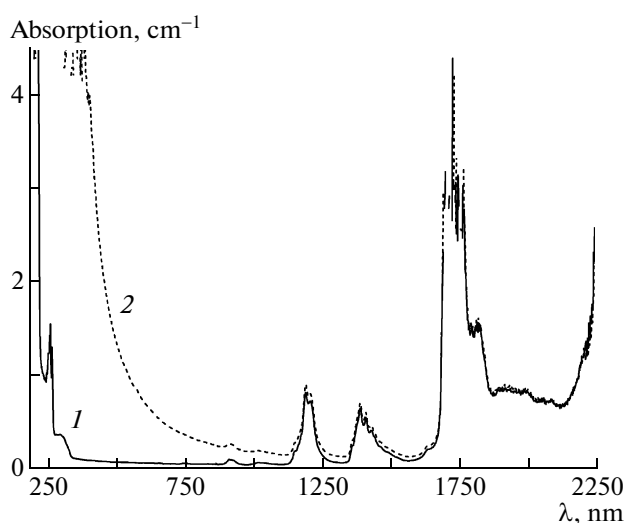
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Absorption, cm^{-1}

Fig. 1. Absorption spectra of (*1*) petrol and (*2*) solution of oil O1.

transition metals in oil or in its processing products. Along with the methods of absorption spectroscopy, which are widely used in analysis of oil, the methods of spectroscopy of optical and magneto-optical activity yield additional possibilities of rapid analysis and more profound analysis of laboratory samples. In [12−14], the spectroscopy of natural circular dichroism was applied for the first time in studies of structural peculiarities of oil systems. However, these publications caused controversy [15], which was related to certain drawbacks of the experimental technique for studying circular dichroism. The spectroscopy of magnetic circular dichroism is devoid of these drawbacks. As a rule, the spectra of magnetic circular dichroism are characterized by narrow lines, which makes it possible to obtain reliable information on optical resonances in the substance. In organic chemistry, the spectroscopy of magnetic circular dichroism has been used rather widely (e.g., [16, 17]), whereas, as far as we are aware, data in the literature on the investigation of the magnetic circular dichroism of crude oil are unavailable.

In connection with this, the objectives of this work were to determine whether it is possible to observe magnetic circular dichroism in solutions both of oil from different fields and of its derivatives; to compare the spectra of the magnetic circular dichroism, of the optical absorption, and of the ESR with the data on the elemental composition of samples obtained with X-ray fluorescence analysis; and to elucidate the nature of the magneto-optical activity and particular features of the observed spectra of magnetic circular dichroism.

SAMPLES AND EXPERIMENTAL TECHNIQUE

We studied samples of crude oil taken from the following three oilfields: (O1) the Tatar oilfield, (O2) the

Mongolian oilfield, and (O3) the West Siberian (Pikhtovoe) oilfield. The samples were dissolved in petroleum ether or toluene in required concentrations. We also investigated toluene solutions of asphaltite from the Orenburg field (A1) and asphaltenes from the Pikhtovoe (A2) and Orenburg (A3) fields. All optical and magneto-optical measurements were performed both for solutions and for solvents using identical cells.

The elemental composition of these samples was determined by X-ray fluorescence analysis using a Quant'x EDXRF spectrometer (situated at the Joint-Use Open Research Center of Siberian Federal University) and an ARL Advant'x instrument (the analytical laboratory of the Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences). X-ray fluorescence spectra were recorded using a pinhole collimator. To measure ESR spectra, we used a Bruker ELEXSYS 500 radio spectrometer, which was equipped with an attachment that allowed one to operate in a temperature range from 77 to 500 K. In the range 250−2250 nm, optical absorption spectra were recorded using a Shimadzu UV-3600 instrument.

