Effect of Hexadecyltrimethylammonium Bromide to Control Corrosion on Mild Steel in Oilfield Brackish Water and Effluent Water

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Abstract:- The aim of study is to check the effective control on corrosion by Hexadecyltrimethylammoniumbromide as corrosion inhibitor on mild steel in the aqueous environment containing Brackish Water (BRW) and Effluent Water (EFW). Corrosion is a natural process and it occurs on mild steel producing severe destructive problems in systems such as equipment and piping systems as well as pipelines. The use of chemical treatment has found to be an inexpensive and easiest method for corrosion protection in BRW and EFW. The chemical treatment slows down the general corrosion and pitting corrosion rate and thus inhibit economic losses due to metallic corrosion. In this paper, the effects of Hexadecyltrimethylammoniumbromide on mild steel were investigated by weight loss methods keeping consideration of International Standard procedures i.e. NACE SP-0775 2018 and ASTM G1–03. Corrosion Inhibitor film efficiency depends on the chemical concentration and contact time with the mild steel metal surface. The results were supplemented with Fourier Transform Infrared spectroscopy (FT-IR) spectroscopy. The results showed that HDTMABr can control corrosion, so this is an effective corrosion inhibitor.
Key Words:- Hexadecyltrimethylammoniumbromide (HDTMABr), corrosion inhibitors, mild steel, Fourier Transform infrared spectroscopy (FT-IR) spectra.

Introduction:- In Oil and Gas industry it is the foremost problems facing low to severe corrosion. Brackish water is used as wash water and utilized in the desalter to clean crude oil. Brackish and Effluent water can be corrosive on mild steel resulting in catastrophic failures of piping, elbows and tees. The destruction caused by corrosion may result very high cost on operation and maintenance and unexpected shut down of the operating equipment, loss of valuable products, safety risk and low reliability. The main objective for current research in corrosion is economic factor. Corrosion is a naturally occurring process. In oil and gas industries corrosion is a serious and foremost problems. Mild steel is extensively used in oil and gas industry for various types of vessels, storage tanks and many other equipment.**[1]** The corrosive properties of the brackish water in mild steel corrosion was due to the higher the concentration of the inorganic ions present, Chloride typically represents the most significant percentage of the total dissolved solids to promote extremely aggressive corrosion, particularly localized (pitting, crevice, etc.) corrosion.**[2]** The Effluent water shows high corrosivity due to its high total dissolved solids more or less same as produced water and high contents of sodium chloride, which could lead to premature failures in effluent water disposal plant and injection lines.**[3]** The chances of higher corrosion is influenced by the following corrosion variables, namely: conductivity, Total dissolved solids, pH, dissolve gases, intensity of microbiological activities, temperature, pressure, and velocity. In history it was notice that severe general corrosion in carbon steel equipment/piping due to effluent water which is coming from all the gathering centers to effluent water disposal plant. There are number of chemicals to prevent corrosion, scaling deposit and growth of bacteria in these facilities.

EXPERIMENTAL

Materials and methods

Surface Preparation of the Corrosion Coupon:-Mild steel refers to low carbon steel which is usually used for structural applications. The specimens used for corrosion tests were square solid mild steel (MS) coupons with a dimension of 2 x 2 cm area have been used. Chemical composition of Mild steel coupons (C=0.20%, Mn=1.00%, Si=0.05%, S=0.025%, P=0.25% and Fe=98%) have been used.**[4]** The surface of the specimens was polished using emery paper (Silicon carbide, grade 200 - 800), rinsed with distilled water, dried and immersed in acetone for 5 sec, and finally dried at room temperature and then weighed. These polished coupons were subjected to water test in agreement as per international standards i.e. NACE SP-0775 2013 and ASTM G1–03 to make sure the metal surfaces were free of scratches and other apparent defects like pits. All reagents that were used for the study were of analytical grades and double distilled water. **[5]**

Organic Compound:-Hexadecyltrimethylammonium bromide is a quaternary ammonium surfactant. The cetrimonium (hexadecyltrimethylammonium) cation is an effective antiseptic agent against bacteria and fungi. The molecular formula of HDTMABr bromide is $C_{19}H_{42}BrN$. HDTMABr purchased from Sigma-Aldrich and used as the inhibitor, the molecular structure of HDTMABr compound is:

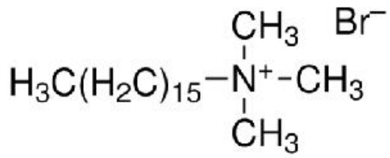


Fig 1: Molecular Structure of Hexadecyltrimethylammonium bromide

Preparation of Hexadecyltrimethylammonium bromide (HDTMABr) Solution

Brackish and Effluent water were used for weight loss method. It was used to make different concentrations range from (0.1 – 0.3) Molarity prepared for Hexadecyltrimethylammonium bromide solutions in 50 ml volume. The inhibitor is soluble in hot water.

