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Electrochemical and eclipsometric study of iron corrosion inhibition in sodium sulphate solutions containing aliphatic acids

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The inhibition effect of normal aliphatic acids with 6–10 carbon atoms in the molecule has been investigated in aerated solutions of 0·05 M sodium sulphate at 6–12 pH. It was found that the depolarization of oxygen is not the only factor responsible for the passivation of iron in aerated solution containing a critical concentration of the inhibitor. The inhibiting ability of aliphatic acids in Na_2SO_4 solutions is brought about by a synergistic action of dissolved oxygen and of molecules (or anions) of the aliphatic acid.

1. Introduction

Fatty acids containing more than four carbon atoms in the molecule are known to inhibit corrosion of iron in solutions of 1 N sulphuric acid [1] and 5 N ammonium nitrate [2]. Being due to adsorption, the ability of fatty acids to inhibit corrosion increases with increasing coverage of the iron surface with organic molecules.

The exact mechanism by which the fatty acids inhibit corrosion of iron in neutral and alkaline solutions has not yet been established. In distilled water the protective ability of normal fatty acids was found to occur in the presence of dissolved oxygen and at $\text{pH} > 7$, and to increase with increasing molecular weight of the organic compound. At lower concentrations than that which is necessary to produce full protection, the fatty acids with less than seven carbon atoms in the molecule were found to stimulate corrosion [3].

The purpose of the present work was to assess the effect of normal aliphatic monocarboxylic acids containing four to ten carbon atoms in the molecule on the corrosion rate of iron in aerated 0·05 N sodium sulphate solutions of pH ranging from 6–12.

The results of electrochemical and ellipsometric studies of processes occurring on the surface of iron in de-aerated sodium sulphate solutions in the presence and absence of fatty acids were given previously [4, 5]. The optical and protective properties of surface films formed on iron were shown to depend upon both the composition of electrolyte and the electrode potential. Within the 6–10 pH range in the absence of fatty acid and at lower potentials than $500\,\text{mV}_{\text{NHE}}$, the surface films were found to exhibit low complex refractive indices $\hat{n} = n(1 - \kappa i)$, where n varied from 1·36–1·50, and κ from 0·002–0·1. These films grew according to linear kinetics. They were probably composed of iron sulphates or hydroxysulphates.

Within the same pH range as above but at more positive potentials than 500 mV, and also in solutions of pH 12, the growth kinetics were logarithmic, and the complex index of refraction was larger, namely, $\hat{n} = 2{\cdot}4(1 - 0{\cdot}08i)$. This value characterizes the iron oxides.

Added to the solution in a sufficient concentration (for example, $2 \times 10^{-2}\,\text{mol}\,\text{l}^{-1}$ of caprylic acid at pH 6), the fatty acids reduce both the anodic current density and the capacity of the iron electrode. These additions affect the growth kinetics and widen the potential range for the formation of oxide films to values lower than 500 mV.

The effectiveness of fatty acids as inhibitors decreases with increasing pH.

2. Experimental

The experiments were carried out using Armco iron. The composition of the specimens and the details of the electrochemical and ellipsometric methods employed were given in previous papers [4, 5].

Measurements of the corrosion rate were performed at 25 ± 0·1° C by the gravimetric method using flat, fully immersed iron specimens. These were ground with no. 300–600 polishing papers, washed with methanol and hung on glass hooks. The solution was bubbled with argon, air or oxygen. A constant stream of the gas dispersed into fine bubbles was used. After a certain exposure time the specimens were cleaned from corrosion products and weighed.

3. Results

The effect of pH on the corrosion rate of iron in sodium sulphate solutions bubbled with different gases using the same stream intensity is given in Fig. 1. It is seen that changes in pH within the 6–9 range do not affect the rate of corrosion. In aerated solutions at pH $\geqslant$ 11·5, and in those bubbled with oxygen at pH $\geqslant$ 11·0, passivation takes place and corrosion ceases.

As shown in Fig. 2, beginning from a critical concentration, c_{crit}, dependent upon the number of C atoms in the molecule of the fatty acid added to the sodium sulphate solution, the corrosion rate is significantly reduced. At pH 6 the critical concentrations for caproic, caprylic, and capric acids are equal to 10^{-1}, 2×10^{-2}, and 10^{-3} mol l^{-1}, respectively. In solutions of pH 8·5 and 10 similar relationships are observed, but the curves are shifted to higher concentrations of inhibitors: the critical concentrations are about 1·5 times greater than at pH 6.

