

THERMODYNAMIC APPROACH TO PURPOSEFUL DESIGN OF SYNERGISTIC INHIBITIVE COMPOSITIONS FOR CORROSION PROTECTION IN AQUEOUS SALINE MEDIUM

V. LEDOVSKYKH¹, Yu. VYSHNEVSKA^{2,3}, I. BRAZHNYK⁴, S. LEVCHENKO¹

¹ National Aviation University, Kyiv;

² National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", Kyiv;

³ Institute for Renewable Energy, Kyiv;

⁴ Gimasi SA Ukraine R&D Centre Via L. Lavizzari, Switzerland

The protective ability of inhibitors against corrosion of steel in aqueous saline solutions is ensured under such metal potentials and pH values that according to the Pourbaix diagram transfer the Fe–H₂O system to a thermodynamically stable state of hydrated oxides of Fe (III). Under such conditions the binary mixtures of inhibitors of oxidation and salt passivation form highly efficient synergistic compositions that may provide a full metal protection. For aqueous saline solutions the isomolar series method is proposed and its expediency is proved for the purposeful design, investigation and composition optimization of inhibitive mixtures with synergistic effects. It is shown that the complex-forming process has a predominant role in the protective mechanism of inhibitive mixtures based on organic ligands that are capable to form the slightly soluble complexes with metal ions. The highly efficient inhibitive mixtures for steel protection in aqueous saline solutions based on the proposed approach are developed.

Keywords: *corrosion, iron, inhibitor, metal protection, isomolar series, complex, phase layers.*

Protection of steel in aqueous saline solutions using inhibitor methods is usually achieved with suppression of the anodic partial reaction by transferring the metal surface to a passive state. A wide range of passivators with different mechanism of protective action are proposed [1–4]. At the same time, individual inhibitors and their technical analogues demonstrate a moderate protective efficiency. Furthermore, such passivation inhibition may be considered as dangerous due to high risks of development of the localized corrosion damage in the case of the passive film discontinuity that may lead to the equipment faults even with the minor metal losses.

Higher protective properties and better cost efficiency may be achieved using specially designed synergistic compositions that demonstrate the overadditive effect of their components. Such compositions are widely used for protection of metals in acidic [1, 3] and neutral media [2, 4], and can be designed based on byproducts and Industrial waste materials [5]. Thus, the purposeful design of mixtures that utilize the synergy phenomena is a promising approach to the development of the high-performance inhibitive compositions that may be implemented using the isomolar series method [6–7].

The presented paper is focused on the thermodynamic analysis of conditions for the electrochemical corrosion of steel in aqueous saline solutions and preconditions to achieve its passivation. A wide range of topics including further development of concepts about the mechanism of action of individual inhibitors and their synergistic mixtures, correlation between the protective efficiency and the nature of the mixture components and their concentration ratio, as well as the role of the metal potential and pH of the medium are discussed.

Materials and experimental methods. Individual inhibitors and their binary compositions based on XO_n^- anions (NO_2^- , ClO_3^- , BrO_3^- , IO_3^-), and based on anions, that may form the slightly soluble salts with Fe^{2+} cations (SiO_3^{2-} , PO_4^{3-} , polyhexamethylene guanidine (PHMG)), as well as the adsorption type surfactants (monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA)) for inhibiting the carbon steel corrosion in neutral media are investigated. Aqueous saline solutions have the composition: 0.3 g/l NaCl; 0.3 g/l Na_2SO_4 and 0.3 g/l $NaHCO_3$.

Corrosion tests and determination of the inhibitor efficiency were performed gravimetrically according to the standard procedure. Exposure time at 25°C temperature of carbon steel 08kp in neutral solutions was 168 h. The ratio of the solution volume (ml) to the area of metal sample (cm^2) was 10:1. The inhibition efficiency was determined by the equation $Z = [(K_m - K'_m) / K_m] \cdot 100\%$, the inhibition coefficient – by the equation $\gamma = K_m / K'_m$, where K_m, K'_m is the corrosion rate of metal in solutions without and with inhibitor ($K_m = \Delta m / (S \cdot \tau)$, where Δm is the loss of the sample weight, g; S is the sample area, m^2 ; τ is the exposure time, h).

Polarization measurements were carried out using a potentiostat P5827 M in potentiostatic regime in a three-electrode cell with separated cathodic and anodic compartments. Carbon steel 08kp was used as the working electrode, platinum – as the counter-electrode and an $Ag|AgCl|KCl(sat.)$ electrode – as the reference one. In this paper the potential values are given with respect to the normal hydrogen electrode potential.

