

Synergistic Inhibition Between Polyvinylpyrrolidone and Iodide Ions on Corrosion of Aluminium in HCl

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Abstract: The effect of iodide ions on the corrosion inhibition of aluminium in 2M HCl in the presence of polyvinylpyrrolidone (PVP) was studied using gasometric (hydrogen evolution) technique at 30-60°C. Results obtained showed that PVP effectively reduces the corrosion rates of aluminium in the acid medium. Inhibition efficiency (%I) increases with increase in concentration of PVP. Increase in temperature increases corrosion rate but decreases inhibition efficiency. The addition of iodide ions enhanced the inhibition efficiency of PVP considerably. Adsorption of PVP and PVP + KI followed Temkin adsorption isotherm. Phenomenon of physical adsorption is proposed from the obtained E_a and ΔG_{ads}^o values. The synergistic parameter (S_1) obtained was found to be greater than unity, which indicates that the enhanced inhibition efficiency caused by the addition of iodide is only due to synergistic effect.

Keywords: Polyvinylpyrrolidone, iodide ions, corrosion inhibition, synergism, aluminium, adsorption isotherm.

INTRODUCTION

Aluminium generally exhibits passive behaviour in aqueous solution due to the formation of strong and compact adherent passive oxide film on its surface which influences its corrosion susceptibility. The adhesive passivating surface oxide film is amphoteric and consequently the metal dissolves readily when exposed to aggressive acidic and alkaline solutions [1]. In an attempt to mitigate electrochemical corrosion of Al, the main strategy is to effectively isolate the metal from corrosion agents. This can be achieved by the use of corrosion inhibitors. Numerous organic and inorganic compounds including polymers have been proved to be effective corrosion inhibitors for metals in acidic medium [2-10]. Polymeric compounds are of interest as corrosion inhibitors in acid baths due to their inherent stability and cost effectiveness. Furthermore, the inhibitive powers of these polymers are related structurally to the cyclic rings and heteroatoms (oxygen and nitrogen), which are the centres of adsorption.

Synergism has become one of the most important effects in inhibition processes and serves as the basis for all modern corrosion inhibitor formulations. A series of reports from our laboratory highlighted the synergistic effect of halide ions on the corrosion inhibition of aluminium/mild steel in acidic solution by polyvinyl alcohol (PVA) and polyethylene glycol (PEG) [11-13] and gum Arabic (GA) [14]. In each case, the synergistic effect of the halide ions increased in the order $Cl^- < Br^- < I^-$. The synergistic inhibition between iodide ions and some organic compounds have been reported by some authors. For instance Oguzie *et al.* [15, 16] reported a synergistic effect between iodide ion and methoinine on mild steel

corrosion inhibition. Zhang *et al.* [17] observed a synergistic effect of iodide ion and 2-mercapto benzimidazole on the corrosion inhibition of copper in aerated sulphuric acid solution. Feng *et al.* [18] as well pointed out that phenomenon of synergism existed between KI and propargyl alcohol (PA) on mild steel corrosion in H_2SO_4 , with an optimum ratio of $[PA]/[KI] = 1/1$. Harek and Larabi [19] studied the effect of KI on the inhibition efficiency of oxalic N-phenylhydrazide N'-phenylthiosemicarbazide on mild steel in hydrochloric acid and reported a maximum synergistic effect for KI mass fraction of 0.1%. Influence of iodide ions on inhibitive performance of tetraphenyl-dithia-octaaza-cyclotetradeca-hexane (PTAT) during pickling of mild steel in hot sulphuric acid has also been reported [20]. Results of the study show enhancement in inhibition efficiency for 500ppm PTAT in the presence of 0.25% KI as synergent. However, available literature to date has revealed that the synergistic effect of halides generally and iodide ions in particular using polymers as inhibitors in acid media is not widely studied. Larabi and Harek [21] and Larabi *et al.* [22] have reported that addition of iodide ions to poly (4-vinylpyridine) (P4VP) in 0.5M H_2SO_4 and 1M HCl respectively yield the required enhancement of inhibition efficiency. Synergism parameter (S_1) evaluated from inhibition efficiency was found to be greater than unity suggesting that the phenomenon of synergism exists between P4VP and iodide ions. We have reported on the synergistic effect of iodide ions and polyacrylamide on the corrosion inhibition of mild steel [23] on our earlier publications.

