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Efficiency of Azodyes in Retarding the Dissolution of Aluminium in Hydrochloric Acid

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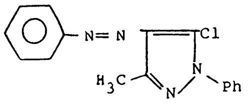
The inhibition of the corrosion of aluminium in hydrochloric acid solution by some 4-(*m*-Substituted phenylazo)pyrazoles has been studied by three different techniques. The inhibitor efficiency calculated from the three techniques are in good agreement. The corrosion rate is a function of temperature, concentration, and nature of the inhibitor. The inhibitors appear to function through general adsorption following the Langmuir adsorption isotherm. Thermodynamic parameters for adsorption of inhibitors have been calculated and discussed.

The industrial importance of corrosion inhibitors is widespread, ranging from pickling to water-cooled systems. The selection of inhibitor for a given system depends on the corrosive medium, the nature of the metal, the magnitude of the charge at the metal-solution interface, and the cathodic reaction.[1] The study of adsorption of organic compounds at electrode-electrolyte interfaces is a subject with pronounced practical significance in view of its relevance to electrochemical energy conversion, electro-organic synthesis, and corrosion inhibition. The latter is most popular since such compounds effectively inhibit the corrosion process even when present in trace amounts.[2] It is known that inhibitor efficiency depends on the mode of adsorption of inhibitor molecule, electron density at the electroactive center[3] and the state of the surface.[4]

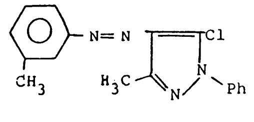
Aluminium is extensively used in various industrial operations and the study of its corrosion inhibition is of great importance. Oxygen- and nitrogen-containing organic compounds have been tried as corrosion inhibitors for metals.[2,5-7]

The aim of this article is to throw some light on the mechanism of inhibition of these bulky molecules on the corrosion of aluminium in hydrochloric acid.

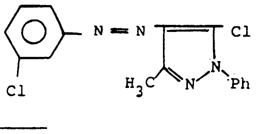
4-Phenylazo-1-phenyl-3-methyl-5-chloropyrazole (**1**)



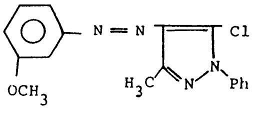
4-(*m*-Tolylazo)-1-phenyl-3-methyl-5-chloropyrazole (**2**)



4-(*m*-Chlorophenylazo)-1-phenyl-3-methyl-5-chloropyrazole (**3**)



4-(*m*-Methoxyphenylazo)-1-phenyl-3-methyl-5-chloropyrazole (**4**).



Experimental

Thermometric Method. Chemicals used were of analytical grade and were used without further purifications. The solutions were made from freshly prepared twice distilled water. The procedure for the determination of metal dissolution rate by the thermometric method has been described previously,[8] the reaction tube being placed inside a vacuum flask to minimize heat losses. Aluminium strips measuring 100×10×1 mm were lightly abroaded with 2/0 and 3/0 emery paper, then degreased with alkaline solution (($15\ \mathrm{g}\ Na_2CO_3+15\ \mathrm{g}\ Na_3PO_4)\cdot l^{-1}$) and washed with running twice distilled water. The specimens were then dried between two filter papers. Each experiment was carried out with a new Al strip and 15 ml of the corroding solution, and repeated to ensure reproducibility of the results.

