

Effect of Ultrasonic Treatment on the Composition and Properties of Waxy High-Resin Oil

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Abstract—The composition and viscosity–temperature properties of waxy, high-resin crude oil treated in ultrasonic field have been studied by gas chromatography–mass spectrometry, IR and ¹H NMR spectroscopy, and rotational viscometry techniques. It has been shown that the ultrasonic treatment leads to an increase in the proportion of lower *n*-alkanes in the oil fraction of the treated crude and a reduction in viscosity and the pour point of the crude oil.

Keywords: oil, component composition, ultrasonic treatment, viscosity, pour point

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Due to depletion of active reserves of light crude oil, the deposits of heavy oils become more and more in demand [1]. Such problematic oils are characterized by high concentrations of high-molecular *n*-alkanes and resin-asphaltene components and high values of viscosity, pour point, and density.

Recent years have seen an increase in interest to use of ultrasonic technology for enhancement of oil refining, producing, and transportation processes by introducing complexes based on ultrasonic systems. Until the middle of XX century, it was believed that reactions in ultrasonic field (sonochemical reactions) can be accomplished only in aqueous solutions. The first successful works on sonochemistry in nonaqueous systems showed that they also feature a substantial increase in the rate and selectivity of sonochemical reactions [2].

Nowadays, it is generally accepted that ultrasound-induced degradation of organic molecules follows the radical chain mechanism. Suslick et al. showed [3] that ultrasonic treatment of *n*-decane leads to the cleavage of its intramolecular bonds followed by recombination of different radicals and formation of new compounds (H₂, CH₄, C₂H₄, C₃H₆, C₂H₂, etc.). The feasibility of effective, cracking-like chemical destruction of hydrocarbons (HC) was shown with the use of *n*-decane and *n*-octane as representative examples [4].

Although there are numerous reports on studying to the effect of ultrasonic treatment (UST) on structural–rheological characteristics of oil and oil products, they are often controversial.

According to Klokov et al. [5], sonication of an aromatic oil, leads to a cleavage of alkylaromatic HC and formation of both free radicals of linear structure and radicals containing an aromatic ring (or rings).

It was shown [6–9] that the efficiency of UST depends on the component composition of oil. The sonication of high-resin waxy oil from the Al'met'evskoe field resulted in pour point depression by 16°C and a sixfold decrease in viscosity at 10°C. The relaxation time of the structural–mechanical parameters of the treated oil is rather long: the initial values of viscosity and pour point were not recovered within several days [6]. The ultrasonication high-wax, low-resin oils leads to an increase in viscosity, pour point, and amount of wax deposits [7].

The ultrasound-induced reduction in the structural viscosity of high-resin oil is also associated with a change in the concentration of resins and asphaltenes in the oil and their effect on the disperse structure, while an increase in the viscosity of waxy oil is explained by an increase in the degree of dispersion of the crystalline phase of paraffin hydrocarbons and their interaction with asphaltenes [10]. However, Omaroaliev et al. [11] using waxy oils from Kazakhstan oilfields as representative examples, showed that an increase in the sonication time and ultrasonic radiation power leads to a substantial reduction in their density and kinematic viscosity; the pour point decreased +8°C to –6°C after 5-min treatment.

The presented review suggests that UST has an ambiguous effect on the structural–rheological properties of oils of different types. Furthermore, the

