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Nonionic Surfactants as Corrosion Inhibitors for Carbon Steel in Hydrochloric acid Medium

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Abstract

The utilization of surfactants is one of the several means for protecting a metallic surface from lectrochemical oxidation or corrosion. The amphiphilic nature of these surfactants encourages the preparation of a self-protective layer on the metallic surface, adequately reducing the area of contact between the liquids and the metal, therefore preventing corrosion. Most of the cationic surfactants like CTAB (Cetyltrimethylammonium bromide) have been utmost frequently used as a corrosion inhibitor of mild steel in acidic medium, yet since it is not eco-friendly its utilization has been depressed. As a substitute, the utilization of non-ionic surfactants like TritonX100, Tween 20, Tween 80 and Brij 35 which are considerably more eco-friendly were observed as inhibitors in this paper. It is well known that carbon steel is a usual material of construction of various mechanical vessels and equipment's used in industrial practice which on continuous usage leads to corrosion of material. Here in this paper we investigate that by using nonionic surfactants which are ecofriendly and sustainable as corrosion inhibitors, in interaction with hydrochloric acid (HCL) to deliberate their mechanism of action and how it can be a substitute to cationic surfactants. In this study it is found that the non-ionic surfactants indicated inhibition efficiencies around 91-92%, which is extremely nearer to that of CTAB (97%) which is cationic surfactant at concentrations of 300-500 ppm with 1M HCL at 30°C. Tween 20 and Tween 80 also demonstrated closer outcomes nearer to CTAB, intently pursued by TritonX100, while Brij 35 slacked. The inhibiting effect of Tween 80 on corrosion of steel in 1M HCL is studied by weight loss technique. Meanwhile, the concentrations of the non-ionic surfactants utilized are in ppm (parts per million), and it is proven that nonionic surfactants which are more environment friendly compared to cationic surfactants pl ay a major role in coatings for carbon steel equipment and is alsoexceptionally cost-effective and hence can be a worthy substitute to CTAB which is a cationic surfactant. And, cationic surfactants are very expensive than nonionic because of the high-pressure hydrogenation reaction carried out during their synthesis hence a better substitute for corrosion inhibition is nonionic surfactant.

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1. Introduction

Formation of gas hydrates and corrosion in pipelines are major challenges in flow assurance[1]–[9]. These issues cause a huge impact to the production in terms of the cost involved, the engineering effort and maintenance that have to be invested [10], [11]. While the study on hydrate inhibitors [12]–[15], and corrosion inhibitors [10], [16],

[17], the researches on environmentally friendly dual functioning gas hydrate and corrosion inhibitor are ongoing as the presence of one causes negative impact on the another's performance [18], [19]. Some non-ionic surfactants show the ability to be Anti-Agglomerate (AA) hydrate inhibitor along with corrosion inhibiting property[20],[21]. In this paper, the corrosion inhibition of certain surfacetants is analyzed.

Corrosion takes place in the presence of oxygen, moisture and involves two electrochemical reactions. The regular techniques used to avoid corrosion in iron-based materials include surface coatings anodization, anodic and cathodic protection. Coatings are comprised of specific atoms which structure a defensive boundary between the outside of the metal and the environment. These particles are otherwise called "corrosion inhibitors" and are essentially natural, inorganic, a surfactant or blended material substances. Corrosion inhibitors have proven to be one of the best ways of enhancing corrosion resistance[22]. Numerous technical studies/investigations deal with corrosion inhibitors. Organic compounds are notable corrosive inhibitors utilized in industries. These organic compounds have numerous bonds which essentially contain nitrogen, sulfur, and oxygen atoms through which they get adsorbed on the metal surface. Impact of temperature on the inhibiting procedure is of vast impact in the industry.

Efficient inhibitors are relied upon to perform under a wide scope of conditions. The inhabitance efficiency/productivity relies upon the parameters of the framework (temperature, pH, time, and metal composition analysis) and on the structure of the inhibitor particle.

Surfactants or surface-active compounds have been demonstrated to be economic friendly anti-corrosive substances.

