Corrosion Inhibitors For Zinc in 2 M HCl Solution

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Inhibiting action of semicarbazide, thiosemicarbazide, sym. diphenylcarbazide towards corrosion of zinc in hydrochloric acid has been investigated. The rate of corrosion depends on the nature of the inhibitor and its concentration. The values of inhibition efficiency from, weight loss, thermometric measurements are in good agreement with those obtained from polarization studies. From the polarization studies, the inhibitors used act as mixed adsorption type inhibitors, increased adsorption resulting from an increase in the electron density at the reactive C=S and C=O groups and N-atoms. The thermodynamic parameters of adsorption obtained using Bockris-Swinkels adsorption isotherm reveal a strong interaction of these carbazides on zinc surface.

Introduction

Because of the wide spread use of zinc, the study of its corrosion has turned to be an outstanding subject in corrosion with the industry of today. Researchers on the corrosion of zinc in HCl have been accumulated in the literature.[1~6] Among nitrogen containing compounds, quinoline,[7] aniline[8] and ephedrine, narcotine, brucine, strychine, etc.,[9] have shown good inhibition towards zinc in acidic medium. Quinine sulphate, piperazine, caffine, barbitone etc. and pyridine derivatives have been investigated as corrosion inhibitors for aluminium and zinc in acidic medium.[10,11]

Unlike many other inhibitors, thiourea and its derivatives show a maximum in concenteration-efficiency curves. Thiourea progressively loses its efficiency and eventually becomes a corrosion promoter.

There are many conflicting reports on the mechanism of inhibition by thiourea. Thus it has been characterized as either anodic, cathodic or mixed inhibitors.[12~14]

The present study was undertaken to investigate the inhibition of corrosion of zinc in HCl by some carbazide derivatives (Scheme 1) and also to throw some light on their mechanism of inhibition.

Experimental

**Electrodes.** The test electrodes were cut from zinc sheet containing the following impurities in weight percent.

Fe	Cd	Pb
0.001	0.01	0.1

They were abraded successively with 4/0 emery paper before degreasing with methanol and washing with bidistilled water.
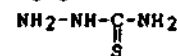
Solutions. All the chemicals used were of the AR grade. The solutions were prepared from freshly bidistilled water.

Experimental systems. (1) Galvanostatic polarization measurements. A three- electrode cell was used with a Pt counter electrode and silver-silver chloride as reference elec-
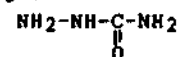
1) Sym.diphenylcarbazide (C13H14N4O)
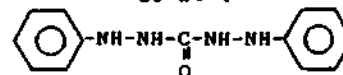
2) Thiosemicarbazide (CH5N3S)

3) Semicarbazide (CH5N3O)

Scheme 1. Carbazide derivatives.

trode. Current from constant current device was measured with a multimeter with an accuracy of ±4%. Corrosion potentials were recorded using a digital ionalizer device (Orion model 701A) with an accuracy of ±7%.

(2) Weight-loss measurements. The specimens of zinc used for the weight loss measurements were of $20 \times 20 \times 1$ mm size. The zinc pieces were degreased in methanol for half an hour, then washed thoroughly with bidistilled water. After specified periods of time, 3 spieces of zinc were taken out of the rest solution and weighed again. The average weight loss at a certain time for each set of three samples was taken. All experiments were carried out at 25 ℃.

(3) Thermometric determination. The variation of the temperature with time for the dissolution of zinc in acids was determined according to the method of Mylius[15] developed and extended by Shams El-Din et al.[16] Details of the procedure and reaction vessel were described elsewhere.[16]

The rate of corrosion is represented by the loss in weight of zinc sample and by the reaction number R.N.

