Inhibition of magnesium corrosion by triazoles

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Abstract

The inhibitive action of some azoles (1,2,4-triazole, 1,2,3-benzotriazole, 5-chlorobenzo-triazole, and IFKhAN-92 corrosion inhibitor) on the corrosion of magnesium was investigated in aqueous buffer solutions and humid atmosphere. Increasing the hydrophobicity and decreasing the pK_a of NH-acids enhance the protection of Mg by triazoles, that is why 5-chlorobenzotriazole and IFKhAN-92 – a mixture of substituted triazoles – are more efficient inhibitors. Small additions of dioctylphosphate increase the protection of Mg in aqueous solution by IFKhAN-92 inhibitor, and addition of trialkoxysilane to the mixed inhibitor allows one to enhance the protection of Mg in a humid atmosphere.

Introduction

Due to the increase in the interest in Mg alloys not only in aerospace but also in many other industries in the past decades, protection of these alloys from corrosion deserves special attention. It is well known that while Mg alloys have many technological advantages over other alloys, including very low specific density, high specific strength and heat capacity, as well as excellent machinability, they are markedly inferior to aluminum alloys in corrosion resistance, especially in chloride-containing environments. The standard electrode potential of magnesium is $E^0_{Mg/Mg^{2+}} = -2.37$ V, which itself already indicates its high thermodynamic tendency to oxidation and corrosion. For this reason, it becomes the anode even in contact with Al and Zn, not to mention the less electronegative metals. Not surprisingly, the corrosion rate of technical Mg (99.9%) is hundreds of times larger than that of the high purity metal (99.99%) due to harmful effects of Fe, Ni and Cu impurities [1]. The corrosion rate of Mg in wet but clean atmosphere is low due to a protective layer of its hydroxide formed by slow hydration of magnesium oxide [2].

The traditional methods of Mg alloy corrosion protection (chromate treatment and paint coatings containing chromate pigments or inhibitors) have been facing serious environmental objections in recent years. Furthermore, even chromate conversion coatings (CC) on technical Mg and alloys do not provide long term protection, especially in industrial atmosphere, where corrosion, *e.g.*, on passivated ML 5 alloy, already appears

after 20 days. In this regard, development of efficient protective means for Mg and its alloys is particularly relevant.

Attempts to create a protective film on Mg and its alloys by phosphate treatment, including electrochemical methods, were made a long time ago [3]. However, little success was achieved, despite the fact that Mg underwent phosphatizing more easily than Al. In some cases it was possible to obtain conversion coatings with a better protective effect than after Mg treatment with selenious acid or HF, however, according to M.A. Timonova, they failed to surpass the films obtained by chromate treatment.

As early as in 1910, V.A. Kistyakovsky observed Mg passivation in alkaline solutions, and later it was found [4] that its corrosion rate decreased with increasing pH and corrosion nearly ceased at pH 11−12. However, in alkaline media, small additions of chloride, sometimes a few mg/l, can disrupt the passive state of alloys.

Some of oxide coatings obtained on Mg alloys by various methods are formed in chromate-free solutions. It is essential that despite the variety of protection methods, the most attention of researchers, according to patent literature [5], belongs to CC (41% of all patented technologies). This is due to their excellent adhesion to the metal substrate and low cost. A detailed review of these methods is given in [5−8]. Besides the already noted type of CC obtained in phosphating compositions that contain not only cations of various metals but also phosphonate corrosion inhibitors, attempts to obtain CC in molybdate, vanadate, and tartrate solutions should be noted. The use of silanes in this process is noteworthy. According to [9], addition of a silane to a vanadate solution increased not only the adhesion of the paint to the CC, but also protection against corrosion in a 5% salt fog chamber.

Development of electrochemical anodizing of Mg alloys as a method for application of functional and protective coatings also continued in recent years. For example, plasma electrolytic oxidation (PEO) makes it possible to obtain thicker coatings on Mg alloys. Addition of TiO_2 nanoparticles to the electrolyte or filling the coating with tetrafluoropolyethylene enhances its protective properties and can improve its durability and provide super-hydrophobization of the surface [6].

However, many protective coatings suffer from the same drawback: they have defects (cracks, pores, *etc*.) which are not only present inherently, but also appear in time upon exposure to the environment or upon destruction of the coating. The problem of "self-healing" of protective coatings for Mg alloys, as well as other metals, is very serious if chromates are no longer used. As correctly observed in [10], it can be solved by incorporation of Mg corrosion inhibitors into the coating, and the most efficient ones should be selected for this purpose.

It is easy to notice that success in the application of chromate inhibitors discouraged for a long time the interest in other corrosion inhibitors for Mg. Recently, it was noted that corrosion inhibitors of Mg alloys undeservedly received little attention [11, 12]. A good overview of studies on this subject is given in the article by Frignani *et al*. [12]. Apparently, sodium dodecylbenzenesulfonate is the best-studied nontoxic organic

corrosion inhibitor for Mg. It is not only very efficient in the protection of Mg alloys, but also demonstrates synergy in protection of AZ91D alloy with 8-hydroxyquinoline [13], which is known for its ability to form sparingly soluble complexes with Mg^{2+} [14].

It is known that organic inhibitors are able to create thin or even ultrathin protective coatings on a metal from aqueous solutions [15−17]. Unfortunately, almost no systematic studies of organic inhibitors and creation of nano-sized and thin (≤2 μm) coatings on Mg on their basis have been carried out. Therefore, this paper presents some new options for the protection of technical Mg in aqueous solutions by compounds of triazole class that are often efficient corrosion inhibitors for ferrous and non-ferrous metals [17, 18].

Experimental

Corrosion and electrochemical tests were conducted using samples of technical Mg (Mg-90) with the composition: Mg − 99.9%, Fe − up to 0.04%, Mn − up to 0.03%, Al − up to 0.02%, Ni − up to 0.001%, Cu − up to 0.004%, Si − up to 0.009%, Cl − up to 0.005%. Electrochemical measurements were carried out using cylindrical electrodes with a working surface area of 0.72 cm^2 mounted in epoxy resin. Borate buffer solution with pH 7.36 was mainly used as the background solution, but borate solution with pH 9.2 was also used in some experiments. Polarization curves of Mg were recorded in a glass cell with separate electrode spaces using a PI 50-1.1 potentiostat. Potentials (*E*) of Mg were measured relative to a silver chloride electrode and converted to the normal hydrogen scale. A platinum auxiliary electrode was used. Before experiments, the electrodes were polished and degreased with acetone.

1,2,4-Triazole (TA), 1,2,3-benzotriazole (BTA), 5-chloro-benzotriazole (Cl-BTA), and IFKhAN-92 inhibitor ware studied as Mg corrosion inhibitors. Working solutions were prepared by dissolving a triazole in water (TA, BTA) or in isopranol (Cl-BTA, IFKhAN-92) with continuous stirring for 30 min.

A triazole solution to be tested was introduced into the electrochemical cell, then the magnesium electrode was immersed into it. The electrode was kept for 15 minutes to establish the free corrosion potential E_c, then anodic polarization curves were recorded in potentiodynamic mode with a potential sweep rate of 0.2 mV/s.

Corrosion tests in borate solutions with pH 7.36 and 9.20 were carried out with Mg-90 samples sized $3.3 \times 2 \times 0.5$ cm. The exposure duration of samples in solution ranged from 0.5 to 12 hours. Corrosion products were removed from the surface of magnesium samples by keeping them for 30 seconds in an aqueous solution containing 60 g L^{-1} potassium dichromate acidified with sulfuric acid to pH 1.0−1.4. Generally, three samples were tested in parallel per data point; the relative measurement error did not exceed 5−7%. The corrosion rate of Mg was calculated by the formula:

$$K\,[\mathrm{g \cdot (m^2 \cdot h)^{-1}}] = \Delta m / S \cdot t,$$

where S is the sample surface area [m²]; t is the test duration [h]. The value of Δm included the correction for the loss of mass of the blank sample exposed to similar etching treatment [0.03 mg/cm^2].