The magnetic circular dichroism was measured in the range 500−650 nm using a setup for spectral–polarimetric investigations that was manufactured at the Kirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences, on the basis of an MDR-12 monochromator. In this case, the state of polarization of the light wave was modulated from the right-hand to the left-hand circular polarization. A modulator was made of a fused quartz prism to which a piezoelectric ceramic element was glued. Application of a alternating electric signal at a frequency ω of natural oscillations of the system to the piezoceramic element leads to the excitation of a standing elastic wave in the quartz prism. If there are no acoustic excitations, the prism is optically isotropic. As a half-wave of compression propagates through the prism along its horizontal axis, the direction of propagation of the acoustic excitation becomes a "slow" axis of the prism. Upon propagation of the second half-wave, the half-wave of extension, the pattern reverses; i.e., the axis of extension becomes a "fast" axis of the prism. Let linearly polarized light be incident on the prism such that the plane of polarization of the light makes an angle of 45° with respect to the horizontal axis of the prism, and let a standing acoustic wave be excited in the prism. Then, the emergent light will be circularly polarized and this circular polarization will alternate between the right- and left-hand with the frequency of the acoustic oscillations of the prism. If a sample under study exhibits a magnetic circular dichroism, the absorption coefficients of light waves that are right- and left-hand circular polarized with respect to the direction of the magnetic moment of the sample will be different. As a result, the light flux transmitted through the sample and incident on the photomultiplier proves to be modulated in intensity. Upon variation of the light wavelength, the constant
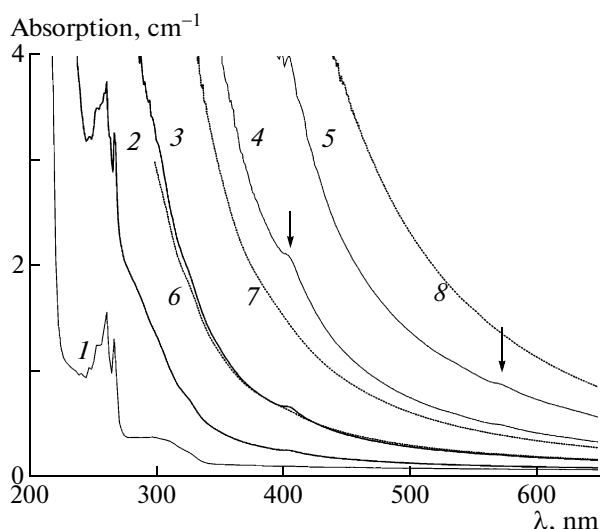
Fig. 2. Absorption spectra of (*1*) petrol, solutions of oil O1 ((*2*) 0.006, (*3*) 0.025, (*4*) 0.1, and (*5*) 0.2%), and solutions of oil O2 ((*6*) 0.025, (*7*) 0.1, and (*8*) 0.6%).

Fig. 3. Spectra of magnetic circular dichroism (MCD) of (*1*) solution of oil O1 with a concentration of 1.6%, (*2*) solution of oil O2 with the same concentration, and (*3*) petroleum ether (solvent).

