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THE INHIBITION EFFECT OF TWO COMMERCIAL COMPOUNDS ON INTERFACE STEEL / NATURAL SOFTENED WATER

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Introduction

The steel remains the more used material in industry although it is inevitably subject of corrosion. The addition of inhibitors has for objective to attenuate the consequences of corrosion. Several compounds are proposed to the industry as inhibitors, often presented without precision of the chemical composition and the system adapted (material, medium, operative conditions). The objective of this work is to study the protective power of two commercial compounds on carbon steel in aqueous environment. The two tested products are basis of nitrites and alkanolamine. It concerned the compounds the more used like commercial inhibitors [1].

The nitrites act while slowing down the anodic reaction, but associated at organic compounds, they can also accelerate the cathodic reaction. They adsorbed to the metallic interface, reduce the free energy of the system and prevent the metallic dissolution toward the solution. The inhibitory effect is less obvious in acidic environment because of the reduction of the nitrites ions. The presence of other aggressive ions in solution which can occupy the interface and prevent inhibitor adsorption is possible [2–3]. According to other authors, the protection is due to the formation of iron oxide (Fe_3O_4 and Fe_2O_3) following the oxidation of the iron hydroxides by the nitrites to the metallic interface to pH between 6.2 and 6.4 [1].

This type of inhibitor is used for the tubular industrial system protection in aqueous environment. The more used industrially is the $NaNO_2$.

The alkanolamines are used like inhibitor in acidic environment. They react by chemical adsorption followed of a dehydration of the OH function and a polymerization [4]. They are considered like cathodic inhibitor. In presence of the amines function, the chemical adsorption takes place by N-Fe links and the inhibitory effect is both anodic and cathodic [5].

The inhibitor forms a thick and compact layer that presents an effect of blockage and gate to the diffusion [6]. Different authors showed that more the chain carbonate is long, better is the protection.

The compounds bases of amines are commonly used such as inhibitors of steel to the carbon against the corrosion in rich environment in H_2S or CO_2 [1].

The performances of these two inhibitors are studied according to the time of immersion and while being based on the electrochemical impedance spectroscopy supported by analytic methods.

Experimental techniques

Material: The plain steel has been appropriated on a work belonging to a factory of sugar is present the following composition in %: C <0,07; S <0,0002; Min.: 0,38; P: 0,021; S <0,004; Cr <0,004; Cu <0,002; Al: 0,03; V <0,004.

The electrodes have a surface of 1cm², coated by an inert resin. They are polished with the abrasive papers of active grid from 80 until 1200 then immersed in the ethanol and rinsed to the distilled water.

Electrolyte: it is constituted by underground water pumped of a boring situated within the factory and exploited for these needs. This water is produced by resins exchanged of ions. Its chemical composition is indicated in the table1.

Table 1. Water analyses

pH	TH (^{0}F)	TA (ppm $CaCO_3$)	CAT (ppm) $CaCO_3$)	Cl^- (ppm)	SO_4^{2-}(mg $SO_4^{=}l^{-1}$)	P_2O_5(ppm)
8.4	0.5	5	270	639	315	1.13

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Inhibitory: The table 2 carried the relative information to the two inhibitors, extracted of their technical charts. The inhibitory Kebecor n (Kn) is basis of nitrites, to use for the tubular systems without precision of the nature of water and the material. No indications for his toxicity are found. The dose of injection recommended varies from 0.2 to 0.5% according to the application method. The dose applied to the studied system is of 0.2%.

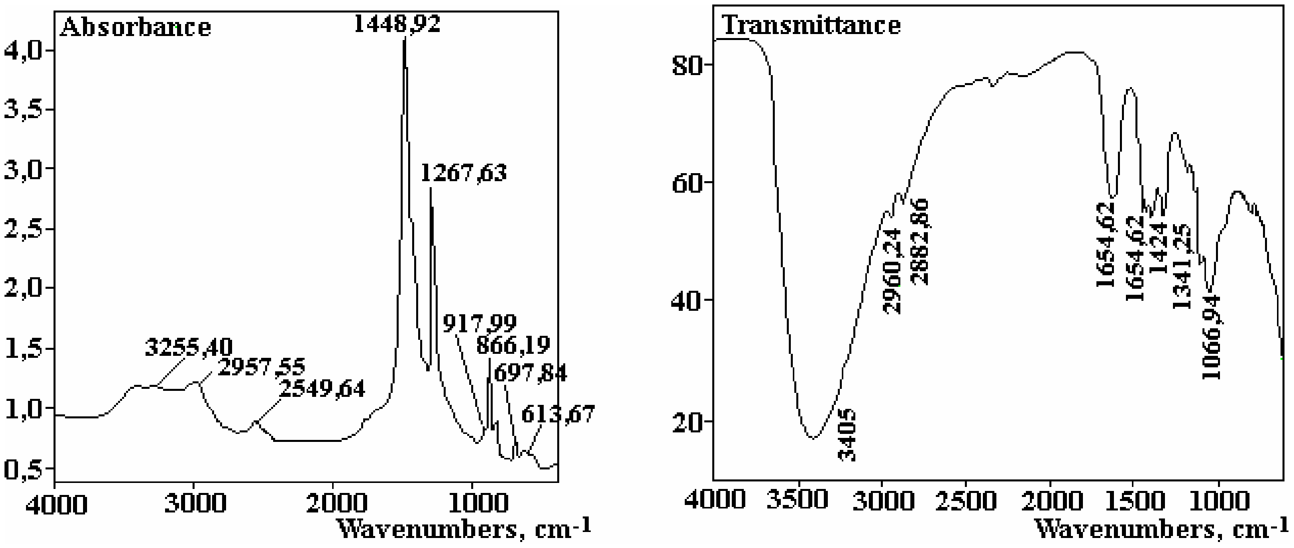
As noted, the inhibitory Sulfazur ATS is composed of derivatives of boron and alknolamines, efficient on plastic, stainless steel to the contact of a drinking water. It is considered like non dangerous compound. The injection dose recommended varies from 0.5 to 1%. The dose applied to the studied system is 0.75%.