The passivating effect of inhibitors was also estimated from the results of corrosion tests of Mg plates in a heat-and-moisture cabinet after immersing them for 10 minutes in distilled water containing 5 mM of the inhibitor being tested at $t = 20$ and 60°C. In some cases, passivation was achieved with stirring the solution on a magnetic stirrer at a speed of $V \sim 0.3$ m/s. The time until the first corrosion damage on the samples served as the criterion of passivation efficiency. The cabinet operated in the mode: $t = 40$°C for 8 h and no heating for the rest of the day, which resulted in abundant condensation on the samples.

Results and discussion

As noted above, chromate is the most studied and very efficient corrosion inhibitor of Mg and its alloys. However, its toxicity and hazard to the environment makes it necessary to replace chromate in various technologies. Sodium molybdate is most similar to it in chemical properties. It has low toxicity and is often suggested as a substitute for chromate [19].

As one can see from the time–potential curves shown in Figure 1, the starting electrode potential of Mg (E_s) upon immersion in borate buffer (pH 7.4) containing no chlorides is very negative, $E_s = -1.68$ V, but increases with time. This is due to the formation of an oxide–hydroxide layer accompanied by evolution of hydrogen at the electrode, which slows down with time. The E_s value is established in 3 hours and reaches -1.4 V. In solutions containing potassium dichromate, E_s is considerably less negative, which is particularly noticeable at a higher concentration ($C = 10$ mmol/l) and the final potential (E_f) is attained more quickly. Its value in a dilute dichromate solution is even slightly more negative than in the background solution. However, in 10 mmol/l $K_2Cr_2O_7$ solution, not only E_s but E_f are hundreds of millivolts more positive than the similar values for Mg in pure borate buffer. This is because, as an oxidant, dichromate can undergo reduction on magnesium surface to form thereon a protective film containing hardly soluble compounds, for example Cr_2O_3, which results in inhibition of both electrode reactions and metal passivation.

