Probability density fittings of corrosion test-data: Implications on $C_6H_{15}NO_3$ effectiveness on concrete steel-rebar corrosion

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Abstract. In this study, corrosion test-data of steel-rebar in concrete were subjected to the fittings of the Normal, Gumbel and the Weibull probability distribution functions. This was done to investigate the suitability of the results of the fitted test-data, by these distributions, for modelling the effectiveness of $C_6H_{15}NO_3$, triethanolamine (TEA), admixtures on the corrosion of steel-rebar in concrete in NaCl and in H_2SO_4 test-media. For this, six different concentrations of TEA were admixed in replicates of steel-reinforced concrete samples which were immersed in the saline/marine and the microbial/industrial simulating test-environments for seventy-five days. From these, distribution fittings of the non-destructive electrochemical measurements were subjected to the Kolmogorov–Smirnov goodness-of-fit statistics and to the analyses of variance modelling for studying test-data compatibility to the fittings and testing significance. Although all fittings of test-data followed similar trends of significant testing, the fittings of the corrosion rate test data followed the Weibull more than the Normal and the Gumbel distribution fittings, thus supporting use of the Weibull fittings for modelling effectiveness. The effectiveness models on rebar corrosion, based on these, identified 0.083% TEA with optimal inhibition efficiency, $\eta = 72.17 \pm 10.68\%$, in NaCl medium while 0.667% TEA was the only admixture with positive

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effectiveness, $\eta = 56.45 \pm 15.85\%$, in H_2SO_4 medium. These results bear implications on the concentrations of TEA for effective corrosion protection of concrete steel-rebar in saline/marine and in industrial/microbial environments.

Keywords. Steel-reinforced concrete; probability distribution functions; corrosion test-data; triethanolamine admixture; corrosion inhibitor effectiveness; statistical tests of significance.

1. Introduction

Buildings and many infrastructural developments, globally, depend on the use of steel reinforced concrete materials because of its durability and relative cost effectiveness compared to other materials (Al-Amoudi *et al* 2003; Zhao *et al* 2010; Shi *et al* 2012; Tang *et al* 2012). However, corrosion degradation of concrete steel rebar, in aggressive environments, affect these properties by inducing low structural strength, cost intensive repairs, rehabilitation and maintenance and, if the corrosion remains unchecked, ultimate premature failure of the concrete structure (Zhang & Li 2006; Duffó *et al* 2009; Junzhi *et al* 2010; Sharifi & Rahgozar 2010; Zhao *et al* 2010; Dong *et al* 2011; Zhao *et al* 2011; Huang *et al* 2012; Omotosho *et al* 2012). Several methods have been proposed for tackling corrosion problems of reinforcing steel in concrete. They include surface coating, cathodic protection, waterproofing membranes and corrosion inhibitors. Among these, the use of corrosion inhibitor admixture in concrete had been identified as an easy, effective and economical approach for mitigating corrosion of steel reinforcement in concrete structures (Etteyeb *et al* 2007a; Ormellese *et al* 2009; Sastri 2011; Okeniyi *et al* 2012).

For a corrosion inhibitor admixture in concrete to effectively mitigate rebar corrosion, it had to be present in the corrosive system at a suitable concentration (Holoway *et al* 2004; Söylev & Richardson 2008). For this reason, studies involving corrosion inhibitor admixtures in concrete had not always been preoccupied with studying effectiveness of the inhibitor substance alone but had also been studying the concentration at which studied effectiveness had been attained (Al-Amoudi *et al* 2003; Ormellese *et al* 2006; Söylev & Richardson 2008). In recent studies, however, issues of conflicting and contradicting reports of inhibition effectiveness are generating concerns because this is militating against responsible application of inhibitors in corrosive environments (Ngala *et al* 2002; Jamil *et al* 2003; Sideris & Savva 2005; Söylev & Richardson 2008; Ormellese *et al* 2009; Feng *et al* 2011). While positive effectiveness were reported in some studies, the needs for further research works, bordering, especially, on admixture concentration for acceptable reduction in corrosion rate had been recommended by others.

The American Society for Testing and Materials, ASTM G16-99 R04, had recognised that many factors and complexities (Vaysburd & Emmons 2004) in the corrosion system introduce randomised scatter in measured readings of corrosion test data which induce deviations of such measured values from the expected values for the prevailing condition in the corrosion system. By these, dataset from such measurements could lead to conflicting interpretations that could in turn culminate in contradictory reports. This could be reason that well known and even commercial inhibitors are not spared from the contradictory inhibition effectiveness in literature (Ormellese *et al* 2006, 2009).

According to the specifications of ASTM G 16-99 R04, addressing the inherent scatter in corrosion test data begins from the identification of the distribution function which the measured test data scattered like or, in statistical terms, followed or come from. Such identification do not usually involve the distribution fittings of the test data alone but also that of studying how well the distribution function represent the pattern of the scatter by the test data. An

approach recommended for this include the use of a goodness of fit (GoF) statistics, for which the Kolmogorov–Smirnov (K–S) GoF test method could be employed (Roberge 2003, 2005, 2008; Izquierdo *et al* 2004). The importance of these fittings, the fitting reliabilities and the relevant GoF tests is that the analyses and evaluations that could be representative of the prevailing conditions in the datasets would only be appropriate through the distribution followed by the scattered test data (Izquierdo *et al* 2004). This bear direct implication from ASTM G16 that using evaluated models, for the scattered data, obtained from distribution not followed by the data, could lead to results that are deviated from the prevailing condition in the corrosive system.

In spite of the foregoing, there is paucity of studies where either the use of probability density fittings or that of the techniques of ASTM G16 had been applied for inhibition effectiveness investigation on concrete steel-rebar corrosion. While the use of probability distribution was upheld as a method of paramount importance in corrosion experiments, it was also identified as the most neglected method of corrosion test data treatment in literature (Haynie 2005). Although Castrellon-Uribe *et al* (2008) and Cuevas-Arteaga (2008) had recently employed ASTM G16 for analysing time series test data of electrochemical noise for alloy steel corrosion and Izquierdo *et al* (2004) had previously employed distribution fittings based on GoF tests for chloride thresholds, none of these were applications for inhibitor effectiveness in steel-reinforced concrete. Also, some authors in this research work had been involved in distribution fitting applications to half-circuit potential test data of other inhibitors in reported studies that had been submitted elsewhere (Okeniyi *et al* 2012; Omotosho *et al* 2010, 2012). However, the results from those studies were only suitable for modelling probabilistic performance but not for representing absolute rebar corrosion activity (Berke & Hicks 2004).

Therefore, the objective of this paper is to investigate the probability density function that could be appropriately used for describing the corrosion test data of reinforcing steel in concrete admixed with different concentrations of $C_6H_{15}NO_3$, triethanolamine (TEA) and immersed in NaCl and in H_2SO_4 test media. By this, the reliability and testing, using K–S GoF criteria, of the fitting models by the Normal and the extreme value distribution functions of the Gumbel and the Weibull will be studied with the aim of employing the reliably tested fitting for inhibition effectiveness. This study had drawn motivation from considerations including the previous studies of TEA as an encapsulated nano-coatings for corrosion protection of steel sheet (Choi *et al* 2012) and, especially, as an inhibitor for chloride induced steel-rebar corrosion in alkaline pore, simulating concrete, solution (Ormellese *et al* 2009). Requirements from this latter and literature had, however, include need for studying inhibitor effectiveness on the corrosion protection of steel-rebar embedded in physically cast concrete block, admixed with the inhibitor, for complementing that of the rebar in simulated, alkaline, pore solution (Etteyeb *et al* 2007b; Ormellese *et al* 2009).

2. Materials and methods

2.1 Materials

2.1a Chemicals used: (i) Solutions: distilled water was used to prepare all solutions (Muralidharan *et al* 2004), except concrete mixing for which drinkable tap water was used (Chung *et al* 2008; Abdelaziz *et al* 2009; Aveldaño & Ortega 2011). (ii) Inhibitor: triethanolamine (TEA), $C_6H_{15}NO_3$, (Surechem Products, ScP). (iii) Aggressive agents: (a) Sodium chloride, NaCl, (Eurostar Scientific) (b) Sulphuric acid, H_2SO_4 , (Sigma-Aldrich) (iv) Others: (a) Acetone, $(CH_3)_2CO$, for degreasing (Sigma-Aldrich) (b) Iso-propyl alcohol, $CH_3CHOHCH_3$, for wetting fluid (J T Baker).

