

# Synergistic Effect of Halide Ions and Polyethylene Glycol on the Corrosion Inhibition of Aluminium in Alkaline Medium

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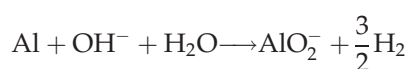
**ABSTRACT:** The corrosion inhibition of aluminium in alkaline medium was studied at 30 and 40°C in the presence of polyethylene glycol (PEG) using gravimetric (weight loss) and thermometric techniques. The effect of halides (KCl, KBr, and KI) on the inhibitory action of PEG was also studied. It was found that PEG acted as inhibitor for aluminium corrosion in the alkaline medium. Inhibition efficiency increased with increasing inhibitor concentration. An increase in temperature led to increase in both the corrosion rate and inhibition efficiency in the absence and presence of inhibitor and halides. Phenomenon of chemical adsorption mechanism is proposed from the values of  $E_a$ ,  $Q_{ads}$ , and  $\Delta G_{ads}^{\circ}$  obtained. The adsorption of PEG on the surface of aluminium was found to obey

Flory–Huggins and Temkin adsorption isotherms. The synergism parameter,  $S_1$  evaluated was found to be greater than unity indicating that the enhanced inhibition efficiency caused by the addition of halides is synergistic in nature. The inhibition efficiency, surface coverage and synergism parameter increased in the order;  $I^- > Br^- > Cl^-$  showing that a joint adsorption of PEG and halide ions on aluminium plays a significant role in the adsorption process. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3533–3543, 2009

**Key words:** adsorption; adsorption isotherms; cooperative effect; polyethylene glycol; corrosion inhibition; aluminium

## INTRODUCTION

Aluminium owes its corrosion resistance to the development of a strong adherent and continuous film on its surface on exposure to the atmosphere or aqueous solutions. However, in some instances, aluminium may be exposed to high concentration of acids or alkalis. These solutions dissolve the passive films. In alkaline environment, the dissolution of Al is represented by:



Because of its prime importance, there is great need to protect aluminium by adding corrosion inhibitors to these aggressive solutions. Several investigations have been carried out on the electrochemical and corrosion behavior of aluminium in

various aqueous media using diverse inhibitors.<sup>1–10</sup> The use of organic and inorganic inhibitors has been reported. It has been shown that organic inhibitors establish their inhibition via the adsorption of their molecules on the metal surface forming a protective layer<sup>3,7,9,10</sup> whereas the inorganic inhibitors act as anodic inhibitors and their metallic atoms are enclosed in the film improving its corrosion resistance.<sup>1,2,6,8</sup>

Recently, the use of polymers as corrosion inhibitors has attracted considerable attention because they have been shown to be low cost, stable, and non-toxic. The use of polyacrylamide, polyacrylic acid, polyaniline, polyvinylimidazoles, polyethylenimine, polyvinylpyrrolidone, polyvinylpyrrolidine, polyvinylbipyridine, polyvinylpyridine, polyvinylbenzyltrimethyl ammonium chloride, poly(4-vinylpyridine), and its derivative poly(4-vinylpyridine poly-3-oxide ethylene) as potential corrosion inhibitors have been reported.<sup>11–18</sup> However, most of the investigations were conducted in acidic medium. A survey of available literature reveals that the inhibition of aluminium by polymers in alkaline medium has not been widely studied. It has been reported that an increase in adsorption of organic molecules on addition of halide ions has been observed,

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thereby enhancing the inhibitory action of an organic compound to acid environments.<sup>19</sup> Available literature provides a series of reports that have highlighted the synergistic effect of halide ions on the corrosion inhibition of aluminium in acidic solution by Congo red dye,<sup>20</sup> hexamine,<sup>21</sup> 2-acetylphenothiazine,<sup>22</sup> methylene blue dye,<sup>23</sup> polyvinyl alcohol (PVA) and polyethylene glycol (PEG)<sup>24</sup>, methyl red,<sup>25</sup> gum Arabic,<sup>26</sup> *Pachylobus edulis* exudates gum,<sup>27</sup> *Sansevieria trifasciata* extract,<sup>28</sup> *Raphia hookeri* exudates gum,<sup>29</sup> and *Ocimum basilicum* extract.<sup>30</sup> In each case, the synergistic effect of the halide ions increased in the order— $I^- > Br^- > Cl^-$ . Oguzie et al. reported a synergistic effect of halide ions on the corrosion inhibition of aluminium in alkaline medium by Congo red dye<sup>31</sup> and methylene blue dye.<sup>32</sup> However, there is no report to our knowledge on the effects of halide ions in combination with polymers in alkaline medium. We have reported on the effect of halide ions on the corrosion inhibition of aluminium in alkaline medium using polyvinyl alcohol in our research group.<sup>26</sup>

The present work is aimed at investigating the corrosion inhibition of aluminium in alkaline medium using PEG in combination with halide ions and to propose a suitable mechanism for the inhibition action in the PEG-halides system using gravimetric (weight loss) and thermometric methods at 30 and 40°C.

## EXPERIMENTAL

Aluminium sheet provided by the System Metals Industries Limited, Calabar, Nigeria was used. Each sheet was 0.4 mm thickness. The sheet was mechanically press cut into 5 cm × 4 cm coupons. The coupons were used as cut without further polishing. However, they were degreased in absolute ethanol, dried with acetone and stored in a moisture free dessicator before their use in corrosion studies. Polyethylene glycol (PEG) used as inhibitor is of molecular weight 10,000 g/mol and was obtained from BDH Laboratory Supplies, England. It was used as obtained without further purification. Concentrations of  $1 \times 10^{-4}$  to  $1 \times 10^{-3}M$  were used in the study. Concentrations of NaOH (BDH chemicals) prepared and used in the study were 0.02 to 1M. KCl, KBr, and KI salts were used in the concentration range of 0.01 to 0.1M. 0.05M KCl, 0.05M KBr, and 0.05M KI were used for the synergistic studies.

Gravimetric measurements were carried out as described elsewhere.<sup>33–36</sup> The inhibition efficiency (%I) of PEG, halides, and PEG-halides mixtures acting as inhibitor was calculated using the equation:

$$\%I = \left(1 - \frac{W_o}{W_1}\right) \times 100 \quad (1)$$

where  $W_o$  and  $W_1$  are the weight losses in free and inhibited alkaline solution, respectively.

The degree of surface coverage ( $\theta$ ) is given by the equation:

$$\theta = 1 - \frac{W_o}{W_1} \quad (2)$$

The corrosion rates of aluminium in different concentration of NaOH, PEG and halides have been determined for a 7 days (168 h) immersion period from the gravimetric measurement using the formula:<sup>33–36</sup>

$$\text{Corrosion rate (mpy)} = \frac{534 W}{\rho A t} \quad (3)$$

where  $W$  is the weight loss (g),  $\rho$  is the density of the specimen ( $g/cm^3$ ),  $A$  is the area of the coupon ( $cm^2$ ) and  $t$  is the exposure time (h).