Indeed, if follows from the analysis of polarization curves on Mg (Figure 2a) that even at $C = 1$ mmol/l dichromate increases significantly the cathodic polarization of the electrode, although its effect on the anodic dissolution of the metal, at least up to $i_{an} \leq 40$ mA/cm^2, is rather small. Increasing C to 5 mmol/l, and especially to 10 mmol/l $K_2Cr_2O_7$, leaves no doubt as to the passivating ability of chromate, as well as improving to the efficiency of its inhibitive effect on the cathodic reaction on Mg as well.
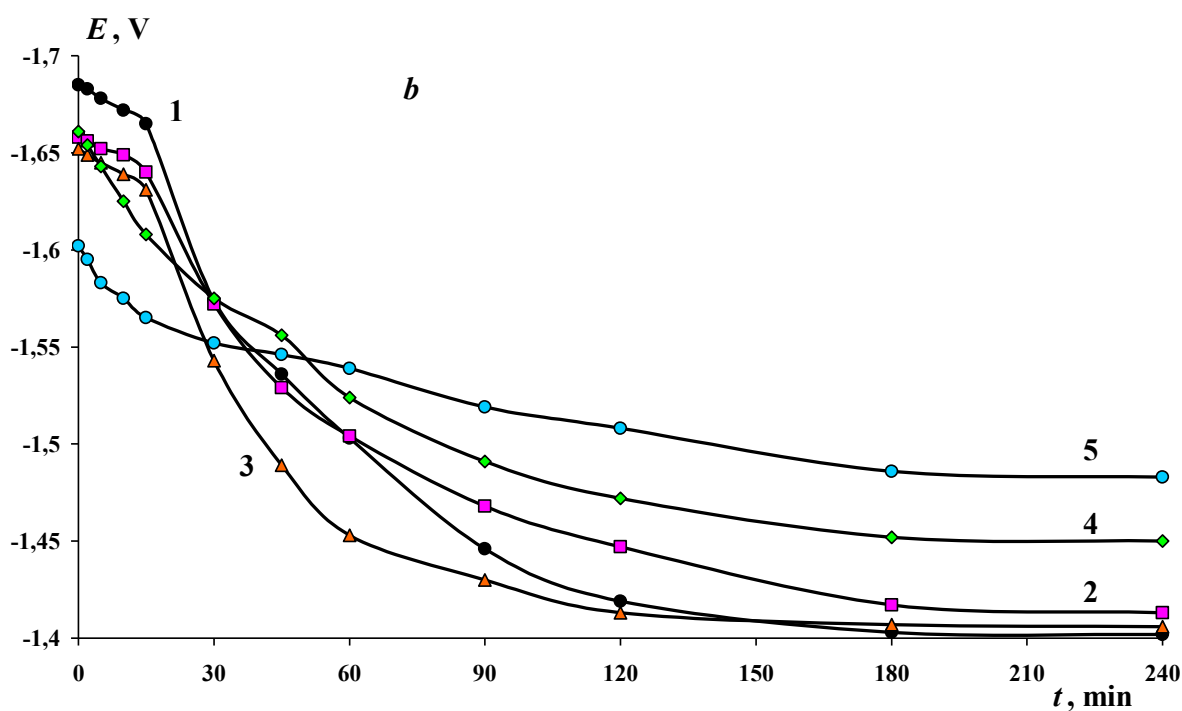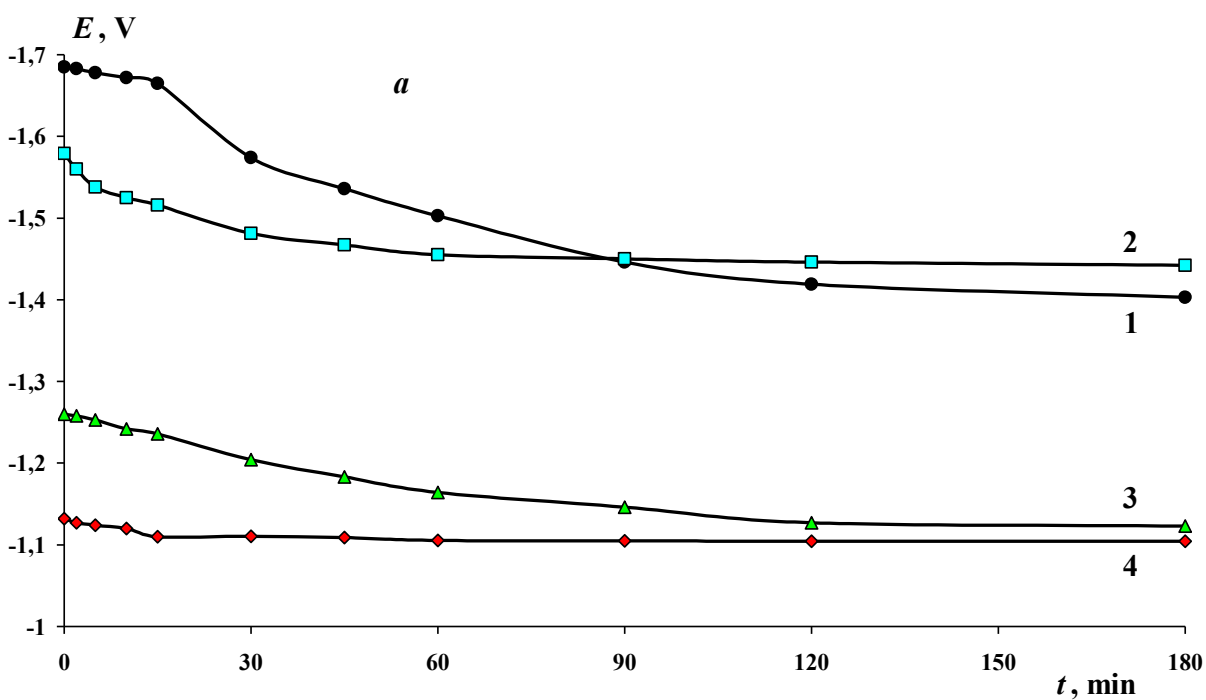
Figure 1. Variation in electrode potential of magnesium in borate buffer with pH 7.4 without (1) and with addition of *a*) potassium dichromate (2 – 1.0, 3 – 10 mmol·L^{-1}); sodium molybdate (4 – 10 mmol·L^{-1}); *b*) 10 mmol·L^{-1} of triazoles (2 – TA; 3 – BTA; 4 – Cl-BTA; 5 – IFKhAN-92.
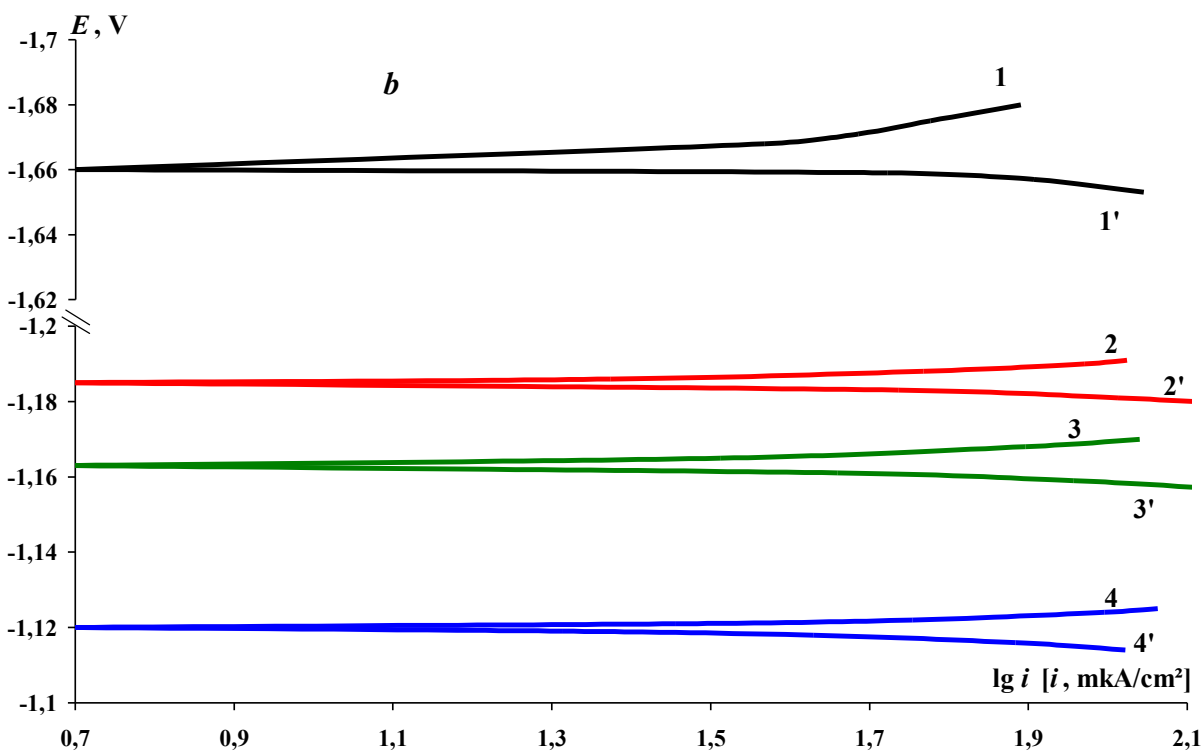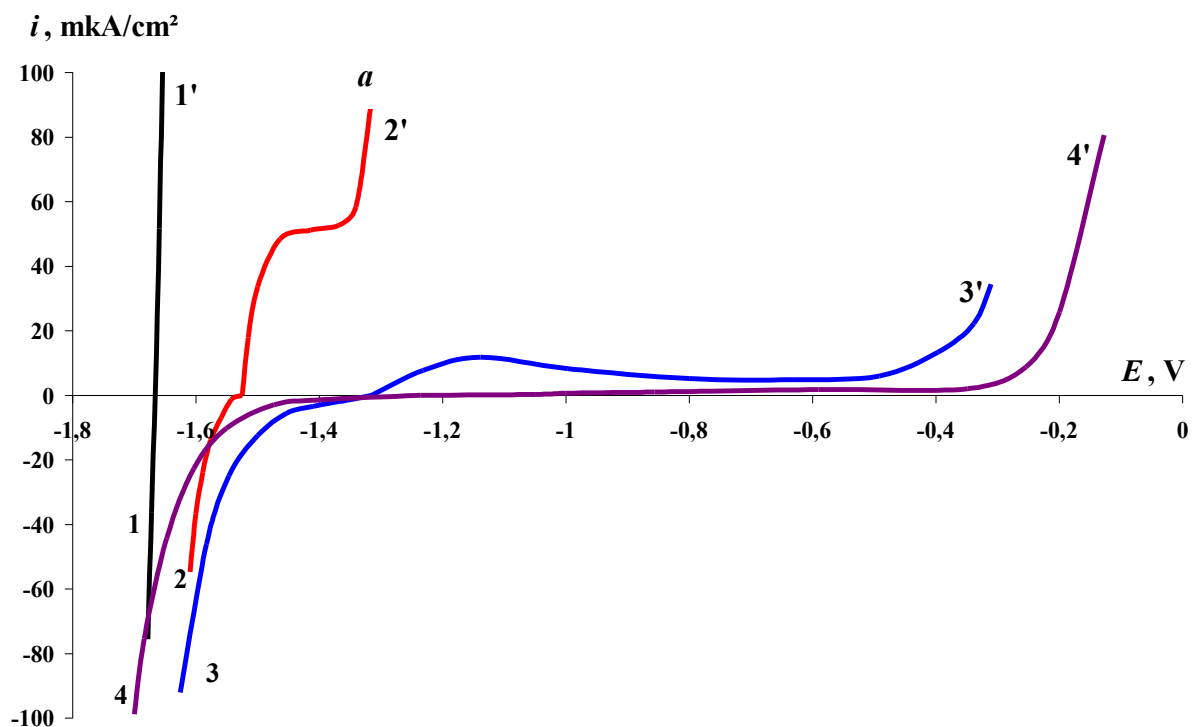
Figure 2. Polarization curves of magnesium in borate buffer with pH 7.4 without (1) and with addition of *a*) potassium dichromate (2 − 1.0; 3 − 5.0; 4 − 10 mmol·L^{-1}); *b*) sodium molybdate (2 − 1.0 mM; 3 − 5 mM; 4 − 10 mM).

It could be assumed that sodium molybdate, which increases the potential of Mg even more considerably (Figure 1a), would reduce the rate of electrode reactions similarly to chromate. However, this is not confirmed by polarization measurements (Figure 2b): no significant changes in Mg polarization upon potential shift both in the cathodic and anodic region are observed, whereas the increase in E_c is only due to molybdate reduction, *i.e.*, its oxidizing properties that presumably lead to acceleration of the overall cathodic reaction. This can cause stimulation rather than inhibition of metal corrosion, as corrosion tests confirm (Table 1).