The reaction number (RN) is defined as $\mathrm{RN}=(T_m-T_i)/t$ °C min^{-1}. T_m, T_i are the maximum and initial temperatures, respectively and t is the time in min, taken to reach T_m. All experiments were started at 25±0.1 °C (T_i). The percentage inhibition, I, is taken as:

$$\%I=(\mathrm{RN}_{\mathrm{pure}}-\mathrm{RN}_{\mathrm{inh}})\ 100/\mathrm{RN}_{\mathrm{pure}} \quad (1)$$

Weight Loss Method. The test pieces measuring 20×20×1 mm were prepared as before, weighed, then immersed in 50 ml of the test solution at a temperature of 25±0.1 °C for a period of 15 min. They were then cleaned and washed with distilled water, dried and re-weighed.

$$\%I=\frac{\mathrm{Wt.\ loss_{pure}}-\mathrm{Wt.\ loss_{inh}}}{\mathrm{Wt.\ loss_{pure}}}\times 100\,\% \quad (2)$$

Gasometeric Method. The reaction vessel and procedure for determining the rate of dissolution of aluminium in HCl were the same as described before.[9] The test pieces measuring 20×20×1 mm were prepared as before.

The efficiency of the inhibitors used can be evaluated as the percentage reduction in RR, viz.

$$\%\ \text{Reduction in RR}=(R_{\mathrm{free}}-R_{\mathrm{inh}})\ 100/R_{\mathrm{free}} \quad (3)$$

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where R_{free} and R_{inh} are rates of Al dissolution in the absence and presence of the additive, respectively, both measured at the same reaction time.

Results and Discussion

By following the temperature changes of the system in absence and presence of different concentrations of 4-(*m*-substituted phenylazo)pyrazoles, the temperature of the system was found to change slightly during the initial stages of the reaction (due to the originally formed oxide film). After a certain period which depended upon the concentration of the additives, the temperature rose to attain a maximum value. A representative temperature-time relationship obtained in presence of varying concentrations of compound **1** is shown in Fig. 1. The relationship between the reaction number (RN) of the system and the logarithm of the concentration (C) of compound **1** is indicated by the curve shown in Fig. 2. Curves having the same character are obtained with the other tested materials.

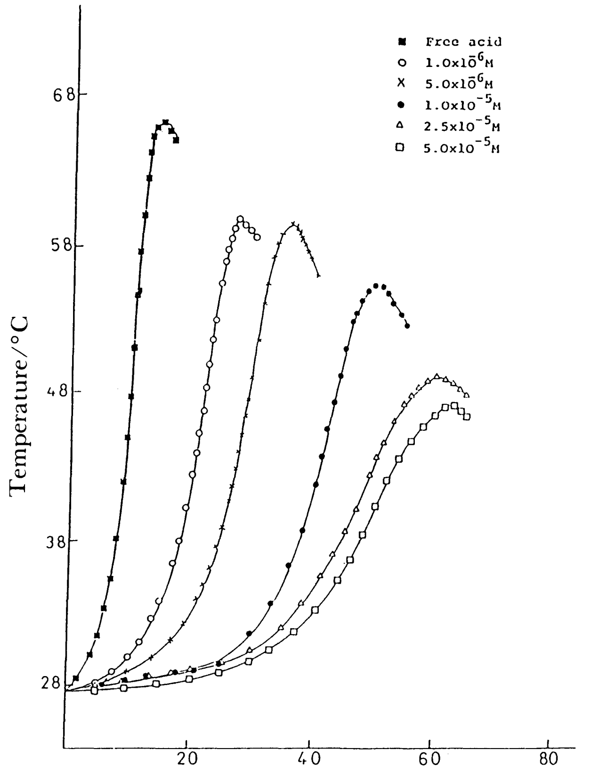


Fig. 1. Temperature-time curves obtained in the absence and presence of varying concentrations of compound **1**.

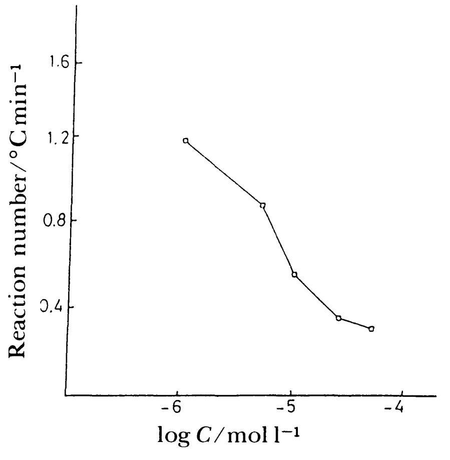


Fig. 2. Variation of the reaction number with the logarithm of concentration of compound **1**.

