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Synergistic inhibition between cetyltrimethyl ammonium bromide (CTAB) and NaCl on the corrosion of cold rolled steel in the various concentrations of sulfuric acid*

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Abstract: The effect of cetyltrimethyl ammonium bromide (CTAB) and NaCl on the corrosion of cold rolled steel in 0.5—2.0 mol/L sulfuric acid was investigated by using weight loss and electrochemical methods. The complex of CTAB and NaCl acts as a mixed type inhibitor, which mainly inhibits cathodic reaction. The adsorption of complex follows with the Langmuir adsorption isotherm. A synergistic inhibition between CTAB and NaCl against steel corrosion in sulfuric acid was demonstrated.

Key words: synergistic inhibition; cetyltrimethyl ammonium bromide; NaCl; cold rolled steel; sulfuric acid
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Cetyltrimethyl ammonium bromide (CTAB) is a cationic surfactant, and the corrosion action of steel in HCl, oxalic acid and nitric acid in the presence of different concentrations of CTAB was investigated by Xueming Li[1], et al. using weight loss method. The investigation shows that CTAB acts as a good corrosion inhibitor for steel corrosion in HCl, but behaves as a corrosion accelerator for steel corrosion in nitric acid.

Sulfuric acid is a widely used corrosion medium, but CTAB can not effectively inhibit steel corrosion in sulfuric acid. In order to expand the usage of CTAB as an inhibitor in various acid media, the authors investigated the corrosion inhibition by CTAB for steel corrosion in sulfuric acid and the improvement in inhibition efficiency of CTAB by addition of chloride ion, and the authors explained the synergism mechanism between CTAB and chloride ion for steel corrosion in sulfuric acid.

1 Experimental method

1.1 Materials The experiments were performed with cold rolled steel specimens with the following composition: w (C) ≤0.10%, w (Mn) ≤0.50%, w (P) ≤0.025%, w (S) ≤0.025%, and Fe remainder.

1.2 Solutions The aggressive solutions used were made of AR grade sulfuric acid. Appropriate concentrations of acid were prepared using distilled water. The concentrations of inhibitor employed were 1—5 $\times 10^{-5}$ mol/L CTAB and 0.1 mol/L NaCl in 0.5—2.0 mol/L sulfuric acid.

1.3 Gravimetric method and electrochemical method The specific method of operation is same as described earlier[1,2].

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2 Experimental results and discussion

2.1 Effect of sulfuric acid concentration on corrosion rate of steel The values of corrosion rate were calculated based on the method used in reference[1].

Fig. 1 indicates that corrosion rate linearly increases with the increase in concentration of sulfuric acid in the absence and presence of inhibitor. It is worth noting that the corrosion rate for the solution in the presence of CTAB and NaCl is very close to zero, indicating that the corrosion of steel is greatly inhibited by the conjunct action of CTAB and NaCl.

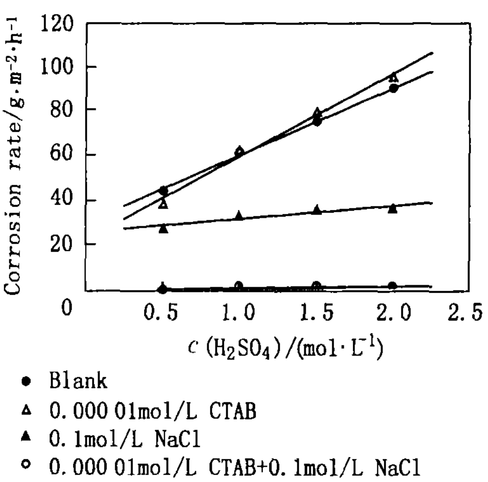

Fig. 1 Dependence of corrosion rate on concentration of sulfuric acid at 40℃

2.2 Effect of concentration of CTAB and sulfuric acid concentration on inhibition efficiency Inhibition efficiencies of inhibitors were calculated by using the following equation

$$E(\%) = 100 \times (V_0 - V)/V_0, \quad (1)$$

where V_0 and V are the corrosion rate of the specimens without and with the addition of inhibitor, respectively.

