MECHANISM OF THE OXIDATIVE AND SALT PASSIVATORS COACTION WITHIN BINARY INHIBITIVE MIXTURES

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The regularities of joint action of the additives that are characterized by a different inhibition mechanism for the protection of mild steel in aqueous saline media have been investigated. Total 14 inhibitive mixtures have been studied at different concentration ratio and the obtained results on the protective efficiency and produced morphological and structural changes of the metal surface have been interpreted in regard to a coaction of individual inhibitive factors. Different kinds of interaction that may result in synergistic and antagonistic effects have been discussed. The schematic representation of the inhibitor mechanism aliasing effects has been presented and the theoretical model that reflects the joint action of individual additives within multicomponent inhibitive systems has been further extended and refined.

Keywords: *corrosion, mild steel, inhibitive mixtures, metal protection, isomolar series, coaction, mechanism aliasing effects.*

Досліджено закономірності спільної дії додатків, які характеризуються різним механізмом інгібувальної дії, для захисту сталі у водно-сольових середовищах. Вивчено 14 інгібіторних сумішей за різних співвідношень концентрацій. Отримані результати захисної ефективності та спричинених морфологічних і структурних змін поверхні металу інтерпретовано з точки зору взаємодії окремих інгібувальних чинників. Розглянуто різні види їх взаємодії, які можуть спричиняти синергетичні та антагоністичні ефекти. Наведено схематичне подання ефектів взаємного накладання інгібувальних механізмів. Теоретична модель, яка відображає спільну дію окремих додатків у багатокомпонентних інгібіторних системах, додатково розширена та вдосконалена.

Ключові слова: *корозія, сталь, інгібувальні суміші, захист металів, ізомолярні серії, ефекти накладання механізмів.*

Introduction. Oxidative and salt passivators are commonly used for the protection of steel in neutral aqueous saline media. Inhibitive mixtures that may exhibit synergistic effects within their components to provide improved protective performance and overcome or minimize the shortcomings of the individual inhibitors are of specific interest. Despite extensive studies of the inhibitive action of individual additives the mechanism of their combined effect is still understood incompletely [1–7].

It is shown [8–10] that the binary mixtures of such inhibitors, characterized by a different mechanism of action under certain conditions – pH range, metal potential, concentration and concentration ratio – may deliver excellent protective efficiency within a synergistic extrema. At the same time, for the binary mixtures with certain combination of inhibitive mechanisms the negative aliasing effects may be observed that result in reduction of efficiency at specific concentration ratios. Furthermore, nega-

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tive aliasing effects may be exhibited by the same mixture depending on the concentration ratio of the components [3].

Thus, the development of the theoretical representation of the mechanism of joint action should take into account the structure of the additives and possible interaction of the mixture components that is crucial for purposeful design of efficient multicomponent inhibitors.

Materials and methods. Corrosion tests and determination of the inhibitor efficiency were performed gravimetrically according to the standard procedure. Tests were performed on steel 08 kp in the aqueous saline solutions with the composition: 0.3 g/l NaCl, 0.3 g/l Na_2SO_4 and 0.3 g/l $NaHCO_3$, exposure time at 25°C was 72 h.

The inhibition efficiency was determined by the equation $Z = [(K_m - K'_m) / K_m] \times \times 100\%$, 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 exposure time, h).

The morphological characteristics and elemental composition of the surface protective films of the inhibitive compositions were investigated by 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. The energy of the electron beam was 3 keV and the current was 0.5 μA. During profiling, the surface of the samples was bombarded with argon ions (ion etching) with the energy of 4 keV. The pickling rate was 40 Å/min.

Results and discussion. Investigation of the mechanism aliasing effects and determination of the coaction regularities on the basis of total 14 binary inhibitive mixtures with components of different mechanism of action were studied at various concentration ratio using the isomolar series method (Fig. 1).

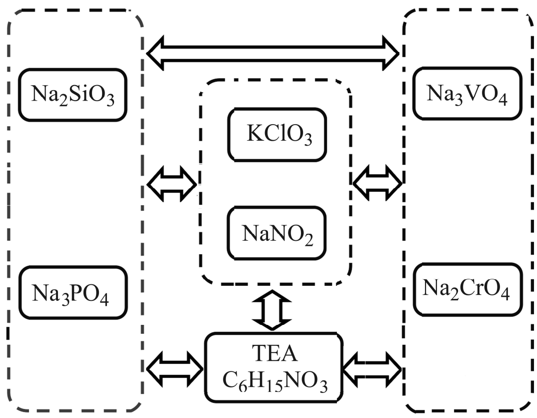

Fig. 1. Schematic representation of studied binary systems.