Investigation of the morphological characteristics and elemental composition of the surface protective films of the inhibitive compositions was carried out with the scanning electron microscope (EVO-50, Zeiss, Germany) equipped with the energy-dispersive detector (INCA PENTA FET×3, Oxford Instruments, Co., UK) and using Auger microprobe JAMP-9500F in the scanning electron microscopy mode.

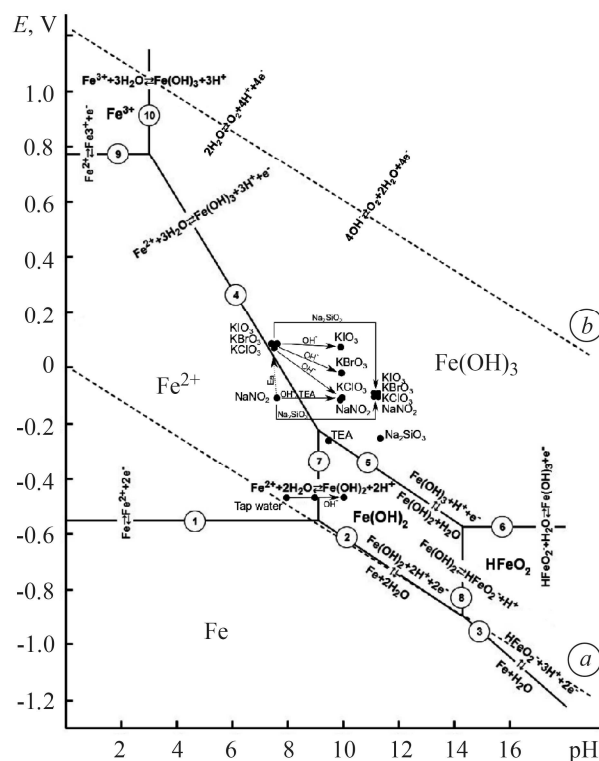


Fig. 1. Pourbaix diagram for the Fe–H₂O system.

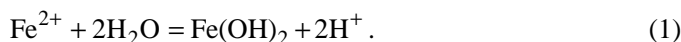
Results and discussion.

Investigation of the main kinetic regularities of the target system, taking into account specific electrochemical behaviors of individual additives for obtaining the complete theoretical model, will enable purposeful engineering of favorable conditions for synergy effects that allow to maximize the protective performance of their binary mixtures.

The Pourbaix diagram for the Fe–H₂O system (Fig. 1) [8] was used for determination of the required conditions for the formation of the phase protective films of the thermodynamically stable hydrated iron oxides and achieving the metal surface passivation.

A pH value of the blank aqueous saline solution has a significant influence on the

steel corrosion resistance. According to the Pourbaix diagram, the increase in the pH value leads to a transition from the corrosion products – hydrated cations of iron (II) toward the iron (II) hydroxide. A vertical line 7 on the E -pH diagram (Fig. 1) corresponds to the change of the stable form of the products according to reaction (1) that is also in line with the obtained SEM images and elemental composition of the surface (Fig. 3):



Increase in pH value leads to the rise in oxygen content that is observed in the surface layer that is especially strongly marked in the $\text{Fe}(\text{OH})_2$ stability area. Analysis of elemental composition of the surface layer shows that after exposure to the modeled aqueous saline solutions with different pH value the oxygen content tends to increase the pH that is also accompanied by the corrosion rate decrease.

Polarization measurements show that the increase in the pH value leads to a gradual shift of the corrosion potential toward a positive direction and a slight inhibition of anodic reaction of metal ionization that occurs in the active area. In the area of thermodynamically stable $\text{Fe}(\text{OH})_2$ (Fig. 1) a small passivation section due to formation of the protective film on the metal surface may be observed (Fig. 2).

The mechanism of action of the individual nitrite ion may be attributed to its adsorption on the metal surface via the active electron pair on sp^2 – hybridized orbital on the central nitrogen atom. The proposed interpretation is also supported by the fact that the nitrate ion, despite being its coordinated analogue, does not exhibit inhibitive properties due to a lack of such electron pair.

