ХИМИЯЛЫҚ ТЕХНОЛОГИЯ

ХИМИЧЕСКАЯ ТЕХНОЛОГИЯ

DOI: 10.53360/2788-7995-2024-2(14)-49

IRSTI: 81.33.29

N.V. Akatyev*, M.K. Khapiyeva, R.Z. Kenzhegalieva, T.B. Seilova
M. Utemisov West Kazakhstan University,
090000, Republic of Kazakhstan, Uralsk, N. Nazarbayev Ave. 162
*e-mail: nikolay.akatyev@wku.edu.kz

BLACKCURRANT (*RIBES NIGRUM)* FROM WESTERN KAZAKHSTAN – A NOVEL NATURAL ECO-FREINDLY CORROSION INHIBITOR OF CARBON STEEL

Annotation: *In the current study, weight loss measurements and electrochemical methods were used to examine the inhibitory characteristics of the aqueous extract of Ribes nigrum leaves on the corrosion of carbon steel in hydrochloric acid medium. It has been determined that in 1.0 mol·dm*$^{-3}$ *HCl, the inhibition efficiency of the extract can reach up to 92,66%. Metal protection ability was found to increase with increasing inhibitor concentration. It was observed that high inhibition efficiency is a result of spontaneous physisorption of the inhibitor (*$\Delta G^0_{abs} > -20$ *kJ·mol*$^{-1}$*) on the carbon steel surface directly obeys the Langmuir absorption model. The polarization curves analysis revealed the mixed-type inhibition behavior of the studied extract with the highest inhibition efficiency achieved at inhibitor concentration of 2.0 g·dm*$^{-3}$*. The electrochemical and gravimetric data were found in great agreement. The assumption that the inhibitory effect of the extract is caused by the adsorption of phenolic compounds was made by the performing of UV-vis spectrophotometric analysis of the corrosive medium before and after the immersion of the carbon steel specimen. Aqueous extract of the R. nigrum leaves was proposed as a low-cost, environmentally friendly and effective corrosion inhibitor.*

Key words: *Ribes nigrum; plant extracts; leaves aqueous extract; inhibition efficiency; «green» inhibitors; metal protection.*

Introduction

The chemical or electrochemical process that occurs when metals or alloys come into the contact with a chemically aggressive environment is commonly referred as corrosion. The metallic material is frequently destroyed during the corrosion process and its properties are also rapidly deteriorate [1]. To prevent corrosion damage of metals various methods are used, including electroplating, alloying, cathodic and anodic protection, laser treatment and the use of inhibitors [2].

Inhibitors of corrosion can be classified as either organic or inorganic. However, the majority of them are not «green» or environmentally friendly [3]. On the other hand, it is commonly known that organic compounds bearing N, S, and O heteroatoms in spite of their strong inhibition efficiency are not only expensive but also harmful to humans and animals. Therefore, there is no need to overstate the significance of corrosion inhibitors that are readily available, low-cost, and eco-friendly [4].

Plants are considered as the most perspective source of «green» inhibitors [5]. Throughout history, people have used plants to meet their needs for clothing, food, shelter, fertilizer, and medicine [6]. Nonetheless, the first application of plant extracts in H_2SO_4 pickling baths occurred in the 1930s. This time frame may be seen as the start of their application as natural products for metal protection [7].

Plants are abundant sources of natural organic compounds, such as phenolics, flavonoids, alkaloids etc. These compounds have a high ability to sorb onto metallic surface and thus they can shield various metals and alloys from the damaging impacts of diverse corrosion media [8]. For this purpose, it is possible to successfully use both whole plants and parts of the plants [9]. Plant extracts are now considered as the most essential eco-friendly, affordable, and renewable sources for successful anti-corrosion applications [10].

The West Kazakhstan region (WKR) has more than 1500 plant species, which belong to more than 700 families. This biodiversity offers unique opportunities in the various «green» technology fields include development of antioxidants [11], protection of human skin against solar radiation [12] and prevention of metals against corrosion [13].

Blackcurrant (*Ribes nigrum*) is a small deciduous shrub 1 - 2 m tall belonging to *Grossulariaceae* family (Fig. 1). Being widely available for study and usage, it is among the most prevalent plants in the WKR.

Figure 1 – Blackcurrant (*Ríbes nígrum*), (*fam. Grossulariaceae*): whole plant (A) and leaves (B)

Among the 150 species of shrubs from the genus *Ribes R. nigrum* berries are differ with the wide range of bioactive components, phytonutrients, and antioxidants. These berries contain high levels of beneficial plant compounds like anthocyanins, along with vitamins A, C, and E, essential fatty acids, omega-6 fatty acids, and gamma-linolenic acid [14-16]. Delphinidin-3-rutinoside, cyanidin-3-glucoside, and delphinidin-3-rutinoside are the primary anthocyanins was also found in *R. nigrum* [17]. Ascorbic acid plays a key role as a phytocomponent in enhancing the potent antioxidant properties found in blackcurrant [18]. It was earlier been reported that vitamin C level of *R. nigrum* is up to 50 times higher than in apples and 3.4-7 times higher than in oranges [19]. The *R. nigrum* seeds may be used to extract oil, which is often used in cosmetics [20] because they are a great source of gamma-linolenic acid, or omega-6 fatty acids [21].

Blackcurrants' beneficial properties are able to reduce the risk of a number of serious diseases, including postmenopausal osteoporosis and glaucoma [22, 23]. In addition, compared to other fruits and berries, *R. nigrum* is low in calories and salt but contains significant amounts of Ca, K, Mg etc [24].

In this work we turn our attention to the ability of aqueous extracts of *R. nigrum* leaves to prevent corrosion on carbon steel. The choice of leaves is based on the fact that they typically contain higher concentrations of active phytochemicals such as polyphenols, flavonoids and alkaloids, which can act as effective corrosion inhibitors [25]. In addition, the extraction of active components from leaves is generally easier and more efficient [26], and harvesting the leaves is significantly less harmful to the plant than harvesting roots or stems [27], allowing continuous use of the plant without killing it, making the process more environmentally friendly. Inhibition efficiency, thermodynamics, kinetics, and absorption behavior of obtained inhibitor was the focus of our investigation. Gravimetric and electrochemical techniques were used for this purpose.

Materials and methods

Reagents and solvents. All of the reagents were used without additional purification and are of analytical grade. The extraction and preparation of the corrosion media were performed with double-distilled water (DDW) obtained from glass distillation apparatus.