The influence of pH on corrosion in solutions containing caprylic acid is illustrated in Fig. 3. As is seen, at 2×10^{-2} mol l^{-1}, which is sufficient to inhibit corrosion at pH 6, an increase of pH to 8·5 or 10 accelerates the corrosion process. In solutions of pH > 11, the corrosion rate is reduced to values found in the absence of any inhibitor. In aerated solutions of pH 8·5 and 10, the presence of $3{\cdot}3 \times 10^{-2}$ mol l^{-1} of caprylic acid produces immunity.

Fig. 4 shows the anodic polarization curves for iron in sodium sulphate solutions containing caprylic acid. At 10^{-2} mol l^{-1} this inhibitor reduces the anodic current density within the potential range from − 190 to 500 mV, whereas at 2×10^{-2} mol l^{-1}, the current density is decreased over the whole range of anodic potentials, and iron becomes passive.

The corrosion potential of iron in aerated solutions of pH 6–10 in the presence of fatty acids at lower concentrations than c_{crit} is $E_{\text{corr}} = -390 \pm 5$ mV. This value is 100–200 mV more positive than that occurring in de-aerated solutions of equal pH. A higher inhibitor content produces a still more noble potential. In an aerated solution of pH 12, the corrosion potential is about 500 mV higher than in de-aerated solution, and is not affected by the presence of the inhibitor.

The effect of the aeration on the resistance–potential relationship for iron immersed in sodium

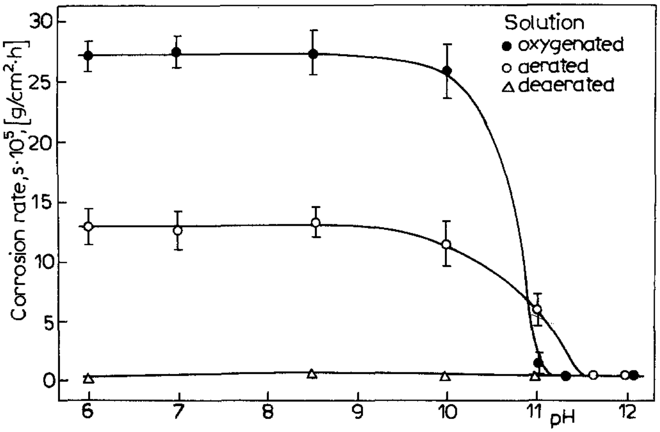

Fig. 1. Corrosion rate of iron in sodium sulphate solutions as a function of pH and oxygen concentration.

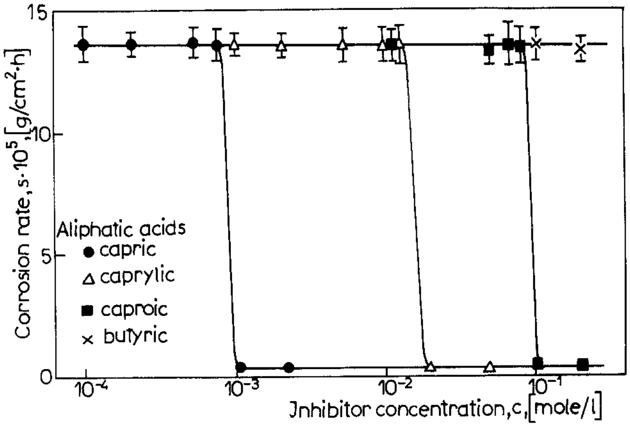

Fig. 2. Effect of the concentration of various fatty acids on the corrosion rate of iron in aerated sodium sulphate solution of pH 6.