component of the photocurrent of the multiplier was maintained at the same level and, therefore, the alternating signal at the output of the photomultiplier was proportional to the magnitude of the magnetic circular dichroism. The magnetic circular dichroism was measured as a difference of signals for two opposite directions of an external magnetic field. The absolute value of the magnetic circular dichroism was calibrated by the technique described in [18]. The magnetic circular dichroism was measured at room temperature in a magnetic field of 0.5 T. The measurement error of the magnetic circular dichroism was 10^{-5}, and the spectral resolution was ~20 cm^{-1}.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the survey absorption spectra of petroleum ether, which was used as a solvent, and a solution of a sample of oil O1 with a concentration of 0.2 wt %. It can be seen that, for wavelengths longer than 1000 nm, these spectra completely coincide. In this range, many narrow bands are observed, which correspond to known data from the literature. In the short-wavelength spectral range, the absorption intensity in the spectrum of the oil sample sharply increases. Figure 2 presents the short-wavelength part of the absorption spectra for petroleum ether and solutions of oils O1 and O2 at different concentrations. The edge of the strong absorption of oil solutions is considerably shifted toward longer wavelengths compared to the absorption edge of petroleum ether, which is especially clearly pronounced for the sample of oil O1. The absorption edge solutions of oil O1 exhibits a particular feature near 400 nm and a considerably weaker fea-
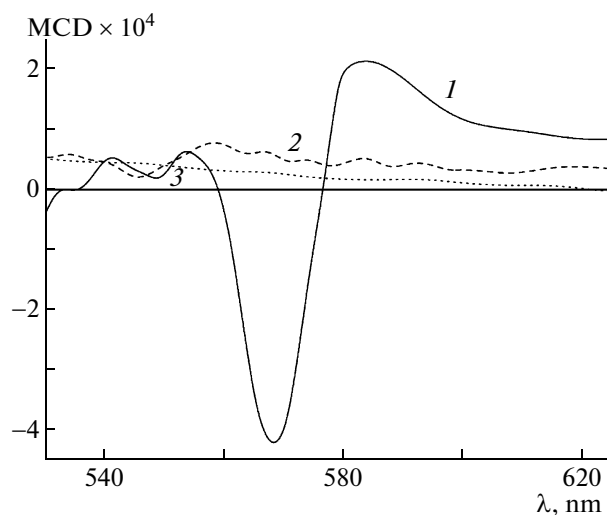
ture in the vicinity of 570 nm. In the spectrum of the solution of oil O2, these features are not observed. Sample O1 also shows a deviation from the smooth behavior of the absorption edge in the range of 320 nm and a pronounced structured peak near 250 nm. The latter two features are also observed in the spectrum of the solvent, which indicates that, in the process of obtaining petroleum ether from oil, components that are responsible for the short-wavelength absorption are preserved. Particular features in the absorption spectra of oil samples at these wavelengths were previously also observed by some authors. Thus, e.g., in [11], by subtracting the smooth curve of the strong absorption from the measured curve, an absorption maximum at 400 nm and a structured band in the range 550–650 nm were revealed, which were attributed by the authors of that work to porphyrin complexes of vanadyl complexes.