Synergistic effects are observed within all systems based on $:NO_2^-$ and $:ClO_3^-$ (Fig. 2*c*–*f*) that may be attributed to the presence of active electron pair on the hybrid *sp*^{2}- and *sp*^{3}-orbitals, respectively, of the acidifying anion, thus it is considered as coordinately unsaturated.

Synergistic maximum for $NaNO_2$–Na_2SiO_3 system at 99.9% is observed at concentration ratio 1:2 that may be considered as full protection (Fig. 2*c*). Despite $NaNO_2$ and Na_2SiO_3 individually demonstrate high inhibitive efficiency in terms of weight loss performance the presence of surface defects and tendency to provoke local corrosion damage (Fig. 3*c*, *d*) is limiting their application. In contrast, $NaNO_2$ and Na_2SiO_3

within a binary mixture at optimal concentration ratio provide efficient pitting control and ensure uniform surface morphology (Fig. 3*f*).

Inhibitive efficiency of $KClO_3$ is poor and barely reaches the value of 20%, while within a mixture it may significantly improve its performance in terms of protection efficiency and surface morphology. Inhibitive mixture $KClO_3$–Na_2SiO_3 demonstrates high protective efficiency within a wide range of concentration ratio 2:1–1:1 reaching a peak value that may be considered as full protection (Fig. 2*f*). The surface morphology is also significantly improved compared to both individual components that are found to be in line with the gravimetric results.

