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Der Pharma Chemica, 2012, 4(5):1803-1811
(<http://derpharmachemica.com/archive.html>)



ISSN 0975-413X
CODEN (USA): PCHHAX

Effect of iodide ion on corrosion inhibition of mild steel in 1M H₂SO₄ by polyacrylamide with different macromolecular weight and polyacrylamide poly4-vinylpyridine mixture

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ABSTRACT

The effect of iodide ions on the corrosion inhibition of mild steel in 1 M sulfuric acid in the presence of polyacrylamide (PAM) with different macromolecular weight and polyacrylamide poly4-vinylpyridine (PAM/P4VP) (50%/50%) mixture were studied by weight loss measurements at 18°C. The obtained results showed that the inhibition efficiency increased with increasing PAM concentration. The macromolecular weight of the PAM polymer has not any effect in the inhibition efficiency. It was also found that inhibition efficiency increased with addition the P4VP solution to PAM solution. The addition of potassium iodide (KI) enhanced the inhibition efficiency (P%). A synergistic effect was observed between PAM, KI and (PAM/P4VP) (50%/50%) mixture, KI.

Keywords: mild steel, corrosion inhibition, PAM-P4VP mixture, sulfuric acid, weight loss measurement.

INTRODUCTION

Acid solutions are widely used in many service environments such as pickling, cleaning, descaling and oil well acidizing. In the order to reduce the corrosion of the metal, inhibitors are usually used in these processes. Most of the well-known acid inhibitors are organic compounds containing nitrogen, sulfur and oxygen [1–11].

The adsorption of these molecules depends mainly on some physico-chemical properties of the inhibitor such as the functional groups, steric factors, aromaticity, electron density at the donor atoms and p-orbital character of donating electrons [12–14], and the electronic structure of the molecules [15].

For polymer inhibitors, Polymer amines have been found to be efficient corrosion inhibitors for iron in acidic solutions because of the presence of abundance of π -electrons and unshared electrons pairs on nitrogen atom which can interact with the empty d-orbital of iron [16]. Polyacrylamide [17, 18], polyacrylic acid [19], poly(4-vinylpyridine) [20], poly(4-vinylpyridine isopentyl bromide) [21] and poly(4-vinylpyridine poly-3-oxide ethylene) [22] have been reported as efficient corrosion inhibitors for iron in acidic media..

Some authors have reported synergistic inhibition between halide ions and some compounds including polymers. Earlier studies have shown that halide ions synergistically increased the corrosion inhibition efficiency of polyethylene glycol, polyvinyl alcohol, polyacrylamide, polyvinyl pyrrolidone and poly(4-vinylpyridine) for mild steel in acidic media [17, 23–27].

In this work, the gravimetric was made using mild steel immersed in molar sulphuric acid without and with addition of polyacrylamide (PAM) for different macromolecular weight and polyacrylamide poly4-vinylpyridine mixture (PAM/P4VP) in absence and in presence of iodide ions.

MATERIALS AND METHODS

PAM was prepared by radical adiabatic polymerization of acrylamide in aqueous solution, with ammonium persulfate (APS) as initiating agent. The polymer was precipitated in ethanol. The structure was checked by ^1H NMR, ^{13}C NMR and FTIR spectroscopy. The molecular weight was estimated by the viscosity technique using water as solvent.

P4VP was prepared by radical polymerization of 4-vinylpyridine in methanol, under vacuum, with azobisisobutyronitrile as initiating agent, as described previously [28]. The polymer was fractionated by partial precipitation from methanol–ethylacetate mixture solution. The structure was checked by ^1H -NMR and FTIR spectroscopy. The molecular weight was estimated by the viscosity technique using methanol as solvent [29].

The mixture PAM/P4VP (50%/50%) was obtained by addition polyacrylamide (PAM) solution to poly4-vinylpyridine (P4VP) solution. The mixture contained 50% of PAM and 50% of P4VP (weight percentage w/w).

Solution of 1M H_2SO_4 was prepared from an analytical reagent grade 98% H_2SO_4 and bidistilled water and was used as corrosion media. For the measurement, the experiments were carried out in solutions of 1M sulfuric acid (uninhibited and inhibited) on mild steel containing 0.14% C, 0.21% Si, 0.01% Al, 0.012% S, 0.09% Mn, 0.006% Cu. The mild steel samples were polished successively with different grades of emery paper up 1200 grade.