The strong absorption makes it almost impossible to measure the magnetic circular dichroism in the range of 400 nm. At the same time, in the range of ~570 nm, in which a scarcely noticeable feature is observed in the absorption spectrum of sample O1 (Fig. 2), we succeeded in revealing a clearly pronounced spectrum of the magnetic circular dichroism (Fig. 3). The main asymmetric S-shaped line of the magnetic circular dichroism corresponds to the center of gravity of the observed feature (Fig. 2). At higher concentrations, two more weak peaks are observed in the shorter-wavelength range of this line, which can be put into correspondence with the absorption line at 530 nm that was previously observed in [14]. For sample O2, the intensity of the signal of the magnetic circular dichroism is very low.
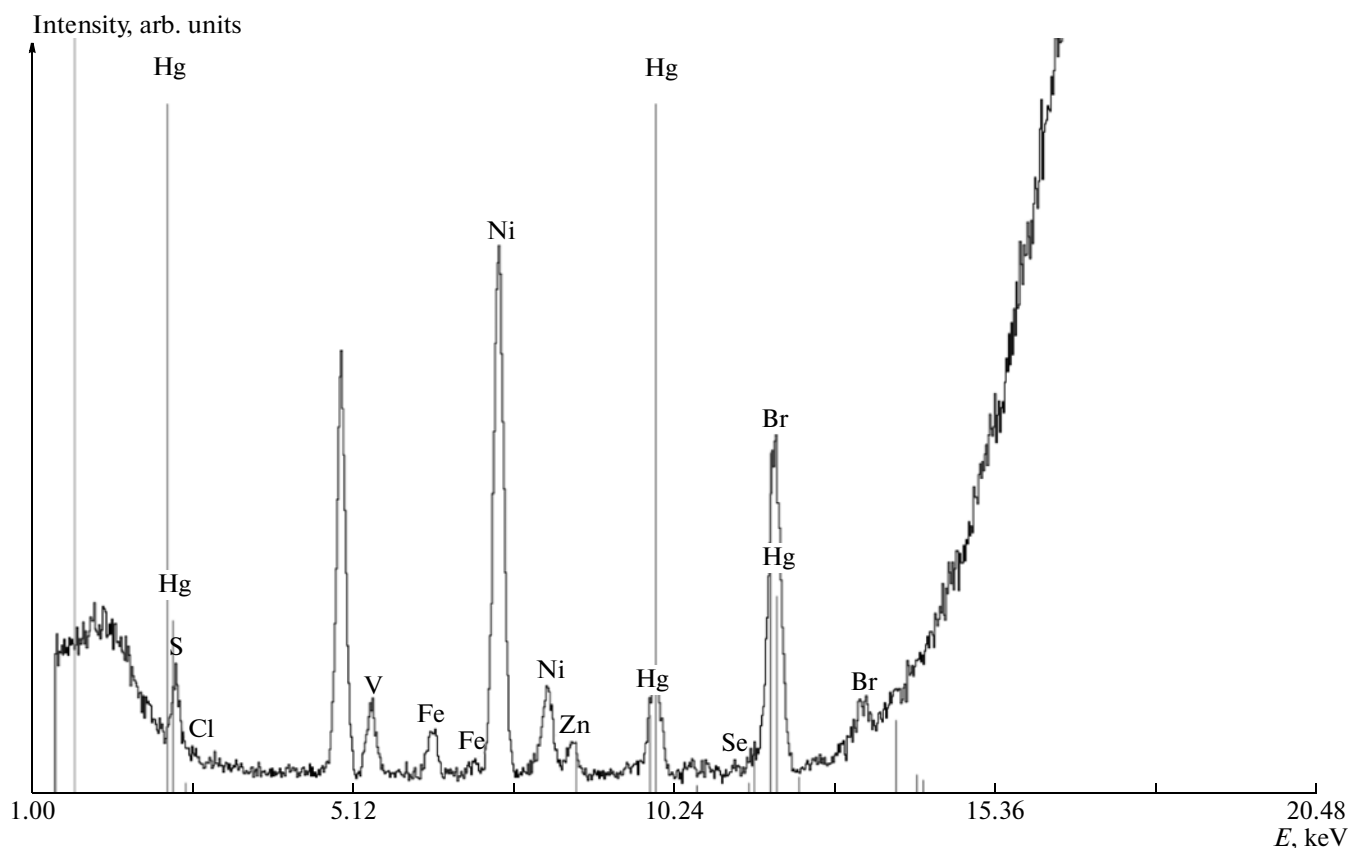
Fig. 4. Part of the X-ray fluorescence spectrum of sample of oil O1 measured with an ARL Quant'x setup.

To elucidate the nature of the magneto-optical activity of heavy oil fractions, we performed a comparative analysis of the elemental composition of samples. For all the samples under study, the concentration of the main elements of oil (H, C, O, N) varies from 95 to 99.8 wt %. The remaining mass consists of impurity elements from Mg to Hg. Figure 4 shows the X-ray fluorescence spectrum for Tatar oil that includes only impurity elements. The total content of these elements was taken as a unit. The table presents the total elemental composition of oil samples of the three types (O1−O3). It can be seen from this table that elements of the transition group are contained in all samples, but at strongly different concentrations. Thus, a maximal concentration of vanadium is observed in Tatar oil (0.019 wt %), whereas, for Mongolian oil (sample O2), within the sensitivity limits of the X-ray fluorescence analysis, this method fails to detect vanadium. An increase in the content of vanadium in oil is accompanied by an increase in the concentration of sulfur.

Attention should be drawn to the fact that the spectra of magnetic circular dichroism are observed for sample O1 in which the concentration of vanadium is the highest, whereas samples of Mongolian oil in which vanadium has not been detected do not exhibit any magneto-optical activity. We can assume that the observed effects are related to the occurrence of vanadium complexes, which, as is known, is contained in oil as porphyrin complexes of VO^{2+}.