The reaction vessel used and the procedure followed for the thermometric technique was the same as previously described elsewhere.<sup>37–39</sup> The variation in temperature of the system is measured to  $\pm 0.5^\circ C$  as a function of reaction time. The reaction number is defined as:

$$RN(^{\circ}C \text{ min}^{-1}) = \frac{T_m - T_i}{t} \quad (4)$$

where  $T_m$  and  $T_i$  are the maximum and initial temperatures, respectively, and  $t$  is the time in min elapsed to reach the maximum temperature,  $T_m$ . The inhibition efficiency (%I) is the percent reduction in reaction namely:

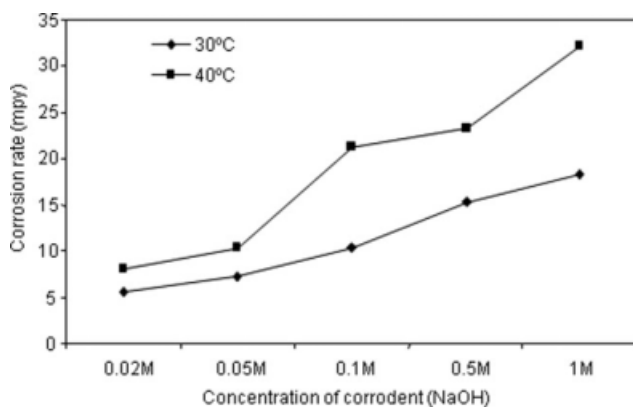
$$\%I = \frac{RN_{aq} - RN_{wi}}{RN_{aq}} \times 100 \quad (5)$$

where  $RN_{aq}$  and  $RN_{wi}$  are the reaction numbers of aluminium dissolution in free alkaline and in the presence of PEG, halides, and PEG-halide mixtures, respectively.

## RESULTS AND DISCUSSION

### Effect of corrodent and inhibitor/halides concentration on the inhibition efficiency from gravimetric and thermometric methods

The dissolution of aluminium in different concentrations of NaOH in the absence of halides or inhibitor (PEG) was investigated using gravimetric method at 30 and 40°C. Results obtained showed that the weight loss of aluminium increases with increase in concentration of the corrodent at 30°C. Similar trend was observed at 40°C but with higher values. Figure 1 shows the plot of corrosion rate against corrodent (NaOH) concentrations at the temperatures studied. Inspection of the figure revealed that corrosion rate



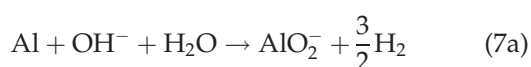
**Figure 1** Plot of corrosion rate against corrodent concentration for aluminium corrosion in NaOH at 30 and 40°C.

increased with increasing concentration of the corrodent and also with rise in temperature. Some authors<sup>32,40</sup> have pointed out that the dissolution of aluminium in aqueous solutions is dependent on the concentration of the anions and identified the controlling step in the process as the complexation reaction of hydrated aluminium cations with the anions present.

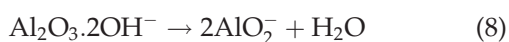


The insoluble complex ion formed catalyzes the dissolution of the metal at a rate which depends on the initial anion concentration and consequently the metal loses weight.

The free corrosion of aluminium in NaOH can be represented by the following equations:<sup>41,42</sup>



An actual mechanism for the process must, however, consider the influence of the passivating surface oxide film which has been reported to possess a high affinity for  $\text{H}^+$  and  $\text{OH}^-$  ions.<sup>41</sup> Consequently, when aluminium metal is introduced into aqueous NaOH solution,  $\text{OH}^-$  ions are primarily adsorbed on the surface oxide film before subsequent dissolution as represented by the reaction.



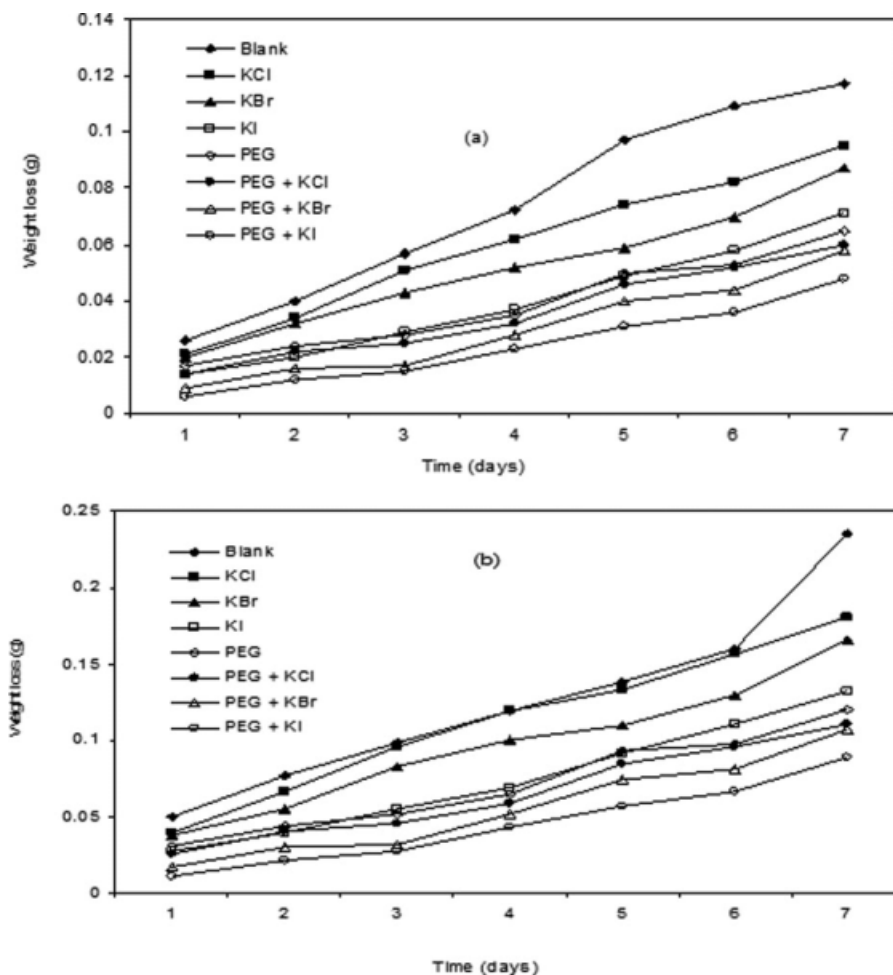
The above reaction is exothermic and the heat generated accelerates further dissolution of the oxide film and this initiates the corrosion of the bare aluminium surface sites exposed to the corrodent.

The highest corrodent concentration studied (1M) was used in subsequent gravimetric measurements involving the halides and inhibitor (PEG). Figure 2

shows the variation of weight loss with time (days) for aluminium dissolution in blank (1M NaOH), halides (0.05M KCl, 0.05M KBr, 0.05M KI), the inhibitor (PEG) (at the highest concentration,  $1 \times 10^{-3}$ M studied) and inhibitor in combination with halides at (a) 30°C and (b) 40°C. Similar plots were obtained for other concentrations of the inhibitor studied at the temperature range. Inspection of the figures revealed that there was a reduction in weight loss of aluminium in the presence of halides and PEG compared to the blank. Further reduction in weight loss was obtained upon addition of halide ions to the inhibitor (PEG).

