

CORROSION INHIBITION PROPERTIES OF SOME NOVEL N-METHYL DIETHANOLAMMONIUM BROMIDE CATIONIC SURFACTANTS

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ABSTRACT:

A series of novel cationic surface-active agents containing two hydrophobic chains were evaluated for their corrosion inhibition efficiency at different doses using the weight loss method at 25°C. The applicability of these inhibitors for mild steel was examined using (4M HCl) at 50, 100 and 200 ppm of the inhibitor concentrations. The results were correlated to their chemical structures and their geometry. The results showed that increasing the hydrophobic chain length, as well as, the number of conjugated double bonds along the alkyl chains of these inhibitors increases their corrosion inhibition efficiency. The maximum corrosion inhibition efficiency of the synthesized inhibitors containing similar hydrophobic groups was discussed.

INTRODUCTION:

Corrosion process is one of the most dangerous action proceeded by the corrosive environments either liquids or vapours upon metal tools in industry ⁽¹⁾. This process leads to great damages in the metallic parts, joints and pipes which costs numerous losses in the industrial projects, specially in pipe lines. The needs of corrosion inhibitors increased largely in the present

time to prevent the corrosion problems in the petroleum projects. That is due to the contamination of the oil with several corrosive components such as sulfur dioxide (SO₂) and hydrogen disulfide (H₂S). Hence, investigators dealt with synthesis of several types of corrosion inhibitors like amides ⁽²⁾, amines ⁽³⁻⁴⁾, quaternary ammonium compounds ⁽⁵⁻⁶⁾, polyamines ⁽⁷⁾, nonionic ethoxylates ⁽⁸⁻¹⁰⁾ and isothiuronium derivatives ⁽¹¹⁾. Quaternary ammonium compounds are considered as one of the most economical class of corrosion inhibitors, which are widely used.

In this work, a series of novel cationic surface-active agents based on methyl diethanolamine were evaluated as corrosion inhibitors for mild stainless steel in acidic medium (4N-HCl) at different doses (50, 100 and 200ppm) using weight loss technique.

Corrosion Inhibition Measurements:

Weight loss experiment was performed at 25°C to measure the inhibiting efficiency of the prepared cationic surfactants for mild steel in HCl solutions. The experiments were performed with mild steel specimen having composition (wt per cent): 0.2C, 0.03Si, 0.5Mn, 0.8P, and the remainder is Fe. The specimen was machined into regular form of 4cm² cross-sectional area. The specimen was sequentially abraded with different grades of emery papers, degreased with acetone, washed with bi-distilled water and dried. Aggressive solutions of 4N-HCl in absence and presence of the prepared surfactants at different doses of 50, 100 and 200ppm were prepared from doubly distilled water⁽¹³⁾. In order to make it easier to determine corrosion (%), the results of the weight loss have been directly converted into loss of thickness, expressed in microns per annum, using the following formula⁽¹⁴⁾:

$$\mathbf{P \times 365}$$

$$\mathbf{Corrosion\ in\ microns\ per\ annum. = \frac{\quad}{\quad}}$$

$$\mathbf{10 \times J \times S \times D}$$

where in, **P** = loss of weight given in milligrams, **J** = number of days of exposure in corrosive medium, **S** = external surface area of the metal specimen given in cm², **D** = specific mass of the used metal given in g/cm³.

Control sample (the test specimen without any inhibitors in the same corrosion conditions) shows 95microns loss in thickness for 30day duration (100%).

Biodegradability:

The biodegradability of the prepared cationic surfactants was performed at 25°C using Die-away test in river water. The test was preceded by preparing 1% surfactant solution in freshly obtained river water, and then the surface tension was measured periodically (each day) for each sample during

the degradation test ⁽¹⁵⁾. The change in the surface tension of the tested inhibitors was used as indicator for their degradation due to the surface activity of these inhibitors. Hence, any change in their composition, i.e. concentration of the active matter, changes the surface tension of their solutions.

RESULTS AND DISCUSSION:

The synthesis routes of the used inhibitors were illustrated in our earlier work ⁽¹²⁾ including elucidation of their structures which, were established according to:

1. Corrected elemental analysis.
2. Spectroscopically (FTIR, ¹H-NMR and MS)

Corrosion Inhibition:

The mechanism of corrosion inhibition of surfactant molecules being either molecular or micellar one ⁽¹⁶⁾ depend on the initial inhibitor concentration applied in the medium. The used inhibitor concentrations are 50, 100 and 200ppm, which is widely lower than their critical micelle concentrations. Hence, the mechanism of inhibition process could be, as expected, the molecular one through the adsorption process.