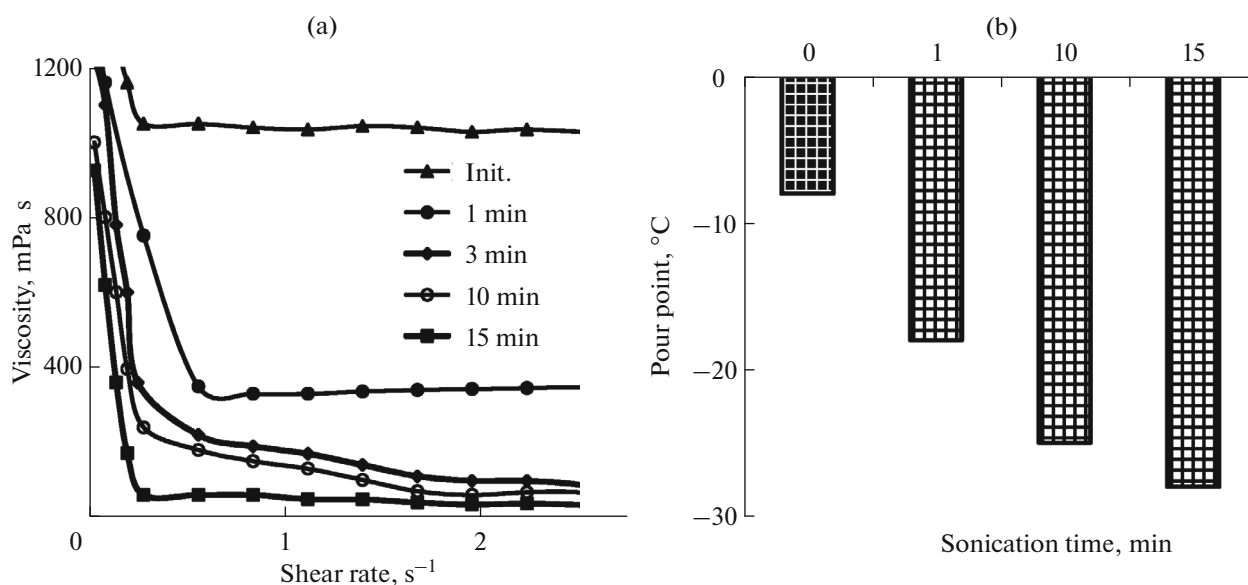


Fig. 1. Effect of sonication time on (a) the dynamic viscosity at 20°C and (b) the pour point of the crude oil.

change in the structural-group composition of oil and its components after ultrasonic treatment still remains an open question.

The goal of this work is to study the effect of ultrasonic treatment on the structural–rheological properties and composition of waxy, high-resin- oil.

EXPERIMENTAL

The object of study was waxy high-resin crude oil (crude) with the pour point -19°C , containing 76.8 wt % of lube oils (including 4.0 wt % *n*-alkanes), 16.1 wt % silica gel resins, and 7.1 wt % asphaltenes. The component compositions of the initial and sonicated oils were determined according to standard procedures [12].

The sonication of the crude was carried out on a UD-20 ultrasonic disintegrator operating at a frequency of 22 ± 1.65 kHz, an amplitude of vibrations at the probe tip of 16 μm , and an intensity of 6.2 W/cm². A sample in amount of 70–80 g was taken to be processed for a specified period of time.

The rheological parameters of the crude samples were measured with a Brookfield DV-III ULTRA viscometer over a wide range of shear rates. The pour points of the samples were determined using an INPN instrument (KRISTALL).

The IR spectra of the crude and its components were recorded on a NICOLET 5700 FTIR-spectrometer in the range of 400–4000 cm⁻¹. The samples of oil and resin fractions from CHCl₃ solutions were applied on KBr plates in the form of films. The spectra of asphaltenes were recorded in KBr discs. The processing of the IR spectra and absorbance determination

were carried out with the OMNIC 7.2 Thermo Nicolet Corporation software. The absorbance values at absorption bands were normalized by the absorbance at 1465 and 1610 cm⁻¹.

The oil fraction of the crude was analyzed by gas chromatography–mass spectrometry (GC–MS) on a Termo Scientific GSMS-DFS chromatographic mass spectral quadrupole system in the multiple ion monitoring mode, scanning mass chromatograms by the characteristic ions in the temperature programming mode of starting temperature, 80°C; final temperature, 300°C, heating rate 4 °C/min. A fused silica capillary column of 30 m in length and of 0.25 mm in inner diameter with the DB-5MS stationary phase (film thickness was 0.35 μm) was used. The reference standard was deuterioacenaphthene. The results obtained were processed using the Xcalibur program package.

The proton distribution in asphaltenes isolated from the crude before and after sonication was determined by analyzing NMR spectra obtained on a Bruker AVANCE AV 300 Fourier-transform spectrometer (Germany). The spectra were recorded in CDCl₃, the chemical shifts were reported relative to tetramethylsilane at room temperature. The areas of the H_{ar}, H_α, H_β, and H_γ regions proportional to the number of protons that give these signals were determined by the values of the integral curve of the resulting spectrum [13].

The elemental analysis of asphaltenes was carried out on a Vario el cube CHNS analyzer (Germany) [12].