Analyses by IR spectroscopy, achieved in the domain 4000-400 cm^{-1} (fig. 1), permitted us to get the following information, referring in the works of Bellamy and Avrans [7] and Kodama [8], and confirm the presence of the nitrites and of amino respectively for the two inhibitors The picks to 1448 cm^{-1} and 866 cm^{-1} identified for Kn, characterized carbonates whereas the nitrites appear toward 1267 cm^{-1}.

The peak situated to 1654 cm^{-1} relative the ATS compound can correspond to a primary alkylamine, and the peaks situated toward 1341, 1424 cm^{-1} and 1458 cm^{-1} to a secondary alkanolamine [9]. According to the technical chart, ATS would be a mixture of primary and secondary amines.

Table 2. Summary of the technical charts of the inhibitors

Commercial noun	**Nature/Proprities**	**Density pH**	**Water quality**	**Application's conditions**	**Action according to technical charts**
Kebocor *n*= (Kn)	Contain nitrites	1,03±0,05 11	No precision	Evaporators, thermical-exchanged, tubular system.	no indication
Sulfazur ATS= (SATS)	Derived of bore and alkanolamines	1,2±0,02	Drinking water	Application for plastic materials, joints, stailness and carbon steel.	Formed a protector film at linterface.



a *b*

Fig. 1. IR- spectres of the compound Kn (a) et ATS (b)

EIS measurements: they were performed using static electrode. The reference electrode is one the saturated calomel one (SCE). The platinum electrode is used a auxiliary electrode. The diagrams of impedance are carried out in potentiostatic–mode at the corrosion potential, using Solartron Schlumberger model (a potentiostat 1286 linked to 1250 frequency response analyser) piloted by the software FRACOM. The amplitude of variation E sinusoidal is ±10 mV, the frequency range varies from 60 kHz to 10 mHz. The experimental results are fitted by the ARIANE software.

Atomic force Microscopy (AFM): these analyses are achieved using (AFM SII SPI 3700) with one constant interaction fashion. It is used to observe the surface after immersion in the solutions in presence of inhibitors.

X-Ray Photoelectron Spectroscopy (XPS): the samples are irradiated with MgK_α. The peak corresponding for C1s (contamination) is at 184.0 eV. The analyses are carried out using VG Escalab MK II. The samples are prepared by the same procedure for the AFM experiments.

Experimental results

Interface polished steel /softened water:

To the contact of water softened, the steel corrodes and the surface is covered by a corrosion product layer that is developed during the immersion time. In a previous work [10], the answer of the interface after a short time of immersion (fig. 2) has been assigned by the presence of HF (high frequency) loop relative of the formation of porous layer. This loop is more developed according to the time (26 and 84 days). The second loop refers to diffusion phenomena. According to the time, the HF loop is more complex (fig. 2,*b*, 2,*c*). It is equivalent to the superposition of the different oxides layers [11]. These layers offer any considerable protection for studied interface because the L_{LF} decreases according immersion time.

