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Study of an Oil Component in Model Solutions of Oil-field Waters

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The processes of oil dissolution in water with different mineralization, pH and time of "mineralized water-oil" contact, were examined in present work. It is shown, that a maximum quantity of oil components extracts from water in the conditions of a weak mineralization and the acid medium. It is established, that the group composition of oil hydrocarbons dissolved in water is influenced by contact time on intersection of "mineralized water-oil" mixture. The growth of quantity of aromatic compounds passed to water from light oil along with increasing of contact time indicates formation of steady disperse system in a solution. For heavy oil the small content of aromatic hydrocarbons is connected with presence of a considerable quantity of high-molecular compounds which form unsTable disperse system in a solution. The behavior of relative content of oxygenic compounds testifies to reversibility for process of light oil components dissolution along with contact time increasing, whereas increasing of their concentration in "mineralized water-oil" mixture is marked for heavy oil.

Keywords: a water mineralization, the emulsion phase reversal, oil components, oil disperse system, pH, spectral coefficients, contact time, IR-spectrometry.

Introduction

The investigations of oil component of oil-field waters are topical at present. Results of these researches allow to find out a source of migrant aquabitumoids in oil-and-gas bearing basin, and also to study natural transformations of oil components in the migration process [1]. Nowadays, the oil-field waters of Western and Eastern Siberia contain considerable quantity of migrant oil and hydrocarbon gases. Therefore, despite big number of water exchange cycles in sedimentation basin, and considerable dispersal of oil components in underground layers, it can be assumed oil and gas presence in investigated territory by results of the analysis of oil component of oil-field waters.

It is known, that all oil-and-gas bearing layers contain waters of various mineralization. However, the problem of mineralization influence on the content and composition of an oil component in oil-field waters is studied insufficiently [2, 3]. At the same time, the presence of oil-origin

organic substance in oil-field waters is a direct sign of oil-and-gas content.

The work purpose – is to show on an example of "mineralized water – oil" model mixtures the influence of water mineralization and pH on the content and group composition of the oil components dissolved in water.

Experimental part

The model solutions on the basis of oil and mineralized waters having composition, similar to composition of natural oil-field waters have been prepared for work. Compositions of mineralized waters are presented in Table 1, characteristics of oils used in work are resulted in Table 2. The only oil components which dissolved in water were extracted from model mixtures through certain time intervals, by a technique described in work [4]. The analysis of the content and group composition of oil components extracted from water was carried out with methods: gravimetry [5], gas-liquid method and infra-red spectrometry.

Fractions of hydrocarbons were obtained from an oil extracts by means of liquid adsorption chromatography on a column with aluminium

Table 1. Chemical composition of mineralized solutions

Composition of salt ions	Content of salt ions in solutions, g/dm³		
	1	2	3
Mg^{2+}	10,214	5,800	6,445
Na^+	51,372	45,200	45,859
K^+	11,500	-	3,250
NH_4^+	1,350	0,050	0,375
Fe^{2+}	-	-	0,033
Fe^{3+}	-	-	0,003
Sr^{2+}	-	0,470	-
Al^{3+}	-	-	0,006
Ca^{2+}	-	21,600	19,439
SO_4^{2-}	0,425	1,100	0,681
Cl^-	209,356	124,300	125,954
Br	3,019	2,100	2,653
J^-	-	0,005	0,032
HCO_3^-	-	0,490	-
Total Mineralization, g/dm³	287,236	201,115	204,731

Table 2. Physical and chemical characteristics of oils from Usinskoye and Kiev -Yoganskoye fields

Characteristics	Oil from Usinskoye field	Oil from Kiev-Yoganskoye field
Depth, m	1248-1254,5	3415-3426,0
Oil density, g/cm³	0,9620	0,82970
Oil viscosity, mm² / s, at 20 °C at 50 °C	1500,00 -	4,60 2,00
Hard wax, %	0,3	1,3
Resins, %	10,00	4,30
Asphaltenes, %	8,10	0,40

oxide of IV degree of activity, hexane was used as eluent.