Each run was carried out in glass vessel containing 50 ml test solution. A clean weighed mild steel sample was completely immersed at an inclined position in the vessel. After 4 hours of immersion in 1M H_2SO_4 , with and without addition of inhibitor at different concentration. The specimen was withdraw, rinsed with bidistilled water, washed with acetone, dried and weighed. The weight loss was used to calculate the corrosion rate.

The inhibition efficiencies P% was calculated as follow equation 1:

$$p\% = \frac{W - W'}{W} \times 100 \quad (1)$$

Where W and W' are the corrosion rate of steel due to the dissolution in 1M H_2SO_4 in the absence and the presence of definite concentrations of inhibitor, respectively.

RESULTS AND DISCUSSION

3.1. Inhibitors effect

3.1.1. Concentration effect of polyacrylamide

Table. 1 gives the values of inhibition efficiency obtained from the weight loss measurements for different concentrations of polyacrylamide with molecular weight $M_v=1,5 \times 10^6$ g/mol in 1M H_2SO_4 at 18°C after 4h immersion.

Table. 1 Inhibition efficiency for corrosion of mild steel in 1M H_2SO_4 with different concentrations of PAM ($M_v=1,5 \times 10^6$ g/mol) obtained from weight loss measurements at 18°C.

Concentration of PAM (mg /l)	Corrosion rate W (mg/cm ² . h)	Inhibition efficiency P(%)
Blank	0.1686	–
10 ⁻¹	0.1060	37.03
1	0.1012	40.00
10	0.0970	42.46
100	0.0806	52.20

The inhibition efficiency increases with increasing inhibitor concentration. The inhibition by PAM can be explained in terms of adsorption on the metal surface. The compound can be adsorbed by the interaction between the lone pair of electrons of the nitrogen, oxygen atoms and metal surface. The optimum concentration required to achieve an efficiency of 52.20 % is found to be 100 mg/l.

3.1.2. Polyacrylamide macromolecular weight effect

Table. 2 gives the values of inhibition efficiency for the corrosion of mild steel in 1M H_2SO_4 obtained from the weight loss measurements for different macromolecular weight of polyacrylamide (PAM) at 18°C after 4h immersion.

Table. 2 Inhibition efficiency for corrosion of mild steel in 1M H₂SO₄ with different macromolecular weight of PAM obtained from weight loss measurements at 18°C after 4h immersion

Concentration of PAM (mg/l)	Macromolecular weight (g/ mol)	Corrosion rate W (mg/ cm ² .h)	Inhibition efficiency P (%)
10	10 ⁴	0.0698	58.60
	10 ⁶	0.0698	58.60
	1.5 ×10 ⁶	0.0970	42.46
10 ⁻¹	10 ⁴	0.1092	35.20
	10 ⁶	0.1094	35.10
	1.5 ×10 ⁶	0.1060	37.03

In examination of these results, we note two effects:

- The values of inhibition efficiencies are independent of the macromolecular weight for the low concentration of polymer (C_p= 10⁻¹ mg/l).
- For the height concentration of polymer (C_p= 10 mg/l), the values of inhibition efficiencies depend on the macromolecular weight of polymer. In this case the inhibition efficiencies are inversely proportional to the macromolecular weight of PAM.

3.1.3. Effect of addition P4VP to PAM

We note that the molecular weight of polyacrylamide in this case was M_v=1,5×10⁶ g/mol and the molecular weight of poly4vinylpyridine was M_v=1,5×10⁴ g/mol.

Table. 3 gives the values of inhibition efficiency obtained from the weight loss measurements for different concentrations of the mixture PAM-P4VP (50%/50%) in 1M H₂SO₄ at 18°C after 4h immersion.

The inhibition efficiency increases with addition the P4VP solution to PAM solution. The addition of P4VP increases the adsorption phenomena onto the metal surface.

Table. 3 Inhibition efficiency for corrosion of mild steel in 1M H₂SO₄ with different concentrations of the mixture PAM-P4VP (50%/50%) obtained from weight loss measurements at 18°C after 4h immersion.