RESULTS AND DISCUSSION

The previous investigations showed that the changes in structural–mechanical properties of petroleum systems treated in ultrasonic field depend on their component composition. The maximal depression of the pour point and viscosity was achieved for waxy resinous crudes at the resins–asphaltenes: *n*-alkanes ratio of 2–8 [6–9]. For the waxy, high-resin crude examined in this study, this ratio is 5.8. Even a short treatment of this crude (1 min) leads to a reduction in dynamic viscosity by more than a factor of 2.5 (Fig. 1a). An increase in the sonication time leads to enhancement of the depression effect, for example, the viscosity at low shear rates drops from 1060 to 60 mPa s after 15-min sonication.

Simultaneously with the change in viscosity, the pour point of the crude is lowered: the of pour point depression is 10°C 1 after min of sonication and becomes 20°C in 15 min (Fig. 1b).

A transition of the excited petroleum system to the equilibrium state after termination of ultrasonic impact takes a rather long period of time. The viscosity and pour point of the crude treated for 15 min remain unchanged for 5 days. In 7 days, the viscosity–temperature characteristics of the relaxing crude increase, but they do not reach the initial values.

To explain the effects observed, the compositions of the crude and its components were studied by different instrumental methods.

By the GC–MS method, the presence of C₁₄–C₃₃ *n*-alkanes in the oil fraction of the crude was detected, with the distribution maximum in the homologous series being at the C₁₈H₃₈ paraffin (Fig. 3). After ultrasonic treatment of the test crude, the position of the *n*-alkane distribution maximum remains unchanged, but the proportion of solid hydrocarbons C₁₇–C₃₃ becomes smaller (Table 1). An increase in the proportion of lower homologues in the oils of the sonicated crude is reflected by coefficient $K = n - (C_{14} - C_{20}) / n - (C_{21} - C_{33})$, which characterizes the ratio of light to heavy paraffin hydrocarbons with the normal chain structure (Table 1).

The following aromatic components were identified in the oil fraction of the crude samples: normal alkylbenzenes (*n*-AB), methylalkylbenzenes (MAB), ethylalkylbenzenes (EAB), and trimethylalkylbenzenes (TMAB). According to the calculation data, the amount of EAB decreases and the amount of TMAB increases in the oils from the sonicated crude (Table 1).

The total amount of all the identified components, including *n*-alkanes, in the oils made about 56%, therefore, the wax fraction can contain other hydrocarbons (isoalkanes, naphthenes, and aromatic HC) that migrated from the composition of complex structural units into the dispersion medium, thereby, along

with the lower *n*-alkanes causing a reduction in the viscosity and pour point of the crude.

The results of the IR study of the samples are presented in the form of normalized absorbance at the absorption bands in the range of 1850–650 cm⁻¹. To determine the relative content of structural fragments in the samples under study, the spectral coefficients were calculated using the absorption bands at 1465 and 1600 cm⁻¹ as references [14]. The aromaticity of oils, resins, and asphaltenes was determined by the ratio of intensities of the absorption bands of all aromatic C=C bonds (1600 cm⁻¹) and aliphatic C–H bonds (1465 cm⁻¹). The structure of the hydrocarbon part of the crude oil components was estimated in terms of aliphaticity and branching, which characterize the proportion of the paraffin to the aromatic moiety and the constitution of the paraffin structures, respectively. The aliphaticity was calculated by the ratio of total intensity of the absorption bands of methylene groups in paraffin chains with the number of carbon atoms >4 (720 cm⁻¹) and methyl groups (1370 cm⁻¹) relative to the aromatic C=C_{arom} bonds (1600 cm⁻¹) ($\Sigma \text{CH}_2 + \text{CH}_3 / \text{C}=\text{C}_{\text{arom}}$); the degree of branching was estimated from the ratio of intensities of CH₃/CH₂ absorption bands [14]. The amount of heteroatomic substituents was calculated by the absorption bands of heteroatomic groups including the oxygen atom. The absorption bands at 1030, 1640, and 1700 cm⁻¹ were used to estimate the contents of sulfoxide (SO) substituents, carbonyl groups (CO) in amides, and CO in acids, respectively.

