

# Effect of NaBr on the corrosion of cold rolled steel in 1.0 M phosphoric acid

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The inhibition of NaBr on the corrosion of cold rolled steel in 1.0 M phosphoric acid was studied by using weight loss method and polarization method. It was found that the adsorption of bromide ion can prevent steel from corrosion and the adsorption follows the Langmuir adsorption isotherm. Polarization studies showed that NaBr is a mixed-type inhibitor for steel corrosion in 1.0 M phosphoric acid. Thermodynamic parameters such as adsorption heat, adsorption entropy and adsorption free energy were obtained from the experimental data of temperature studies for the inhibition process at four temperatures ranging from 30 to 45°C. The kinetic data such as apparent activation energies and pre-exponential factors at different concentrations of the inhibitor were calculated, and the effects of the apparent activation energy and pre-exponential factor on the corrosion rate of cold rolled steel were discussed. The inhibitive action was satisfactorily explained by using thermodynamic and kinetic models. The results obtained from polarization experiment were in good agreement with those obtained from weight loss measurement. © 2006 Springer Science + Business Media, Inc.

## 1. Introduction

Corrosion problems have received considerable attention because of their attack on materials. The use of inhibitors is one of the most practical methods for protecting materials against corrosion, especially in acidic media. Acid solutions are widely used in industry, for example, acid pickling, acid cleaning and acid descaling. Because of the general aggression of acidic solutions, inhibitors are generally used to reduce the corrosive attack on metallic materials.

Some works have studied the influence of organic compounds containing nitrogen [1–9], sulphur [3, 6, 8–10], oxygen [4, 5, 7, 9, 11–13] and phosphorus [12, 14, 15] on the corrosion of steel in acidic media. The results showed

kinetic models, hoping to gain some useful information about the mechanism of adsorption of halide ions.

## 2. Experimental method

### 2.1. Materials

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

### 2.2. Solutions

The aggressive solutions used were made of AR grade phosphoric acid. Appropriate concentrations of acid were

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prepared using distilled water. The concentration range of inhibitor employed was from 0.001 to 0.3 M in 1.0 M phosphoric acid.

### 2.3. Gravimetric measurements

Prior to experiment, the cold rolled steel sheets of 30×15×0.5 mm were abraded with a series of emery paper from 220 to 1000 grades. Then, the specimens were washed several times with distilled water then with acetone and dried using a stream of forced air. After weighing accurately, the specimens were immersed in 100 ml beaker, which contained 100 ml 1.0 M phosphoric acid with and without addition of different concentrations of NaBr. All the aggressive acid solutions were open to air. After 4 h, the specimens were taken out, washed, dried and weighed accurately. Then the tests were repeated at different temperatures.

### 2.4. Electrochemical measurements

For polarization studies, the steel specimen was embedded in PVC holder using epoxy resin with an exposed area of 1.0 cm<sup>2</sup> (0.155 in.<sup>2</sup>) as a working electrode. A platinum foil was used as an auxiliary electrode. The reference electrode was a saturated calomel electrode (SCE) coupled to a Luggin capillary whose tip was located between the working electrode and the auxiliary electrode.

Before measurement, the electrode was immersed in test solution at natural potential for ca. 2 h until a steady state was reached. All polarization measurements were performed using PARSTAT 2263 Potentiostat/Galvanostat (Princeton Applied Research) at 25°C under aerated condition, and the scanning rate was 0.5 mV s<sup>-1</sup>.

## 3. Experimental results and discussion

### 3.1. Effect of concentration of NaBr and experimental temperature on the corrosion rate of steel

The value of corrosion rate is calculated from the following equation [1, 18]:

$$v = (m_1 - m_2)/(S \cdot t) \quad (1)$$

where  $m_1$  is the mass of the specimen before corrosion,  $m_2$  is the mass of the specimen after corrosion,  $S$  is the area of the rectangular steel,  $t$  is corrosion time and  $v$  is corrosion rate.

Fig. 1 shows the effect of concentration of NaBr on the corrosion rate of steel in 1.0 M phosphoric acid.