To clarify the role played by VO^{2+} complexes in the magneto-optical activity of oil, we analyzed the ESR spectra of samples of oils O1−O3 (Fig. 5). It appeared that, if the resonance signal is unsaturated, the mass-normalized integral intensity of the ESR spectrum of vanadyl complexes is maximal in sample O1 (Tatar oil), whereas the intensity of the singlet of the radical origin in the Tatar oil is minimal compared to other samples (Fig. 6). These results indicate that magnetic circular dichroism is indeed observed in oil samples with a maximal concentration of vanadium porphyrins.

Figure 7 presents a series of the spectra of magnetic circular dichroism for different concentrations of oil O1 in petroleum ether. It can be seen that, as the oil concentration decreases, the amplitude of the signal decreases. Furthermore, although the intensity of short-wavelength maxima decreases somewhat faster compared to the intensity of the main maximum, the overall shape of the spectrum is retained, which indicates that the spectra of magnetic circular dichroism are specific for oils of different compositions. There-
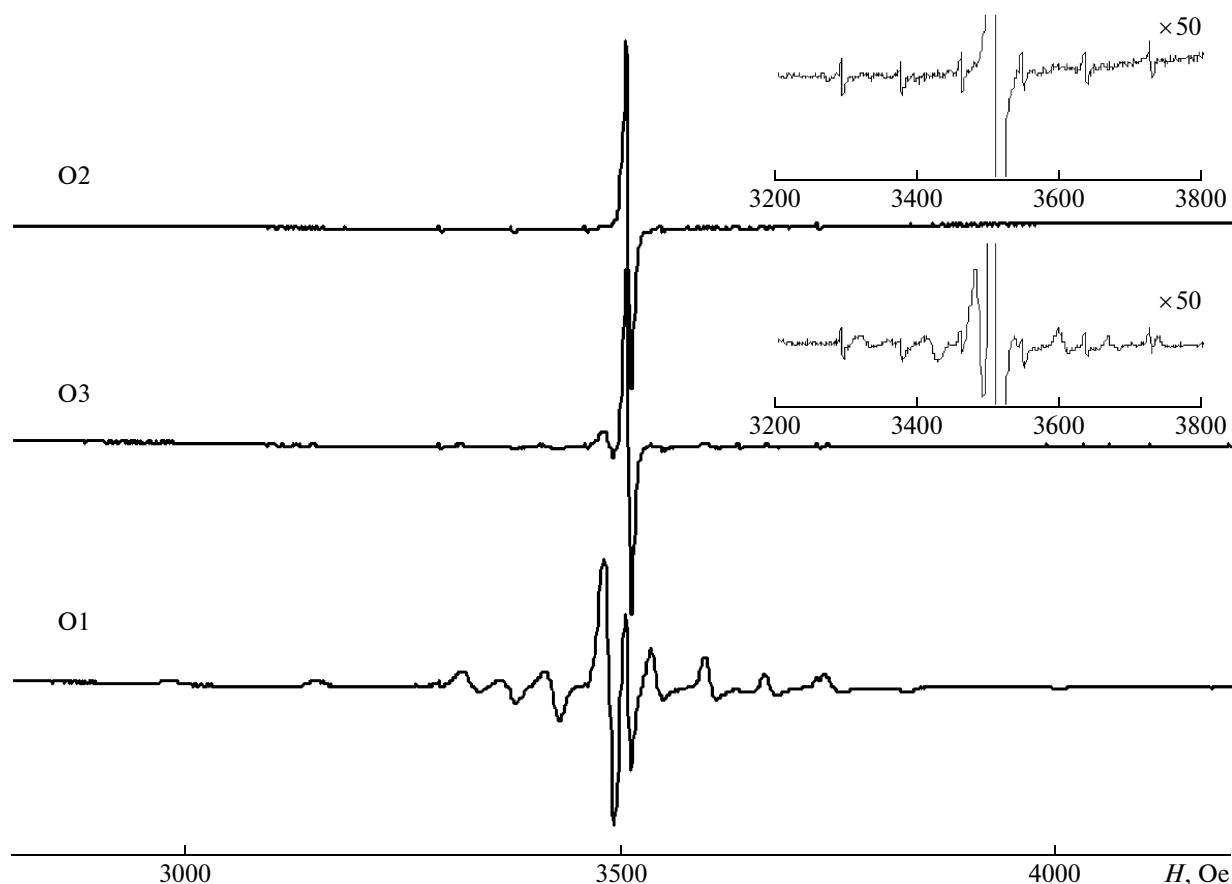
Fig. 5. ESR spectra of oil samples O1−O3 normalized to the sample mass and measured in the presence of reference Mn^{2+} in MgO at $T = 300$ K.