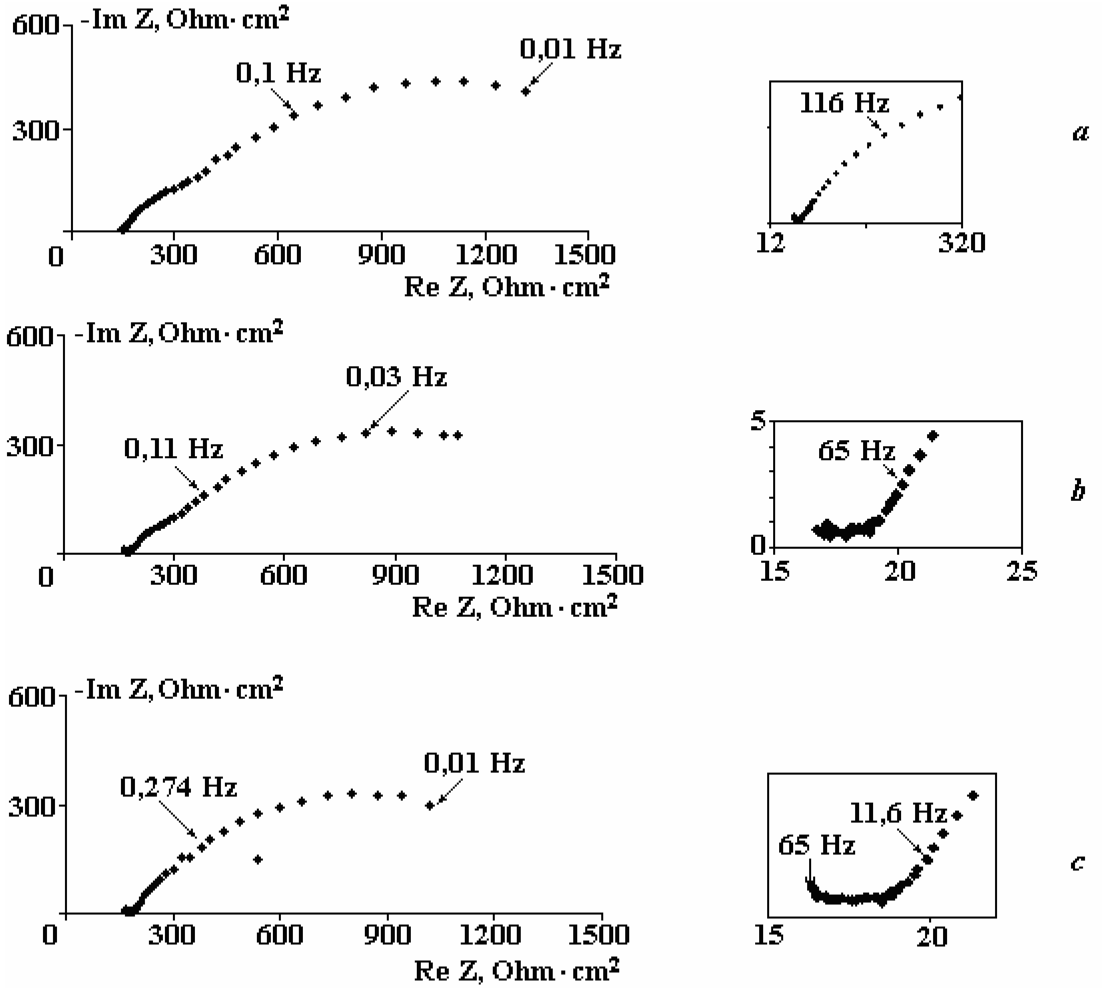
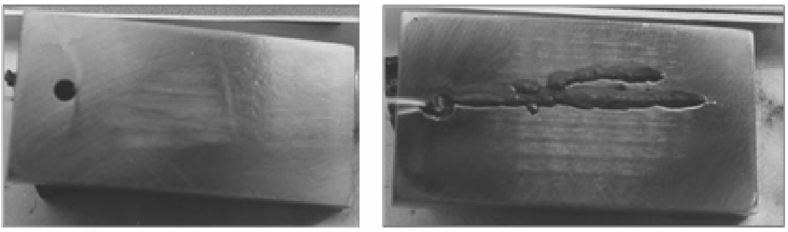


Fig. 2. Evolution of EIS diagrams of the system polished steel / softened water according to the time: (a) 1 day, (b) 26 days, (c) 84 days

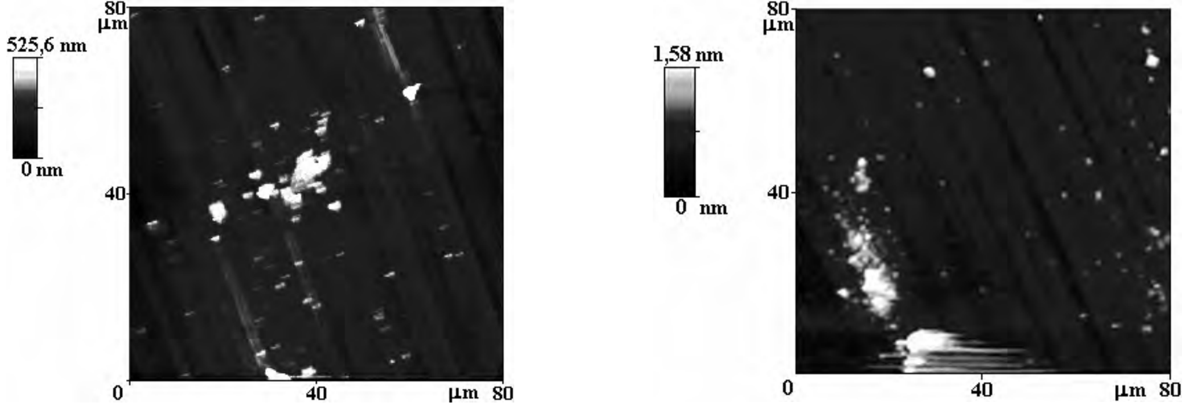
Inhibitory basis of nitrites (Kn):