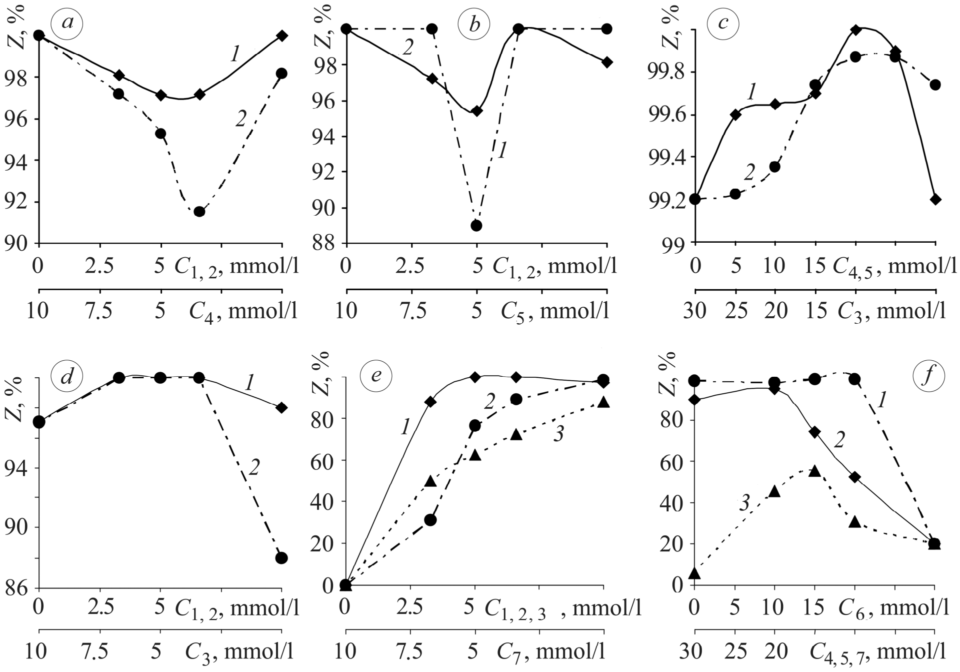

Fig. 2. Inhibitive efficiency vs concentration ratio of the binary mixture components.
a: *1* – Na_3VO_4 + Na_2SiO_3; *2* – Na_2CrO_4 + Na_2SiO_3;
b: *1* – Na_3VO_4 + Na_3PO_4; *2* – Na_2CrO_4 + Na_3PO_4;
c: *1* – Na_2SiO_3 + $NaNO_2$; *2* – Na_3PO_4 + $NaNO_2$;
d: *1* – Na_3VO_4 + $NaNO_2$; *2* – Na_2CrO_4 + $NaNO_2$;
e: *1* – $NaNO_2$ + TEA; *2* – Na_3VO_4 + TEA; *3* – Na_2CrO_4 + TEA;
f: *1* – Na_2SiO_3 + $KClO_3$; *2* – Na_3PO_4 + $KClO_3$; *3* – TEA + $KClO_3$.
Key: 1 – Na_3VO_4; 2 – Na_2CrO_4; 3 – $NaNO_2$; 4 – Na_2SiO_3; 5 – Na_3PO_4; 6 – $KClO_3$; 7 – TEA.

The elemental composition analysis of the protective films formed in the presence of $NaNO_2$–Na_2SiO_3 and $KClO_3$–Na_2SiO_3 synergistic mixtures using the Auger spectroscopy method shows that the nitrogen and halogen atoms, respectively, are not included into the protective film. The obtained results are found to be in a good agreement with theoretical expectations that imply reduction of $:NO_2^-$ and $:ClO_3^-$ ions that facilitate formation of the protective film of hydrated iron (III) oxides with inclusion of slightly soluble salts originating from the salt passivator components of the mixture [9, 10]. The inhibitive mixtures based on $NaNO_2$ or $KClO_3$, that also exhibit synergistic behavior (Fig. 2*c*–*f*) and tend to improve finishing of the metal surface, are studied.

In contrast, binary inhibitive mixtures composed according to a similar schema as oxidative passivators (Na_3VO_4, Na_2CrO_4) but with coordinately saturated acidizing anions with addition of salt inhibitors (Na_2SiO_3, Na_3PO_4) demonstrate negative mechanism aliasing that results in noticeable antagonistic effects both in terms of protection efficiency and the amount of surface corrosion damage (Fig. 2*a*, *b*, *e*). Such behavior may be attributed to a concurrence among the individual inhibitive action factors that take place between the mixture components due to structural similarities that reduce efficiency at specific concentration ratio.

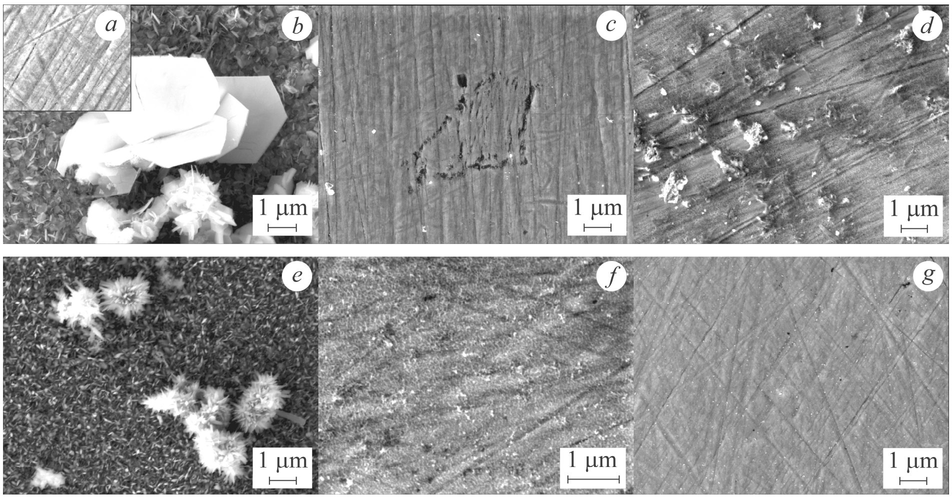

Fig. 3. SEM images of carbon steel after exposure to aqueous saline solution in the presence of inhibitors (total concentration 30 mmol/l): *a* – without exposure; *b* – background aqueous saline solution; *c* – $NaNO_2$ (30 mmol/l); *d* – Na_2SiO_3 (30 mmol/l); *e* – $KClO_3$ (30 mmol/l); *f* – 10 mmol/l $NaNO_2$ + 20 mmol/l Na_2SiO_3; *g* – 10 mmol/l $KClO_3$ + 20 mmol/l Na_2SiO_3. Exposure time 168 h.