Surfactant inhibitors have numerous favourable benefits, for instance, high inhibition throughput, low cost, low toxicity, and easy to manufacture. The high activity of the micelles to adsorb onto interfaces is the thing that makes surfactants perfect to use as corrosion inhibitors. Surfactants can stabilize mechanical and cost-effective loss because of their being inexpensive and competent. The best concentration for inhibition is typically much lower than the Critical Micellar Concentration (CMC) of the surfactant [23].

The cationic surfactant, CTAB is a good inhibitor for the corrosion of C-steel in 1M and 2M HCLsolution, and Inhibition Efficiency (IE) was 87% in 2M HCL. CTAB pursued the Langmuir adsorption isotherm[24]. However, CTAB surfactant is not eco-friendly and needs to be replaced. Masroor et al [25] observed the non-ionic surfactant, Triton X-100 to be an efficient corrosion inhibitor for Al in 1M HCL, with an efficiency of 76%. With an increase in temperature, the inhibition efficiency decreased. An addition of Gemini surfactant (GS) synergistically improved the inhibition efficiency of Triton X-100 and higher efficiency of 94.26% is perceived. The weight reduction and SEM analysis concur sensibly and further affirm the inhibitory activity of Triton X100 on Al [25]. Sobhi et al [26] have tested nonionic surfactants such as Polysorbate 20 (Tween 20), 40 and 80, for their corrosion inhibition performance. The tested polysorbate mixtures restrained the corrosion of C-steel in 2.0 M HCL. Polysorbate compounds made a passive oxide film on the surface of the metal by forming a protective layer. With the increase in the hydrocarbon chain of polysorbate and increase in acid concentrations, the inhibition efficiency increased [26]. The adsorption of Tweens on C-steel obeys Langmuir adsorption isotherm[27]. Using nonionic surfactants which are eco-friendly it was found that the non- ionic surfactants indicated inhibition efficiencies around 91-92%, which is extremely nearer to that of CTAB 97%at concentrations of 300-500 ppm with 1M HCL at 30°C When the temperature of the setup was increased, inhibition efficiency was found to diminish considerably, down to practically 30% at 80°C. The inhibition efficiency diminished to half with an incremental increase in acid concentration up to 4M HCL. Tween 20 and Tween 80 demonstrated closer outcomes nearer to CTAB, intently pursued by TritonX100, while Brij 35 slacked[28]. With nonionic surfactants like Tween 20 & Tween 60, the inhibiting effect on corrosion of C-steel in 0.5M HCL was studied by weight loss method. It showed that IE increases with increase in inhibitor concentration while decreases with increase in temperature.

Salem [29] experimented on the impact of nonionic surfactant, Brij 58 as co-surfactant with anionic surfactant, sodium dodecyl sulphonate (SDSO). SDSO indicated corrosion inhibition efficiency of about 84% at a reasonably higher concentration of SDSO. The inhibition impact of SDSO was disclosed to be because of its adsorption on the cathodic locales on the carbon steel surface. The optimal quantity of SDSO was observed to be very lower than the CMC of SDSO. Addition of a co-surfactant Brij 58 improved the anticorrosion property of SDSO [29]. The corrosion efficiency of Sodium dodecyl sulfate was examined here. At lower pH (pH=6) IE diminished and in alkali medium (pH=8) IE improved. Intensifying the surface action of inhibitors extended their IE. The adsorption of the various inhibitors on C-steel surface followed Langmuir adsorption isotherm. Recent non-ionic surfactants (I and II) indicated high IE even at low concentrations where the inhibitors performed as blended inhibitors. The percentage IE (η%) of the surfactants expanded by increasing the molecule size. The IE was ascribed to the sturdy adsorption capacity of the chosen surfactants on C-steel surface, shaping a decent protective film, which separates the surface from the hostileconditions[31].

In this paper, the corrosion inhibition efficiency of nonionic surfactants TritonX100, Tween 20, Tween 80 and Brij 35 are analysed and compared with CTAB. Economic evaluation has been done based on the IE and cost per 100ml of the chemical.