In presence of Kn, the surface of a specimen remains intact after an immersion of 54 days (fig. 3(*a*)). The observation of the surface state by AFM after 86 days of immersion reveals the presence of an uniform layer, of thickness about 0.8 µm and maximal thickness about 1.58 µm localized in some points (fig. 4 (*a*)). The XPS analyses of the surface corresponding to the Fe, O, C, N, Na transition are carried out (fig. 5(*a*)). The different percentages are presented on the fig. 5(*a*). The presence of N (4.9%) demonstrates that the inhibitor is adsorbed at the surface. The relative spectre in O1s, indicates the presence of an important peak at 533 eV relative to the OH of the water molecule and a little peak at 530 eV corresponding to the oxygen bounding of ferric oxides [11]. In the same way on the spectre of Fe 2p, the relative peak to the oxides of iron (711 eV) is weak, whereas the iron is mostly bound in the metallic Fe suggesting that the film is thin.



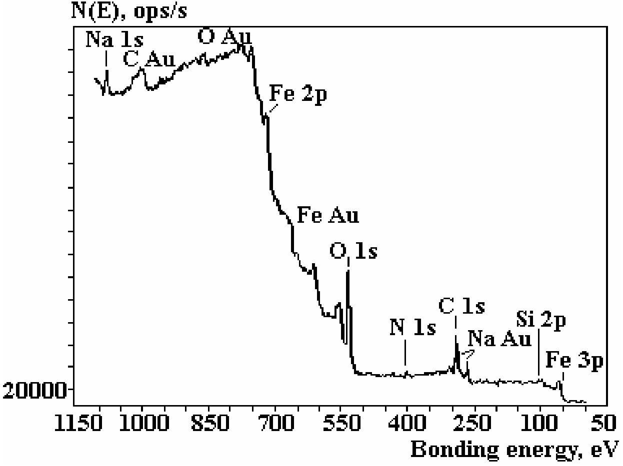
a *b*

Fig. 3. States of the polished surfaces immersed in the softened water + 0,2% Kn during 54 days (a), + 0,75% ATS during 22 days (b)



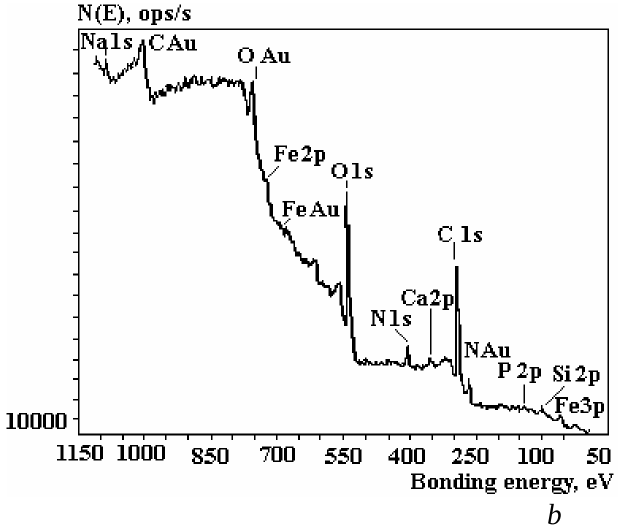
a *b*

Fig. 4. AFM pictures of the surface of the polished steel immersed in the softened water + 0,2% Kn during 86 days (a), + 0,75% ATS during 102 days (b)



Pick	B.energy	Air	%
O 1s	531,05	783,21	41
C 1s	285,2	660,75	34,6
Fe 2p	725,1	192,28	10,1
N 1s	400,15	109,05	4,9
Na 1s	1071,55	204,09	10,7
Si 2p	102,35	37,29	2

a



Pick	B.energy	Air	%
O 1s	532,6	726,82	32,5
C 1s	285,55	1227,26	54,8
Fe 2p	724,7	50,08	2,2
N 1s	400,6	109,05	4,9
Na 1s	1071,9	83,5	3,7
Si 2p	102,25	26,45	1,2
Ca 2p	352,15	6,33	0,3
P 2p	133,9	9,12	0,4

b

Fig. 5. XPS spectra for the polished surface steel immersed in the softened water + 0,2% Kn during 86 days (a), + 0,75% ATS during 102 days (b)

The EIS diagram presents a different form for the interface polite steel / softened water, it is formed by an ascending branch, with a very important L_{LF} which is about 15 kΩ.cm^2 after one day and reaches 150 kΩ·cm^2 after 59 days. This demonstrates an important protective effect (fig. 6).