Table 1. Results of corrosion tests of magnesium in borate buffer solution containing corrosion inhibitors.

| No.	Solution composition		K, g·(m²·h)⁻¹	Z (%)
		Test duration = 1 hour		
1	Borate buffer solution (pH 7.4)		6.20	–
2	same + sodium molybdate	1 mM	8.48	−36.7
3		5 mM	7.98	−28.7
4		10 mM	7.06	−13.8
5	same + 1,2,4-triazole	10 mM	6.28	−1.2
6		30 mM	5.89	5.0
7	same + 1,2,3-benzotriazole	10 mM	6.08	1.9
8	same + 5-chlorobenzotriazole	10 mM	3.48	43.9
9	same + 1 mM DOPh + 1.0 mM IFKhAN-92		0.14	97.7
10	Borate buffer solution (pH 9.2)		3.91	–
11	same + 5-chlorobenzotriazole	1.0 mM	1.70	56.5
12		5.0 mM	0.87	77.7
13		10.0 mM	0.38	90.3
14	same + 10.0 mM 1,2,4-triazole		4.39	−12.3
15	same + 10.0 mM 1,2,3-benzotriazole		4.26	−8.9

On the other hand, as mentioned above, corrosion inhibition of Mg alloys was also observed upon surface treatment or incorporation of organic compounds into the coating. Of these compounds, various triazoles are noteworthy that are still little studied for protection of Mg and its alloys. According to [11], TA proved to be an efficient corrosion inhibitor for Mg alloy AZ31 containing 3% Al and 1% Zn, therefore it was interesting to study this compound and its derivatives as corrosion inhibitors of Mg in a neutral aqueous solution.

In the solutions containing 10 mmol/l of the triazoles being studied, E_s is less negative than in pure borate buffer and also increases with time (Figure 1b). In the case of additives such as TA, BTA or Cl-BTA, E_f of magnesium becomes by 20–30 mV more positive than in the background solution. However, a particularly noticeable increase to $E_s = -1.60$ occurs in a solution containing IFKhAN-92. Although in all the solutions studied the potential of Mg increases with time, the established E_f value in pure borate buffer is less negative than in the presence of organic additives. Only in the BTA solution, E remains more positive than in the background solution for 2 hours, but it is still established at the same value $E_f = -1.40$ V. It is important that the most negative E_f is found in solutions of substituted triazoles with considerable hydrophobicity, *i.e.*, Cl-BTA and IFKhAN-92.[1] (For individual compounds, *i.e.*, all the additives studied except IFKhAN-92, the criterion of hydrophobicity is considered to equal the logarithm of the partition coefficient (log *P*) of the compound of interest in two immiscible liquids, octanol–water, or log *D* with adjustment for acid dissociation [20]. For example, the log *P* value in the series TA – BTA – Cl-BTA increases from hydrophilic TA to the most hydrophobic Cl-BTA: –0.58, 1.34 and 2.10.

The anodic polarization curves of Mg in borate buffer containing various C_{TA} almost do not differ from those obtained in the absence of a triazole, which indicates that this triazole poorly inhibits the metal dissolution (Figure 3a). This confirms the results of the corrosion tests carried out at $C_{TA} = 10$ and 30 mmol/l (Table 1). It is possible that the hydrophilic TA can provide a good level of protection of technical Mg, similar to that observed for Mg alloys in [10], but at higher C_{TA}. However, preference should clearly be given to the more hydrophobic Cl-BTA, which significantly increases the anodic polarization of the electrode (Figure 3b). It increases *Z* by more than an order at the same *C* as TA (Table 1). It is also more efficient than BTA, which may be due not only to its higher hydrophobicity. Another reason is the increase in acidity in the series TA (pK_a 10.0) < BTA (pK_a 8.38) < Cl-BTA (pK_a 5.46), because as pK_a of NH-acids decreases, their dissociation is facilitated and the amount of triazolate anions in solution increases. If the surface of the metal being protected is positively charged, then anions are adsorbed more readily than neutral organic molecules. Therefore, their inhibitive properties may increase upon transition from neutral to slightly alkaline solution. Indeed, upon increasing the pH of borate solution from 7.36 to 9.20, its corrosivity with respect to Mg decreases by 37%, but the degree of protection of 1.0 and 10 mM Cl-BTA increases from 3.95 and 47.0% to 56.5 and 90.0%, respectively (Table 1). Unfortunately, such an increase in the pH of borate solution, which has such a beneficial effect on the inhibitive properties of Cl-BTA, at least at *C* = 10 mM, fails to provide protective properties to TA or BTA.

