458 *Bull. Korean Chem. Soc.* **1995**, Vol. 16, No. 5

M. M. El-Fass et al.

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.

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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

Behaviour of Some Acid Dyes in Aqueous Media

Bull. Korean Chem. Soc. 1995, Vol. 16, No. 5   459

two ionic dye molecules is small compared to the affinity of the hydrophobic association. In addition dislocation of hydration sheath (Franks icebergs)[8] surrounding the dye molecules by the added salts contributes to an entropy directed share to increase the aggregation tendency. Recently, further work on this point has confirmed and extended this interpretation.[9-11] The interaction of counter-ion with chromophoric groups of the dye ion has been investigated previously through different techniques. In view of all these studies, the formation of micelles seems very important in considering dye association as a model for the association of subunits in molecular biology.[12-13]

This study endeavors to investigate the aggregation ability of two monoazo disulphonic dyes by visible absorption measurements in the absence and presence of a coutner-ion such as Na^+. The effect of adding such foreign ions was discussed only in terms of the dimerization process of dye in aqueous media based on the Beer's law deviation data. The concentration range of 10^{-5} to 10^{-4} mol dm^{-3} where the dye species exists only in monomer $\rightleftharpoons$ dimer equilibrium was used. The effect of the electrostatic repulsion on dye aggregation is used to elucidate the molecular interaction of the system.

Experimental

The spectrophotometric measurements were performed with a Beckman spectrophotometer model 25 using a 1 cm width cell. The dye sample of C.I. Acid Red 14 (Edicol Carmoisine) was obtained from ICI (Imperial Chemical Industries Ltd, Dyestuff Division, England). C.I. Acid Red 17 (Naphthalene Bardaux) was obtained from Ciba Geigy Ltd, Basel, Switzerland. The dye samples were purified by recrystallization twice from 50% ethanol/water and dried in vacuum oven at 40 ℃. Their structures are given below:
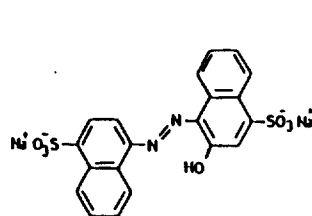

C.I. Acid Red 14 (Dye I)
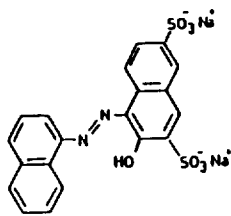
C.I. Acid Red 17 (Dye II)

The visible absorption spectra of solutions of the dyes were recorded. Each solution was prepared by dilution from a stock solution. Sodium chloride A.R. grade was used.

Different molarities (0.01-1.00 M) of salt were added to the dye solutions and left overnight in the dark before the spectrophotometric measurements were taken and to ensure attaining equilibrium.

Results and Discussion

The application of the maximum slope method[14] on C.I. Acid Red 14. & C.I. Acid Red 17 which is based on a simple equilibrium between monomer and a polymer of one distinct degree of association in aqueous media proved that these dyes give a good example of the dimeric state at 25 ℃. Anal-
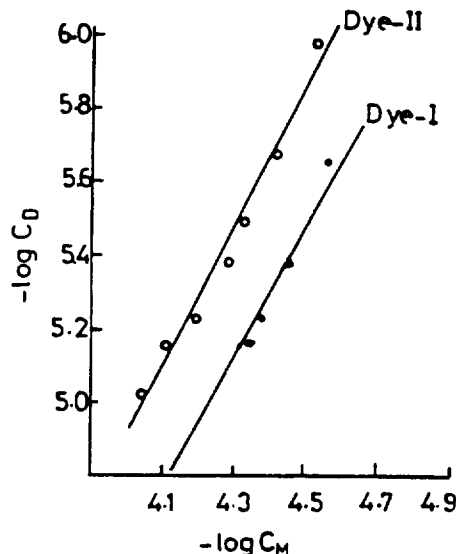

Figure 1. Logarithm monomer concentration as a function of dimer concentration of dye-I and dye-II in aqueous media at 25 ℃.
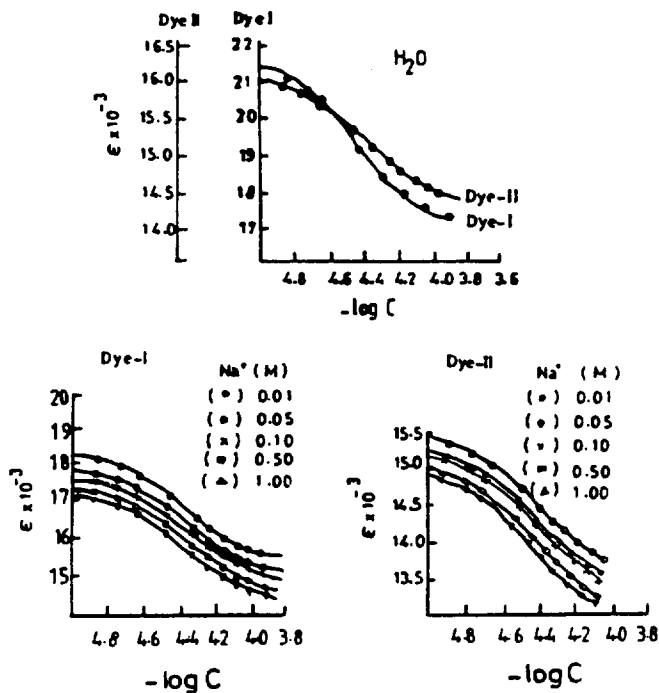
Figure 2. Relation between molar absorptivity and concentration for dye-I and dye-II in water and in different molarities of Na^+.