2.1b Steel reinforced concrete specimens: Steel reinforcement was obtained from Federated Steel Rolling Mills, Ota, Ogun State, Nigeria, for use in the study. The Ø 12 mm deformed steel-rebar was cut into 190 mm rod of specimens, for each of which surface preparation was maintained uniformly in accordance with literatures (Muralidharan *et al* 2004; Loto & Popoola 2011; Singh *et al* 2012) and designation (ASTMG109-99a 2005). Length of 150 mm of each rod of steel-rebar, leaving 40 mm steel protrusion for electrochemical connections, were embedded in 100 mm × 100 mm × 200 mm replicate blocks of concrete samples that totaled twenty-eight reinforced concrete blocks. These were made in moulds containing four block samples each and into which different concentrations of TEA were admixed. These admixed TEA concentrations, in percentage of cement content include: 0% control (Ctrl) samples, 0.083%, 0.167%, 0.25%, 0.333%, 0.417% and 0.667% TEA admixture per block sample within each of the batch mixings of replicated moulds, see table 1. The last replicate samples admixed with the 0.667% TEA was included, as a jump in the concentration trend, for a model study of how such high concentration affects steel-rebar corrosion.

Ordinary Portland Cement (OPC) of type CEM II/A-L 42.5N according to EN 197-1 (2000) was used for the reinforced concrete formulation (Bertolini *et al* 2012). This formulation had a

Table 1. Triethanolamine, $C_6H_{15}NO_3$: TEA, (in % of cement content) admixed in steel reinforced concretes.

S/No	Specimen by admixed $C_6H_{15}NO_3$ percentage
1.	0.0% $C_6H_{15}NO_3$ (Control in NaCl)
2.	0.0% $C_6H_{15}NO_3$ (Control in H_2SO_4)
3.	0.0% $C_6H_{15}NO_3$ (Control in NaCl_Rep)
4.	0.0% $C_6H_{15}NO_3$ (Control in H_2SO_4 _Rep)
5.	0.083% $C_6H_{15}NO_3$ in NaCl
6.	0.083% $C_6H_{15}NO_3$ in H_2SO_4
7.	0.083% $C_6H_{15}NO_3$ in NaCl_Rep
8.	0.083% $C_6H_{15}NO_3$ in H_2SO_4 _Rep
9.	0.167% $C_6H_{15}NO_3$ in NaCl
10.	0.167% $C_6H_{15}NO_3$ in H_2SO_4
11.	0.167% $C_6H_{15}NO_3$ in NaCl_Rep
12.	0.167% $C_6H_{15}NO_3$ in H_2SO_4 _Rep
13.	0.25% $C_6H_{15}NO_3$ in NaCl
14.	0.25% $C_6H_{15}NO_3$ in H_2SO_4
15.	0.25% $C_6H_{15}NO_3$ in NaCl_Rep
16.	0.25% $C_6H_{15}NO_3$ in H_2SO_4 _Rep
17.	0.333% $C_6H_{15}NO_3$ in NaCl
18.	0.333% $C_6H_{15}NO_3$ in H_2SO_4
19.	0.333% $C_6H_{15}NO_3$ in NaCl_Rep
20.	0.333% $C_6H_{15}NO_3$ in H_2SO_4 _Rep
21.	0.417% $C_6H_{15}NO_3$ in NaCl
22.	0.417% $C_6H_{15}NO_3$ in H_2SO_4
23.	0.417% $C_6H_{15}NO_3$ in NaCl_Rep
24.	0.417% $C_6H_{15}NO_3$ in H_2SO_4 _Rep
25.	0.667% $C_6H_{15}NO_3$ in NaCl
26.	0.667% $C_6H_{15}NO_3$ in H_2SO_4
27.	0.667% $C_6H_{15}NO_3$ in NaCl_Rep
28.	0.667% $C_6H_{15}NO_3$ in H_2SO_4 _Rep

mix proportion of 300.0 kg/m³ of the cement, 890.6 kg/m³ of sand of 2.80 fineness modulus (which conforms to ASTM C33-03 (2005)), 1106.3 kg/m³ of granite stones of maximum size 19 mm and 149.7 kg/m³ of water thus having water–cement ratio of 0.499 (ASTM G109-99a (2005); Ormellesse *et al* 2006). Each mould of concrete batch mixings were made with wood which was covered with non-absorbent polyvinyl-chloride (PVC) material that is non-reactive with the concrete to prevent leaching of the admixture solution into the wooden mould. Each of the moulded batches of concrete blocks were externally vibrated on an electric vibrator (Matest equipment) and cured in a curing room for 28 days, in accordance with the specifications of ASTM C192/192M-02 (2005). The rebar protrusion was painted with glossy paint after the casting of concrete specimens.

2.2 Experimental methods

2.2a Setup for corrosion test-experiment: Steel reinforced concrete samples were partially immersed, longitudinally, in plastic bowls containing respective test solution of aggressive agent. Each of the first replicated set of fourteen samples was partially immersed in 3.5% NaCl solution (Mehta *et al* 2010; Zafeiropoulou *et al* 2011; Zhou *et al* 2012) while the second replicated set was partially immersed in 0.5 M H₂SO₄ solution (Moretti *et al* 2004; Obot *et al* 2010). By these, the NaCl test medium simulates saline/marine (Tang *et al* 2012; Muralidharan *et al* 2004) while the H₂SO₄ test medium simulates industrial/microbial (Dexter 2005; Roberge 2008; Hunting & Kampfraath 2013) or sewage (Hewayde *et al* 2007; Wei *et al* 2010) environments. In each bowl, the test solution was made up to just below the reinforcing steel rebar without touching it and was replenished every three weeks in the bowls to prevent dryness and induce continuous system of corrosive environment (Muralidharan *et al* 2004).

2.2b Setup for corrosion test data measurements: Corrosion test data of non-destructive electrochemical measurements (Broomfield 2003; Song & Saraswathy 2007; Zafeiropoulou *et al* 2011) were taken from the described reinforced concrete test setup, first, in five days interval for forty days and thereafter in seven days interval for the following five weeks. This totals seventy-five days experimental period for this study. These electrochemical test methods include:

- (i) Half-cell potential (HCP) measurements were measured through the experimental period versus Cu/CuSO₄ electrode (CSE), Model 8-A (Tinker & Rasor®) using a high impedance digital multimeter, Model DT-9205A, figure 1a, according to ASTM C876-91 R99 (2005).
- (ii) Electrochemical cell current (ECC) measurements: in the concrete-test solution system were measured, versus the CSE, using zero resistance ammeter, (ZRA), Model ZM3P (Corrosion Service) (Jäggi *et al* 2001; McCarter & Vennesland 2004; Abdelaziz *et al* 2009; Sastri 2011). This constitutes the Daniel cell model (Broomfield 2003) of measuring reinforcing steel dissolution activity (McCarter & Vennesland 2004) in the aggressive test solution systems which shares porous partitioning with the Cu/CuSO₄. The concept of premise for this include the consideration that the porous partition of the CSE's semi-permeable membrane permits charge exchange, when reference and working electrodes are joined, but remains impervious to ion movement. Therefore, the zero resistance ammeter connection was idealised for the measurement of the current ensuing from the charge movement system of the Daniel cell model.
- (iii) Corrosion rate (CR) measurements were obtained through direct instrument conversion to mpy (Abosrra *et al* 2011) using the three-electrode LPR Data Logger®, Model MS1500 L

(a)

(b)

Figure 1. Set-ups for corrosion test-variable measurements (a) HCP, (b) LPR set-up for CR.

(Metal Samples®) (Sastri 2011). As described in Song & Saraswathy (2007) and in Broomfield (2003), the three electrodes of this equipment were correspondingly connected, as shown in figure 1b, to Ag/AgCl SCE reference electrode (EDT direct-ION double junction), brass plate auxiliary and the steel-rebar working electrode (Kahlert 2010; Stojek 2010). By this connection, the instrument, through a true potentiostatic circuit, null any residual potential difference between the reference electrode and the reinforcing steel working electrode after which current was made to flow between the auxiliary and the working electrode until the potential of the working electrode was shifted by $\Delta E = 10$ mV relative to the reference electrode. The current increase (ΔI) required to sustain the 10 mV potential (ΔE) was employed for direct readout of the corrosion rate in mpy by the instrument. For this, the Stern–Geary relationship (Song & Saraswathy 2007; Mehta *et al* 2010) between the

corrosion current i_{cor} and the polarisation resistance $\Delta E/\Delta I$ find usefulness, by the LPR Data Logger® instrument, for evaluating i_{cor} as

$$i_{cor} = \frac{\beta_a \cdot \beta_c}{2.3(\beta_a + \beta_c)} \cdot \frac{\Delta I}{\Delta E} \equiv K \Delta I. \quad (1)$$

This i_{cor} is then employed by the LPR Data Logger® instrument for computing its direct readout of corrosion rate CR (in mpy unit) through Faraday law application:

$$CR = \frac{i_{cor} \times S}{A \times F} \times \frac{E}{d} \times \frac{1000}{254}, \quad (2)$$

where β_a and β_c are anodic and cathodic Tafel constants (volt/decade) and by these a constant B (ranging from 26 to 52 mV depending on the passivity or active condition of the steel-rebar) had been proposed in literature (Broomfield 2003; Song & Saraswathy 2007) for the ratio $(\beta_a \cdot \beta_c)/[2.3 \times (\beta_a + \beta_c)]$, however, the commercial instrument of the LPR Data Logger® Model MS1500L used in this study had been configured from factory to internally estimate this empirical constant, based on an absorbed form of the ratio constituting the average constant of proportionality derived from a large number of factory-based E/I measurements, for requisite computation of the direct readout of corrosion rate in mpy by the LPR instrument;

S = number of seconds in a year (31,536,000 s);

A = surface area of working electrode (cm²);

F = Faraday's constant (96,494 coulombs·(g.equ)⁻¹);

E = equivalent weight (27.92 g·(g.equ)⁻¹, for iron (Mehta *et al* 2010));

d = density of corroding metal (7.86 g/cm³, for iron (Mehta *et al* 2010)).