Plant collection. The fresh plants were gathered away from roads and industrial structures in the suburbs of Uralsk, in their natural habitat. The World Flora Online database [28] and the herbarium of M. Utemisov West Kazakhstan University's Faculty of Natural Sciences both provided confirmation of the plant species. The plants were thoroughly cleaned with tap water and twice washed with DDW followed by the drying in a shaded area on air for two weeks. The samples were then ground into a fine powder, sieved through a 1.0 mm, and stored at 4°C.

Preparation of the extract. 10 g of ground-up, dried plant material was transferred into a 250 ml Erlenmeyer flask, and extracted 3 times in a water bath with 100 ml of DDW at 60°C for 8 hours.

The temperature was maintained using a TW-2.02 water thermostat with an accuracy of ±0.1°C. The extracts were then combined and evaporated. After being dried to constant weight at 50°C extracts were kept in dark, sealed vials at 4°C until further use for anti-corrosion tests.

Sample preparation. Carbon steel specimens with composition of (wt. %) 97,8 – Fe; 0,22 – C; 0,65 – Mn; 0,30 – Si; 0,04 – P; 0,05 – S; 0,30 – Cr; 0,30 – Ni; 0,30 – Cu; 0,01 – N; 0,08 and dimensions of 25,0 x 35,0 x 3,0 mm were obtained from industry and used for corrosion tests. Prior to the experiment specimens were sequentially polished with emery paper ranging in grit numbers from 250 to 1200. Then, after being washed in running water and DDW from oxides and dust, the abraded specimens were cleaned and degreased using ethanol and acetone. Prepared specimens were stored in a desiccator over silica gel until the following corrosion experiments.

Weight loss (gravimetric) method

The corrosion rate (CR), degree of surface coverage (θ), and inhibition efficiency (IE) were assessed through the weight loss experiments. Each specimen was submerged in an open-air beaker filled with 100 ml of room-temperature corrosion medium. Specimens were removed from the beaker after the immersion period and cleaned with soft brush under running water, DDW, and thereafter, in a solution containing 50% NaOH and 100 g of zinc dust [29] to eliminate any remaining corrosion product residues. Before reweighting, the specimens were again washed under running water, DDW, rinsed in ethanol, acetone, and dried. The Ohaus Adventurer Pro AV264 analytical balance, with an accuracy of ±0.1mg, was used for all weight measurements.

Equations 1-3 were used to calculate the corrosion rate (CR $g\cdot m^{-2}\cdot h^{-1}$), inhibition efficiency (IE%), and degree of surface coverage (θ) respectively:

$$CR(g\cdot m^{-2}\cdot h^{-1}) = \frac{\Delta m}{S\cdot \tau} \tag{1}$$

$$IE(\%) = \frac{CR_0 - CR_i}{CR_0}\cdot 100 \tag{2}$$

$$\theta = \frac{IE(\%)}{100} \tag{3}$$

where Δm – is the weight loss of the carbon steel specimen (g) after the immersion time (h), CR_0 – the corrosion rate of carbon steel without inhibitor, CR_i – the corrosion rate of carbon steel with the addition of the inhibitor.

Absorption and thermodynamics. The Langmuir adsorption isotherms were used to describe the adsorption mechanism of the inhibitor on the carbon steel surface [30]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{abs}} + C_{inh} \tag{4}$$

where C_{inh} is the concentration of the inhibitor, θ is the degree of surface coverage, and K_{abs} is the absorption-desorption process equilibrium constant. The intercepts of the isotherms provided the values of the absorption equilibrium constants (K_{abs}). Equation 5 represents the relationship between the absorption equilibrium constant and the Gibbs free energy:

$$\Delta G^0_{abs} = -RT\ln(55.5K_{abs}) \tag{5}$$

where ΔG^0_{abs} is the Gibbs free energy of absorption, R is the universal gas constant (8.314 $J\cdot K^{-1}\cdot mol^{-1}$), T is the system's thermodynamic temperature, and 55.5 is the molar concentration of water $mol\cdot dm^{-3}$.

Electrochemical measurement. The same pretreatment was applied to the steel specimens for the electrochemical experiment as for the weight loss test. The Autolab PGSTAT 101 Metrohm potentiostat/galvanostat, equipped with the NOVA 2.1.6 software, was used for the electrochemical test. Three-electrode setup was used to electrochemical measurements: reference electrode (Ag/AgCl filled with 3.0 $mol\cdot dm^{-3}$ KCl), counter electrode (platinum), and working electrode (steel specimen). A beaker containing 100 ml of 1.0 $mol\cdot dm^{-3}$ HCl, both with and without inhibitor, served as the electrochemical cell. The working electrode, with an exposed area 0,82 cm^2 was stabilized during open circuit potential (OCP) testing. The linear sweep voltammetry (LSV) staircase and corrosion rate analysis were used to perform linear polarization measurements right after the OCP. Potentiodynamic scanning was performed with a step voltage of 0.01V and a scan rate of 0.01 V/s between -0.50 and +0.50 V. From the Tafel polarization curves, the corrosion potential (E_{corr}) and corrosion current density (j_{corr}) were established.

Equation 6 was used to obtain the inhibition efficiency (IE_i%) through the corrosion current [31]:

$$IE_i(\%) = \frac{i_{inh} - i_{corr}}{i_{inh}} \cdot 100 \qquad (6)$$

where i_{inh} and i_{corr} are the corrosion current densities determined by extrapolating the Tafel slopes with and without inhibitors respectively, $A \cdot cm^{-2}$.

Using the equation (7), the inhibition efficiency through the polarization resistance (IE_R%) was determined [32]:

$$IE_R(\%) = \frac{R_p^{inh} - R_p^0}{R_p^{inh}} \cdot 100 \qquad (7)$$

where R_p^{inh} and R_p^0 represent the charge transfer resistance with and without inhibitor respectively, Ω.

The experimental results are given as the average of three independent determinations (n = 3) ± standard deviation (SD) with α = 0.95.

Results and discussion

Weight loss assay.

The inhibitory effect of the aqueous extract of *R. nigrum* leaves was examined for the typical corrosion media including the model medium recommended by the National Association of Corrosion Engineers (NACE) of USA [33]. Screening results are shown in Table 1.