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2. Methodology

Materials

TritonX100 (assay≈ 98%), Tween 20 (assay≈ 98%), Tween 80 (assay 99%), Brij 35 (assay 99%), C16TAB (assay 99%), and HCL (assay 32-38%) are purchased from MERCK. The Carbon steel plates with the respective metal composition C-23%, Mn-30%, P-3.5%, S-4%, Fe- 35%, Cu-1.5%, Ni-1.8%, Cr- 1.2% and dimensions of 3.0 x 2.5 x 0.3cm are used as the test material to be submerged in test medium that is HCL medium.

Preparation method

The test materials, C-steel are roughened with emery paper to eliminate the surface impurities. C-steel plates is then washed with 1M HCL to remove oxides, washed with acetone to remove grease, then washed with distilled water and then dried. Various nonionic surfactants like Triton X100, Tween 20, Tween 80, Brij 35, C16TAB are used for experimental study as corrosion inhibitors using 1M HCL in different beakers. 1M HCL of 36% assay is used where 87.33cm3 of HCL is diluted with 912.67cm3 of distilled water. 1L Triton X 100 stock solution of 1000 ppm is prepared. Various concentrations of 100, 200, 300, 400 and 500ppm are weighted and added to the investidated solution.. 5cm3 of Triton X 100 solution is taken from 1000ppm stock solution and diluted with 45cm3of 1M HCL to prepare 100ppm of Triton X 100 solution and similarly 10cm3 for 200ppm, 15cm3 for 300ppm, 20cm3 for 400ppm and 25cm3 for 500ppm. Similarly, other non-ionic surfactants like Tween 20, Tween 80, Brij and CTAB stock solutions are also prepared.

Weight Loss Method

C-steel plate is accurately weighed electronic digital weighing balance Mettler Toledo which has a sensitivity of 0.01mg and a standard deviation of ±0.02 mg and immersed in 50mL of the prepared acid solution with the surfactant of a predetermined concentration.

The setup, as shown in Fig.1 is then left for 24 hours at room temperature of 26°C or kept in an oven for analysis using different temperatures. After 24 hours, eachplate is then carefully removed, washed, dried and weighed again.

Figure 1: The experimental setup

The corrosion rate (Cr), material remaining after corrosion (θ), surface coverage, inhibition efficiency (η%) of the surfactants were determined using equations (1)-(3).

$$v\boldsymbol{Cr} = \frac{wo-wi}{At\rho} \quad (1)$$

$$\boldsymbol{\theta} = \frac{Cr1-Cr2}{Cr1} \quad (2)$$

$$\boldsymbol{\eta}\,\% = \theta \times 100 \quad (3)$$

where,

wi = weight before corrosion (g)
wo = weight after value (g)
A = total area of the specimen (cm2)
ρ = density of carbon steel (7.833g/cm3)
t = immersion time (hr)
Cr = Corrosion rate (cm/hr)
θ = Material remaining after corrosion
η% = Inhibition efficiency
C = Concentration of inhibitor (mol/g)
Cr1 = Corrosion rate without inhibitor for the conditions (cm/hr)
Cr2 = Corrosion rate with inhibitor for the conditions (cm/hr)

3. Results And Discussions

Illustration with the help of graph is shown below based on different parameters like effectof PPM on IE, effect of immersion time on IE, effect of concentration of acid on the IE, effect of temperature on the IE, weight loss curve of C-steel in 1M HCL in the absence and presence of Tween 80 at 20°C were plotted. The other parameters are kept constant when one parameter is tested. The results were then compared.

Based on Fig. 2, it is observed that CTAB showed a maximum IE of 97.61%. Though this is a basis for comparison against the non-ionic surfactants, it almost offered complete surface protection for 1M HCL, 30°C for 24 hours. Tween80 showed the maximum IE among all the non-ionic surfactants at 92.38%, while Tween 20 and TritonX100 were closely at 91.63% whereas Brij 35 did not show much efficiency when compared to the others from Fig 2. This larger efficiency could be attributed to the number of functional groups present in each surfactant which latch on to the metallic surface.