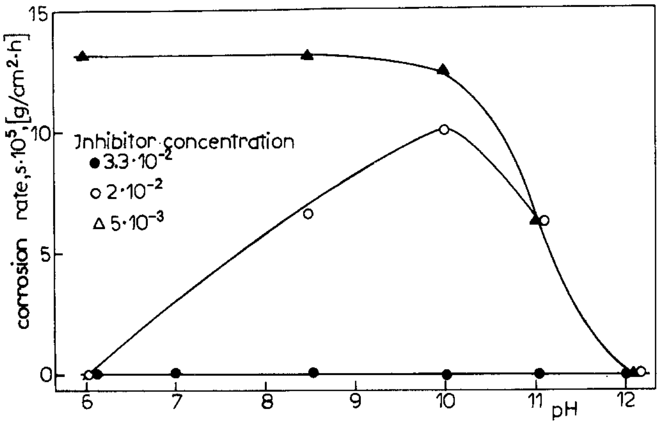

Fig. 3. Effect of pH and concentration of caprylic acid on the corrosion rate of iron in aerated sodium sulphate solution.

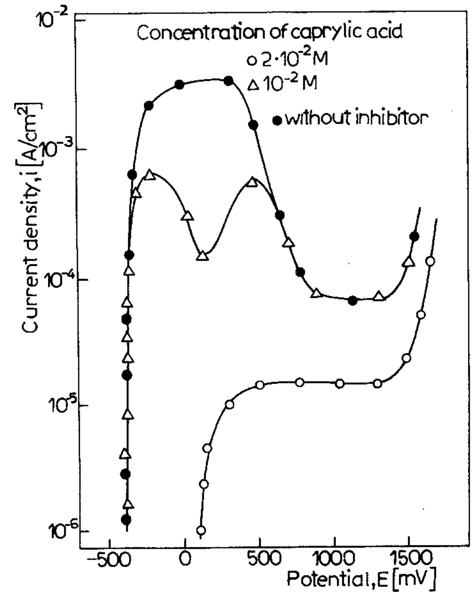

Fig. 4. Effect of the concentration of caprylic acid on the course of polarization curves in aerated sodium sulphate solution of pH 6.

sulphate solution containing 2×10^{-2} mol l^{-1} of caprylic acid is shown in Fig. 5. The aeration increases the resistance at pH 6 but has no effect at pH 12.

Figs. 6 and 7 and Table 1 give the optical parameters of surface films formed on iron in aerated solutions. Films grown on iron under open circuit conditions in solutions containing caprylic acid at 10^{-2} mol l^{-1} and pH 8·5 and 10 exhibit low refractive indices and absorption coefficients: $n = 1{\cdot}36$–$1{\cdot}40$; $\kappa = 0{\cdot}005$–$0{\cdot}06$. At higher inhibitor concentration, for example 2×10^{-2} mol l^{-1} at pH 8·5 and 10, the initial film formed immediately on the surface of iron exhibits optical properties characteristic of iron oxides, but after a few minutes of exposure the film shows $n = 1{\cdot}45$–$1{\cdot}55$, and $\kappa = 0{\cdot}05$–$0{\cdot}10$. A further increase in the fatty acid concentration up to c_{crit}, i.e. to 2×10^{-2} mol l^{-1} for caprylic acid at pH 6, and $3{\cdot}3 \times 10^{-2}$ mol l^{-1} at pH 8·5 and 10, results both at open circuit potential and within the whole

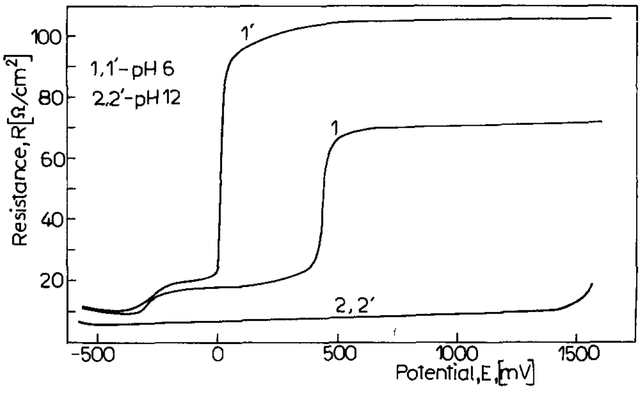

Fig. 5. Relationship between the resistivity and electrode potential of iron in de-aerated (curves 1 and 2) and aerated (1' and 2') solutions of sodium sulphate solution with addition of 2×10^{-2} mol l^{-1} of caprylic acid.

