Inhibitory protection of copper in acetic acid solutions

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Abstract

The kinetics of copper corrosion and the effect of convection on this process were studied in freely aerated acetic acid solutions. The copper corrosion rate in this medium does not depend significantly on the duration of contact between copper and the corrosive medium (1-20 days)and H₃CCOOH concentration (0.25-4 M). There are no fundamental differences in the corrosivity of this medium toward copper upon transition from static to dynamic experimental conditions. The corrosivity of H₃CCOOH solutions toward metallic copper is enhanced in the presence of the corrosion product, Cu(II) acetate. This effect is especially pronounced if metallic copper contacts a dynamic corrosive medium. A triazole derivative, IFKhAN-92, is recommended for copper protection in freely aerated H₃CCOOH solutions. The efficiency of this compound does not depend considerably on the duration of contact between the metal and the corrosive medium, H₃CCOOH content, and hydrodynamic characteristics of the solution. An important feature of the IFKhAN-92 inhibitor is that its protective ability toward metallic copper is preserved even if Cu(II) acetate is accumulated in the corrosive medium, which is true not only in static but also in dynamic media. The dependence of the copper corrosion rate on the convective factor in freely aerated 2 M H₃CCOOH + 0.05 M Cu(H₃CCOO)₂, both in the absence and in the presence of the corrosion inhibitor, is formally described by the equation $k=a+b\cdot n^{1/2}$, where a and b are empirical parameters and n is the rotation frequency of the magnetic stirrer. The addition of IFKhAN-92 decreases the parameters a and b in this equation.

Keywords: corrosion, corrosion inhibitors, copper, acetic acid, copper(II) acetate, triazole.

Received: January 6, 2021. Published: March 2, 2021

doi: <u>10.17675/2305-6894-2020-10-1-17</u>

Introduction

Acetic acid solutions, alongside with hydrochloric and sulfuric acid solutions, are process liquids for removal of mineral impurities and corrosion products from metal surfaces [1]. An advantage of acetic acid in comparison to HCl and H_2SO_4 is that its corrosivity toward the most important engineering materials, such as steels, is low. This allows using them in industry, as opposed to inorganic acids, without additional inhibitor protection [2]. Technological equipment that often contacts acidic solutions is partly or wholly made of copper or its alloys. The corrosion stability of copper in HCl and H_2SO_4 solutions and the

possibility of its inhibitor protection in these media are widely discussed [3-15]. In contrast, the stability of copper in H₃CCOOH solutions and the possible ways of its corrosion protection are not covered in the available literature. Our earlier studies on the corrosion ability of low carbon steel in H₃CCOOH solutions showed the possibility of its efficient protection in this medium by formulations based on a triazole derivative, the IFKhAN-92 inhibitor [16]. The result obtained allows one to hope that efficient protection of copper in H₃CCOOH solutions by this inhibitor is possible.

It should be noted that no direct reaction is possible between metallic copper and acetic acid. Copper corrosion occurs only in the presence of atmospheric oxygen in the corrosive medium that acts as its oxidant:

$$2Cu + O_2 + 4H_3CCOOH = 2Cu(H_3CCOO)_2 + 2H_2O$$

It is reasonable to assume a multistage mechanism of this corrosion process. It is important to point out that the final corrosion product, Cu(II) cations, are also involved in metal corrosion. As Cu(II) cations are accumulated in the solution, their reaction with metallic copper becomes possible [17]:

$$Cu^{2+} + Cu = 2Cu^{+}$$

In turn, the Cu(I) cations formed in the solution will be reoxidized by oxygen to Cu(II) cations. Altogether, this effect must lead in time to acceleration of copper corrosion. It is known that in the case of acid solutions containing additional oxidants (oxygen, metal cations), participation of the latter in metal corrosion causes acceleration of the cathodic process. Besides, reduction of such additional oxidants occurs under diffusion control [18]. As oxygen and Cu(II) cations are the oxidants in the system under consideration, one might make the assumption that the corrosion process on the whole is controlled by diffusion and its rate must considerably depend on the hydrodynamic parameters of the corrosive medium.