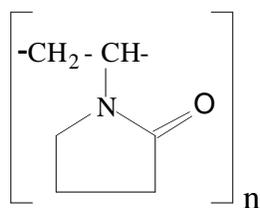
In continuation of our quest of exploring more polymeric materials as corrosion inhibitors and improvement of their inhibition efficiency using halide ions coupled with encouraging results obtained from previous studies, the present work reports on the synergistic inhibition between iodide ions and polyvinylpyrrolidone on the corrosion inhibition of

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Al in HCl using hydrogen evolution (*via* gasometric assembly) at 30-60°C.

EXPERIMENTAL

Aluminium sheet provided by the First Aluminium Company, Port Harcourt, Nigeria was used. Each sheet was 0.4mm in thickness. Preparation of the sheet was as previously reported [12, 14]. Polyvinylpyrrolidone (PVP), structure of the repeat unit shown below, used as inhibitor is a product of Hi-Tek polymers, Japan has the average molecular weight of 44, 000 g/mol and was used as sourced without further purification. The concentrations of PVP used for this study were 2×10^{-5} - 1×10^{-4} M. The concentration of HCl (BDH Laboratory Supplies Chemicals, England) used was 2M. The halide used (KI) was obtained from BDH Laboratory Supplies Chemicals, England, and the concentrations prepared were 1- 6mM. However, 6mM KI was used for the synergistic study. The studies were carried out at 30-60°C.



Structure of PVP repeat unit

The method of hydrogen evolution (*via* gasometric assembly) was determined as previously described elsewhere [11-14, 24]. The progress of corrosion reaction was monitored by careful measurement of the volume of hydrogen gas evolved at fixed time intervals. From the volume of hydrogen evolved during the corrosion reaction, the corrosion rate (CR) was determined using the expression:

$$CR_H = \frac{V_t - V_i}{t_t - t_i} \quad (1)$$

where V_t and V_i are the volume of hydrogen gas evolved at time t_t and t_i respectively.

The inhibition efficiency (%I) was calculated using the equation:

$$\%I = \left(\frac{CR_{blank} - CR_{inh}}{CR_{blank}} \right) \times 100 \quad (2)$$

where CR_{blank} and CR_{inh} are the corrosion rate in the absence and presence of inhibitor respectively.

RESULTS AND DISCUSSION

Hydrogen Evolution and Corrosion Rates

The gas-volumetric technique provides a rapid and sensitive method of monitoring any perturbation by an inhibitor regarding gas evolution at the metal-corrodent interphase. The corrosion of aluminium in free (2M) acid solution was characterized by rapid effervescence resulting from hydrogen gas evolution. The corrosion rates of aluminium in the absence and presence of inhibitors were assessed by measuring the volume of H_2 gas evolved during the corrosion reaction. Fig. (1) shows the variation of volume of H_2 evolved with time for Al dissolution in 2M HCl in the absence and

presence of 1×10^{-4} M PVP, 6mM KI and 1×10^{-4} M PVP + 6mM KI at (a) the lowest (30°C) and (b) highest (60°C) temperatures studied. Similar plots were obtained at other temperatures (40 and 50°C) also studied. Inspection of Fig. (1) reveals that the volume of H_2 evolved increases linearly with time. The rate of evolution was very small at the commencement of the reaction as evident in the constant volume of H_2 evolved with time. This is known as the incubation period and it is the time required to breakdown the pre-immersion oxide film on aluminium surface before the start of the metal attack by the acid. After the consumption of the pre-immersion oxide film, the volume of H_2 evolved increases. Volume of H_2 evolved also increases with increase in temperature. Addition of the inhibitors (PVP and KI) reduces markedly the rate of H_2 evolution compared to the free acid. Further reduction in the volume of H_2 gas was observed in the presence of PVP in combination with 6mM KI.

