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The synergistic inhibition between hexadecyl trimethyl ammonium bromide (HTAB) and NaBr for the corrosion of cold rolled steel in 0.5 M sulfuric acid

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The synergistic effect of the mixture of hexadecyl trimethyl ammonium bromide (HTAB) and various concentrations of NaBr on the corrosion of cold rolled steel in 0.5 M sulfuric acid has been investigated using weight loss method and polarization method. The results reveal that the corrosion of cold rolled steel has been efficiently inhibited by HTAB in the presence of NaBr in sulfuric acid, and inhibition efficiency increases with increasing concentration of NaBr at the same temperature. A synergistic effect has been observed for HTAB with NaBr at every experimental temperature. The polarization curves show that the complex of HTAB and NaBr is a mixed-type inhibitor. The experimental results suggest that the presence of bromide ion in the solution stabilizes the adsorption of HTAB molecules on the metal surface and improves the inhibition efficiency of HTAB. Langmuir adsorption isotherm equation was obeyed at all the temperatures studied. The synergism parameters have been calculated and discussed. The results obtained from weight loss method and polarization method are in good agreement.

1. Introduction

Corrosive environments have received a considerable amount of attention because of their attack on materials. Using inhibitors is one of the most important applications in corrosion protection, and many compounds containing nitrogen, oxygen, sulphur or phosphorous have been widely reported as efficient corrosion inhibitors in acidic solutions [1–5]. Except for these traditional inhibitors, the applications of various surfactants as inhibitor have been received a great attention. Some investigations [6–12] showed that surfactants can also be used to protect the steel surface against corrosion in acidic solutions. Hexadecyl trimethyl ammonium bromide (HTAB) is a common cationic surfactant, and it has been reported [13] that alone HTAB behaves as an effective inhibitor in sulfuric acid as well as in hydrochloric acid solutions. The study of Lu et al [14] has shown that HTAB is also an efficient inhibition for copper in acidic solutions.

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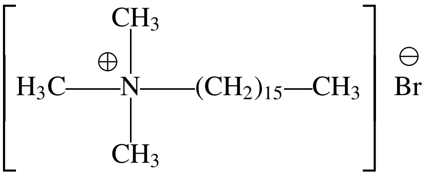
Synergistic effects describe the increase in the effectiveness of a corrosion inhibitor in the presence of another substance in the corrosive medium. This phenomenon has been frequently used in practice [15–20]. Recent studies of Li et al. [21, 22] have shown that there is synergistic effect between some surfactants such as Tween 60, OP etc and halide ions. In this paper, the synergistic effect of HTAB and bromide ion on the corrosion inhibition of cold rolled steel in sulfuric acid has been investigated using weight loss method and polarization method. The possible synergistic mechanism has been proposed on the basis of results obtained.

2. Experimental method

The molecular formula of HTAB used as inhibitor is shown as follows:



$$\left[H_3C - \underset{CH_3}{\overset{CH_3}{\overset{\oplus}{N}}} - (CH_2)_{15} - CH_3 \right] \overset{\ominus}{Br}$$

2.1. Materials

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

2.2. Solutions

The aggressive solutions used were made of AR grade sulfuric acid, and the appropriate concentrations of acid were prepared using distilled water. In this paper, the concentration of sulfuric acid is 0.5 M in all the experiments, and the concentration range of HTAB employed was 10 μM, and the concentration range of NaBr was 0.001 to 0.3 M.

2.3. Gravimetric measurements

Prior to experiment, the cold rolled steel specimens of $30 \times 15 \times 0.5$ mm were abraded with a series of emery paper from 220 to 1000 grades. The specimens were washed several times with distilled water then with acetone and dried using a stream of air. After weighing, the specimens were immersed in beaker, which contained 100 ml sulfuric acid with and without addition of 10 μM HTAB and different concentrations of NaBr. Six samples were prepared for gravimetric measurements in different concentrations of NaBr without the addition of HTAB, and seven samples were prepared for gravimetric measurements in different concentrations of NaBr in the presence of 10 μM HTAB. The sensitivity of the balance is 0.0001 g. The weight loss deviation is less than 1%. All the aggressive acid solutions were open to air. After 4 h, the specimens were taken out, washed, dried and weighed with precision. Then the tests were repeated at 30°C, 35°C, 40°C and 45°C. The corrosion rate (v) and inhibition efficiency (IE) over the exposure period at each temperature were calculated from the following equations [1, 6]:

$$v = \frac{m_1 - m_2}{S.t} \tag{1}$$

$$IE(\%) = \frac{(v_0 - v)}{v_0} \times 100 \tag{2}$$

where m_1 is the mass of the specimen before corrosion, m_2 is the mass of the specimen after corrosion, S is the total area of the specimen, t is corrosion time, v_0 and v are the corrosion rates of the specimen in sulfuric acid without and with the addition of inhibitor, respectively.

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^2 (0.155 $in.^2$) 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^{-1}.

The inhibition efficiency (IE) was evaluated from the potentiodynamic polarization data by the formula [10]:

$$\mathrm{IE}(\%) = 100 \times \frac{(i_{\mathrm{corr}} - i'_{\mathrm{corr}})}{i_{\mathrm{corr}}} \tag{3}$$

where i_{corr} and i'_{corr} are the corrosion current densities in the absence and presence of inhibitor, respectively.

3. Experimental results and discussion

3.1. Effect of HTAB and NaBr on the corrosion of cold rolled steel in sulfuric acid

The corrosion rate of cold rolled steel in different concentrations of NaBr in the presence of 10 μM HTAB at different temperatures was investigated using Eq. (1) and shown in Table I. From Table I, it is shown that the corrosion rate is the highest in the blank (acid without inhibitor) at all the temperatures studied. With the addition of 10 μM HTAB, the corrosion rate decreased at four temperatures studied, but at rather higher values at higher temperature. Addition of NaBr to the inhibitor (HTAB) further significantly decreases the corrosion rate values. The most significant decrease is observed at relative higher concentration of NaBr (above concentration of 0.005 M) with the addition of 10 μM HTAB.

TABLE I. Corrosion rate obtained from the weight loss for different concentrations of NaBr with the addition of 10 μM HTAB in 0.5 M sulfuric acid at different temperatures

NaBr	HTAB	Corrosion rate (g m^{-2}h^{-1})			
(M)	(μM)	30°C	35°C	40°C	45°C
0	0	20.30	33.34	41.96	67.58
0	10	9.01	24.07	35.21	63.39
0.001	10	4.11	11.36	23.08	51.87
0.005	10	1.73	2.97	3.23	6.24
0.010	10	0.87	1.95	1.99	4.20
0.050	10	0.48	0.89	0.94	1.44
0.100	10	0.49	0.72	0.88	1.22
0.300	10	0.58	0.55	0.52	0.89

TABLE II. Inhibition efficiencies obtained from the weight loss method for different concentrations of NaBr with the addition of 10 μM HTAB in 0.5 M sulfuric acid at different temperatures

NaBr	HTAB	Inhibition efficiency (%)			
(M)	(mM)	30°C	35°C	40°C	45°C
0.001	0	14.49	10.56	11.34	8.41
0.005	0	29.09	24.99	26.21	23.28
0.010	0	36.29	32.35	33.36	33.05
0.050	0	62.05	55.99	58.30	51.57
0.100	0	67.97	65.14	65.89	62.77
0.300	0	79.27	76.47	75.95	72.76
0	10	55.64	27.80	16.09	6.20
0.001	10	**79.76**	**65.92**	**44.99**	**23.25**
0.005	10	**91.46**	**91.10**	**92.30**	**90.76**
0.010	10	**95.74**	**94.16**	**95.25**	**93.79**
0.050	10	97.64	**97.32**	**97.75**	**97.87**
0.100	10	97.59	**97.83**	**97.91**	**98.20**
0.300	10	97.13	98.35	98.75	**98.68**