The reaction number-log$C$ curves consist of an initial descending portion along which RN decreases slowly followed by a sharp descending portion to a certain limit of concentration. On further increase of the concentration of the additive, the values of RN decreases linearly with concentration and then become more or less constant. This behavior is explained on the basis of one-step adsorption process. The inhibiting action of tested compounds on Al dissolution is manifested by a decrease in T and an increase in the incubation period. The increase in the incubation period indicates that the additive acts in the acid solution as a strong cathodic inhibitors[10,11] and the lowering in T_m shows the strong adsorbability of the additive.[11]

The results obtained (Table 1) support the view that tested compounds have an inhibitive effect on the corrosion of Al in HCl. This apparent from the reduction of the values of RN of the metal by increasing the concentration of the additive. The percentage reduction in RN for all tested compounds are presented in Table 2.

Table 1. Efficiency of Corrosion Inhibition of 4-(*m*-Substituted phenylazo)pyrazoles as Determined by Percentage Reduction in Reaction Number in 2 M HCl

Concn of the additive in mol l^{-1}	% Reduction in RN			
	1	**2**	**3**	**4**
1.0×10^{-6}	55.3	50.8	36.0	33.0
2.5×10^{-6}	—	53.6	43.3	36.7
5.0×10^{-6}	67.0	63.4	51.3	48.0
1.0×10^{-5}	70.3	74.8	65.0	60.7
2.5×10^{-5}	86.8	81.2	72.7	68.5
5.0×10^{-5}	88.5	82.6	75.1	69.4

Table 2. Comparison between Efficiency of 4-(*m*-Substituted phenylazo)pyrazoles as Determined by Thermometric Weight Loss and Hydrogen Evolution Techniques in 2 M HCl at 10^{-5} M Inhibitors Concentration

Inhibitor	% Reduction in RN	% Inhibition	Reduction in RR
1	79.3	94.0	70.7
2	74.8	92.4	69.6
3	65.0	89.4	59.0
4	60.7	87.4	48.4

Figure 3 shows the volume of hydrogen evolved in ml cm^{-2} vs. the reaction time of compound **1**. The slope of the curve at specified times gives the reaction rate in l m^{-2} min^{-1}. The percentage reduction in RR, after 60 min, for all the studied compounds are presented in Table 2.

Figure 4 represents the relation between the weight loss and time for compound **1**. The inhibition efficiences of the additives after 60 min are included in Table 2. In this table the 4-(*m*-substituted phenylazo)-pyrazoles examined are arranged in the order of decreasing inhibition efficiency. The same order is obtained from both the experimental methods employed.

According to Damaskin[12] the surface coverage (θ) can be determined as follows:

$$\theta = 1 - \frac{I}{I_0} \qquad (4)$$

where I and I_0 are the current densities of the given potentials in electrolytes with and without inhibitor, respectively. But Rozenfeld[13] and Gardner[14] replace the current density by the capacitance of the double layer, dissolution rates, adsorption potential, or weight losses. Accordingly, it seemed promising to use U values instead of any of these variables. Equation 4 can thus be written as:

$$\theta = 1 - \frac{U_i}{U} \qquad (5)$$

where U_i and U are corrosion rates in solution with and without inhibitor, respectively in case of weight loss method. It is available from the results of the present investigation to calculate the surface coverage, θ. The Langmiur adsorption isotherm may be written in the form:[15]

$$\log \frac{\theta}{1-\theta} = \log BC - G/2.303\,RT \qquad (6)$$

where B is the adsorption equilibrium constant and G is the free energy of adsorption. Plotting $\log[\theta/(1-\theta)]$ against $\log C$ of compound **1** gives straight line, Fig. 5,