Figure 3 shows representative temperature-time curves for the dissolution of aluminium in 1M NaOH in the absence and presence of halides, the highest concentration of PEG studied and PEG-halide mixtures. Examination of the figures show that the dissolution of aluminium starts after a certain time from the immersion of the aluminium coupon in the test solution as evident from the constant temperature with time. It may be expected that this time correspond to the period needed by the base to destroy the pre-immersion oxide film and is known as the incubation period. After the consumption of the pre-immersion oxide film, the temperature of the system rises gradually due to the exothermic corrosion reaction to reach a maximum value,  $T_m$ . The blank (1M NaOH) recorded the highest maximum temperature reached and with the shortest time. It is also seen in the figure that on addition of the halides and PEG, there was a decrease in the maximum temperature reached and an increase in time taken to reach the maximum temperature. Further decrease in maximum temperature was also observed in the presence of PEG in combination with halides. The most profound effect was noticed with PEG-KI combination. This behavior reflects the high inhibition efficiency ( $I\%$ ) obtained for the PEG-halide mixtures toward aluminium dissolution in the alkaline medium. The inhibition efficiency increases with increase in the concentration of PEG. Further inspection of Figure 3 reveals that the temperatures of all systems decreased again after reaching their maximum values. This could be attributed to decreasing corrodent concentration with increasing reaction time which in turn decreases the corrosion rate, hence a decrease in the quantity of heat evolved.

The calculated values of corrosion rate (mpy), inhibition efficiency ( $I\%$ ) and degree of surface coverage ( $\theta$ ) for aluminium dissolution in 1M NaOH for the various systems studied at 30 and 40°C are presented in Table I. From the table, it is seen that corrosion rate increases with decrease in concentration of the inhibitor (PEG) and also with rise in temperature. The free alkali gave the highest value of

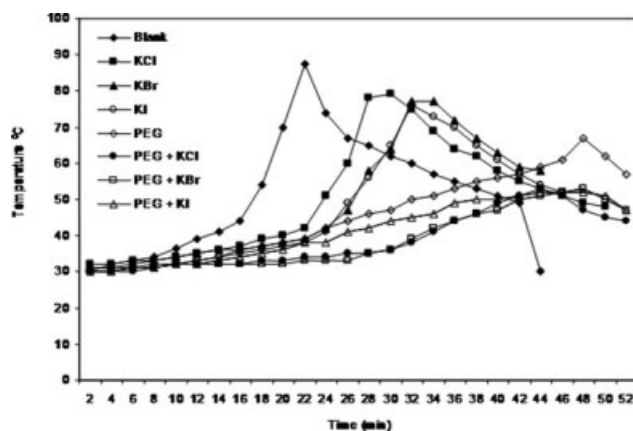


**Figure 2** Variation of weight loss with time for aluminium dissolution in 1M NaOH in the absence and presence of halides. PEG and PEG-halide mixture at (a) 30°C (b) 40°C.

corrosion rate at all the temperatures studied. Results presented in Table I also revealed that corrosion rate was significantly reduced in the presence of the halides with the most decrease observed with KI at 30°C. A similar trend was observed at 40°C but higher values of corrosion rates. Addition of halide ions to PEG leads to a further decrease in corrosion rate in the order; PEG + KCl > PEG + KBr > PEG + KI at 30°C. A similar trend is also observed at 40°C. The most significant decrease obtained was with PEG + KI.

Table I also shows the calculated values of inhibition efficiency obtained from eq. (1) and degree of surface coverage evaluated using eq. (2) for aluminium dissolution in 1M NaOH containing halides, various concentrations of PEG, and varying concentration of PEG in combination with 0.05M KCl, 0.05M KBr, and 0.05M KI at the temperatures studied. Figure 4 shows the plot of inhibition efficiency against inhibitor concentration for aluminium in 1M NaOH containing different concentrations of PEG at 30 and 40°C. From the Table and Figure, it is also

seen that with increasing temperature and inhibitor concentration, there is a corresponding increase in inhibition efficiency with the highest value (49%) obtained for  $1 \times 10^{-3}M$  PEG at 40°C. This



**Figure 3** Temperature – time curves for the dissolution of aluminium in 1M NaOH in the absence and presence of halides, PEG and PEG – halide mixtures.

TABLE I  
Calculated Values of Corrosion Rate (mpy), Inhibition Efficiency (%I) and Degree of Surface Coverage ( $\theta$ ) for Aluminium Dissolution in 1M NaOH in the Presence of halides, PEG, and PEG- Halide Mixtures at 30 and 40°C

Systems/concentration	Corrosion rate (mpy) $\times 10^{-4}$		Inhibition efficiency (%I)		Degree of surface coverage ( $\theta$ )	
	30°C	40°C	30°C	40°C	30°C	40°C
Blank	103	212	–	–	–	–
0.05M KCl	83	163	18.8	23.0	0.19	0.23
0.05M KBr	75	140	25.6	29.1	0.26	0.29
0.05M KI	64	118	39.3	43.3	0.39	0.43
$1 \times 10^{-3}$ M PEG	55	103	44.4	49.0	0.44	0.49
$7 \times 10^{-4}$ M PEG	60	113	39.3	43.8	0.39	0.44
$5 \times 10^{-4}$ M PEG	63	119	35.9	40.9	.36	0.41
$3 \times 10^{-4}$ M PEG	78	150	19.7	26.0	0.20	0.26
$1 \times 10^{-4}$ M PEG	88	167	10.3	17.4	0.10	0.17
$1 \times 10^{-3}$ M PEG + 0.05M KCl	55	98	48.7	52.8	0.49	0.53
$7 \times 10^{-4}$ M PEG + 0.05M KCl	58	104	45.3	49.9	0.45	0.50
$5 \times 10^{-4}$ M PEG + 0.05M KCl	65	115	39.3	44.3	0.39	0.44
$3 \times 10^{-4}$ M PEG + 0.05M KCl	81	145	23.9	29.8	0.24	0.30
$1 \times 10^{-4}$ M PEG + 0.05M KCl	90	161	15.4	22.1	0.15	0.22
$1 \times 10^{-3}$ M PEG + 0.05M KBr	52	97	50.4	54.5	0.50	0.55
$7 \times 10^{-4}$ M PEG + 0.05M KBr	54	101	48.7	52.8	0.49	0.53
$5 \times 10^{-4}$ M PEG + 0.05M KBr	61	115	41.9	46.4	0.42	0.46
$3 \times 10^{-4}$ M PEG + 0.05M KBr	73	136	35.9	36.1	0.36	0.36
$1 \times 10^{-4}$ M PEG + 0.05M KBr	84	157	20.5	26.8	0.21	0.27
$1 \times 10^{-3}$ M PEG + 0.05M KI	39	86	59.0	62.1	0.59	0.62
$7 \times 10^{-4}$ M PEG + 0.05M KI	45	101	52.1	55.7	0.52	0.56
$5 \times 10^{-4}$ M PEG + 0.05M KI	48	105	49.6	53.6	0.50	0.54
$3 \times 10^{-4}$ M PEG + 0.05M KI	61	134	38.9	40.9	0.39	0.41
$1 \times 10^{-4}$ M PEG + 0.05M KI	70	154	26.5	32.3	0.27	0.32

concentration was therefore used to evaluate the effect of halides in most cases.