In view of this, it appears expedient to study the regularities of copper corrosion in H₃CCOOH solutions and also to consider the possibility of its protection by inhibitors. The corrosion inhibitor studied is IFKhAN-92, while the compound used as a reference is the commercial cationic surfactant, Catamine AB (alkylbenzyldimethylammonium chloride $[C_nH_{2n+1}N^+(CH_3)_2CH_2C_6H_5]Cl^-$, where n=10-18). The factors to be assessed include the duration of corrosion tests, H₃CCOOH concentration, the presence of the corrosion product $[Cu(H_3CCOO)_2]$, the presence of corrosion inhibitors, and convection that may affect copper corrosion in the medium in question.

Experimental

The corrosion rate of M1 copper (up to 0.005 Fe; up to 0.002 Ni; up to 0.004 S; up to 0.002 As; up to 0.005 Pb; up to 0.004 Zn; up to 0.05 O; up to 0.002 Sb; up to 0.001 Bi; up to 0.002 Sn; Cu (99.90)) in H₃CCOOH solutions was determined from the sample mass loss (at least three samples per point) using the sample size of 50.0 mm × 30.0 mm × 1.0 mm per 165 ml of the acid solution at a temperature of $t=20\pm2^{\circ}$ C. Prior to an experiment, the samples were

cleaned on P600 sandpaper and degreased with acetone. The experiment duration was 1-20 days.

The effect of convection on the copper corrosion rate was studied in H₃CCOOH solutions stirred with a magnetic stirrer at rotation rates of n = 0, 250, 420, and 750 rpm.

The efficiency of inhibitors was estimated by protection degrees $Z = [(k_0 - k_{in})/k_0] \cdot 100\%$, where k_0 and k_{in} are the corrosion rates in the background solution and in a solution with an additive being studied.

70% H₃CCOOH (GOST R 55982-2014), copper(II) acetate, and distilled water were used for solution preparation. The basic concentration of IFKhAN-92 and Catamine AB was $C_{in} = 0.5$ mM. As the solubility of IFKhAN-92 in H₃CCOOH solutions is low, it was added in the form of a solution in ethanol.

Copper(II) acetate was obtained by dissolution of basic copper(II) carbonate in 70% H_3CCOOH . Basic copper(II) carbonate was obtained by precipitation with sodium hydrocarbonate ("chemically pure" grade) from copper(II) sulfate ("pure" grade) solution followed by long-term rinsing of the precipitate with distilled water.

Results and Discussion

Copper corrosion in 2 M H₃CCOOH occurs relatively slowly (Table 1). Note that the sample mass loss (Δm) in the course of long-term corrosion tests (20 days) reaches a significant value of 37 g/m². The mean copper corrosion rate *k* weakly depends on the duration of exposure of metallic samples to the corrosive medium. The maximum *k* value was obtained after 2 days of tests: 0.096 g/(m²·h). An increase in the test duration results in a decrease in the *k* of copper. The content of H₃CCOOH in a solution weakly affects the *k* value of copper (Table 2); *e.g.*, its 16-fold increase results only in 1.3-fold acceleration of copper corrosion. The result obtained is in good agreement with the fact that copper is oxidized by the air oxygen dissolved in a corrosive medium studied whose content is similar in these solutions, rather than by acetic acid. Accumulation of copper(II) acetate in the corrosive medium enhances its corrosivity somewhat (Table 3). In fact, the *k* value of copper grows 1.2-fold in the presence of 0.05 M Cu(H₃CCOO)₂, but a further increase in the content of this salt in the solution does not result in corrosion acceleration.

The above results on the copper corrosion in H_3CCOOH solutions correspond to static conditions that are rarely encountered under industrial conditions. More often, metals contact a stream of a corrosive medium. In ceases where the corrosion process is controlled by diffusion limitations, this may result in a considerable acceleration of metal degradation.