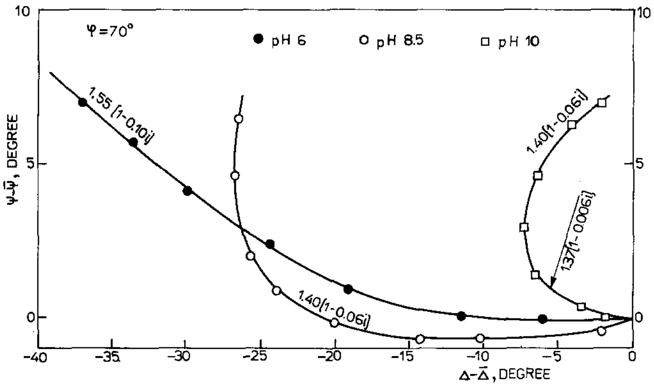

Fig. 6. Relationship between $\Psi - \bar{\Psi}$ and $\Delta - \bar{\Delta}$ for films formed under open circuit conditions in aerated sodium sulphate solution containing 10^{-2} mol l^{-1} of caprylic acid.

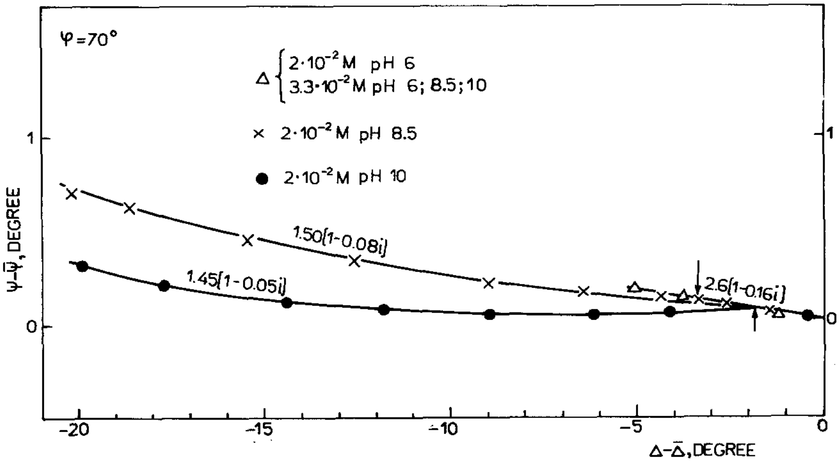

Fig. 7. Relationship as in Fig. 6 but in the presence of 2×10^{-2} mol l^{-1} and $3{\cdot}3 \times 10^{-2}$ mol l^{-1} of caprylic acid, respectively.

Table 1. Optical properties of films formed on iron at open circuit potentials in sodium sulphate solutions containing caprylic acid

	Concentration of caprylic acid (mol l^{-1})			
pH	*0*	*10^{-2}*	*2×10^{-2}*	*$3{\cdot}3 \times 10^{-2}$*
6	1·36 (1 − 0·006 *i*)	1·55 (1 − 0·10 *i*)	2·6 (1 − 0·16 *i*)	2·6 (1 − 0·16 *i*)
8·5	I 1·36 (1 − 0·006 *i*)* II 1·38 (1 − 0·02 *i*)*	I 1·36 (1 − 0·005 *i*) II 1·37 (1 − 0·016 *i*)	I 2·6 (1 − 0·16 *i*) II 1·45 (1 − 0·05 *i*)	2·6 (1 − 0·16 *i*)
10	I 1·36 (1 − 0·006 *i*) II 1·40 (1 − 0·06 *i*)	I 1·37 (1 − 0·016 *i*) II 1·40 (1 − 0·006 *i*)	I 2·6 (1 − 0·16 *i*) II 1·45 (1 − 0·05 *i*)	2·6 (1 − 0·16 *i*)
12	2·6 (1 − 0·16 *i*)	2·6 (1 − 0·16 *i*)	2·6 (1 − 0·16 *i*)	2·6 (1 − 0·16 *i*)

* I, optical parameters of the film adhering to the metal surface; II, optical parameters of the film grown on the top of film I

$n = (1{\cdot}36 \div 1{\cdot}40) \pm 0{\cdot}1;\ \kappa = \pm\, 0{\cdot}001$

$n = (1{\cdot}45 \div 1{\cdot}55) \pm 0{:}2;\ \kappa = \pm\, 0{\cdot}005$

$n = 2{\cdot}6 \pm 0{\cdot}1;\ \kappa = \pm\, 0{\cdot}02$

range of anodic potentials in the formation of oxide films. The oxide films also form at open circuit potential and at anodic potentials in aerated inhibitor-free solution of pH 12.