fore, we can conclude that the necessary condition for the occurrence of the magnetic circular dichroism in oil samples is indeed the occurrence of vanadium ions in the samples in the form of vanadyl porphyrin complexes.

However, the question of whether this condition is sufficient is open. It is known that transition metals, including vanadium, are mainly concentrated in heavy oil fractions, in particular, in asphaltenes. Figure 8 shows the distribution of impurity elements in samples of asphaltenes and asphaltites A1−A3, which was normalized to the total mass of impurities in each sample. All three samples contain a considerable amount of vanadium and, also, a small amount of nickel. In this

case, an increase in the concentration of vanadium from sample to sample is also accompanied by an increase in the concentration of nickel. A reverse pattern is observed for sulfur: the higher the content of vanadium in the sample, the lower the content of sulfur.

Figure 9 shows parts of the spectra of magnetic circular dichroism for samples of oil derivatives A1−A3. As should be expected for samples obtained from the oil of the same origin, the shapes of the spectra of magnetic circular dichroism for asphaltite (A1) and asphaltene (A3) from the Orenburg oilfield coincide; for the sample of asphaltene A2, which was extracted from West Siberian oil, no spectrum of magnetic cir-

Content of elements in oil samples of different origin (wt %) according to X-ray fluorescence analysis performed on an ARL Advant'x setup

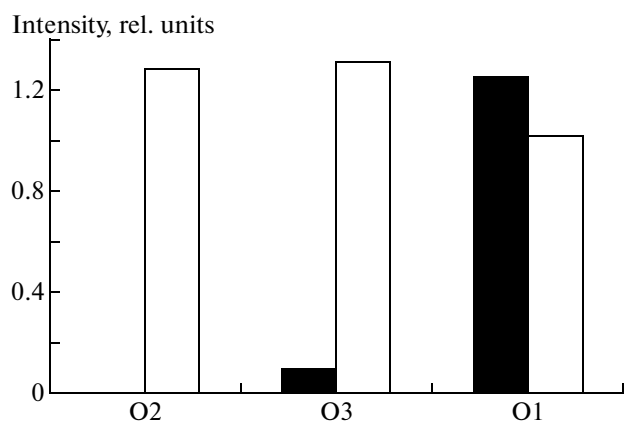| Oil sample	H, C, O, N	Mg	S	Cl	V	Fe	Ni
O1 (Tatar oilfield)	95.2339	0.0369	4.7037	—	0.0193	0.0011	0.0051
O2 (Mongolian oilfield)	99.7824	—	0.1969	0.0182	—	0.0006	0.0019
O3 (West Siberian oilfield)	98.8000	—	1.196	—	0.0019	0.001	0.0011

Intensity, rel. units

Fig. 6. Normalized integral intensity of ESR spectra of vanadyl complexes (dark columns) and singlet of a radical nature (light columns) in samples of oils O1, O2, and O3.

cular dichroism is observed. The amplitude of the signal in samples A1 and A3 decreases with decreasing vanadium concentration, as can be seen from comparison of the histograms in Fig. 8 and the curves in Fig. 9; however, there is no direct proportionality between these quantities.

Therefore, we can conclude that the occurrence of V^{4+} ions cannot be a sufficient condition for observation of spectra of magnetic circular dichroism. Indeed,

e.g., according to the data of the X-ray fluorescence analysis and ESR, sample A2 contains an appreciable amount of vanadium in the form of vanadyl complexes and this sample does not exhibit any magnetic circular dichroism.