The inhibition of mild steel corrosion by halide ions has been reported to be caused by the adsorption on the metal surface and by the formation of surface compounds which are insoluble in the corrosive media.<sup>43,44</sup> The adsorption ability on the metal surface and hence inhibition potential of the halides has been estimated in the order  $I^- > Br^- > Cl^-$ .<sup>45,46</sup> Generally, the absorbability of anions is related to

the degree of hydration, the less hydrated ion is preferentially adsorbed on the metal surface. The ease of adsorption (greater inhibition efficiency) shown in case of iodide ions may be due to its lesser degree of hydration. The inhibitive effect of halide ions found in this study is in the same order as that of adsorption ability.<sup>47</sup>

The Table also reveal that the inhibition efficiency for the halides increases with increase in temperature and in the order KCl (23%) < KBr (29.2%) < KI (43.3%) at 40°C.

It can also be seen from Table I and Figure 5 that inhibition efficiency of PEG increases synergistically on addition of halide ions with the highest value obtained when PEG is combined with iodide ion. The synergistic effect increases in the order;  $I^- > Br^- > Cl^-$ . Gomma<sup>48</sup> and Ebenso<sup>22</sup> have shown that a cooperative effect results on addition of a halide salt to sulphuric acid solution containing an organic compound, which inhibits the corrosion of iron. Halides have been reported to inhibit the corrosion of some metals in strong acids and this effect depends on the ionic size through the electrostatic field set up by the negative charge of the anion on adsorption sites.<sup>22,49–54</sup> A similar trend has been observed in this study involving alkaline medium. The stabilization of adsorbed halide ions by means of interaction with PEG leads to greater surface coverage as

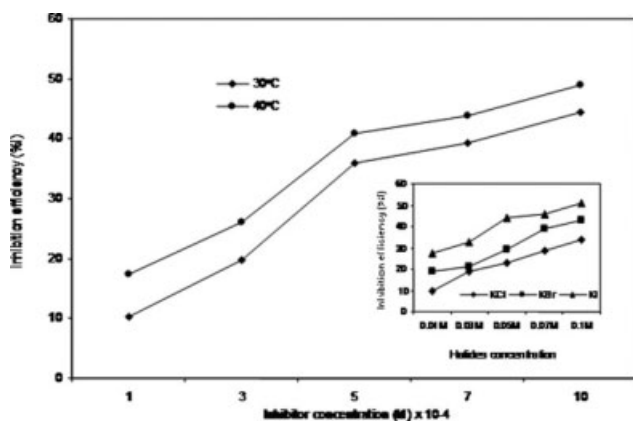
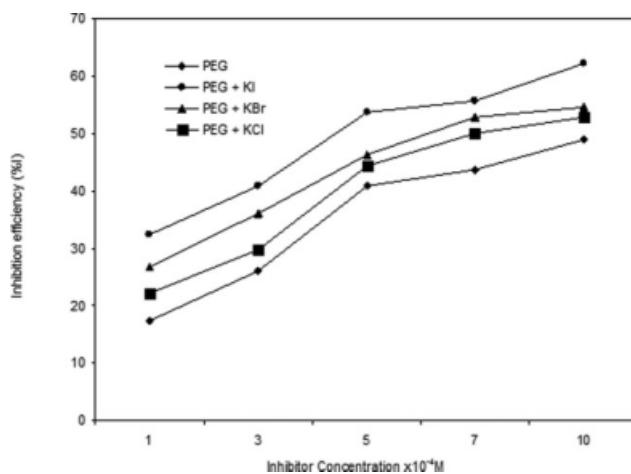


Figure 4 Plot of inhibition efficiency (%I) against inhibitor (PEG) concentration at 30 and 40°C (inset shows plot of %I vs halides concentration at 30°C)



**Figure 5** Plot of inhibition efficiency (%) against inhibitor concentration for PEG and PEG – halide mixtures at 40°C.

we go from  $\text{Cl}^-$  to  $\text{I}^-$  and hence greater inhibition efficiency (Table I). Halide ions are good ligands because they exhibit low electronegativity (less than 3.5) except fluoride.<sup>21</sup> Electronegativity values decrease from  $\text{Cl}^-$  to  $\text{I}^-$  ( $\text{Cl}^- = 3.0$ ,  $\text{Br}^- = 2.8$ ,  $\text{I}^- = 2.5$ ) whereas atomic radius increases from  $\text{Cl}^-$  to  $\text{I}^-$  ( $\text{Cl}^- = 0.090$  nm,  $\text{Br}^- = 0.114$  nm,  $\text{I}^- = 0.135$  nm).<sup>55</sup> Hence, aluminium can form compounds with the halide ions. It has also been reported<sup>21</sup> that the inhibitive effect decreases in the order;  $\text{I}^- > \text{Br}^- > \text{Cl}^-$ , which suggests that the radii and electronegativity of the halide ions may have an important role to play in the adsorption process. The iodide ion is more readily adsorbed than the bromide ion or the chloride ion.

Table II shows the comparison of inhibition efficiency (%I) values obtained from the gravimetric measurement (obtained from eq. (1) at 40°C and the thermometric method (obtained from eq. (5)). The values obtained as indicated in the table shows some reasonable level of agreement from the two independent methods.

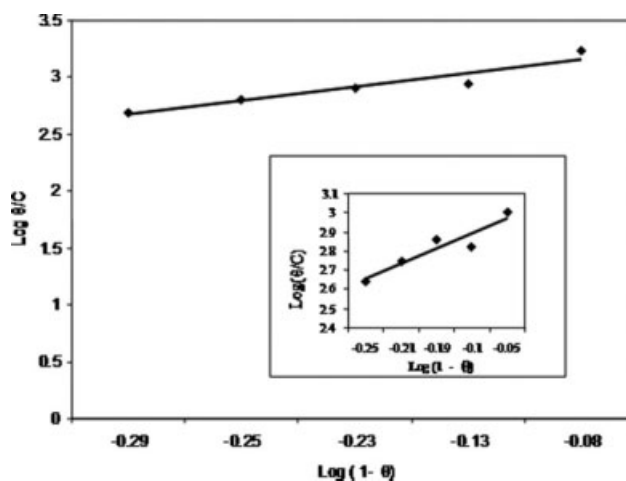
### Adsorption considerations

Figures 4 and 5 show that inhibition efficiency increases with increase in inhibitor concentration and with rise in temperature which is suggestive of a chemical adsorption mechanism and it is known that compounds that obey chemical adsorption have isotherms at lower temperatures below those at higher temperatures. This is clearly seen in Figures 4 and 7. Adsorption isotherms are very useful in discussing the adsorption process and give detailed information on adsorption mechanisms. Classical adsorption isotherms<sup>56</sup> of Freundlich, Temkin, and Frumkin as well as substitutional isotherms<sup>57</sup> of Flory-Huggins, Dhar-Flory-Huggins, and Bockris-

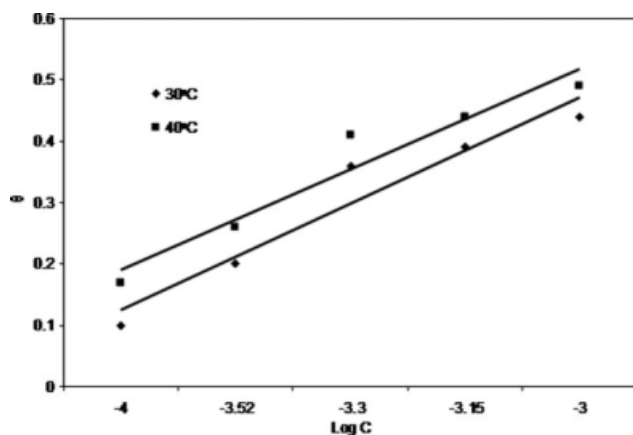
**TABLE II**  
Comparison of Inhibition Efficiency (%I) Obtained From Gravimetric Measurement at 40°C and Thermometric Methods