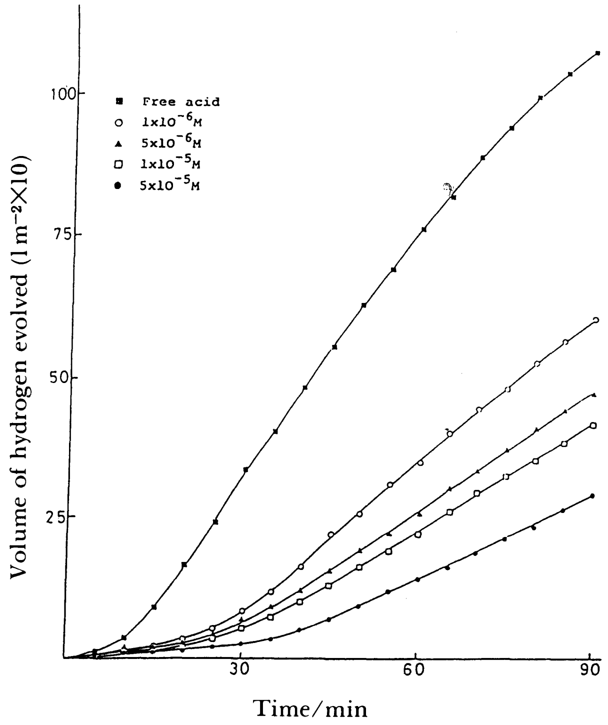


Fig. 3. Volume of hydrogen evolved-time curves obtained in the absence and presence of varying concentrations of compound **1**.

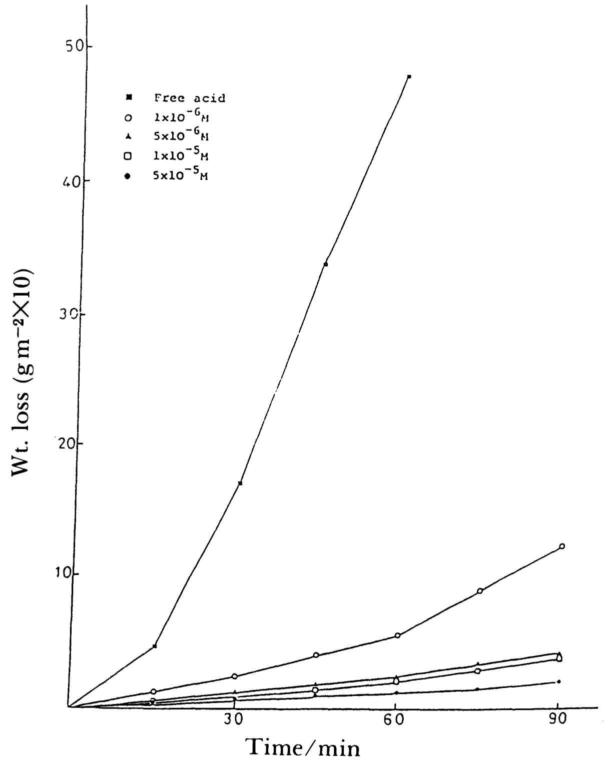


Fig. 4. Weight loss-time curves obtained in the absence and presence of varying concentrations of compound **1**.

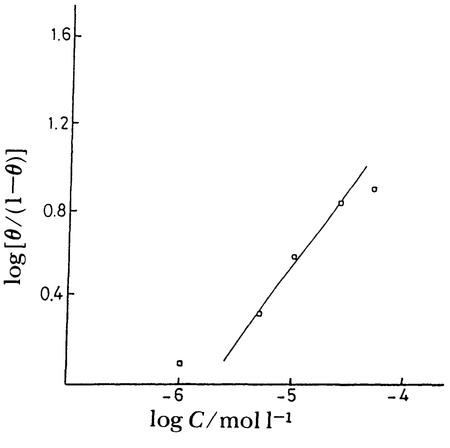


Fig. 5. Dependence of $\log[\theta/(1-\theta)]$ on logarithm of concentration of compound **1**.