Different shapes of the spectra of magnetic circular dichroism for oil samples of different origin and the dependence of the intensity of observed lines of the dichroism on the oil concentration in the solution and, as a consequence, on the concentration of vanadyl complexes in the sample under study allow us to assume that the environment of the vanadium ion strongly affects the formation of the spectrum of magnetic circular dichroism of crude oils. Particular features in optical spectra of vanadyl are, as a rule, related both to $d-d$ electron transitions in the V^{4+} ion and to the charge transfer transition V^+-O^-. Thus, e.g., in the absorption spectrum of a crystal of diglycine calcium chloride $[(NH_2CH_2COOH)_2 \cdot CaCl_2 \cdot 4H_2O]$ doped with VO^{2+}, four bands were observed at 682, 646, 479, and 382 nm [4]. Three long-wavelength bands were attributed to the $d-d$ transitions $^2B_{2g} \rightarrow {}^2E_g$ $(d_{xy} \leftrightarrow d_{xz,yz})$, $^2B_{2g} \rightarrow {}^2B_{1g}$ $(d_{xy} \leftrightarrow d_{x^2-y^2})$, and $^2B_{2g} \rightarrow$ $^2A_{1g}$ $(d_{xy} \leftrightarrow d_{z^2})$, respectively. The short-wavelength band was assigned to the charge transfer transition between the bonding (e_π^b) and antibonding (b_2) orbitals. It is reasonable to assume that the well-resolved
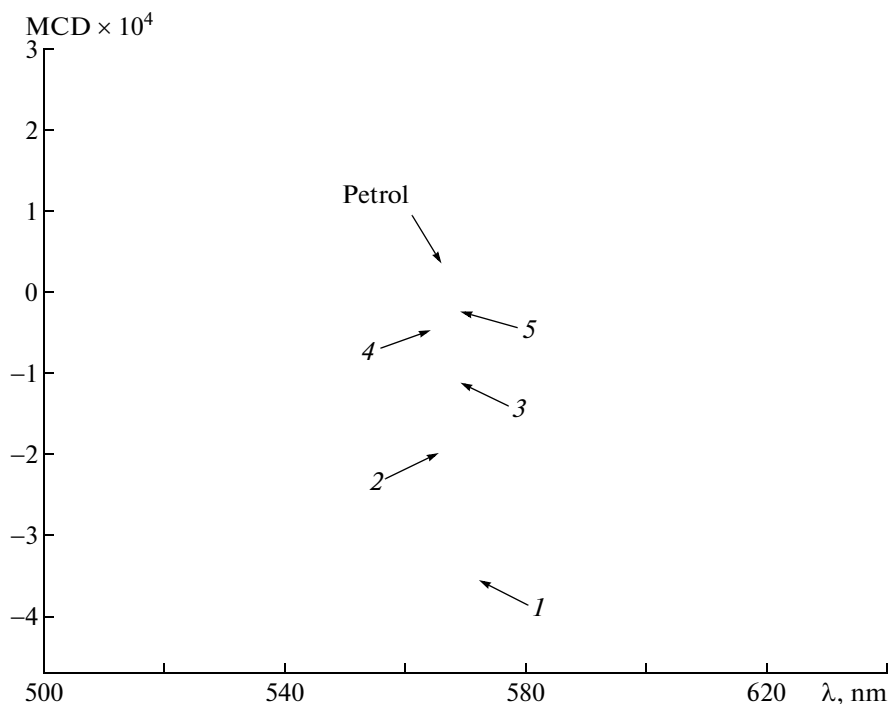