Concentration of PAM/P4VP Mixture (mg/ l)	Corrosion rate W (mg/ cm ² . h)	Inhibition efficiency P (%)
Blank	0.1686	-
10 ⁻¹	0.0982	41.75
1	0.0784	53.50
10	0.0730	56.70
100	0.0622	63.12

The results indicate that the corrosion rate is reduced from 0.1686 mg/ cm². h in the free acid solution to 0.0806 mg/ cm². h in the presence of PAM (M_v = 1.5×10⁶ g/mol, C_p = 100mg/l). These values were further reduced to 0.0622 mg/ cm².h in the presence of the same concentration of PAM/P4VP (50%/50%) mixture.

3.2. Effect of iodide ion

3.2.1. In PAM for different macromolecular weight

The obtained results of the inhibition efficiency for the corrosion of mild steel in 1M H₂SO₄ in the presence of 10 mg l⁻¹ of PAM with different macromolecular weight and various concentrations of KI are listed in Table. 4.

The results obtained in Table. 4 are illustrated in Fig. 1.

Fig. 1 shows Inhibition efficiency for various concentrations of KI of mild steel in 1M H₂SO₄ in the presence of 10 mg/l of PAM with different macromolecular weight obtained from weight loss measurements at 18°C after 4h immersion.

Table. 4 Inhibition efficiency for different concentrations of KI of mild steel in 1M H₂SO₄ in presence of 10 mg/l of PAM with different macromolecular weight obtained from weight loss measurements at 18°C after 4h immersion

Macromolecular weight (g/ mol)	KI concentration (%)	Corrosion rate W (mg/ cm ² . h)	Inhibition efficiency P (%)
10 ⁴	0	0.0698	58.60
	0.005	0.0274	83.75
	0.008	0.0236	86.00
	0.010	0.0258	84.47
	0.012	0.0275	83.66
	0.015	0.0294	82.53
10 ⁶	0	0.0698	58.60
	0.005	0.0277	83.57
	0.008	0.0244	85.50
	0.010	0.0226	86.60
	0.012	0.0206	87.77
	0.015	0.0186	88.97
	0.018	0.0236	86.00
1.5× 10 ⁶	0	0.0970	42.46
	0.005	0.0372	77.90
	0.008	0.0305	81.90
	0.010	0.0295	82.50
	0.012	0.0291	82.72
	0.015	0.0243	85.56
	0.018	0.0234	86.12
	0.020	0.0248	85.27

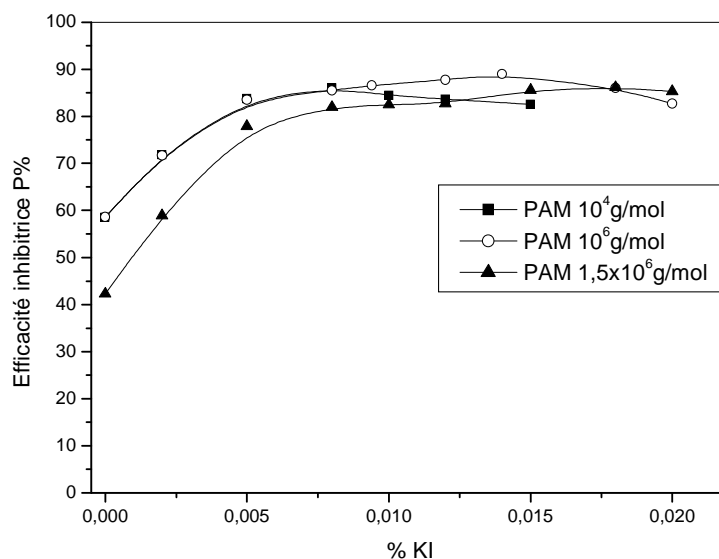


Fig. 1 Variation of inhibition efficiency of mild steel in 1M H₂SO₄ in the presence of PAM with different macromolecular weight according to the KI concentration at 18°C.

The Fig.1 shows a clear increase in inhibition efficiencies according to the concentration of the KI. This result indicates the synergetic effect between PAM and KI. The maximum of synergy is observed for a concentration of KI precise for each case. Any later increase in the concentration of KI is accompanied by a reduction in the value of the inhibition efficiency. These results are in agreement with the literature [18, 24].