The kinetics of film growth vary with the properties of the films being formed. The thickness–time relationships for films grown under open circuit conditions in aerated inhibitor-free solutions and in the presence of caprylic acid are represented in Fig. 8. In the absence of fatty acid the surface film exhibits $\hat{n} = 1{\cdot}36\ (1 - 0{\cdot}006i)$ and linear growth kinetics, whereas in the presence of 10^{-2} mol l^{-1} of caprylic acid the kinetics are nearly parabolic. At the critical concentration of caprylic acid, logarithmic growth kinetics are observed.

4. Discussion

The results show that in neutral and alkaline solutions of sodium sulphate the active dissolution of iron occurs within the 6–11·5 pH range. In solutions of higher alkalinity the corrosion process is restrained by passivation (Fig. 1). The rate of corrosion is controlled by the concentration of oxygen dissolved in the electrolyte and by the quality of surface films formed on iron. These films affect the course of the anodic processes.

In the presence of fatty acids the corrosion rate is reduced but a significant influence is observed only for acids containing at least six carbon atoms in the molecule (Fig. 2). Similarly as in sulphuric acid [1] and in ammonium nitrate solutions [2],

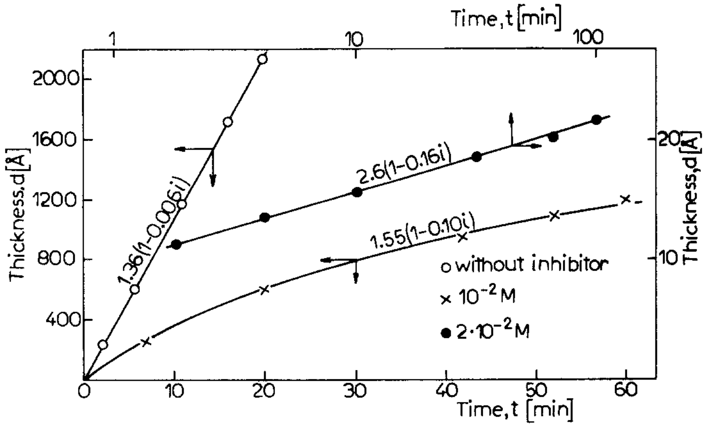

Fig. 8. Effect of exposure time on the thickness of films grown on iron in aerated sodium sulphate solution of pH 6 without and with addition of caprylic acid.

the effectiveness of unbranched fatty acids as inhibitors in Na_2SO_4 increases with increasing length of the hydrocarbon chain. Conforming to Frumkin's adsorption isotherm, in sulphuric acid proportionality occurs between corrosion rate and coverage of iron surface with inhibitor molecules. Neutral and alkaline solutions behave differently. In solutions of pH 6–10, the reduction of the corrosion rate occurs only after a certain critical inhibitor concentration is attained. At c_{crit} or above, the corrosion is practically eliminated, i.e., almost 100% inhibitor efficiency is attained.

Supposedly, at c_{crit} the anions or molecules of the inhibitor cover the majority of active sites of the surface of iron and eliminate the adsorption of the sulphate ions. This prevents the dissolution of iron and the formation of thick layers of corrosion products [5].

As indicated by the results of capacity measurements [5], at higher pH and at the same fatty acid concentration (e.g., pH 8·5, $c = 2 \times 10^{-2}$ mol l^{-1} caprylic acid), the coverage of iron with the inhibitor is decreased and this leads to lower inhibition efficiency and higher corrosion rate (Fig. 3). A similar effect is obtained by decreasing the inhibitor concentration at constant pH.

The optical properties of films grown on iron under open circuit conditions in aerated inhibitor-free solutions or in those containing fatty acids at concentrations lower than c_{crit} resemble the optical parameters of films formed in de-aerated solutions [4, 5]. These films exhibit weak protective ability and their growth kinetics are linear. The loss of weight is a linear function of exposure time to solutions of pH 6–10.