Fig. 1 clearly shows that at a certain experimental temperature, corrosion rate of specimen reduces with increasing concentration of NaBr, while at a certain concentration of NaBr, corrosion rate of specimen increases with increasing in experimental temperature. It is worth noting

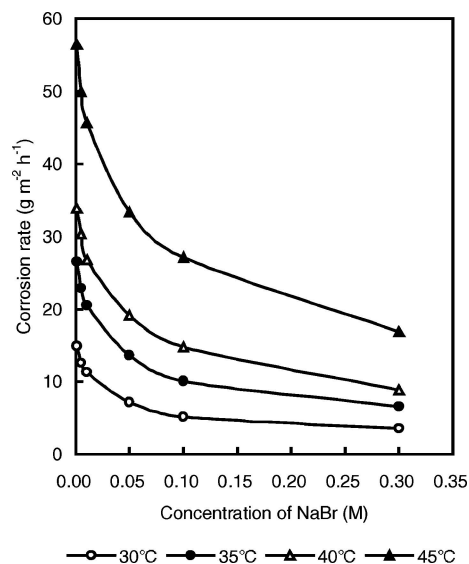


Figure 1 Dependence of the concentration of NaBr on the corrosion rate of steel at different temperatures.

that the higher the experimental temperature, the more remarkable change of the corrosion rate of specimen.

### 3.2. Effects of inhibitor concentration and experimental temperature on inhibition efficiency

The inhibition efficiency of NaBr for the corrosion of cold rolled steel was calculated by using the following equation [2]:

$$E(\%) = (v_0 - v)/v_0 \times 100 \quad (2)$$

where  $v_0$  and  $v$  are the corrosion rates of the specimens in the solutions without and with inhibitor, respectively.

The values of inhibition efficiency are calculated and summarized in Table I, and the variation of inhibition efficiencies with concentration of NaBr at different temperatures is given in Fig. 2. It can be seen from the Table I and Fig. 2 that inhibition efficiency rapidly increases with an increase in concentration of NaBr at the same temperature. At the same concentration of NaBr, however, inhibition efficiency decreases with increasing experimental temperature. The results show that inhibition efficiency of NaBr is jointly affected by concentration of NaBr and experimental temperature in 1.0 M phosphoric acid.

### 3.3. Adsorption isotherm for bromide ion

Assuming the corrosion inhibition was caused by the adsorption of bromide ion, and the degree of surface coverage ( $\theta$ ) for different concentrations of NaBr in 1.0 M phosphoric acid was evaluated from weight loss measurement using the Sekine and Hirakawa's method [14]:

$$\theta = (v_0 - v)/(v_0 - v_m) \quad (3)$$

where  $v_m$  is the smallest corrosion rate.

TABLE I Inhibition efficiency obtained from the weight loss method for different concentrations of NaBr in 1.0 M phosphoric acid at different temperatures

NaBr (M)	Inhibition efficiency (%)			
	30°C	35°C	40°C	45°C
0.001	10.714	7.335	6.891	5.644
0.005	24.557	20.265	16.751	16.510
0.01	32.203	28.429	26.335	23.668
0.05	57.130	52.549	47.410	44.241
0.1	69.350	64.945	59.456	54.737
0.3	78.784	77.154	75.718	71.798

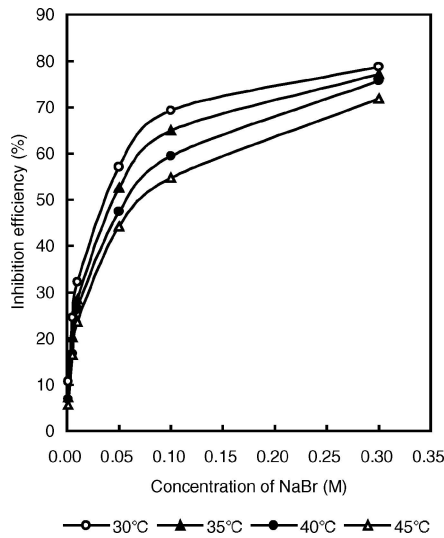


Figure 2 Relationship between inhibition efficiency and concentration of NaBr at different temperatures.