Table 1 – Inhibition efficiency (IE%) of the aqueous extract of *R. nigrum* leaves against corrosion of carbon steel in typical corrosion media at the inhibitor concentration of 1.0 $g \cdot dm^{-3}$ at room temperature

Entry	**Corrosion media**	**Concentration**	**CR, $g \cdot m^{-2} \cdot h^{-1}$**		**θ**	**IE, %**
			Blank	**With inhibitor**		
1	CH_3COOH	1,0 $mol \cdot dm^{-3}$	2,62	1,21	0,5393	53,93 ± 4,93
2		0,5 $mol \cdot dm^{-3}$	1,44	0,87	0,3939	39,39 ± 2,58
3		0,1 $mol \cdot dm^{-3}$	1,65	1,07	0,3530	35,30 ± 2,88
4	H_2SO_4	1,0 $mol \cdot dm^{-3}$	24,23	5,39	0,7773	77,73 ± 4,19
5		0,5 $mol \cdot dm^{-3}$	5,11	2,45	0,5197	51,97 ± 4,01
6		0,1 $mol \cdot dm^{-3}$	9,42	5,06	0,4629	46,29 ± 2,05
7	HNO_3	1,0 $mol \cdot dm^{-3}$	3,68	2,26	0,3857	38,57 ± 3,03
8		0,5 $mol \cdot dm^{-3}$	36,66	23,14	0,3687	36,87 ± 2,51
9		0,1 $mol \cdot dm^{-3}$	15,86	11,12	0,2990	29,90 ± 2,12
10	H_3PO_4	1,0 $mol \cdot dm^{-3}$	3,50	1,15	0,6704	67,04 ± 3,26
11		0,5 $mol \cdot dm^{-3}$	6,81	2,31	0,6605	66,05 ± 4,11
12		0,1 $mol \cdot dm^{-3}$	4,05	2,38	0,4113	41,13 ± 3,56
13	HCl	1,0 $mol \cdot dm^{-3}$	5,72	0,68	0,9048	88,06 ± 4,85
14		0,5 $mol \cdot dm^{-3}$	3,87	0,56	0,8543	85,43 ± 4,73
15		0,1 $mol \cdot dm^{-3}$	4,16	0,65	0,8428	84,28 ± 5,06
16	NACE medium	NaCl 5,0 $g \cdot dm^{-3}$ + CH_3COOH 0,25 $g \cdot dm^{-3}$	0,39	0,35	0,5229	52,29 ± 3,48
17	NaCl	3.0%	0,46	0,22	0,1070	10,70 ± 2,22
18	DDW	-	0,50	0,30	0,3980	39,80 ± 2,96

The data from Table 1 show that aqueous extract of *R. nigrum* leaves exhibits inhibitory properties in all corrosion media tested, with an IE range of 10.70 (3,0% NaCl, Entry 17) to 88,06% (1,0 $mol \cdot dm^{-3}$ HCl, Entry 13). The extract also demonstrated high IE in HCl solutions at 0,5 $mol \cdot dm^{-3}$ (85,43%) and 0,1 $mol \cdot dm^{-3}$ (84,28%) (Entries 14 and 15 respectively). The lowest IE values for tested extract were observed in HNO_3 solutions (Entries 7-9) and for the saline and neutral environment (Entries 17 and 18 respectively).

Finding the kinetic and thermodynamic parameters of inhibition in the specified medium was the next step in our investigation because the aqueous extract of *R. nigrum* leaves had the highest IE in a 1.0 mol·dm^{-3} HCl solution. The tests were carried out at room temperature over an exposure time of 2-24 hours and inhibitor concentrations of 0,1-2,0 g·dm^{-3}.

Figure 2 shows the effect of exposure time and inhibitor concentration on the IE of aqueous extract of *R. nigrum* leaves in 1,0 mol·dm^{-3} HCl solutions.

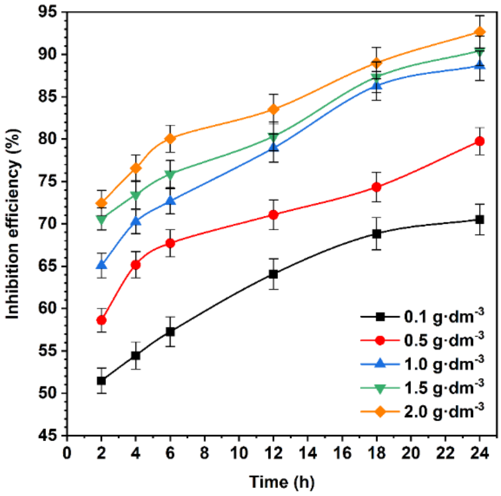

Figure 2 – Relationship between the IE (%) of aqueous extract of *R. nigrum* leaves on carbon steel in 1.0 mol·dm^{-3} HCl solution from the different inhibitor concentration and immersion time at room temperature

As can be seen, the IE of the aqueous extract of *R. nigrum* leaves in 1,0 mol·dm^{-3} HCl solution at different inhibitor concentrations increases over time. The presence of an induction period demonstrates that at least 6 hours are needed in a given corrosive medium for the inhibitor to form a maximally effective protective layer. An increase in inhibitor concentration leads to an increase in protective properties. The most effective corrosion inhibition was observed at the inhibitor concentration of 2,0 g·dm^{-3}. Therefore, higher concentrations of the inhibitor should be used for the most optimal inhibition effectiveness. These results suggest that the aqueous extract of *R. nigrum* leaves has good prospects for use in preventing metal corrosion in highly acidic environments.

The inhibitor can adsorb on the metal surface by chemical, physical or combined way. Finding the values of the Gibbs free energy (ΔG^0_{abs}) is necessary to characterize the absorption mechanism. The electrostatic interaction (physisorption) between charged inhibitor molecules and metal surfaces is represented by ΔG^0_{abs} values up to -20 kJ·mol^{-1}. A value less than or equal to about -40 kJ·mol^{-1}, commonly considered the threshold between chemisorption and physisorption, indicates the chemical character of the sorption [34].

Langmuir absorption isotherms of the aqueous extract of *R. nigrum* leaves in 1,0 mol·dm^{-3} HCl solution at experimental temperatures was shown in Fig. 3.

Fig. 3 illustrates that the plots of C/θ against inhibitor concentration exhibit as straight lines at both temperatures. The linear approximation with values of the correlation coefficient greater than 0.99 clearly shows that the Langmuir model is suitable for describing of the adsorption of R. nigrum leaves aqueous extract on carbon steel surface. This confirms that the inhibition is due to the adsorption of the active organic compounds from plant extract on the carbon steel surface. Additionally, this demonstrates that due to the absorption from the solution, there is an exchange between the water molecules and the inhibitor molecules on the metal surface [35].

