

Effect of Asphaltenes on Wettability of Gas and Oil Saturated Reservoir Rocks

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Abstract—The wettability by asphaltenes of siliciclastic and carbonate drill-cores from oil and gas condensate fields extracted with *n*-hexane and chloroform was studied. The values obtained for the drill-cores of wetting by asphaltenes indicate the effect of asphaltenes on the wettability change for various rocks.

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One of the reasons for the low recoverability of hydrocarbons from the reservoir is molecular–surface processes at the interface between the rock and fluids. The composition of oil and the change in the temperature and pressure conditions during extraction influence the deposition of polar molecules on the surface of the pore channels. These polar molecules have a high adsorption capacity and, therefore, can change the wettability of a rock stratum. Wettability plays a key role in any process of extracting oil and gas and affects the precipitation and mobility of the condensate in the reservoir extraction process. Neglecting these wetting effects causes erroneous estimates of the saturation distribution in geological modeling, as well as poor quality prediction of exploration in hydrodynamic modeling. Many oil fields have a hydrophobic characteristic of the reservoir rocks, precluding their efficient exploitation using traditional waterflooding; thus, oil reserves in such reservoirs are difficult to extract [3].

Asphaltenes are the most prone to adsorption. Adsorption of asphaltenes leads to a change in the component composition of an oil dispersion medium, that is, to a change in the internal structure and loss of the kinetic stability of a system. Adsorption is also one of the causes of asphaltene occlusion of an oil reservoir.

Asphaltenes can be adsorbed not only directly from oil, but also as resinous asphaltene micelles of a colloidal nature. An increased concentration of asphaltenes in the pore space contributes to the formation of dense

polymolecular layers. Even a minimal adsorption of asphaltenes by rock can lead to a change in its wettability. In this paper, the effect of asphaltenes on the change in reservoir wettability has been studied experimentally.

For this study core samples of siliciclastic and carbonate rocks have been selected from the gas, gas–condensate, and petroleum zones of the Karachaganak deposit (carbonate rocks) and siliciclastics from the Romashka and Chernaya Gora oil fields.

EXPERIMENTAL PART

The samples of the core, initially containing adsorbed oil in pores, were saturated in a vacuum with distilled water, then dried in a drying unit at 25°C and air humidity of 33%. As a result of this, the first drying curve was obtained: it represents the dependence of the sample moisture content against drying time. Then the samples were treated in a Soxhlet extractor. In order to retain asphaltenes on the surface of the pore channels in the samples, extraction was carried out with *n*-hexane, since asphaltenes do not dissolve in alkane hydrocarbons, while oils and resins of adsorbed petroleum do dissolve [5, 8]. Then, the samples were dried at a temperature of 70°C to remove *n*-hexane. After its removal, a second drying curve was obtained in the manner described above. The third drying curve was obtained after treatment of the samples with chloroform (Fig. 1). After this procedure, the core samples become hydrophilic. In all cases, extraction was carried out until the UV-induced luminescence of the solvents was terminated [1, 4].

Analysis of the curves prior to extraction, after extraction with *n*-hexane, and after extraction with chloroform allowed calculation of the hydrophobization coefficients of the pore channel surface of the core samples by adsorbed petroleum and separately by asphaltenes. The coefficient of hydrophobization cor-

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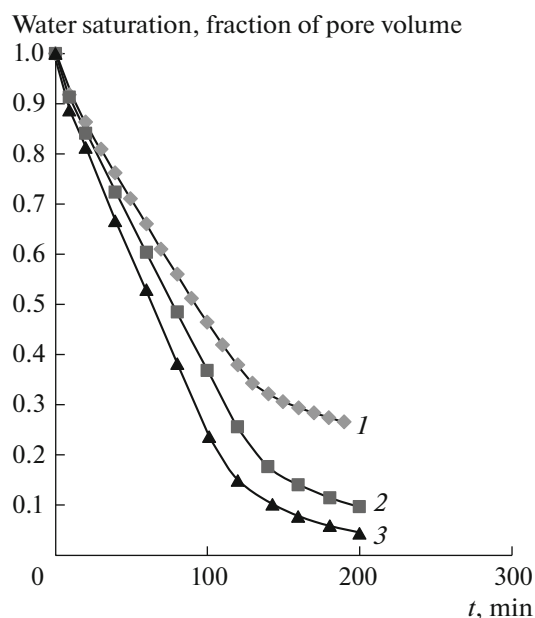


Fig. 1. Evaporation of water from a sample with adsorbed oil (curve 1), from the sample with adsorbed asphaltenes (curve 2), from a hydrophilic sample (curve 3).

responds to the fraction of the pore surface area occupied by hydrophobic substances [6].