It should be noted that the non-usage of a guard ring configuration for the LPR measurement is expected to double the corrosion rate measurements, as had been indicated in literature (Broomfield 2003; Song & Saraswathy 2007). Also, the flowing current from the potentiostatic circuit of the LPR Data Logger is expected to accelerate the corrosion process as an impressed current configuration, of the type employed in Abosrra *et al* (2011). It is opined that the high range of corrosion rate measurements that could be obtained from these would facilitate noticeable corrosion rate variations within the scheduled experimental period (Abosrra *et al* 2011) suitable for studying effectiveness of the different TEA admixture concentrations employed.

To ensure good electrical contact for these electrochemical measurements, a water retentive conducting sponge was employed for the point of contact of the measuring probes and the reinforced concrete (Song & 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), to improve the wetting characteristics of the conducting solution.

2.3 Probability density fittings and modelling

Each measured entity of electrochemical data was denoted as proceeding from system of independent and identically distributed (i.i.d.) random samples (Kvam & Lu 2006; Lovric 2011). By this, they were subjected to the statistical analysis of the Normal and the extreme value fitting functions of the Gumbel and the Weibull distributions for modelling quality, uniformity and the reliability of the electrochemical test data (Roberge 2003, 2005, 2008; Karian & Dudewicz 2011; Lovric 2011).

2.3a The normal distribution fittings and tests of significance: The statistical tool of the Normal probability density function (pdf) used for studying measurements of corrosion test data (Montgomery & Runger 2003; Soong 2004; Haynie 2005; Okeniyi *et al* 2013) is given by

$$f(x) = \frac{1}{\sigma(2\pi)^{1/2}} \exp \left[-\frac{(x - \mu)^2}{2\sigma^2} \right], \quad (3)$$

where μ is the mean and σ is the standard deviation of x , the corrosion test data variable. The maximum likelihood equation for the Normal μ and σ are well known (Haynie 2005). The Normal cumulative density function, CDF, could be obtained from (Montgomery & Runger 2003; Okeniyi *et al* 2013)

$$F(x) = \frac{1}{\sigma(2\pi)^{1/2}} \int_{-\infty}^x \exp \left[-\frac{(x - \mu)^2}{2\sigma^2} \right] dx. \quad (4)$$

Estimated value of the cumulative density function, $F(x)$, at x gives cumulative probability of obtaining at least x within the dataset of the modelled corrosion test variable. By this, $F(x)$ find usefulness, in probability density fittings, for modelling reliability of the quality and uniformity of the dataset by the distribution fitting model, especially in accordance with how it had been employed for corrosion test-data in studies (Omotosho *et al* 2010, 2012).

2.3b The Gumbel distribution fittings: The type I extreme-value fittings of the Gumbel distribution, for modelling corrosion test data of reinforced concrete samples, are given by (Kotz & Nadarajah 2000; Roberge 2005):

$$f(x) = \frac{1}{k} \exp \left[-\left(\frac{x - c}{k} \right) \right] \exp \left\{ -\exp \left[-\left(\frac{x - c}{k} \right) \right] \right\}, \quad (5)$$

$$F(x) = 1 - \exp \left\{ -\exp \left[-\left(\frac{x - c}{k} \right) \right] \right\}, \quad (6)$$

where k is the scale parameter and c is the location parameter. Estimations of these parameters were obtained, for sample size n , from the solution of the simultaneous maximum likelihood equations (Kotz & Nadarajah 2000; Kvam & Lu 2006; Reiss & Thomas 2007):

$$\hat{k} + \hat{c} + \frac{1}{n} \sum_{i=1}^n x_i \exp \left\{ -\frac{x_i - \hat{c}}{\hat{k}} \right\} - \frac{\hat{c}}{n} \sum_{i=1}^n \exp \left\{ -\frac{x_i - \hat{c}}{\hat{k}} \right\} = \bar{x}, \quad (7)$$

$$\sum_{i=1}^n \exp \left\{ -\frac{x_i - \hat{c}}{\hat{k}} \right\} = n. \quad (8)$$

For these, the combined fixed point iterative–Aitken Δ^2 procedures were employed (Hoffman 2001; Lange 2010; Waldemar 2010). The unbiased estimated values of k and c , from these, were used to compute the Gumbel mean model from (Reiss & Thomas 2007)

$$\mu_G = c - k\Gamma'(1), \quad (9)$$

where $\Gamma'(1) = \gamma$, Euler's constant and the value of $d\Gamma(n)/dn$ evaluated at $n = 1$.

2.3c *The Weibull distribution fittings:* The type III extreme-value fittings of the Weibull pdf, for analysis of rebar corrosion test data takes the form (Kotz & Nadarajah 2000; Roberge 2005; Reiss & Thomas 2007):

$$f(x) = \frac{k}{c} \left(\frac{x}{c}\right)^{k-1} \cdot \exp \left\{ -\left(\frac{x}{c}\right)^k \right\}, \quad (10)$$

$$F(x) = 1 - \exp \left[-\left(\frac{x}{c}\right)^k \right]. \quad (11)$$

Here, k is the shape parameter and c is the scale parameter. Estimations of these parameters were obtained, for sample size n , from the solution of the simultaneous maximum likelihood equations (Kotz & Nadarajah 2000; Kvam & Lu 2006; Reiss & Thomas 2007):

$$\frac{n}{\hat{k}} - n \ln(\hat{c}) + \sum_{i=1}^n \ln x_i - \sum_{i=1}^n \left(\frac{x_i}{\hat{c}}\right)^{\hat{k}} \ln \left(\frac{x_i}{\hat{c}}\right) = 0, \quad (12)$$

$$\hat{c} - \left\{ \frac{1}{n} \sum_{i=1}^n x_i^{\hat{k}} \right\}^{\frac{1}{\hat{k}}} = 0. \quad (13)$$

For these also, the combined fixed point iterative–Aitken Δ^2 procedures were employed (Hoffman 2001; Lange 2010; Waldemar 2010). The unbiased estimated values of k and c , from these, were used to compute the Weibull mean, μ_W , model as (Reiss & Thomas 2007; Omotosho *et al* 2010; Ajayi *et al* 2011)

$$\mu_W = c\Gamma \left(1 + \frac{1}{k} \right), \quad (14)$$

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

2.3d *Goodness-of-fit test statistics:* Compatibility of the scatter of each variable of electro-chemical data to each of the probability distribution models employed for fitting the dataset were verified using the Kolmogorov–Smirnov (K–S) goodness-of-fit (GoF) test statistics (Roberge 2003, 2005; Shabri & Jemain 2006; Omotosho *et al* 2010; Thas 2010; Ajayi *et al* 2011; Fagbenle *et al* 2011; Okeniyi & Okeniyi 2012; Okeniyi *et al* 2012, 2013). 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, through the statistics

$$D_n = D(x_1, \dots, x_n) = \sup_{-\infty < x < \infty} |F^*(x) - F(x)|. \quad (15)$$

The D -value evaluation from Eq. (15) was used for direct computation of the K–S p -value using procedures that had been described in Okeniyi & Okeniyi (2012). By this approach, K–S p -value $\geq \alpha$ for a probability distribution model of corrosion test data indicate the scattering of such data like the distribution while K–S p -value $< \alpha$ showed that the test data were not scattered like the distribution model. For all these statistical tests, the significant level $\alpha = 0.05$ was employed, which corresponds to 95% confidence interval (Aguilar *et al* 2012).

2.3e Statistical tests of significance of differences of corrosion test-variables: It is also of interest to test significance of differences encountered between measurements of corrosion test-data for replicate samples as well as the modelled performance between different admixture concentrations in the concretes immersed in their respective media. For these, procedures prescribed in ASTM G16-95 R04 for executing these types of tests of significance were employed in this study. For the between-replicate test of significance of differences encountered in the measured test-data, the student's *t*-test statistics, including the homoscedastic *t*-test which assumes equal variance (EV) and the heteroscedastic *t*-test of the unequal variance (UV), were employed. For studying test of significance of differences, in the probabilistic performance models among the different admixture concentrations, the one-way factorial analysis of variance, ANOVA (Aguilar *et al* 2012), was applied to the test-variable modelling by each of the distribution fitting functions.