Systems/concentration	Inhibition efficiency (%I)	
	Thermometric	Weight loss
0.05M KCl	28.2	23.0
0.05M KBr	33.9	29.1
0.05M KI	48.7	43.3
$1 \times 10^{-3}$ M PEG	52.8	49.0
$7 \times 10^{-4}$ M PEG	47.3	43.8
$5 \times 10^{-4}$ M PEG	41.3	40.9
$3 \times 10^{-4}$ M PEG	34.5	26.0
$1 \times 10^{-4}$ M PEG	18.9	17.4
$1 \times 10^{-3}$ M PEG + 0.05M KCl	60.7	52.8
$7 \times 10^{-4}$ M PEG + 0.05M KCl	51.1	49.9
$5 \times 10^{-4}$ M PEG + 0.05M KCl	46.1	44.3
$3 \times 10^{-4}$ M PEG + 0.05M KCl	30.6	29.8
$1 \times 10^{-4}$ M PEG + 0.05M KCl	26.5	22.1
$1 \times 10^{-3}$ M PEG + 0.05M KBr	56.7	54.5
$7 \times 10^{-4}$ M PEG + 0.05M KBr	55.2	52.8
$5 \times 10^{-4}$ M PEG + 0.05M KBr	45.2	46.4
$3 \times 10^{-4}$ M PEG + 0.05M KBr	36.3	36.1
$1 \times 10^{-4}$ M PEG + 0.05M KBr	28.3	26.8
$1 \times 10^{-3}$ M PEG + 0.05M KI	63.6	62.1
$7 \times 10^{-4}$ M PEG + 0.05M KI	56.4	55.7
$5 \times 10^{-4}$ M PEG + 0.05M KI	55.2	53.6
$3 \times 10^{-4}$ M PEG + 0.05M KI	41.9	40.9
$1 \times 10^{-4}$ M PEG + 0.05M KI	39.5	32.3

Swinkles have been used to represent the adsorption behavior and characteristic of organic compounds on metal surfaces. In this study, an attempt was made to fit the  $\theta$  values to some of the above mentioned adsorption isotherms for the inhibitor (PEG) and correlation coefficients ( $R^2$ ) were used to determine the best fit isotherm. The best results were obtained for Flory-Huggins ( $R^2 = 0.91$ ) and Temkin ( $R^2 = 0.94$ ) adsorption isotherms for PEG. The linear plot obtained when  $\log \theta/C$  was plotted as a



**Figure 6** Flory – Huggins adsorption isotherm plot for PEG at 40°C (inset shows similar plot at 30°C).



**Figure 7** Temkin adsorption isotherm plot for PEG at 30 and 40°C.

function of  $\log(1-\theta)$  shown in Figure 6 indicates that the experimental data fit Flory–Huggins adsorption isotherm given by<sup>58</sup>:

$$\log \frac{\theta}{C} = \log K + x \log(1 - \theta) \quad (9)$$

where  $\theta$  is the degree of surface coverage,  $x$  is the number of inhibitor molecules occupying an active site (or the number of water molecules replaced by one molecule of PEG),  $K$  is equilibrium constant of adsorption process, and  $C$  is the concentration of inhibitor (PEG).

Figure 7 shows Temkin adsorption isotherm plotted as  $\theta$  vs  $\log C$  for the dissolution of aluminium in 1M NaOH containing PEG at the temperatures studied. The linear plots obtained show that Temkin isotherm, which is given by:

$$\exp(-2a\theta) = KC \quad (10)$$

where  $a$  is molecular interaction parameter,  $\theta$  is the degree of surface coverage,  $K$  is equilibrium constant of adsorption process, and  $C$  is the inhibitor concentration, was obeyed.

Thus, the inhibition of aluminium by PEG may be due to the presence of hetero oxygen atom in the molecule which makes possible its adsorption by coordinate type linkage using lone pairs of oxygen atom (chemisorption). To further support the assertion that chemical adsorption is proposed, the values of activation energy ( $E_a$ ) were evaluated using the Arrhenius equation;<sup>59</sup>

$$\log \frac{r_2}{r_1} = \frac{E_a}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (11)$$

where  $r_1$  and  $r_2$  are the corrosion rates at temperature  $T_1$  and  $T_2$ , respectively. The values obtained as presented in Table II are greater than 40 kJmol<sup>-1</sup> which agrees with report by Martinez.<sup>57</sup>

### Kinetics and thermodynamics considerations

The calculated values of activation energy  $E_a$  (kJ/mol), heat of adsorption  $Q_{ads}$  (kJ/mol), rate constant  $K$  (day<sup>-1</sup>) and half-life (day) for the dissolution of aluminium in 1M NaOH in the absence and presence of 0.05M KCl, 0.05M KBr, 0.05M KI, various concentration of PEG and varying concentration of PEG in combination with halides are presented in Table III. From the table, it can be seen that  $E_a$  values increases with decrease in the concentration of the inhibitor. The values of heat of adsorption  $Q_{ads}$  were calculated using the equation.<sup>60</sup>

$$Q_{ads} = 2.303R \left[ \log \left( \frac{\theta_2}{1 - \theta_2} \right) - \log \left( \frac{\theta_1}{1 - \theta_1} \right) \right] \left( \frac{T_1 T_2}{T_2 - T_1} \right) \quad (12)$$

where  $\theta_1$  and  $\theta_2$  are the degrees of surface coverage at the temperatures  $T_1$  and  $T_2$ , respectively. Results obtained are shown in Table III. It is seen that the  $Q_{ads}$  values are positive and ranges from 3.5 kJ/mol to 48.2 kJ/mol. The positive values are because the degree of adsorption and the inhibition efficiency increase with rise in temperature which also supports the chemical adsorption mechanism. Free energy of adsorption  $\Delta G_{ads}^{\circ}$  for aluminium dissolution in 1M NaOH containing halides, the highest concentration of PEG studied and this concentration in combination with the halides at 30 and 40°C were obtained from the plot of  $\log \%I$  vs  $\log$  inhibitor concentration (Fig. 8) and calculated from the intercepts of the plots using the following equation.<sup>61</sup>

$$\log C = \log \left( \frac{\theta}{1 - \theta} \right) - \log B \quad (13)$$

where  $\log B = -1.74 - (\Delta G_{ads}^{\circ} / 2.303RT)$  and  $C$  is the concentration of the systems studied. The calculated values are presented in Table IV. From the Table it is evident that in all cases the values of  $\Delta G_{ads}^{\circ}$  are negative. The negative values suggest that the inhibitor molecules are strongly adsorbed on the metal surface. It also indicates a spontaneous adsorption of the inhibitor molecules and usually characterize their strong interactions with the metal surface. Generally values of  $\Delta G_{ads}^{\circ}$  up to -20 kJ/mol are consistent with electrostatic interactions between the charged molecules and the charged metals, which imply physical adsorption.  $\Delta G_{ads}^{\circ}$  values more negative than -40 kJ/mol (as obtained in this study) involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond, which implies chemisorption.<sup>62,63</sup>

Figure 9 shows the representative plot of  $\log W_f$  ( $W_f$  means final weight loss) for aluminium dissolution in 1M NaOH in the absence and presence of