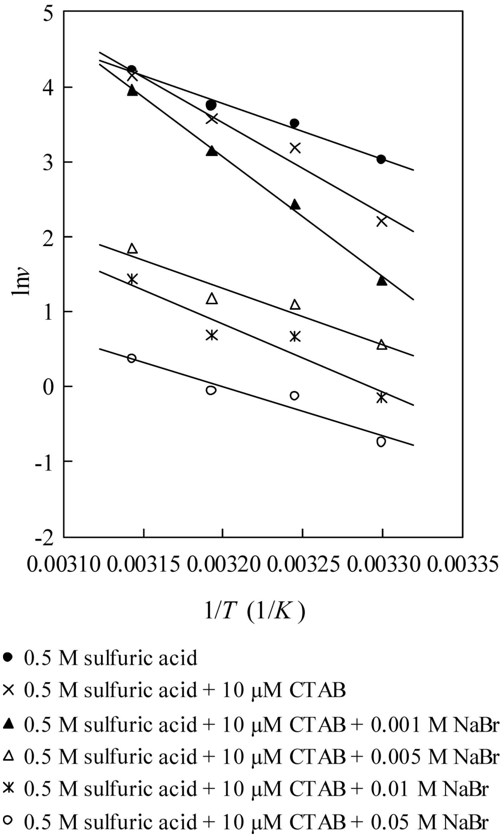


Figure 1 Relationship between ln$v$ and 1/T.

Correspondingly, inhibition efficiencies offered by NaBr to cold rolled steel in sulfuric acid in the absence and presence of 10 μM HTAB at different temperatures are calculated using Eq. (2) and given in Table II. The inhibition efficiency of NaBr, on the whole, increases with a rise in concentration at every temperature studied, both in the absence and presence of 10 μM HTAB. The higher the concentration of inhibitor, the more the inhibitor molecules adsorb on the steel surface, leading to the higher values of surface coverage. Thus, H^+ can attack less area of steel surface, resulting to higher values in inhibition. It is found that alone NaBr shows good inhibition efficiency, but as far as 10 μM HTAB is concerned, the inhibition efficiency is significantly decreases with increasing of temperature. However, the complex of NaBr and 10 μM HTAB has a better inhibition efficiency (IE), that is to say, the addition of NaBr further strengthens the values of inhibition efficiency. The higher the concentration of NaBr, the more the negatively charged Br^- may adsorb on positively charged steel surface [9], which leads to the increase in the number of positively charged HTAB on steel surface because of the static attraction between the negatively charged Br^- and the positively charged HTAB. For example, at 35°C 0.005 M NaBr has 24.99% IE and 10 μM HTAB has 27.80% IE, while their complex has 91.10% IE. This suggests there is a synergistic effect between HTAB and NaBr. The bold-faced values of inhibition in Table II means synergistic inhibition. It can be seen from the Table II that the higher the temperature, the more prominent the synergistic effect.

Tang et al. [1] have shown that logarithm of corrosion rate (v) can be represented as a straight line function of 1/T, ie. Arrhenius equation:

$$\ln v = -\frac{Ea}{RT} + \ln A \tag{4}$$

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.

Fig. 1 represents the relationship between ln$v$ and 1/T. Straight lines obtained show that the reaction obeys the Arrhenius Eq. (4) for the blank, HTAB alone and for the mixtures of HTAB and NaBr.

3.2. Adsorption isotherm for the complex of HTAB and NaBr

Assuming the corrosion inhibition was caused by the adsorption of HTAB and NaBr, and the degree of surface coverage (θ) for different concentrations of NaBr in

TABLE III. The values of coverage obtained from the weight loss for different concentrations of NaBr with the addition of 10 μM HTAB in 0.5 M sulfuric acid at different temperatures

NaBr (M)	HTAB (μM)	Coverage 30°C	35°C	40°C	45°C
0	10	0.57	0.28	0.16	0.06
0.001	10	0.82	0.67	0.46	0.24
0.005	10	0.94	0.93	0.94	0.92
0.01	10	0.98	0.96	0.96	0.95
0.05	10	1.00	0.99	0.99	0.99
0.1	10	1.00	0.99	0.99	0.99
0.3	10	0.99	1.00	1.00	1.00

sulfuric acid was evaluated from weight loss measurements using the Sekine and Hirakawa's method [23]:

$$\theta = \frac{v_0 - v}{v_0 - v_m} \tag{5}$$

where v_m is the smallest corrosion rate.