2.3f Inhibition efficiency: The mean model from the optimal probability fitting function of the corrosion rate test (CR) data was applied for evaluating inhibition efficiency, η . This was done from the consideration that such modelled mean from pdf of similar scatter with the dataset would adequately represent the prevailing condition in the corrosive system, according to ASTM G16. Thus, for each replicate of admixture concentration employed, relative to each replicate of control sample, the inhibition efficiency, η , was obtained from (Holloway *et al* 2004; Etteyeb *et al* 2007a; Behpour *et al* 2009; Obot *et al* 2010; Zhou *et al* 2012):

$$\eta = \frac{\mu_{pdf,ctrl} - \mu_{pdf,inh}}{\mu_{pdf,ctrl}} \times 100. \quad (16)$$

3. Results and discussion

3.1 Experimental data measurements

Corrosion test data, from non-destructive electrochemical measurements of half-cell potential (HCP) and corrosion rate (CR) of steel-rebar in concrete through the seventy-five days experimental period, are presented for samples in NaCl in figure 2, and in H₂SO₄ in figure 3.

From the plots, it could be noted that both readings of the half cell potential (HCP), figures 2a and 3a, and that of the electrochemical cell current (ECC), figures 2b and 3b, are negative, that is in $-mV$ and $-\mu A$ units, respectively. The negative potential readings are due to the dissolution model of steel-rebar, within the concentrated cell of concrete in aggressive media, which instigates more build up of negatively charged electrons at the steel-rebar in concrete than at the CSE. In comparison, the copper electrode in the CSE half cell is positively charged, relative to the steel-rebar because copper from the copper sulphate solution plates out on the copper electrode in the Daniel cell model application to steel-rebar corrosion in concrete (Broomfield 2003). Since the high impedance voltmeter for measuring HCP is meant to disallow flow of current, it measures negative potential difference across the rebar connected to its positive terminal (but more negative by electrons build-up) and the CSE electrode connected to its negative terminal (Song & Saraswathy 2007). This negative potential difference forms the basis for the negative ECC measurement by the Zero Resistance Ammeter (ZRA) which measures its current as the applied voltage, equivalent to voltage drop, across a resistor divided by the resistance of the resistor. By

Figure 2. Corrosion test data measurements for steel-reinforced concrete samples partially immersed in NaCl medium: (a) half-circuit potential; (b) electrochemical cell current; and (c) corrosion rate.

this, the negative measure of potential difference divided by positive resistance yields negative current readout by the ZRA as the ECC measurements plotted in figures 2b and 3b.

The plots in figures 2 and 3 also showed that the datasets of the corrosion test variables were well attended with variability or experimental scatter that would make interpretation difficult. This necessitates needs for statistical tools utilisation for aiding result interpretation for each steel-reinforced concrete specimen through requisite analysis of the scattered measured data.

Figure 3. Corrosion test data measurements for steel-reinforced concrete samples partially immersed in H_2SO_4 medium: (a) half-circuit potential; (b) electrochemical cell current and (c) corrosion rate.

3.2 Modelled results from normal distribution fittings of test-data and tests of significance

Results of the corrosion test data models by the normal distribution functions are presented in table 2 for samples immersed in NaCl medium and in table 3 for samples in H_2SO_4 medium. The Normal mean models exhibited monotonous cumulative probability of attaining at least each of the mean, i.e., the reliability of 50%, bearing implications that each of the Normal mean models equal the 50th percentile or the median of their datasets. Though these Normal mean models were better form of order than the stochastic scatter of the measured data, a good number of

Table 2. Results of normal pdf modelling of corrosion test data for samples in NaCl medium.

S/No	Admixture in concrete (NaCl medium)	Half-cell potential (HCP)			Electrochemical cell current (ECC)			Corrosion rate (CR)		
		Mean μ_{N-HCP} (-mV CSE)	Reliability F (μ_{N-HCP})	K-S p -value	Mean μ_{N-ECC} (- μ A)	Reliability F(μ_{N-ECC})	K-S p -value	Mean μ_{N-CR} (mm/y)	Reliability F(μ_{N-CR})	K-S p -value
1.	0% TEA-Ctrl	597.83	0.5	0.3688	705.25	0.5	0.9989	2.549	0.5	0.0702
2.	0% TEA-Ctrl _(Rep)	570.93	0.5	0.2646	764.11	0.5	0.8546	2.554	0.5	0.0702
3.	0.083% TEA	445.38	0.5	0.2199	257.53	0.5	0.9718	0.891	0.5	0.0179
4.	0.083% TEA _(Rep)	461.98	0.5	0.2524	196.81	0.5	0.5075	1.110	0.5	0.1017
5.	0.167% TEA	516.76	0.5	0.4599	358.14	0.5	0.9343	1.662	0.5	0.0431
6.	0.167% TEA _(Rep)	442.36	0.5	0.5078	175.97	0.5	0.5488	1.198	0.5	0.0569
7.	0.25% TEA	440.71	0.5	0.0559	228.25	0.5	0.7832	0.996	0.5	0.0378
8.	0.25% TEA _(Rep)	363.29	0.5	0.9555	162.08	0.5	0.4792	1.609	0.5	0.0621
9.	0.333% TEA	529.57	0.5	0.3112	465.13	0.5	0.9440	2.359	0.5	0.1105
10.	0.333% TEA _(Rep)	497.02	0.5	0.0764	503.92	0.5	0.4393	1.714	0.5	0.0965
11.	0.417% TEA	467.24	0.5	0.9412	262.89	0.5	0.8180	1.981	0.5	0.1702
12.	0.417% TEA _(Rep)	458.33	0.5	0.3912	323.11	0.5	0.8999	1.945	0.5	0.0795
13.	0.667% TEA	552.45	0.5	0.0294	385.47	0.5	0.5459	1.860	0.5	0.0180
14.	0.667% TEA _(Rep)	534.29	0.5	0.0790	424.08	0.5	0.9092	1.886	0.5	0.0317

Table 3. Results of normal pdf modelling of corrosion test data for samples in H₂SO₄ medium.

S/No	Admixture in concrete (H ₂ SO ₄ medium)	Half-cell potential (HCP)				Electrochemical cell current (ECC)				Corrosion rate (CR)			
		Mean μ_N -HCP (-mV CSE)	Reliability $F(\mu_N$ -HCP)	K-S p -value	Mean μ_N -ECC (- μ A)	Reliability $F(\mu_N$ -ECC)	K-S p -value	Mean μ_N -CR (mm/y)	Reliability $F(\mu_N$ -CR)	K-S p -value			
1.	0% TEA-Ctrl	298.52	0.5	0.2417	91.81	0.5	0.1426	0.256	0.5	0.0457			
2.	0% TEA-Ctrl(Rep)	453.83	0.5	0.9064	152.51	0.5	0.9703	0.218	0.5	0.0668			
3.	0.083% TEA	119.38	0.5	0.0858	15.25	0.5	0.9655	0.266	0.5	0.0038			
4.	0.083% TEA(Rep)	78.05	0.5	0.2383	70.51	0.5	0.0004	0.238	0.5	0.0189			
5.	0.167% TEA	93.74	0.5	0.9007	45.71	0.5	0.0006	0.411	0.5	0.0014			
6.	0.167% TEA(Rep)	181.62	0.5	0.7572	23.82	0.5	0.0329	0.252	0.5	0.0309			
7.	0.25% TEA	105.81	0.5	0.4255	8.43	0.5	0.5618	0.080	0.5	0.4490			
8.	0.25% TEA(Rep)	134.48	0.5	0.2295	12.92	0.5	0.9498	0.760	0.5	0.0085			
9.	0.333% TEA	116.79	0.5	0.9221	12.50	0.5	0.3835	0.320	0.5	0.0057			
10.	0.333% TEA(Rep)	135.50	0.5	0.1162	24.40	0.5	0.5044	0.437	0.5	0.0067			
11.	0.417% TEA	154.14	0.5	0.0786	26.23	0.5	0.0769	0.109	0.5	0.0444			
12.	0.417% TEA(Rep)	123.74	0.5	0.7237	16.70	0.5	0.9052	0.366	0.5	0.0705			
13.	0.667% TEA	117.95	0.5	0.4091	6.40	0.5	0.8392	0.130	0.5	0.0183			
14.	0.667% TEA(Rep)	157.21	0.5	0.1597	15.63	0.5	0.2082	0.077	0.5	0.0038			

the corrosion rate dataset were not well fitted by the Normal pdf. According to the K-S GoF statistics, p -values were less than 0.05 for CR dataset of five concrete samples in the NaCl and for CR dataset of nine samples in the H_2SO_4 medium.

Thus, even while it could be considered that only the HCP dataset of a sample in NaCl and the ECC dataset of three samples in H_2SO_4 medium did not scatter like the Normal, the fittings of the CR test data by the Normal distribution bear much more significance. Reason for this significance includes the fact that the corrosion rate test-variable is the quantitative measure which finds usefulness for modelling inhibitor effectiveness and for detailing absolute inhibitor performance. Conflicting effectiveness could ensue from the consideration that the non-compatibility of these CR datasets could be implicative of their Normal mean models not being representative of the prevailing conditions in their respective corrosive system, according to ASTM G16.