Weight Loss Corrosion Coupon Analysis:-The mild steel corrosion coupons were immersed in BRW and EFW at different concentrations for 30 days weight loss. The experiments were carried out to study the corrosion inhibition effects of HDTMABr as inhibitor at different concentrations.In the weight loss experiment, the mild steel coupons were accurately weighed and then immersed in 50 ml each of test solution contained in a plastic bottle. The first bottle was used as blank and rest were used to contained as corrosion inhibitor at different concentrations of 0.1M, 0.2M and 0.3M prepared for HDTMABr kept at constant temperature 25±1°C throughout the experiment. After the period of 30 days, the mild steel coupons were removed, scrubbed with 000 grade steel wool in soap solution, degreased with acetone, dried in warm air and re-weighed. A calculation of average corrosion rate, expressed as uniform rate of thickness loss per unit time in mils per year (mpy), is shown in equation (1)

$$CR = \frac{WX365X1000}{ATDX\,(2.54)^3} = \frac{2.227X10^4\,XW}{ATD} \qquad (1)$$

Where CR = Average corrosion rate, mils per year (mpy)

W = Weight loss in grams (g)

A = Coupon surface area in square inches (in^2)

T = Exposed time in days (d)

D = Density of the metal coupon in grams per cubic centimeter (g/cm^3)

Guidelines for general and pitting corrosion rates are classified 'Low, Moderate, High and Severe' as per NACE as shown in **Table-1**

Table. 1 Corrosion and Pitting Rates classification as per NACE SP0775-2018 (mpy = mils per year)

General Corrosion	Corrosion rate	Pitting Corrosion	Pitting Rate
Low	<1 mpy	Low	<5 mpy
Moderate	1-4.9 mpy	Moderate	5-7.9
High	5-10 mpy	High	8-15
Severe	>10 mpy	Severe	>15 mpy

The inhibition efficiency of all the inhibitors was determined for three different concentrations was measured using the equation (2)

$$\text{Inhibition Efficiency (I\%)} = \frac{W_O\text{-}W}{W_O} \text{ X } 100 \qquad (2)$$

Where W is the loss in weight with inhibitor in the solution and W_0 is the loss in weight without inhibitor in solution.

During the weight loss study of mild steel in BRW and EFW, Hexadecyltrimethylammonium Bromide (HDTMABr) used as inhibitor.

RESULTS AND DISCUSSION:-

Analysis of Weight Loss Study

The effect of inhibition efficiencies (IE) and corrosion rates (CR) of HDTMABr in controlling corrosion of mild steel immersed in BRW and EFW with and without inhibitor for a period of 30 days of varying concentration of 0.1M, 0.2M and 0.3M at 25±1°C temperature was studied, and it is given in Table 2.

Table 2. Different concentration of HDTMABr for 30 Days exposure at room temperature 25±1°C in the presence and absence of inhibitor by weight loss parameters of mild steel coupons in BRW and EFW.

	Conc. (M)	Initial Wt.	Final Wt.	Wt. Loss (mg)	CR (mpy)	IE (%)
BRW	0	9.3002	9.1154	0.1848	2.38	0.00
	0.10	9.6282	9.5968	0.0314	0.41	83.01
	0.20	11.5499	11.5315	0.0184	0.24	90.04
	0.30	11.6468	11.6364	0.0104	0.13	94.37
EFW	0	9.7058	9.2668	0.4390	7.35	0.00
	0.10	9.5287	9.5064	0.0223	0.37	94.92
	0.20	10.3506	10.3407	0.0099	0.13	97.74
	0.30	11.7442	11.7379	0.0063	0.08	98.56

It was observed that as the increase in the inhibitor concentration was accompanied by a decrease in corrosion rate and an increase in the percentage inhibition efficiency. It has been observed that in 30 days weight loss inhibition efficiency of inhibitor improved from 0.1M to 0.3 M in HDTMABr and attain maximum inhibition efficiency in 0.3M are 94.37 % in BRW and 98.56 % in EFW respectively. The corrosion rate was calculated in 0.3M are 0.13 mpy in BRW and 0.08 mpy in EFW respectively. From the above results it was observed that HDTMABr is proved to be an effective corrosion inhibitor in BRW and EFW. The inhibition efficiency of corrosion inhibitor was found to be dependent on the inhibitor concentration. The addition of HDTMABr reduces metal dissolution in an aqueous environment and this may be due to adsorption and complex formation at the metal surface. The adsorbed layer combats the action of Brackish and Effluent water and enhances protection of the metal surface.