All the values of coverage have been calculated and listed in Table III.

It was found that the experimental data obtained within the temperature range from 30–45°C fit Langmuir adsorption isotherm which is given by [1, 15]

$$C/\theta = 1/k + C \tag{6}$$

where θ is the degree of coverage on the metal surface, C is the concentration of inhibitor in mol l^{-1} and k is the equilibrium constant.

With the obtained values of coverage, the regressions between C/θ and C at different temperatures have been completed using computer. Fig. 2 is the relationship between C/θ and C at 35. The straight line means that there is a good linear relationship between C/θ and C, suggesting that the experimental data can be explained by the Langmuir adsorption isotherm. The obtained adsorption coefficients, slopes, and linear correlation coefficients from the regressions between C/θ and C are listed in Table IV. It is found that all the linear correlation coefficients are equal to 1.00 and all the slopes are very close to 1, so the good linear relationship between C/θ and C also indicates that the adsorption of inhibitor onto steel surface accords with the Langmuir adsorption isotherm.

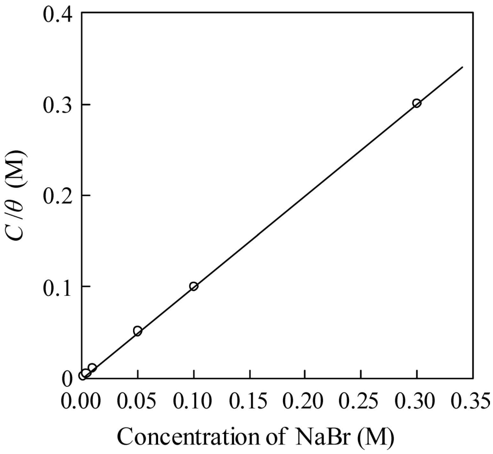


Figure 2 Dependence of C/θ on concentration of NaBr in the presence of 10 μM HTAB at 35°C.

TABLE IV. Some parameters of the linear regression between C/θ and C

Temperature (°C)	k	Slope	Linear correlation coefficient
30	18912.74	1.00	1.00
35	1939.89	1.00	1.00
40	1416.26	1.00	1.00
45	819.03	0.99	1.00

3.3. Thermodynamic parameters for the complex of NaBr and HTAB

Using the obtained adsorption coefficients, the values of adsorption free energy, adsorption heat and adsorption entropy can be calculated.

The adsorption heat was calculated according to the Van't Hoff equation [1, 21]:

$$\ln k = \frac{(-\Delta H_{\text{ads}})}{RT} + \text{Constant} \tag{7}$$

To obtain the adsorption heat, the regression between ln$k$ and $1/T$ was dealt with. 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 (ΔH°).

To obtain the standard adsorption free energy (ΔG°), the following equation was employed [1, 21]:

$$k = (1/55.5)\exp[-\Delta G^\circ/(RT)] \tag{8}$$

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

Fig. 3 indicates that there is good relationship between ln$k$ and $1/T$. For the NaBr in the presence of 10 μM HTAB, all the obtained thermodynamic parameters are summarized in Table V. The negative values of ΔG° indicate the spontaneous adsorption of inhibitor on the surface of cold rolled steel. The negative values of adsorption heat suggest that the adsorption of inhibitor molecule onto the steel surface in sulfuric acid is an exothermic process. The driving force for the adsorption is the decrease in enthalpy rather than the increase in entropy. The magnitude of adsorption heat means that the adsorption is mainly chemical adsorption. The negative values of adsorption entropy indicate that the adsorption is a process accompanied by a reduction in entropy.

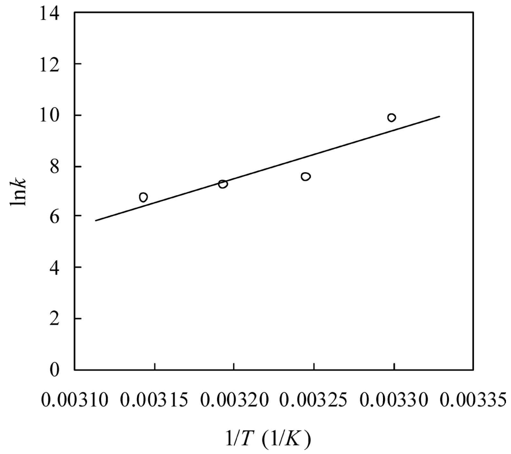


Figure 3 The relationship between ln*k* and 1/*T*.