The relationship between inhibition efficiency and concentration of CTAB is shown in Fig. 2. It is obvious that the highest inhibition efficiency is smaller than 90%, and CTAB drastically loses its inhibition action below the concentration of 2×10^{-5} mol/L. In order to improve the inhibition efficiency of CTAB and decrease the inhibitor concentration, chloride ion is added in sulfuric acid.

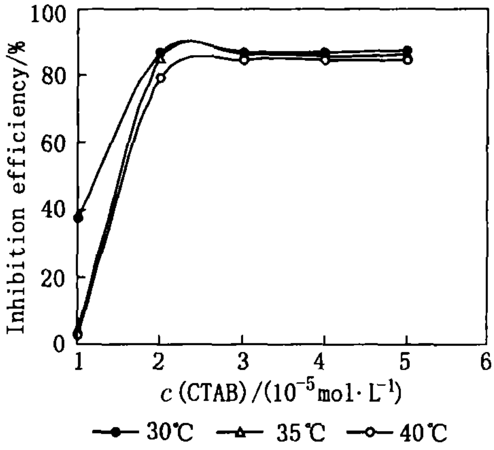

Fig. 2 Dependence of inhibition efficiency on concentration of CTAB in 1.0 mol/L sulfuric acid

The inhibition efficiencies for steel corrosion in 0.5 mol/L sulfuric acid were calculated and listed in Tab. 1. Obviously, 1×10^{-5} mol/L CTAB only has 13.762% protection against steel corrosion. Single NaCl exhibits low inhibition efficiency (< 60%), in the presence of both CTAB and NaCl, however, inhibition efficiency can reach 97%, indicating the synergistic inhibition between CTAB and NaCl.

Tab. 1 Inhibition efficiency calculated from weight loss method in 0.5 mol/L sulfuric acid at 40℃

c(NaCl)/ ($\mathrm{mol \cdot L^{-1}}$)	c(CTAB)/ ($\mathrm{mol \cdot L^{-1}}$)	Inhibition efficiency /%
0.005	0	11.496
0.01	0	18.735
0.05	0	46.278
0.1	0	38.424
0.3	0	51.659
0.5	0	55.885
0	1×10^{-5}	13.762
0.005	1×10^{-5}	56.347
0.01	1×10^{-5}	90.016
0.05	1×10^{-5}	95.952
0.1	1×10^{-5}	96.574
0.3	1×10^{-5}	97.344
0.5	1×10^{-5}	97.648

The relationship between inhibition efficiency and sulfuric acid concentration is shown in Fig. 3. It is obvious that inhibition efficiency for single NaCl increases with an increase in acid concentration, inhibition efficiency for single CTAB and the mixture, however, decreases with an increase in acid concentration. In Fig. 3, "▲" represents the sum of the inhibition efficiency for single NaCl and single CTAB. Clearly, the inhibition efficiency is smaller than that for the presence of the mixture of NaCl and CTAB ("△"), this is the result of the synergistic inhibition between CTAB and NaCl.

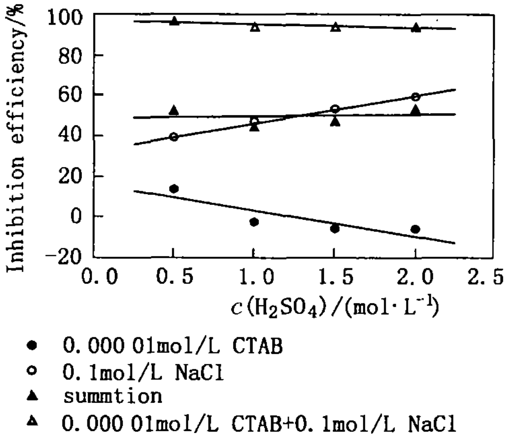

Fig. 3 Dependence of inhibition efficiency on concentration of sulfuric acid at 40℃

It is worth noting that with the increase in sulfuric acid concentration, the synergistic inhibition, on the whole, remains as a constant and the values are very close to 100%.