The results of corrosion inhibition efficiency of the synthesized inhibitors are listed in Table (1). Rationalization of the chemical structure of these inhibitors by their corrosion inhibition efficiency could be done through classifying them into three classes:

Class 1: Longer hydrophobic chains posses higher inhibition efficiency, which can be seen for surfactants (I_c, III_d), Figures (1,2).

Class 2: The presence of conjugation within the inhibitor molecules increases the inhibiting efficiency (IV_b, V_a, V_b, V_c, V_d), Figure (3).

Class 3: The similarity between the two hydrophobic chains raises the inhibiting efficiency to higher extent as in case of surfactants (I_b, II_c, III_d).

The three mentioned classes of inhibitors showed the maximum corrosion inhibition efficiencies between the synthesized surfactants ranging between 93.57% and 93.13%.

The inhibition mechanism of the studied compounds is attributed to the adsorption of positively charged n-alkyl quaternary ammonium ions on the metal surface, accompanied by co-adsorption of halide ions ⁽¹⁷⁾. The first adsorbed ions of inhibitors are attached to the most active anodic sites, usually considered to be the corners or edges of incomplete layers of atoms on the metal surface ⁽¹⁸⁾. Hence, the factors, which enhance the adsorption of inhibitor molecules at the surfaces, facilitate also the inhibition efficiency of these inhibitors.

The standard free energy changes of adsorption for the synthesized inhibitors were found to be more negative than those of the micellization values ⁽¹²⁾. Hence, it can be concluded that these surfactants prefer the adsorption at the interfaces rather than the micellization in the bulk of their solutions. As a result, it is expected that these surfactants could be used as interfacial influencing materials (i.e. emulsifiers, corrosion inhibitors and phase transfer catalysts).

The hydrophobic chain length plays an important role in corrosion inhibition of the inhibitor molecules. That role is exhibited through the isolation of the corrosive media away from the metal surfaces by means of the hydrophobes. Hence, increasing the hydrophobic chain lengths increases the distance between the corrosive medium and the metal surface, as shown in class (1).

The presence of unsaturated sites within the hydrophobic chains increases the ability of inhibitors towards adsorption at the interfaces, which could be seen in class (2).

Many studies have revealed that inhibition efficiency of n-alkyl quaternary ammonium salts increases with increase in chain length. For a family of molecules, which differ in length of carbon chain the inhibitory action obeys Traube's rule⁽²⁰⁾ for values of hydrophobicity corresponding to chain lengths of less than 11-12 methylene groups. Above this length, this rule is no longer observed, and the inhibitory action either decreases or remains the same depending on the type of molecules.

The geometrical structure of the adsorbed inhibitors at the metal-liquid interface plays an important role in the surface protection of the metal surfaces. The well arranged hydrophobes at the interface were provided by the identical chains, hence the inhibitor molecules containing symmetrical hydrophobes possess higher inhibition efficiency rather than the asymmetrical hydrophobic groups, as can be seen in class (3).

Perceptibly from Figure (3), surfactants IV_d and V_d provided the most effective inhibitors for mild steel against the corrosive media consisting of

4N-HCl. That is due to the presence of unsaturation sites in their chemical structure, which produces higher adsorption at the metal/liquid interface. Also, the symmetry of the hydrophobic chains yielding the maximum arrangement and well tighten and packed layers of them, which provided higher corrosion inhibitory action.

Increasing the corrosion inhibitor concentrations up to 100 or 200ppm has an increasing influence on the inhibition efficiency of the applied inhibitors, Table (2,3). That is due to the accumulation of the adsorbed ions at the metal/liquid interface due to van der waal's forces between the inhibitor molecules and the metal surface. The driving force of the accumulation process at the interface is the Hydrophilic – Lipophilic Balance (HLB) values and the hydrophobicity of these molecules. Decreasing the HLB values of the compounds increases their tendency towards adsorption at the interfaces, and vice versa. The inhibition of corrosion reaction proceeded via steric hindrance of the escaped Fe^{2+} ions, also because of the adverse electric field from the positively charged layer of the adsorbed cationic ions of the inhibitors at the interfaces.

Biodegradability:

The results of biodegradation die-away test ⁽²¹⁾ in river water is clear from Table (4). The biodegradation ratio ranged between 95%–99% for the 7th day, Figure (4-6).

Hence, the synthesized surfactants have the applicability in the open environment (sea water or river water) without any dangers of pollution or accumulation in the soil due to their ability to degrade biologically within 7 days by the action of water microorganisms including bacteria and fungi ⁽²¹⁾.