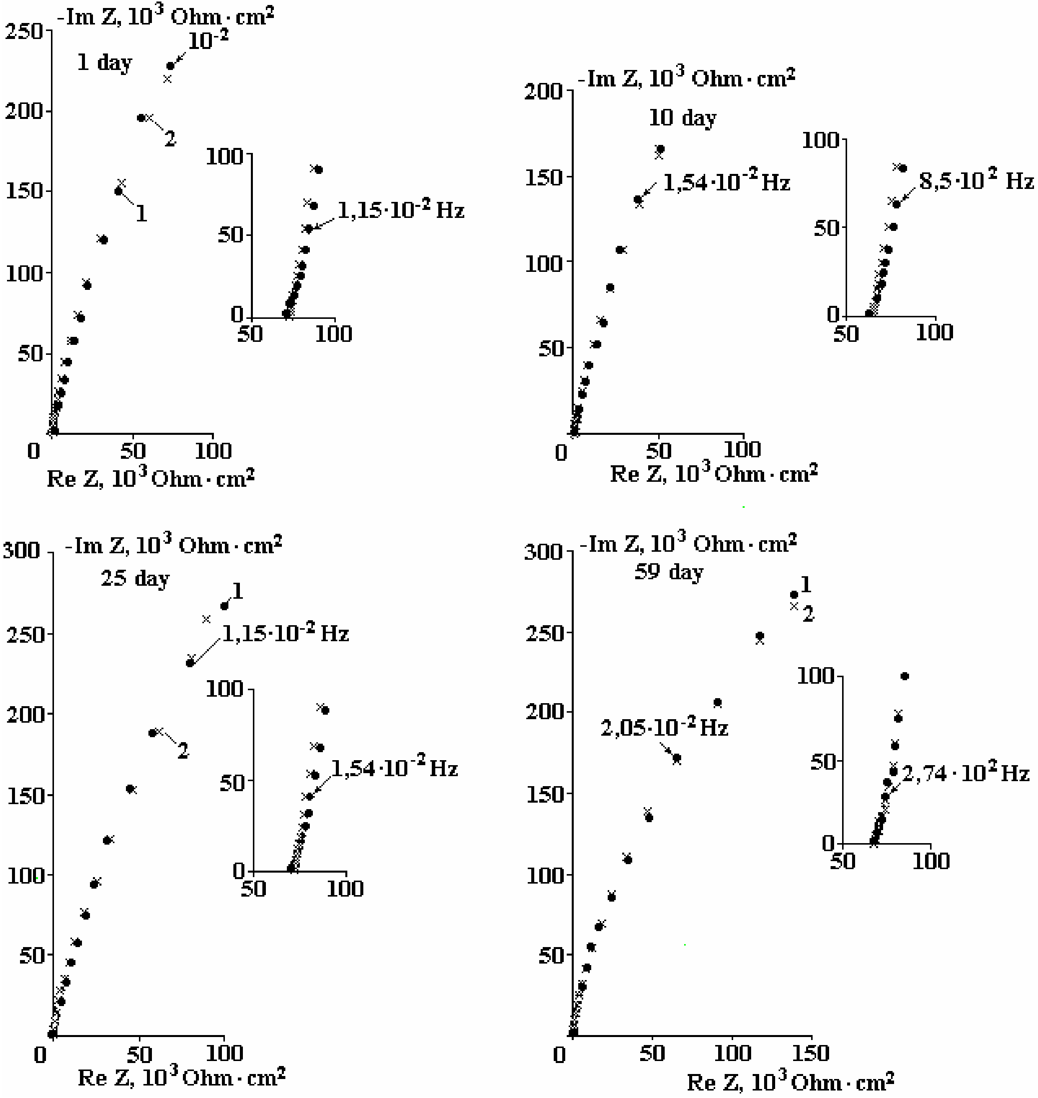


Fig. 6. The evolution of the EIS diagrams of steel impedances in the /eau carbon softened + 0,75% ATS during the time. 1 – exp; 2– adj

The experimental data are fitted with the equivalent electric circuit represented in fig. 7 that is the combination of a resistance – CPE (constant phase element). Because of the non idealist of the interface behaviour, an element of constant phase (CPE1) is used to estimate the double layer capacity [12] in parallel with the transfer resistance localized in the pores or the imperfections of interface layer [13–15].

