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$C_{10}H_{18}N_2Na_2O_{10}$ inhibition and adsorption mechanism on concrete steel-reinforcement corrosion in corrosive environments



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Abstract $C_{10}H_{18}N_2Na_2O_{10}$ (ethylenediaminetetra-acetic acid disodium salt) inhibition and adsorption mechanism on the corrosion of steel-reinforcement corrosion in concrete immersed in corrosive environments were investigated in this paper. For this, seven different concentrations ranging from 0% to 0.667% $C_{10}H_{18}N_2Na_2O_{10}$ per weight of cement were admixed in steel-reinforced concretes immersed in saline and in acidic sulphate test-media and these were monitored using electrochemical techniques. Statistical analyses of the scatter of measured data from these, as per ASTM G16-95 R04, showed that $C_{10}H_{18}N_2Na_2O_{10} > 0\%$ admixtures portrayed excellent efficiency at inhibiting steel-reinforcement corrosion in the saline environment. However, attaining comparably high inhibition of steel-reinforcement corrosion in concrete immersed in the acidic sulphate environment exhibited greater dependency on high $C_{10}H_{18}N_2Na_2O_{10}$ admixture concentration in the steel-reinforced concretes. Different models of adsorption isotherms bear indications of chemical adsorption, chemisorptions, as the prevalent adsorption mechanism of $C_{10}H_{18}N_2Na_2O_{10}$ on steel-reinforcement in both of the corrosive environments.

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1. Introduction

Steel reinforced concrete is a material of choice in the construction industry worldwide because of its desirable structural strength properties, relative cost and durability. Usually, steel reinforced concrete durability is ensured by high alkalinity (pH > 12.5) of the concrete pore environment which protects the steel rebar by a thin stable passive oxide film, from hydrated product of cement pastes, strongly adherent to the

steel surface (Tang et al., 2012). However, environmental agents of corrosion reduce concrete alkalinity and break down the protective passive oxide film on the steel-rebar thus rendering it susceptible to corrosion attacks (Tang et al., 2012; Garcés et al., 2011). These environmental agents take the form of carbonation from the atmosphere, chloride ingress from saline (e.g. from de-icing salts) or marine and sulphate attack from acid rain in industrial or microbial activities in sewage environments (Okeniyi et al., 2014a; Gerengi et al., 2013; De Muyne et al., 2009; Tommaselli et al., 2009). By-products from the attacks of these on steel-rebar are expansive within the concrete, induce low structural strength and lead to cracks, spalling, delamination and, if unchecked, eventual catastrophic

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collapse of the concrete structure. The premature and progressive deterioration of concrete structures and infrastructures due to corrosion of steel reinforcement (steel-rebar) in the concrete militates against safe and sustainable infrastructure worldwide (Dong et al., 2012; Feng et al., 2011; Fedrizzi et al., 2005).

Many studies had deliberated on methods for mitigating corrosion degradation of reinforcing steel in concrete (Okeniyi et al., 2014a; Dong et al., 2012; Parthiban et al., 2008; Valcarce and Vázquez, 2008). Some of the methods proposed include cathodic protection, coatings of the steel-rebar and/or the reinforced concrete, concrete realkalization and the use of admixtures for inhibiting steel rebar corrosion in concrete. Among these methods, the use of corrosion inhibiting admixtures is considered a simple and less costly technique for protecting reinforcing steel, embedded in concrete, from corrosion degradation (Fedrizzi et al., 2005).

Generally, corrosion inhibitors could be broadly classified as inorganic and organic (Qian and Cusson, 2004). While many inorganic inhibitors like nitrites and chromates had been known to be effective for rebar corrosion protection in concrete they suffered many drawbacks that are limiting their usage in many countries of the world. These drawbacks include environmental restrictions due to toxicity, inhibition mechanism limitation to the anodic sites, corrosion aggravation potency from insufficient quantity applications in the corrosive system and relatively high costs of the inorganic chemicals (Feng et al., 2011; Fu et al., 2010; Mennucci et al., 2009; Vaysburd and Emmons, 2004). In contrast, organic corrosion inhibitors are environmentally friendly, mixed, i.e. both anodic and cathodic, inhibitors and relatively cheaper than their inorganic counterparts (Feng et al., 2011; Sastri, 2011; Fu et al., 2010).

$C_{10}H_{18}N_2Na_2O_{10}$ (ethylenediaminetetra-acetic acid disodium salt) is an organic chemical that is non-toxic and non-hazardous to the environmental ecosystem and which had been found as a suitable agent in studies for stripping corrosion products from metals (Keny et al., 2006; Huda, 2002). Although, Qu et al. (2007) had employed $C_{10}H_{18}N_2Na_2O_{10}$ for inhibiting metallic corrosion in acidic chloride (HCl), there is still dearth of studies on the inhibition and the adsorption mechanism by $C_{10}H_{18}N_2Na_2O_{10}$ on concrete steel-reinforcement in corrosive environments. This paper therefore studies inhibition and adsorption mechanisms of $C_{10}H_{18}N_2Na_2O_{10}$ on steel-reinforcement corrosion in concrete slabs immersed in NaCl medium, simulating saline/marine environment and in H_2SO_4 medium simulating industrial/microbial environment.

2. Materials and methods

2.1. Materials

2.1.1. Chemicals employed

Distilled water was employed for solution preparations (Muralidharan et al., 2004), except for concrete mixing whereby drinkable tap water was used (Zafeiropoulou et al., 2011). Also, all chemicals used were of commercially pure quality. These include $C_{10}H_{18}N_2Na_2O_{10}$ (ethylenediaminetetra-acetic acid disodium salt) as inhibitor, sodium chloride (NaCl) and sulphuric acid, (H_2SO_4) as aggressive agents, acetone (C_3H_6O) for degreasing and iso-propyl alcohol (C_3H_8O) for wetting fluid.