TABLE V. The thermodynamic parameters of adsorption of different concentrations of NaBr with the addition of 10 μM HTAB on the steel surface at different temperatures

Temperature (°C)	ΔG° ($\mathrm{kJ \cdot mol^{-1}}$)	ΔH° ($\mathrm{kJ \cdot mol^{-1}}$)	ΔS° ($\mathrm{J \cdot mol^{-1} K^{-1}}$)
30	−34.943	−156.965	−402.515
35	−29.685	−156.965	−413.046
40	−29.347	−156.965	−407.529
45	−28.367	−156.965	−404.205

3.4. Synergism considerations

According to studies by Gomma [24], the synergism parameter (S_I) can be calculated using the relationship given by Aramaki and Hackermann [25]:

$$S_I = \frac{1 - I_{1+2}}{1 - I'_{1+2}} \tag{9}$$

where $I_{1+2} = I_1 + I_2$, I_1 is the inhibition efficiency of the NaBr, I_2 is the inhibition efficiency of HTAB and I'_{1+2} is the measured inhibition efficiency for HTAB in combination with NaBr.

The calculated values are listed in Table VI for different concentrations of inhibitors. From Table VI, it can be seen that the most values of S_I are greater than 1, which clearly shows that the corrosion inhibition brought about by the complex of HTAB and NaBr is synergistic. It is obvious that the higher experimental temperature, the higher the value of synergism parameter.

TABLE VI. Synergism parameter (S_I) for various concentrations of inhibitor

NaBr	HTAB	S_I			
(M)	(μM)	30°C	35°C	40°C	45°C
0.001	10	1.48	1.81	1.32	1.11
0.005	10	1.79	5.30	7.49	7.63
0.010	10	1.89	6.82	10.64	9.78
0.050	10	−7.50	6.05	11.38	19.83
0.100	10	−9.80	3.25	8.62	17.24
0.300	10	−12.16	−2.59	6.37	15.94

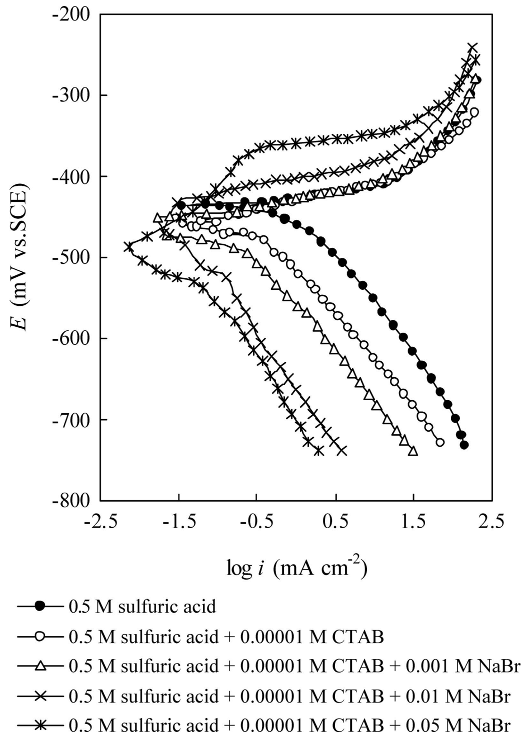


Figure 4 Polarization curves for steel in 0.5 M sulfuric acid solutions with and without various inhibitors.

3.5. Polarization measurements

In the absence and presence of HTAB and NaBr, the polarization experiments were carried out at 25°C, the polarization curves are shown in Fig. 4. The electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}), anodic Tafel slope (β_{a}) and cathodic Tafel slope (β_{c}) were calculated using Tafel fit. All the electrochemical parameters and inhibition efficiency calculated using the corrosion current density were listed in Table VII.