The values of coverage have been calculated and listed in Table II. Apparently, the value of coverage increases with an increase in concentration of NaBr at each experimental temperature, while at a certain concentration of NaBr, the value of coverage, on the whole, decreases with increasing in experimental temperature.

Assuming the adsorption of bromide ion on steel surface followed the simplest adsorption isotherm, i.e., the Langmuir adsorption isotherm, and the Langmuir adsorption isotherm was applied to investigate the adsorption

TABLE II The values of coverage obtained from the weight loss method for different concentrations of NaBr in 1.0 M phosphoric acid at different temperatures

NaBr (M)	Coverage			
	30°C	35°C	40°C	45°C
0.001	0.136	0.095	0.091	0.079
0.005	0.312	0.263	0.221	0.230
0.01	0.409	0.368	0.348	0.330
0.05	0.725	0.681	0.626	0.616
0.1	0.880	0.842	0.785	0.762
0.3	1.000	1.000	1.000	1.000

TABLE III Some parameters of the linear regression between  $c/\text{coverage}$  and  $c$

Temperature (°C)	$K$	Slope	Linear correlation coefficient
30	73.285	0.963	0.999
35	57.191	0.953	0.998
40	46.766	0.947	0.996
45	43.871	0.945	0.996

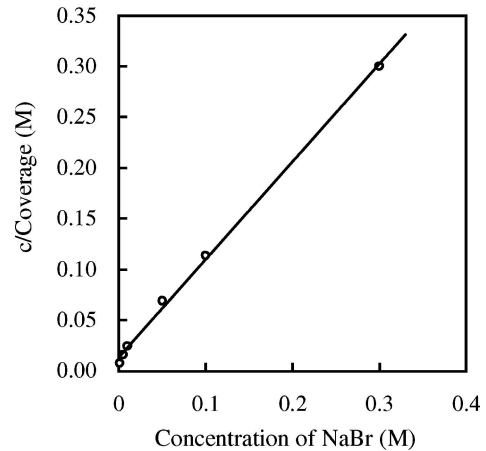


Figure 3 Dependence of  $c/\text{coverage}$  on concentration of NaBr at 30°C.

mechanism by the following equation [1, 19, 20]:

$$c/\theta = 1/K + c \quad (4)$$

where  $K$  is the equilibrium constant of the adsorption process, and  $c$  is the inhibitor concentration.

The regression between  $c/\text{coverage}$  and  $c$  was completed using computer, and Fig. 3 clearly shows the good linear relationship between  $c/\text{coverage}$  and  $c$  at 30°C. The corresponding parameters were listed in Table III. Obviously, the linear correlation coefficients and slopes are close to 1.000, which means that the assumption is correct, i.e., the adsorption of bromide ion on steel surface obeys the Langmuir adsorption isotherm. Table III also shows that the equilibrium constant of the adsorption process ( $K$ ) decreases with increasing temperature. It is well known that  $K$  indicates the adsorption ability of inhibitor onto the steel surface. In Table III, NaBr gives high values of  $K$  at lower temperatures, indicating that bromide ion absorbs strongly onto the steel surface. Therefore, the inhibition efficiency decreases with increasing temperature as the result of the improvement for the desorption of bromide ion from the steel surface.

### 3.4. Thermodynamic parameters for NaBr

Thermodynamic model can be used to explain the adsorption phenomenon of inhibitor molecule. Using the obtained adsorption coefficients, the values of adsorption free energy, adsorption heat and adsorption entropy can be calculated.

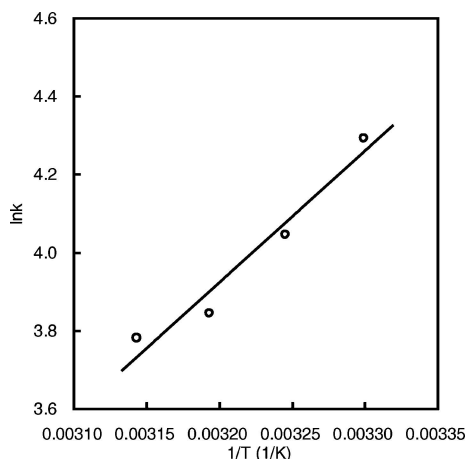


Figure 4 Dependence of  $\ln K$  on  $1/T$ .