2.1.2. Steel reinforced concrete materials

Deformed steel-rebar employed in the study was of 12 mm diameter. This has the composition: 0.273% C, 0.403% Si, 0.780% Mn, 0.039% P, 0.037% S, 0.142% Cr, 0.109% Ni, 0.016% Mo, 0.240% Cu, 0.0086% Co, 0.0083% Nb, 0.0063% Sn, 0.0032% V, 0.0037% Ce and the balance Fe. This reinforcing steel was cut, for the corrosion test-experiment, into lengths of 190 mm, and for each of these lengths of rods, surface preparation was maintained uniformly as prescribed from reported study (Muralidharan et al., 2004) and from the specifications of ASTM G109-99a (2005). 150 mm length of each steel rod was embedded in each 100 mm × 100 mm × 200 mm concrete block sample, such that the remaining 40 mm steel protrusion could be used for electrochemical connections. This protrusion was painted with glossy paint, for each block after concrete casting.

Four block samples were made in each mould, in a replicated experimental design (Haynie, 2005) that totalled twenty-eight reinforced concrete blocks, for the study. These facilitate seven variations of $C_{10}H_{18}N_2Na_2O_{10}$ admixture concentrations, as presented in Table 1, whereby duplicate samples of blocks (tagged with “_Dup” or simply “Dup”) with similar $C_{10}H_{18}N_2Na_2O_{10}$ concentrations were tested in each aggressive test medium. In the first six moulds, $C_{10}H_{18}N_2Na_2O_{10}$ admixtures were varied from 0%, for the blank specimens, in increments of 0.0833% (i.e. a part by weight of $C_{10}H_{18}N_2Na_2O_{10}$ in 1200 parts by weight of cement) up to 0.4167% of $C_{10}H_{18}N_2Na_2O_{10}$ for each block sample. These translate to 0 M $C_{10}H_{18}N_2Na_2O_{10}$ admixture in increment of 0.00448 M $C_{10}H_{18}N_2Na_2O_{10}$ to 0.024 M $C_{10}H_{18}N_2Na_2O_{10}$ relative to cement mixing water, where 1 M ≡ 1 mol/dm³. The last mould of four blocks had 0.6667% (0.03584 M) of $C_{10}H_{18}N_2Na_2O_{10}$ admixture per block sample for studying the effect of such a high concentration on steel-rebar corrosion.

Formulation of steel-reinforced concrete in the study employed mixed proportion of Ordinary Portland Cement = 300.0 kg/m³, river sand, of 2.80 fineness modulus, conforming to ASTM C33-03 (2005), = 890.6 kg/m³, granite stone coarse aggregate (of 7.54 fineness modulus) = 1106.3 kg/m³ and 149.7 kg/m³ of water. The sieve analyses for the fine and coarse aggregates were studied as prescribed in ASTM C136-01 (2005). Water-cement ratio employed for the concrete mix = 0.499 (Ormellese et al., 2006; ASTM G109-99a, 2005). Preparations and casting of the steel-reinforced concrete specimens were carried out as specified by ASTM C192/192M-02 (2005) and as described in Okeniyi et al. (2014b).

2.2. Experimental methods

2.2.1. Setup of concrete test-specimens

The steel reinforced concrete test-specimens were divided into two sets of duplicated specimens. Specimens in each set were immersed, partially along the lengths of the concretes, in plastic bowls containing their respective corrosive test-environments. Samples of the first duplicated set of fourteen specimens were partially immersed in 3.5% NaCl solution (Zhou et al., 2012; Zafeiropoulou et al., 2011) for simulating saline/marine medium while samples of the second duplicated set were partially immersed in 0.5 M H_2SO_4 solution (Gerengi et al., 2013; Obot and Obi-Egbedi, 2010; Moretti et al., 2004) for simulating

Table 1 Concentrations in wt% of C₁₀H₁₈N₂Na₂O₁₀ admixtures in steel-reinforced concrete samples.

S/no	Specimen by C ₁₀ H ₁₈ N ₂ Na ₂ O ₁₀ concentration	S/no	Specimen by C ₁₀ H ₁₈ N ₂ Na ₂ O ₁₀ concentration
1	0% C ₁₀ H ₁₈ N ₂ Na ₂ O ₁₀ (blank in NaCl)	2	0% C ₁₀ H ₁₈ N ₂ Na ₂ O ₁₀ (blank in H ₂ SO ₄)
3	0% C ₁₀ H ₁₈ N ₂ Na ₂ O ₁₀ (blank in NaCl_Dup)	4	0% C ₁₀ H ₁₈ N ₂ Na ₂ O ₁₀ (blank in H ₂ SO ₄ _Dup)
5	0.0833% C ₁₀ H ₁₈ N ₂ Na ₂ O ₁₀ in NaCl	6	0.0833% C ₁₀ H ₁₈ N ₂ Na ₂ O ₁₀ in H ₂ SO ₄
7	0.0833% C ₁₀ H ₁₈ N ₂ Na ₂ O ₁₀ in NaCl_Dup	8	0.0833% C ₁₀ H ₁₈ N ₂ Na ₂ O ₁₀ in H ₂ SO ₄ _Dup
9	0.1667% C ₁₀ H ₁₈ N ₂ Na ₂ O ₁₀ in NaCl	10	0.1667% C ₁₀ H ₁₈ N ₂ Na ₂ O ₁₀ in H ₂ SO ₄
11	0.1667% C ₁₀ H ₁₈ N ₂ Na ₂ O ₁₀ in NaCl_Dup	12	0.1667% C ₁₀ H ₁₈ N ₂ Na ₂ O ₁₀ in H ₂ SO ₄ _Dup
13	0.25% C ₁₀ H ₁₈ N ₂ Na ₂ O ₁₀ in NaCl	14	0.25% C ₁₀ H ₁₈ N ₂ Na ₂ O ₁₀ in H ₂ SO ₄
15	0.25% C ₁₀ H ₁₈ N ₂ Na ₂ O ₁₀ in NaCl_Dup	16	0.25% C ₁₀ H ₁₈ N ₂ Na ₂ O ₁₀ in H ₂ SO ₄ _Dup
17	0.3333% C ₁₀ H ₁₈ N ₂ Na ₂ O ₁₀ in NaCl	18	0.3333% C ₁₀ H ₁₈ N ₂ Na ₂ O ₁₀ in H ₂ SO ₄
19	0.3333% C ₁₀ H ₁₈ N ₂ Na ₂ O ₁₀ in NaCl_Dup	20	0.3333% C ₁₀ H ₁₈ N ₂ Na ₂ O ₁₀ in H ₂ SO ₄ _Dup
21	0.4167% C ₁₀ H ₁₈ N ₂ Na ₂ O ₁₀ in NaCl	22	0.4167% C ₁₀ H ₁₈ N ₂ Na ₂ O ₁₀ in H ₂ SO ₄
23	0.4167% C ₁₀ H ₁₈ N ₂ Na ₂ O ₁₀ in NaCl_Dup	24	0.4167% C ₁₀ H ₁₈ N ₂ Na ₂ O ₁₀ in H ₂ SO ₄ _Dup
25	0.6667% C ₁₀ H ₁₈ N ₂ Na ₂ O ₁₀ in NaCl	26	0.6667% C ₁₀ H ₁₈ N ₂ Na ₂ O ₁₀ in H ₂ SO ₄
27	0.6667% C ₁₀ H ₁₈ N ₂ Na ₂ O ₁₀ in NaCl_Dup	28	0.6667% C ₁₀ H ₁₈ N ₂ Na ₂ O ₁₀ in H ₂ SO ₄ _Dup