Compositions of saturated hydrocarbons were defined by gas-liquid chromatograph «Perkin-Elmen Sigma 2B» with application of gas-ionizing detector. Helium was used as gas-carrier. The shooting was carried out with rate of 4 degrees per minute in temperature interval from 100 ^{0}C up to 290 ^{0}C. The sample input was carried out with microsyringe of 0,5 microliters volume.

The general IR spectra of analyzed samples of oils and oil extracts were registered on IR Fourier spectrometer Nicolet 5700 (the resolution of 4 sm^{-1}, number of sample scans – 64) in the range of 1800-600 sm^{-1} in a thin layer between KBr glasses. The spectral coefficients required for the analysis of group composition of oil compounds, dissolved in water, were counted by means of the spectra. The quantity of oil hydrocarbons was defined in the range of 3100-2700 sm^{-1} by a technique [6] in NaCl cuvet with the thickness of an absorbing layer of 10 mm.

Results and their discussion

Influence of pH and water mineralization on efficiency of solubility of oil components in water was investigated in work. The influence of pH on solubility of oil components in mineralized water was not discussed in the literature earlier. The data presented in Table 3, have shown, that a maximum quantity of oil components extracts from the model mixture, prepared on the basis of a solution with a smaller mineralization, having more acid medium (3rd composition). The extraction data on oil components from water of identical composition of mineral salts, but of a different mineralization and pH solutions are cited in Table 4.

The reason for high content of oil components in composition 3, apparently, is the fact that in the acid medium the water molecule forms stronger hydrogen bonds with ones for oil, i.e. transition of oil components in water is facilitated. It is known, that the influence of oil-field waters mineralization on solubility of oil hydrocarbons into them during migration process, consists in the fact that oil compounds will pass to the water with more difficulties if it has the high content of mineral salts because the presence of salts increases entropy factor of this disperse system [7]. The results received in given work, do not contradict to this. Really, in studied "water-oil" systems the degree of oil components extraction is the highest for less mineralized solution.

Thus, the calculated extraction degrees of oil compounds are maximum for more acid model solutions. All the compounds move from oil to less acid medium (the pH of solutions 1 and 2 are 5,0 and 5,4), that is gravimetrically defined. Mainly alkanes, which are well quantitatively defined by means of IR spectrometer method, easier move to the acid medium. Extraction degrees values for oil components from a solution 3, received by means of gravimetric and IR spectrometer methods, are practically identical (Table 3).

The processes of oil components transition in water depending on time of "water-oil" contact under various water mineralizations are studied in work. Model mixtures on basis of oil and mineralized solutions of composition 3 were in contact from 1 up to 27 days at temperature 60 ^{0}C. The extraction of oil components was periodically spent. The results presented in Fig. 1, 2 show that in high mineralization water the content of oil components is lower in comparison with weak mineralization water, irrespective of type of oil and time of its contact to water. Besides, curves, presented in Fig. 1, indicate that the process of oil components transition on interface of two phases from light Kiev-Yoganskoye oil to mineralized water is process of emulsion phase reversal, 2 maxima are observed under this condition. The same regularity is for heavy Usinskoye oil

Table. 3. Efficiency of extraction of oil components from the water, depending on the composition of minerals (oil from Kiev-Yoganskoye field)

Solu-tion	Composition	pH	Minerali-zation, g/dm³	Degree of oil extraction*, %	
				Gravimetric analysis	Infrared analysis
1	NH₄CI, K₂SO₄, KBr, MgCI₂, NaCI, KCI, CaCI₂	5,4	287,236	62, 5	26,0
2	MgCI₂, NaCI, NH₄CI, NaBr, NaI, SrCI₂, CaCI₂, Na₂SO₄, NaHCO₃	5,0	201,115	72, 5	33,5
3	AICI₃, FeCI₃, FeCI₂, KI, NH₄CI, NaBr, MgCI₂, NaCI, CaCI₂, Na₂SO₄ , HCI (1N)	4,3	204,731	86,0	82,0

* initial oil concentration − 0,5 g/dm³

Table 4. Efficiency of oil components extracting from the water depending on the mineralization of model mixtures and pH (oil from Kiev-Yoganskoye field)