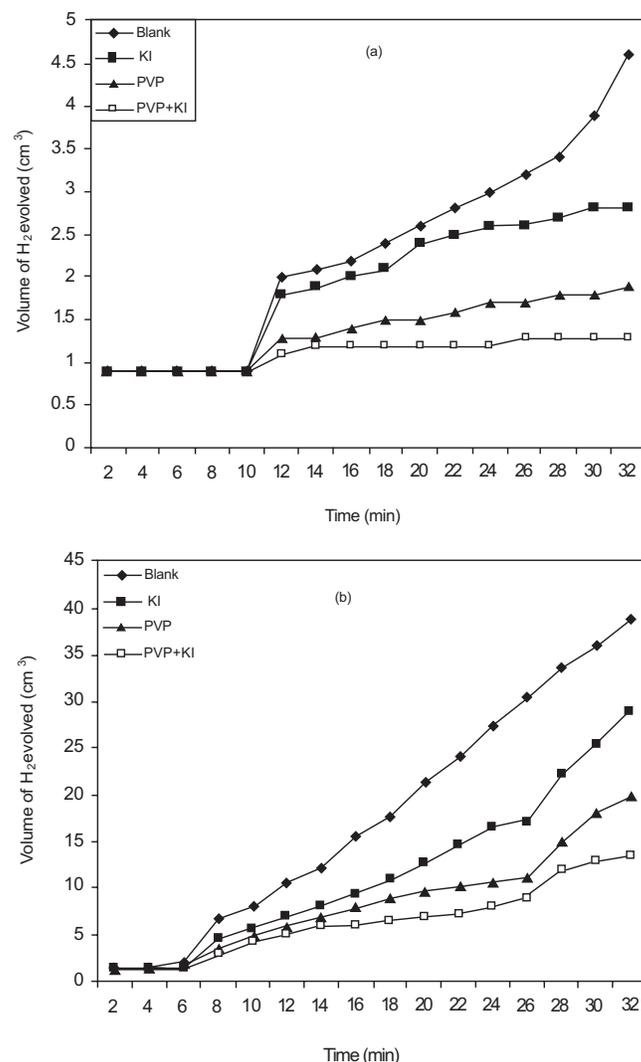


Fig. (1). Variation of volume of H_2 evolved with time for Al dissolution in 2M HCl in the absence and presence of PVP, KI and PVP + KI at (a) 30°C and (b) 60°C.

Table 1 shows the calculated values of corrosion rate ($mL \text{ min}^{-1}$) using equation (1) and inhibition efficiency (%I) using equation (2) for aluminium dissolution in 2M HCl in the absence and presence of different concentrations of PVP

Table 1. Calculated Values of Corrosion Rate (mL min^{-1}) and Inhibition Efficiency (%I) for Aluminium Corrosion in 2M H_2SO_4 for Different Systems at Different Temperatures

Systems/Concentration	Corrosion Rate (mL min^{-1})				Inhibition Efficiency (%I)			
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
Blank	0.0072	0.0281	0.0429	0.0606	-	-	-	-
0.06 M KI	0.0044	0.0177	0.0303	0.0453	39	37	29	25
2×10^{-5} M PVP	0.0045	0.0186	0.0344	0.0490	36	33	20	19
4×10^{-5} M PVP	0.0042	0.0170	0.0306	0.0450	41	39	28	26
6×10^{-5} M PVP	0.0038	0.0156	0.0270	0.0414	47	44	37	32
8×10^{-5} M PVP	0.0033	0.0141	0.0239	0.0375	54	50	44	38
1×10^{-4} M PVP	0.0029	0.0128	0.0211	0.0344	58	54	50	43
2×10^{-5} M PVP+6mM KI	0.0038	0.0166	0.0308	0.0452	47	41	28	25
4×10^{-5} M PVP+6mM KI	0.0033	0.0150	0.0275	0.0409	54	46	36	32
6×10^{-5} M PVP+6mM KI	0.0029	0.0136	0.0241	0.0377	58	51	44	38
8×10^{-5} M PVP+6mM KI	0.0025	0.0122	0.0213	0.0311	65	56	50	48
1×10^{-4} M PVP+6mM KI	0.0020	0.0109	0.0178	0.0271	71	61	58	55

and different concentrations of PVP + 6mM KI at different temperatures. The corrosion rate (mL min^{-1}) obtained at the highest concentration of inhibitor (1×10^{-4} M PVP) was lowest compared with other concentrations. The decrease in corrosion rate of Al in the presence of PVP is an indication that PVP actually inhibited the corrosion of the metal in the acid medium. Addition of the iodide ions to inhibitor (PVP) further decreased corrosion rate values. The most significant change being observed with the 1×10^{-4} M PVP + 6mM KI at 30°C. Similar trend were observed at 40, 50 and 60°C.