In accordance with the slopes and intercepts of the linear plots, the Gibbs free energy (ΔG^0_{ads}) and K_{abs} values for the aqueous extract of *R. nigrum* leaves were calculated. Obtained values are presented in Table 2.

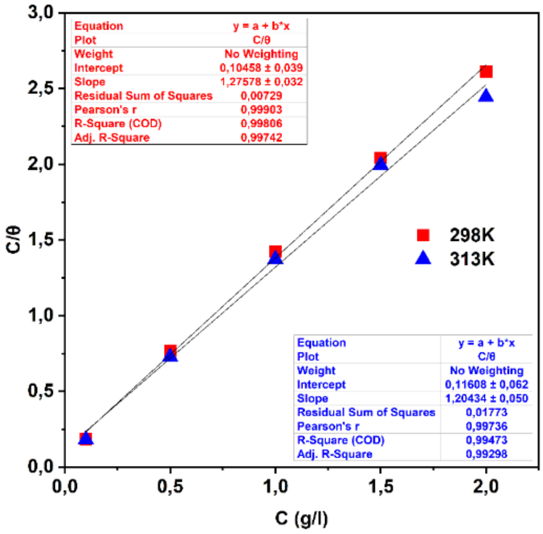

Figure 3 – Langmuir isotherms for adsorption of *R. nigrum* leaves aqueous extract in 1.0 mol·dm^{-3} HCl solution for 4 hours immersion period at 298 and 313K

Table 2 – Thermodynamic parameters of adsorption of aqueous extract of *R. nigrum* leaves on carbon steel surface in 1.0 mol·dm^{-3} HCl solution

Temperature, K	**Slope**	**Intercept**	**R^2**	**K$_{abs}$**	**ΔG$^0_{abs}$, kJ·mol^{-1}**
298	1,27578	0,10458	0,99806	9,5621	-15,55
313	1,20434	0,11608	0,99473	8,6147	-16,06

Negative values of ΔG$^0_{ads}$ indicate that the absorption of aqueous extract of *R. nigrum* leaves onto the carbon steel surface occurs spontaneously [36]. The value of ΔG$^0_{ads}$ > -20 kJ·mol^{-1} clearly shows that the adsorption is physical (physisorption) and occurs as a result of an electrostatic interaction between charged inhibitor molecules and the steel surface [37]. Increasing the temperature and concentration of the inhibitor accelerates the adsorption-desorption processes and promotes the formation of a stable protective barrier on the metal surface [38].

Metal surface analysis. Micrographs of the steel surface were also used to investigate the protective effect of the *R. nigrum* leaves aqueous extract. The polished specimen and the test specimens were observed under an optical microscope. Fig. 4 displays micrographs of carbon steel surfaces taken both before and after they were submerged in 1.0 mol·dm^{-3} HCl solution with and without the inhibitor.

Figure 4 – Micrographs (^{x}50) of the carbon steel surface after 24 hours of immersion in 1.0 mol·dm^{-3} HCl solution: before immersion (a), in the absence (b) and in the presence (c) of aqueous extract of *R. nigrum* leaves at a concentration of 1,0 g·dm^{-3}

The steel plate's surface had a noticeable metallic luster and was uniform before it was exposed to a corrosive environment (Fig.4a). The surface structure changes significantly when exposed to an acid solution without the presence of an inhibitor. A dark, porous, loose layer with obvious pits and cracks forms (Fig.4b). Conversely, in the presence of an inhibitor, the protective coating develops and the metallic shine disappears, but the metal's structure remains intact (Fig.4c).

UV–visible spectroscopy analysis. In addition, to confirm that the protective effect is due precisely to the absorption of the aqueous extract of *R. nigrum* leaves on the metal surface, UV-spectrometric analysis of the corrosive environment was carried out. UV-vis spectra were recorded before and after immersion a carbon steel specimen for 24 h at presents of the inhibitor. Results are given in Fig. 5.

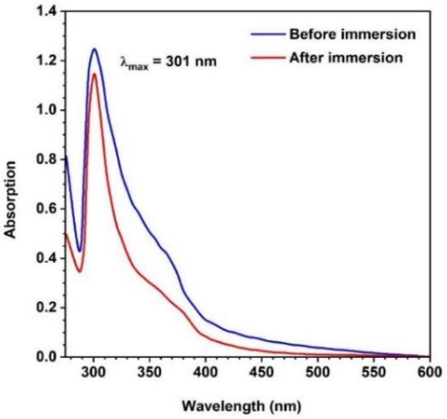

Figure 5 – UV–vis spectra of 1.0 mol·dm^{-3} HCl solution containing 0.1 g·dm^{-3} of *R. nigrum* leaves aqueous extract before (blue line) and after 24 h immersion (red line) of carbon steel specimen

The UV-vis spectrum of the solution of *R. nigrum* leaves aqueous extract in 1.0 mol·dm^{-3} HCl before and after immersion shows the maximum absorbance at 301 nm that is typical for phenolic phytocomponents. Nevertheless, after immersion of the steel specimen the intensity of the absorption decreased. However, there are no any shifts of maximum absorbance in the UV-vis spectra were observed. Since absorption in given wavelength range is due only to the presence of the extract, the decrease in absorption intensity is caused by a decrease in its concentration, which in turn can be explained by sorption of *R. nigrum* leaves aqueous extract components from the solution on the metal surface. It is well known that absorption at 340-360 nm is typical for flavonols [39]. The most intensive hypochromic effect localized in this region of the UV-vis-spectra allows to propose that the inhibitory activity of *R. nigrum* leaves aqueous extract is determined by absorption of the phenolic compounds, predominantly flavonols.

Electrochemical experiment. The OCP evaluation for the carbon steel was carried out both with and without the *R. nigrum* leaves aqueous extract, during a 60-second immersion in 1.0 mol·dm^{-3} HCl solution. Fig. 6A indicates that the OCP achieve a condition of equilibrium before the 60 s was over. Shift of OCP value at presents of different concentrations of the aqueous extract of *R. nigrum* leaves could be a sign that inhibitor molecules had been adsorbed to the carbon steel surface. Nevertheless, a positive shift in OCP reveals that *R. nigrum* leaves aqueous extract mostly inhibits the anodic process [40].