The adsorption heat was calculated according to the Van't Hoff equation [1, 19]:

$$\ln K = (-\Delta H)/RT + \text{Constant} \quad (5)$$

To obtain the adsorption heat, the regression between  $\ln K$  and  $1/T$  was dealt with. The relationship between  $\ln K$  and  $1/T$  was shown in Fig. 4. Clearly, the adsorption heat can be obtained by using the slope of the regression. Under the experimental conditions, the adsorption heat can be approximately regarded as the standard adsorption heat ( $\Delta H^\circ$ ).

To obtain the standard adsorption free energy ( $\Delta G^\circ$ ), the following equation was employed [1, 21]:

$$K = (1/55.5) \exp[-\Delta G^\circ/(RT)] \quad (6)$$

According to the thermodynamic basic equation  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ , the standard adsorption entropy  $\Delta S^\circ$  could be calculated.

All the obtained thermodynamic parameters were listed in Table IV. The negative values of  $\Delta G^\circ$  mean that the adsorption of bromide ion on steel surface is a spontaneous process. The negative values of  $\Delta H^\circ$  suggest that the adsorption is an exothermic process, and the magnitudes of  $\Delta H^\circ$  mean that physical adsorption might take place in the system. The negative values of  $\Delta S^\circ$  suggest that the adsorption is a process accompanied by a decrease in entropy.

TABLE IV The thermodynamic parameters of adsorption of bromide ion on the steel surface at different temperatures

Temperature (°C)	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )
30	-20.946	-28.003	-23.280
35	-20.656	-28.003	-23.842
40	-20.468	-28.003	-24.064
45	-20.626	-28.003	-23.190

### 3.5. Kinetic parameters for NaBr

It is found that the natural logarithm of corrosion rate acts as a linear function of the reciprocal of absolute temperature, i.e [1]:

$$\ln v = -Ea/RT + \ln A \quad (7)$$

Where  $Ea$  represents the apparent activation energy,  $R$  is the universal gas constant,  $T$  is the absolute temperature, and  $A$  is the pre-exponential factor.

The regression between  $\ln v$  and  $1/T$  was completed using computer, and the results indicated that all the regression coefficients are very close to 1. The dependence of  $\ln v$  on  $1/T$  was showed in Fig. 5. The apparent activation energy and pre-exponential factor can be calculated from the slope and intercept of the regression, respectively. All the kinetic parameters were calculated and listed in Table V.

Table V suggests that with increasing concentration of NaBr the values of  $Ea$  increase firstly, and then decrease with increasing concentration of NaBr. That is to say, in the present system there is a "peak-like"

$Ea$ . At lower concentrations (0.001–0.1 M) of NaBr,  $Ea$  increases with increasing concentration of NaBr, while at concentrations above 0.1 M,  $Ea$  decreases with increasing concentration of NaBr. The variation in  $Ea$  is the same as that of Libin Tang's previous study [1]. The relationship between  $Ea$  and concentration of NaBr was shown in Fig. 6. It is noticeable that all values of  $Ea$  in the presence of NaBr are higher than that in uninhibited phosphoric acid. The result indicates that the energy barrier for the corrosion of steel has been enlarged by the presence of NaBr in 1.0 M phosphoric acid.