Composition of model mixture	pH	Mineralization, g/dm³	Degree of extraction of oil *, %
AICI₃, FeCI₃, FeCI₂, KI, NH₄CI, NaBr, MgCI₂, NaCI, CaCI₂, Na₂SO₄, HCl (1н)	3	204,731	25,5
	3	102,365	32,0
	3	51,182	57,4
	5	204,731	25,0
	5	102,365	29,0
	5	51,182	47,9
	8	204,731	20,0
	8	102,365	32,7
	8	51,182	44,3

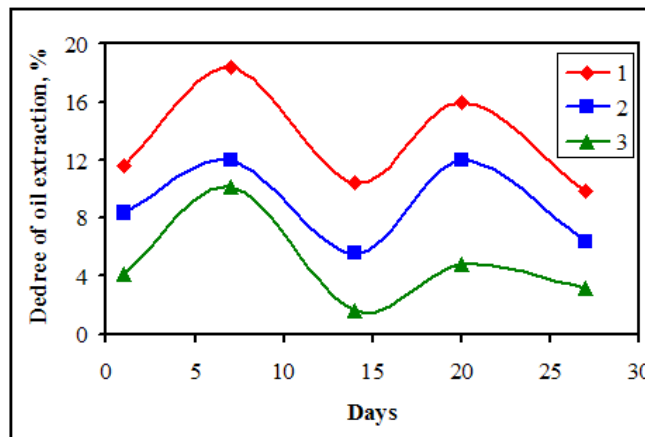* initial oil concentration − 0,5 g/dm³

Fig. 1. The efficiency of extraction of oil components of oil from Kiev-Yoganskoye field depending on contact time, "water-oil" solutions at pH = 3, T = 60-80 ⁰C and water mineralization: 1 − 5,118 g/dm³; 2 − 51,182 g/dm³; 3 − 204,731g/dm³
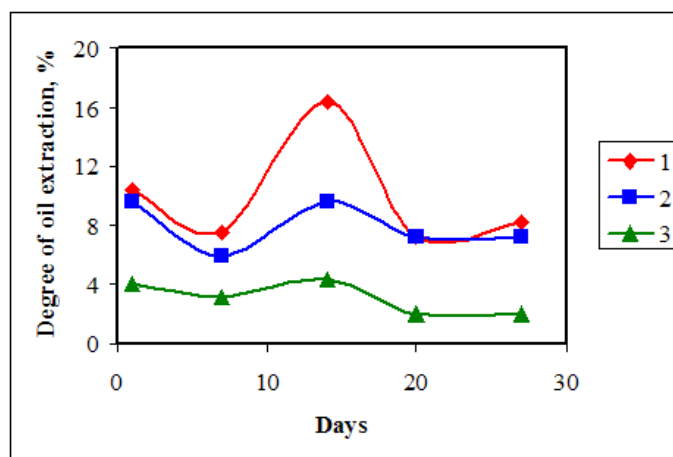
Fig. 2 – The efficiency of extraction of oil components of oil from Usinskoye field depending on contact time, "water-oil" solutions at pH = 3, T = 60-80 ^{0}C and water mineralization: 1 – 5,118 g/dm^3; 2 – 51,182 g/dm^3; 3 – 204,731g/dm^3

Table 5. Spectral coefficients for oil and oil components extracted from model mixtures (oil from Kiev-Yoganskoye field)

The objects	The time of contact, days	$C_1=D_{1610}/D_{720}$	$C_2=D_{1720}/D_{1470}$	$C_3=D_{1380}/D_{1470}$	$C_4=D_{975}/D_{720}$	$C_5=D_{720}/D_{745}$
Oil		0,42	0,59	0,51	0,28	1,28
Oil components	1	0,59	0,49	0,55	0,62	1,22
	7	1,12	1,18	0,69	1,24	0,88
	14	1,17	0,89	0,65	1,02	0,86
	21	2,64	0,15	0,29	0,90	1,87
	27	1,90	0,09	0,25	0,75	1,60

Table 6. Spectral coefficients for oil and oil components extracted from model mixtures (oil from Usinskoye field)

The objects	The time of contact, days	$C_1=D_{1610}/D_{720}$	$C_2=D_{1720}/D_{1470}$	$C_3=D_{1380}/D_{1470}$	$C_4=D_{975}/D_{720}$	$C_5=D_{720}/D_{745}$
Oil		1,82	0,16	0,61	1,09	0,73
Oil components	1	1,18	0,36	0,66	1,06	1,03
	7	0,73	1,26	0,71	1,31	0,88
	14	1,65	1,11	0,68	1,25	0,58
	21	0,45	0,89	0,58	1,13	0,87
	27	0,30	0,74	0,47	1,02	0,22

(Fig. 2); however a maximum for it comes much later (in 14th day).