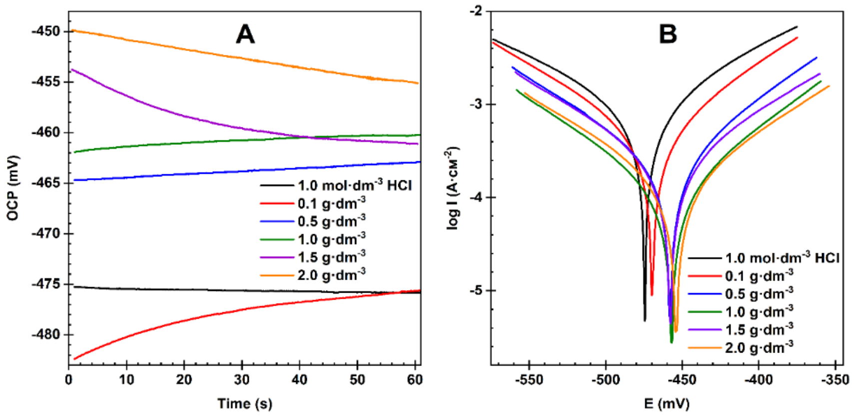

Figure 6 – OCP *vs* time diagram (A) and Tafel polarization curves (B) for carbon steel in 1.0 mol·dm^{-3} HCl solution with and without of the aqueous extract of *R. nigrum* leaves at room temperature

Figure 6B shows the potentiodynamic polarization curves for carbon steel in 1,0 mol·dm^{-3} HCl solutions with different concentrations and without aqueous extract of *R. nigrum* leaves*.* The electrochemical data of the corrosion process derived from polarization curves using corrosion rate analysis are shown in Table 3.

Table 3 – The electrochemical corrosion parameters of carbon steel in 1.0 mol·dm^{-3} HCl in the absence and presence of different concentrations of aqueous extract of *R. nigrum* leaves at room temperature

Concentration, g·dm^{-3}	**-E$_{corr}$, mV**	**J$_{corr}$, A·cm^{-2}**	**IE$_i$, %**	**|b$_a$|, mV·dec^{-1}**	**|b$_c$|, mV·dec^{-1}**	**R$_p$, Ω**	**IE$_R$, %**
0,0	474,52	$1{,}04 \cdot 10^{-3}$	-	108,78	127,25	29,84	-
0,1	469,61	$5{,}33 \cdot 10^{-4}$	72,39	86,20	101,47	46,31	79,89
0,5	457,95	$2{,}72 \cdot 10^{-4}$	73,88	81,98	99,12	87,16	82,99
1,0	457,84	$2{,}35 \cdot 10^{-4}$	76,39	87,04	95,84	102,60	83,37
1,5	454,04	$1{,}57 \cdot 10^{-4}$	78,55	91,85	96,06	158,29	83,70
2,0	457,11	$1{,}31 \cdot 10^{-4}$	80,65	79,41	90,71	170,04	86,18

The presence of aqueous extract of *R. nigrum* leaves results in a significant decrease in the corrosion rate of carbon steel in 1.0 mol·dm^{-3} HCl. The corrosion current density (J_{corr}) values are significantly lower in the presence of the inhibitor, indicating that aqueous extract of *R. nigrum* leaves effectively protect the metal surface from corrosion [41]. The values of polarization resistance (R_p) increase with the addition of inhibitor, which confirms the formation of a protective layer on the steel surface consequently preventing corrosion damage [42]. As can be seen, both the cathodic and anodic parts of the polarization curves noticeably shift in the presence of an inhibitor. Thus, the aqueous extract of *R. nigrum* leaves acts as a mixed type inhibitor, slowing down both the cathodic and anodic reactions [43]. Nevertheless, the cathodic site shifts $|b_c|$ are larger than the anodic $|b_a|$. This implies that the cathodic polarization is more strongly affected by the inhibitor than the anodic one.

In the presence of the aqueous extract of *R. nigrum* leaves, the inhibitory effect values determined using equations 6 and 7 from corrosion current and polarization resistance, respectively, increase significantly with increasing in inhibitor concentration. This also indicates that the studied inhibitor has a high potential to prevent the corrosion of carbon steel in 1.0 mol·dm^{-3} HCl solution. The electrochemical and gravimetric data were found to be in excellent agreement.

Analysis of literary sources revealed that plants of the genus *Ribes*, with the exception of *Ribes rubrum*, have not been studied as “green” corrosion inhibitors. An aqueous extract of *Ribes rubrum* berries at a concentration of 800 ppm in a 1 M HCl solution was shown to provide 64% protection of mild steel [44], which is slightly lower than the results obtained for *Ribes nigrum* leaves in our investigation. Thus, our study can be considered as the first example of the effective use of aqueous extracts of *Ribes nigrum* leaves as an environmentally friendly corrosion inhibitor.

Conclusion

Despite enormous scientific and technological progress, including the field of material protection, modern industry needs to develop environmentally friendly and effective approaches to protecting metals from corrosion destruction. The creation of inhibitors based on natural products plays a key role in this scientific direction.

In this work, the corrosion protection potential of the aqueous extract of *R. nigrum* leaves was investigated gravimetrically and electrochemically. The aqueous extract of *R. nigrum* leaves in 1.0 mol·dm^{-3} HCl solution was found to have excellent protective effect on carbon steel, providing an inhibitory effect of up to 92.66%. According to the Langmuir model a stable protective monolayer is formed as a result of the inhibitor's adsorption on the steel surface. Negative values of Gibbs free energy revealed the spontaneous physisorption of the inhibitor. The inhibitory effect of the extract is probably due to the adsorption of phenolic compounds. Investigation results suggest that the aqueous extract of *R. nigrum* leaves is one of the most promising candidates for the development of "green" corrosion inhibitors for multiple industrial and technical applications.