industrial/microbial medium. The corrosive test-environments in the bowls were made up to just below the reinforcing steel but without touching the rebar. These corrosive test-solutions were then replenished every three weeks in the bowls, both for preventing dryness and for ensuring continuity of the corrosive environments in the bowls (Muralidharan et al., 2004).

Non-destructive electrochemical measurements as detailed in the literature (Zafeiropoulou et al., 2011; Song and Saraswathy, 2007; Broomfield, 2003) were taken from each specimen of steel-reinforced concrete, in five day interval for forty days and thereafter in seven day interval for the following three weeks. This totalled sixty-one days. The non-destructive electrochemical test-techniques employed include:

- I. Half-cell potential (HCP), also known as corrosion potential, measurements versus copper/copper sulphate electrode (CSE), as per ASTM C876-91 R99 (2005) (Okeniyi et al., 2014a,b; Gulikers, 2010).
- II. Electrochemical cell current (ECC) measurements versus CSE, using zero resistance ammeter (Okeniyi et al., 2013a, b; Sastri, 2011; McCarter and Vennesland, 2004; Jäggi et al., 2001).
- III. Corrosion rate (CR) measurement: was obtained using the 3-electrode LPR Data Logger, Model MS1500L, from Metal Samples® (Okeniyi et al., 2014b; Abosrra et al., 2011; Sastri, 2011).

A water retentive conducting sponge was employed for the point of contact of the measuring probes and the reinforced concrete to ensure good electrical contact for the electrochemical measurements (Okeniyi et al., 2014a; Gulikers, 2010; Song and Saraswathy, 2007). This sponge was wetted before measurements using contact solution consisting of drinkable tap water, small addition of iso-propyl alcohol and some local detergent, as prescribed in ASTM C876-91 R99 (2005), for improving the wetting characteristics of the conducting solution.

2.3. Data analyses

2.3.1. Statistical probability distribution analyses

As per ASTM G16-95 R04 (2005), the scatter of electrochemical test-data, from each corrosion test variable, was subjected

to the descriptive statistics of the Weibull probability density function for detailing prevalent condition in the corrosive test system (Okeniyi et al., 2012, 2013b; Omotosho et al., 2011, 2012; Izquierdo et al., 2004; Roberge, 2003). This probability density function (pdf) is given by (Kotz and Nadarajah, 2000):

$$f(x) = \frac{k}{c} \left(\frac{x}{c}\right)^{k-1} \cdot \exp \left\{ -\left(\frac{x}{c}\right)^k \right\} \quad (1)$$

where x is measured corrosion test data, k is the shape parameter and c is the scale parameter. Estimations of these parameters were obtained, for sample size $n = 12$ data points of measurements of each electrochemical test-variable, from the solution of the simultaneous maximum likelihood equations (Okeniyi et al., 2014b; Reiss and Thomas, 2007; Kotz and Nadarajah, 2000):

$$\frac{n}{\hat{k}} - n \log(\hat{c}) + \sum_{i=1}^n \log x_i - \sum_{i=1}^n \left(\frac{x_i}{\hat{c}}\right)^{\hat{k}} \log \left(\frac{x_i}{\hat{c}}\right) = 0 \quad (2)$$

$$\hat{c} - \left\{ \frac{1}{n} \sum_{i=1}^n x_i^{\hat{k}} \right\}^{\frac{1}{\hat{k}}} = 0 \quad (3)$$

For these, the combined fixed point iterative–Aitken Δ^2 procedures were employed (Lange, 2010; Hoffman, 2001). The unbiased estimated values of k and c , from these, were used to evaluate the Weibull mean, μ , model of corrosion test variables over the test-period, as proposed by Bungey et al. (2006), through (Okeniyi et al., 2013b; Omotosho et al., 2011):

$$\mu = c\Gamma\left(1 + \frac{1}{k}\right) \quad (4)$$

where $\Gamma(\cdot)$ is the gamma function of (\cdot) .

2.3.2. Goodness-of-fit test statistics

As prescribed in the literature (ASTM G16-95 R04, 2005; Roberge, 2003), the Kolmogorov–Smirnov (K–S) goodness-of-fit (GoF) test statistics was employed to verify scattering of experimental data from each electrochemical test-variable like the Weibull distribution at the significant level $\alpha = 0.05$ (Okeniyi et al., 2012, 2013b,c; Okeniyi and Okeniyi, 2012; Roberge, 2003). The K–S GoF method measures the absolute difference between empirical distribution function $F^*(x)$ and theoretical distribution function $F(x)$, for n data points, using:

$$D_n = D(x_1, \dots, x_n) = \sup_{-\infty < x < \infty} |F^*(x) - F(x)| \quad (5)$$

2.3.3. Testing of statistical significance between steel-reinforced concrete samples

Significance of differences between corrosion test-data of the duplicated samples of each admixture concentration was investigated by using the student's *t*-test statistics (ASTM G16-95 R04, 2005). This includes the homoscedastic (hom) *t*-test of equal variance assumption, and the heteroscedastic (het) *t*-test of unequal variance assumption. This *t*-test statistics finds usefulness for indicating whether differences in test-responses encountered in duplicated samples were due to chance and thus not significant or otherwise.