In naturally aerated 2 M H₃CCOOH, the effect of forced convection (n=750 rpm) on corrosion is minor. The corrosion loss gain is as small as 38% (Table 4). In contrast, the effect of forced convection on k of copper in naturally aerated 2 M H₃CCOOH + 0.05 M Cu(H₃CCOO)₂ is significant (Table 4, Figure 1). The k values of copper in a static and dynamic (n=750 rpm) medium differ by a factor of 4.0. In freely aerated 2 M H₃CCOOH + 0.05 M Cu(H₃CCOO)₂, copper corrosion occurs due to the presence of two oxidants in the corrosive medium: molecular oxygen and Cu(II) cations. It seems of interest to establish the

effective copper corrosion rates in this medium related solely to the presence of Cu(II) cations by calculating them as a difference in the *k* of copper in aerated acid solutions in the presence and in the absence of 0.05 M Cu(H₃CCOO)₂. This approach is correct on the assumption of independent corrosion processes on copper caused by the presence of molecular oxygen and Cu(H₃CCOO)₂ in an H₃CCOOH solution. The effective *k* of copper due only to the presence of Cu(II) cations is sensitive to convective effects. The effective *k* values of copper in static and dynamic (*n*=750 rpm) media differ 8.5-fold.

Corrosion process	Exposure time, days							
parameter	1	2	4	8	13	20		
Without an inhibitor								
$\Delta m, g/m^2$	1.4	4.6	8.9	17	23	37		
k, g/(m ² ·h)	0.058	0.096	0.093	0.089	0.074	0.077		
	0.5 mM Catamine AB							
Δm , g/m ²	0.34	0.67	0.99	2.2	2.6	6.2		
k, g/(m ² ·h)	0.014	0.014	0.010	0.011	0.008	0.013		
Z, %	75.9	85.4	89.2	87.4	89.2	83.1		
0.5 mM IFKhAN-92								
Δm , g/m ²	0.17	0.41	0.56	1.6	1.9	4.4		
k, g/(m ² ·h)	0.007	0.009	0.006	0.008	0.006	0.009		
Z, %	87.9	90.6	93.5	91.0	91.2	88.3		

Table 1. Effect of the duration of exposure of copper samples in 2 M H₃CCOOH ($20\pm2^{\circ}$ C) on the mass loss (Δm), corrosion rate (*k*), and degree of metal protection by the inhibitor (*Z*).

Analysis of the dependence of the copper corrosion rate on the magnetic stirrer rotation frequency in freely aerated 2 M H₃CCOOH + 0.05 M Cu(H₃CCOO)₂ (Table 5, Figure 1) showed that, formally, it is fairly described by the equation: $k=a+b\cdot n^{1/2}$. The form of this equation is typical of concurrent processes under kinetic and diffusion control [19]. Parameter *a* characterizes the kinetic component, while *b* corresponds to diffusion. In our system, however, it is more correct to relate parameter *a* to metal corrosion due to natural convection of the corrosive medium in long-term static tests.

Thus, H₃CCOOH solutions, especially in the absence of prolonged contact with copper, are relatively weakly corrosive to the latter. This is typical of both static and dynamic corrosion conditions. Under static conditions, accumulation of the corrosion product, Cu(H₃CCOO)₂, in the acid also fails to affect copper corrosion. Meanwhile, accumulation of Cu(II) cations in acetate solutions together with dynamic corrosion conditions is capable of considerably enhancing the solution corrosivity, which is extremely undesirable.

Corrosion process	C(H ₃ CCOOH), M							
parameter	0.25	0.5	1	2	4			
Without an inhibitor								
k, g/(m ² ·h)	0.073	0.075	0.089	0.089	0.094			
	0.5 mM Catamine AB							
k, g/(m ² ·h)	0.008	0.010	0.010	0.011	0.008			
Z, %	89.0	86.7	88.8	87.4	91.5			
0.5 mM IFKhAN-92								
k, g/(m ² ·h)	0.013	0.009	0.009	0.008	0.005			
<i>Z</i> , %	82.2	88.0	89.9	91.0	94.4			

Table 2. Effect of the concentration of H₃CCOOH ($20\pm 2^{\circ}$ C) on the rate of copper corrosion (*k*) and degree of metal protection by the inhibitor (*Z*) based on the data of 8-day tests.