It is also in line with the investigation of the film on the steel surface after exposure to the aqueous saline solution with addition of NaNO_2 at pH 7.3 using SEM. Despite moderate reduction in corrosion rate ($Z = 99\%$) in the presence of sodium nitrite, a significant corrosion damage may be observed on the metal surface (Fig. 3d). Elemental composition of the surface layer shows the appearance of nitrogen that indicates the presence of adsorbed NO_2^- -ions.

Addition of sodium nitrite to the tap water model at pH 7.3 leads to the inhibition of anodic reaction of the steel corrosion, shifts its potential toward the positive direction thus providing a moderate decrease in the corrosion rate. According to the Pourbaix diagram for the $\text{Fe}-\text{H}_2\text{O}$ system, the corrosion products would be the hydrated Fe (II) ions that are found to be a thermodynamically stable form under these conditions. According to the polarization measurements the sodium nitrite has virtually no influence on the kinetics of the cathodic reaction. Cathodic portion of the polarization curve contains the diffusion wave of the depolarizer reduction while the anodic process of metal ionization occurs in the active area (Fig. 4). Oxide passivation may only be achieved in the potential area above the Flade potential (0.1 V) that corresponds to an external anodic protection (Fig. 4). According to the Pourbaix diagram, this also corresponds to the $\text{Fe}-\text{H}_2\text{O}$ system transition to the state of stability of the hydrated iron (III) oxides that may form dense passive films (Fig. 1).

It is shown that the corrosion rate in the presence of nitrite ions may be significantly decreased and virtually complete metal protection may be ensured by shifting the pH value to the region where the system will be transferred to a passive state owing to hydrated iron oxides, according to reaction (2) that corresponds to crossing of line 4 (Fig. 1):

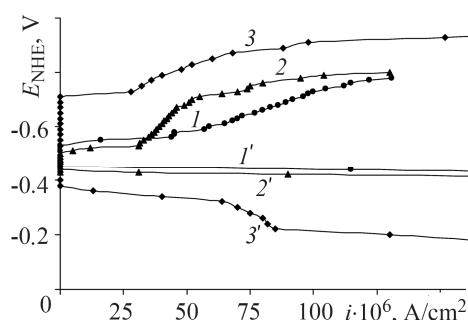


Fig. 2. Cathodic (curves 1–3) and anodic (curves 1'–3') polarization curves for carbon steel 08kp in background aqueous saline solution at pH: 1, 1' – 8; 2, 2' – 9; 3, 3' – 10.

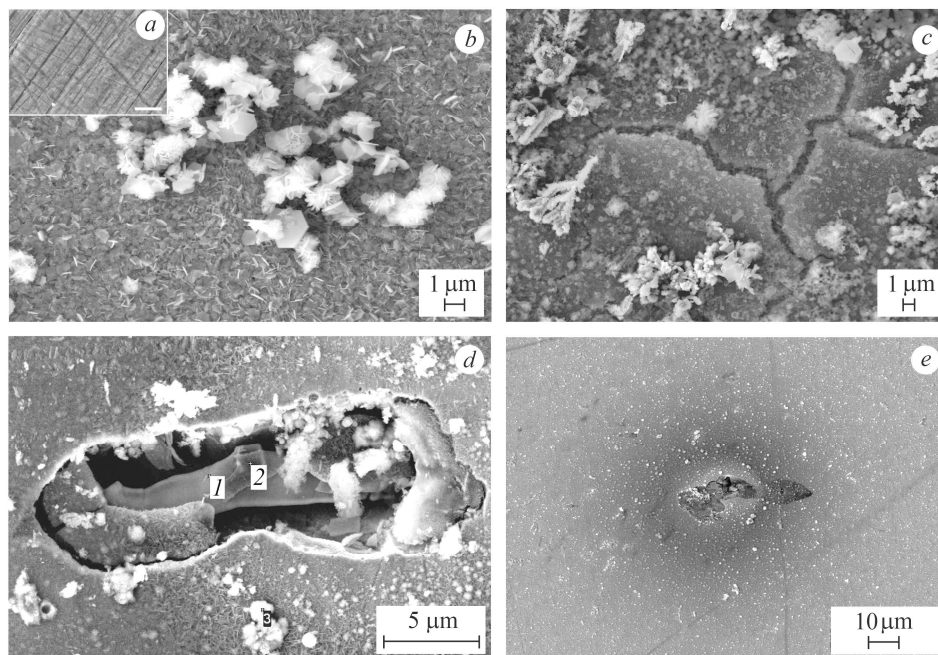
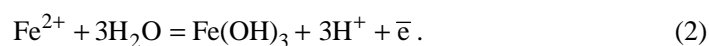


Fig. 3. SEM images of carbon steel after exposure to: *a* – without exposure; *b* – background aqueous saline solution at pH 7.3; *c* – background aqueous saline solution at pH 10; *d* – presence of NaNO_2 (30 mmol/l) at pH 7.38; *e* – presence of NaNO_2 (30 mmol/l) at pH 10. Exposure time 168 h.

