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ELECTROCHEMICAL METHOD FOR EVALUATING THE WETTABILITY OF STEEL IN A TWO-PHASE DYNAMIC SYSTEM OF ELECTROLYTE AND LIQUID HYDROCARBONS

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In a dynamic system of 2 immiscible liquids, only that part of the electrode (St-3 steel) which is wetted by the electroylte is corroded. This affects the polarization resistance of the electrodes. In tests with identical electrode pairs with different areas of exposure (3-18 cm. (to the second power), formation water as the corrosive medium, of 100-500 mv., and const. stirring for 1 hr., the resistance (R) between the electrodes due to the medium increased from 2 to 9 ohms with decrease in the area exposed. The ratio of R to the total resistance showed that the corrosion process was controlled not by the elec. resistance of the medium but by the resistance of the electrodes to polarization. In 2-phase systems contg. petroleum in addn., even a small amt. (3 percent) of the latter led to a sharp drop in the polarization current (I) values; this drop was explained by the formation of a hydrophobic oily layer on the metal surface which inhibited the electrode processes. The addn. of 100 mg./l of oil or water-sol. inhibitors considerably reduced the wettability of the metal surface and this inhibited corrosion. The electrode surface area wetted by the electroylte (and the oil) was calcd. from the actual I values for the given exptl. conditions and compared with the graphical relation between the area exposed and the I values for the same metal in a 1-phase electrolyte medium. Thus, at 3 percent oil concn. in the medium with no inhibitors, 58 percent of the metal surface was covered by an oily film; this rose to about 85 percent at 10 percent oil concn.

U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	*А а*	A, a	Р р	*Р р*	R, r
Б б	*Б б*	B, b	С с	*С с*	S, s
В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
З з	*З з*	Z, z	Ч ч	*Ч ч*	Ch, ch
И и	*И и*	I, i	Ш ш	*Ш ш*	Sh, sh
Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

ELECTROCHEMICAL METHOD FOR EVALUATING THE WETTABILITY OF STEEL IN A TWO-PHASE DYNAMIC SYSTEM OF ELECTROLYTE AND LIQUID HYDROCARBONS

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During the study of the mechanism and dimensions of corrosion of steel in systems of two immiscible liquids (formation mineral water and liquid hydrocarbons – oil, gasoline) much attention is allotted to the question of selective wetting of the surface of the metal.

It is known that corrosion of steel in a system of the two immiscible liquids mentioned above is conditioned by the presence of an electrolyte. Oil, even with a high content of organic acids and sulphur, does not cause considerable corrosion at usual temperatures. However, the presence of a mixture of oil and salty water saturated by corrosion-aggressive gases, leads to a serious form of corrosion destruction-pitting of the steel surface, corrosion fatigue and, as a result mechanical failure.

All of this is in many respects determined by the unequal selective wetting of the steel surface in the shown systems. In those cases when the liquid hydrocarbons, due to the presence of dissolved surface active substances, wet the surface of the metal well, replacing the water solution, one should expect a smaller corrosion rate thanks to the protective action of the hydrocarbon film.

Under conditions of dynamic and mobile systems of two immiscible liquids the petroleum (hydrocarbon)film on the surface of steel is constantly washed off by the moving flow. Thus, the surface of the metal is subjected to variable wetting by water and oil.

Of great value for judgement about causes of corrosion of steel in a flow of oil and water is the correct determination of the phenomenon and degree of wetting of the steel surface by components of the examined mixture.

Among existing methods for evaluating wettability of a metallic surface by two immiscible liquids the most widespread is that proposed by Menk [1] a method for determining the contact angle formed on the interface of the metal and liquid 1-liquid 2.

The method for determining contact angles is widely used by corrosion researchers in their investigations. Thus, for example, Fayerman and others [2, 3] in works on the study of corrosion fatigue of rod steel in a system of formation water and oil, by way of contrasting wetting contact angles on the boundary of the rod steel, formation water and oil phases and fatigue limit of the same steel, have shown a dependence between these two characteristics.

Gonik [4] used values of wetting contact angles for a study of the influence of surface active substances, inhibitors of hydrosulphide corrosion, on selective wetting of iron in a two-phase system of electrolyte and hydrocarbon.

However, the method for determining wetting contact angle has a number of deficiencies:

1. Wetting contact angles are determined in static conditions. They can give a correct representation of moistening of the surface

by some liquid under rest conditions, but in those cases when wetting occurs under dynamic conditions and mixing of the medium, they do not completely reflect the influence of all factors on the studied phenomenon.

2. Wetting contact angles, due to reactions on the surfaces of steel and changes in composition of the liquid, do not remain time-independent for the same liquids and metal.

3. Contact angles can give an idea about selective wetting of a metal by one or another liquid of a two-phase liquid system, but here one cannot consider the influence of the quantity of and the relationship of the immiscible liquids in the studied system, which under dynamic conditions and washing of the protective layers is of some significance.