It can be seen from Table VII that compared with the blank, in the presence of inhibitor the value of corrosion current density become smaller, meaning that the corrosion of steel is inhibited by HTAB and NaBr. Table VII also suggests that inhibition efficiency increases with an increase in concentration of NaBr, which is similar to the regular obtained from weight loss method. The exact values between weight loss and electrochemical methods remain different, this may be the result that the electrochemical experiment was carried out at 25°C, while weight loss experiment was carried out in the temperature range from 30°C to 45°C, and the lower the experimental temperature, the higher the value of inhibition efficiency. Another possible reason may be due to the inhibition efficiency calculated from weight loss method is an average value, while the inhibition efficiency obtained from electrochemical method is a instantaneous value rather than an

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

NaBr (M)	HTAB (μM)	E_{corr} (mV vs. SCE)	i_{corr} (μA cm^{-2})	βa (mV dec^{-1})	βc (mV dec^{-1})	IE (%)
0	0	−434.85	6.75×10^2	19.38	112.55	0
0	10	−456.78	2.34×10^2	33.61	105.55	65.38
0.001	10	−467.04	8.24×10^1	47.55	89.15	87.79
0.010	10	−435.50	1.10×10^1	17.36	116.55	98.36
0.050	10	−494.76	2.22×10^1	117.10	124.54	96.70

average value. The electrochemical result, on the whole, is in good agreement with the weight loss result.

Fig. 4 clearly indicates that both anodic and cathodic reactions are dramatically inhibited by the presence of HTAB and NaBr, especially at relatively higher concentration of NaBr (above 0.01 M). Fig. 4 also indicates that the corrosion potential for the mixture of HTAB and NaBr have not been obviously shifted, meaning that the mixture behaves as a mixed–type inhibitor for the steel corrosion in sulfuric acid. It is also found that for the mixture of 10 μM HTAB and 0.05 M NaBr, when potential reaches a certain value the corrosion current density increases rapidly with the little increase in potential, meaning the existence of desorption potential. Fig. 4 suggests that jointed with NaBr, HTAB acts as an excellent inhibitor for steel corrosion in sulfuric acid, showing that there is a strong synergistic inhibition between HTAB and NaBr, the result is in agreement with that obtained from weight loss technique.

The inhibition efficiency calculated from corrosion current density for the mixture reaches a considerable value (98.36%). There is a small difference in the inhibition efficiencies calculated from corrosion current density and weight loss method, and the reason may be the difference of two methods.

4. Explanation for synergism

T.Y. Soror et al. [13] have proposed the possible mechanism for the inhibition of carbon steel corrosion by single HTAB. They attributed the effect of HTAB to the C-steel–Br$^-$ cetyl trimethyl N$^+$ composite film has a greater inhibiting effect due to its protective and compact nature.

In the present system, the possible mechanism is in the following way: it is well known that HTAB is a kind of cationic surfactant, and in strong acidic solution, HTAB ionizes and charge positive charge. It is also well known that steel surface is positively charged in presence of acidic medium [9, 26] because of $E_{\mathrm{corr}} - E_{\mathrm{q=0}}$ (zero charge potential) >0, while halide ion is negatively charged. As a result, the specific adsorption of halide ion adsorbs onto the steel surface, which causes the negatively charged surface of steel. By means of electrostatic attraction (physical adsorption), ionized HTAB easily reaches steel surface, and the dipoles of the surface compound are oriented with their negative ends towards the solution, and prevents the acid solution attach directly to the steel surface. So, Br$^-$ ion acts as an adsorption mediator for bonding the metal surface and HTAB. This gives rise to the formation of an adsorption composite film in which the bromide ions are sandwiched between the metal and positively charged part of the inhibitor. This film acts as a barrier facing the corrosion process.

5. Conclusion

1. Corrosion of cold rolled steel in sulfuric acid is efficiently inhibited by HTAB in the presence of NaBr, and inhibition efficiency increases with increasing concentration of NaBr at the same temperature.

2. At every experimental temperature, there is a synergistic effect of HTAB and NaBr in inhibiting the corrosion of steel, and the adsorption of HTAB on the cold rolled steel surface in the presence of NaBr obeys the Langmuir adsorption isotherm.

3. The polarization curves show that the complex of HTAB and NaBr is a mixed-type inhibitor.

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