For hydrocarbons separated by extraction with *n*-hexane and chloroform, IR spectra have been obtained (Figs. 2, 3). The IR spectra were determined by the FTIR method using a Nicolet iSiO FTIR spectrometer with St Se crystal.

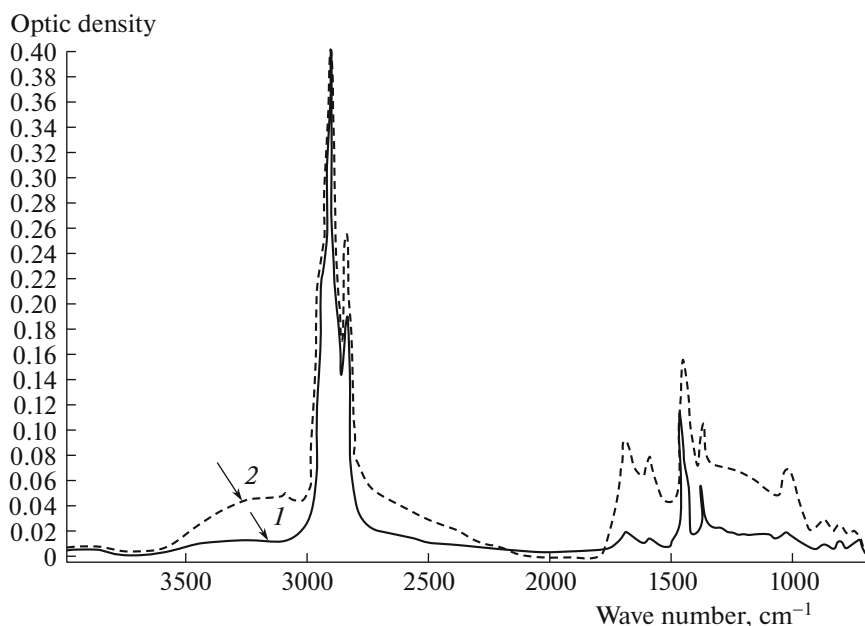


Fig. 2. IR spectrum of hydrocarbons extracted from sample 1: (1) with *n*-hexane (oils and resins); (2) with chloroform (asphaltenes).

EXPERIMENTAL RESULTS

Table 1 shows the results of the hydrophobization coefficient determinations of the pore space of core samples by adsorbed petroleum and separately by asphaltenes, oils, and resins.

As follows from Table 1, the fraction of the pore surface area occupied by the adsorbed petroleum in the studied siliciclastic samples varies.

For carbonate rocks, this parameter increases from the sample of the gas zone to the sample of the petroleum zone.

After extraction of the core samples with *n*-hexane, the coefficient of hydrophobization ($\Theta_{h \text{ asphaltenes}}$) became lower than that of samples with adsorbed petroleum. In sample 2 of the oil field, the surface of the pore channels became hydrophilic ($\Theta_{h \text{ asphaltenes}} = 0$).

Hence, the hydrophobization of the studied samples increases with the presence of hydrocarbons extracted by *n*-hexane in the adsorbed petroleum (Table 1; $\Theta_{h \text{ oils \& resins}}$). To determine the difference in the composition of hydrocarbons extracted from samples by *n*-hexane, and then chloroform, IR spectral analysis was applied for a sample from the Romashka oil field and for a sample from the oil zone of the Karachaganak field.

Analysis of the IR spectra of the matter extracted by *n*-hexane and chloroform from the samples of carbonate and siliciclastic rocks showed that the spectra are almost the same; that is, they contain the same structures. The IR bands differ only in intensity.