To confirm the choice of the electric circuit used in the case of the Kn compound, it is interesting to estimate the number of the time constants from the relative slopes to the diagram of the *Ln (-ImZ) = f*(*Ln* (frequency)). This slope is different from the unity which confirms the choice of a CPE instead of an ideal capacity.

An example correspondent 10 days (fig. 8) confirms the presence of only one slope and therefore only one constant of the time (τ =RC).

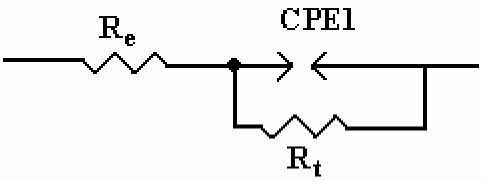


Fig. 7. Equivalent Circuit to the interface polished steel /softened water + 0.2 % Kn, Re: electrolyte resistance; CPE1: CPE relative of the double layer; R_t: transfer resistance

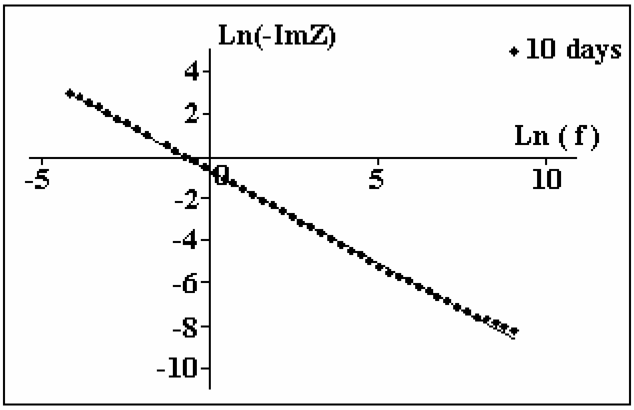


Fig. 8. An example for Ln (-ImZ) = f (Ln (f)) for the Kn compound. y = - 0,8693x – 0,6734

The table 3 summarizes the evolution of the theorical values at the corrosion potential which is obtained and stabilized after 59 days to reach -158 mV/SCE. It translates an effect of nitrites compound on the anodic metallic dissolution.

Table 3. Theorical parameters for EIS diagrams according to polished steel / softened water + 0.2 % Kn

Time(days)	E_{corr} (mV/ECS)	R_e (Ω·cm²)	CPE·10^6/ Ω cm² $s^{-(1-\alpha)}$	α_{theo}	R_t/ 10^4 Ω.cm²	C_0/ µF·cm^{-2}
1	-265	72.58	79.3	0.89	141	48.43
3	-224	68.59	56.6	0.90	101	30.54
10	-198	64.73	62.3	0.89	86	31.54
25	-189	72.41	53.0	0.90	94	28.57
44	-165	79.02	44.0	0.91	90	60.41
59	-158	68.92	41.7	0.91	70	55.25
73	-158	85.01	38.4	0.91	56	57.27

The values of the transfer resistance increase greatly and this behaviour demonstrate the protective effect of the inhibition film. The inhibitor would rather act on the activate sites blocking the anodic reaction; this hypothesis being compatible with the action of the nitrites [1]. However, R_t decreases according to the time, this behaviour can result from the partial deterioration result of the penetration of water following the protective layer [16]. The value on angular α varies from 0,89 to 0,91. The constant Q has the dimension of Ω.cm².$s^{-(1-\alpha)}$ represents the CPE. The value of double layer capacity is determined by the following equation: $C_0 = [Q(R_e^{-1} + R_t^{-1})]^{\frac{1}{\alpha}}$ [16]. The double layer capacity evolutes inversely with the resistance variation. It increases slightly that means a partial alteration of inhibitor film.

Inhibitory basis of alkanolamine (ATS):

The continuous immersion of a steel sample in the softened water added of this inhibitor during 22 days put in evidence a localized corrosion on fixation hole (fig 3-b). The AFM analyses show the recovery of the surface by a homogeneous layer of thickness 262 nm and maximal 525.6 nm after 102 days of immersion (fig. 4,*b*).

The XPS analyses show that it formed an organic layer containing Fe and Na (10%), and rich in N (4.9%) (fig. 5,*b*). The percentage of nitrogen suggests that there is a good recouvrement of the surface by the inhibitor. The relative spectre in O1s, indicates the presence of a peak relative at 530 eV attributed to the oxygen bound to an iron oxide. The Fe 2p spectra present a peak at (711 eV) what is more important for this inhibitor.

The potential of corrosion becomes more anodic according to the time. Their evolution according to the time shows that it is about a chemical adsorption.

The EIS diagrams show a linear part 45° to the very low characteristic frequencies of a very slow diffusion phenomenon that can take place within a layer (fig. 9).