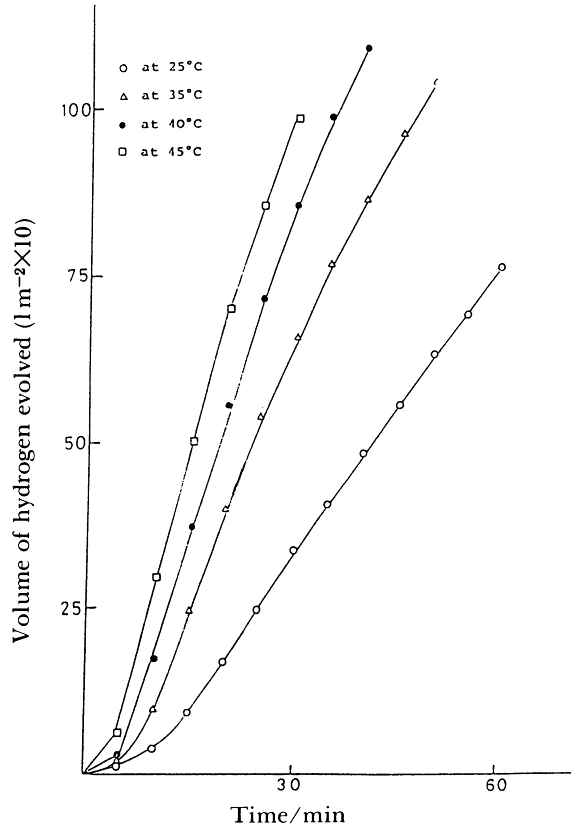


Fig. 6. Volume-time curves for 2 M HCl at different temperatures.

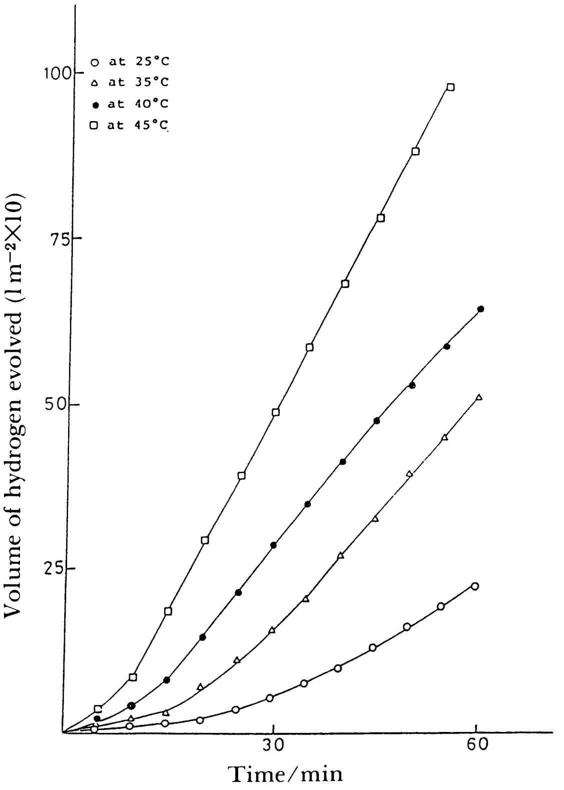


Fig. 7. Volume-time curves for compound **1** at different temperatures.