The corrosion rate of iron in de-aerated inhibitor-free sodium sulphate solution is 3×10^{-6} g cm^{-2} h. Aeration increases the rate by a factor of about 40, this being due to the acceleration of the cathodic process (Fig. 1). Bubbling with oxygen produces an effect twice as large, whereas the concentration of oxygen in a solution saturated with this gas is about 4·8 times greater than in an aerated one. As shown by the results of measurements performed with a rotating disc electrode, the limiting current density for the diffusion of oxygen in sodium sulphate solution is a linear function of the concentration of O_2. This suggests that the corrosion rate of iron in such a solution is not only controlled by the cathodic depolarization process, but is controlled also by the anodic process; namely by the formation of deposits of hydroxides on the surface of iron.

The curves of anodic polarization of iron in neutral and alkaline solutions show (Fig. 4) that the passivation can occur in two potential ranges, one from -190 to 500 mV and another at $E >$ 500 mV. The latter region can be attained only by polarization of the electrode with an external current. After switching off, the potential drops below 500 mV. Spontaneous passivation is restricted to the lower potential range.

Polarization curves measured in the absence of inhibitors at pH 6–10 do not exhibit the formation of passivating films at potentials lower than 500 mV (Fig. 4). Although immediately after immersion the presence of an oxide film can be established ellipsometrically, after a few minutes of exposure a secondary layer of corrosion products replaces the previous film. The secondary layer exhibits a low complex refractive index and a poor protective ability.

The complex refractive index of oxide films formed in inhibitor-containing solutions at potentials lower than 500 mV is close to that of films formed at $E >$ 500 mV; the approximate value is $\hat{n} = 2{\cdot}6\,(1 - 0{\cdot}16i)$. However, in the absence of inhibitors and at much lower concentrations of the fatty acid than c_{crit}, a prolonged polarization of the iron electrode at $E >$ 500 mV leads to the formation of oxide films, and no changes in optical parameters of the iron surface are observed. On the other hand, polarization at $E <$ 500 mV in these solutions induces the growth of deposits of corrosion products. The thickness of oxide films grown at $E >$ 500 mV is greater than that of less protective films grown at $E <$ 500 mV. It seems that the lower protective capability of the latter films is not only due to their thinness, but also to some differences in their chemical composition. So, for example, at lower potentials the film might contain occluded sulphate ions or water molecules.

At potentials lower than 500 mV the growth rate of oxide films is higher than that within the more positive potential range; the rates are 10 Å/decade and 3–4 Å/decade, respectively.

The presence in the sulphate solutions of fatty acids at concentrations higher than c_{crit} induces, even at lower potentials than 500 mV, the formation of stable and protective oxide films which prevent the formation of surface films with low refractive indices, and eliminate pitting [5].

The protective capacity of oxide films grown in the presence of inhibitors at potentials lower than 500 mV is greatly increased by oxygen. In the presence of oxygen dissolved in the electrolyte the resistivity of the film increases significantly (Fig. 5). The formation of such a film which promotes the passivation process and protects the metal against corrosion is brought about by a synergistic action of the fatty acid and the dissolved oxygen.

5. Conclusions

(a) In aerated neutral and alkaline solutions of sodium sulphate (pH 6–11) the iron undergoes a relatively rapid corrosion. Above pH 11 the corrosion rate decreases because of passivation.

(b) The corrosion is accompanied by the formation of surface films having low refractive indices and feeble protective capacity.

(c) In the presence of fatty acids containing more than six carbon atoms in the molecule, the corrosion of iron is inhibited if the concentration of the fatty acid exceeds some critical value, c_{crit}. This critical concentration depends on the length of the hydrocarbon chain and on the pH of the solution. In solutions of pH > 10 the fatty acids do not affect the processes occurring on the iron electrode.

(d) In 0·05 M sodium sulphate solution the inhibitive efficiency of fatty acids increases with the length of the hydrocarbon chain.

(e) The inhibitive effect of fatty acids is probably caused by hindering the adsorption of sulphate ions on iron and preventing the dissolution of iron and from the formation of thick layers of corrosion products on the surface of iron; and also, by increasing the stability and the protective capability of the oxide films grown on iron during the anodic process.

(f) The reduction of the corrosion rate of iron in aerated sodium sulphate solutions results from a synergistic action of fatty acids and of oxygen dissolved in the electrolyte.

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