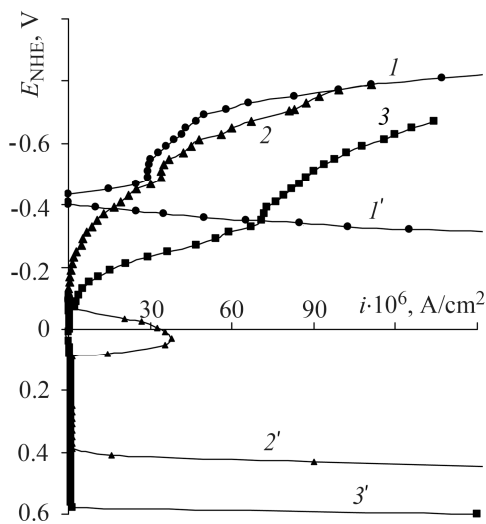


Fig. 4. Cathodic (curves 1–3) and anodic (curves 1'–3') polarization curves for carbon steel 08kp in: 1, 1' – background aqueous saline solution; 2, 2' – in the presence of NaNO_2 (30 mmol/l) at pH 7.38; 3, 3' – in the presence of NaNO_2 (30 mmol/l) at pH 10.

The SEM images of the film formed at pH10 in the presence of nitrite ions show mostly uniform morphology while some signs of local corrosion damage may still be observed (Fig. 3e). This is also supported by the analysis of elemental composition that shows the increased content of oxygen at pH 10 that is in line with theoretical expectations. It should also be noted that some amount of nitrogen is registered for the film formed at pH 10. By the given presence of nitrogen in the protective film we may conclude that under these conditions two individual factors – adsorption of nitrite ion that caused the positive shift of the potential and increased pH value of the environment results in the oxide passivation of the metal surface with thermodynamically stable hydrated iron (III) oxide (Fig. 1).

Inhibitive action of XO_3^- oxyanions ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) is usually attributed to their reduction and acceleration of the cathodic partial reaction [9] that may also

be supported by the representation based on the Pourbaix diagram (Fig. 1).

In the presence of such strong oxidizing agents the steel potential rises to the values where Fe–H₂O system shifts to the state with thermodynamically stable hydrated iron (III) ions that result in oxide passivation of the metal surface. According to the electrochemical measurements the anodic portion of the polarization curves in the presence of studied oxyanions contains the full passivation zone at both pH 7.38 (Fig. 6a) and pH 10 (Fig. 6b). At the same time the cathodic polarization of steel rises significantly, while the oxygen reduction waves are not recorded in the presence of such additives.

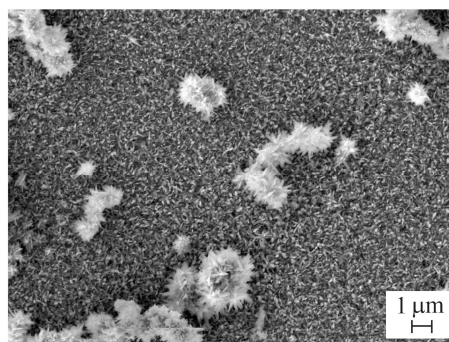


Fig. 5. SEM image of carbon steel after exposure to aqueous saline solution in the presence of 30 mmol/l KClO₃.

Analysis of the morphology of the iron (III) oxide film formed in the presence of KClO₃ (Fig. 5) shows a uniform structure without signs of pitting damage that is in good agreement with electrochemical measurements, while its elemental composition does not include halogen atoms which is also in line with the proposed interpretation.