Figure 4 shows results of student's t -test of significance between the replicate reinforced concrete samples admixed with same concentration of TEA admixtures in their respective test-media and with the linear plot of $\alpha = 0.05$ shown for direct interpretation of significance. Thus, plots reaching or towering beyond this $\alpha = 0.05$ line represent test-variables exhibiting no significant difference, while plots falling short of it represent test-variables exhibiting significant difference, at 95% confidence level. From this, it could be observed that, except for the ECC test data of the replicated samples admixed with 0.167% TEA, differences in the between-replicate measurements of corrosion test-variables are not significant for all replicated concrete samples in NaCl medium. For these other samples in NaCl medium, encountered differences in the measurements of their corrosion test variables were not significant according to the t -test statistics. However, the test-data of the ECC test-variable of the 0.167% TEA replicates showed that differences encountered in this test-variable among the 0.167% TEA replicates are significant and are not due to chance. For samples in H_2SO_4 medium, between-replicate differences encountered in the HCP test data of 0.083% TEA, 0.167% TEA and the 0.667% TEA as well as the ECC test data of the 0.25% TEA, 0.333% TEA and the 0.667% TEA samples were not due to chance but were significant. The remaining test-data of measured corrosion test variables in the medium exhibited differences that were not significant at 95% confidence level. Also, all datasets of corrosion rate of TEA-admixed replicated concrete samples, both in NaCl and in H_2SO_4 media (figure 4), exhibited differences that were not significant.

Figure 4. Student's t -test of significance between TEA admixed replicated concretes immersed in corrosive media.

In spite of these student's t -test results, the one-way ANOVA results, table 4, showed that differences in the normal mean models of HCP and ECC of different TEA-admixed samples in both media and CR of the samples in NaCl are significant within 95% confidence level. These exhibited p -values <0.05 . However, the ANOVA results showed that differences encountered in the Normal mean models of corrosion rate of the different TEA admixed samples in H_2SO_4 medium are not significant but due to chance or unaccounted complexities in the corrosive test-system (Vaysburd & Emmons 2004; ASTM G16-95 R04 2005). The CR ANOVA for these H_2SO_4 -immersed samples had p -value >0.05 .

3.3 Modelled results from Gumbel distribution fittings of corrosion test data

Results of the corrosion test data fittings by the Gumbel pdf are presented for samples in NaCl medium in table 5, and in H_2SO_4 medium in table 6. From the tables, it could be observed that the Gumbel means were modelled with also monotonous 57.04% reliability (or the cumulative probability of attaining at least the mean values) which was however higher than were obtained for the Normal mean models. By this, each of the Gumbel mean models exhibited 57.04th percentile of their datasets. Also, the K-S GoF tests of how the test data were fitted by the Gumbel pdf are shown in figure 5 for samples in the saline/marine and those in the industrial/microbial simulating environments. In the figure, the linear plot of the significant level $\alpha = 0.05$ was also included for direct identification of dataset well fitted and the test data not well-fitted by the Gumbel pdf. From this, it could be observed that the corrosion rate of twelve samples, three in the NaCl, nine in the H_2SO_4 medium were included, along with two ECC and three HCP test data, in the datasets from seventeen samples not scattering like the Gumbel probability density function. That so many CR test data were not well-fitted by the Gumbel pdf also suggested caution in the applicability of the Gumbel fitting models of mean for representing prevailing conditions in the corrosive systems in the study and for modelling inhibition effectiveness in the samples.

The variability of how the different test-variables followed or did not follow the Gumbel fittings further deepens interest in studying analyses of variances of the different test variables relative to the different concentrations of admixed TEA in concretes in their media. Results of these ANOVA are presented in table 7 for each test-variable of samples immersed in NaCl medium and in H_2SO_4 medium. From the table, the results showed that differences encountered in the Gumbel fittings of the test-data of all the corrosion test-variables for the NaCl-immersed samples admixed with different concentrations of TEA are not due to chance but are significant. Also, differences in the Gumbel fittings of HCP and ECC test-data of the different TEA concentration-admixed samples immersed in H_2SO_4 are not due to chance but are significant. The ANOVA p -values are less than 0.05 for all these test variables of samples. However, the ANOVA p -values >0.05 for the corrosion rate fittings of the samples in H_2SO_4 medium by the Gumbel distribution, thus, showing that differences encountered in the corrosion rate of the different TEA-admixed samples in the medium are not significant.

3.4 Modelled results from Weibull distribution fittings of corrosion test data

Results obtained from the fittings of the corrosion test data by the Weibull probability density function are presented in table 8 for samples immersed in NaCl and in table 9 for samples immersed in H_2SO_4 medium. It could be noted from these tables that the Weibull models were attended with non-monotonous reliabilities, with that of the CR datasets higher than reliabilities obtained from the Normal and from the Gumbel pdf. The least 69.53% reliability of the Weibull

Table 4. One-way ANOVA of Normal pdf models of corrosion test-variables.

	Source of variations	df	Samples in NaCl medium				Samples in H ₂ SO ₄ medium			
			SS	MS	F	p-value	SS	MS	F	p-value
HCP ANOVA	Admixed TEA	6	44399.28	7399.87	7.4014	0.00922	109268.94	18211.49	6.855537	0.011427
	Replication	7	6998.53	999.790			18595.25	2656.47		
	Total	13	51397.81				127864.20			
ECC ANOVA	Admixed TEA	6	429545.71	71590.95	19.523	0.00048	18489.87	3081.64	5.710373	0.018774
	Replication	7	25668.82	3666.97			3777.60	539.66		
	Total	13	455214.53				22267.47			
CR ANOVA	Admixed TEA	6	3.296307	0.549384	7.2763	0.00968	0.134918	0.022486	0.550111	0.758046
	Replication	7	0.528524	0.075503			0.286132	0.040876		
	Total	13	3.824831				0.42105			

Table 5. Results of Gumbel pdf modelling of corrosion test data for samples in NaCl medium.

S/ No	Admixed TEA in concrete (NaCl)	Half-cell potential (HCP)				Electrochemical cell current (ECC)				Corrosion rate (CR)			
		Scale parameter k	Location parameter c	Mean μ_{G-HCP} (-mV CSE)	Reliability $F(\mu_{G-HCP})$	Scale parameter k	Location parameter c	Mean μ_{G-ECC} (- μA)	Reliability $F(\mu_{G-ECC})$	Scale parameter k	Location parameter c	Mean μ_{G-CR} (mm/y)	Reliability $F(\mu_{G-CR})$
1.	Ctrl	279.91	473.74	635.31	0.5704	432.21	478.90	728.38	0.5704	2.35	1.30	2.650	0.5704
2.	Ctrl(Rep)	243.54	468.29	608.87	0.5704	448.21	535.99	794.70	0.5704	2.34	1.30	2.656	0.5704
3.	0.083%	213.93	356.93	480.41	0.5704	156.07	181.88	271.97	0.5704	0.84	0.28	0.762	0.5704
4.	0.083%(Rep)	212.40	372.15	494.75	0.5704	148.68	113.82	199.64	0.5704	1.00	0.45	1.024	0.5704
5.	0.167%	151.96	452.11	539.82	0.5704	226.25	250.83	381.42	0.5704	1.61	0.68	1.603	0.5704
6.	0.167%(Rep)	105.49	392.15	453.04	0.5704	121.70	106.74	176.99	0.5704	1.13	0.45	1.103	0.5704
7.	0.25%	97.76	401.94	458.37	0.5704	159.18	151.14	243.02	0.5704	0.92	0.36	0.887	0.5704
8.	0.25%(Rep)	143.76	291.28	374.26	0.5704	123.22	91.90	163.02	0.5704	1.55	0.64	1.534	0.5704
9.	0.333%	262.98	419.61	571.41	0.5704	331.67	292.98	484.42	0.5704	2.13	1.19	2.421	0.5704
10.	0.333%(Rep)	158.97	436.85	528.61	0.5704	295.53	369.17	539.75	0.5704	1.61	0.74	1.667	0.5704
11.	0.417%	65.05	436.91	474.46	0.5704	178.43	171.12	274.11	0.5704	1.87	0.90	1.973	0.5704
12.	0.417%(Rep)	75.81	422.44	466.20	0.5704	211.89	219.10	341.41	0.5704	1.87	0.85	1.930	0.5704
13.	0.667%	180.00	480.43	584.33	0.5704	236.21	277.09	413.43	0.5704	1.84	0.76	1.823	0.5704
14.	0.667%(Rep)	108.38	488.43	550.99	0.5704	252.91	307.61	453.60	0.5704	1.83	0.79	1.851	0.5704

Table 6. Results of Gumbel pdf modelling of corrosion test data for samples in H₂SO₄ medium.