2.3.4. Surface coverage and inhibition efficiency

The mean model, μ , of the Weibull fittings of corrosion rate test data was employed for evaluating the surface coverage, θ , and the inhibition efficiency, η , for each concentration of $C_{10}H_{18}N_2Na_2O_{10}$ admixture in concrete relative to the blank using the relationships (Anejar et al., 2014; Karthikaiselvi and Subhashini, 2014; Singh et al., 2012):

$$\theta = \frac{\mu_{(\text{blank})} - \mu_{(\text{admixed})}}{\mu_{(\text{blank})}} \quad (6)$$

$$\eta = \frac{\mu_{(\text{blank})} - \mu_{(\text{admixed})}}{\mu_{(\text{blank})}} \times 100 \quad (7)$$

2.3.5. Modelling of adsorption mechanism

For studying the mechanisms of $C_{10}H_{18}N_2Na_2O_{10}$ adsorption on the metallic steel-reinforcement three models of adsorption isotherms were fitted to the experimental data and the concentration of $C_{10}H_{18}N_2Na_2O_{10}$ in mol/dm^3 . These include the Langmuir, the El-Awady and the Freundlich models of adsorption isotherms. For these adsorption isotherm models, characteristic equations and parameter estimations/interpretations that have been detailed in studies (Anejar et al., 2014; Karthikaiselvi and Subhashini, 2014; Obi-Egbedi et al., 2012; Singh et al., 2012; Foo and Hameed, 2010; Vijayaraghavan et al., 2006) were employed.

In addition, the Langmuir model of adsorption isotherm facilitates estimation of the separation factor, R_L , using the relationship (Foo and Hameed, 2010):

$$R_L = \frac{1}{1 + K_{\text{ads}}\mu_{\text{blank}}} \quad (8)$$

where K_{ads} is the Langmuir equilibrium constant of the adsorption-desorption process; R_L a dimensionless constant for indicating $C_{10}H_{18}N_2Na_2O_{10}$ adsorption nature on steel-rebar as either irreversible if $R_L = 0$ or favourable if $0 < R_L < 1$ or linear if $R_L = 1$ or unfavourable if $R_L > 1$.

Also from the Langmuir and the El-Awady models of adsorption isotherms, the Gibbs free energy of adsorption $\Delta G_{\text{ads}}^\circ$ was calculated from its relationship with K_{ads} according to (Anejar et al., 2014; Karthikaiselvi and Subhashini, 2014):

$$\Delta G_{\text{ads}}^\circ = -2.303RT \log(55.5K_{\text{ads}}) \quad (9)$$

where $R = 8.314\text{J/mol}\cdot\text{K}$ is the molar gas constant, T is absolute temperature (K) and 55.5 is the concentration of water in solution expressed in molar. The Gibbs free energy

of adsorption $\Delta G_{\text{ads}}^\circ$ finds usefulness for indicating adsorption mechanism on the metallic surface. For instance, it is well known that value of $\Delta G_{\text{ads}}^\circ$ around -20 kJ/mol or lower is indicative of physical adsorption mechanism or physisorption while value around -40 kJ/mol or higher is indicative of chemical adsorption mechanism or chemisorptions (Anejar et al., 2014; Karthikaiselvi and Subhashini, 2014; Obi-Egbedi et al., 2012; Singh et al., 2012).

Also, the value of $1/\lambda$, the slope obtained from the fitting of Freundlich isotherm model, is useful for indicating adsorption mechanism on the metallic surface. Value of $1/\lambda < 1$ implies chemical adsorption mechanism, chemisorptions, while $1/\lambda > 1$ indicates cooperative adsorption effects of physical adsorption mechanism, physisorption (Foo and Hameed, 2010). This was therefore employed in this study for comparison with the adsorption mechanism interpreted from the Gibbs free energy of adsorption $\Delta G_{\text{ads}}^\circ$ from the Langmuir and the El-Awady models of adsorption isotherm.

3. Results and discussion

3.1. Results of statistical analyses of corrosion test data

Results of the analysis techniques of the Weibull probability distribution function for the corrosion test data of electrochemical variables are presented as graphical plots in Fig. 1 for steel-reinforced concrete samples immersed in the NaCl and in H_2SO_4 media. From these plots, it is worth noting that the Weibull mean of test responses from the blank samples in NaCl medium exhibited higher severity of corrosive activities than the Weibull mean of test-responses from the blank samples in H_2SO_4 medium. This could be due to the availability of chloride ions for continuous dissolutions and corrosion accelerations of concrete steel-reinforcement in the NaCl corrosive environment because they, the chloride ions, were not consumed in the corrosion process (Wei et al., 2013; Fontana, 1987). In contrast, the acidic sulphate ions were usually consumed in concrete attacks even before the ions could attain the steel-rebar for corrosion attacks (Hewayde et al., 2007).

It could also be noted that the plots of Weibull mean of half-cell potential in Fig. 1(a) find pattern agreements with the plots of Weibull mean of electrochemical cell current in Fig. 1(b). However, the high corrosion rates from the blank samples in NaCl medium make visualising the pattern of the Weibull mean of corrosion rate from the blank samples in H_2SO_4 and the $C_{10}H_{18}N_2Na_2O_{10}$ admixed samples in both corrosive media impossible as shown in Fig. 1(c). This necessitates the plotting of the corrosion rate from the $C_{10}H_{18}N_2Na_2O_{10}$ admixed samples, without the high corrosion rate-valued blank samples, in NaCl medium in Fig. 1(d) and the plotting of the samples (including the blanks) in H_2SO_4 medium in Fig. 1(e). These latter figures bear indications of more reductions in the corrosion rate of concrete steel-reinforcement in $C_{10}H_{18}N_2Na_2O_{10}$ admixed samples in NaCl medium than the corrosion rate of concrete steel-reinforcement in $C_{10}H_{18}N_2Na_2O_{10}$ admixed samples in H_2SO_4 medium.