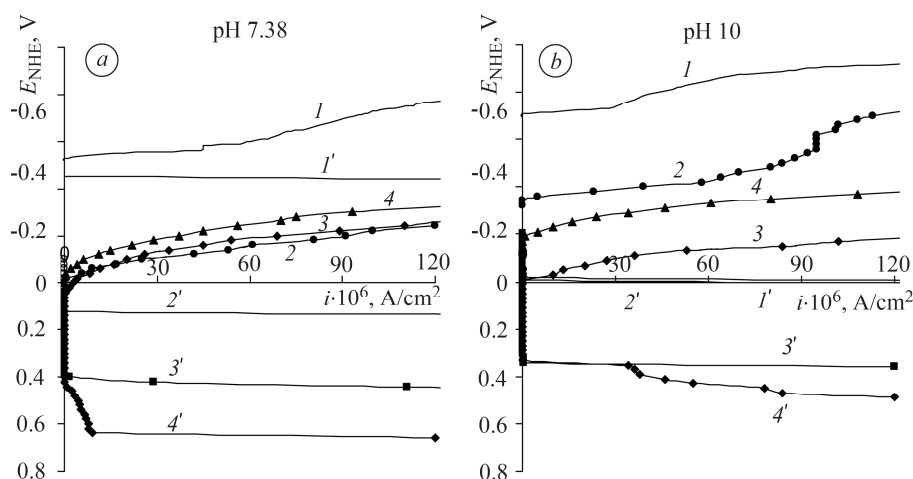
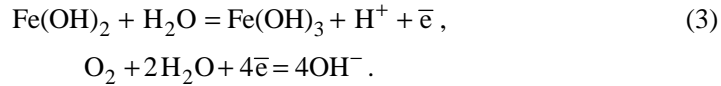


Fig. 6. Cathodic (curves 1–4) and anodic (curves 1'–4') polarization curves for carbon steel 08kp at pH 7.38 (a) and 10 (b): 1, 1' – background aqueous saline solution; 2, 2' – in the presence of KClO₃ (30 mmol/l); 3, 3' – in the presence of KBrO₃ (30 mmol/l) and 4, 4' – in the presence of KIO₃ (30 mmol/l).

The inhibitory properties of silicates, phosphates, and borates are usually attributed to the steel surface blocking with their slightly soluble salts with the iron (II) cations that are formed in the previous stages of corrosion. At the same time the factor of hydrolysis of additives as salts of weak acids and strong bases is usually not taken into account. Hydrolysis results in a significant alkalization of the medium, which depending on the inhibitor concentration, may reach pH ≥ 10...11. The steel corrosion potential and pH value increase that leads to the Fe–H₂O system transition to the metal passive state (Fig. 1). It can be assumed that an increase in the pH value of the solution due to addition of silicate or phosphate causes the formation of the hydrated iron (II) oxides. This process occurs when the system crosses the vertical line 7 of the diagram with subsequent oxidation by oxygen in the aerated corrosive medium (at the intersection of line 5 of the diagram) due to the corrosion potential shift in the presence of slightly soluble salts of iron (II):



Such interpretation is supported by the composition analysis using Auger spectroscopy that shows the presence of significant amount of oxygen and silicon in the formed film (61.7 at.% and 10.3 at.%, respectively).

Under these conditions there is a combined action of two factors that affect the corrosion process – the formation of the iron (III) oxide film and insoluble salts of the iron (II) on the metal surface. As a result the full passivation zones are recorded on the anodic portion of the polarization curves (Fig. 7).

Inhibitors of a number of organic amines in aqueous solutions behave like weak bases and cause alkalization of the medium. The corrosion potential of the steel in the presence of TEA is shifted toward the positive direction and the pH value reaches pH 9.5 at the additive concentration of 30 mmol/l. According to the Pourbaix diagram, under these conditions the hydrated oxides of iron (II) become thermodynamically stable. However, they are not capable to ensure significant metal passivation compared to the hydrated oxides of iron (III) (Figs. 1 and 7b). It can be assumed that in the presence of the individual amines additives there is also a mutual superimposition of the adsorption of the surfactant and the oxide passivation of the metal with iron (II) hydroxides.