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[1]This is evidenced by the fact that due to low solubility in water, they were injected into the buffer solution in the form of a solution in isopropanol. The addition of the same amount of isopropanol (≤ 10%) little affected the corrosion-electrochemical behavior of Mg.
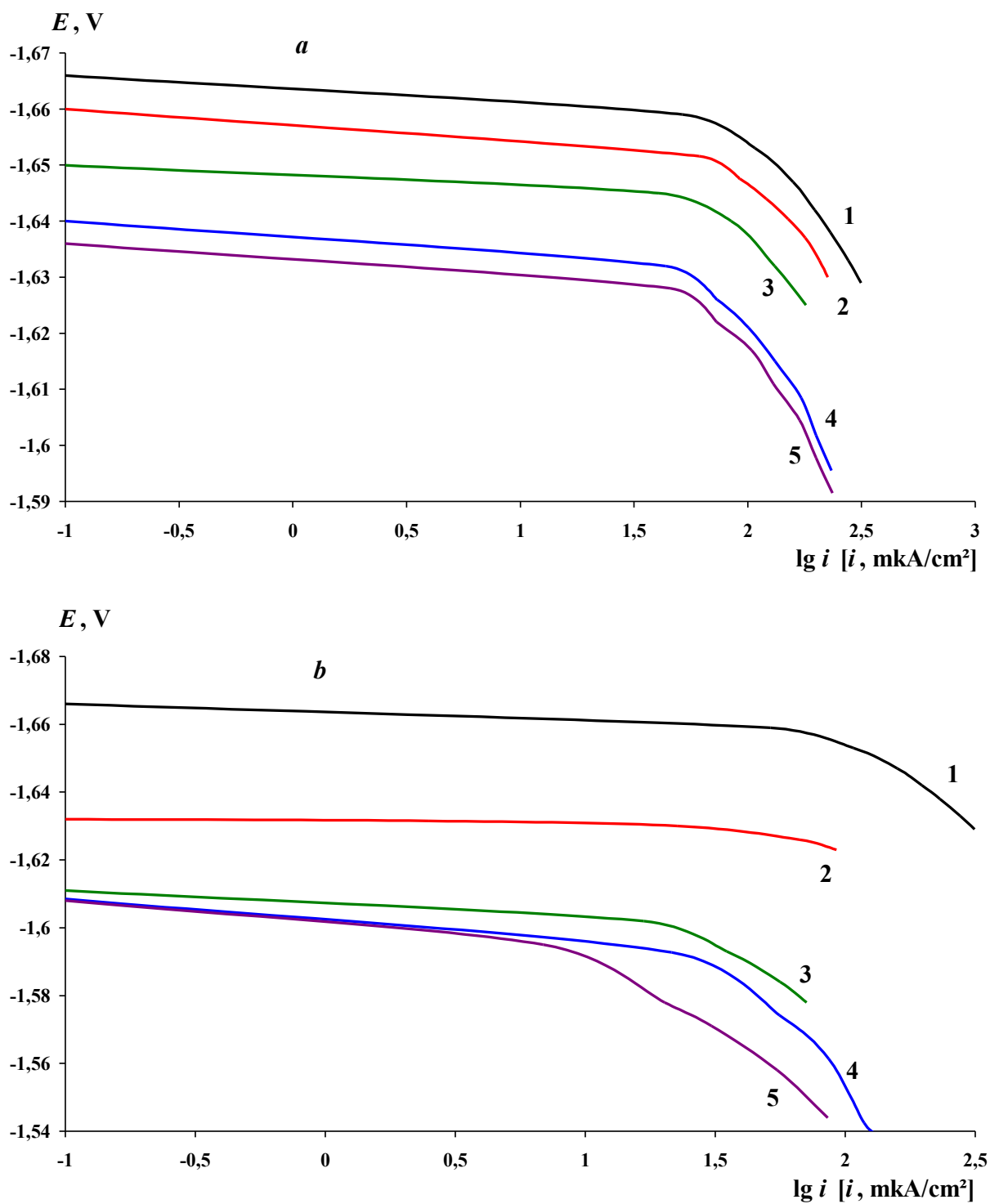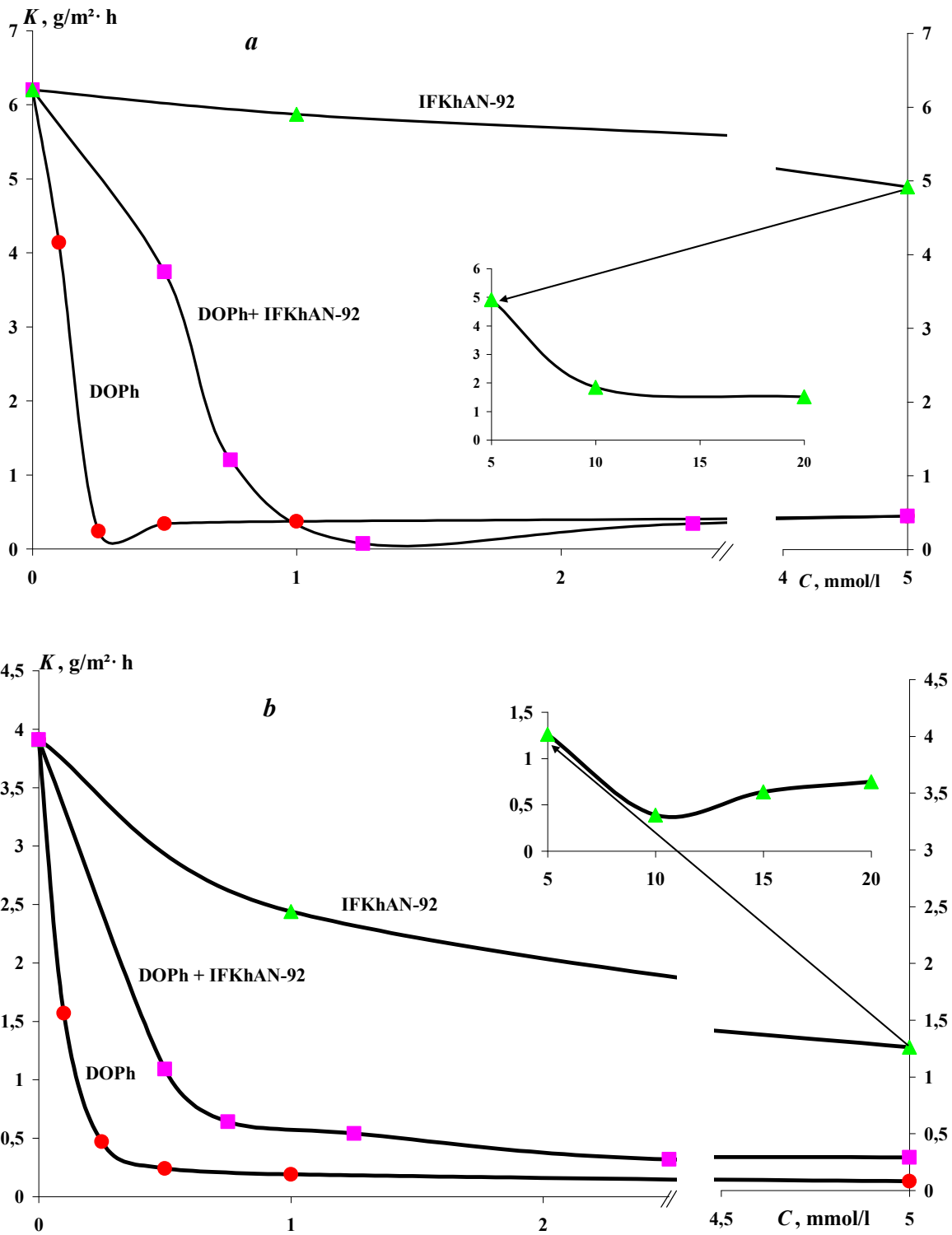
Figure 3. Polarization curves of magnesium in borate buffer with pH 7.4 without (1) and with addition of TA (*a*) and Cl-BTA (*b*), mmol·L^{-1}: 2 − 1.0; 3 − 5.0; 4 − 10.0; 5 − 25.0.

In neutral solution, IFKhAN-92 inhibitor, which is a mixture of triazole derivatives, is the most efficient in Mg protection. It proved itself as a good inhibitor of steel corrosion and hydrogen absorption in highly corrosive H_2S-containing environments and solutions of various acids [21–23]. As expected, IFKhAN-92 can significantly increase not only anodic but also cathodic electrode polarization and, although it requires its relatively high $C \geq 10$ mmol/l (Figure 4). Corrosion tests proved that with IFKhAN-92, $Z = 74.7–75.5\%$ can be reached in neutral solution, but higher protection is prevented by limited water solubility of the inhibitor, even with its improvement by 10% isopropanol addition (Figure 5a). In this context, of interest are data obtained in weakly alkaline borate solution, where Z can be raised to 90% at $C = 10$ mM (Figure 5b). For smaller $C = 1.0$ and 5.0 mM, though it is somewhat less efficient than Cl-BTA, but it can still significantly reduce the rate of Mg corrosion. However, an increase in C to 15 or 20 mM decreases Z somewhat, to 83.6 and 80.8%, respectively, though it is still higher than the best results in neutral borate solution.
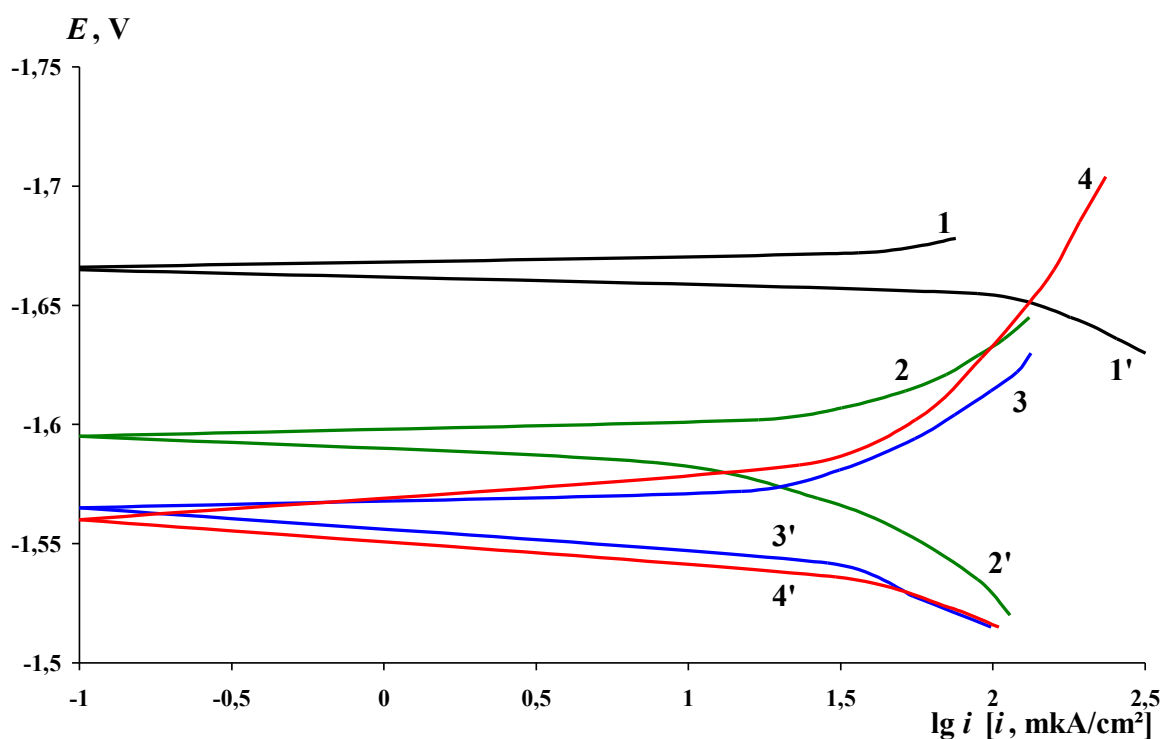
Figure 4. Cathodic (1–4) and anodic (1′–4′) polarization curves of magnesium in borate buffer with pH 7.4 without (1,1′) and with addition of IFKhAN-92 (mmol·L^{-1}): 2 – 1.0; 3 – 10.0; 4 –25.0.