Table 3. Effect of the concentration of copper(II) acetate on the rate of copper corrosion in 2 M H₃CCOOH $(20\pm2^{\circ}C)$ based on the data of 4-day tests.

Corrosion process	$C(Cu(H_3CCOO)_2), M$							
parameter	0	0.025	0.05	0.1				
	Without an inhibitor							
k, g/(m ² ·h)	0.093	0.100	0.110	0.110				
0.5 mM Catamine AB								
k, g/(m ² ·h)	0.010	0.014	0.019	0.041				
<i>Z</i> , %	89.2	86.0	82.7	62.7				
0.5 mM IFKhAN-92								
k, g/(m ² ·h)	0.006	0.007	0.007	0.010				
<i>Z</i> , %	93.5	93.0	93.6	90.9				

According to the data of 8-day tests, the Catamine AB additive ($C_{in}=0.05-5$ mM) in 2 M H₃CCOOH inhibits copper corrosion 4.5–8.9 fold (Table 6). At $C_{in} \ge 0.1$ mM, Z > 80%, while at $C_{in} \ge 1$ mM, Z is independent of the inhibitor content. A similar amount of IFKhAN-92 lowers the *k* of copper 5.2–15 fold. In the C_{in} range studied, Z > 80%, while at $C_{in} \ge 1$ mM, Z is independent of IFKhAN-92.

Compain	Without inhibitor		0.5 mM Catamine AB		0.5 mM IFKhAN-92			
process	Rotation rate of the magnetic stirrer, rpm							
parameter —	0	750	0	750	0	750		
		2 M H ₃	CCOOH (free a	eration)				
k, g/(m ² ·h)	0.058	0.080	0.014	0.029	0.007	0.014		
Z, %	-	-	75.9	63.8	87.9	82.5		
	2 M	$H_3CCOOH + 0$.05 M Cu(H ₃ CC	$COO)_2$ (free aera	ation)			
k, g/(m ² ·h)	0.092	0.370	0.032	0.051	0.014	0.029		
Z, %	-	-	65.2	86.2	84.8	92.2		
$2 \text{ M H}_3\text{CCOOH} + 0.05 \text{ M Cu}(\text{H}_3\text{CCOO})_2^*$								
$k, g/(m^2 \cdot h)$	0.034	0.290	0.018	0.022	0.007	0.015		
Z, %	-	-	47.1	92.4	79.4	94.8		

Table 4. Effect of the convective factor on the copper corrosion in 2 M H₃CCOOH ($20\pm2^{\circ}$ C) based on one-day tests.

*Effective contribution of the 0.05 M Cu(H₃CCOO)₂ addition to the corrosion process.



Figure 1. Plots of the copper corrosion rate in 2 M H₃CCOOH ($20\pm2^{\circ}$ C) based on the data of one-day tests *versus* the frequency of solution stirring by a magnetic stirrer. 1 – without an inhibitor, 2 – 0.5 mM Catamine AB, 3 – 0.5 mM IFKhAN-92.

Both studied inhibitors retain their protective effect in 2 M H₃CCOOH for at least 20 days (Table 1). The addition of 0.5 mM Catamine AB slows down copper corrosion by a factor of 4.1-9.3, while IFKhAN-92 inhibits it by a factor of 8.3-16, *i.e.*, more strongly. Judging by the sample mass loss with time in the presence of both inhibitors, copper

corrosion is the slowest in the time range of 8-13 days, after which the process accelerates. Both organic compounds studied inhibit copper corrosion in a wide range of $C(H_3CCOOH) = 0.25-4$ M (Table 2). With the exception of the most dilute solutions, the protective effect of IFKhAN-92 is better than that of Catamine AB.