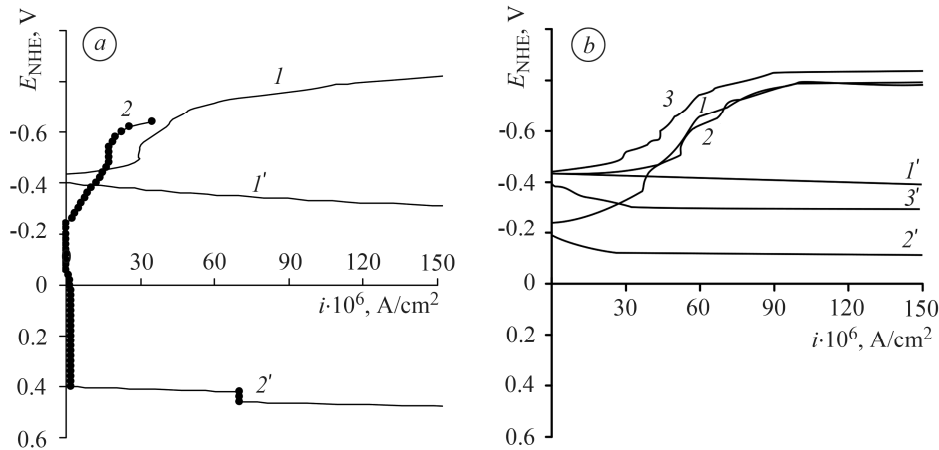


Fig. 7. Cathodic (curves 1–3) and anodic (curves 1'–3') polarization curves for carbon steel 08kp: *a*: 1, 1' – background aqueous saline solution; 2, 2' – in the presence of Na_2SiO_3 (30 mmol/l), and *b*: 1, 1' – background aqueous saline solution, 2, 2' – in the presence of MEA (30 mmol/l), 3, 3' – in the presence of TEA (30 mmol/l).

It is shown that individual additives have specific drawbacks that may be addressed by combining inhibitors of different nature for obtaining the synergistic mixtures. The binary mixtures of inhibitors with different mechanisms of action of a number of oxo-anions XO_3^- that have active unbound electron pairs of sp^3 -hybrid orbitals of an acidifier with such inhibitors as silicates, phosphates, guanidines or amines, are capable to simultaneously shift the metal potential toward the positive direction and pH of the medium toward higher values (Fig. 1). That leads to the formation on the metal surface of the thermodynamically stable hydrated oxides of iron (III) that according to the results of the X-ray diffraction and phase analysis has a goethite structure modified with insoluble salts of iron (II) or adsorbed amines.

Analysis of the morphology of the protective films formed in the presence of different inhibitive mixtures at optimal concentration ratio of the components ($\text{NaNO}_2:\text{Na}_2\text{SiO}_3$ as 1:2; $\text{KClO}_3:\text{Na}_2\text{SiO}_3$ as 1:2; $\text{NaNO}_2:\text{PHMG}$ as 2:1) shows that anticorrosive performance has been significantly improved compared to any individual additives (Fig. 8).

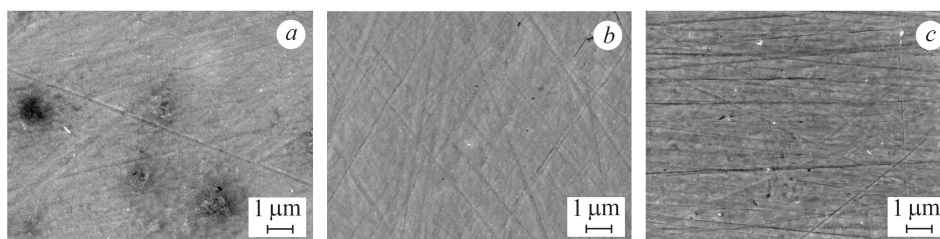


Fig. 8. SEM images of carbon steel after exposure to aqueous saline solution in the presence of synergistic mixture (total concentration 30 mmol/l): *a* – 10 mmol/l NaNO₂ + 20 mmol/l Na₂SiO₃; *b* – 10 mmol/l KClO₃ + 20 mmol/l Na₂SiO₃; *c* – 10 mmol/l PHMG + 20 mmol/l NaNO₂.

Elemental composition of the carbon steel surface (by the results of Auger-spectroscopy) after treatment in: 1 – 10 mmol/l NaNO₂ and 20 mmol/l Na₂SiO₃; 2 – 10 mmol/l KClO₃ and 20 mmol/l Na₂SiO₃; 3 – 10 mmol/l PHMG and 20 mmol/l NaNO₂

Spectrum	C	N	O	Na	Si	S	Cl	Ca	Fe	Total
1 (key to Fig. 8a)	25.4	1.0	59.1	0.2	12.8	0.2	–	0.1	1.20	100.00
2 (key to Fig. 8b)	19.7	1.4	63.6	–	12.8	–	–	–	1.80	100.00
3 (key to Fig. 8c)	37.6	25.5	21.2	0.4	–	0.1	0.1	–	15.2	100.00