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Table (1): Corrosion Inhibition Efficiency of the Synthesized Quaternary Ammonium Surfactants at 50 ppm

Surfactant	Corrosion (microns)	Corrosion %	Inhibition Efficiency %
Blank	95.5	100	0.00
I_b	7.54	8.00	82.00
I_c	6.70	7.10	92.90
I_d	6.53	6.87	93.13
II_b	6.95	8.00	92.00
II_c	7.36	7.75	88.25
II_d	14.30	15.0	84.95
III_b	6.59	8.94	91.13
III_c	6.14	7.46	92.54
III_d	6.93	7.30	92.70
IV_b	8.27	8.71	91.30
IV_d	6.42	6.76	93.24
V_a	7.11	7.50	88.25
V_b	9.76	10.27	89.73
V_c	5.67	6.00	92.00
V_d	6.11	6.43	93.57

Table (2): Corrosion Inhibition Efficiency of the Synthesized Quaternary Ammonium Surfactants at 100 ppm

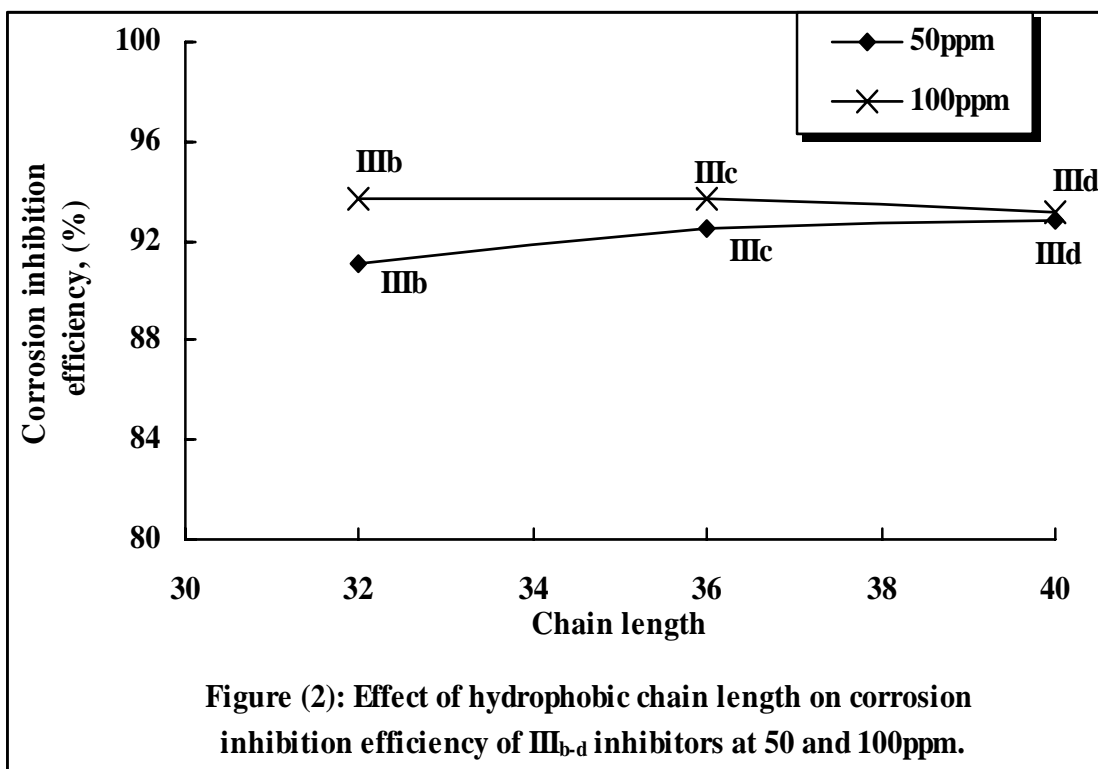
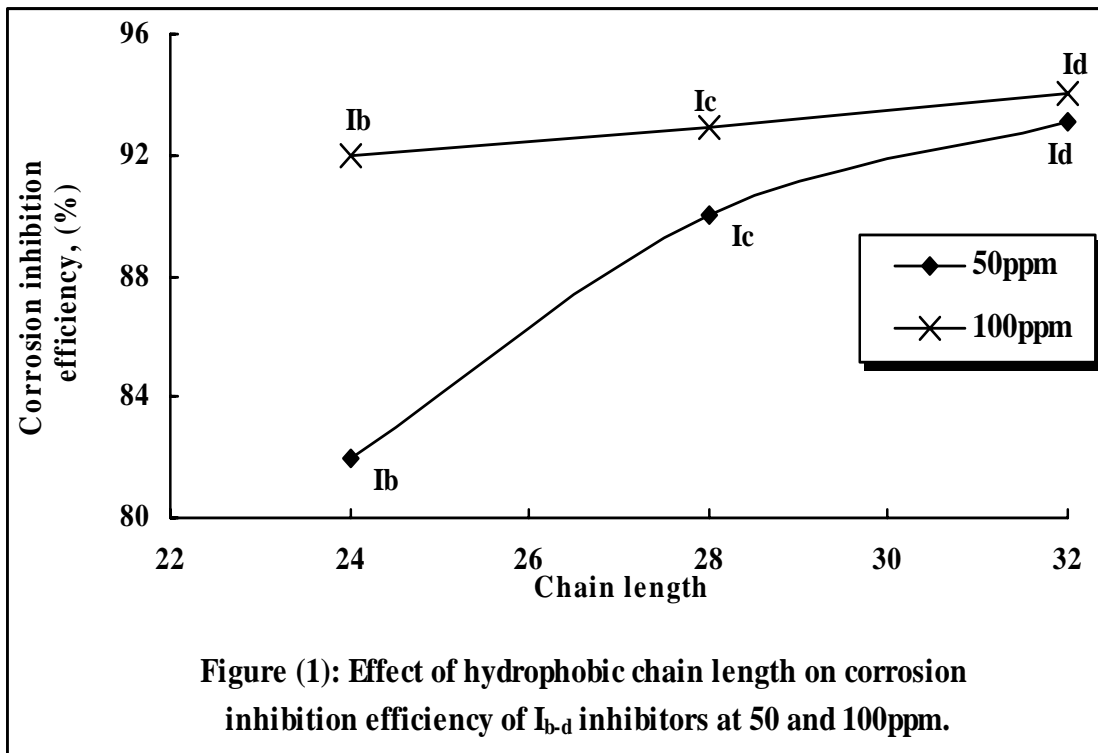
Surfactant	Corrosion (microns)	Corrosion %	Inhibition Efficiency %
Blank	95.00	100.00	0.00
I_b	7.50	7.96	92.10
I_c	5.97	6.28	93.72
I_d	6.40	5.74	94.30
II_a	6.40	7.90	92.10
II_c	6.01	6.33	93.67
II_d	8.00	8.43	91.60
III_b	6.00	6.32	93.68
III_c	5.50	6.30	93.70
III_d	6.49	6.83	93.17
IV_b	6.22	6.55	93.45
IV_d	9.27	6.10	93.90
V_a	5.95	7.26	92.64
V_b	7.91	7.00	93.00
V_c	5.67	6.00	94.00
V_d	5.76	5.40	94.70