Table 5. Parameters *a* and *b* of the kinetic equation $k = a + b \cdot n^{1/2}$ for copper corrosion in 2 M H₃CCOOH + 0.05 M Cu(H₃CCOO)₂ (20±2°C) based on 1-day tests.

Inhibitor	$a, g/(m^2 \cdot h)$	$b, g/(m^2 \cdot h \cdot rpm^{1/2})$
Without an inhibitor	0.082	0.0098
0.5 mM Catamine AB	0.032	0.0007
0.5 mM IFKhAN-92	0.014	0.0005

Table 6.* Effect of the inhibitor concentration on the copper corrosion rate in 2 M H₃CCOOH ($20\pm2^{\circ}C$) based on 8-day tests.

Corrosion process	$C_{ m in}, m mM$						
parameter –	0.05	0.1	0.5	1	5		
		Catamine	AB				
k, g/(m ² ·h)	0.020	0.017	0.011	0.010	0.010		
<i>Z</i> , %	77.5	80.9	87.4	89.2	89.2		
IFKhAN-92							
k, g/(m ² ·h)	0.017	0.015	0.008	0.006	0.006		
<i>Z</i> , %	80.9	83.1	91	93.5	93.5		

*The copper corrosion rate in 2 M H₃CCOOH ($20\pm2^{\circ}$ C) is 0.089 g/($m^{2}\cdot$ h).

In a static corrosive medium, the presence of $Cu(H_3CCOO)_2$ has an adverse effect on the copper protection by Catamine AB (Table 3). The presence of 0.1 M Cu(II) enhances the *k* of copper by a factor of 4.1 compared to the medium free of Cu(H₃CCOO)₂. In contrast, IFKhAN-92 accelerates corrosion only 1.7-fold under similar conditions. This is rather an interesting result, as it is known that the presence of metal cations with oxidizing properties in a corrosive medium causes a significant weakening of the protective effect of acid corrosion inhibitors [20]. This regularity is clearly demonstrated by Catamine AB in the medium we were studying. In contrast, the effect of IFKhAN-92 is rather stable in the presence of Cu(II) cations in the corrosive medium. Earlier [21, 22], the unique ability of IFKhAN-based composite inhibitors to preserve their protective effect was shown in the case of mild steel corrosion in acid media containing Fe(III) salts. It is important to understand whether efficient copper corrosion inhibition is maintained in H₃CCOOH solutions on transition from static corrosion to corrosion under dynamic conditions. Indeed, the *k* values of copper in freely aerated 2 M H₃CCOOH in the presence of 0.5 mM Catamine AB under static conditions and under dynamic (n=750 rpm) conditions differ 2.1-fold (Table 4). In this case, the protective effect of the inhibitor decreases to 63.8%. In the case of 0.5 mM IFKhAN-92, corrosion is also accelerated 2.0-fold, but the *Z* value remains much higher (82.5%), since the *k* of copper is considerably lower in the presence of this compound.

The addition of Catamine AB demonstrates a poorer result than that of IFKhAN-92 in freely aerated 2 M H₃CCOOH + 0.05 M Cu(H₃CCOO)₂. Interestingly, corrosion is accelerated in the presence of both inhibitors under dynamic conditions (n=750 rpm) in comparison with the data of static tests. Nevertheless, on the whole, the protective effect is better under dynamic conditions. This effect is due to a significant acceleration of copper corrosion in the background medium in a stirred solution. Similar regularities are also typical of the effective contribution of Cu(II) cations to the corrosion process.

In inhibited media, the dependences of the copper corrosion rate on the magnetic stirrer rotation rate in freely aerated 2 M H₃CCOOH + 0.05 M Cu(H₃CCOO)₂, like in the background medium, are satisfactorily described by the equation: $k=a+b\cdot n^{1/2}$ (Table 5, Figure 1). In the presence of 0.5 mM Catamine AB, parameter *a* is 2.6 times smaller and parameter *b* is 14 times smaller. In the presence of 0.5 mM IFKhAN-92, these parameters are even smaller: they decrease 5.9- and 20-fold.