For instance, the highest corrosion rate, of 0.0102 mm/y from the 0.1667% $C_{10}H_{18}N_2Na_2O_{10}$ admixed sample, among the other admixed samples in NaCl medium, just surpassed the “ $0.001\text{--}0.01\text{ mm/y}$ ” “low/moderate” range of corrosion

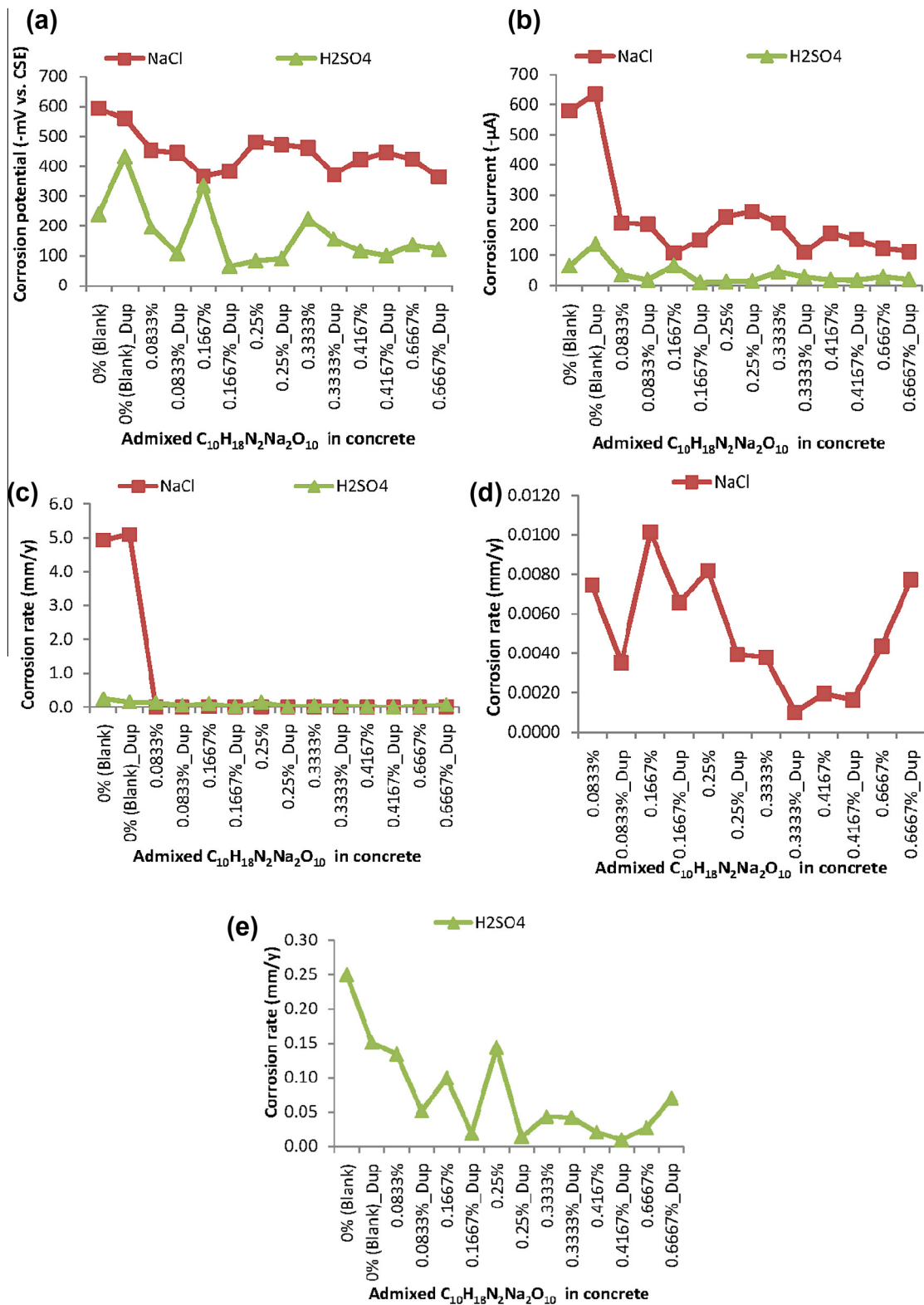


Figure 1 Graphical plots of Weibull mean of electrochemical test-data from steel-reinforced concretes (a) half-cell potential (HCP) (b) electrochemical cell current (ECC) (c) corrosion rate (d) corrosion rate for samples in NaCl medium without the blank samples (e) corrosion rate of samples in H₂SO₄ medium including the blank samples in the medium.

rate classifications in the literature (Söylev et al., 2007; Bungey et al., 2006; Millard et al., 2001). This was in spite of the corrosion rate models of the blank samples in the NaCl medium

which surpassed the “0.1–1 mm/y” that represented the “very high” corrosion rate classifications from the cited studies. In contrast, while the corrosion rate of the blank samples in

H₂SO₄ medium classified to the “very high” corrosion rate, only the 0.4167% C₁₀H₁₈N₂Na₂O₁₀ admixed sample in the H₂SO₄ exhibited corrosion rate of 0.0095 mm/y that classified to the “low/moderate” corrosion rate. The other C₁₀H₁₈N₂Na₂O₁₀ admixed samples in the acidic medium were modelled with corrosion rate ranging from the “very high” to the “high” rate of corrosion classifications. It is worth noting that both the beyond “very high” corrosion rate by the blank samples in the NaCl and the “very high” corrosion rate from the blank samples in the H₂SO₄ medium lay credence that the two test-media represented severe conditions of corrosive test-systems. These therefore followed the prescription of the preferred practice by Roberge (2003) for reducing the time for effects to be observed so that the dominant factor could be employed as the rank ordering factor of performance in the conduct of laboratory corrosion tests. However, these prevailing corrosion conditions in each of the corrosive test-systems, by the Weibull mean models of corrosion test-data, necessitate ascertaining that the fitted test-data by the Weibull descriptive statistics scatter like the Weibull probability distribution function.

The results of K–S GoF test applications to the Weibull fitting of corrosion test-data are presented in Fig. 2 for steel-reinforced concrete samples immersed in the corrosive environments of NaCl and of H₂SO₄ medium. In the figure, the linear plot of significant level $\alpha = 0.05$ was included for easy ascertaining of test-data not scattering like the Weibull probability distribution function. From the plots, it could be noted that the K–S p -value > 0.05 for the test-data of corrosion test-variables subjected to the fittings of the Weibull probability distribution function. These bear indications that the scatter of non-destructive electrochemical test-data in this study distributed like the Weibull probability distribution thus bearing support for the suitability of the Weibull distribution as the statistics for describing the test-data.