References

1. Ukoba O.K. Corrosion behaviour of ductile iron in different environment / O.K. Ukoba, P.K. Oke, M.C. Ibegbulam // Journal of Science and Tech. – 2012. – T.2. – P. 618-612.
2. Corrosion inhibitors. A review / A. Kadhim et al // International Journal of Corrosion and Scale Inhibition. – 2021. – T.10, № 1. – P. 54-67.
3. Epoxy pre-polymers as new and effective materials for corrosion inhibition of carbon steel in acidic medium: Computational and experimental studies / O. Dagdag et al // Scientific reports. – 2019. – T.9, № 1. – 11715 P.
4. Dariva C.G. Corrosion inhibitors–principles, mechanisms and applications / C.G. Dariva, A.F. Galio // Developments in corrosion protection. – 2014. – T.16. – P. 365-378.
5. Verma C. Phytochemistry in Corrosion Science: Plant Extracts and Phytochemicals as Corrosion Inhibitors / C. Verma, A. Kumar, A. Thakur // CRC Press, 2024.
6. Jamshidi-Kia F. Medicinal plants: Past history and future perspective / F. Jamshidi-Kia, Z. Lorigooini, H. Amini-Khoei //J herbmed pharmacol. – 2018. – T.7, № 1. – P. 1-7.
7. Sanyal B. Organic compounds as corrosion inhibitors in different environments – a review / B. Sanyal // Progress in Organic Coatings. – 1981. – T.9, № 2. – P. 165-236.
8. Dehghani A. Green Eucalyptus leaf extract: A potent source of bio-active corrosion inhibitors for mild steel / A. Dehghani, G. Bahlakeh, B. Ramezanzadeh // Bioelectrochemistry. – 2019. – T.130. – 107339.
9. A comparative study of the accumulation of trace elements in Brassicaceae plant species with phytoremediation potential / Drozdova I. et al // Applied Geochemistry. – 2019. – T.108. – 104377.
10. Hossain N. An overview of green corrosion inhibitors for sustainable and environment friendly industrial development / N. Hossain, M. Asaduzzaman Chowdhury, M. Kchaou // Journal of Adhesion Science and Technology. – 2021. – T.35, № 7. – P. 673-690.
11. Investigation of antioxidant properties of aqueous extracts of Chenopódium album linn / D.D. Suyungaliyeva et al // Vestnik WKU. – 2023. – № 1. – P. 187-193.
12. Akatyev N.V. Investigation of sun protection capacity of Plantago major roots, leaves and seeds extracts against UVB-rays by UV-Vis-spectroscop / N.V. Akatyev, A.K. Jamanbaliyeva, T.B. Seilova // International scientific and practical conference «Trends in the development of natural and technical sciences in the modern world». – Petropavlovsk, 2022. – P.194-198.
13. Seilova T.B. Narrow-Leaved Pepperwort (*Lepidium Ruderale L.*) From Western Kazakhstan - A New «Green» Corrosion Inhibitor For Carbon Steel / T.B. Seilova, N.V. Akatyev // Vestnik WKU. – 2023. – № 2. – P. 172-182.
14. The health benefits of blackcurrants / A. Gopalan et al. // Food & function. – 2012. – T. 3, № 8. – P. 795-809.
15. Quantitative trait loci mapping of polyphenol metabolites in blackcurrant (Ribes nigrum L.) / I.N. Abreu et al // Metabolomics. – 2020. – T.16. – P. 1-23.
16. Wijekoon C. Bioactive Phenolic and Fatty Acid Composition of Canadian Wild Gooseberry and Blackcurrant / C. Wijekoon, S. Sura // SLIIT Journal of Humanities and Sciences. – 2021. – T. 2, № 1.
17. Bordonaba G.J. Maximising blackcurrant anthocyanins: temporal changes during ripening and storage in different genotypes / G.J. Bordonaba, G.A. Chope, L.A. Terry // Journal of Berry Research. – 2010. – T. 1, № 2. – P. 73-80.
18. Oczkowski M. Health-promoting effects of bioactive compounds in blackcurrant (Ribes nigrum L.) Berries / M. Oczkowski // Roczniki Państwowego Zakładu Higieny. – 2021. – T. 72, № 3. – P. 229-238.
19. Dale A. Potential for Ribes cultivation in North America / A. Dale // HortTechnology. – 2000. – T. 10, № 3. – P. 548-554.
20. Flavonoid intake and coronary mortality in Finland: a cohort study / P. Knekt et al // BMJ. – 1996. – T. 312, № 7029. – P. 478-481.
21. Bakowska-Barczak A.M. Characterization of Canadian black currant (Ribes nigrum L.) seed oils and residues / A.M. Bakowska-Barczak, A. Schieber, P. Kolodziejczyk // Journal of agricultural and food chemistry. – 2009. – T. 57, № 24. – P. 11528-11536.
22. Blackcurrants reduce the risk of postmenopausal osteoporosis: a pilot double-blind, randomized, placebo-controlled clinical trial / B.M. Nosal et al // Nutrients. – 2022. – T. 14, № 23. – P. 4971.