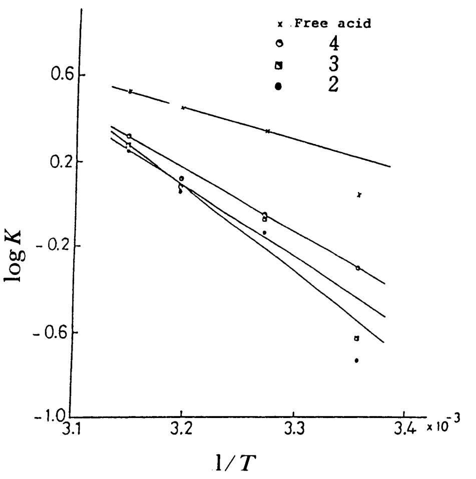


Fig. 8. log$K$-1/T curves for aluminium dissolution in presence and in absence of 4-(*m*-substituted phenylazo)pyrazoles.

Table 3. Effect of Temperature on the % Reduction in RR in Presence of 10^{-5} M 4-(*m*-Substituted phenylazo)pyrazoles at 30 min

Temp/°C	**1**	**2**	**3**	**4**
25	83.5	82.4	78.8	55.1
35	76.0	66.8	60.4	58.5
40	67.0	59.7	57.2	53.3
45	50.0	45.1	41.2	36.0

indicating almost a general agreement with Langmiur adsorption isotherm.

To study the effect of temperature on the rate of hydrogen evolution, hydrogen evolved was determined in 2 M HCl (1 M=1 mol dm^{-3}) without (Fig. 6) and with 10^{-5} M (Fig. 7) from compound **1** at solution temperatures of 25, 35, 40, and 45 °C. It was observed from the results of Table 3 that the inhibitive efficiency of all tested compounds decreases with the rise in temperature from 25 to 45 °C. This indicates that these compounds are physically adsorbed on aluminium surface.

The values of energy of activation, E, were calculated from the slopes of the Arrhenius plots of log k vs. 1/T, where k is the corrosion rate and T the absolute temperature (Fig. 8). The E values are given in Table 4. From Table 4 it is evident that the E values in presence of additives are significantly lower than in its absence. This indicates that the four compounds function as effective inhibitors. The almost similar values of E suggest that the inhibitors are similar in their mechanism of action and the order of efficiency may be related to the preexponential factor A by the equation:

$$\log k = \log A - E/RT \tag{7}$$

This is further related to concentration, steric effects, metal surface characteristics etc.

For calculating the values of heat of adsorption of the various inhibitors, plots were drawn of log

Table 4. Thermodynamic Parameters for Adsorption of Inhibitors on to an Aluminium Surface in 2 M HCl Containing 10^{-5} M Inhibitors

Inhibitor	E	$-\Delta G^{\circ}_{\text{ads}}$	$\Delta S^{\circ}_{\text{ads}}$	$-Q$	Slope of
	kcal mol^{-1}	kcal mol^{-1}	cal K^{-1} mol^{-1}	kcal mol^{-1}	$\log[\theta/(1-\theta)]$vs.$(1/T)$
Free acid	6.4	—	—	—	—
4	14.1	10.3	51.6	5.1	1.1
3	17.8	10.4	50.4	4.6	1.0
2	15.5	10.6	49.5	4.2	0.9
1	17.4	10.8	47.1	3.2	0.7

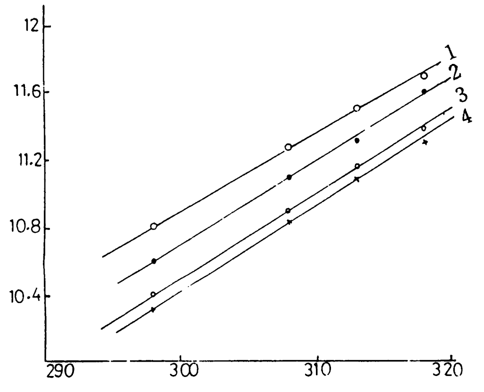


Fig. 9. Relation between $-\Delta G^{\circ}_{\text{ads}}$ and temperature for different 4-(*m*-substituted phenylazo)pyrazoles.