For the low macromolecular weight of PAM ($M_V = 10^4$ g/mole), we observe two fields of variations. The first is an increase in the synergy effect which reaches a maximum for a weak concentration of the KI (0.008%). By increasing of the KI concentration, the value of the inhibition efficiency decreases.

For the high macromolecular weight of PAM ($M_V = 10^6$ g/mole and $M_V = 1.5 \times 10^6$ g/mole), we observe three fields of variations:

First, an increase in the synergy effect according to the KI concentration. By increasing of the KI concentration, the value of the inhibition efficiency remains almost constant. Finally we observe a decrease in this effect. We note, the

maximum of synergy is reached for a concentration of KI (0.015% and 0.018%) which is high compared to the first case.

3.2.2. In PAM-P4VP (50%/50%) mixture

Fig. 2 gives the values of inhibition efficiency for various concentrations of KI of mild steel in 1M H₂SO₄ in the presence of 10 mg/l of PAM alone ($M_v = 1.5 \times 10^6$ g/mol) and of PAM/P4VP (50% /50%) mixture obtained by weight loss measurements at 18°C.

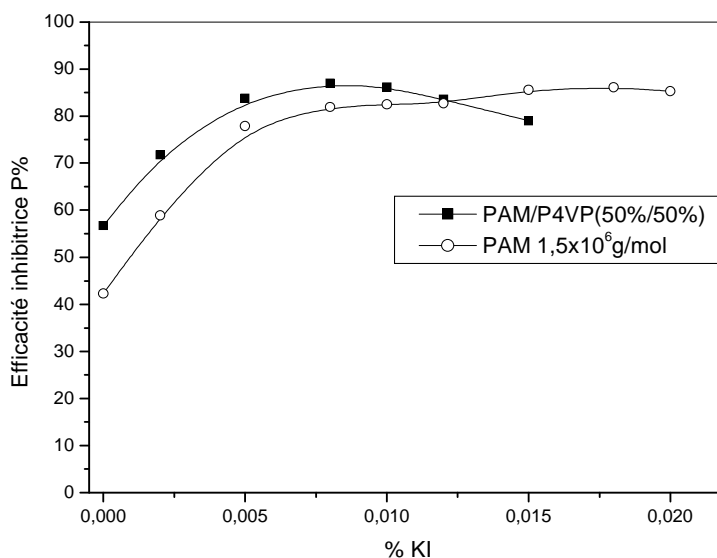


Fig. 2 Variation of inhibition efficiency of mild steel in 1M H₂SO₄ in the presence of 10 mg/l of PAM alone and PAM/P4VP (50%/50%) mixture according to the KI concentration at 18°C.

The addition of the iodide ions increases inhibition efficiency values. This can be attributed to the enhanced adsorption of the inhibitors in the presence of KI because of the synergistic effect of iodide ions. So we note that, the increases of the synergistic effect are rapidly in addition of KI to PAM/P4VP mixture than to the PAM alone.

The maximum of synergy of the (PAM-P4VP) mixture with I⁻ ion is obtained for a weak KI concentration (0.008%). In the case of PAM only the maximum of synergy is obtained for a high KI concentration (0.018%). In both cases, the maximum of inhibition efficiency reaches the same value.

3.3 Effect of temperature

Temperature can affect the steel corrosion in the acidic media in the presence and absence of inhibitor. To investigate the mechanism of inhibition and to calculate the activation energies of the corrosion process, gravimetric measurements are taken at various temperatures (291–323 K) in the absence and presence of 10mg/l of PAM ($M_v = 1.5 \times 10^6$ g/mole) and PAM/P4VP (50%/50%) mixture alone and with 0.008% KI at 2 h of immersion. Corresponding data are given in Table. 5.

The inhibition efficiency (P%) and degree of surface coverage (Θ) of the inhibitor in the presence and absence of KI were calculated using equations 1 and 2 [6,30].

$$\Theta = \frac{W - W'}{W} \quad (2)$$

Where W and W' are the corrosion rate of steel due to the dissolution in 1M H₂SO₄ in the absence and the presence of definite concentrations of inhibitor, respectively. Θ is the degree of surface coverage of the inhibitor.