According to the Equation 7, the corrosion rate of steel is jointly affected by  $Ea$  and  $A$  at a certain temperature. Generally speaking, the influence of  $Ea$  on the corrosion rate of steel is more obvious than that of  $A$ . However, if the variation of  $A$  is more prominent than that of  $Ea$ , the value of  $A$  might be the dominant factor to decide the corrosion rate of steel. In this system, in the range of inhibitor concentration from 0.001 to 0.1 M, the increase in concentration of NaBr leads to the increase in  $Ea$ , and accordingly reduces the corrosion rate of steel. As far as  $A$  is concerned, the value of  $A$  increases with increasing

TABLE V Some parameters of the linear regression between  $\ln v$  and  $1/T$

NaBr (M)	Pre-exponential factor (g m <sup>-2</sup> h <sup>-1</sup> )	$Ea$ (kJ mol <sup>-1</sup> )	Linear correlation coefficient
0	$3.001 \times 10^{12}$	65.235	0.991
0.001	$8.024 \times 10^{12}$	67.980	0.990
0.005	$2.106 \times 10^{13}$	70.828	0.992
0.01	$2.371 \times 10^{13}$	71.410	0.991
0.05	$3.794 \times 10^{14}$	79.550	0.994
0.1	$3.979 \times 10^{15}$	86.333	0.995
0.3	$2.082 \times 10^{14}$	79.866	0.991

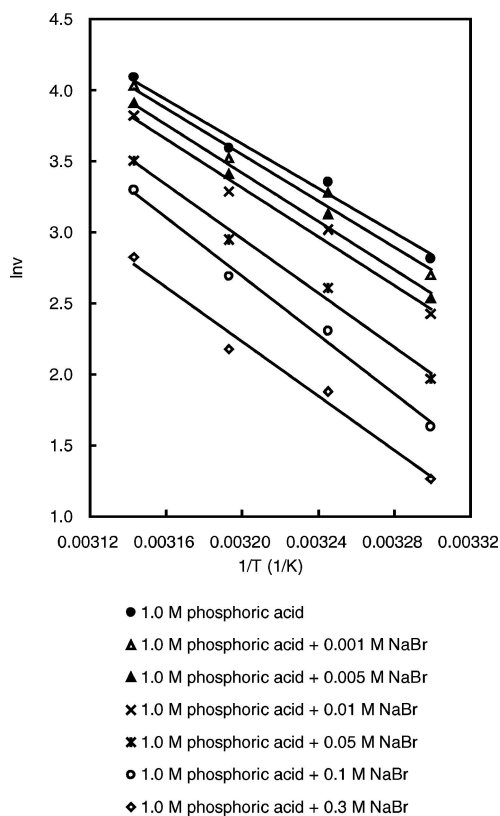


Figure 5 Relationship between  $\ln v$  and  $1/T$ .

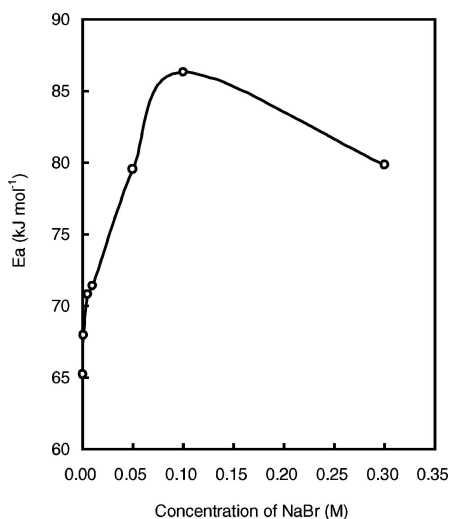


Figure 6 Relationship between  $E_a$  and concentration of NaBr.

of inhibitor concentration. The experimental data show that the values of corrosion rate decrease with increasing concentration of NaBr. So, it is clear that in this system the increase of  $E_a$  is a crucial factor for the inhibitor to decrease the corrosion rate of steel in 1.0 M phosphoric acid.