23. Yoshida K. Black currant anthocyanins normalized abnormal levels of serum concentrations of endothelin-1 in patients with glaucoma / K. Yoshida, I. Ohguro, H. Ohguro // Journal of ocular pharmacology and therapeutics. – 2013. – T. 29, № 5. – P. 480-487.
24. Staszowska-Karkut M. Phenolic composition, mineral content, and beneficial bioactivities of leaf extracts from Black Currant (Ribes nigrum L.), raspberry (Rubus idaeus), and aronia (Aronia melanocarpa) / M. Staszowska-Karkut, M. Materska // Nutrients. – 2020. – T. 12, № 2. – 463.
25. Green corrosion inhibitors based on plant extracts for metals and alloys in corrosive environment: a technological and scientific prospection / W.R. de Souza Morais et al // Applied Sciences. – 2023. – T. 13, № 13. – P. 7482.
26. Singh A. Corrosion inhibition of carbon steel in HCl solution by some plant extracts / A. Singh, E.E. Ebenso, M.A. Quraishi // International Journal of corrosion. – 2012. – № 1. – P. 897430.
27. Corrosion inhibition mechanism and extraction technology of plant corrosion inhibitors: a review / X. Wang et al // Journal of Adhesion Science and Technology. – 2023. – T. 37, № 21. – P. 2919-2943.
28. https://www.worldfloraonline.org/taxon/wfo-0000405161
29. ISO 8407-2021. Corrosion of metals and alloys - Removal of corrosion products from corrosion test specimens. – Geneva, Switzerland, 2021.
30. Nickel and zinc effects, accumulation and distribution in ruderal plants Lepidium ruderale and Capsella bursa-pastoris / A.D. Kozhevnikova et al // Acta physiologiae plantarum. – 2014. – T. 36. – P. 3291-3305.
31. Corrosion inhibition effect of magnolia grandiflora leaves extract on mild steel in acid solution / B. Li et al // International Journal of Electrochemical Science. – 2023. – T. 18, № 4. – 100082.
32. Adsorption isotherm, kinetic and mechanism studies of some substituted phenols on activated carbon fibers / Q.S. Liu et al // Chemical engineering journal. – 2010. – T. 157, № 2-3. – P. 348-356.
33. Mahgoub F.M. Corrosion inhibition of mild steel in acidic solution by leaves and stem extract of Acacia nilotica / F.M. Mahgoub, A.M. Hefnawy, E.H. Abd Alrazzaq // Desalin. Water Treat. – 2019. – T. 169. – P. 49-58.
34. Miralrio A. Plant extracts as green corrosion inhibitors for different metal surfaces and corrosive media: a review / A. Miralrio, A. Espinoza Vázquez // Processes. – 2020. – T. 8, № 8. – P. 942.
35. Polyphenolic Compouds of Plant of Lepidium Ruderale Linn. and Their Biololical Activity / S. Nailya et al // Journal of Biochemical Technology. – 2018. – T. 9, № 4. – P. 77.
36. Adsorption and thermodynamics study of the inhibition of corrosion of mild steel in H_2SO_4 medium using Vernonia amygdalina / J.T. Nwabanne et al // Journal of Minerals and Materials Characterization and engineering. – 2012. – T. 11, № 09. – P. 885 - 890.
37. Corrosion inhibition of mild steel in 1 M HCl solution by henna extract: A comparative study of the inhibition by henna and its constituents (Lawsone, Gallic acid, α-d-Glucose and Tannic acid) / A. Ostovari et al // Corrosion Science. – 2009. – T. 51, № 9. – P. 1935-1949.
38. Corrosion inhibition of carbon steel in 1 M hydrochloric acid solution by aqueous extract of Thevetia peruviana / A.S. Fouda et al // Journal of Bio-and Tribo-Corrosion. – 2016. – T. 2. – P. 1-13.
39. Characterization of antioxidants from Detarium microcarpum Guill. et Perr. leaves using HPLC-DAD coupled with pre-column DPPH assay / N.R. Meda et al // European Food Research and Technology. – 2017. – T. 243. – P. 1659-1666.
40. Studying the temperature influence on carbon steel in sour petroleum media using facilely-designed Schiff base polymers as corrosion inhibitors / O.E. El-Azabawy et al // Journal of Molecular Structure. – 2023. – T. 1275. – P. 134518.
41. Raja P.B. Natural products as corrosion inhibitor for metals in corrosive media – a review / P.B. Raja, M.G. Sethuraman // Materials letters. – 2008. – T. 62, № 1. – P. 113-116.
42. Adsorption and corrosion inhibitive properties of 2-amino-5-mercapto-1, 3, 4-thiadiazole on mild steel in hydrochloric acid media / R. Solmaz et al // Colloids and Surfaces A: Physicochemical and Engineering Aspects. – 2008. – T. 312, № 1. – P. 7-17.
43. Peculiarities of protective efficiency of nitrogen containing inhibitors of steel corrosion / L.E. Tsygankova et al. // International Journal of Corrosion and Scale Inhibition. – 2013. – T. 2, № 4. – P. 304-310.

44. Pourmohseni M. Preparation of corrosion inhibitor from natural plant for mild stil immersed in an acidic environmental: experimental and theoretical study / M. Pourmohseni, A Rashidi, M. Karimkhani // Scientific Reports. – 2024. – T. 14. – № 1. – P. 7937.

Н.В. Акатьев*, М.Қ. Хапиева, Р.Ж. Кенжегалиева, Т.Б. Сейлова
Западно-Казахстанский университет им. М. Утемисова,
090000, Республика Казахстан, Уральск, проспект Н. Назарбаева, 162
*e-mail: nikolay.akatyev@wku.edu.kz

ЧЕРНАЯ СМОРОДИНА (RIBES NIGRUM) ИЗ ЗАПАДНОГО КАЗАХСТАНА – НОВЫЙ ПРИРОДНЫЙ ЭКОЛОГИЧЕСКИ ЧИСТЫЙ ИНГИБИТОР КОРРОЗИИ УГЛЕРОДИСТОЙ СТАЛИ

В настоящем исследовании метод потери массы и электрохимические методы были использованы для изучения ингибирующих свойств водного экстракта листьев Ribes nigrum относительно коррозии углеродистой стали в солянокислой среде. Установлено, что в 1,0 моль·дм$^{-3}$ HCl эффективность ингибирования экстрактом может достигать 92,66%. Показано, что защитная способность ингибитора возрастает с увеличением его концентрации. Обнаружено, что высокая эффективность ингибирования является результатом самопроизвольной физиосорбции ингибитора (ΔG^0_{abs} > -20 кДж·моль$^{-1}$) на поверхности углеродистой стали, которая подчиняптся модели Ленгмюра. Анализ поляризационных кривых выявил смешанный тип ингибирующего действия исследуемого экстракта, при этом наибольшая эффективность ингибирования достигается при концентрации ингибитора 2,0 г·дм$^{-3}$. Электрохимические и гравиметрические данные оказались в хорошем согласии. На основании УФ-спектрофотометрического анализа коррозионной среды до и после погружения образца углеродистой стали, сделано предположение о том, что ингибирующее действие экстракта обусловлено адсорбцией фенольных соединений. Водный экстракт листьев R. nigrum был предложен в качестве недорогого, экологически чистого и эффективного ингибитора коррозии.

Ключевые слова: *Ribes nigrum; растительные экстракты; водный экстракт листьев; эффективность ингибиторов; «зеленые» ингибиторы; защита металла.*

Н.В. Акатьев*, М.Қ. Хапиева, Р.Ж. Кенжегалиева, Т.Б. Сейлова
М. Өтемісов атындағы Батыс Қазақстан университеті,
090000, Қазақстан Республикасы, Орал қ., Н. Назарбаев даңғылы, 162
*e-mail: nikolay.akatyev@wku.edu.kz