2.3 Effect of 1×10^{-5} mol/L CTAB and 0.1 mol/L NaCl on the corrosion of steel in 0.5—2.0 mol/L sulfuric acid In order to investigate the effect of sulfuric acid concentration on the corrosion of steel, an empirical equation has been employed, i.e.

$$V = N \cdot \exp(Bc) \tag{2}$$

or

$$\ln(V) = \ln(N) + Bc, \tag{3}$$

where V is the corrosion rate, N is defined as concentration pre-exponential factor, B is defined as acid concentration constant, and c is the acid concentration.

Clearly, the regression between $\ln V$ and c gives a straight line with the intercept of $\ln N$ and slope of B, and all the calculated parameters at 40℃ were listed in Tab. 2.

Tab. 2 Some parameters of the linear regression between $\ln V$ and c in 0.5—2.0 mol/L sulfuric acid at 40℃

c(CTAB)/ (mol·L^{-1})	c(NaCl)/ (mol·L^{-1})	N/ (g·m^{-2}·h^{-1})	B/ (L·mol^{-1})	R
0	0	36.593	0.466	0.989
1×10^{-5}	0	30.965	0.598	0.976
0	0.1	25.612	0.196	0.936
1×10^{-5}	0.1	1.254	0.786	0.922

The regression coefficients listed in Tab. 2 indicate that there is a good linear relationship between $\ln V$ and c, and the good linear relationship between $\ln V$ and acid concentration is also proved by Fig. 4.

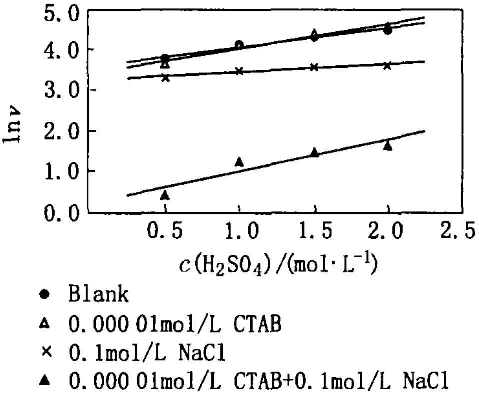

Fig. 4 Relationship between $\ln V$ and concentration of sulfuric acid in the absence and presence of various kinds of inhibitors at 40℃

Equation 2 indicates that N is directly proportional to V, and implies that the bigger the value of N, the bigger the value of corrosion rates.

Tab. 2 obviously suggests that in the presence of inhibitors, there is a decrease in N, leading to the decrease in corrosion rate. Especially in the presence of 1×10^{-5} mol/L CTAB and 0.1 mol/L NaCl, the value of N sharply decreases compared with the blank solution, resulting in the decrease in corrosion rate. Equation 3 also indicates that B is directly proportional to $\ln V$, obviously, in the system, it is the decrease in N rather the change in B leads to the reduction in corrosion rate.

2.4 Adsorption model Surface coverage is evaluated from weight loss measurement using the Sekine and Hirakawa's method[3]

$$\theta = (V_0 - V)/(V_0 - V_m), \qquad (4)$$

where V_m is the smallest corrosion rate.

The experimental data were studied by using the Langmuir isotherm[4]

$$\theta/(1-\theta) = kc, \qquad (5)$$

where c is the inhibitor concentration, k is the equilibrium constant of adsorption.

Fig. 5 shows that $\theta/(1-\theta)$ linearly increases with an increase in concentration of NaCl, revealing the adsorption follows the Langmuir adsorption isotherm. Furthermore, the slope (k) of 1×10^{-5} mol/L CTAB + NaCl is much higher than that of NaCl, indicating the presence of CTAB can improve the adsorption of chloride ion.