Besides, the relative content of hydrocarbons by results of calculation of spectral coefficients (Table 5, 6) was defined in present work, according to work [8].

The aromaticity coefficient C_1, that defines aromatic and aliphatic compounds ratio, increases throughout all time of contact for light oil of Kiev-Yoganskoye field. It testifies that aromatic compositions form steadier disperse system with formation of "oil in water" inclusion compounds [9]. Whereas, the reduction of coefficient C_1 is observed for oil components of oil from Usinskoye field. It can be explained with the fact that aromatic hydrocarbons of heavy oil contain more high-molecular compounds, therefore they form less steady disperse system.

Coefficient C_2 reflecting the quantity of oxygenic compounds, for oil components of light oil, increases in 7th and 14th days, and decreases in 1st, 21st and 27th days in comparison with initial oil, this testifies to fluctuation process of transition of carboxyl groups (-COOH) – from oil in water and vice versa, i.e. to reversibility of process of oil components dissolution. As for heavy oil of the Usinskoye field, the increasing of coefficient C_2 noted throughout all time of contact, testifies to increasing of oxygenic compounds quantity in "water-oil" emulsion, i.e. to higher dissolution of oxygenic components in water.

Relative contents of the branched compositions (coefficient C_3) specify that they are inclined to formation of small quantity of steady disperse compositions in water because of wider molecular diameter and it is difficult for them to pass water phase with formation of inclusion compounds. This tendency is observed, both for heavy oil, and for light one.

Fluctuation of values of the relative content of naphthenic structures (coefficient C_4) specifies that transition process of naphthenic hydrocarbons in a water phase is non-constant in time. Decrease in their relative content for light oil by 27th day testifies that their associates with water are not sTable because of reversibility of processes of inclusion compounds formation. In heavy oil, the naphthenes with the long not branched side-chain prevail most likely.

Relative contents of n-Alkanes (coefficient C_5) up to C_{20}, both for light and heavy oils change throughout all time of contact. Apparently, the phenomenon of the emulsion phase reversal
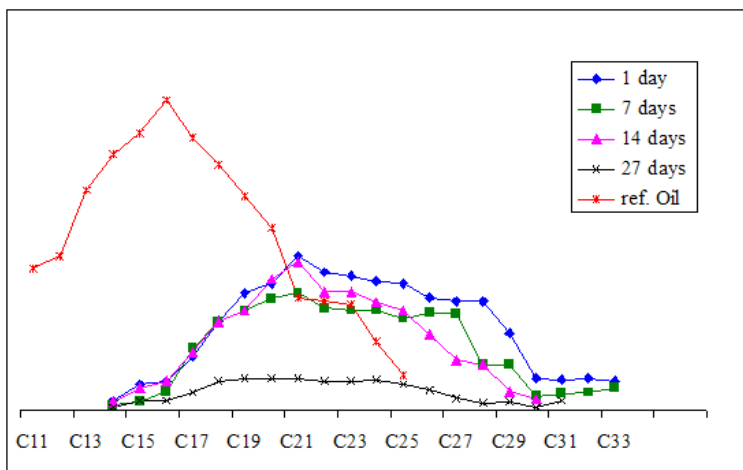