It should be noted that elemental composition of the obtained film in the case of KClO₃ + Na₂SiO₃ (see Table, spectrum 2) shows no presence of chlorine what is an evidence of partial or full reduction of XO₃[–] oxyanions on the metal surface creating the preconditions for the protective film formation. In the case of NaNO₂+PHMG mixture (see Table 1, spectrum 3) the oxygen content is notably lower while the concentration of nitrogen is significantly higher compared to other mixtures. The obtained results correspond to the structure of the phase film of slightly soluble PHMG-Fe complexes with some inclusion of iron oxide indicating that the complexation process has a predominant role in the protective mechanism of the mixture.

The efficiency of the mixtures depends on the components nature, their mechanism of action and the concentration ratio in an aggressive medium that should be adjusted to obtain the optimal protective performance. Using the isomolar series method it is shown that the dependence of the efficiency of binary compositions in relation to the ratio of molar concentrations of its components at a constant total concentration has an extreme character where in the maxima the best protection of steel is achieved. The gravimetric measurements showed that binary compositions XO_n[–] (NO₂[–], ClO₃[–], BrO₃[–], IO₃[–]) with salts of type Na₂SiO₃; Na₃PO₄, PHMG or amines are able to significantly exceed the protective efficiency of their individual components, exhibit the synergy phenomena and provide full protection of steel against corrosion (Fig. 9). According to the polarization studies of the electrochemical behavior of steel in aqueous saline solutions, synergistic inhibitive mixtures cause a shift in the metal corrosion potential toward the positive direction and the transition of its surface to a passive state (Fig. 10).

The passivation zone extends over a wide range of anode potentials while the pitting potential is significantly distant from the corrosion one that is in line with the gravimetric and morphology studies. A significantly wider passivation zone than in the case of individual components, some inhibition of cathodic processes and low current density of full passivation (that does not exceed few microamperes per square centimeter) result in a greatly improved performance of the synergistic mixture.

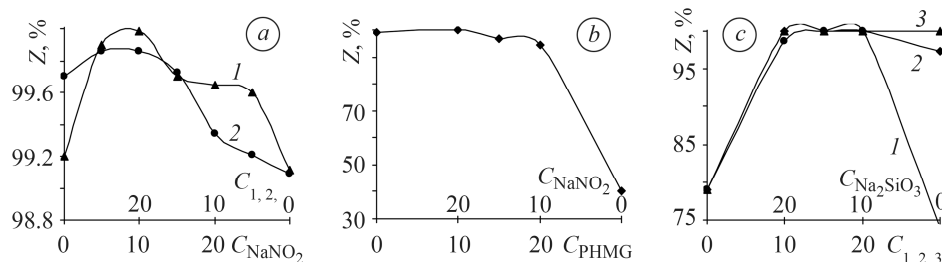


Fig. 9. Dependence of the inhibition efficiency for carbon steel in the aqueous saline solution on the ratio of molar concentrations of the individual components in isomolar mixtures (total concentration 30 mmol/l): *a* – 1 – $\text{NaNO}_2 + \text{Na}_2\text{SiO}_3$; 2 – $\text{NaNO}_2 + \text{Na}_3\text{PO}_4$; *b* – $\text{PHMG} + \text{NaNO}_2$; *c* – 1 – $\text{KClO}_3 + \text{Na}_2\text{SiO}_3$; 2 – $\text{KBrO}_3 + \text{Na}_2\text{SiO}_3$; 3 – $\text{KIO}_3 + \text{Na}_2\text{SiO}_3$.

Important advantage of synergistic binary compositions is that they are capable to retain high efficiency at elevated temperatures and in the presence of 3% NaCl [7, 10].