Table. 5 Various corrosion parameters for mild steel in 1M H₂SO₄ in absence and presence of 10 mg/l of inhibitors alone and with 0.008% KI at different temperatures

Inhibitor	Temperature(K)	W(mg/cm ² .h)	P (%)	Θ
Blank	291	0.1686	—	—
	298	0.3329	—	—
	313	2.5665	—	—
	323	6.0103	—	—
PAM 10 mg/l	291	0.0970	42.4	0.424
	298	0.1954	41.3	0.413
	313	1.3910	45.8	0.458
	323	3.1734	47.2	0.472
PAM /P4VP mixture 10 mg/l	291	0.0730	56.7	0.567
	298	0.1461	56.1	0.561
	313	1.0061	60.8	0.608
	323	2.2659	62.3	0.623
PAM 10mg/l + KI 0.008%	291	0.0305	81.9	0.819
	298	0.0592	82.2	0.822
	313	0.3619	85.9	0.859
	323	0.7813	87.0	0.870
PAM /P4VP mixture 10mg/l + KI 0.008%	291	0.0219	87.0	0.870
	298	0.0416	87.5	0.875
	313	0.1745	93.2	0.932
	323	0.3305	94.5	0.945

From these results, we can deduce that the corrosion rate increases in the blank with the rise of temperature, but in the presence of the PAM polymer, PAM/P4VP mixture, PAM+KI and PAM/P4VP mixture + KI, the dissolution of mild steel is widely retarded. The values of inhibition efficiency obtained from the weight loss at various temperatures show that the inhibition efficiency increases with increasing temperature indicating that higher temperature favourite the adsorption of inhibitor and inhibitor with KI on the dissolution of steel at the surface. The corrosion process and protectiveness of an inhibitor are significantly dependent on the temperature.

3.4. Adsorption isotherm

Fig. 3 shows Arrhenius plots for mild steel corrosion rate for both blank, inhibitors and inhibitors + KI solution.

Straight lines with coefficients of correlation (c. c) of 0.99 are obtained for the supporting electrolyte and all compounds. The values of the slopes of these straight lines permit the calculation of the Arrhenius activation energy using equation 3.

$$\ln(W) = \frac{-E_a}{RT} + A \quad (3)$$

T is the absolute temperature. A is a constant and R is universal gas constant.

The E_a values were determined from the slopes of these plots. The calculated values of E_a in the absence and the presence of inhibitors and inhibitors with KI are given in Table. 6.

Inspection of these data reveals that the apparent activation energy E_a in 1 M H₂SO₄ in absence of inhibitors was 87.25 kJ/mol. The addition of inhibitors (PAM, PAM/P4VP mixture) to the acid solution decreases the activation energy and the extent of the decrease is very pronounced with addition inhibitors + 0.008KI. Note that the reduction of the activation energy in the presence of inhibitors may be attributed to the chemisorption of the inhibitors on mild steel surface [31, 32].

Table. 6 Values of activation energy E_a for mild steel in 1 M H₂SO₄ in absence and presence of additives

Sample	E _a / KJ mol ⁻¹
H ₂ SO ₄ 1M	87.25
PAM 10 mg/l	85.05
PAM/P4VP mixture 10mg/l	84.08
PAM + KI 0.008%	79.19
PAM/P4VP mixture + KI 0.008%	66.23

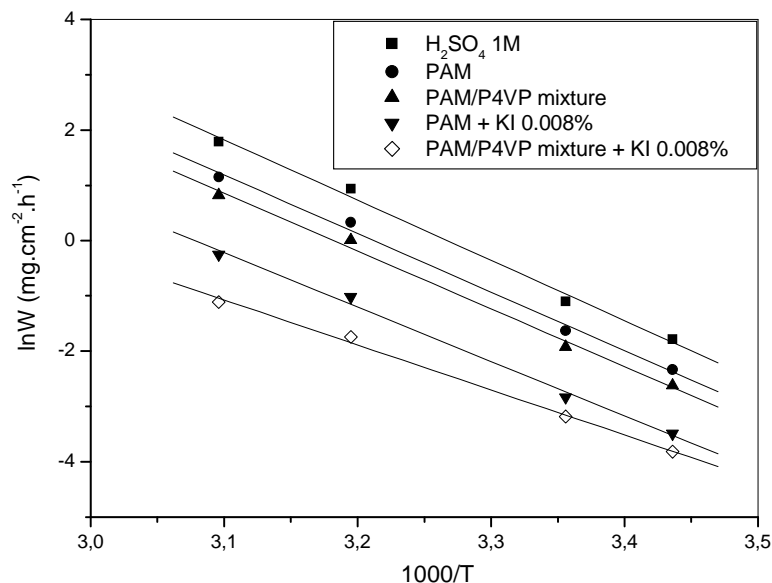


Fig. 3 Arrhenius plots for mild steel in 1M H₂SO₄ in the absence and the presence of 10 mg/l of inhibitor alone and with 0.008% KI