Figure 5. Dependence of magnesium corrosion rate in borate solution with pH 7.4 (*a*) and 9.2 (*b*) on the concentration of DOPh (1), IFKhAN-92 (2) and an IFKhAN-92 + DOPh mixture (1:4).
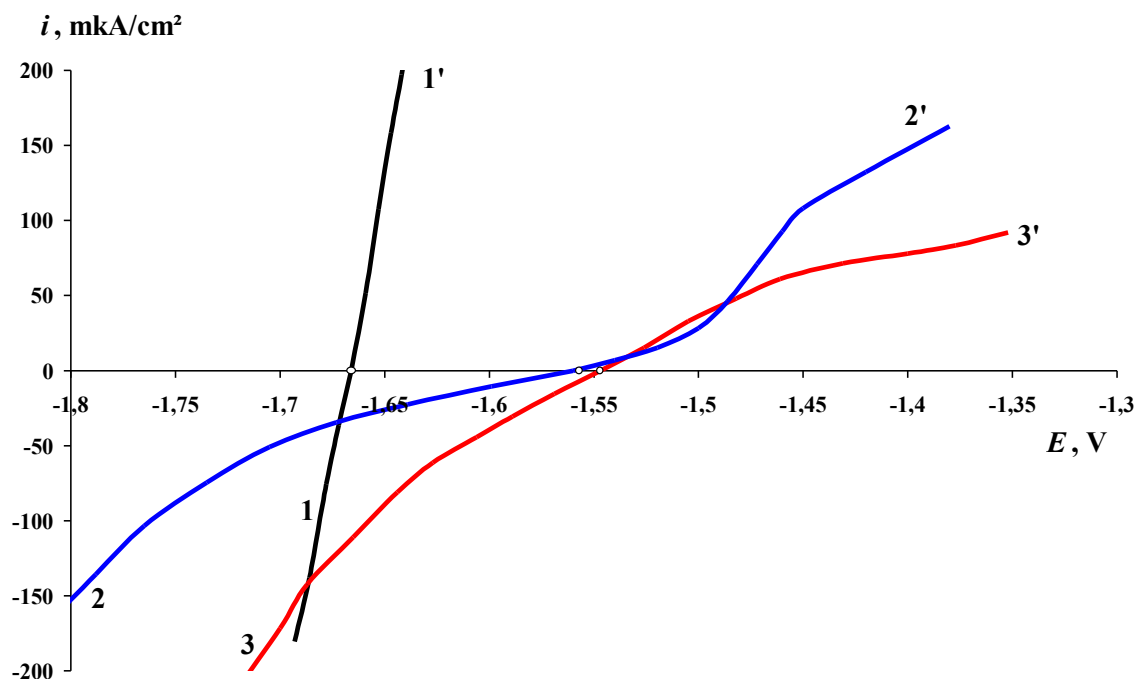
Figure 6. Polarization curves of magnesium in borate buffer solution with pH 7.4 without (1) and with addition of DOPh (mmol·L^{-1}): 2 – 1.0; 3 – 5.0.

It seemed worthwhile to explore yet another approach for increasing the protective properties of the best inhibitors – triazole derivatives. It can be done using IFKhAN-92 together with small additions of an anion-active metal corrosion inhibitor such as sodium dioctyl phosphate (DOPh) that has high adsorption and passivation ability on some metals [24, 25]. Indeed, even small amounts of DOPh can slow down not only the anodic dissolution of Mg but also the cathodic reaction on its surface (Figure 5). It is interesting that at low C_{DOPh} = 1.0 mmol/l its inhibitive effect on the cathodic reaction is stronger, but decreases markedly with a concentration increase. It is possible that under such negative E, the DOPh anion can undergo reduction, just as it was observed with inorganic phosphate ions on zinc [26, 27]. Their reduction to phosphites was confirmed not only in slightly acidic and neutral solutions at $E \leq -0.86$ V, but also in alkaline media at $E \leq -0.97$ [27].

Corrosion tests have demonstrated the high efficiency of small DOPh amounts and their ability to increase the protection of Mg to even greater values when combined with IFKhAN-92 (Figure 6a). It is characteristic that at the ratio DOPh:IFKhAN-92 = 1:4, the consumption of the substituted triazole decreases abruptly and Z_{mix} increases compared to Z_{DOPh} at the same C. In weakly alkaline medium, this was observed only at low C_{DOPh} < 0.25 mM, whereas with C_{DOPh} increase, DOPh became more efficient than the mixture (Figure 6b). On the other hand, the advantage of the mixture over any of its components in neutral buffer is also observed with an increase in the fraction of DOPh. In fact, Z at C = 1.0 mM is 94% for DOPh, 3.5% for IFKhAN-92, and a 97.7% for their mixture. The latter value is higher than even that of 5 mM DOPh (Z = 92.7%).