S/No	Admixed TEA in concrete (H ₂ SO ₄)	Half-cell potential (HCP)				Electrochemical cell current (ECC)				Corrosion rate (CR)			
		Scale parameter k	Location parameter c	Mean μ_{G-HCP} (-mV CSE)	Reliability F (μ_{G-HCP})	Scale parameter k	Location parameter c	Mean μ_{G-ECC} ($-\mu A$)	Reliability F (μ_{G-ECC})	Scale parameter k	Location parameter c	Mean μ_{G-CR} (mm/y)	Reliability F (μ_{G-CR})
1.	Ctrl	198.63	183.65	298.30	0.5704	72.93	47.81	89.91	0.5704	0.25	0.08	0.224	0.5704
2.	Ctrl(Rep)	178.02	378.91	481.67	0.5704	60.19	122.46	157.20	0.5704	0.17	0.11	0.206	0.5704
3.	0.083%	25.46	102.39	117.08	0.5704	6.36	12.13	15.81	0.5704	0.27	0.07	0.233	0.5704
4.	0.083%(Rep)	33.98	57.86	77.48	0.5704	71.17	11.31	52.40	0.5704	0.23	0.08	0.215	0.5704
5.	0.167%	24.86	81.10	95.44	0.5704	37.57	14.78	36.47	0.5704	0.41	0.07	0.312	0.5704
6.	0.167%(Rep)	68.51	149.90	189.44	0.5704	13.41	14.87	22.62	0.5704	0.25	0.08	0.220	0.5704
7.	0.25%	34.21	86.37	106.11	0.5704	3.75	6.44	8.60	0.5704	0.07	0.04	0.080	0.5704
8.	0.25%(Rep)	34.11	115.31	135.00	0.5704	5.09	10.67	13.60	0.5704	0.77	0.21	0.657	0.5704
9.	0.333%	36.30	99.45	120.40	0.5704	7.17	8.13	12.27	0.5704	0.32	0.07	0.259	0.5704
10.	0.333%(Rep)	31.87	116.51	134.90	0.5704	12.17	17.78	24.80	0.5704	0.44	0.09	0.340	0.5704
11.	0.417%	68.35	107.22	146.67	0.5704	19.44	13.73	24.95	0.5704	0.09	0.04	0.098	0.5704
12.	0.417%(Rep)	24.79	109.85	124.16	0.5704	8.05	12.78	17.43	0.5704	0.33	0.14	0.329	0.5704
13.	0.667%	28.75	102.93	119.52	0.5704	2.91	4.95	6.63	0.5704	0.13	0.04	0.109	0.5704
14.	0.667%(Rep)	29.54	142.54	159.59	0.5704	7.35	11.34	15.58	0.5704	0.07	0.02	0.064	0.5704

Figure 5. K–S goodness of Gumbel probability fittings of corrosion test data for samples in corrosive media.

model of CR test data obtained from the CR dataset of the Ctrl_(Rep) in H₂SO₄ medium was higher than the reliabilities of samples in the Normal and the Gumbel models. Reliabilities of samples in the NaCl medium were all greater than 80%. These implies that the probability of attaining at least the Weibull mean models of CR from each of their dataset measurements is $\geq 69.53\%$ in the H₂SO₄-immersed concrete samples and $\geq 80.94\%$ in the NaCl-immersed concrete samples. Also, in continuance of these comparisons, the Weibull mean models of the CR test data of each of the replicates of control samples in the NaCl medium more than doubled the normal and the Gumbel mean models of these samples.

These more than doubled Weibull mean values find explanations from their >0.82 cumulative probability of attaining them since increased cumulative probability implies increased value of modelled parameter among the ordered data required for probability density fittings. However, these higher Weibull mean models still engender keen interest for ascertaining how well the corrosion test data of samples in their corrosive media were fitted by the Weibull probability density function through use of the goodness of fit test statistics.

The p -values obtained from the K–S GoF tests of the fittings of corrosion test data by the Weibull pdf are shown in figure 6, for samples in NaCl and the samples in H₂SO₄ media. In the figure the linear plot of the significant level $\alpha = 0.05$ was also shown for identifying dataset scattering or not scattering like the Weibull fitting function directly. By this it could be seen that three datasets, of an HCP and two ECC did not scatter like the Weibull pdf. However, all CR datasets of samples in both medium followed the Weibull probability density function according to the K–S GoF statistics. Also, the K–S p -value of the control sample (0.0895) and that of its replicate (0.0934) showed that the dataset of these samples followed the fittings of the Weibull pdf in spite of the double mean models by this pdf compared to the mean models by the Normal and the Gumbel pdf's. These followings of the Weibull fittings by the CR test data bear credence of the suitability of the Weibull pdf for representing the prevalent conditions in the studied corrosive systems and for modelling inhibition effectiveness of TEA on the corrosion of steel-rebar in the concrete samples.

In spite of the scattering like the Weibull fitting function by the corrosion test-variables, according to the K–S GoF criteria, the results of the ANOVA of the Weibull fittings, shown in table 10, followed the same trends encountered with the Normal and with the Gumbel pdf. As obtained in the other probability density fittings studied, the p -values of the ANOVA of the

Table 7. One-way ANOVA of Gumbel pdf models of corrosion test-variables.

	Source of variations	df	Samples in NaCl medium				Samples in H ₂ SO ₄ medium			
			SS	MS	F	p-value	SS	MS	F	p-value
HCP ANOVA	Admixed TEA	6	56586.80	9431.13	7.1289	0.01025	121209.98	20201.66	5.99385	0.016494
	Replication	7	9260.60	1322.94			23592.79	3370.40		
	Total	13	65847.40				144802.77			
ECC ANOVA	Admixed TEA	6	465229.22	77538.20	16.196	0.00087	18946.51	3157.75	6.932406	0.011079
	Replication	7	33513.45	4787.64			3188.54	455.51		
	Total	13	498742.67				22135.05			
CR ANOVA	Admixed TEA	6	4.239165	0.706528	7.5597	0.00869	0.091855	0.015309	0.531222	0.77072
	Replication	7	0.654219	0.09346			0.201731	0.028819		
	Total	13	4.893384				0.293585			

Table 8. Results of Weibull pdf modelling of corrosion test data for samples in NaCl medium.

S/No	Admixed TEA in concrete (NaCl)	Half-cell potential (HCP)				Electrochemical cell current (ECC)				Corrosion rate (CR)			
		Shape parameter k	Scale parameter c	Mean μ_{W-HCP} (-mV CSE)	Reliability F (μ_{W-HCP})	Shape parameter k	Scale parameter c	Mean μ_{W-ECC} ($-\mu A$)	Reliability F (μ_{W-ECC})	Shape parameter k	Scale parameter c	Mean μ_{W-CR} (mm/y)	Reliability F (μ_{W-CR})
1.	Ctrl	2.30	666.41	590.39	0.5308	1.25	768.29	715.83	0.5997	0.35	1.09	5.454	0.8276
2.	Ctrl(Rep)	2.82	632.51	563.34	0.5141	1.36	840.71	769.73	0.5880	0.35	1.11	5.561	0.8275
3.	0.083%	3.06	490.60	438.47	0.5080	1.35	280.80	257.35	0.5888	0.38	0.31	1.243	0.8142
4.	0.083%(Rep)	2.84	510.91	455.21	0.5133	0.73	179.11	218.34	0.6851	0.38	0.49	1.822	0.8094
5.	0.167%	5.23	560.83	516.30	0.4772	1.11	375.38	360.98	0.6161	0.37	0.68	2.839	0.8164
6.	0.167%(Rep)	4.76	481.39	440.74	0.4816	0.94	179.01	184.14	0.6419	0.37	0.47	2.039	0.8188
7.	0.25%	9.84	464.43	441.54	0.4556	0.87	225.75	242.60	0.6551	0.38	0.40	1.587	0.8138
8.	0.25%(Rep)	2.37	409.66	363.08	0.5281	0.79	153.08	174.38	0.6701	0.33	0.53	3.501	0.8424
9.	0.333%	2.46	582.90	517.00	0.5249	0.93	471.26	486.11	0.6428	0.38	1.21	4.553	0.8102
10.	0.333%(Rep)	7.27	529.50	496.29	0.4644	1.61	554.93	497.27	0.5675	0.38	0.76	3.023	0.8136
11.	0.417%	7.50	493.60	463.37	0.4634	0.95	267.17	273.55	0.6404	0.34	0.77	4.305	0.8339
12.	0.417%(Rep)	5.87	490.07	454.08	0.4723	1.17	345.32	327.26	0.6091	0.33	0.70	4.135	0.8366
13.	0.667%	6.73	592.51	553.10	0.4671	1.23	409.46	382.77	0.6016	0.35	0.68	3.452	0.8284
14.	0.667%(Rep)	9.23	565.25	535.87	0.4573	1.50	464.29	419.20	0.5760	0.37	0.77	3.333	0.8188

Table 9. Results of Weibull pdf modelling of corrosion test data for samples in H₂SO₄ medium.