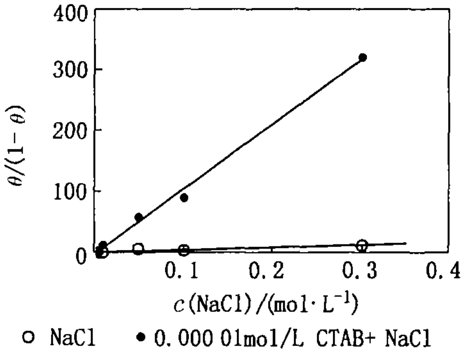

Fig. 5 Dependence of $\theta/(1-\theta)$ on concentration of NaCl at 40℃

2.5 Polarization studies The polarization measurement was conducted at 25℃, the polarization curves were shown in Fig. 6.

Fig. 6 shows that only the cathodic reaction of electrode is inhibited by the presence of single CTAB or single chloride ion, and the corrosion potentials slightly shift to the negative direction compared with the blank. But in the presence of the complex of CTAB and chloride ion, both anodic and cathodic reactions are significantly inhibited, and the corrosion potentials slightly shift to the negative direction either. The results indicate that the complex is a mixed type inhibitor that mainly inhibits the cathodic reaction of electrode.

It is worth noting that either CTAB or chloride ion can only trivially inhibits the cathodic reaction of polarization, the complex of CTAB and chloride ion, however, drastically retards both anodic and cathodic reactions, this may be the result of the synergism.

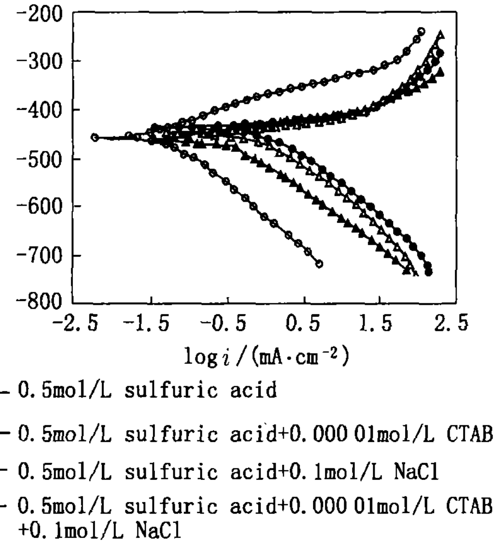

Fig. 6 Polarization curves for steel in 0.5 mol/L sulfuric acid in the absence and presence of various kinds of inhibitors at 25℃

2.6 Explanation for Synergism Obviously, CTAB is a cationic surfactant, which may exist in the cationic form. It is also well known that steel surface contains positive charge due to $E_{\mathrm{corr}} - E_{q=0}$ (zero charge potential) > 0, thus, it is difficult for the positively charged CTAB to approach the positively charged steel surface because of the electrostatic repulsion, this is why single CTAB can not acts as an excellent inhibitor for steel corrosion in sulfuric acid without containing halide ion. With the presence of halide ion, the specific adsorption of halide ion causes the negatively charged surface of steel, thus, by means of electrostatic attraction at the steel/solution interface.

Another possible reason for the synergism is that the addition of chloride ion in aqueous solution reduces the amount of the free water molecule in solution, leading to the increase in concentration of CTAB in solution.

3 Conclusions

Weight loss and electrochemical methods show that there is a synergistic inhibition between CTAB and chloride ion against steel corrosion in sulfuric acid. The adsorption of complex of CTAB and NaCl accords with the Langmuir adsorption isotherm. The complex acts as a mixed type inhibitor, which mainly inhibits cathodic reaction.

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十六烷基三甲基溴化铵与氯化钠对不同浓度硫酸中冷轧钢的缓蚀协同作用*

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摘要: 用失重法和电化学方法研究了 0.5-2.0 mol/L 硫酸中十六烷基三甲基溴化铵(CTAB)与氯化钠对冷轧钢的腐蚀影响. 研究表明: CTAB 与 NaCl 的混合物表现为阴极为主的混合型缓蚀剂, 混合物的吸附符合 Langmuir 等温式. 失重法和电化学方法都表明 CTAB 与 NaCl 对硫酸中钢的腐蚀存在缓蚀协同作用.

关键词: 缓蚀协同作用; 十六烷基三甲基溴化铵; NaCl; 冷轧钢; 硫酸

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