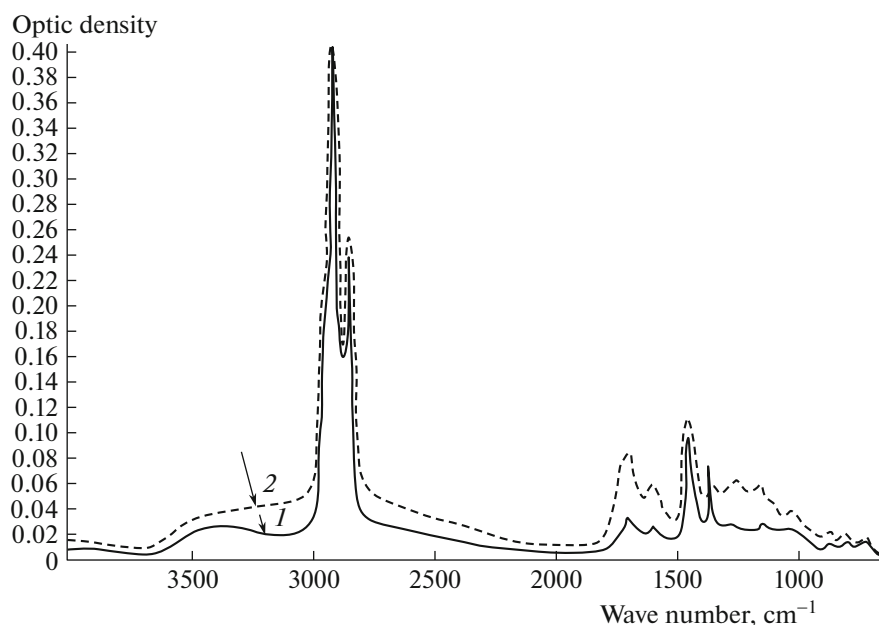


Fig. 3. IR spectrum of hydrocarbons extracted from sample 5: (1) with *n*-hexane (oils and resins); (2) with chloroform (asphaltenes).

For the hydrocarbons studied, absorption bands in the range of 3369–722 cm^{-1} are typical. Based on the analysis of the characteristic bands, it was found that extracts of *n*-hexane and chloroform from the siliciclastic and carbonate core samples are represented by polyaromatic hydrocarbons, which include oxygen- and sulfur-bearing compounds. These data permitted calculation of the spectral coefficients that characterize C_1 , aromaticity; C_2 , oxidation; C_3 , branching; C_4 , aliphaticity; and C_5 , sulfurization (Table 2) [2].

As follows from Table 2, the chloroform extracts consisting of asphaltenes contain more aromatics,

have a larger branching, and contain more sulfur compounds. They are more oxidized, but they contain fewer long aliphatic chains. Possibly this determines the lesser hydrophobization with asphaltenes than in the presence of oils and resins in the adsorbed petroleum.

This study has shown the following:

(1) Asphaltenes hydrophobize the pore space of reservoir rocks to varying degrees.

(2) The hydrophobization of the studied samples with asphaltenes is less than with the oil–resin fraction due to the smaller number of long aliphatic chains in their composition.

Table 1. Hydrophobization coefficient of adsorbed petroleum, asphaltenes, oils, and resins

Sample	Hydrophobization coefficient, Θ_h , of the fraction of area units of pores		
	$\Theta_{h \text{ ads petrol}}$	$\Theta_{h \text{ asphaltenes}}$	$\Theta_{h \text{ oils \& resins}}$
1	0.238	0.065	0.173
2	0.074	0	0.074
3	0.093	0.044	0.049
4	0.100	0.02	0.098
5	0.312	0.104	0.208

Table 2. IR Spectral coefficients

Sample/rock	Fraction	Spectral coefficients				
		C_1	C_2	C_3	C_4	C_5
1 siliciclastic	Oils, resins	1.16	0.256	0.588	3.67	0.216
	Asphaltenes	4.17	0.610	0.706	1.54	0.474
2 carbonate	Oils, resins	1.375	0.301	0.585	3.24	0.2
	Asphaltenes	3.07	0.759	0.734	1.713	0.34

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