Therefore during the study of wetting contact angles the rod of the surface of the metal, covered by water and participating in corrosion remains unknown.

4. Knowledge of value of the wetting contact angle during the study of wettability of surface-active substances is insufficient. Under dynamic conditions there is a rapid saturation of the metal surface by the surface-active substances, neatly influencing the degree of wetting of metal by one or another liquid of a two-phase system. In static conditions, adsorption of the surface-active substance on the surface occurs very slowly due to the low concentration of it in a droplet and hampered diffusion of the flow.

Negeyev and others [5] offered a new method for evaluating wetting of a steel surface in a dynamic system of solutions of water and hydrocarbons by determining the corrosion rate of steel.

Corrosion of steel in the examined system is determined by its surface of contact with the electrolyte and the degree of corrosivity of this electrolyte. Therefore in systems of one and the same electrolyte and hydrocarbon (oil, gasoline) the corrosion rate of steel is determined by the degree of wetting of its surface in dynamic conditions during contact with a two-phase liquid.

There is no doubt that at the same wetting angle of steel by a drop of oil on the border with formation water, measured in a static state under conditions of motion of the mixture of oil and water, the dimensions of the water-moistened surface of steel will be increased with an increase in the content of water in the mixture.

However this will in large part depend on the presence of the surface-active substance in the oil (liquid hydrocarbons) and in the aqueous solution.

Therefore the creation of a method allowing us to characterize the ability of steel to be moistened by water and oil in dynamic conditions at various volumetric ratios of mixture components is very important for studying the corrosive action of petroleum and gas products in oil wells.

In this work we attempt to develop a new method for evaluating wetting of metal (steel) in dynamic systems of two immiscible liquids, allowing us to give a quantitative characteristic of the area of the steel surface in contact with liquid hydrocarbons and with water.

It is well-known that the rate of a corrosion process is determined by the strength of a corrosion current flowing between two electrodes $I=\frac{V_{к}-V_{а}}{r+P_{к}+P_{а}}$,
where I – corrosion current; more exact, current density, i.e., a value depending on dimensions of the surface of the metal; $V_{к}$ - V_{a} – potential difference between electrodes of the corrosion pair; r – resistance of the corroding medium; $P_{к}$ and P_{a} – polarization resistances of cathode and anode respectively.

Corrosion rate and strength of the corrosion current, its determining factor, when the process flows in a media with low ohmic resistance, is controlled by work of a micropair and depends on the process of cathode and anode polarization, and as a result on the potential difference of cathode and anode, i.e., $I=f(V_k-V_a)$.

Measurement of these indices is possible with the help of instruement IKP-1, developed in the corrosion laboratory of the Institute of Chemistry, AN of the Azerbaydzhan Soviet Socialist Republic jointly with NIPINeftekhimavtomat (in the town of Sumgait), allowing one to determine the current intensity in a pair of two steel electrodes during superposition on it of an assigned potential difference.

Since in a dynamic system consisting of two immiscible liquids, electrolyte and hydrocarbon, the determinants of corrosion and, consequently, polarization resistance and current intensity will be only the sections contacting the electrolyte, then quantitatively it is possible to determine the area of steel moistened by the hydrocarbon for different ratios of electrolyte and hydrocarbon in a state of motion (during stirring).

The first stage of our work was construction of a curve of the dependence of the strength of the polarizing current of the pair of steel electrodes for selected values of the potential difference at which these electrodes are polarized, on area of the corroding surfaces of the cathode and anode in formation water.

For this we prepared 6 pairs of electrodes with areas of working surfaces equal to 18, 15, 12, 9, 6 and 3 cm^2 respectively.

In all cases we used steel samples (St-3) with dimension 60 × 30 × 2 mm. Ends and all nonoperating parts of the surface were insulated by perchlorovinyl varnish.

The aggressive corrosion medium was formation water from drill-well 803 of the 8th trade NPU Ordzhonikidzeneft'.

Each pair of steel electrodes, preliminarily polished and degreased, was placed vertically in a plexiglas vessel parallel to each other at a distance of 1.5 cm. The vessel is then filled with 350 ml of formation water. Experiments were conducted with constant mixing of the formation water for 60 minutes. Every 5, 15, 30, 45 and 60 minutes after the beginning of the experiment we measured the force of the polarizing current of the pair necessary for polarizing the steel electrodes to the assigned potential difference.

Table 1 gives results of tests conducted during a time equal to 15 minutes from the beginning of the experiment, since up to this time the values of currents had become stabilized.

Table 1.