Results and Discussion

1-Polarization measurements. Anodic and cathodic polarization studies were carried out galvanostatically in 2 M HCl with various concentrations of the inhibitors at 25 ℃. Figure 1 shows the polarization curves for zinc in the inhibited 2 M HCl in presence of different concentrations
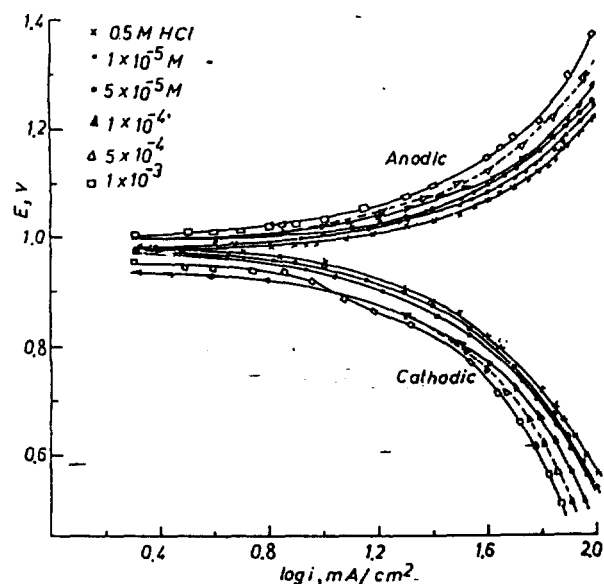
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Figure 1. Polarization curves of zinc in 2 M HCl in the presence of different concentration of thiosemicarbazide at 30 °C.

Table 1. Electrochemical parameters of zinc in the presence of different concentrations of thiosemicarbazide (CH$_5$N$_3$S)

Conc.(m)	0.00	1×10^{-5}	5×10^{-5}	1×10^{-4}	5×10^{-4}	1×10^{-3}
$-E_{corr}$ [vs(Ag/AgCl)]	0.99	0.995	0.995	0.995	0.995	0.995
i_{corr} mAcm^{-2}	70.79	19.5	17.38	15.85	14.79	12.59
$-\beta_c$ [V/decade]	0.080	0.082	0.080	0.081	0.080	0.080
β_a [V/decade]	0.075	0.076	0.077	0.077	0.075	0.075
%inhib.	—	72.5	75.5	77.6	79.1	82.2

Where; E_{corr} is the corrosion potential. i_{corr} is the corrosion current density. β_c is the cathodic Tafel slope. β_a is the anodic Tafel slope.

of thiosemicarbazide. Thiosemicarbazide produces a parallel displacement of both the anodic and cathodic Tafel lines. The polarization curves for zinc in 2 M HCl containing different concentrations of sym. diphenylcarbazide and semicarbazide gave similar results. These curves show that the carbazides under consideration influence both the cathodic and the anodic processes. The electrochemical parameters of zinc in 2 M HCl are given in Table 1. The slope of cathodic and anodic Tafel lines, β_c and β_a, remains unchanged and is 75-82 mV per current decade. This indicates that the addition of thiosemicarbazide did affect the anodic and cathodeic Tafel slopes but reduced the corrosion rate. Hence, the mechanism of inhibition of the dissolution of zinc involves the blockage of the surface by the adsorbed organics. Figure 2 shows the variation of the degree of surface coverage (θ) with the logarithm of bulk concentration. The three carbazides exhibit clear adsorption patterns as indicated by the S-shaped curves. Table 2 shows the electrochemical parame-
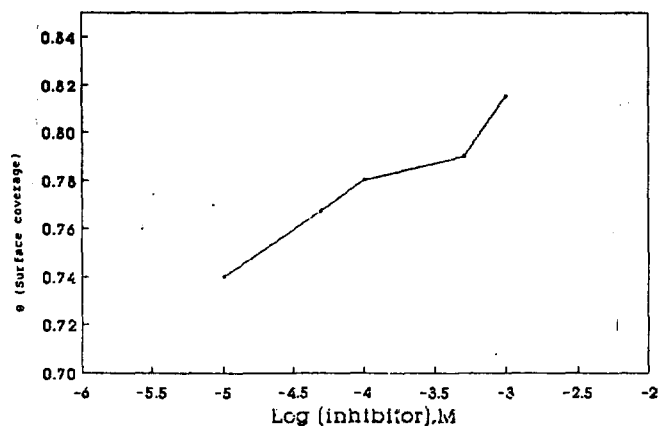

Figure 2. The relationship between degree of coverage (θ) and the concentration of thiosemicarbazide at 25 °C.

Table 2. Electrochemical parameters of zinc in the presence of 5×10^{-4} M of each of carbazides used at 25 °C

Compound	C$_{13}$H$_{14}$N$_4$O	CH$_5$N$_3$S	CH$_5$N$_3$O
$-E_{corr}$ [vs.(Ag/AgCl)]	0.993	0.995	0.996
i_{corr} [mAcm^{-2}]	11.32	14.79	16.78
$-\beta_c$ [V/decade]	0.079	0.080	0.081
β_a [V/decade]	0.074	0.075	0.075
%inhibition	84.0	79.1	76.3
$-\Delta G^o_a$ KJmol^{-1}	26.42	23.91	23.53