Although the K–S GoF statistics showed that the test-data of corrosion variables from samples in the corrosive media scattered like the Weibull distribution, the Weibull mean of corrosion responses from duplicates of concrete samples still exhibited differences. For this, it is further needful to ascertain whether the between-duplicate differences encountered in the Weibull mean of corrosion response from the steel-reinforced concrete duplicates were due to chance or were significant.

The results of student’s t -test statistics using the homoscedastic (hom) and the heteroscedastic (het) applications to the corrosion test-data of the duplicates of steel-reinforced concrete samples were presented in graphical plots in Fig. 3. In this figure, the linear plots of significant level $\alpha = 0.05$ were also included for direct identification of significance of differences from the charts. From this, it could be observed that except for the ECC of the 0.3333% C₁₀H₁₈N₂Na₂O₁₀, the differences in test-data of the other corrosion test-variables encountered between the duplicates of the concrete samples in NaCl medium were due to chance but were not significant. While the ECC of the 0.3333% C₁₀H₁₈N₂Na₂O₁₀ exhibited p -value $\approx 0.02 < 0.05$, data of other test-variables from the NaCl-immersed samples exhibited p -values > 0.05 by student’s t -test statistics of the homoscedastic (hom) and the heteroscedastic (het) applications, Fig. 3(a). By this, the differences encountered in the ECC measurements of the duplicate samples admixed with 0.3333% C₁₀H₁₈N₂Na₂O₁₀ were not due to chance but were significant at $\alpha = 5\%$ level of significance.

Also, Fig. 3(b) showed that the between-duplicate differences encountered in the HCP test-data of the 0% (the blank samples), the 0.0833% C₁₀H₁₈N₂Na₂O₁₀ and of the 0.1667% C₁₀H₁₈N₂Na₂O₁₀ admixed concretes in H₂SO₄ medium were not due to chance but were significant. It could also be deduced from Fig. 3(b) that the ECC test-data from the concrete samples admixed with these 0% (blank), 0.0833% and 0.1667% C₁₀H₁₈N₂Na₂O₁₀ admixtures in H₂SO₄ medium exhibited differences that were not due to chance but that were significant. The p -values from student’s t -test statistics were less than the significant level of 0.05 by the “hom” and by the “het” t -test applications.

However, student’s t -test results in Fig. 3(a), from the NaCl-immersed samples, and in Fig. 3(b), from the H₂SO₄-immersed samples, showed that the differences encountered in the corrosion rate of the duplicate samples were due to chance but were not significant. This bears support for the electrochemical test-variable of corrosion rate as the dominant factor that could be used as rank ordering factor, as per Roberge (2003), for detailing C₁₀H₁₈N₂Na₂O₁₀ performance on steel-reinforcement corrosion in the corrosive environments.

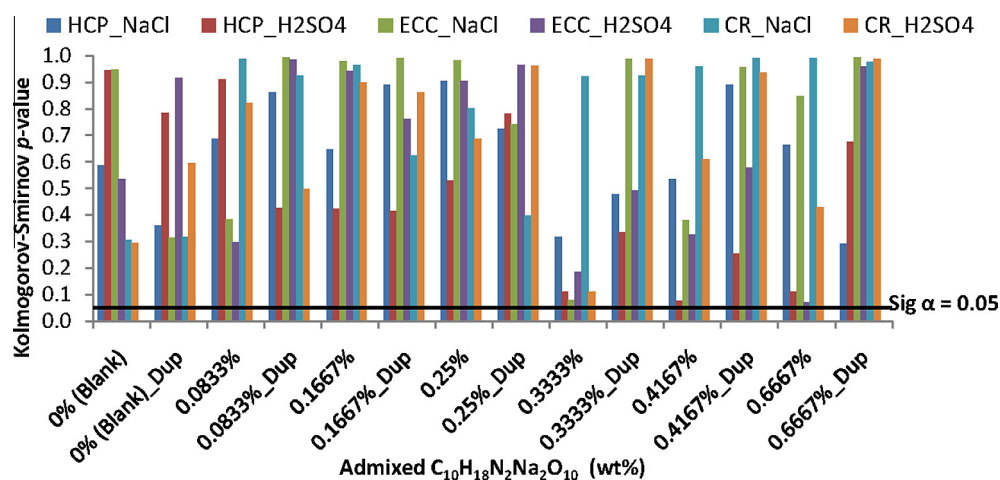


Figure 2 Kolmogorov-Smirnov goodness-of-fit (K-S GoF) test results of the Weibull fittings of the test-data from steel-reinforced concrete samples in corrosive environments.