The inhibition efficiency values are observed to increase with increase in concentration of PVP at all the temperatures studied (Table 1). The addition of iodide ions synergistically increased the inhibition efficiency values. The values of the %I decreased with increase in temperature with the highest value of 71% obtained at 30°C. Similar observations have been reported elsewhere [25, 26]. The observed decrease in inhibition efficiency (%I) with increase in temperature suggests that the inhibitors were physically adsorbed onto the aluminium surface [27] such that an increase in temperature resulted in desorption of the adsorbed molecules. It is also possible that at higher temperatures, the enhanced corrosion rates as well as the increased agitation of the solution resulting from the higher rates of hydrogen gas evolution reduced the ability of the inhibitor to be adsorbed on the metal surface. Similar observation has been reported by Ebenso *et al.* [28]. The physical adsorption mechanism suggested by the results obtained in this study results from the electrostatic attractive forces between inhibiting organic ions or dipoles and the electrically charged surface of the metal due to the electric field existing at the metal/solution interface. The protonated species can be adsorbed on cathodic sites on the aluminium and reduce H_2 gas evolution.

The adsorption of PVP through the O and N atoms on the Al surface makes a barrier for mass and charge transfer. Consequently, the metal is protected from the aggressive anion of the acid. The addition of KI improves the inhibition

efficiency significantly. This may be attributed to initial specific adsorption of iodide ions on the aluminium surface which then facilitates the adsorption of protonated PVP, leading to improved surface coverage hence higher inhibition efficiency.

It is also worthy to mention that the result obtained by the gasometric technique employed in the present study are corroborated by other well established methods including weight loss and thermometry [29, 30], potentiostatic polarization [31] and impedance spectroscopy [32]

Adsorption Considerations

The values of degree of surface coverage, θ , for different concentrations of inhibitor (PVP) and PVP-KI mixtures at the temperatures studied have been employed and are useful in discussing the adsorption process. The degree of surface coverage (θ) was calculated using the expression:

$$\theta = \left(\frac{CR_{blank} - CR_{inh}}{CR_{blank}} \right) \quad (3)$$

Attempts were made to fit the, θ values to different adsorption isotherms and correlation coefficients (R^2) were used to determine the best fits. By far, best results were obtained for Temkin adsorption isotherm. Fig. (2) shows the plot of, θ against $\log C$ for Al dissolution in 2M HCl in the presence of (a) PVP and (b) PVP + KI at different temperatures. Linear plots were obtained which indicate that the experimental data obtained obeys Temkin adsorption isotherm given by:

$$\exp(-2a\theta) = Kc \quad (4)$$

where a is molecular interaction parameter, θ is the degree of surface coverage, K is the equilibrium constant of adsorption process and C is the inhibitor concentration. The value

of K is related to the free energy of adsorption ΔG_{ads}^0 by the equation:

$$K = \frac{1}{55.5} \exp \left[\frac{-\Delta G_{ads}}{RT} \right] \quad (5)$$

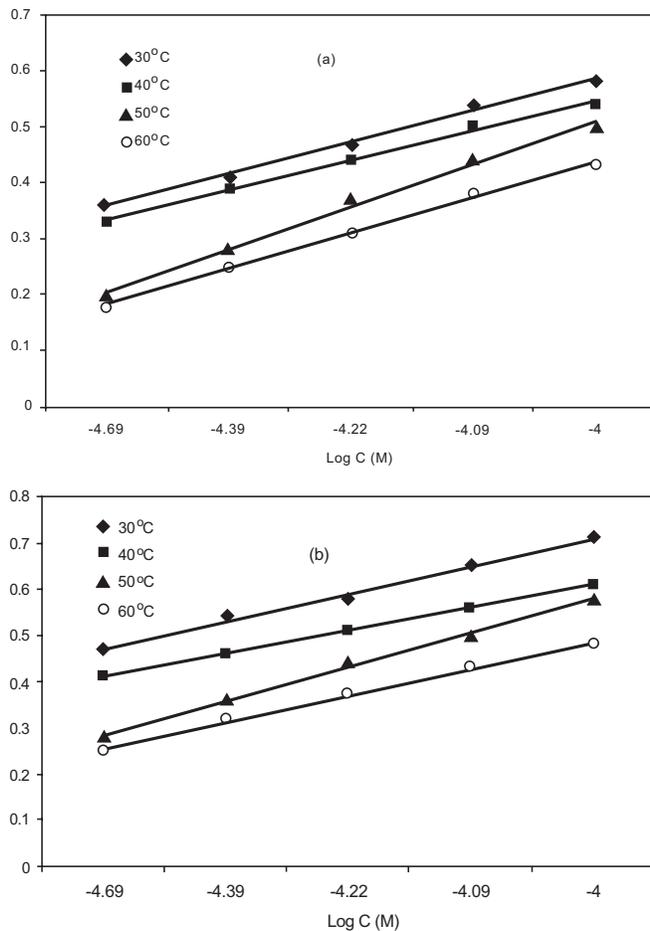


Fig. (2). The plot of θ against $\log C$ for Al dissolution in 2M HCl in the presence of (a) PVP and (b) PVP+KI at different temperatures.

The Temkin isotherm characterizes the chemisorption of uncharged molecules on a heterogeneous surface [33]. In acid solution PVP may exist in both protonated and molecu-

lar species which can affect the corrosion process to different extents, depending on their relative proportion. Physical adsorption is a result of electrostatic attraction between charged metal surface and protonated species in the bulk solution. Though physisorption of the protonated species by the electrostatic interaction with chloride ion adsorbed on the aluminium surface should prevail, the observed adherence to the Temkin adsorption isotherm suggests the participation of some molecular species. These do not however, significantly influence the corrosion process as the free energy of adsorption (ΔG) is quite low. It could therefore be concluded that in addition to protonated species, PVP can also be present as molecular species and that both protonated and molecular species can be adsorbed on the aluminium surface and influence the corrosion process differently.

The calculated values of molecular interaction a , equilibrium constant of adsorption process, K and correlation coefficient R^2 obtained from Temkin plot are shown in Table 2. The values of a are negative in all cases showing that repulsion exist in adsorption layer [34]. The values of K decrease with increasing temperature suggesting that the inhibitor is physically adsorbed on the Al surface. At any particular temperature, the value of K was found to be in order (PVP + KI) > PVP. The correlation coefficients are very good and very close to unity indicating that the adsorption of PVP + KI and PVP followed Temkin adsorption isotherm.

Kinetic/Thermodynamic Considerations

Fig. (3) shows the plot of logarithm of corrosion rate (CR) versus the reciprocal of absolute temperature ($1/T$). Linear plots were obtained for Al in 2M HCl in the absence and presence of (a) different concentrations of PVP and (b) different concentrations of PVP + 6mM KI which indicates that it follows Arrhenius equation given by:

$$\log CR = \log A - \frac{E_a}{2.303RT} \quad (6)$$

where CR is the corrosion rate; A is the constant called the frequency factor; E_a is the activation energy; R is the molar gas constant and T is the absolute temperature.

The values of E_a obtained from the slope the Arrhenius plot for PVP and PVP + KI are shown in Table 3. It is clearly

Table 2. Some Parameters of the Linear Regression from Temkin Adsorption Isotherm

Inhibitor	Temperature (°C)	ΔG (kJ/mol)	Temkin Isotherm		
			a	K	R^2
PVP	30	-20.09	-3.81	1.92×10^5	0.994
	40	-19.84	-4.09	1.97×10^5	0.996
	50	-14.47	-2.86	51.58	0.995
	60	-14.69	-3.45	83.71	0.997
PVP+KI	30	-20.77	-3.68	1.00×10^7	0.995
	40	-21.55	-4.34	1.57×10^7	1.000
	50	-19.75	-2.93	6.82×10^2	0.998
	60	-19.21	-3.81	3.11×10^3	0.997

seen from the results obtained that E_a increases in the presence of the additives. This may be attributed to an appreciable decrease in adsorption process of the inhibitors on the metal surface with rise in temperature [27]. The most noticeable increase in activation energy is observed with PVP + KI combination.