ysis of the present spectral data of these dyes in the concentration range used was ascertained by plotting the logarithmic monomer dye concentration C_M as a function of dimer dye concentration C_D (Figure 1). This plot shows good linearity for both dye-I and dye-II with correlation coefficient≈ 0.99. The aggregation number was found to be around 2 from the values of the slopes shown in Figure 1. In the present work a trial was made to investigate further the capability of the dimeric dye system to be extended to several other species more than the dimer. It is well known that
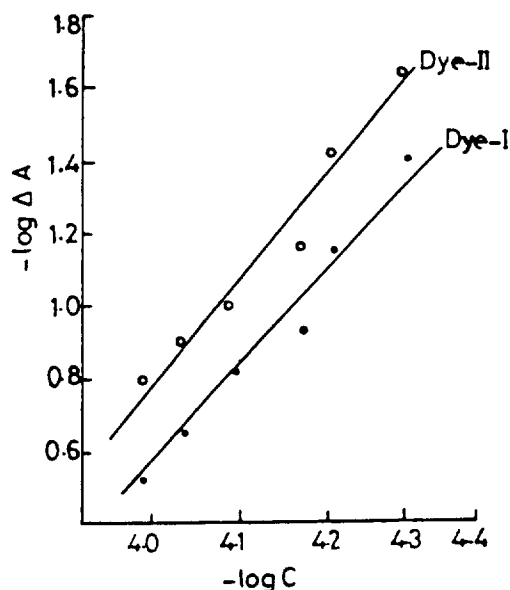
Figure 3. Plots of log ΔA against log C according to Pugh equation.

addition of salt increases the extent of dye association. Accordingly, the apparent deviation from Beer's law has been used to calculate the average aggregation number and constant as reported by Pugh *et al.*[15] and Moulik *et al.*[7] respectively in presence of NaCl using the following equation.

$$\text{Log } \Delta A = \log\left(K\frac{a^2}{b}\right) + \frac{3}{2}\log C \qquad (1)$$

where ΔA is the deviation in the absorbance A of the solution from the linear Beer's law plot, a is the probability of a photon being absorbed by a dye monomer which is equal to $\varepsilon_M \times 10^{-6}$ as ε_M is the extinction coefficient at infinite dilution obtained from Figure 2, C is the number of monomeric dye molecules, K and B are constnats. Thus a plot of log ΔA against log C should be linear with a slope of 3/2. These plots (Figure 3) for dye-I and dye-II are linear as predicted by Pugh theory and the slopes are 2.2 and 2.1 respectively which vary around the predicted value of 1.5, but in view of the simplified model, agreement is good.

Pugh *et al.* have proposed equations from 2-4 to calculate the average aggregation number N,

$$1 - \alpha = Aa/\Delta A \qquad (2)$$

$$M = M_o/1 - \alpha \qquad (3)$$

and

$$N = M/M_o \qquad (4)$$

where α is the monomer fraction, M is the average molecular weight of the aggregated molecule and M_o is the molecular weight of the monomer. Table 1 summarizes the different parameters obtained using these equations for dye-I and dye-II in aqueous media.

The hypochromic effect of added salts on the dimerization process of dye-I and dye-II in aqueous media (Figure 4) can be described quantitatively using equation 5 suggested by Moulik *et al.*[7]

Table 1. Variation of average aggregation number, with dye concentration in aqueous media

Dyc conc $\times 10^3$ mol dm^{-3}	Dye-1				Dye-II			
	a	1-α	M	N	a	1-α	M	N
10.96	0.018	0.136	3683	7.30	0.015	0.166	3021	6.00
9.00	0.018	0.146	3444	6.80	0.015	0.171	2945	5.80
7.67	0.018	0.182	2754	5.40	0.015	0.179	2804	5.50
6.00	0.018	0.186	2701	5.40	0.015	0.110	2395	4.70
5.48	0.018	0.273	1843	3.70	0.015	0.247	1451	2.80
4.38	0.018	0.395	1270	2.50	0.015	0.340	1142	2.20
3.28	0.018	0.500	1004	2.00	0.015	0.526	950	1.90