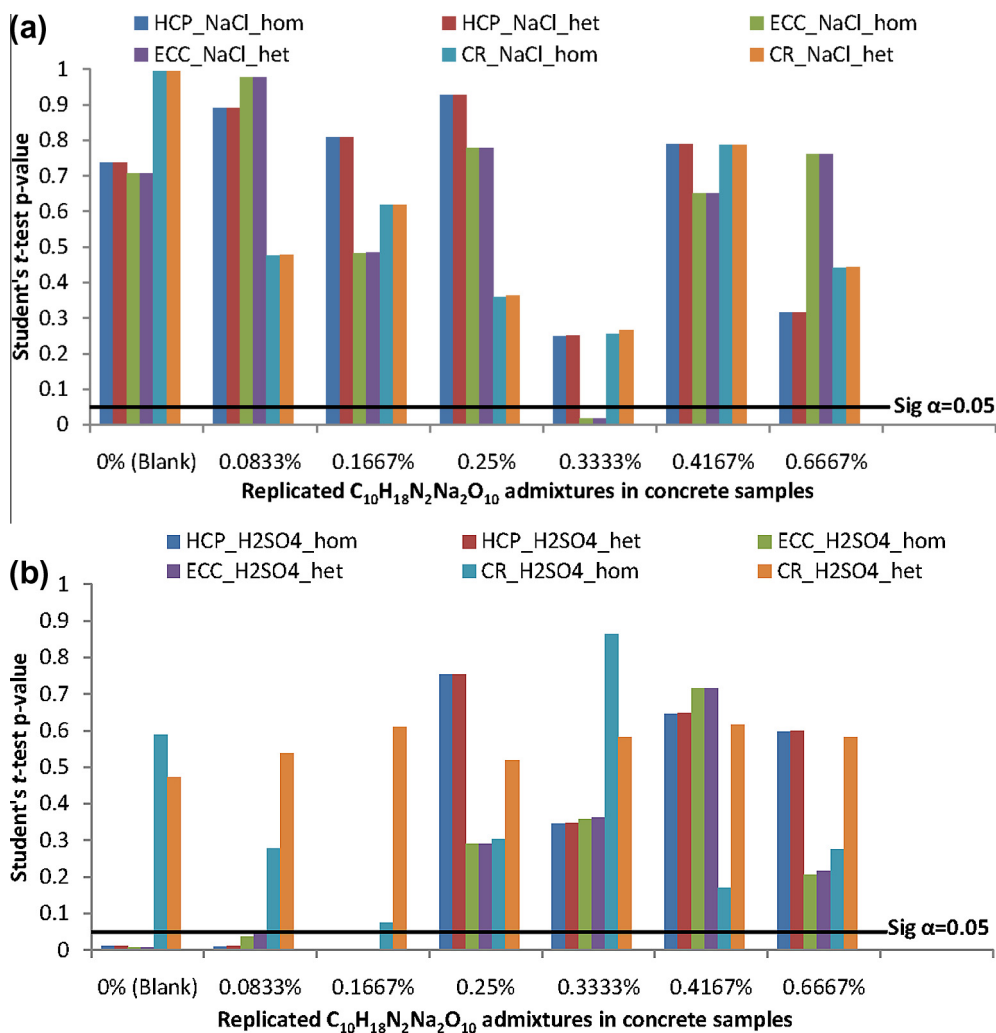


Figure 3 Plots of student's *t*-test statistics for significance of differences between replicates of steel-reinforced concrete samples (a) in NaCl medium (b) in H₂SO₄ medium.

3.2. Inhibition effectiveness ranking

The lack of significant differences in the corrosion rate test-response from the duplicates of steel-reinforced concretes being studied facilitates estimations of averaged corrosion rate from each duplicate of steel-reinforced concretes in each of the corrosive test-media. To these averages, Eq. (7) was relevantly applied for evaluating inhibition efficiency, η , by each of the admixed $C_{10}H_{18}N_2Na_2O_{10}$ concentrations on the concrete steel-reinforcement corrosion in the corrosive test-media. These inhibition efficiency results of $C_{10}H_{18}N_2Na_2O_{10}$ admixture on concrete steel-reinforcement corrosion are presented in ranking order of inhibition effectiveness in Fig. 4.

From Fig. 4(a), it could be noted that $C_{10}H_{18}N_2Na_2O_{10}$ admixtures exhibited very strong effectiveness at inhibiting concrete steel-reinforcement corrosion in the also highly aggressive NaCl medium. Also, the inhibition efficiency by $C_{10}H_{18}N_2Na_2O_{10}$ admixture on concrete steel-reinforcement corrosion could be described as invariant to the concentrations of $C_{10}H_{18}N_2Na_2O_{10}$ admixed in concrete. In spite of this concentration invariance, however, the 0.4167% $C_{10}H_{18}N_2Na_2O_{10}$

admixture exhibited optimal inhibition effectiveness, $\eta = 99.96 \pm 0.004\%$, at inhibiting concrete steel-reinforcement in the saline/marine simulating environment. The 0.1667% $C_{10}H_{18}N_2Na_2O_{10}$ admixture exhibited inhibition efficiency of $\eta = 99.83 \pm 0.04\%$ as the least effective among the $C_{10}H_{18}N_2Na_2O_{10}$ admixtures in the NaCl medium.

The kind of concentration invariance encountered in the NaCl medium was not exhibited by $C_{10}H_{18}N_2Na_2O_{10}$ admixture on concrete steel-reinforcement corrosion in the H₂SO₄ medium, Fig. 4(b). Although, the 0.4167% $C_{10}H_{18}N_2Na_2O_{10}$ admixture still exhibited optimal inhibition efficiency of $\eta = 92.04 \pm 4.13\%$, the 0.0833% $C_{10}H_{18}N_2Na_2O_{10}$ admixture exhibited least effectiveness of $\eta = 50.67 \pm 19.04\%$, at inhibiting reinforcing steel corrosion in the H₂SO₄ medium. It is worth noting from Fig. 4(b) that inhibition efficiency of $\eta > 74\%$ was attained by the higher $C_{10}H_{18}N_2Na_2O_{10}$ concentrations, i.e. the 0.4167%, the 0.3333% and the 0.6667% $C_{10}H_{18}N_2Na_2O_{10}$ admixtures. These bear suggestions that high $C_{10}H_{18}N_2Na_2O_{10}$ concentrations were required for high effectiveness of the $C_{10}H_{18}N_2Na_2O_{10}$ admixture at inhibiting concrete steel-reinforcement corrosion in H₂SO₄ medium.