S/No	Admixed TEA in concrete (H ₂ SO ₄)	Half-cell potential (HCP)				Electrochemical cell current (ECC)				Corrosion rate (CR)			
		Shape parameter	Scale parameter	Mean μ_{W-HCP} (-mV CSE)	Reliability F (μ_{W-HCP})	Shape parameter	Scale parameter	Mean μ_{W-ECC} (- μ A)	Reliability F (μ_{W-ECC})	Shape parameter	Scale parameter	Mean μ_{W-CR} (mm/y)	Reliability F (μ_{W-CR})
1.	Ctrl	1.04	314.90	309.78	0.6258	0.78	84.92	98.14	0.6735	0.43	0.10	0.286	0.7866
2.	Ctrl _(Rep)	3.41	500.90	450.06	0.5006	2.55	171.86	152.57	0.5218	0.69	0.19	0.239	0.6953
3.	0.083%	2.18	134.53	119.14	0.5359	2.33	17.19	15.23	0.5299	0.38	0.08	0.327	0.8124
4.	0.083% _(Rep)	1.56	88.41	79.45	0.5709	0.43	18.78	51.10	0.7859	0.43	0.11	0.301	0.7878
5.	0.167%	3.50	103.66	93.27	0.4989	0.59	27.81	42.93	0.7250	0.34	0.07	0.357	0.8309
6.	0.167% _(Rep)	3.13	202.45	181.14	0.5062	0.99	24.87	24.99	0.6338	0.37	0.08	0.315	0.8154
7.	0.25%	2.21	119.65	105.97	0.5346	1.76	9.54	8.49	0.5572	0.49	0.05	0.108	0.7598
8.	0.25% _(Rep)	3.02	149.90	133.90	0.5089	3.12	14.36	12.84	0.5066	0.28	0.12	1.579	0.8705
9.	0.333%	3.06	129.73	115.95	0.5079	1.17	13.67	12.94	0.6085	0.33	0.06	0.382	0.8399
10.	0.333% _(Rep)	2.32	152.16	134.81	0.5301	1.52	27.41	24.72	0.5746	0.32	0.07	0.479	0.8465
11.	0.417%	1.27	171.90	159.61	0.5976	0.82	24.99	27.76	0.6639	0.49	0.06	0.131	0.7616
12.	0.417% _(Rep)	3.45	136.21	122.46	0.4998	1.97	18.81	16.68	0.5454	0.45	0.18	0.465	0.7793
13.	0.667%	3.05	130.74	116.83	0.5082	2.13	7.24	6.42	0.5379	0.39	0.04	0.147	0.8082
14.	0.667% _(Rep)	4.12	170.90	155.17	0.4891	1.56	17.69	15.90	0.5709	0.44	0.03	0.079	0.7812

Figure 6. K–S goodness of Weibull probability fittings of corrosion test data for samples in corrosive media.

Weibull fittings of all the test-variables of samples in the NaCl medium as well as of the HCP and the ECC test variables of samples in the H₂SO₄ medium were less than 0.05. By this, the differences encountered in the test-variables among the different TEA-admixed samples were not due to chance but are significant. But like the results from the other distribution fittings studied, the differences in the Weibull fittings of the test-data of corrosion rate for samples in H₂SO₄ are not significant among the different TEA-admixed concrete samples at 95% confidence level. For these H₂SO₄-immersed samples, ANOVA *p*-values = 0.698198 which is greater than 0.05.

3.5 Correlation analyses of Weibull distribution fittings of corrosion test-variables

That the other corrosion test-variables, other than the corrosion rate, of samples in the H₂SO₄ medium exhibit differences among the different concentrations of TEA admixture engender implications of lurking information of corrosive activities in these other test-variables. This engender interest in studying correlation analyses of the Weibull fittings of the corrosion test-variables of concrete samples in their respective test-media, as prescribed by ASTM G16 and as employed by Izquierdo *et al* (2004) for potential and chloride threshold values.

For the samples in NaCl medium, the Weibull probability density fittings exhibit correlation between the corrosion rate, $CR_{(NaCl)}$ (mm/y), and the admixed TEA concentration, τ (%), half cell potential, V (–mV) and electrochemical cell current, I (– μ A) which takes the form:

$$CR_{(NaCl)} = e^{\tau} \left\{ 3.0575\sqrt{I} \left(1 - 0.04368\sqrt{V} \right) \right\} - 19.5454\sqrt{V} \left(1 - 0.0267\sqrt{V} \right) + 177.6738. \quad (17)$$

For this model for NaCl-immersed samples, the correlation coefficient $r = 88.67\%$.

For the H₂SO₄-immersed samples, the Weibull fittings of test-variables exhibit correlation between corrosion rate, $CR_{(H_2SO_4)}$, and the admixed TEA concentration, τ (%), half cell potential, V (–mV) and electrochemical cell current, I (– μ A) in the form:

$$CR_{(H_2SO_4)} = 0.9107 \sin V \left(1 - 0.1782\tau - \log I^{0.1919} \right) + 0.2187 \cos I \left(\sin V + \log V^{0.17} \right) + 0.4265. \quad (18)$$

For this model for samples immersed in H₂SO₄, correlation coefficient $r = 84.61\%$.

Table 10. One-way ANOVA of Weibul pdf models of corrosion test-variables.

	Source of variations	df	Samples in NaCl medium				Samples in H ₂ SO ₄ medium			
			SS	MS	F	p-value	SS	MS	F	p-value
HCP ANOVA	Admixed TEA	6	42835.91	7139.32	7.3013	0.00958	112513.35	18752.22	7.964722	0.007488
	Replication	7	6844.68	977.81			16480.87	2354.41		
	Total	13	49680.58				128994.22			
ECC ANOVA	Admixed TEA	6	424042.70	70673.78	22.139	0.00032	19477.76	3246.29	9.196523	0.004935
	Replication	7	22345.55	3192.22			2470.94	352.99		
	Total	13	446388.24				21948.70			
CR ANOVA	Admixed TEA	6	20.77624	3.46271	6.8919	0.01126	0.629699	0.10495	0.640508	0.698198
	Replication	7	3.517024	0.50243			1.146979	0.163854		
	Total	13	24.29326				1.776677			

It could be noted from these correlation fittings that the correlations of test variables of samples from the NaCl medium assumed square root models of the independent variables of potential and current. This bears similarity with the root models of independent variable of chloride thresholds in Izquierdo *et al* (2004) which is also a study of concrete steel-rebar corrosion in NaCl medium. However, the correlation fittings of test variables in the H₂SO₄ medium did not exhibit such root models but rather they exhibit trigonometric, combined with logarithmic, models of the independent variables of the potential and the current. Also, it is especially worth noting that the admixed TEA concentration term, τ , in the correlation fitting function of CR (in H₂SO₄), contributes to the corrosion rate in the medium as a product with sinusoidal function of the half cell potential; $0.9107\sin V \times 0.1782\tau$. This predominant dependency on the cyclic model of trigonometric fittings by the corrosion rate of samples in the H₂SO₄ medium finds suggestion as the analytical reason their CR exhibited differences that were not significant among the different TEA concentrations.

However, this analytical position requires ascertaining that there is statistically significant relationship between the correlated test-variables in the correlation fitting functions. For this therefore, further analysis of variance is needed. The results of the ANOVA for each medium, NaCl and H₂SO₄, are as tabulated in table 11. From the table, p -value = 0.0044 for the correlation fitting of samples in NaCl medium and p -value = 0.04 for samples immersed in H₂SO₄ medium. Both of these p -values are less than 0.05 thus implying that the relationships between the correlated corrosion test-variables, in each of the test-media of concrete immersions, are statistically significant at 95% confidence level.

3.6 Inhibition effectiveness modelling

The results of inhibition efficiency, η , from relevant application of Eq. (16) to the Weibull mean models are presented in effectiveness ranking order in figure 7, for replicated concrete samples in NaCl medium, figure 7a, and for those in H₂SO₄ medium, figure 7b. These effectiveness ranking identified the 0.083% TEA admixture in concrete with optimal inhibition efficiency, $\eta = 77.21\%$ and $\eta_{(rep)} = 77.21\%$, relative to the control sample (Ctrl) and to the control replicate (Ctrl_(Rep)), respectively, in the NaCl medium. From table 8, this admixture exhibited Weibull mean of corrosion rate $\mu_{W-CR} = 1.243$ mm/y at 81.42% reliability, -257.35 μ A highly reduced rebar dissolution activity and -438.47 mV (CSE) more anodic corrosion potential compared to that of the Ctrl and of the Ctrl_(Rep). The 0.083% TEA replicate sample ($\eta = 66.20\%$, $\eta_{(rep)} = 67.25\%$) just lagged behind the 0.25% TEA sample ($\eta = 70.91\%$, $\eta_{(rep)} = 71.47\%$) in following the effectiveness of its first 0.083% TEA sample. However, both replicates of 0.167% TEA samples followed each other in effectiveness.