Fig. 7. Spectra of magnetic circular dichroism (MCD) of solutions of oil O1 in petroleum ether at different oil concentrations: (*1*) 1.6, (*2*) 0.6, (*3*) 0.4, (*4*) 0.2, and (*5*) 0.1%.
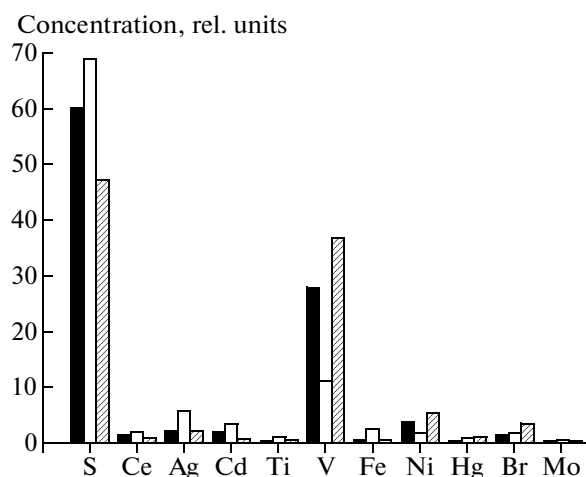
Concentration, rel. units

Fig. 8. Relative contents of atoms of elements from sulfur to molybdenum in samples A1 (dark columns), A2 (light columns), and A3 (gray columns) obtained using an ARL Quant'x setup.
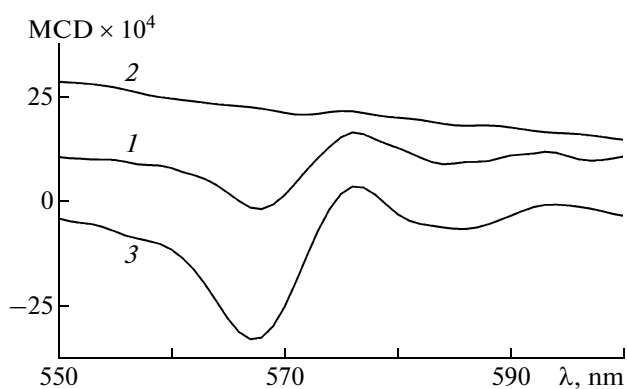

Fig. 9. Magnetic circular dichroism (MCD) at room temperature of (*1*) asphaltite from the Orenburg field, (*2*) asphaltene from the Pikhtovoe field, and (*3*) asphaltene from the Orenburg field.

band at 570 nm and a weaker feature at 530 nm that we observed in the spectrum of magnetic circular dichroism are caused by the $^2B_{2g} \rightarrow {}^2E_g$ and $^2B_{2g} \rightarrow {}^2B_{1g}$ transitions. The spacing between the centers of gravity of these bands (40 nm) is roughly consistent with the similar spacing in the spectrum of the crystal mentioned above (36 nm). If we further use this analogy, then the band that corresponds to the transition $^2B_{2g} \rightarrow {}^2A_{1g}$ should be observed near 430 nm. It is this range in which the feature in the absorption spectrum is observed (Fig. 2). A certain shift of the main band of the magnetic circular dichroism (570 nm) that occurs upon a decrease in the concentration of oil in the solution can be attributed to a decrease in the axial component of the crystal field, i.e., to a slight change in the

conformation of vanadyl. This possibility was previously observed in [11].

Our results provide evidence that the spectra of magnetic circular dichroism contain information on specific features of crude oils and their heavy fractions, which can considerably complement data of absorption spectroscopy. Measurement and analysis of spectra of magnetic circular dichroism of oil can form the basis of a new method of certification of crude oil (including heavy oil fractions) and products of its processing.

CONCLUSIONS

We studied optical and magneto-optical spectra of samples of crude oils of different origins and their heavy fractions in the visible range of the optical radiation. We revealed a magnetic circular dichroism of oil in the wavelength range of ~550 nm. Comparison of the spectra of magnetic circular dichroism, optical absorption, and ESR with the elemental composition of oils showed that the observed magneto-optical activity is caused by vanadyl complexes that are present in the samples under study. We showed that the shape of the spectra of magnetic circular dichroism depends on the origin of oil and their intensity is proportional to the concentration of oil in the solution. The performed analysis of the observed spectra allowed us to assume that the observed magnetic circular dichroism is caused by electron $d–d$ transitions in tetravalent vanadium ions.

The observed magneto-optical activity of crude oil can form the basis of a unique method of analysis of the composition and properties of oils of different origins and their heavy fractions.

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