### 3.6. Functions obtained from transition-state equation

The thermodynamic functions for dissolution of steel in uninhibited and inhibited solutions can be obtained by

TABLE VI Functions obtained from transition-state equation

NaBr (M)	$\Delta H_a^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta S_a^\circ$ (J·mol <sup>-1</sup> K <sup>-1</sup> )	$r$
0	62.653	-14.704	0.990
0.001	65.399	-6.525	0.989
0.005	68.247	1.491	0.992
0.01	68.829	2.484	0.991
0.05	76.969	25.535	0.994
0.1	83.751	45.074	0.995
0.3	77.248	20.546	0.990

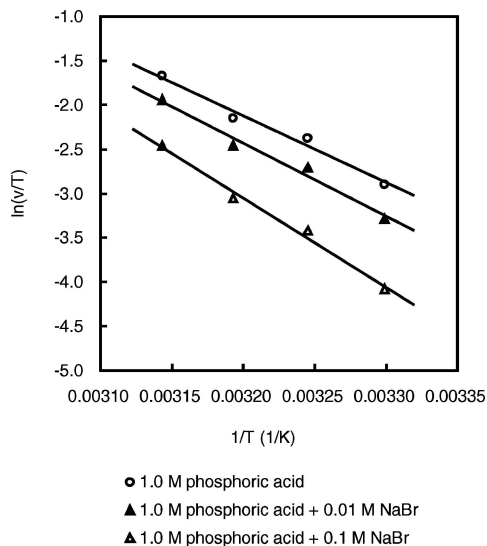


Figure 7 The relationship between  $\ln(v/T)$  and  $1/T$ .

applying the transition-state equation [22, 23]:

$$\ln(v/T) = \ln(R/N_A h) + \Delta S_a^\circ/R - \Delta H_a^\circ/RT \quad (8)$$

where  $N_A$  is the Avogadro's number,  $h$  is the Plank's constant,  $\Delta S_a^\circ$  and  $\Delta H_a^\circ$  are the apparent entropy and apparent enthalpy of activation, respectively.

Fig. 7 suggests that for the system in the absence and presence of inhibitor, there is a good linear relationship between  $\ln(v/T)$  and  $1/T$ , indicating the transition-state equation can be used in the present study.

The values of  $\Delta S_a^\circ$  and  $\Delta H_a^\circ$  can be calculated from the intercept and slope of the regression between  $\ln(v/T)$  and  $1/T$ , respectively. The values were calculated and listed in Table VI.

Linear correlation coefficients listed in Table VI show that the relationship between  $\ln(v/T)$  and  $1/T$  is linear. Clearly, all the inhibited values of  $\Delta H_a^\circ$  are bigger than the uninhibited value (62.653 kJ mol<sup>-1</sup>), meaning higher barrier for the steel dissolution in the inhibited solutions. The values of  $\Delta S_a^\circ$  are positive except the systems in the absence and presence of 0.001 M NaBr, implying the activated complex in the rate-determining step represents a dissociation rather than an association step, meaning that an increase in disordering takes place on going from reactants to the activated complex.

TABLE VII Electrochemical parameters obtained from polarization measurements at 25°C

NaBr (M)	$E_{\text{corr}}$ (mV vs. SCE)	$i_{\text{corr}}$ ( $\mu\text{A cm}^{-2}$ )	$\beta_c$ (mV dec $^{-1}$ )	$\beta_a$ (mV dec $^{-1}$ ) (%)	IE (%)
0	-465.131	$1.406 \times 10^2$	91.208	20.537	0
0.01	-467.779	$1.130 \times 10^2$	87.560	20.951	19.630
0.1	-455.687	$1.283 \times 10^1$	77.041	19.777	90.875

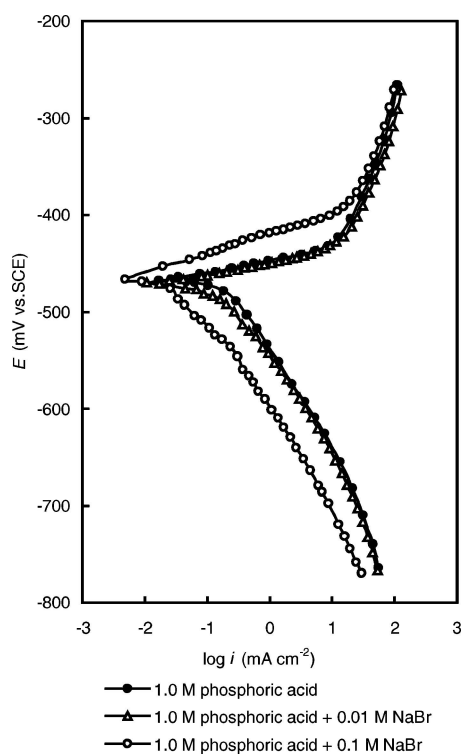


Figure 8 Polarization curves for steel corrosion in the absence and presence of various concentrations of NaBr in 1.0 M phosphoric acid at 25°C.