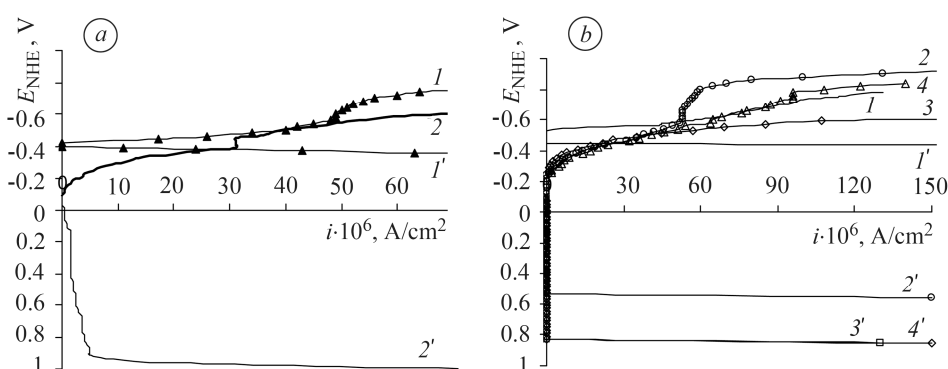


Fig. 10. Cathodic and anodic (with ') polarization curves for carbon steel 08kp in the presence of: *a* – 1, 1' – background aqueous saline solution; 2, 2' – NaNO_2 (10 mmol/l) + Na_2SiO_3 (20 mmol/l); *b* – 1, 1' – background aqueous saline solution; 2, 2' – KClO_3 (15 mmol/l) + Na_2SiO_3 (15 mmol/l); 3, 3' – KBrO_3 (10 mmol/l) + Na_2SiO_3 (20 mmol/l) and 4, 4' – KIO_3 (10 mmol/l) + Na_2SiO_3 (20 mmol/l).

It is worth noting that the extreme character of the dependence in binary mixtures also applies to such parameters as corrosion potential, current density of full passivation, and the pitting potential that should be taken into account during development and optimization of the novel high-performance metal protection methods [7].

CONCLUSIONS

It is shown that the protective action of the inhibitors and their synergistic mixtures on the corrosion of steel in aqueous saline solutions is ensured under such metal potentials and pH values that according to the Pourbaix diagram transfer the system to the state of thermodynamically stable hydrated iron (III) oxide. Specifically designed binary mixtures of inhibitors with different mechanism of action exhibit the synergistic effects that allow one to achieve the high inhibitive efficiency. Such compositions are capable to retain high protective efficiency in aggressive medium and at elevated temperatures. The isomolar series method has been proposed and its feasibility for purposeful development and composition optimization of inhibitive mixtures with synergistic effects has been demonstrated. Highly efficient inhibiting compositions have been developed for steel protection in aqueous saline solutions as well as for application as inhibiting components of technological fluids for the processes of electro-spark and mechanical processing of steel. It has been shown, that the complex-forming process has a predominant role in the protective mechanism of inhibitive mixtures based on organic ligands that are capable to form the slightly soluble complexes with the metal ions.

РЕЗЮМЕ. Показано, що захисну здатність інгібіторів під час корозії сталі у водно-сольових розчинах забезпечено за таких потенціалів металу та рН середовища, які за діаграмою Пурбе переводять систему Fe–H₂O у термодинамічно тривкий стан гідратованих оксидів феруму (III). За цих умов бінарні суміші інгібіторів оксидної і сольової пасивації утворюють високоефективні синергічні композиції, які здатні забезпечувати повний захист металу. Для водно-сольових розчинів запропоновано метод ізомольарних серій та доведено доцільність його застосування для цілеспрямованої розробки, оптимізації складу і дослідження сумішей інгібіторів з ефектами синергізму. Також показано, що комплексоутворення відіграє визначальну роль у захисному механізмі при застосуванні сумішей на основі органічних лігандів, які здатні утворювати малорозчинні комплексні сполуки з іонами металів. На основі запропонованих підходів розроблені високоефективні інгібіторні суміші для захисту сталі у водно-сольових розчинах.

РЕЗЮМЕ. Показано, что защитная способность ингибиторов при коррозии стали в водно-солевых растворах обеспечивается при таких потенциалах металла и рН среды, которые по диаграмме Пурбэ переводят систему Fe–H₂O в термодинамически устойчивое состояние гидратированных оксидов железа (III). В этих условиях бинарные смеси ингибиторов оксидной и солевой пассивации образуют высокоэффективные синергические композиции, которые способны обеспечивать полную защиту металла. Для водно-солевых растворов предложен метод изомольарных серий и доказана целесообразность его использования для целенаправленной разработки, оптимизации состава и исследования смесей ингибиторов с эффектами синергизма. Также показано, что комплексообразование оказывает доминирующее влияние в защитном механизме при использовании смесей на основе органических лигандов, которые способны образовывать слаборастворимые комплексные соединения с ионами металлов. На основании предложенных подходов разработаны высокоэффективные ингибирующие смеси для защиты стали в водно-солевых растворах.

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