Table 2. The values of ΔA and N of dye-I and dye-II in different molarities of Na$^+$

Dyc conc $\times 10^3$ mol dm^{-3}	Dye-I									
	0.01 M		0.05 M		0.10 M		0.50 M		1.00 M	
	ΔA	N	ΔA	N	ΔA	N	ΔA	N	ΔA	N
10.96	0.26	7.80	0.27	8.20	0.27	8.50	0.31	9.90	0.32	10.30
9.00	0.19	6.90	0.21	7.80	0.21	8.10	0.23	9.00	0.23	9.20
7.67	0.13	5.70	0.15	6.60	0.15	6.70	0.16	7.30	0.17	7.70
6.00	0.11	5.80	0.12	6.50	0.11	6.60	0.12	7.10	0.12	7.20
5.48	0.05	3.90	0.07	4.40	0.07	4.60	0.09	5.50	0.09	5.70

Dyc conc $\times 10^3$ mol dm^{-3}	Dye-II									
	0.01 M		0.05 M		0.10 M		0.50 M		1.00 M	
	ΔA	N	ΔA	N	ΔA	N	ΔA	N	ΔA	N
10.96	0.17	6.70	0.18	7.10	0.17	7.20	0.18	7.50	0.83	7.60
9.00	0.14	6.70	0.14	6.80	0.14	6.80	0.14	7.10	0.15	7.50
7.67	0.10	5.60	0.10	5.80	0.10	5.90	0.11	6.40	0.11	6.50
6.00	0.08	5.30	0.07	5.10	0.07	5.30	0.08	5.80	0.08	6.10
5.48	0.05	3.80	0.06	4.70	0.06	5.00	0.06	5.20	0.07	5.70

$$K_A = \varepsilon_M(\varepsilon_M C - A)/2A \qquad (5)$$

where ε_M, C and A are as defined before and K_A is the aggregation constant. The values of ΔA, N and K_A are given in Tables (1-3) for dye-I and dye-II in aqueous media and in the presence of Na$^+$. Apart from the region of great ionic strength, the interaction between dye ions and counter-ions would not be merely because of the Debye-Hückel effects. This could be due to the high solubility of the disulphonic acid dye in water than in the presence of NaCl.[16-17] Usually amphiphilic interaction as on the following scheme is choice.

In addition, the location of sulphonic groups in dye-I and dye-II also should affect the aggregation of dye molecules. The apparent high solubility of dye-II due to the presence of sulphonic groups in two different aromatic rings gives low K_A values of dye-II than dye-I as reported in Table 3 in aqueous media. More association is observed from the results in Table 3 in presence of NaCl. This could be due

Table 3. Values of aggregation constant K_A in water and different molarities of Na^+ calculated from Moulik equation

Dye conc$\times 10^3$ mol dm^{-3}	Dye I					
	H_2O	0.01 M	0.05 M	0.10 M	0.50 M	1.00 M
10.96	678	729	771	792	949	949
9.00	584	601	682	762	706	763
7.67	419	542	594	538	588	622
6.00	310	429	475	475	476	448
5.48	207	284	306	255	315	342
	Dye II					
	H_2O	0.01 M	0.05 M	0.10 M	0.50 M	1.00 M
	423	554	570	563	595	598
	330	478	536	537	595	566
	329	368	467	476	501	532
	240	294	312	340	395	395
	153	230	231	282	337	360
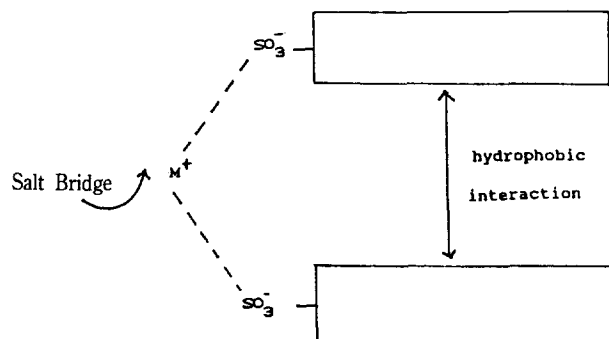
to the melting of the iceberg structure with rearrangement of the dye molecules.[7] Similar. explanation to the one but forward by Robinson[13] and Mukherjee[18] could demonstrate the behaviour of Acid Red 14 and 17 in the presence of NaCl. The inorganic salt when present at higher concentrations can function as a water structure disrupting agent with entropy gain and help in dimerization. Besides altering the water structure may also bestow an electrostatic compression on two dye molecules by the positive atmosphere surrounding the central dye anions thus leading to increase associa-

tion phenomenon.

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