An important feature of the action of the inhibitors studied on the corrosion of Mg is that Z changes in time (Table 2). In the pure buffer with pH 7.36, the corrosion rate passes through a small maximum, *i.e.*, it increases in the time range from 0.5 to 4.0 hours, which is probably due to destruction of the oxide layer formed in the air, and then decreases due to the protective properties of the resulting gray-colored film of corrosion products. After 12.0 hours it apparently reaches a constant value of $K = 5.53 \pm 0.02$ g/m^{2}h. Addition of a small $C_{\text{IFKhAN-92}}$ amount slightly reduces the corrosion rate, but its dependence on the test time is little different from that of the original buffer. An even smaller amount of DOPh efficiently reduces the corrosion rate, but its inhibitory effect changes in time in a different way: it slowly decreases initially and then decreases abruptly. It is essential that the abrupt decrease in the protective effect of DOPh cannot be explained by the fact that C_{DOPh} is just small and insufficient to block the entire metal surface. This is indicated by the fact that the growth of $C_{\text{DOPh}} > 0.25$ mM itself (at the same test time) does not increase but reduces the Z of the inhibitor (Figure 6). It can be assumed that DOPh, like organic complex formers that are capable of forming water-soluble compounds with cations of a metal being protected as their content in solution increases, prevents the formation of a protective hydroxide-oxide film on Mg [28]. It is therefore that small C_{DOPh} amounts can be promising for improvement of protective action of IFKhAN-92 with respect to Mg. Indeed, the formulation of 0.25 mmol/l DOPh with 1.0 mmol/l IFKhAN-92 demonstrates particularly high protective properties in the first 4.0 hours, exceeding 2.6–3.4 fold DOPh itself at its optimal concentration. However, an increase in not only C_{DOPh} but also $C_{\text{IFKhAN-92}}$ in this formulation significantly degrades the inhibitor efficiency, apparently due to competition of inhibitor adsorption with formation of an oxide-hydroxide film. This is in good agreement

Table 2. Results of corrosion tests of magnesium in borate buffer solution with pH 7.36 containing corrosion inhibitors.

Solution composition (mmol·L^{-1}):	Corrosion rate of magnesium, g·(m^2·h)$^{-1}$, at test duration (hours):			
	0.5	**1.0**	**4.0**	**12.0**
Borate buffer	5.60	6.20	5.74	5.51
same + 1.0 mM IFKhAN-92	5.30	5.88	5.34	5.24
same + 0.25 mM DOPh	0.18	0.24	0.31	1.88
same + 0.25 mM DOPh + IFKhAN-92				
1.0 mM	0.06	0.07	0.12	1.67
4.0 mM	–	0.27	–	2.95
same + 1.0 mM DOPh + IFKhAN-92				
1.0 mM	–	0.14	0.15	2.83
4.0 mM	–	0.45	0.76	2.43

with the fact that even at the optimum ratio of inhibitor components, a high degree of protection can only be achieved for short-term exposures of Mg in neutral solution and at relatively low inhibitor concentration. In fact, in case of exposure for 1 hour in neutral solution, the most efficient composition (0.25 mM DOPh + 1.0 mM IFKhAN-92) provides $Z = 98.8\%$, but after 12 hours, this value is reduced to 69.7%.

In a slightly alkaline solution, the protective effect of the mixed inhibitor changes considerably. In a solution with pH 9.2, the best protection of Mg is achieved at a higher overall C_{in} (1.5 mM DOPh + 6.0 mM IFKhAN-92) than in the neutral solution, but the Z value decreases with time more slowly (from 95.4 in a 1 h test to only 92.9% in a 12 h test, whereas in the solution with pH 7.4 at the same C_{in}, Z decreases from 92.6 to 82.6%). Therefore, Mg passivation was performed in aqueous solutions (in the absence of borate) with $C_{in} = 5.0–7.5$ mM at various pH and t values (Figure 7).
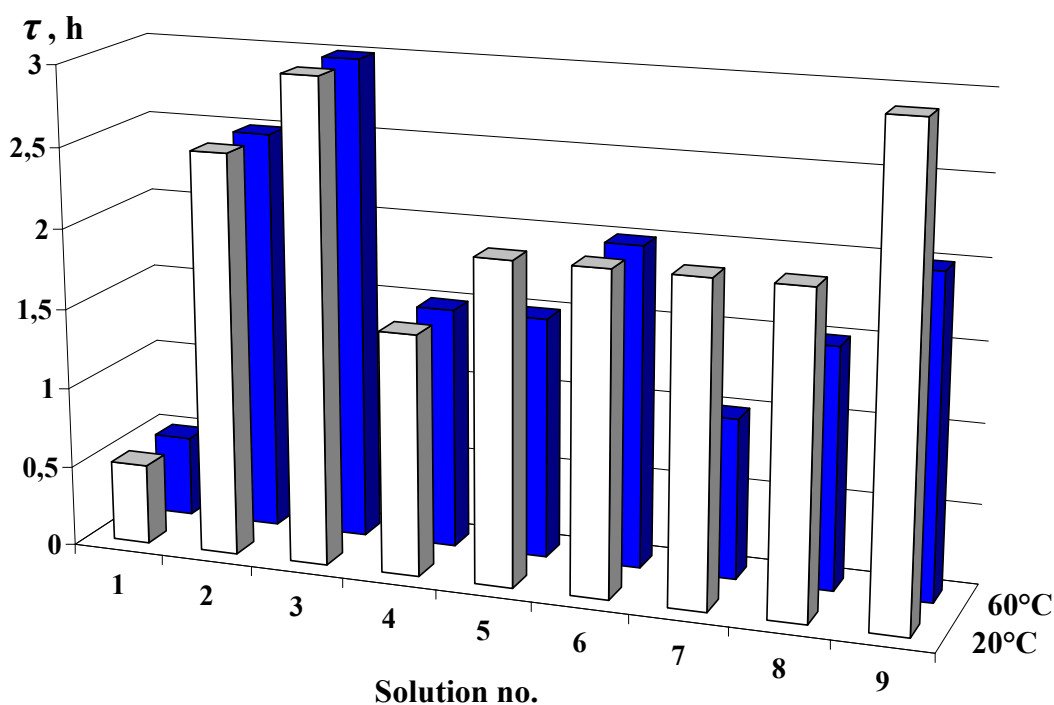
Figure 7. Dependence of the time to appearance of the first corrosion damage (τ) on magnesium specimens placed into a heat and moisture chamber without (1) and with pre-treatment (2–9) in aqueous solutions with $t = 20$ or 60°C and with corrosion inhibitors, $C_{inh} = 5$ mM: 2 – potassium dichromate (pH 4.4); 3 – potassium dichromate (pH 9.2); 4 – DOPh (pH 7.2); 5 – DOPh (pH 9.2); 6 – DOPh + IFKhAN-92 (1:4, pH 6.9); 7 – DOPh + IFKhAN-92 (1:4, pH 9.2). The composition used in variants 8 and 9 contained 2.0 mM DOPh + 8 mM IFKhAN-92, without and with stirring of the passivating solution, respectively.

In the absence of passivating treatment, corrosion spots appear on magnesium samples placed in a 100% relative humidity chamber after 30 minutes and rapidly increase with time. Treatment of Mg in a neutral 5 mM DOPh solution, regardless of treatment

time, protects it from corrosion for $\tau = 1.5$ h. Treatment in the same solution with pH 9.2 at room temperature increased τ to 2 hours, however, an increase in t impaired Mg protection.

Chromate treatment in an acidic solution (pH 4.4), irrespective of treatment duration, provides Mg stability for 2.5 hours, and in slightly alkaline solution – for 3.0 hours. Passivating treatment of Mg, both in neutral and in slightly alkaline solution of the mixed inhibitor (1.0 mM DOPh + 4.0 mM IFKhAN-92), provides the best protection at $t = 20°C$ ($\tau = 2.0$ h). It is superior in efficiency to similar treatment with a DOPh solution but inferior to chromate treatment carried out not only in a weakly alkaline but also in an acidic acidic solution. Also, protection cannot be improved by increasing C_{mix} twofold, but the effect of chromate treatment can be achieved by mixing this slightly alkaline solution (Figure 7). Solution stirring that does not affect the efficiency of chromate passivation increases it slightly for DOPh ($\tau = 2.0$ h), therefore the protective effect of its mixture with IFKhAN-92 is also improved.