Mechanism of Inhibition:-

The inhibitor is a long chain compound with a large molecular weight ($C_{19}H_{42}NBr$ or $C_{16}H_{33}$ - $N+(CH_3)_3Br-$) is shown in Fig. 2

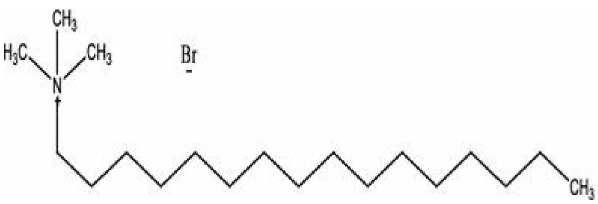


Fig. 2

The mechanism can be discussed based on adsorption of HDTMABr on mild steel in aqueous solution. Since the organic compound is a long hydrocarbon chain which can adsorb on metal/solution interface and enhance adsorption. It consists of hydrophilic group and hydrophobic group. Hydrophilic part $+N(CH_3)_3$ is a polar group which may adsorb at steel/solution interface and hydrophobic part is a non-polar group which spread into the solution.**[6]** The adsorption of positive quaternary ammonium ions (hydrophilic part) on metal depends mainly on the amount of Br- ions adsorbed on mild steel, more number of Br- ions adsorb facilitate the adsorption of $+N(CH_3)_3$ ions and due to the synergistic effect between positively charge nitrogen and negatively charged metal surface which is predominantly covered by Br- ions making it negatively charged through ionic bonds and this leads to a high protection. Br- ions act as intermediate bridge on the metal surface. The chemisorption takes place due to formation of coordinate bond between vacant d-orbitals of metal and lone Pair of nitrogen atom. The inhibition efficiency enhanced with increasing concentration of inhibitor in solution.**[7]** The smaller spacer and long alkyl chain, the denser will be the adsorption layer on the mild steel surface, and thus higher efficiency for inhibition of iron dissolution.

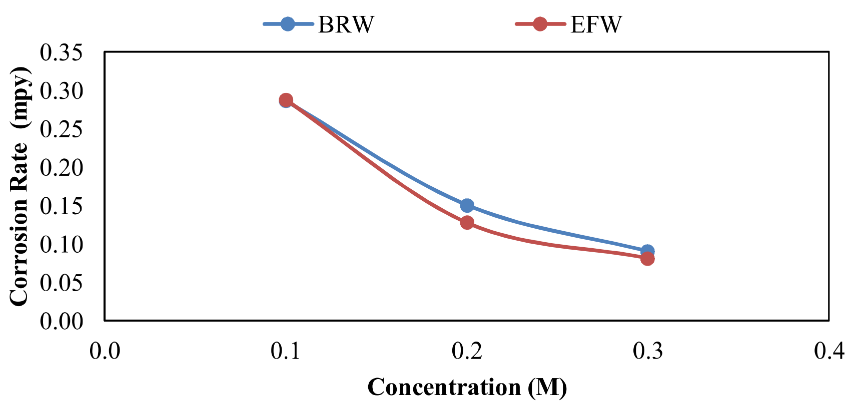


Fig. 3 Corrosion rate vs Conc. at 25°C temperature for HDTMABr for 30 Days exposure in BRW and EFW