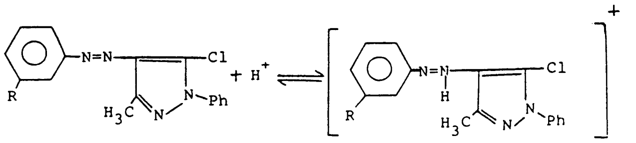
Table 5. Spectroscopic Data for 4-(*m*-Substituted phenylazo)pyrazoles

Compound	λ_{max}/nm	pK
1	334	12.2
2	336	6.4
3	360	5.8
4	334	5.3

$[\theta/(1-\theta)]$ vs. $1/T$ [θ=fraction of the surface covered by the inhibitor$=1-\mu_i/\mu$]. The Q values obtained from the slopes of these plots (ranging from 0.7—1.1) are given in Table 4. From the results it may be generalized that the more efficient inhibitor the less value of Q it has and vice versa.

The values of free energy of adsorption $\Delta G^{\circ}_{\text{ads}}$, are given in Table 4 at 25 °C. The results show that compound **1** which gives maximum efficiency shows more negative free energy of adsorption indicating that it is strongly adsorbed on the metal surface. In general, the negative values of free energy of adsorption, $\Delta G^{\circ}_{\text{ads}}$, indicate the spontaneous adsorption of inhibitors on aluminium. Also the entropy of adsorption, $\Delta S^{\circ}_{\text{ads}}$, was calculated[16] from the slopes of Fig. 9 and its values are recorded in Table 4.

Effect of Chemical Constitution on Inhibition Efficiency. The order of decreased inhibition efficiency for 4-(*m*-substituted phenylazo)pyrazoles **1**, **2**, **3**, and **4** is: $H > CH_3 > Cl > OCH_3$ as indicated by the results in Table 2. Differences in the inhibition efficiency for aluminium corrosion in 2 M HCl as indicated by the above orders probably do not originate from the pyrazole moiety of the molecule, but arise from the substituents in the phenylazo group. It is evident that the electrophilic character of these substituents plays a determining role in imparting inhibition efficiency. Therefore, increase in electron-withdrawing ability of substituents is expected to increase the positive charge on the protonated form (acid form) of the inhibitors which is adsorbed on the aluminium surface. In strong acid solutions at pH 0 the acid-base equilibrium of the azo inhibitors to consider is as follows:



R = H, CH_3, Cl, OCH_3

Moreover, the intensity of the azo bands decreases with increase in pH and isobestic points are observed in the absorption spectra at longer wavelength. This behavior refers to the presence of the acid-base equilibrium and indicates that the acid form is predominant at low pH values. Also pK values were determined spectrophotometrically by well-known procedure.[17] A large value points to the presence of the azo inhibitors more in the acid form. The results of spectrophotometric measurements are summarized in Table 5. The order of decrease of these pK values is: $H > CH_3 > Cl > OCH_3$ which is similar to that of decreased inhibition efficiency.

Fouda[18] and Barradas[19] reported before that the increased protection efficiency for some derivatives of thiophene is due to the presence of electrophilic substituents. This phenomenon was accounted[20] for by the adsorption of the protonated form of the inhibitor species and hence a decrease in the electron density of the functional group leads to an effective increase in its positive charge. Consequently, adsorption is reinforced by electrostatic forces.

The electrophilic character of the substituents used is decreased in the order:[21] $Cl > H > CH_3 > OCH_3$. This order runs parallel to the above mentioned observed sequence of decreased inhibition efficiency of the azo inhibitors (**1**—**4**) with exception of the Cl-substituted one (**3**) which could be accounted for by the operation of a mesomeric effect (+M) involving electron pairs on Cl which acts in opposite direction to the −I effect and the overall mechanism constitutes electron release which reduces the positive charge on the protonated from of the azo inhibitor **3** in a greater extent than the methyl-substituted compound **2** and renders it less inhibitive. Also the increase in red shift for R=Cl over that for R=CH_3 supports the suggestion that +M effect operates in this case.

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