Fig. 3. Molecular weight distribution of n-Alkanes of oil component, depending on the contact time of "mineralized water-oil" (oil from Kiev-Yoganskoye field)
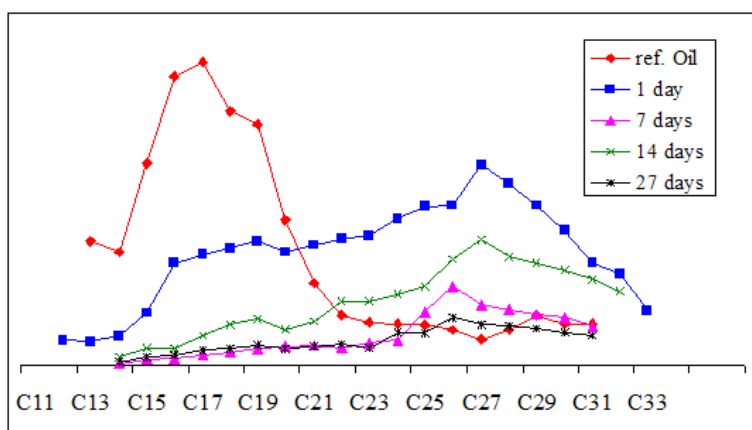
Fig. 4 – Molecular weight distribution of n-Alkanes of oil component, depending on the contact time of "mineralized water-oil" (oil from Usinskoye field)

takes place. Values of coefficient C_5 specify that normal alkanes with molecular weight more than C_{20} prevail in heavy oil from Usinskoye field that is confirmed by data of a gas-liquid chromatography.

Fractions of n-Alkanes were obtained from samples of water-extracted oil components of light and heavy oils by the method of liquid adsorptive chromatography. The molecular weight distribution of the components (Fig. 3, 4) was calculated for these fractions with the method of gas-liquid chromatography.

As it follows from curves of molecular weight distribution, the maximum of n-Alkanes for light oil falls on $C_{20} - C_{24}$, and on $C_{26} - C_{29}$ for heavy one. Thus, using results of molecular weight distribution of n-Alkanes, it is possible to define the type of oil buried in boundaries of oil-and-gas bearing layers.

Conclusion

The processes of oil dissolution in water with different mineralization, pH and time of "mineralized water-oil" contact, were examined in present work. A maximum quantity of oil components extracts from water in the conditions of a weak mineralization and of acid medium. The group composition of the oil hydrocarbons dissolved from water is influenced by contact time on intersection of "mineralized water-oil" mixture. The growth of quantity of light oil aromatic compounds extracted to water along with increasing of contact time indicates formation of steady disperse system in a solution. For heavy oil the small content of aromatic hydrocarbons is connected with presence of a considerable quantity of high-molecular compounds which form unsTable disperse system in a solution. The behavior of relative content of oxygenic compounds testifies to reversibility of process of oil component dissolution for light oil, whereas their increase is noted in "mineralized water-oil" mixture for heavy oil.

It is shown, that using results of molecular weight distribution of n-Alkanes, dissolated in oil-field water, it is possible to define the type of buried oil. Results of work can be used at oilfields investigation, in hydrogeochemical researches of oil-field waters, and also at the analysis of subsoil and foul water in oil production areas.

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Изучение нефтяной составляющей

в модельных растворах пластовых вод

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В работе исследовали процессы растворения нефтей в воде с разной минерализацией, pH среды и временем контакта смеси «минерализованная вода-нефть». Показано, что максимальное количество нефтяных компонентов экстрагируется из воды в условиях слабой минерализации и кислой среды. Установлено, что на групповой состав нефтяных углеводородов, выделенных из воды, влияет время контакта на границе раздела

«минерализованная вода-нефть». С увеличением времени контакта повышается количество ароматических соединений, переходящих в воду из легкой нефти, что свидетельствует об образовании в растворе устойчивой дисперсной системы. Для тяжелой нефти уменьшение содержания ароматических углеводородов связано с наличием большого количества высокомолекулярных соединений, которые образуют неустойчивую дисперсную систему. Характер изменения относительного содержания кислородсодержащих соединений с увеличением времени контакта свидетельствует об обратимости процесса растворения нефтяных компонентов легкой нефти, тогда как для тяжелой нефти отмечается их увеличение в смеси «минерализованная вода-нефть».

Ключевые слова: минерализация воды, обращение фаз эмульсий, нефтяные компоненты, нефтяная дисперсная система, pH среды, спектральные коэффициенты, время контакта, ИК-спектрометрия.