Where; ΔG^o_a is the change in the free energy of activation of the adsorption process.

ters of zinc in 2 M HCl containing 5×10^{-4} M of different carbazides. As shown from Table 2, the order of increasing protection efficiency is C$_{13}$H$_{14}$N$_4$O>CH$_5$N$_3$S>CH$_5$N$_3$O. It appears also from this Table, that the efficiency of the inhibition depends mainly on the molecular size of the carbazide used and the charge density on the active sites (S, N, O) and increases with increasing both. These compouns used are polar molecules with the sulfer atom having a permanent negative charge whereas the nitrogen atom has a positive charge. While in the semicarbazide and sym. diphenylcarbazide, nitrogen atom has a negative charge and oxygen atom has a positive charge. This is because the basicity of these atoms increases in the order S>N>O. As the molecule approaches the electrode surface, the electric field of the double layer increases the polarization of the molecule and induces additional charges on both the S and N or N and O atoms, a condition that enhances the adsorption of the molecule. In spite of, S atom is more strongly adsorbed than N and O[17] and inhibits by way of electron donation to the metal,[18] sym. diphenylcarbazide comes on the top of these compounds used. This due to the fact that the aryl groups protect better than alkyl ones. After this thiosemicarbazide

comes and finally semicarbazide. This is due to the above fact that S atom is more adsorbed than O atom. At similar concentrations of HCl and inhibitor, the inhibition efficiency is higher for thiosemicarbazide than for semicarbazide, this has been also observed by others.[19]
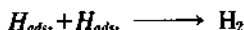
The corrosion of zinc in HCl solutions is an electrochemical process, the anodic reaction of which is:

$$Zn \longrightarrow Zn^{2+} + 2e^-$$
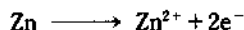
and the cathodic reaction is:

$$H^+ + e^- \longrightarrow H_{ads}.$$

followed by:

$$H_{ads}. + H_{ads}. \longrightarrow H_2$$

The inhibition of the process can take place by:

i) change in the corrosion (or open circuit potential) potential

ii) an increase in the polarization of cathodic and/or anodic processes.

In the present investigation, it was observed that there is no change in the corrosion potentials. Therefore, the inhibition of corrosion is mainly due to an increase in the polarization of the cathodic and anodic processes.

The inhibition by nitrogen-containing compounds is primarily due to the adsorption of these compounds on the surface of the metal, and the greater the adsorption (due to the strength of he adsorption and the amount of inhibitors adsorbed on the metal surface) the greater the inhibition. The adsorption in our case[20] takes place through the nitrogen atoms, $C=O$ and $C=S$ groups, the extent of the adsorption being dependent on the electron density of these atoms and groups. In addition to the nature of the inhibitor, the extent of corrosion inhibition depends on the molecular size, the surface condition and the mode of adsorption of the inhibitor. The nature of the inhibitor interaction with the electrode surface has been deduced in terms of its adsorption characteristics.

The inhibition efficiency (I_e) was calculated from the following equation:

$$\% \ I_e = \left(1 - \frac{i_{inh}}{i_{free}}\right) \times 100 \qquad (1)$$

where, i_{inh} and i_{free} are the corrosion current densities in the presence and the absence of inhibitors.

The surface of the electrode in aqueous solutions is considered to be covered with water dipoles. Therefore, for inhibition to occur, these water dipoles must be replaced by inhibitor molecules in a reaction of the type:

$$nH_2O_{ads}. + Org._{sol} \rightleftharpoons Org._{ads} + nH_2O_{sol}.$$
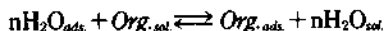
The thermodynamics of the substitution process depends on the number of water molecules (n) removed by the inhibitor molecules.

For the evaluation of the standard free energy change (ΔG°_a) for the adsorption process, adsorption isotherms can be used.[21~25] One of these isotherms is that given by Bockris *et al.*[21~23] which is written in the form:

$$\Delta G^\circ_a = -RT\ln[55.5\theta/C_{org}(1-\theta)^n] \cdot [\theta + n(1-\theta)^{r-1}/n^n] \qquad (2)$$
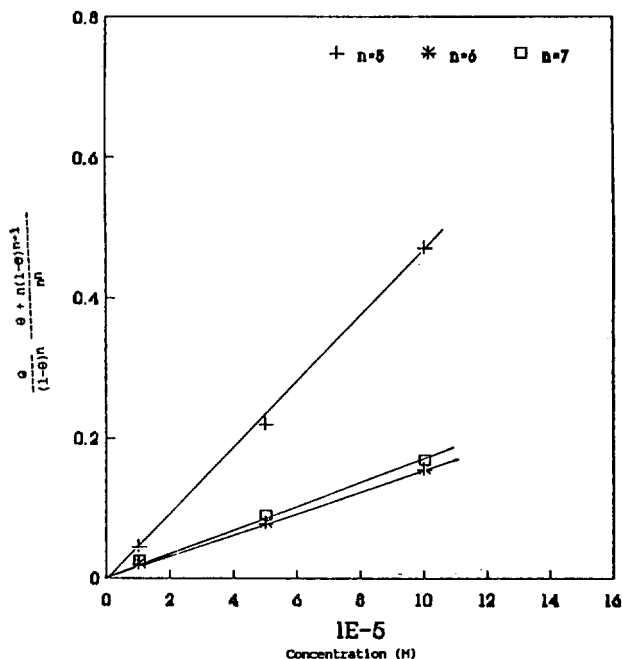

Figure 3. Bockris-Swinkel's adsorption isotherms of different inhibitors in 2 M HCl. (□) sym. diphenylcarbazide, (*) thiosemicarbazide and (+) semicarbazide.
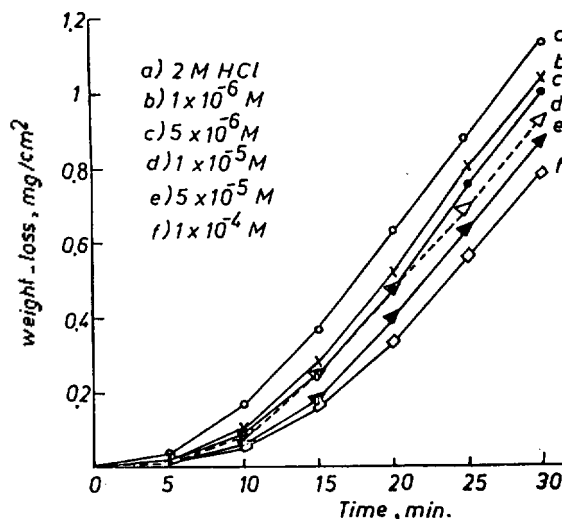

Figure 4. Effect of thiosemicarbazide concentration on weight-loss vs. time curves for zinc in 2 M HCl.

where θ is the surface coverage which calculated from the relation $\theta = (1 - u/u_o)$, where u_o and u are the rate of corrosion in the absence and presence of inhibitor respectively, and C_{org} is the concentration of the added solute in the bulk of solution.

A plot of $\theta/(1-\theta)^n[\theta + n(1-\theta)^{n-1}/n^n]$ against inhibitor concentration was made to evaluate the most probable values of n (Figure 3) shows the adsorption isotherms for different values of n for sym. diphenylcarbazide, thiosemicarbazide and semicarbazide. The straight line with $n=7$, 6 and 5 passes through the origin indicating that 7, 6, 5 are the values for sym. diphenylcarbazide, thiosemicarbazide and semicar-
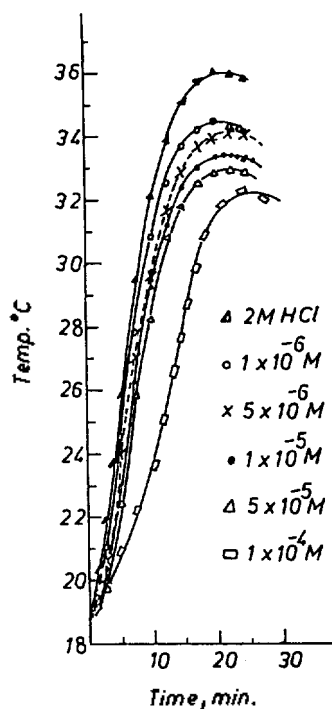
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Figure 5. Effect of thiosemicarbazide concentrations on the thermometric behaviour of zinc in 2 M HCl.