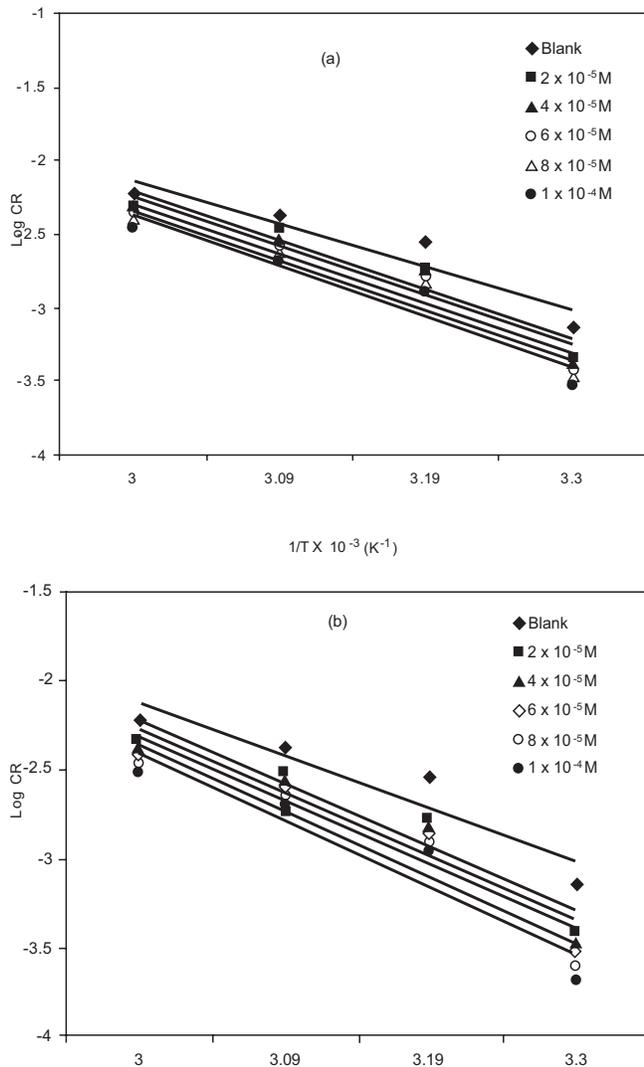


Fig. (3). The plot of logarithm of corrosion rate (CR) against 1/T for Al in 2M HCl in the absence and presence of (a) PVP and (b) PVP + KI.

The free energy of adsorption values, ΔG_{ads}^o were obtained from equation (4) and are presented in Table 2. The values obtained are negative. The negative values ensure the spontaneity of the adsorption process and the stability of adsorbed layer on the Al surface. The values of ΔG_{ads}^o up to -40kJmol^{-1} is usually accepted as a threshold value between chemisorption and physisorption [35]. The values of ΔG_{ads}^o obtained in this study are below the threshold value. This is consistent with electrostatic interactions between the charged metals and the charged molecules, which signifies physical adsorption.

Table 3. Calculated Values of Activation Energy for Different Systems

Systems/Concentration	Activation Energy, E_a (kJ/mol)
Blank	5.63
6M KI	6.54
2×10^{-5} M PVP	6.43
4×10^{-5} M PVP	6.36
6×10^{-5} M PVP	6.43
8×10^{-5} M PVP	6.47
1×10^{-4} M PVP	6.56
2×10^{-5} M PVP+6mM KI	6.72
4×10^{-5} M PVP+6mM KI	6.82
6×10^{-5} M PVP+6mM KI	6.80
8×10^{-5} M PVP+6mM KI	7.07
1×10^{-4} M PVP+6mM KI	7.26

The values of enthalpy of adsorption, ΔH^o and entropy of adsorption, ΔS^o were obtained from the plot of ΔG_{ads}^o versus T (Fig. 4) from the basic thermodynamic equation (7)

$$\Delta G_{ads}^o = \Delta H^o - T\Delta S^o \quad (7)$$

ΔH^o obtained were -12.31 and $-12.99 \text{ kJmol}^{-1}$ for PVP and PVP + KI respectively. Also the values obtained for ΔS^o were 0.39 and $0.46 \text{ kJmol}^{-1}\text{K}^{-1}$ for PVP and PVP + KI respectively. The negative sign of the ΔH^o obtained indicates the exothermic nature of the corrosion process while is spontaneous while the positive sign of the ΔS^o shows a decrease in the systems order [30].