To enhance the passivating effect of inhibitors, it is possible to use a small addition of trialkoxysilane (TAS), though it by itself may fail to provide inhibitive properties with respect to the metal to be protected. Chemical reactions of TAS lead to the formation of poorly soluble siloxane nano-sized layers on the surface of the metal that can increase the stability of inhibitor adsorption films. In this case (Figure 8), replacement of 4 mM DOPh by an equimolar amount of TAS did not change the efficiency of Mg treatment at room temperature but increased it slightly at elevated temperature (up to $\tau = 2.0$ h). It proved to be enough to add as little as 1 mM TAS to a non-stirred solution of the mixed inhibitor (5.0 mM) with pH 9.2 to increase τ to 2.5 hours ($t = 20°C$) or 3.0 hours ($t = 60°C$). Increasing C_{TAS} to 5.0 mM makes the efficiency of Mg passivation treatment with the mixed inhibitor ($t = 20°C$, $\tau = 3.5$ h) higher than that obtained using chromate solutions.

A combination of stirring and optimal temperature, pH and C of the mixed inhibitor in the passivating solution with an addition of TAS to it can improve Mg protection with ultrathin organic coating formed under drastic humid atmosphere conditions. Comparison of the results shown in Figures 7, 8 and Table 3 shows that in the case of a three-component inhibitor, its stirred solutions generally either do not impair or do improve the stability of protective layers. This beneficial effect of C_{TAS} is optimal at 5.0 mM, which provides $\tau = 4.0–4.5$ hours, *i.e.*, it extends the induction period of Mg corrosion under drastic conditions 8–9 fold. This allows one to hope that further studies aimed at optimizing Mg passivation techniques will make it possible to develop an environmentally friendly technology for protection of this metal and its alloys from atmospheric corrosion with thin and ultrathin organic coatings.
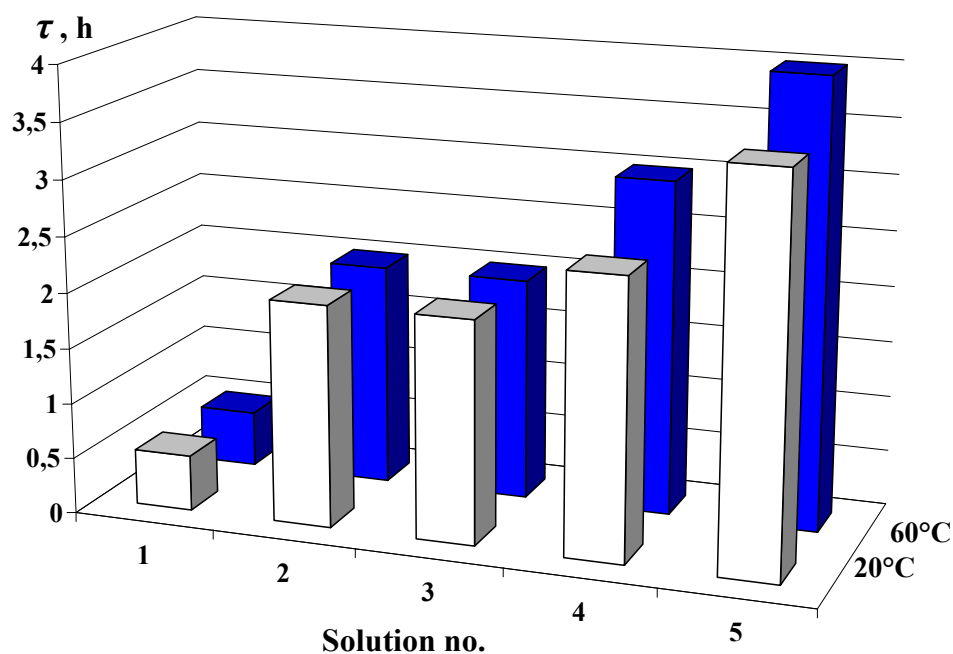
Figure 8. Dependence of the time to appearance of the first corrosion damage (τ) on magnesium specimens placed into a heat and moisture chamber without (1) and with pre-treatment (2–9) in aqueous solutions with *t* = 20 or 60°C at pH 9.2: 2 – 5.0 mM DOPh; 3 – 1.0 mM DOPh + 4 mM TAS; 4 – 1.0 mM DOPh + 4 mM IFKhAN-92 + 1.0 mM TAS; 5 – 1.0 mM DOPh + 4 mM IFKhAN-92 + 5.0 mM TAS.

Table 3. Corrosion results in a heat and moisture chamber for magnesium samples the pre-treated in aqueous solutions of corrosion inhibitors stirred at V=0.3 m·s^{-1}.

No.	Passivation solution composition	pH	Treatment temperature, °C	τ until the first corrosion damage, h
1	without an inhibitor (no treatment)	–	–	0.5
2	5.0 mM DOPh	9.2	60	2.0
3	5.0 mM K$_2$CrO$_4$	9.2	60	3.0
4	1.0 mM DOPh + 4.0 mM IFKhAN-92	7.4	60	2.0
5	same as above	9.2	20	2.5
6	1.0 mM DOPh + 4.0 mM IFKhAN-92 + 1.0 mM TAS	9.2	60	3.0
7	1.0 mM DOPh + 4.0 mM IFKhAN-92 + 5.0 mM TAS	7.4	60	2.5
8	same as above	9.2	20	3.5
9	same as above	9.2	60	4.0
10	1.0 mM DOPh + 4.0 mM IFKhAN-92 + 10.0 mM TAS	9.2	60	3.0
11	1.0 mM DOPh + 4.0 mM IFKhAN-92 + 20.0 mM TAS	9.2	60	2.5

Conclusions

1. Unlike chromate, another inorganic corrosion inhibitor, sodium molybdate, shows no passivating properties with respect to Mg in neutral solution. Moreover, at concentrations $C_{in} \leq 0.01$ M it only stimulates magnesium corrosion in borate buffer with pH 7.4.

2. 1,2,4-Triazole and BTA very slightly slow down Mg dissolution in neutral solution. However, their derivatives (5-chloro-BTA or a mixture of substituted triazoles – IFKhAN-92) inhibit the corrosion of Mg, although they do not passivate it. Not only the increase in hydrophobicity, but also a decrease in pK_a of these NH-acids make a positive contribution to improving the protection of Mg by triazoles. Their efficiency increases in a solution with pH 9.2 where the degree of protection (Z) reaches 90%, indicating the superiority of triazolate anions over the molecules of the same inhibitors.

3. In neutral solution, protection by dioctyl phosphate (DOPh) is more efficient, but the dependences of Z on C_{in} or test duration for this compound have distinct maxima, similarly to triazoles. A possible reason for this is competition between the inhibitor adsorption and the growth of an oxide–hydroxide layer on Mg.

4. Small additions of DOPh to IFKhAN-92 inhibitor increase the degree of magnesium protection. At the ratio of the components DOPh:IFKhAN-92 = 1:4, not only the triazole consumption in neutral solutions decreases, but also Z_{mix} increases compared to Z of DOPh at the same concentration.

5. In the solution with pH 9.2, the best protection of Mg is achieved at a higher total C_{in} (1.5 mM DOPh + 6.0 mM IFKhAN-92) than in neutral solution, but the magnitude of Z decreases slowly with time. Therefore, it is not surprising that passivation treatment of Mg in order to impart stability in humid atmosphere is often more efficient in this solution than in neutral solution.

6. A combination of stirring and optimization of temperature, pH and the concentration of the mixed inhibitor in the passivating solution with addition of TAS can improve Mg protection by ultrathin organic coatings formed under conditions of drastic humid atmosphere and abundant water condensation. This treatment increases the time until the first corrosion damage on Mg in 8−9 fold.

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