At the same time, triethanolamine (TEA) surfactant that is characterized by the presence of inactive electron pair virtually does not affect the corrosion rate at low concentrations (Fig. 2*e*, *f*), showing a noticeable improvement in the mixtures based on $NaNO_2$ and $KClO_3$. Analysis of the TEA behavior within four studied mixtures indicates that $:NO_2^-$ and $:ClO_3^-$ ions facilitate establishing of favorable conditions for TEA, that also results in suppression of local corrosion damage typically caused by $NaNO_2$, while in the case of CrO_4^{2-} and VO_4^{3-} some decrease in protective efficiency may be observed that may be attributed to concurrency effects.

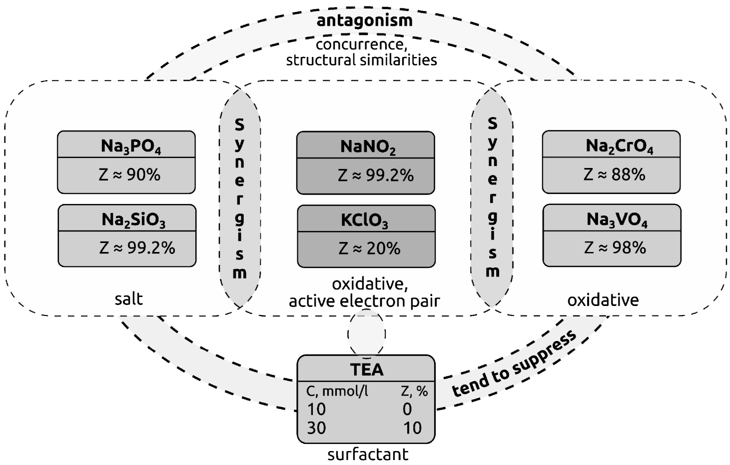

Fig. 4. The inhibitive coaction diagram within studied systems.

Comprehensive analysis of the obtained experimental results enables further refining of the theoretical model that represents combined action of inhibitors within binary inhibitive mixtures (Fig. 4). The analytical approach implies splitting the inhibitive action of the additives into individual factors that have to be weighted in terms of possible aliasing effects with other components of the mixture for a target pH range, metal potentials and other conditions that contribute to the final protective properties of the mixture. Various types of positive and negative mechanism aliasing effects are observed among studied systems including cases where specific inhibitive factor of one component does not affect the corrosion rate individually but significantly improves the performance of the second component due to the formation of favorable conditions that constitute a tandem inhibitive system.

Thus, the enhanced efficiency of the binary inhibitive mixtures may be attributed to a supplementary, complementary or tandem action of their components depending on the nature and magnitude of inter-mixture mechanism aliasing effects that should be taken into account when developing multicomponent synergistic mixtures.

CONCLUSIONS

Total 14 binary inhibitive mixtures for the protection of mild steel in neutral aqueous saline media were investigated at various concentration ratios for determination of the mechanism and regularities of the joint inhibitive action of individual additives within a multicomponent system. It was shown that multiple type of interaction might occur within the inhibitive mixture components that might result in synergistic and antagonistic effects in respect to a mixture protective efficiency and resulting surface morphology depending on the nature of the mechanism aliasing effects. Synergistic effects were observed within all studied systems based on $:NO_2^-$ and $:ClO_3^-$ owing to the presence of active electron pair on a hybrid sp^2- and sp^3-orbitals of the acidifying anion, respectively, thus they were considered as coordinately unsaturated. In contrast, binary inhibitive mixtures that also included oxidative passivators (Na_3VO_4, Na_2CrO_4) but with coordinately saturated acidizing anions with addition of salt inhibitors (Na_2SiO_3, Na_3PO_4) demonstrated negative aliasing mechanism that resulted in noticeable antagonistic effects. Synergistic effects tend to appear in such cases when individual inhibitive action factors of one component facilitated establishing of the favorable conditions for the counterpart component while the antagonistic effects were attributed to shifting from the optimal conditions and a mechanism concurrence. The extended and refined theoretical model that represents the mechanism coaction and the inter-mixture interactions plays a key role in the determination and analytical prediction of preconditions for obtaining reliable synergistic effects in the multicomponent systems.

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Received 17.07.2020