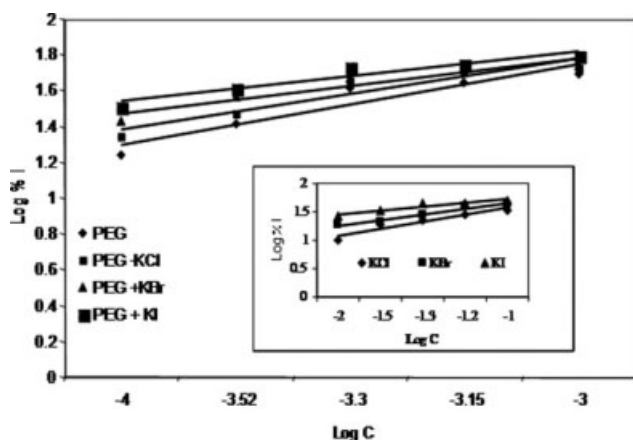
**TABLE III**  
Calculated Values of Activation energy, ( $\text{kJmol}^{-1}$ ), Heat of Adsorption,  $Q_{\text{ads}}$  ( $\text{kJmol}^{-1}$ ), Rate Constant,  $K$  ( $\text{day}^{-1}$ ) and Half-Life,  $t_{1/2}$  (day) for Blank, Halides, PEG, and PEG-Halide Mixtures at 30 and 40°C

Systems/concentration	$E_a(\text{kJmol}^{-1})$	$Q_{\text{ads}}(\text{kJmol}^{-1})$	Rate constant, $K$ ( $\text{day}^{-1}$ ) $\times 10^{-4}$		Half-life, $t_{1/2}$ (day) $\times 10^2$	
	30–40°C	30–40°C	30°C	40°C	30°C	40°C
Blank	54.6		4.5	9.5	15.40	7.30
0.05M KCl	51.1	19.1	4.6	7.3	15.07	9.49
0.05M KBr	47.2	11.9	3.2	5.1	21.66	13.59
0.05M KI	46.2	16.2	2.7	5.1	25.29	13.59
$1 \times 10^{-3}\text{M}$ PEG	47.4	15.9	2.3	4.4	30.13	15.75
$7 \times 10^{-4}\text{M}$ PEG	47.8	16.3	2.5	4.9	27.72	14.14
$5 \times 10^{-4}\text{M}$ PEG	48.2	16.7	2.7	5.1	25.67	13.59
$3 \times 10^{-4}\text{M}$ PEG	49.4	26.8	3.8	6.6	20.38	10.50
$1 \times 10^{-4}\text{M}$ PEG	48.4	48.2	3.4	7.4	18.24	9.37
$1 \times 10^{-3}\text{M}$ PEG + 0.05M KCl	43.7	17.8	2.3	4.2	30.13	16.50
$7 \times 10^{-4}\text{M}$ PEG + 0.05M KCl	43.5	15.3	2.5	4.5	27.72	15.40
$5 \times 10^{-4}\text{M}$ PEG + 0.05M KCl	43.1	16.2	2.8	5.0	24.75	13.86
$3 \times 10^{-4}\text{M}$ PEG + 0.05M KCl	44.0	24.1	3.5	6.4	19.80	10.83
$1 \times 10^{-4}\text{M}$ PEG + 0.05M KCl	44.0	27.5	3.9	7.2	17.77	9.63
$1 \times 10^{-3}\text{M}$ PEG + 0.05M KBr	47.4	15.8	2.2	4.2	31.50	16.50
$7 \times 10^{-4}\text{M}$ PEG + 0.05M KBr	47.3	12.6	2.3	4.4	30.13	15.75
$5 \times 10^{-4}\text{M}$ PEG + 0.05M KBr	48.9	12.8	2.6	5.0	26.65	13.86
$3 \times 10^{-4}\text{M}$ PEG + 0.05M KBr	47.3	3.5	3.1	6.0	22.36	11.55
$1 \times 10^{-4}\text{M}$ PEG + 0.05M KBr	47.2	35.4	3.4	6.9	20.38	10.04
$1 \times 10^{-3}\text{M}$ PEG + 0.05M KI	59.8	9.9	1.6	3.7	43.31	18.73
$7 \times 10^{-4}\text{M}$ PEG + 0.05M KI	61.1	12.7	1.9	4.4	36.47	15.75
$5 \times 10^{-4}\text{M}$ PEG + 0.05M KI	59.2	12.6	2.0	4.6	34.65	15.07
$3 \times 10^{-4}\text{M}$ PEG + 0.05M KI	59.4	6.57	2.6	5.7	26.65	12.16
$1 \times 10^{-4}\text{M}$ PEG + 0.05M KI	59.6	19.0	3.0	6.8	23.10	10.19

halides, and of PEG studied and PEG-halide mixtures at (a) 30°C (b) 40°C. Similar plots were obtained involving other concentrations of PEG and in combination with halides at the temperatures studied. Linear plots were obtained which indicate first order kinetics. Rate constant,  $K$  ( $\text{day}^{-1}$ ) values were obtained from the plot of  $\log W_f$  versus time (Fig. 9) whereas the half-life,  $t_{1/2}$  values were calculated using the equation:

$$t_{1/2} = \frac{0.693}{k} \quad (14)$$

The calculated values are as presented in Table III. From the Table, it is observed that the rate constant increases with decrease in concentration of the inhibitor whereas half-life increases with increase in the concentration of the inhibitor. It was also found that the rate constant increases with increase in temperature whereas half-life decreases with rise in temperature. Adsorbed organic molecules can influence the