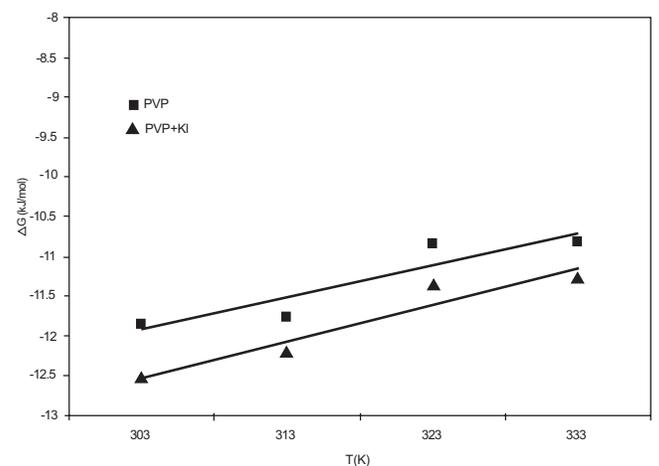


Fig. (4). The plot of ΔG_{ads}^o against T for Al dissolution in 2M HCl containing PVP and PVP+KI.

Synergism Considerations

The synergism parameter (S_1) was calculated using the relationship earlier reported [25, 26]. The synergistic parameter was evaluated from the inhibition efficiency values obtained using equation (2). The calculated values for the different concentrations of PVP at 30°C are presented in Table 4.

Results shown in the Table 4 indicate that the synergistic parameter increases with increase in the concentration of PVP and are greater than unity, which clearly shows that the corrosion inhibition brought about by PVP in combination with iodide ions are synergistic in nature. The result obtained is in agreement with what has been reported by Larabi and Harek [20] and Larabi *et al.* [21] in their study of addition of iodide ions to poly (4-vinylpyridine) (P4VP) in 0.5M H₂SO₄ and 1M HCl respectively.

Table 4. Synergistic Parameter for Different Concentrations of PVP

PVP Concentration	Synergism Parameter, S_1
2x10 ⁻⁵ M PVP	1.32
4x10 ⁻⁵ M PVP	1.35
6x10 ⁻⁵ M PVP	1.49
8x10 ⁻⁵ M PVP	1.53
1x10 ⁻⁴ M PVP	1.55

The observed synergistic effect results from increased surface coverage arising from ion-pair interaction between I⁻ anion and PVP cations. There are different schools of thoughts [17-19, 36] on the actual role of the anions as regards improved adsorption of the organic inhibitors. The ion pairs could be formed in the bulk of the solution and then adsorbed from the solution on to the metal surface as follows:



In the second mechanism, the halide ions is first adsorbed on the metal surface and the inhibitor is then drawn into the double layer by the adsorbed halide ion such that the ion pair formation occurs directly on the metal surface.



where Y_s , X_s and $(YX)_s$ represent inhibitor, halide ion and ion-pair respectively in the bulk solution while Y_{ads} , X_{ads} and $(YX)_{ads}$ refer to the same species in the adsorbed state.

The improvement in the inhibition efficiency of 2-mercapto benzimidazole on addition of iodide ions during copper corrosion was attributed to the first mechanism by Wu *et al.* [17] while results of Oguzie *et al.* [36, 37] and other authors [18, 19] suggest that the ion-pair interaction occur *via* the second mechanism. Stabilization of the ad-

sorbed iodide ions with PVP cations leads to greater surface coverage and thereby improved inhibition efficiency.

The enhanced inhibition efficiency caused by the addition of iodide ions to PVP is only due to synergistic effect. Halide ions are known to improve adsorption of organic cation-type inhibitors in solution by forming intermediate bridges between the positively charged metal surface and the positive end of the organic inhibitor. The phenomenon of synergism observed could be attributed to increased surface coverage arising from ion-pair interaction between organic cations and anions.

CONCLUSION

From the overall experimental results the following conclusions can be deduced: Polyvinylpyrrolidone acts as an inhibitor for the corrosion of aluminium in 2M HCl. Inhibition efficiency increases with increase in inhibitor concentration and decreases with increase in temperature. On addition of iodide ions to 2M HCl containing PVP, a synergistic or cooperative effect occurred thus inhibiting aluminium corrosion. The Temkin adsorption isotherm fits the experimental data obtained in this study. The phenomenon of physical adsorption is proposed from the obtained E_a and ΔG_{ads}^o values. Thermodynamics parameters also revealed that the adsorption process is spontaneous.

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