The ranking effectiveness model identified the 0.667% TEA replicate (Rep) sample with optimal inhibition efficiency $\eta = 72.28\%$ and $\eta_{(rep)} = 66.86\%$ relative to the Ctrl and to the Ctrl_(Rep), respectively, in the H₂SO₄ medium, figure 7b. From table 9, this sample exhibited mean corrosion rate (Weibull) $\mu_{W-CR} = 0.079$ mm/y at 78.12% reliability, -15.90 μ A extensively reduced rebar dissolution activity and -155.17 mV (CSE) more anodic corrosion potential compared to the Ctrl and with the Ctrl_(Rep). Though the optimal sample was followed, in order of effectiveness, by the 0.25% TEA and the 0.417% TEA samples, the effectiveness by these samples relative to the control replicates were conflicting because their replicates aggravated rebar corrosion by having negative effectiveness in H₂SO₄. Only the 0.667% TEA replicate samples exhibited agreements of positive inhibition efficiencies $\eta = 48.39\%$ and $\eta_{(rep)} = 38.29\%$ among the studied replicates of H₂SO₄-immersed concretes.

Figure 7. Ranking of inhibition efficiency for modelling inhibitor admixture effectiveness vs. each replicate of control samples: (a) replicates in NaCl medium; (b) replicates in H₂SO₄ medium.

It is of interest to investigate the averaged model of inhibition effectiveness of each TEA admixture concentration for addressing variations in inhibition efficiency, by replicate samples with similar admixture concentrations, as prescribed by Haynie (2005). The results of this averaged effectiveness model are shown in figure 8. By this, the 0.083% TEA concentration was confirmed with optimum averaged inhibition efficiency model, $\eta = 72.17 \pm 10.68\%$, in the NaCl medium, in which an inverse relationship between effectiveness and TEA concentration almost ensued, save for an interposing 0.667% TEA before the 0.333%, figure 8a. In the H₂SO₄ medium, figure 8b only the 0.667% TEA concentration exhibited positive and thus optimal averaged inhibition efficiency model, $\eta = 56.45 \pm 15.85\%$. Other TEA admixture concentrations, less than 0.667% TEA in the medium, exhibited negative inhibitions which implied rebar corrosion aggravation beyond that obtained in the control.

Figure 8. Ranking of averaged inhibition efficiency model of TEA admixture (a) in NaCl, (b) in H₂SO₄ media.

Table 12. Comparison of effectiveness of different TEA admixture concentrations at inhibiting concrete steel-rebar corrosion in NaCl and in H₂SO₄ medium.

S/No	TEA concentration (%)	Averaged inhibition efficiency η (%) in NaCl	Efficiency classification in NaCl	Averaged inhibition efficiency η (%) in H ₂ SO ₄	Efficiency classification in H ₂ SO ₄
1.	0.083	72.17	Good*	-20.72	Unsatisfactory
2.	0.167	55.71	Good	-29.19	Unsatisfactory
3.	0.25	53.80	Good	-224.24	Unsatisfactory
4.	0.333	31.22	Fair	-65.65	Unsatisfactory
5.	0.417	23.37	Poor	-14.55	Unsatisfactory
6.	0.667	38.40	Fair	56.45	Good*

*Optimum concentration of TEA admixture at inhibiting steel-rebar corrosion in the test-medium, in this study

Based on these, comparisons of the corrosion inhibition effectiveness of the different concentrations of admixed TEA studied on steel-rebar corrosion in concrete immersed in NaCl medium and in H₂SO₄ medium are presented in table 12. For these comparisons, requisite applications of efficiency classifications presented in Coffey *et al* (2013) find usefulness for interpreting the effectiveness criteria of TEA admixtures at inhibiting concrete steel-rebar corrosion in each of the test-media.

These results bear implications on the responsible applications of TEA for the corrosion protection of steel-rebar in concrete immersed in the corrosive test environments studied in this research work. The first implication include the suggestion that just little TEA admixture concentration, e.g., 0.083% TEA, would be required for optimal inhibition of steel-rebar corrosion in the NaCl medium, simulating saline/marine environment. Higher TEA admixture concentrations could culminate in lesser inhibition effectiveness in comparison with that from the control sample without TEA admixture in the corrosive chloride medium. In addition, the results are suggestive of the need for substantially large amount of TEA admixture concentration, e.g., 0.667% TEA, for obtaining positive inhibition in the H₂SO₄ medium, simulating industrial/microbial environment. Also that the corrosion rate models for samples in the NaCl medium were generally greater than those obtained for samples in H₂SO₄ medium bears further suggestion that the chloride ions lead to higher reinforcing steel corrosion than the sulphate ions. From these, it seems most probable to deduce that the higher TEA concentrations required for effective inhibition in the acidic medium may be needed for initial protection of the concrete from damage that could ensue from sulphate attack before inhibition of the rebar corrosion. However, this deduction will require further study of the effect of TEA admixture on concrete strength properties, which is a study usually beyond the non-destructive scope of this present research.

4. Conclusions

Probability density fittings of measured corrosion test data from steel reinforced concretes admixed with different concentrations of triethanolamine (C₆H₁₅NO₃: TEA) and immersed in 3.5% NaCl and in 0.5 M H₂SO₄ media had been studied for TEA effectiveness on steel-rebar corrosion. From these, the following conclusions could be drawn.

- The stochastic scatter of the corrosion test data measurements of steel reinforced concrete samples with TEA admixtures made interpretation of inhibition effectiveness difficult, in both studied test environments, thus necessitating the use of statistical probability density functions for fitting and instilling order in the test data, in accordance with the prescriptions of ASTM G16.
- Although the Normal and the Gumbel probability density functions fitted many of the half-cell potential (HCP) and the electrochemical cell current (ECC) test data fairly well, the two pdf fittings of the corrosion rate (CR) test data were indicative of many of the CR datasets not following the two pdf's according to the Kolmogorov–Smirnov (K–S) goodness of fit (GoF) criteria, and for these reasons, the CR models by these pdf's were considered unsuitable, in the study, for modelling TEA effectiveness on corrosion inhibition of the concrete steel-rebar in their test environments.
- Although, an HCP and two ECC datasets did not scatter like the Weibull pdf, which also more than doubled the CR mean models of each control replicate compared to the Normal and Gumbel models of the same dataset, the Weibull fittings of the CR test data showed that all the CR datasets followed the Weibull distribution, according to the K–S GoF tests, thus bearing implications of the suitability of the Weibull fittings of the CR test-data for modelling inhibition effectiveness of the TEA admixtures.
- Requisite analysis of variance (ANOVA) modelling of the fittings of each probability distribution model showed consistently that the differences encountered in all the test-variables among different admixed-TEA concentrations in NaCl-immersed concrete and in HCP and ECC in the H₂SO₄-immersed concretes were not due to chance but were significant while differences in the corrosion rate of different admixed-TEA in the H₂SO₄-immersed concretes were not significant, for all the studied distribution fitting models, requisite correlation study showed that this could be due to dependency of the corrosion rate of the H₂SO₄-immersed concretes on cyclic models obtained from trigonometric functions of the potential and current variables.
- By the foregoing, the 0.083% TEA admixture exhibited optimal model of inhibition effectiveness $\eta = 72.17 \pm 10.68\%$ in NaCl medium even as an almost inverse relationship was observed between inhibition effectiveness and TEA admixture concentrations, a trend that was only broken by the 0.667% TEA admixture being interposed before the 0.333% TEA admixture in the 0.083% to 0.417% decreasing effectiveness trend relative to the control.
- In the H₂SO₄ medium, the 0.667% TEA admixture exhibited optimal model of inhibition effectiveness $\eta = 56.45 \pm 15.85\%$ even as this admixture concentration was the only one that maintained positive inhibition relative to the control without TEA admixture, among all the studied admixtures in the medium.

Implications from these results on the concentration of TEA admixture for effective protection of steel-rebar corrosion include following points.

- Appropriate choice of statistical fitting function is important for understanding the true picture of prevalent conditions especially of inhibition effectiveness of admixtures in corrosive systems.
- Little concentration of TEA admixture per weight of cement, e.g., 0.083% TEA, would be required for optimal corrosion inhibition of steel-rebar in concrete immersed in the saline/marine environments.

- Quite a substantial amount of TEA admixture concentration, e.g., 0.0895 M TEA, would be needed for positive concrete steel-rebar corrosion inhibition in the industrial/microbial environments.
- The corrosion models of samples in the NaCl medium were generally greater than the CR models of samples in the H₂SO₄ medium support the notion that chloride ions lead to higher corrosion than sulphate ions even as this further bear implication that the higher TEA concentration needed for effective inhibition in the acidic medium, relative to the control in that medium, may be required for initial protection of concrete from sulphate damage before the inhibition of steel-rebar corrosion.

The probability density modelling and analyses of corrosion test data in this study had been rigorously focused on concrete samples immersed in 3.5% NaCl and in 0.5 M H₂SO₄. These concentrations of test-media had been employed due to their common applications for simulating saline/marine and acidic (microbial/industrial) media in studies cited in the work. However, use of other concentrations of these test-media abound in studies also and based on this, further studies investigating probability density fitting of corrosion test data from concrete immersed in the other concentrations of the test-media are recommended.

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