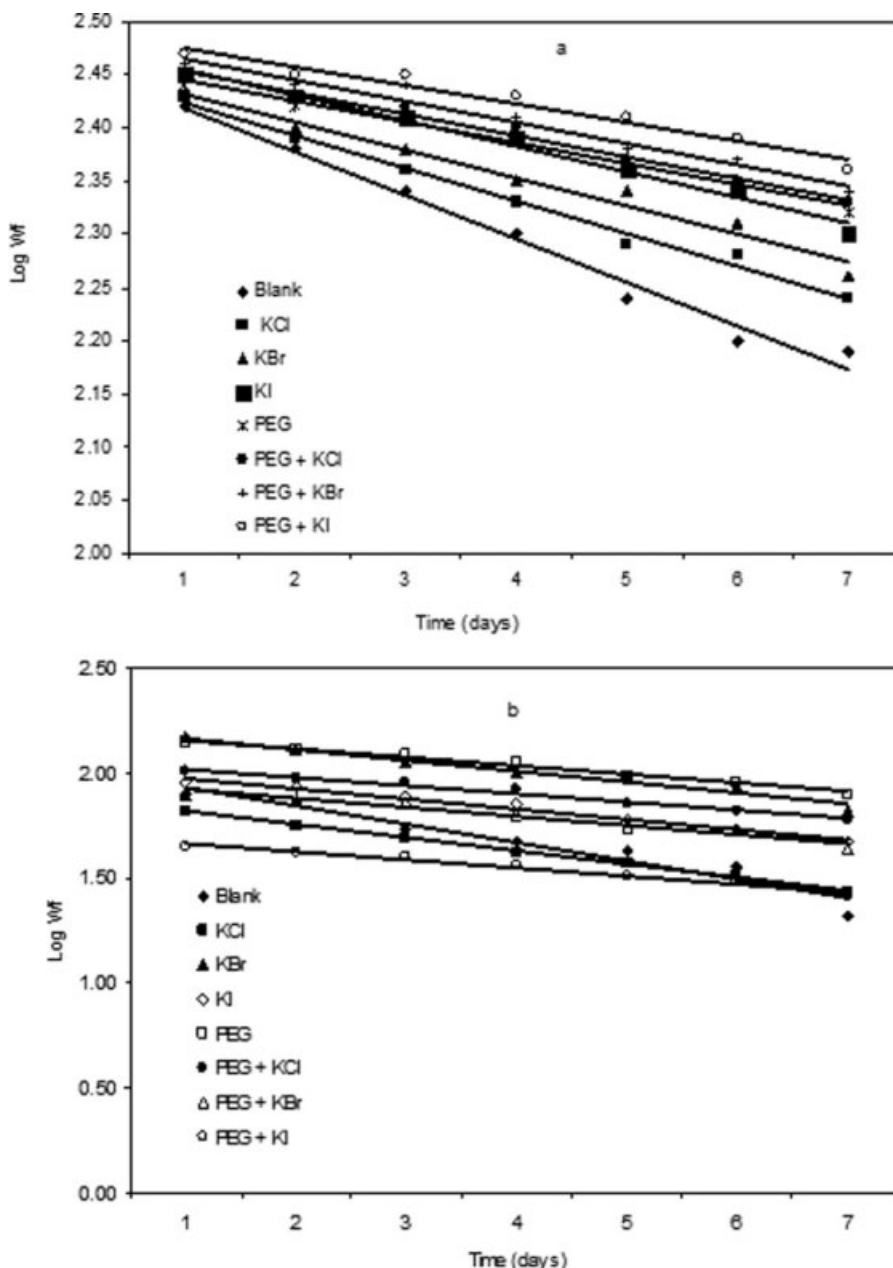


**Figure 8** Plot of  $\log \%I$  against  $\log C$  for PEG and PEG-halide mixtures at 40°C (inset shows plot for the halides at 40°C).

**TABLE IV**  
Calculated Values of Free Energy of Adsorption,  $\Delta G_{\text{ads}}^{\circ}$  for Aluminium Dissolution in 1M NaOH Containing Halides, PEG, and PEG-Halides Mixtures at 30 and 40°C

Systems/concentrations	Free energy of adsorption, $\Delta G_{\text{ads}}^{\circ}$ ( $\text{kJmol}^{-1}$ )	
	30°C	40°C
0.05M KCl	-35.54	-63.47
0.05M KBr	-72.55	-97.45
0.05M KI	-119.12	-154.86
$1 \times 10^{-3}\text{M}$ PEG	-61.33	-100.93
$1 \times 10^{-3}\text{M}$ PEG + 0.05M KCl	-86.22	-124.36
$1 \times 10^{-3}\text{M}$ PEG + 0.05M KBr	-126.65	-157.54
$1 \times 10^{-3}\text{M}$ PEG + 0.05M KI	-152.18	-186.48





**Figure 9** Plot of  $\log W_f$  against time (days) for aluminium dissolution in 1M NaOH in the absence and presence of halides, PEG and PEG – halide mixtures at (a) 30 and (b) 40°C.

behavior of electrochemical reactions involved in corrosion processes in several ways. The action of organic inhibitors also depends on the type of interaction between the substance and the metallic surface. The interaction causes a change in either the electrochemical mechanism or in the surface available for the process.<sup>64,65</sup>

#### Synergism considerations

The synergism parameter ( $S_1$ ) was evaluated using the relationship given by Aramaki and Hackerman<sup>65</sup> and previously described elsewhere;<sup>22,48</sup>

$$S_1 = \frac{I - I_{1+2}}{I - I'_{1+2}} \quad (15)$$

where  $I_{1+2} = I_1 + I_2$ ;  $I_1$  is the inhibition efficiency of the halides,  $I_2$  is the inhibition efficiency of PEG and  $I'$  is the measured inhibition efficiency for PEG in combination with halides. The calculated values are presented in Table V for the halides and are greater than unity. The values obtained for  $S_1$  suggest that the enhanced inhibition efficiency caused by the addition of the halogen atoms to PEG in the order  $I^- > Br^- > Cl^-$  may be only due to synergistic effect. This can be explained on the basis that halides have

TABLE V  
Synergism Parameter,  $S_1$  for the Halides

Halides	$S_1$
KCl	1.336
KBr	1.419
KI	1.466

great tendency to be adsorbed strongly on metal surfaces where the chemisorbed ions enter the metallic part of the double layer and the charge of the ions becomes part of the charge of the metal surface.<sup>42</sup> Thus, the inhibitor is not adsorbed directly on the metal surface but rather by columbic attraction to the adsorbed halide ions on the metal surface. This process is similar to the phenomenon of anion induced adsorption<sup>66</sup> and may be represented by the highly simplified mechanism:



where  $X_s$  and  $M_s$  designate the halide ion and organic species, respectively, in the bulk solution,  $X_{ads}$  and  $MX_{ads}$  refer to the halide ion and ion-pair, respectively, in the adsorbed state. This ion-pair interaction consequently increases the surface coverage thereby reducing metal dissolution.

The increase in inhibition efficiency (and degree of surface coverage values) found in the order  $I^- > Br^- > Cl^-$  is also displayed in the synergistic consideration which clearly indicates that the radii and the electronegativity of the halide ions play a significant role in the adsorption process. It may therefore also be concluded that the iodide ion is strongly adsorbable and facilitates the adsorption of organic cation thus producing inhibition synergism.

## CONCLUSIONS

The study shows that PEG inhibited the corrosion of aluminium in alkaline medium and the inhibition efficiency (%I) increased with increase in PEG concentration and also with increase in temperature. The values of activation energy,  $E_a$  obtained in the absence and presence of PEG or halides were greater than 40 kJ/mol which indicates that inhibition of aluminium corrosion by PEG is due to adsorption on the metal surface by chemical adsorption mechanism. The values of  $Q_{ads}$  and  $\Delta G_{ads}^0$  obtained also support the chemical adsorption mechanism. The experimental data obtained from this study fits well into Flory-Huggins and Temkin adsorption isotherms. On addition of halides to the alkaline medium containing PEG, a cooperative or synergistic effect occurred and the synergism parameter,  $S_1$

obtained for PEG were greater than unity showing that the enhanced corrosion inhibition brought about by PEG and the halides is due to synergism.