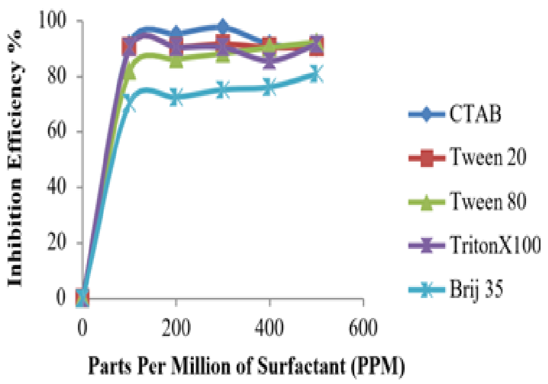

Figure 2: Effect of concentration (ppm) on IE

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The dependency of immersion time on IE is calculated from the observed values, as shown in Fig.3. The immersion times is varied from 3 to 48 hours. From the below graph in Fig.3, it is clearly seen that the immersion time of the metal decreased initially and then increased and kept steady later on. This is due to the adsorption process, where the molecules initially get adsorbed onto the surface. The movement of the molecules may be slow in the medium.

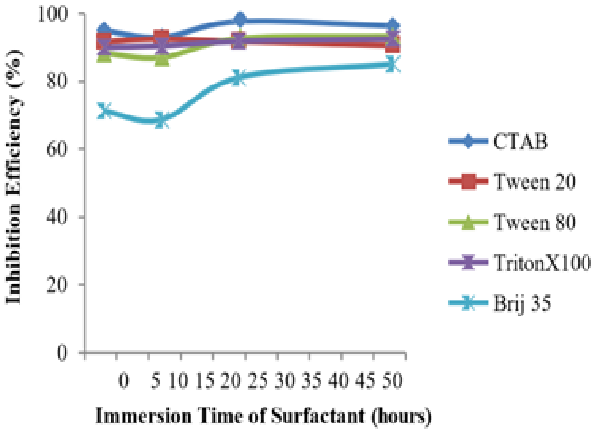

Fig. 3 Effect of Immersion time on IE

It is seen from Fig.4, that the IE decreased with the increase in the concentration of the acid substantially. The number of HCL molecules kept increasing with increasing concentration, while the number of surfactant molecules is kept constant, because of which the surface is exposed. This is the reason for this decrease in IE.

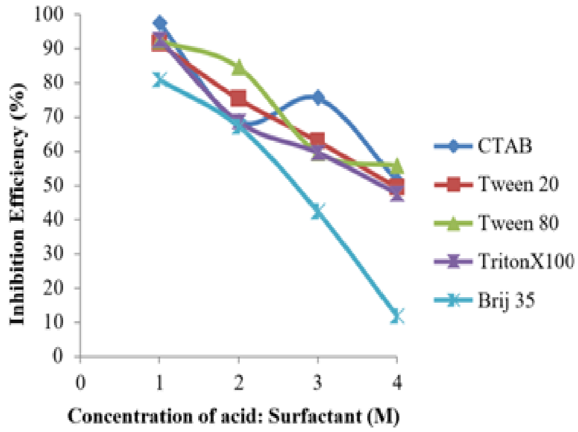

Fig. 4 Effect of concentration of acid on the IE

With the increase in temperature, the surfactant molecules break down hence there is a decrease in IE with an increase in temperature as seen from Fig. 5. With increase in temperature leads to an increase of the dynamic energy for the inhibitor molecules. This raises the rate of their collision with each other. This is turn impedes and slows the formation of the protective film of inhibitors on the metal surface. Thus increase in temperature causes the strength of the adsorption molecules on the metal surface by decreasing the IE.

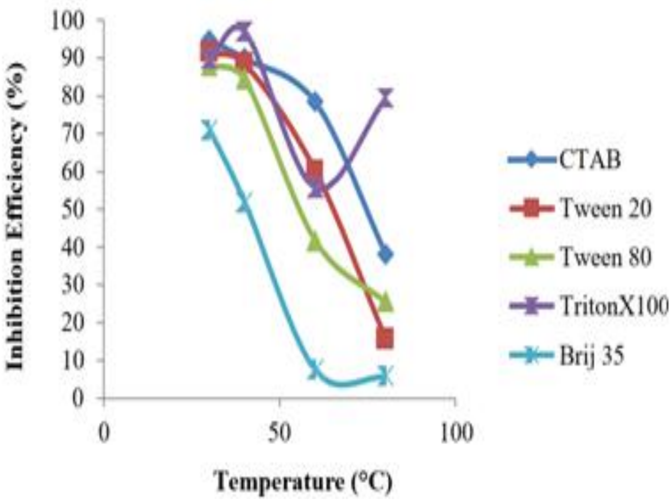

Fig. 5 Effect of temperature on the IE

Weight loss-time curves of C-steel at different concentrations of Tween 80 are shown in Fig 6. The curves show that the weight loss values of C-steel in 1M HCL containing Tween 80 decreases as the concentration of the inhibitor increases that is corrosion inhibition strengthens with non-ionic surfactant concentrations.