Table 3. Variation of percentage inhibitor efficiency (% P) in 2 M HCl containing different inhibitor concentrations at 25 °C and after 30 min. immersion

Inhibitor	% P		
conc. (M)	($C_{13}H_{14}N_4O$)	(CH_5N_3S)	(CH_5N_3O)
1×10^{-6}	10.6	6.8	5.7
5×10^{-6}	20.8	16.9	15.4
1×10^{-5}	29.3	23.7	21.2
5×10^{-5}	34.6	28.0	26.7
1×10^{-4}	40.0	32.2	30.9

Table 4. Effect of thiosemicarbazide (CH_5N_3S) concentration on the parameters of the thermometric curves for zinc in 2 M HCl solution

Concentration (M)	T_i °C	T_m °C	t min.	RN °C/min	% RN
0.00	18.8	36.0	20	0.86	−
1×10^{-6}	18.8	34.4	20	0.78	9.3
5×10^{-6}	18.8	33.8	20	0.75	12.8
1×10^{-5}	18.8	33.4	21	0.70	19.2
5×10^{-5}	18.8	32.8	23	0.61	29.2
1×10^{-4}	18.8	32.3	25	0.54	37.2

bazide, respectively.

Table 2 gives the values of ΔG°_a at 25 °C for inhibitors concentration for example at 5×10^{-4} M.

The negative values of ΔG°_a indicate the spontaneous adsorption of inhibitors on zinc surface. Semicarbazide is a weaker base than thiosemicarbazide and sym. diphenylcarbazide. One could thus expect the degree of adsorption by these inhibitors on zinc to be in the order: sym. diphenylcarbazide>Thiosemicarbazide>semicarbazide. This also in agreement with the observed corrosion data.

2-Weight-loss measurements. Zinc was immersed for 30 min. in unstirred 2 M HCl without and with various concentrations (1×10^{-6} to 1×10^{-4} M) of the three carbazides used at 25 °C. These carbazides had a marked inhibitive effect on the corrosion of zinc in HCl. The weight-loss of zinc decreased appreciably even in the presence of traces of these carbazides. The extent of the decrease in the weight-loss was found to depend on the nature of the inhibitor and its concentration. Figure 4 shows the variation of the weight-loss of zinc with the concentration of this semicarbazide.

The percentage inhibitive efficiency (% P) of each inhibitor on zinc surface, at different concentrations, was calculated using the equation:

$$\% \ P = [(W_o - W)/W_o]\times100 \qquad (3)$$

where W_o and W are the values of the weight-loss of zinc without and with the inhibitor, respectively. Table 3 gives the values of % P in the presence of various concentrations of inhibitors used in 2 M HCl at 25 °C. It is clear from Table 3 that $C_{13}H_{14}N_4O>CH_5N_3S>CH_5N_3O$ in their inhibitive action.

3-Thermometric measurements. In this method the

temperature change of the system involving zinc in 2 M HCl was followed in absence and presence of different concentrations of thiosemicarbazide (Figure 5). The maximum temperature (T_m) measured in acid solution is 36 °C, (The initial temperature $T_i = 18.8$ °C) and is attained after 20 min. This corresponds to an RN of 0.86 °C/min. On increasing the concentration of the inhibitors the time required to reach T_{max}. increases. This indicates that the additives retard the dissolution of zinc, presumbly by adsorption onto the surface of the metal. The extent of retardation due to inhibition depends on the degree of coverage of the metal with the adsorbate, and the temperature-time curves provide a means of differentiating between weak and strong adsorption.[8] Weak adsorption is noted here for sym. diphenylcarbazide and semicarbazide with the exception of thiosemicarbazide. Thiosemicarbazide exhibits strong adsorption (Figure 5) since a simultaneous increase in t and a diminution of T_m take place, and both factors cause a large decrease in the R.N. of the system. The results recorded in Table 4 reveal that the efficiency of corrosion inhibition as determined from the percentage reduction in RN increases with increasing the concentration of the inhibitors in 2 M HCl.

$$RN = (T_{max} - T_i)/t \ \ °C/min. \qquad (4)$$

$$\% \ \text{reduction in } RN = [1 - (RN_{inh}/RN_{uninh})]\times100 \qquad (5)$$

where T_{max} and T_i are the maximum and initial temperatures, respectively, and t is the time (in minutes) required to reach the maximum temperature. The order of increasing inhibition efficiency is: $C_{13}H_{14}N_4O>CH_5N_3S>CH_5N_3O$.

Thus, the same order of inhibitive action obtained by the

three measurements substantiates the given explanation of the arrangement of the additives used in inhibiting the corrosion of zinc metal in acidic solution. However, they showed differences in absolute values for the inhibition efficiency. This observed discrepency could be attributed to the different experimental conditions under which each technique was carried out.