## References

- Mahmoud, S. S. *Bull Electrochem* 1995, 11, 366.
- Lusdem, J. B.; Szklarska, S. Z. *Corrosion*, 1978, 34, 169.
- Muller, B.; Kubitzki, G.; Kinet, G. *Corros Sci* 1998, 40, 1469.
- Mansfield, F.; Lin, S.; Kim, S.; Shih, H. *Corros Sci* 1987, 27, 997.
- Macdonald, D. D. *Electrochem Soc* 1983, 138, 127.
- Bazzi, L.; Kertit, S.; Hamani, M. *Bull Electrochem* 1998, 14, 34.
- Garrigues, L.; Pebere, N.; Dabosi, F. *Electrochim Acta* 1996, 41, 1209.
- Hinton, B. R. W.; Amott, D. R. *Ryan Mater Forum* 1986, 9, 657.
- Khamis, E. *Corrosion* 1990, 46, 476.
- Hefter, G. T.; North, N. A.; Tan, S. H. *Corrosion* 1998, 53, 657.
- Abed, Y.; Azzar, Z.; Aounit, A.; Hammouti, B.; Kertit, S.; Mansri, A. *J Chim Phys* 1999, 95, 1347.
- Jianguo, Lin, W.; Otieno-Alego, V.; Schiweinberg, D. P. *Corros Sci* 1995, 7, 975.
- Schiweinberg, D. P.; Hope, G. A.; Truemann, A.; Otieno-Alego, V. *Corros Sci* 1996, 38, 587.
- Abed, Y.; Hammouti, B.; Taleb, M.; Kertit, S.; Mansri, A. *Anti-Corros Methods Mater* 2001, 48, 304.
- Abed, Y.; Hammouti, B.; Touhami, F.; Aounit, A.; Kertit, S.; Mansri, A.; Elkacemi, K. *Bull Electrochem* 2001, 17, 105.
- Bereket, G.; Yurt, A.; Turk, H. *Anti-Corros Methods Mater* 2003, 50, 422.
- Grchev, T.; Cvetkovska, M.; Schultz, J. W. *Corros Sci* 1991, 32, 103.
- Kraljic, M.; Mandic, Z.; Duie, L. J. *Corros Sci* 2003, 45, 181.
- Rozenfeld, I. L. *Corrosion Inhibitors*; McGraw Hill: New York, 1984; p 109
- Oguzie, E. E.; Ebenso, E. E. *Pigment Resin Technol* 2006, 35, 30.
- El-Dahan, H. A.; Soror, T. Y.; El-Sherif, R. M. *Mater Chem Phys* 2005, 89, 260.
- Ebenso, E. E. *Mater Chem Phys* 2003, 79, 58.
- Oguzie, E. E.; Okolue, B. N.; Ebenso, E. E.; Onuoha, G. N.; Onuchukwu, A. I. *Mater Chem Phys* 2004, 87, 394.
- Ebenso, E. E.; Ekpe, U. J.; Umoren, S. A.; Jackson, E.; Abiola, O. K.; Oforka, N. C. *J Appl Polym Sci* 2006, 100, 2889.
- Ebenso, E. E. *Bull Electrochem* 2004, 20, 551.
- Umoren, S. A.; Ogbobe, O.; Ebenso, E. E. *Trans SAEST* 2006, 41, 74.
- Umoren, S. A.; Obot, I. B.; Ebenso, E. E. *E-J Chem* 2008, 5, 355.
- Oguzie, E. E. *Corros Sci* 2007, 49, 1527.
- Umoren, S. A.; Ogbobe, O.; Ebenso, E. E. *Bull Electrochem* 2006, 22, 155.
- Oguzie, E. E.; Onuchukwu, A. I.; Okafor, P. C.; Ebenso, E. E. *Pigment Resin Technol* 2006, 35, 63.
- Oguzie, E. E.; Onuoha, G. N.; Onuchukwu, A. I. *Anti-Corros Methods Mater* 2005, 52, 293.
- Oguzie, E. E.; Okolue, B. N.; Ogukwe, C. E.; Onuoha, G. N.; Onuchukwu, A. I.; Unaegbu, C. *Bull Electrochem* 2004, 20, 421.
- Umoren, S. A.; Ebenso, E. E.; Ekpe, U. J.; Jackson, E.; Okafor, P. C.; Ogbobe, O. *J Appl Polym Sci* 2007, 105, 3363.
- Ekpe, U. J.; Ibok, U. J.; Ita, B. I.; Offiong, O. E.; Ebenso, E. E. *Mater Chem Phys* 1995, 40, 87.
- Ebenso, E. E.; Ekpe, U. J.; Ita, B. I.; Offiong, O. E.; Ibok, U. J. *Mater Chem Phys* 1999, 60, 79.
- Ebenso, E. E.; Okafor, P. C.; Ekpe, U. J. *Anti-Corros Methods Mater* 2003, 50, 414.

37. ShamsEldin, A. A.; Kherdr, M. G. A. *Metalloberft* 1992, 25, 200.
38. El-Etre, A. Y. *Corros Sci* 2003, 45, 2485.
39. Ebenso, E. E.; Ekpe, U. J.; Ibok, U. J.; Umoren, S. A.; Jackson, E.; Abiola, O. K.; Oforka, N. C.; Martinez, S. *Trans SAEST* 2004, 117.
40. Nguyen, T. H.; Foley, R. T. *J Electrochem Soc* 1982, 129, 27.
41. Moussa, M. N.; Fouda, A. S.; Taha, F. I.; Elnenaa, A. *Bull Korean Chem Soc* 1988, 9, 191.
42. Onuchukwu, A. I.; Trassatti, S. P. *Corros Sci* 1994, 36, 1815.
43. Kirkov, P. *Corros Sci* 1973, 13, 697.
44. Jeyaprabha, C.; Sathiyarayanan, S.; Muralidharan, S.; Venkatachari, G. *J Braz Chem Soc* 2006, 17, 61.
45. Hackerman, N.; Snavely, E. S.; Payne, J. S. *J Electrochem Soc* 1996, 113, 677.
46. Abd Elhamid, M. H.; Ateya, B. G.; Pickering, H. W. *J Electrochem Soc* 2000, 147, 2258.
47. Devanathan, M. A. V.; Tilak, B. V. K. S. R. A. *Chem Rev* 1965, 65, 635.
48. Gomma, G. K. *Mater Chem Phys* 1998, 54, 241.
49. Pryor, M. J. Z. *Electrochemistry* 1962, 62, 782.
50. Cartledge, G. H. *J Phys Chem* 1952, 60, 32.
51. Lorenz, W. I. *Corros Sci* 1965, 5, 121.
52. Hudson, R. M.; Warning, C. J. *Corros Sci* 1970, 10, 121.
53. Arvia, A. J.; Podesta, J. J. *Corros Sci* 1968, 8, 203.
54. Rudresh, H. B.; Mayanna, S. M. *Corros Sci* 1979, 19, 361.
55. Tennen, R. M., Ed. *Science Data Book*; Oliver and Boyd: Edinburgh, 1978; p 56.
56. Martinez, S.; Stern, I. *J Appl Electrochem* 2001, 31, 973.
57. Martinez, S. *Mater Chem Phys* 2002, 77, 97.
58. AbdElRehim, S. S.; Ibrahim, M. A. M.; Khaled, K. F. *Mater Chem Phys* 2001, 70, 369.
59. Talati, J. D.; Modi, R. M. *Trans SAEST* 1981, 16, 259.
60. Subramanian, N.; Ramakrishnaiah, K. *Indian J Tech* 1970, 8, 369.
61. Abdel, A. M. S.; Saeed, A. E. L. *Trans SAEST* 1981, 16.
62. Bilgic, S.; Sahin, M. *Mater Chem Phys* 2001, 70, 290.
63. Granese, S. L. *Corros Sci* 1988, 44, 322.
64. Mayanna, S. M. *J Electrochem Soc* 1975, 122, 252.
65. Aramaki, K.; Hackerman, N. J. *Electrochem Soc* 1969, 116, 568.
66. Fishtik, I. F.; Vataman, I. I.; Spatar, F. A. *J Electroanal Chem* 1984, 165, 1.