Thus, the IFKhAN inhibitor efficiently slows down copper corrosion in H₃CCOOH solutions. It retains its protective effect if the corrosion product, Cu(H₃CCOO)₂, is accumulated in H₃CCOOH solutions. It is important to note that IFKhAN-92 protects copper both in static and dynamic corrosive media. Under all experimental conditions, the IFKhAN-92 inhibitor provides Z>80%, while the largest *k* of copper observed under extremely severe corrosion conditions (0.05 M Cu(H₃CCOO)₂, *n*=750 rpm) is as small as 0.029 g/(m²·h). Under similar conditions, Catamine AB is inferior to IFKhAN-92 as regards the inhibition of copper corrosion.

The results obtained are important from the practical point of view, since they open new prospects for using H₃CCOOH solutions where they potentially can come into contact with metallic copper. The corrosion rate in H₃CCOOH solutions is rather low, k=0.058-0.094 g/(m²·h), but accumulation of the corrosion product, Cu(H₃CCOO)₂, combined with forced convection of the medium may cause its increase to 0.370 g/(m²·h). If 0.5 mM IFKhAN-92 is used for copper protection, then, irrespective of the hydrodynamic mode in an H₃CCOOH solution and the presence of Cu(H₃CCOO)₂, the *k* value for copper is 0.005– 0.029 g/(m²·h), which is a good result.

It is important to understand the origin of the higher inhibitor effect of the IFKhAN-92 triazole derivative in comparison with Catamine AB. They largely due to the unique regularities of the mechanism of the protective action of triazoles [23]. These compounds can be chemosorbed on the surface of a metal being protected [24–27] followed by the

formation of polymolecular protective surface layers that are extremely efficient in corrosion inhibition [28].

The results presented in this paper deal with the specifics of the corrosion behavior of copper in acetic acid media and the effect of corrosion inhibitors on this process. The discussion of the reasons for the observed regularities of the corrosion behavior of copper is tentative and requires additional studies involving electrochemical and physicochemical methods. Their results will be presented in our further papers on this subject.

Conclusions

- 1. The copper corrosion rate in freely aerated acetic acid solutions weakly depends on the duration of contact between copper and the corrosive medium and on the concentration of H_3CCOOH . Moreover, there is no fundamental difference in the corrosivity of these solutions toward copper on transition from static to dynamic conditions.
- 2. The corrosivity of H₃CCOOH solutions toward copper is enhanced in the presence of Cu(II) acetate. This effect is especially pronounced in the case of contact between copper and a flowing corrosive medium.
- 3. The IFKhAN-92 inhibitor can be used for copper protection in freely aerated H₃CCOOH solutions. The efficiency of this compound does not depend considerably on the duration of contact between the metal and the corrosive medium, the H₃CCOOH content, and the hydrodynamic parameters. An important feature of the IFKhAN-92 inhibitor is that it maintains its protective ability toward copper even where Cu(II) acetate is accumulated in the corrosive medium. This effect is observed not only in static but also in dynamic media.
- 4. The protective effect of IFKhAN-92 toward copper in H_3CCOOH solutions is much stronger than that of Catamine AB, a well-known inhibitor of acid metal corrosion.
- 5. The dependence of the copper corrosion rate on the convective factor in freely aerated 2 M H₃CCOOH + 0.05 M Cu(H₃CCOO)₂, both in the absence and in the presence of corrosion inhibitors, is formally described by the equation: $k=a+b\cdot n^{1/2}$, where *n* is the rotation frequency of the magnetic stirrer. The addition of the inhibitors studied, especially IFKhAN-92, decrease the parameters *a* and *b* in this equation.

Acknowledgements

The study was carried out under the Fundamental Scientific Research Program of the State Academies of Sciences for 2013–2020: "Development of the fundamental scientific foundations of the protective effect of metal corrosion inhibitors in gas and condensed media, nanocomposites, paints and conversion coatings" (State registration number AAAA-A18-118121090043-0).

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