Sonication does not lead to noticeable changes in the IR spectra of both the crude and the oil fraction (Table 2). Normalized to 1460 cm⁻¹, the absorbances at the absorption bands of sulfoxides (1030 cm⁻¹), CH₂ groups in alkyl substituents with no more than 4 carbon atoms, and aromatic structures (860, 820 cm⁻¹) for the samples of the crude and oil fractions remain unaltered by sonication, as well as aromaticity (1600 cm⁻¹) and degree of branching (1380 cm⁻¹). Unlike the case of crude, the spectrum of the oil fraction lacks the bands at 1650 and 805 cm⁻¹ attributed to the amide moieties and polysubstituted arenes.

The oils from the sonicated crude show an increase in aliphaticity (Table 3). A growth in the ratio of intensities of CH₃/CH₂ absorption bands (1380/2921 cm⁻¹) suggests a reduction in the average molecular weight [15], which is in agreement with the GC–MS data.

The IR spectra of the resins isolated from the sonicated crude demonstrate a reduction in intensity of the absorption bands at 1700 cm⁻¹ (carbonyl compounds) and at 1600, 850, 805, and 760 cm⁻¹, indicating a decrease in the amount of aromatic structures (Table 2). Furthermore, the intensity of the 1380-cm⁻¹ band characterizing the branching of alkyl chains decreases for the resins isolated from the sonicated

Table 1. Effect of ultrasonication on some parameters of *n*-alkane composition and distribution of petroleum alkylbenzenes

Sonication time, min	Content, %			<i>K</i>	Content, %			
	C ₁₇ –C ₃₃	C ₁₄ –C ₂₀	C ₂₁ –C ₃₃		<i>n</i> -AB	MAB	EAB	TMAB
0	88.7	59.5	40.5	1.47	4.7	9.0	14.7	71.6
5	72.8	62.6	37.4	2.06	4.2	9.2	13.0	75.2
15	75.0	63.6	37.6	1.69	2.8	9.5	9.5	78.3
30	79.9	67.3	32.7	1.75	2.9	9.5	9.3	78.9

Table 2. Normalized absorbance at characteristic bands of the IR spectra of crude, oil fraction, resins, and asphaltenes

Sample/sonication time, min	Absorption bands, cm ⁻¹								
	1700	1650	1600	1380	1030	850	805	760	725
	Normalized optical densities, rel. units*								
Crude/0	–	0.06	0.10	0.53	0.1	0.08	0.11	0.09	0.14
Crude/5	–	0.05	0.10	0.53	0.09	0.08	0.10	0.09	0.13
Crude/15	–	0.06	0.10	0.53	0.09	0.08	0.11	0.09	0.14
Oils/0	–	–	0.06	0.51	0.08	0.07	–	0.11	0.16
Oils/5	–	–	0.06	0.51	0.08	0.07	–	0.11	0.16
Oils/15	–	–	0.06	0.51	0.07	0.07	–	0.11	0.15
Resins/0	0.17	0.14	0.19	0.58	0.26	0.10	0.15	0.13	0.13
Resins/5	0.16	0.13	0.18	0.56	0.24	0.10	0.14	0.12	0.13
Resins/15	0.14	0.11	0.16	0.54	0.21	0.08	0.12	0.11	0.12
Asphaltenes/0	–	–	0.44	0.76	0.24	0.22	0.25	0.21	0.19
Asphaltenes/2	–	–	0.46	0.75	0.21	0.20	0.22	0.19	0.16
Asphaltenes/5	–	–	0.46	0.75	0.24	0.21	0.22	0.19	0.17
Asphaltenes/10	–	–	0.46	0.78	0.27	0.21	0.22	0.21	0.19
Asphaltenes/15	–	–	0.47	0.78	0.28	0.21	0.22	0.20	0.19
Asphaltenes/20	–	–	0.49	0.77	0.23	0.19	0.22	0.20	0.19
Asphaltenes/25	–	–	0.48	0.76	0.23	0.20	0.22	0.19	0.17
Asphaltenes/30	–	–	0.47	0.80	0.28	0.22	0.26	0.23	0.22

* Relative to the absorption band at 1465 cm⁻¹.**Table 3.** IR spectral data of the samples

Sample/sonication time, min	Aliphaticity, CH ₂ + CH ₃ /C=C _{arom}	CH ₃ /CH ₂ ,
Oils/0	10.38	0.20
Oils/5	10.42	0.55
Oils/15	10.55	1.17
Resins/0	3.68	0.20
Resins/5	3.80	0.18
Resins/15	4.08	0.16
Asphaltenes/0	1.77	0.32
Asphaltenes/2	1.66	0.31
Asphaltenes/5	1.68	0.31
Asphaltenes/10	1.67	0.36
Asphaltenes/15	1.70	0.35
Asphaltenes/20	1.57	0.33
Asphaltenes/25	1.62	0.32
Asphaltenes/30	1.72	0.36

samples. A reduction in the sulfoxide content of the resins from the sonicated samples is manifested in a decrease in the normalized absorbance at 1030 cm⁻¹. It should be noted that the tendency toward reduction of the normalized absorbance of these absorption bands is rather weak. The aliphaticity of the resins increases with an increase in the sonication time, the ratio of CH₃/CH₂ absorption bands changes in the antipathic manner (Table 3).