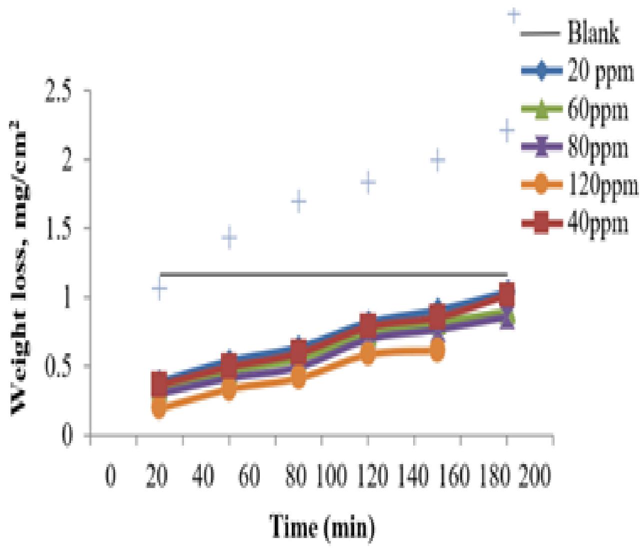

Fig. 6 Weight loss curve of C-steel in 1M HCL in the absence and presence of Tween 80 at 20°C

In comparison to CTAB, all the non-ionic surfactants exhibited very good results. Table 1 shows a comparison carried at different experimental runs. The nonionic surfactants used exhibited more or less similar results to that of CTAB. The Tween 80 surfactants undermined the others because of lower cost and maximum IE, while being eco-friendly version of the toxic CTAB. TritonX100 comes close behind, in terms of all the parameters. Brij 35, on the other hand, did not show a very convincing outcome on IE, and so its use as an ecofriendly alternative CI for C-steel may be discouraged.

Table 1: Comparison chart of surfactants tested in this experiment

Surfactant	CTAB	Tween 20	Tween 80	TritonX100	Brij 35
Max. IE (%) at room temperature	97.61	91.83	92.46	91.70	81.95
PPM for Max. IE	300	300	500	500	500
IE for an immersion time of 48hrs	96.32	90.50	93.11	92.66	84.92
IE at 80°C	38.09	15.59	25.48	79.55	5.88
Environment-friendly	No	Yes	Yes	Yes	Yes
Cost per 100mL/100g	88	210	349	240	244

4. Conclusion

The efficiencies of the non-ionic surfactants remained very near to that of CTAB from 100 – 500 ppm. The inhibition efficiencies of nonionic surfactant is found to increase with the concentration of the surfactants, till the maximum IE is attained. The IE decreased with the increase in the concentration of the acid for all the non-ionic surfactants even with CTAB. TritonX100 worked out to be as the best non-ionic surfactant for varying concentrations from 1M-4M HCL. The inhibition efficiency decreased with increase in temperature up to 80°C. TritonX100 again showed better efficiency for varying temperature conditions from 30°C -90°C.The immersion time did not affect the inhibition efficiency much. Almost all the non-ionic surfactants showed positive results. Tween 20 and Tween 80 showed similar results, very close to TritonX100, while Brij 35 did not show great efficiency. Out of all the non-ionic surfactants, the Tween compounds showed the best efficiencies for effect of ppm, effect of immersion time, concentration of acid and for different concentrations of Tween 80 at different time intervals varying from 10 mins to 200 mins. These results are pretty much comparable to that of CTAB. Moreover, these nonionic surfactants are also economical when compared to TritonX100 and Brij35, though there is not a large difference in costs.

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