Conclusions

The carbazides tested are effective acid corrosion inhibitors for zinc. These carbazides are strongly adsorbed *via* the donation of the lone pair of electrons of O atom in the carbonyl group and S atom in the $C=S$ group and N atoms to zinc surface. The extent of % inhibition depends upon the molecular size and electron charge density on the active groups and atoms. The system was found to follows Bockris-Swinkels adsorption isotherm.

References

1. King, C. B.; Braverman, M. M. *J. Am. Chem. Soc.* **1932**, *54*, 1744.
2. Bergmann, C. W.; Evans, U. R. *Trans. Electrochem. Soc.* **1932**, *65*, 249.
3. Bianchi, G. *Corrosion* **1958**, *14*, 245t.
4. Sekerka, I.; Smreek, K. *Collect. Czech. Chem. Comm.* **1957**, *22*, 712.
5. Ya, Kolotyrkin, M.; Florionovich, G. M. *Itogi Nauk, Electrokhimiya Russia* **1971**, *7*, 5.
6. Evans, U. R. *The corrosion and oxidation of metals*; Edward Arnold London, 1959; p 86.
7. Kawai, S.; Kato, H.; Hayakawa, Y. *Denki Kagaku Oyobi Kogyo Butsuri Kagaku* **1971**, *39*(4), 288.
8. Grigorev, V. P.; Ekilik, V. V. *Protection of metals* **1968**, *4*, 1.
9. Subramanyam, N.; Ramakrishnaiah, K. *Indian J. Technol.* **1970**, *8*, 369.
10. Sharma, P.; Gaur, I. N. *J. Electrochem. Soc., India* **1976**, *25*(4), 183.
11. Jain, B. L.; Gaur, J. N. *Trans. SAEST* **1978**, *13*(1), 63.
12. Cavallavo, L.; Bolognesi, G. *Att. Acd. Sci., Ferrara* **1946-1947**, *24*(1).
13. Kuzntzov, V. A.; Iofa, Z. A. *J. Phys. Chem. (U.S.S.R.)* **1957**, *21*, 201.
14. Elze, J.; Fischer, H. *J. electrochem. Soc.* **1952**, *99*, 259.
15. Mylius, F. *Z. Metallk* **1922**, *14*, 233.
16. Shams El-Din, A. M.; Abd-Elkader, J. M. *Oberflache/surface* **1977**, *18*, 11.
17. Hackerman, N.; Makrides, A. C. *Ind. Eng. Chem.* **1954**, *46*, 523.
18. Evans, U. R. *The corrosion and oxidation of metals*; Edward Arnold, 1960; p 180.
19. Fouda, A. S.; Mdkour, L. H.; El-Shafei, A. A.; El-Asklany, A. H. Matwiss U. Werkstoffech, in press.
20. Moussa, M. N.; Taha, F. I.; Gouda, M. M.; Singab, G. M. *Corros. Sci.* **1976**, *16*, 379.
21. Bockris, J. O'M.; Swinkels, D. A. *J. Electrochem. Soc.* **1964**, *111*, 736.
22. Bockris, J. O'M.; Green, M.; Swinkels, D. A. *J. Electrochem. Soc.* **1964**, *111*, 743.
23. Bockris, J. O'M.; Reddy, A. K. *In Modern Electrochem., II*; Plenum: 1970; p 742.
24. Florry, P. J. *J. Chem. Phys.* **1942**, *10*, 51.
25. Huggins, M. L. *Ann. N.Y. Acad. Sci.* **1912**, *4*, 31.

The Influence of Simple Electrolyte on the Behaviour of Some Acid Dyes in Aqueous Media

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The influence of adding counter-ion such as Na^+ on the dimerization of the two sulphonated azo dyes, C.I. Acid Red 14 and C.I. Acid Red 17 in aqueous media has been studied spectrophotometrically. The observed hypochromic effect on increasing the amount of salt has been described. The dye concentration range where the dimerization equilibrium is applicable was chosen. No metachromatic behaviour was observed on changing the dye concentration and the amount of salt. This behaviour was attributed to the ability of the counter-ion to disrupt the structure of water as well as reducing the electrostatic repulsion forces between dye anions which will lead to the increase of aggregation tendency of the dye species.

Introduction

Ionic azo dyes are characterized by their ability to dye directly protein and polyamide fibers as well as polyacrylonitrile fibers under certain conditions.[1]

Further, aggregation of various classes of dyes is a very well known phenomenon.[2-6] Moulik *et al.*[7] have concluded that in the presence of salt, the π-electron repulsion between