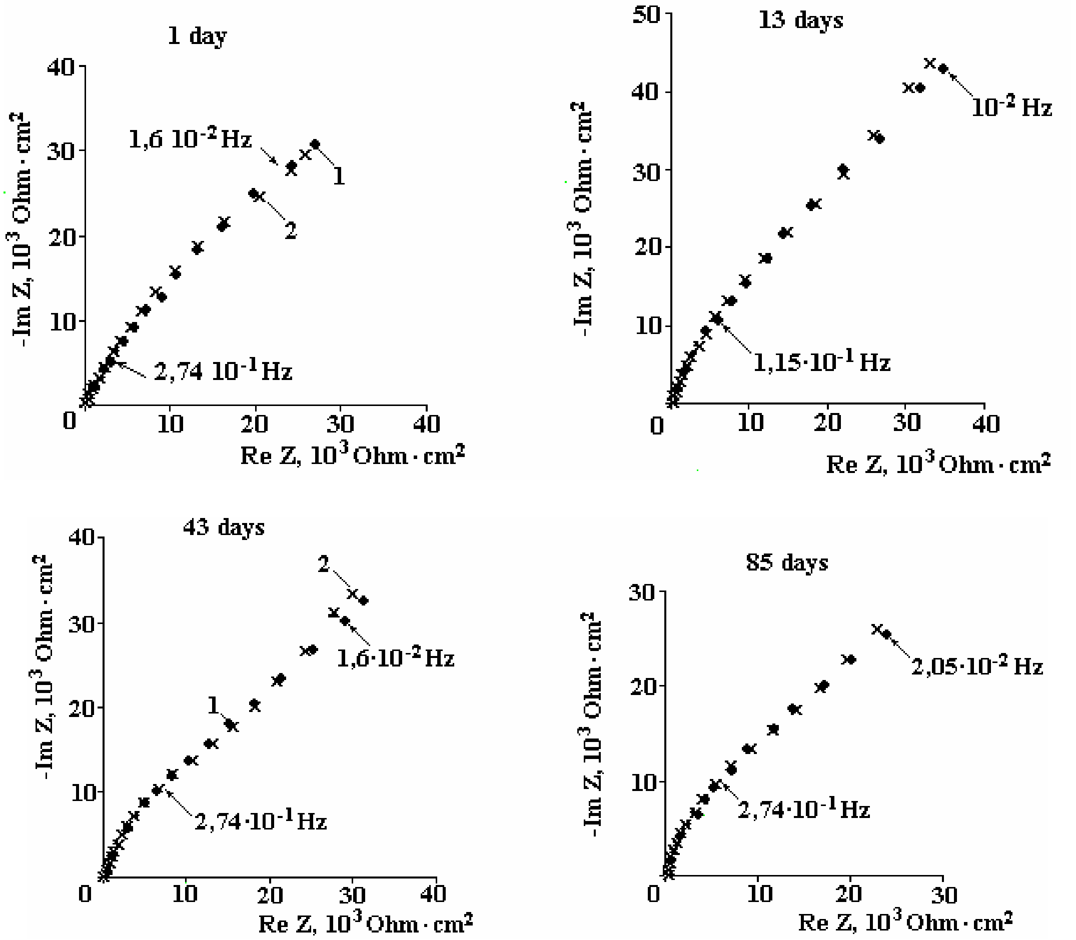


Fig. 9. The evolution of the EIS diagrams of steel impedances in the /eau carbon softened + 0,75% ATS during the time. 1 – exp; 2 – adj

The data of the applied impedance diagrams are fitted by the equivalent electric circuit schematized on the fig. 10. The circuit is formed by a double layer capacity – transfer resistance in parallel, in series with infinite diffusion impedance. The all is in series with an electrolyte resistance.

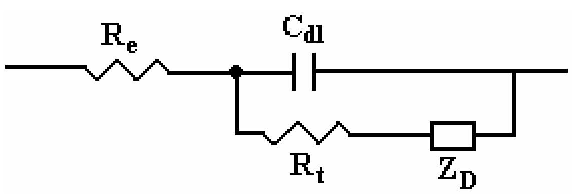


Fig. 10. Equivalent Circuit to the interface polite steel /softened water + 0.75% ATS, Re: electrolyte resistance, C_{dl}: The double layer capacity. R_t: transfer charge resistance, W_1: Z_D: infinite diffusion impedance

Table 4. Theorical parameters of EIS diagrams of polite steel /softened water + 0.75% ATS

Temps (days)	R_e Ω·cm²	R_t/Ω·cm²	C_{dl}/10^{-6} F·cm⁻²	R_d / Ω·cm²	T_d / s
1	102.95	22.05	39.46	9198	2.86
3	107.07	40.83	39.06	14298	5.12
13	102.48	60.88	38.88	11731	5.54
43	103.61	45.84	40.24	10046	1.39
61	111.23	52.44	38.90	10891	1.63
85	97.925	54.22	38.65	10580	1.25

The table 4 gives the theoretical parameters of different elements in the case of the ATS compound. The values of the transfer resistances don't present a considerable variation according to the time while being more important for longer times. The resistance of diffusion is important; it means that it is about diffusion very apparent within the layer formed by the alkanolamines.