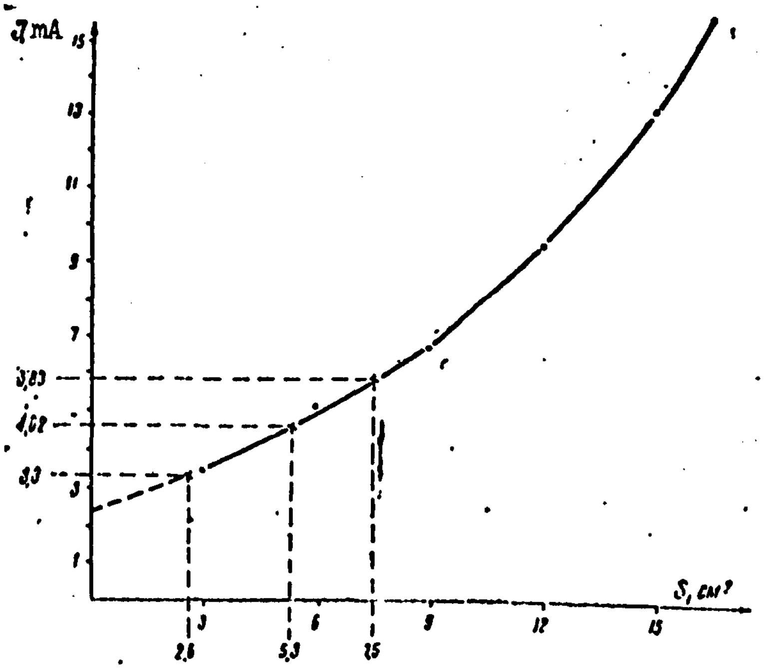
Surface of electrodes, cm^2	Strength of polarizing current mA			Resistance of medium, Ω	Part of ohmic resistance, %			Ohmic voltage drop, V	Strength of polarizing current at $V_K - V_a$ = 500 mV taking into account correction for ohmic voltage drop
	$V_K - V_a$ = 100 mV	$V_K - V_a$ = 250 mV	$V_K - V_a$ = 500 mV		$V_K - V_a$ = 100 mV	$V_K - V_a$ = 250 mV	$V_K - V_a$ = 500 mV		
18	5,0	8,0	13,0	2	1,0	6,4	7,2	35	20,07
15	3,2	5,0	12,0	2	7,4	4.0	4,8	24	12,92
12	1 8	4,1	9,0	3	5,1	5,0	5,0	27	9,32
9	1,5	3,3	6,3	4	6,0	5,3	5,0	25	6,02
6	1,4	2,8	5,2	6	8,4	6 7	6,0	31	5,18
3	0,6	1.4	3,2	9	5,4	5.0	5,7	29	3,46

Resistance of the corrosion medium between electrodes was measured by instrument IKP-1, having an independent circuit for determining the resistance between electrodes during transmission of a variable electrical current.

As represented in Table 1, the shares of ohmic resistance show that in this case the corrosion process is controlled not by resistance of the medium, but by polarization resistances of the cathode and anode processes (P_K and P_a).

However, since ohmic resistance of the medium (pure) is not equal to zero, but in every case has a defined value, then one can construct an exact curve of the dependence of current strength on the surface of the cathode and anode pair at an assigned potential difference only by taking into account the correction for ohmic voltage drop. Ohmic voltage drop $\Delta V_r = Ir$ is calculated from known values of current intensity and resistance of the medium.

By increasing the assigned potential difference (500 mV) by the value of ohmic voltage drop, we can find theoretically the corresponding strength of the polarizing current with the help of the interpolation formula of Lagrange.



Dependence of strength of polarizing current on surface of electrodes in formation water, during polarization of steel electrodes to a potential difference of 500 mV.

The figure graphically represents the dependence of the strength of the polarizing current necessary for polarization of steel electrodes to E = 500 mV on the dimensions of the surfaces of the anode and cathode of the corrosion element moistened by the electrolyte (formation water).

The second stage of the work was a study of wetting of steel in a two-phase system for different ratios of formation water and oil in terms of strength of the polarizing current at assigned potential differences.

Experiments were conducted by the method described above. In all systems consisting of a mixture of formation water and oil at different percentage relationships the area of the steel anode and cathode equaled 18 cm^2.

Data of Table 2 show that even a small amount of oil (3%) in the system leads to a sharp decrease in the strength of the polarizing current. A further percentage increase in the oil content leads to an even greater decrease in the strength of the polarizing current, and at an oil concentration of 70% the polarizing current becomes equal to zero. This should be explained by wetting of steel by oil in a system of formation water and oil with formation on the steel surface of hydrophobic petroleum layer preventing contact of steel with the formation water, braking the flow of depolarizers and thereby leading to a decrease in the polarizing current of the pair.

Regarding the share of ohmic control, for a high content of oil in the system it remains low thanks to the presence of a considerable amount of salts in the formation water.