Asphaltenes from the crude sonicated for 2–30 min were studied in more detail by IR spectral analysis (Table 2). Note a weak tendency growth for the relative amount of aromatic structures (1600 cm⁻¹). The normalized absorbances of the “triplet” of aromatic bands (850, 805, 760 cm⁻¹), the concentration of alkyl units with the chain length of no more than four carbon atoms (725 cm⁻¹), and that of branched alkyl chains (1380 cm⁻¹) remains almost

unchanged. The aliphaticity of the asphaltenes isolated from the sonicated crude increases, and the ratio of CH_3/CH_2 band intensities decreases compared to the initial sample (Table 3).

To characterize the structure of asphaltenes, their ^1H NMR spectra were recorded and elemental composition was determined. The calculation of the ^1H NMR spectra showed that the amount of aromatic protons in the structure of asphaltenes from the sonicated crude does not change, but some reduction in the $\text{H}_\beta/\text{H}_\gamma$ ratio is observed (Table 4).

According to elemental analysis the data, the hydrogen concentration in asphaltenes isolated from the sonicated crude is higher than in the asphaltenes from the initial crude, indicating a reduction in aromaticity (Table 5).

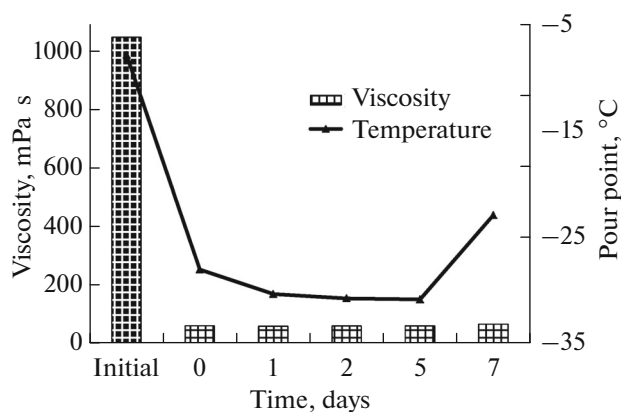


Fig. 2. Relaxation of viscosity (shear rate 0.56 s^{-1}) at 20°C and pour point of the crude after 15-min sonication.

Table 4. Effect of sonication on the concentration of protons in petroleum asphaltenes

Sonication time, min	Groups of characteristic protons (arb. units)				
	H_{ar}	H_α	H_β	H_γ	$\text{H}_\beta/\text{H}_\gamma$
0	0.931	2.179	4.705	1.225	3.841
2	0.934	2.044	4.317	1.310	3.295
5	0.935	2.112	4.483	1.166	3.845
10	0.935	2.306	4.433	1.273	3.482
15	0.963	2.351	5.055	1.310	3.859
20	0.929	2.203	4.864	1.549	3.140
25	0.935	2.154	4.406	1.354	3.254
30	1.000	2.398	5.328	2.099	2.538

Table 5. Elemental composition of petroleum asphaltenes

UST duration, min	Content, wt %					
	C	H	N	S	O (calc.)	C/H ratio
0	78.5	6.1	1.4	7.7	6.3	12.8
5	74.3	6.5	1.3	7.1	3.4	11.4
15	80.2	7.0	1.4	7.9	5.4	11.4
20	71.7	6.2	1.3	6.5	10.8	11.6
30	78.5	6.9	1.4	7.8	14.3	11.4