Discussion

The two inhibitors seem to act on the same way, while forming a protective layer on steel surface, whereas the answer of the interface showed by electrochemical spectroscopy impedance is different. In the case of the alkanolamines, we have a phenomenon of diffusion, limiting the kinetics of the reaction which is absent in the case of the nitrites.

If we compare the inhibitor efficiency, nitrites increases the polarisation resistance by the formation of a uniform layer with 0.8 µm of thickness. It is more efficient than the layer formed by the ATS compound basis of alkanolamine. However, the properties of the first deteriorate slowly according to the time whereas the one of the second inhibitor has the tendency to stabilize. However, the two inhibitors especially bring a very efficient for the industrial materials when water circulates in closed buckle (case of the intersections). The use of the compound basis of nitrites can present a risk for human being because of its toxicity. The ATS compound seems to favrite a localized corrosion, its use wouldn’t be advised for the industrial works with complex shape (containing corners).

In an industrial environment, the works made by steel often present rough surfaces attacked during the storage, transportation or machining. The surface is a parameter influencing considerably the action of the inhibitor, the same tests have been achieved on raw surface metal presenting to its surface several layers of oxides.

In the fig. 11, it is presented the evolution of the limits low frequencies (R_p) in absence and in presence of the two inhibitors on polite and raw surfaces. Only the compound basis of nitrites (*Kn*) presents a weak protection on the raw surface, but remains very limited comparing to the polite state. No action is noted for the inhibitor basis of alkanolamine (ATS sulfazur).

In order to stand always in the industrial conditions, a cleaning of the raw steel has been achieved by a solution 39% of HCl containing 2 g.L^{-1} of hexamethylene-diamine. The limit low frequencies are more important and the protection is improved, but it remains very weak in relation to a polished surface (fig. 11).

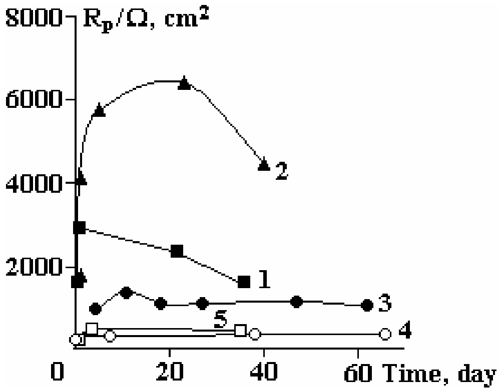


Fig. 11. Evolution of the limits low frequencies (Rp) according to the time. 1 – raw (+Kn); 2 – scoured (+Kn); 3 – polished steel; 4 – raw steel; 5 – raw (+ATS)

Conclusion

The protection of the surface steel offered by two commercial inhibitors basis of nitrites and alkanolmines in aqueous environment (softened water) has been studied by electrochemical impedance spectroscopy supported by analytic methods. The two inhibitors protect the polished steel interface respectively by the formation of protective layers respectively with 0.8 µm and 0.26 µm of thickness.

In the case of alkanolamines, the reaction kinetic is limited by the diffusion following the infinite layer. However, the charge transfer is the phenomena what has the low rate in the reaction.

The protection gotten by the two inhibitors is strongly affected to the state of surface, raw surface interferes with the action of the inhibitors.

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Summary

The protection against the corrosion of the carbon steel in aqueous environment by commercial inhibitors, based of nitrite and alkanolamine, has been studied by electrochemical impedance spectroscopy (EIS) and several analytic methods. An inhibitor's efficiency has been determined with the two compounds on polished surface in presence of softened water. The results show that the two inhibitors act by the formation of protective layer on interface steel/electrolyte but the efficiency is more important in the case of the nitrite compound thanks to the formation of film with thickness estimated by Atomic force microscopy (AFM) at 0.8 µm after 102 days of immersion. In the case of the nitrites, the inhibitor film is a porous layer, weak conductor and presents a considerable increase of the charge transfer resistance with time. This is a result of an interest protection of the surface against corrosion. The low frequencies limit (L_{LF}) reaches about 150 kΩ.cm² after 59 days of immersion. In the case of the alkanolamine, XPS (X-Rray Spectroscopy) show that the film formed is richer of Fe ions but is offered a considerable protection of the interface, its thickness is about 0.26 µm and L_{LF} reaches about 35.5 kΩ.cm² after 61 days of immersion. The influence of surface state is discussed in this paper, in fact on raw surface steel, no inhibitor efficiency is observed. A few protections are given with a crude surface in contact with water softened in presence of the nitrite compound.