The third stage of the investigation was a study of the action oil- and water-soluble corrosion inhibitors leading to an increase of wettability in oil thanks to formation on the steel surface of a hydrophobic protective layer containing liquid hydrocarbons.

Table 2.

Medium: oil-water		Inhibitor	Strength of polarizing current, mA			Resistance of medium, Ω	Part of ohmic resistance, %			Ohmic voltage drop, mV	Force of polarizing current taking into account correction for ΔV = Ir	Area, moistened		% area, moistened	
By oil, %	By water, %		$V_K - V_a = 100$ mV	$V_K - V_a = 250$ mV	$V_K - V_a = 500$ mV		$V_K - V_a = 100$ mV	$V_K - V_a = 250$ mV	$V_K - V_a = 500$ mV			By oil, cm^2	By water, cm^2	By oil	By water
3	97	No inhibitor	0.1	1,4	5,0	8,6	0,86	4,8	8,6	43	5,83	10,5	7,5	58	42
6	94		0,1	1,3	4,2	7,0	0,70	3,6	5,8	29	4,62	12,7	5,3	70	30
10	90	No inhibitor	0,2	0,8	3,0	8,0	1,60	2,5	4,8	24	3,30	15,4	2,6	85,5	14,5
3	97	NChK	0,15	0,40	1,60	40,0	6,0			64,0	2,09	17,47	0,53	93	3

Table 3.

Composition of corrosion medium, %		Corrosion of steel in different mixtures, $g/m^2 \cdot h$	
Oil	Water	Oil and water from oil well 587 NPU Ordzhonikidzeneft'	Oil and water from oil well 803 NPU Ordzhonikidzeneft'
--	100	0,0	2,11
3	97	0,0	0,20
6	94	0,0	0,31
10	90	0,0	0,20
20	80	0,0	0,13
30	70	0,0	0,15
50	50	0,0	0,14
70	30	0,0	0,15

Notes: 1. Oil taken from well 587 is active, oil from well 803 has low-activity.

2. Activity of oil is determined by content of naphthenic acids.

3. To well 587 for separting the emulsion of formating water and oil PAV-NChK.

Results of test in Tables 2 and 4 show that both water- and oil-soluble inhibitors considerably decrease wetting by water of the steel surface and braking of the corrosion process.

Conducted tests (whose results are given in Tables 3 and 4) on determination of the corrosion rate of steel versus a weight loss of oil and water for different ratios of them in the absence, and in the presence of corrosion inhibitors with constant agitation for 3 hours confirmed the electrochemical investigations.

Actually, as a rule, with an increase in the percentage of oil one can observe a regular deceleration of corrosion. Additions of inhibitors (in all cases in an amount of 100 mg/ℓ) to the same system sharply decrease the corrosion rate.

Using the curve of the dependence of polarizing current on steel surfaces of the anode and cathode pairs at an assigned potential

Table 4.

Composition of corrosion medium, %		Corrosion of steel in different mixtures with various inhibitors, g/m^2·h				
Oil	Water	Diaminedioleat	IKSG-1	Katapin A	I-1-B	NChK
—	100	2,63	2,60	0,18	0,18	0,42
3	97	0,06	0,10	0,21	0,05	0,21
6	94	0,01	0,07	0,04	0,02	0,16
10	90	0,07	0,07	0,01	0,06	0,06
20	80	0,01	0,01	0,02	0,04	0,04
30	70	0,01	0,04	0,01	0,03	0,05
50	50	0,01	0,01	0,01	0,01	0,06
70	30	0,00	0,00	0,01	0,01	0,06

Note: All tests with formation water and oil from well 803, NPU Ordzhopikidzeneft'.

difference (figure) and values of the polarizing current in systems with different contents of formation water and oil (from Table 2), we can determine what part of the surface is moistened by formation water and what part is wet by oil.

For example, let us determine the sections of the steel surface moistened by water and oil in a dynamic system containing 3% oil and 97% formation water.

Data of Table 2 give for this system a polarizing current of equal to 5.8 mA at a potential difference of 500 mV. At the same time the pair of steel electrodes in a medium of formation water alone at a potential difference of 500 mV are polarized by a current of 20 mA. This means, in a system of 3% oil and 97% formation water, participation in the process of depolarization is taken not by all the surface of the electrodes, but only that part which is wet by formation water. This part of the surface is found graphically by using the curve on Fig. 1.

Table 2 gives found values of a surface moistened by oil and water. It is possible to see that even for 3% oil in a 2-phase dynamic system best wettability of the steel surface by oil (10.5 cm^2, or 58% is observed. Further increase of the content of oil leads to an even greater increase of the surface covered by the petroleum film.

Conclusion

This article describes the development of a new method for evaluating wetting or a metal (St-3) in dynamic systems of two immiscible liquids on electrolyte and liquid hydrocarbons.

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