БАТЫС ҚАЗАҚСТАННЫҢ ҚАРА ҚАРАҚАТЫ (RIBES NIGRUM) - КӨМІРТАНДЫ БОЛАТТЫҢ ЖАҢА ТАБИҒИ, ЭКОЛОГИЯЛЫҚ ТАЗА КОРРОЗИЯ ИНГИБИТОРЫ

Бұл зерттеу жұмысында тұз қышқылы ортасындағы көміртекті болатта Ribes nigrum жапырақтарының сулы сығындысының коррозияға қарсы қасиеттерін зерттеу үшін масса жоғалту және электрохимиялық әдістер қолданылды. 1,0 моль·дм$^{-3}$ HCl-де сығындының тежеу тиімділігі 92,66%-ға жетуі мүмкін екені анықталды. Сондай-ақ, ингибитор концентрациясы жоғарылаған сайын қорғаныс қабілеті жоғарылайтыны анықталды. Ингибитордың жоғары тиімділігі көміртекті болат бетінде өздігінен физиосорбциялануының (ΔG^0_{abs} > -20 кДж·моль$^{-1}$) нәтижесі болып табылатындығы және Лангмюр моделіне тікелей бағынатындығы байқалды. Поляризация қисықтарын талдау барысында зерттелген сығындының ингибиторлық әсерінің аралас түрге жататындығы анықтады. Ең үлкен тежеу тиімділігі 2,0 г·дм$^{-3}$ ингибитор концентрациясында қол жеткізілді. Электрохимиялық және гравиметриялық деректер сәйкес келді. Көміртекті болат үлгісін батыру алдында және одан кейінгі коррозиялық ортаның ультракүлгін спектрофотометриялық талдауына сүйене отырып, сығындының ингибиторлық әсері фенолды қосылыстардың адсорбциялануымен байланысты деп ұйғарылды. R. nigrum жапырақтарының сулы сығындысы арзан, экологиялық таза және коррозияға қарсы тиімді ингибитор ретінде ұсынылды.

Түйін сөздер: *Ribes nigrum; өсімдік сығындылары; сулы жапырақ сығындылары; ингибиторлардың тиімділігі; жасыл ингибиторлар; металды қорғау.*

Information about the authors

Nikolay Vladimirovich Akatyev* – candidate of chemical sciences, senior lecturer, M.Utemisov West Kazakhstan university, Uralsk, Republic of Kazakhstan; e-mail: nikolay.akatyev@wku.edu.kz. ORCID: https://orcid.org/0000-0001-9248-2753.

Meruyet Kuanyshkyzy Khapiyeva – master student, M. Utemisov West Kazakhstan university, Uralsk, Republic of Kazakhstan; e-mail: missmeruuu@gmail.com. ORCID: https://orcid.org/0009-0009-3540-9475.

Roza Zhalgasovna Kenzhegalieva – master student, M. Utemisov West Kazakhstan university, Uralsk, Republic of Kazakhstan; e-mail: rozka _k90@mail.ru. ORCID: https://orcid.org/0009-0007-9236-6155.

Tomiris Berikovna Seilova – master student, M. Utemisov West Kazakhstan university, Uralsk,Republic of Kazakhstan; e-mail: tomy27@mail.ru. ORCID: https://orcid.org/0009-0001-2327-5977.

Авторлар туралы мәліметтер

Николай Владимирович Акатьев* – химических ғылымдарының кандидаты, аға оқытушы, М. Өтемісов атындағы Батыс Қазақстан университеті, Орал қ., Қазақстан; e-mail: nikolay.akatyev@wku.edu.kz. ORCID: https://orcid.org/0000-0001-9248-2753.

Мерует Куанышкызы Хапиева – магистрант, М. Өтемісов атындағы Батыс Қазақстан университеті, Орал қ., Қазақстан; e-mail: missmeruuu@gmail.com. ORCID: https://orcid.org/0009-0009-3540-9475.

Роза Жалгасовна Кенжегалиева – магистрант, М. Өтемісов атындағы Батыс Қазақстан университеті, Орал қ., Қазақстан; e-mail: k90@mail.ru. ORCID: https://orcid.org/0009-0007-9236-6155.

Томирис Бериковна Сейлова – магистрант, М. Өтемісов атындағы Батыс Қазақстан университеті, Орал қ., Қазақстан; e-mail: tomy27@mail.ru. ORCID: https://orcid.org/0009-0001-2327-5977.

Сведения об авторах

Николай Владимирович Акатьев* – кандидат химических наук, старший преподаватель, Западно-Казахстанский университет им. М. Утемисова, г. Уральск, Республика Казахстан; e-mail: nikolay.akatyev@wku.edu.kz. ORCID: https://orcid.org/0000-0001-9248-2753.

Мерует Куанышкызы Хапиева – магистрант, Западно-Казахстанский университет им. М. Утемисова, г. Уральск, Республика Казахстан; e-mail: missmeruuu@gmail.com. ORCID: https://orcid.org/0009-0009-3540-9475.

Роза Жалгасовна Кенжегалиева – магистрант, Западно-Казахстанский университет им. М. Утемисова, г. Уральск, Республика Казахстан; e-mail: k90@mail.ru. ORCID: https://orcid.org/0009-0007-9236-6155.

Томирис Бериковна Сейлова – магистрант, Западно-Казахстанский университет им. М.Утемисова, г. Уральск, Республика Казахстан; e-mail: tomy27@mail.ru. ORCID: https://orcid.org/0009-0001-2327-5977.

Received 02.04.2024
Revised 28.05.2024
Accepted 29.05.2024

DOI: 10.53360/2788-7995-2024-2(14)-50

МРНТИ: 31.15.37

А. Асанов, С.А. Мамешова*, А.А. Асанов
Таразский региональный университет имени М.Х. Дулати,
080000, Республика Казахстан, г. Тараз, ул. Толе би, 60
*e-mail: sayat.mameshova@icloud.com

ВЛИЯНИЕ ГИБРИДИРОВАННЫХ АМИД ФУНКЦИОНАЛЬНЫХ ПОЛИМЕРОВ НА СТРУКТУРООБРАЗОВАНИЕ ПОЧВ

Аннотация: *В последние годы наблюдается увеличение деградации почв под влиянием антропогенной нагрузки. Это приводит к снижению плодородия и ухудшению качества окружающей среды. В связи с этим, возрастает потребность в разработке новых методов для создания и восстановления почвенной структуры и в статье представлены результаты исследования влияния гибридных амид функциональных полимеров на структурообразование почв. Актуальность работы обуславливается возрастающей потребностью в разработке новых методов для создания и восстановления почвенной структуры, деградирующей под влиянием человеческой деятельности. В работе изучены полимеры, отличающиеся по набору функциональных групп, заряду, конформации и типу противоионов. Проведено комплексное исследование оптических, вязкостных и электропроводных свойств. Идентифицированы типы функциональных групп и установлены количественные соотношения между ними. Определены типы полимеров и влияние*