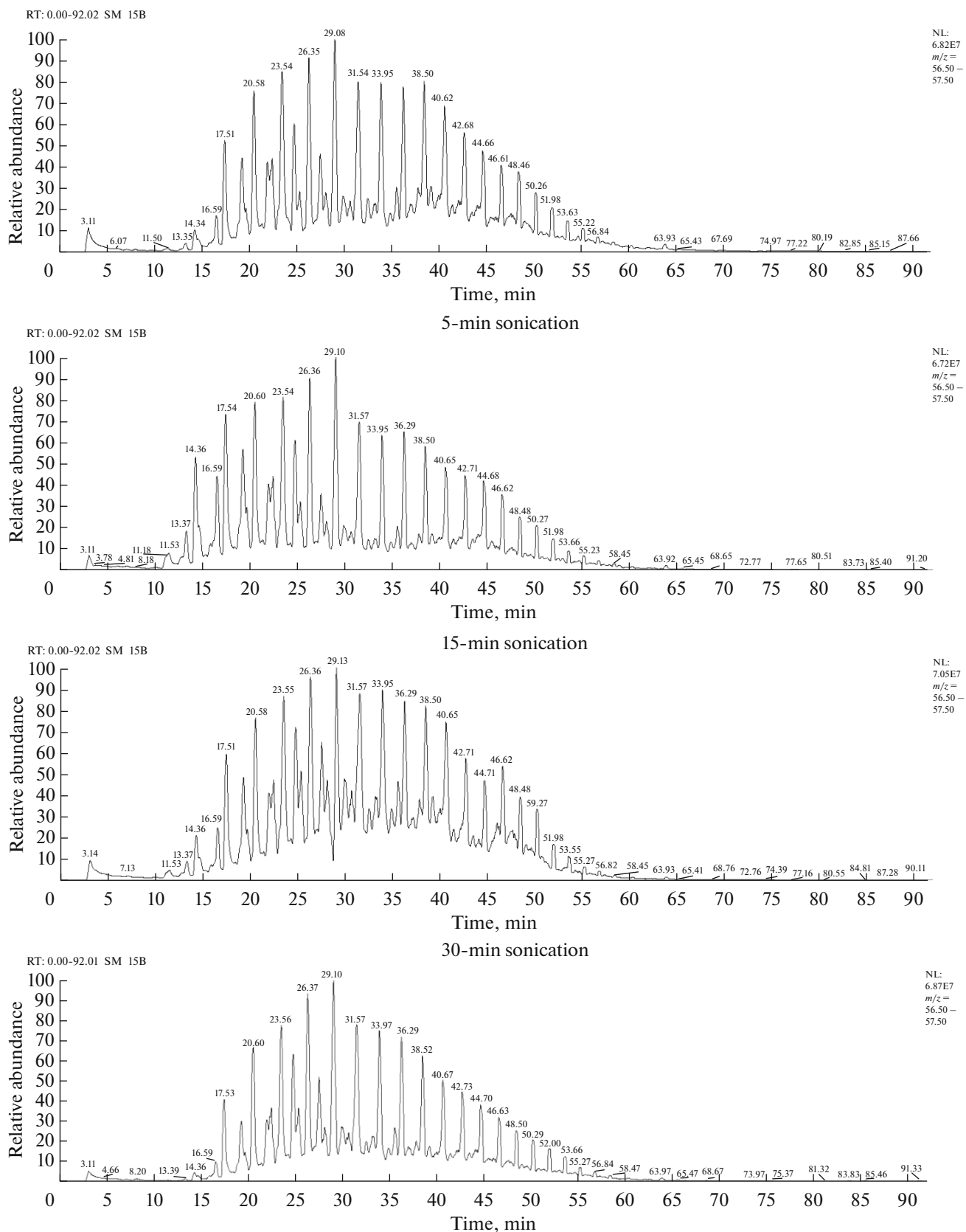


Fig. 3. Mass fragmentograms at m/z 57 (alkanes) of the oil fraction of crude after sonication.

In summary, this investigation shows that the ultrasonic treatment is an efficient tool to improve the viscosity–temperature parameters of waxy crudes with high resin–asphaltene content. The positive effects are enhanced by increasing the sonication time. The achieved viscosity and pour point depression is retained for more than 7 days, which is enough to transport crude oil for long distances.

The results of instrumental studies evidence that sonication under mild conditions (room temperature, treatment time no more than 30 min) does not lead to a substantial change in the composition of petroleum components. The improvement in viscosity–temperature characteristics of the crude by sonication is likely due to the degradation of intermolecular bonds and redistribution of the petroleum components between the disperse phase and dispersion medium of the petroleum disperse system.

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