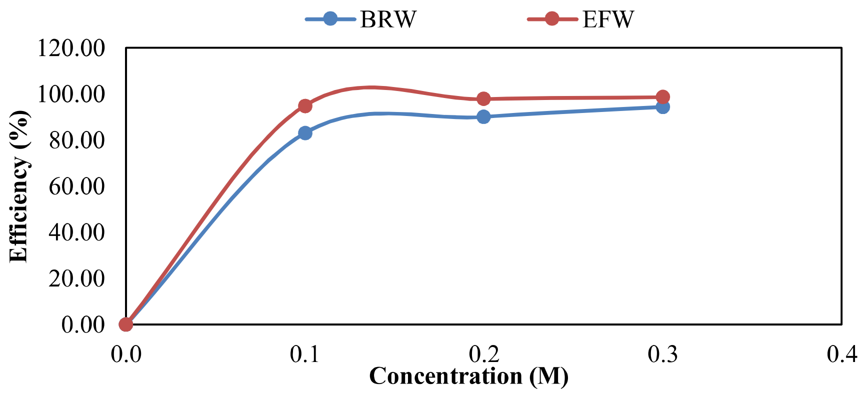
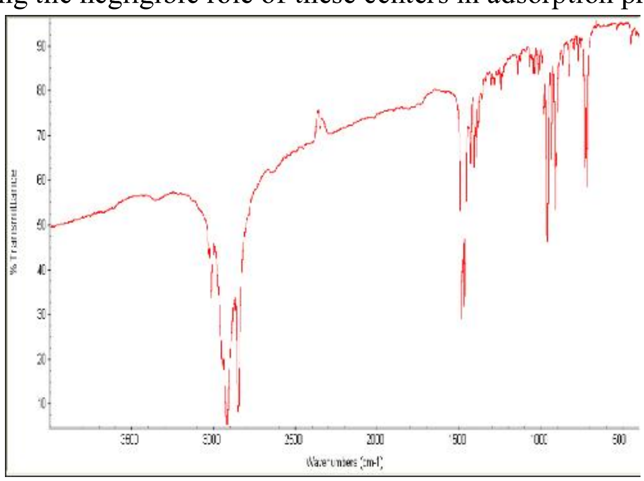
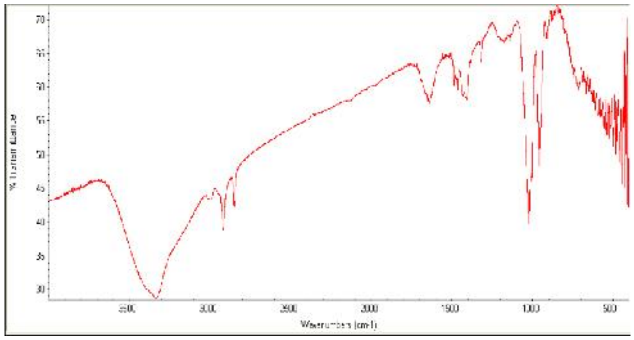


Fig. 4 Efficiency vs Conc. at 25°C temperature for HDTMABr for 30 Days exposure in BRW and EFW

Analysis of FTIR spectra:-Fourier transform infra-red spectroscopy Perkin-Elmer 'Spectrum Two' Spectrophotometer (spectral resolution 0.5 cm^{-1}) was used to record the FT-IR spectra of pure specimen (HDTMABr) and specimens adsorbed on the carbon steel surface. The carbon steel specimens were immersed in various test solutions for one week were taken out cleaned and dried first, and the thin film formed on the metal surface was carefully removed. To record the FT-IR spectra of pure samples, the powder was mixed with KBr and made into the disc. The spectra were recorded in the frequency range of 200 - 4000 cm^{-1}. Data was collected and interpreted by the Spectrum Software.The IR spectrum of film formed on the steel surface (Fe^{2+}- specimen) show all the characteristic peaks of HDTMABr with shifting of the molecular vibrations to either higher or lower wave-numbers. These shifts of the molecular vibrations to higher or lower wavenumber may be due to the formation of the complex between Test Specimens and Fe^{2+} on the carbon steel surface. Comparing the IR spectra of pure specimens HDTMABr with the one adsorbed over carbon steel (Fe^{2+}- HDTMABr), it can be seen that shift in the peaks for -NH stretching vibrations 2840 cm^{-1} has been shifted to 3335 cm^{-1} whereas with the one adsorbed over carbon steel (Fe^{2+}) shows a very small peak at 3383 cm^{-1}. The shift observed in the other peaks of Fe^{2+}-Specimen (scrapped samples) is not so significant suggesting the negligible role of these centers in adsorption process.



(a)



(b)

Figures 5: (a) FTIR Spectrum of pure HDTMABr

(b) HDTMABr adsorbed on metal

Conclusions:-This research investigated the phenomenon of corrosion of mild steel metal in BRW and EFW. Weight loss method, FT-IR analysis were used in this study. From the result and discussions, the following conclusions were derived.

- Hexadecyltrimethylammonium Bromide acts as good inhibitor for mild steel in BRW and EFW.
- From the weight loss study, it is showed that strong electrostatic interaction between the mild steel surface and Hexadecyltrimethylammonium Bromide through physio-chemical adsorption occurred in the inhibition process.
- Inhibition efficiency increased with increase in Hexadecyltrimethylammonium Bromide concentration.
- From the results of FT-IR spectral analysis it is confirmed that the adsorption of inhibitor is good on surface of metal.

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