Table (3): Corrosion Inhibition Efficiency of the Synthesized Quaternary Ammonium Surfactants at 200 ppm

Surfactant	Corrosion (microns)	Corrosion %	Inhibition Efficiency %
Blank	95.00	100.00	0.00
I_b	7.10	7.48	92.53
I_c	6.51	6.85	93.20
I_d	6.73	5.57	94.53
II_a	6.09	6.42	93.60
II_c	2.38	2.50	97.50
II_d	5.02	5.30	94.72
III_b	5.50	5.80	94.22
III_c	4.98	5.25	94.76
III_d	7.31	5.70	94.30
IV_b	6.15	6.07	93.93
IV_d	8.22	5.65	94.35
V_a	4.98	5.24	94.76
V_b	8.81	6.27	93.73
V_c	5.75	5.05	94.95
V_d	4.11	4.33	95.70

Table (4): Biodegradation of the synthesized surfactants

Surfactant	1st day	3rd day	5th day	7th day
I_b	50	68	89	96
I_c	56	69	90	97
I_d	54	75	89	95
II_a	59	86	87	98
II_c	55	74	88	99
II_d	55	83	85	94
III_b	56	66	89	95
III_c	55	69	85	95
III_d	52	68	85	96
IV_b	59	63	83	93
IV_d	57	62	86	99
V_a	58	61	86	95
V_b	53	61	85	95
V_c	52	61	89	98
V_d	51	65	89	94