The lower E_a value obtained in the presence of inhibitors when compared to that in its absence indicates chemisorption of the corrosion inhibitor [33]. According to Radovici, cited by Popova et al. [34], lower E_a values in solutions containing inhibitor indicate a specific type of adsorption of the inhibitors. Szauer and al. [35, 36] state that the lower activation energy value of the process in the presence of the inhibitor compared to that in its absence can be attributed to its chemisorption, while the opposite is the case with physical adsorption.

Basic information on the interaction between the inhibitor and the mild steel can be provided by the adsorption isotherm. The adsorption of the organic compounds can be described by two main types of interaction: physical adsorption and chemisorption. These are influenced by the chemical structure of the inhibitor, the type of the electrolyte and the charge and nature of the metal. The surface coverage Θ of the metal surface by the adsorbed inhibitor was calculated using the equation (2):

The θ values for different inhibitor concentrations at different temperatures were tested by fitting to various isotherms. By far the best fit was obtained with the Langmuir isotherm. According to this isotherm Θ is related to concentration inhibitor C via

$$\frac{C}{\Theta} = \frac{1}{K} + C \quad (4)$$

where K designates the adsorption equilibrium constant.

This equation is the ideal equation that should be applied to the ideal case of the physical and chemical adsorption on a smooth surface with no interaction between adsorbed molecules.

It was found that a plot of C/Θ vs C gives straight lines showing that the adsorption of inhibitors alone and in combination with KI from H₂SO₄ 1 M on the mild steel surface obeys the Langmuir adsorption isotherm (Fig.4).

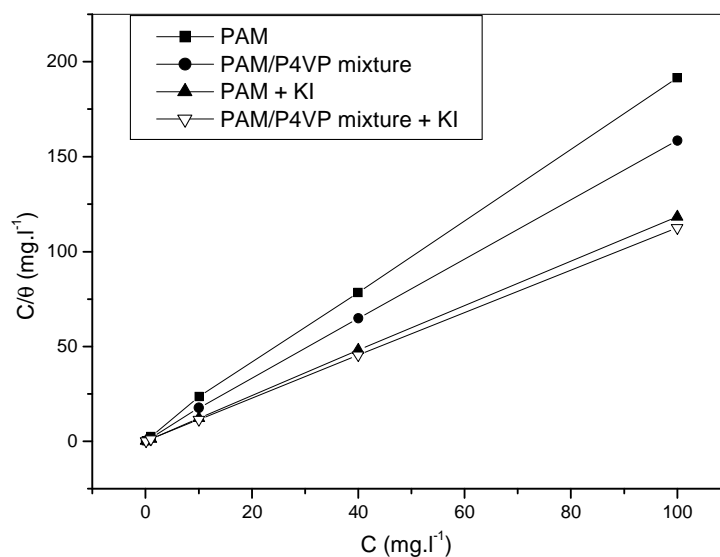


Fig. 4 Langmuir adsorption isotherm of inhibitors and inhibitors + KI on the mild steel surface in 1 M H₂SO₄ from loss measurements.

CONCLUSION

Polyacrylamide (PAM) alone inhibits the corrosion of mild steel in 1M H₂SO₄. Inhibition efficiency increases with addition P4VP solution to PAM solution and with increasing inhibitors concentrations. Synergistic effects between PAM polymer, KI and PAM/PAVP mixture have been observed. The addition of KI enhances the inhibition efficiency of the PAM and PAM/P4VP mixture significantly.

The chemisorption of PAM and PAM/P4VP mixture is stabilized by the presence of iodide ions in the solutions.

The adsorption of inhibitors and (inhibitors + KI) on the metal surface from 1 M H₂SO₄ obeys the Langmuir adsorption isotherm.

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