### 3.7. Polarization studies

The polarization behavior of cold rolled steel in 1.0 M phosphoric acid in the absence and presence of different concentrations of NaBr is shown in Fig. 8. Electrochemical parameters such as corrosion current density ( $i_{\text{corr}}$ ), corrosion potential ( $E_{\text{corr}}$ ) and Tafel slope are given in Table VII.

Inhibition efficiency may also be calculated by corrosion current density using the following formula [24]:

$$E(\%) = 100 \times (i_{\text{corr}} - i'_{\text{corr}}) / i_{\text{corr}} \quad (9)$$

where  $i_{\text{corr}}$  and  $i'_{\text{corr}}$  are the corrosion current densities in the absence and presence of inhibitor, respectively. The values of inhibition efficiency are also listed in Table VII.

Fig. 8 shows that the addition of 0.01 M NaBr to 1.0 M phosphoric acid does not affect the corrosion of steel on the whole, but the presence of 0.1 M NaBr observably inhibits both anodic and cathodic reactions. Because NaBr exhibits the evident anodic and cathodic inhibition and does not shift  $E_{\text{corr}}$  to the anodic or cathodic direction dramatically, NaBr can be defined as a mixed type inhibitor for the corrosion of steel in 1.0 M phosphoric acid.

Once again, the data in Table VII show that inhibition efficiency increases with increasing of concentration of NaBr, which is similar to the results obtained from weight loss measurements, showing that the results obtained from polarization and weight loss method are in good agreement. Further study on Table VII shows that the values of inhibition efficiency obtained from polarization are different from those obtained from weight loss measurements at the same concentrations of NaBr, the difference may be due to the difference in experimental temperature (the polarization was carried out at 25°C, but the weight loss was performed at temperatures ranging from 30°C to 45°C) and the discrepancy in the two experimental methods (the weight loss deals with uniform corrosion, but the polarization deals with uniform and pitting corrosion).

Fig. 8 clearly shows that when the potential reaches about -380 mV, the inhibitor loses its protection against anodic dissolution of steel, which may be the result of the desorption of bromide ion from steel surface. Thus, the desorption potential for steel corrosion in 1.0 M phosphoric acid in the presence of NaBr is about -380 mV.

### 3.8. Explanation for the mechanism of inhibition of bromide ion

It is well known that in the acidic solution steel surface charges positive charge because of  $E_{\text{corr}} - E_{q=0}$  (zero charge potential)  $> 0$ . As far as bromide ion is concerned, by means of electrostatic attraction, the specific adsorption and the smaller degree of hydration make the negatively charged bromide ion easily adsorbed (physical adsorption) onto positively charged steel surface, preventing steel surface from the attack of proton. As a result, the steel corrosion is suppressed.

### 4. Conclusions

NaBr can inhibit steel corrosion in phosphoric acid, and the high temperature is a disadvantage for single NaBr as an inhibitor for steel corrosion in phosphoric acid. In the case of high temperature, NaBr should be used as a component of the complex inhibitor.

The inhibition action of NaBr for the steel corrosion is attributed to the adsorption of bromide ion on the steel surface, and the adsorption behavior of bromide ion on steel surface in 1.0 M phosphoric acid accords with the Langmuir adsorption isotherm.

The adsorption of bromide ion onto the steel surface is a spontaneous, exothermic process accompanied by a decrease in entropy.

With the increase in the concentration of NaBr, the energy barrier for the steel corrosion becomes higher in 1.0 M phosphoric acid.

NaBr acts as a mixed type inhibitor for the steel corrosion in 1.0 M phosphoric acid.

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