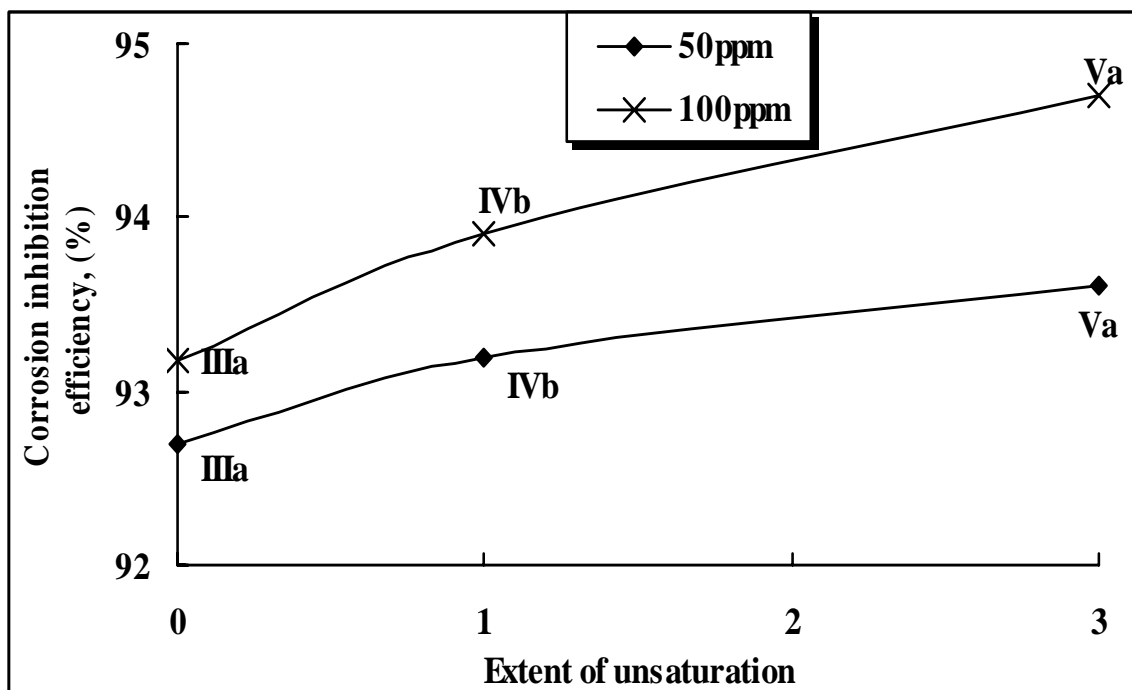


Figure (3): Effect of unsaturation on corrosion inhibition efficiency of inhibitors at 50 and 100ppm.

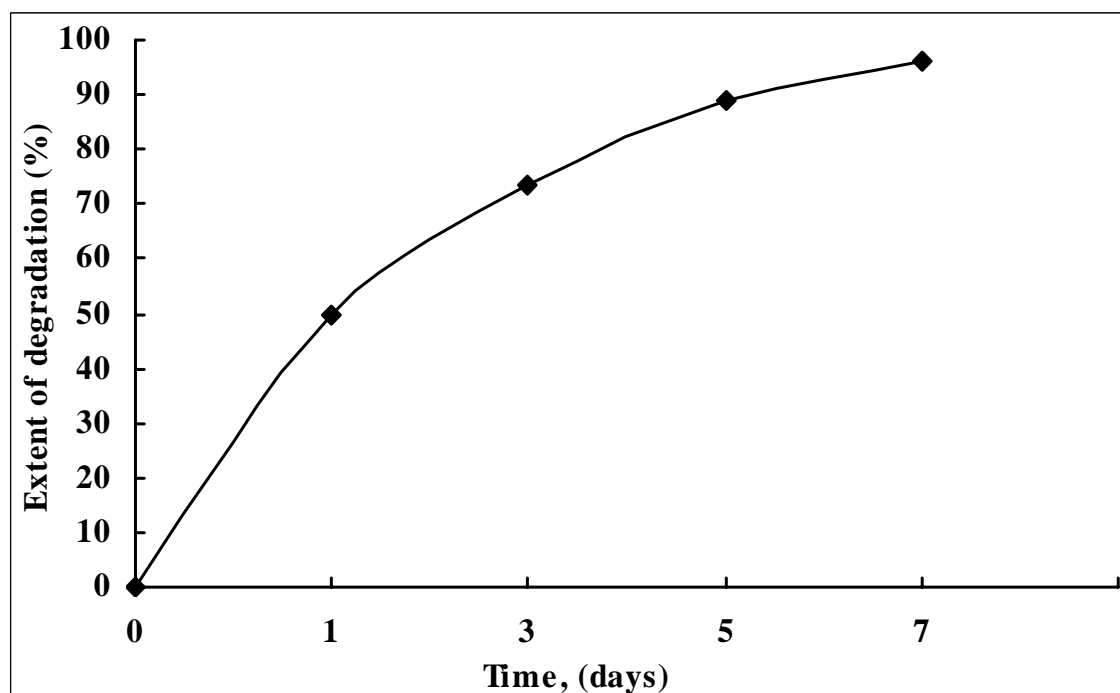


Figure (4): Biodegradation of I_b surfactants in river water.