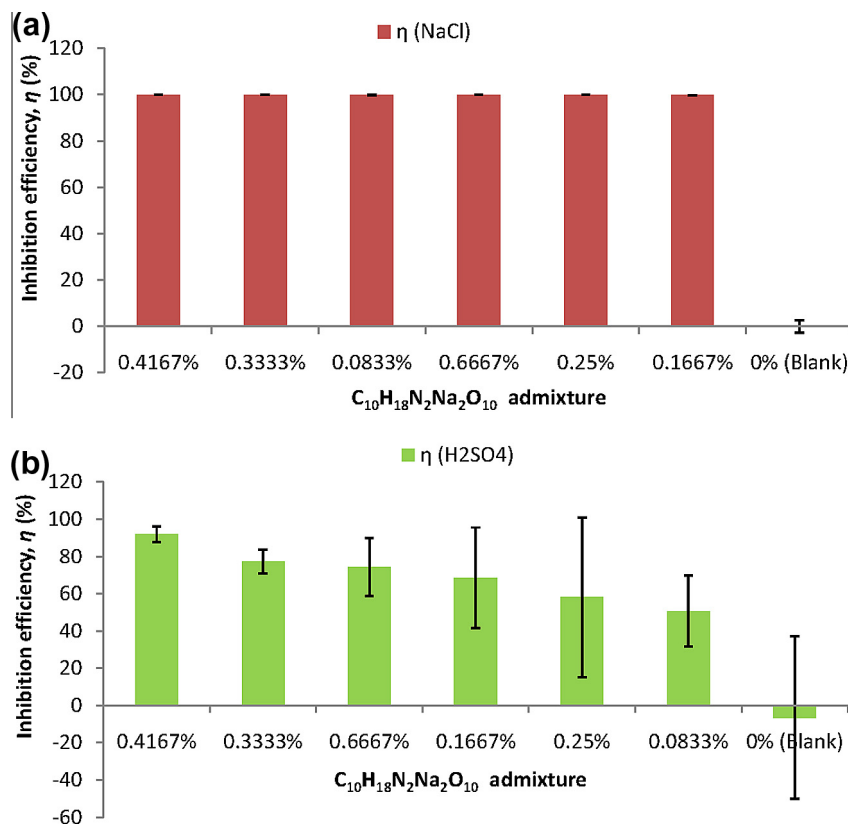


Figure 4 Inhibition efficiency ranking of $C_{10}H_{18}N_2Na_2O_{10}$ admixtures on concrete steel-reinforcement corrosion (a) in NaCl medium (b) in H_2SO_4 medium.

3.3. Mechanism of $C_{10}H_{18}N_2Na_2O_{10}$ adsorption on steel-reinforcement

The resulting parameters from the fittings of the different adsorption isotherm models to the experimental performance of $C_{10}H_{18}N_2Na_2O_{10}$ admixtures on steel-reinforcement corrosion are presented in Table 2. From this, the Langmuir isotherm model could be observed as the best-fitting model of $C_{10}H_{18}N_2Na_2O_{10}$ adsorption on concrete steel-reinforcement in the NaCl environment with $R^2 = 0.9999$ and in the H_2SO_4 environment with $R^2 = 0.9520$.

Apart from the non-fittings of experimental performance of $C_{10}H_{18}N_2Na_2O_{10}$ by the El-Awady and the Freundlich isotherm models, they still bear supports for important inferences that could be drawn from them and from the Langmuir isotherm, which include:

- o Multilayer of $C_{10}H_{18}N_2Na_2O_{10}$ was formed on the metal surface in both corrosive media because “ $1/y > 1$ ” from the El-Awady isotherm;
- o The adsorption was favourable in both media because “ $0 < R_L < 1$ ” from the Langmuir isotherm;
- o The adsorption process was spontaneous and the adsorbed $C_{10}H_{18}N_2Na_2O_{10}$ layer was stable on the metallic surface in both corrosive media due to the negative values of ΔG_{ads}° from both the Langmuir and the El-Awady isotherm models;
- o The adsorption mechanisms of $C_{10}H_{18}N_2Na_2O_{10}$ on concrete steel-reinforcement were more indicative of chemical adsorption or chemisorptions as being prevalent in both corrosive test-media, based on the Freundlich slope “ $1/\lambda < 1$ ” and the ΔG_{ads}° from both the Langmuir and the El-Awady isotherm models that were higher than -40 kJ/mol.

Table 2 Estimated parameters for models of adsorption isotherm.

Medium	Isotherm model	R^2	$1/y$	$1/\lambda$	Equilibrium constant $K_{eq} \equiv K_{ads}$	R_L	ΔG_{ads}° (kJ/mol)
NaCl	Langmuir	0.9999			1.0526×10^6	1.8945×10^{-7}	-102.7236
	El-Awady	0.1371	3.2522		6.1944×10^{11}		-179.0361
	Freundlich	0.1278		2.426×10^{-4}	1.00003		
H_2SO_4	Langmuir	0.9520			385.8963	1.2774×10^{-2}	-57.2803
	El-Awady	0.4260	1.3463		300.7450		-55.8483
	Freundlich	0.5842		0.2032	1.6864		

4. Conclusions

Inhibition and adsorption mechanisms of concentrations of $C_{10}H_{18}N_2Na_2O_{10}$ admixtures on steel-reinforcement corrosion in concrete immersed in NaCl and H_2SO_4 corrosive environments had been studied in this work. The conclusions that could be drawn from these include:

- o Data of non-destructive electrochemical test-measurements from the study distributed like the Weibull probability distribution according to the Kolmogorov-Smirnov test-statistics, thus supporting the use of the Weibull distribution fittings as the descriptive statistics for detailing prevailing corrosion conditions in the corrosive test-systems;
- o Test-data of corrosion rate exhibited differences that were not significant between duplicated steel-reinforced concrete samples admixed with similar $C_{10}H_{18}N_2Na_2O_{10}$ concentrations, in the same test-media, according to student's *t*-test statistics of the homoscedastic and heteroscedastic assumptions at $\alpha = 0.05$ significant level;
- o Although, all the $C_{10}H_{18}N_2Na_2O_{10}$ admixture concentrations in this study exhibited very high, $\eta > 99\%$, inhibition efficiency in concrete immersed in NaCl medium, the 0.4167% $C_{10}H_{18}N_2Na_2O_{10}$ admixture exhibited optimal effectiveness, $\eta = 99.96 \pm 0.004\%$, at inhibiting steel-reinforcement corrosion in concrete immersed in this saline/marine simulating environment;
- o The 0.4167% $C_{10}H_{18}N_2Na_2O_{10}$ admixture also exhibited optimal effectiveness, $\eta = 92.04 \pm 4.13\%$ at inhibiting steel-reinforcement corrosion in concrete immersed in H_2SO_4 medium, where high concentrations, the 0.4167%, the 0.3333% and the 0.6667% of $C_{10}H_{18}N_2Na_2O_{10}$ were required to attain inhibition efficiency of $\eta > 74\%$;
- o Adsorption modelling showed that $C_{10}H_{18}N_2Na_2O_{10}$ admixtures were best fitted by the Langmuir isotherm even as the other two isotherm models employed, the El-Awady and the Freundlich, bear supports with the Langmuir model at indicating chemical adsorption, chemisorptions, as the prevalent adsorption mechanism of $C_{10}H_{18}N_2Na_2O_{10}$ on concrete steel-reinforcement in both the NaCl and the H_2SO_4 corrosive environments.

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