An Amperometric Study of the Aggregation of Some Acid Dyes

AFAF A R EL-MARIAH*, ZAKYA H KAFAFI & EGLAL A MOUSSA

Chemistry Department, Al-Azhar University (Girls), Cairo, Egypt

Received 1 March 1983; revised 14 February 1984; accepted 27 April 1984

Diffusion co-efficients of mono-, di-, and tri-sulphonated acid dyes have been calculated from their diffusion-controlled limiting currents in buffers in aqueous and mixed solvent systems. From these values, the molecular weights of the aggregated dyes are obtained. The results have been interpreted in terms of a monomer-dimer equilibrium. The dimerization constant decreases upon addition of organic solvents. This indicates that organic solvents cause de-aggregation. The results show that the aggregation number increases on decreasing the temperature, even for dilute solutions. Accordingly, the value for the dimerization constant increases.

Hillson and McKay[1] calculated the aggregation number of some dyes by using the polarographic technique. The method has been applied to different types of dyes, and studies on a series of acid dyes have revealed that the solutions are monodisperse until a critical concentration is reached when dimer is formed[2]. The formation of dimer only has been found by other workers using Orange II and Orange 8 (refs 3-5). Malik and Gupta[6] found that Solochrome Yellow 2 GS exists in the monomeric form at low concentrations $(1.0-9.0 \times 10^{-5} M)$. Higher concentrations $(5.0-6.0 \times 10^{-4} M)$ produce dimers. These concentrations vary from one dye to the other. Duff, Kirkwood and Stevenson[7] used polarography to investigate the effect of structural differences on the aggregation of groups of closely related monoazoacid dyes. The results showed that the extent of aggregation increases with increasing concentration within the range $0.5-5.0 \times 10^{-4} M$. We report here the results of our studies on the aggregation of some acid dyes.

Materials and Methods

C.I. Acid Red 88 and 27 (I.C.I., England), C.I. Acid Red 141 (Clayton Aniline Co. Ltd., England), C.I. Acid Red 13 (Bayer A.G., Leverkusen, Germany), were used after purification on ion-exchange resin as described by Coward[8] and El-Mariah[9]. The purification of the different organic solvents was carried out by the method of Moussa[10]. The polarographic measurements were carried out on a recording polarograph Model Lp 7 type 701. The *H*-type cell consisted of two limbs separated by a short agar bridge. Capillary characteristics were: drop time = 1.25 sec; rate of mercury flow = 6.59 mg/sec at a column height of 35 cm. All dye solutions were buffered at *p*H 3.30-8.15 using the universal buffer solutions; these were de-aerated with nitrogen. Measured limiting currents were corrected by subtraction of the residual current at the same potential.
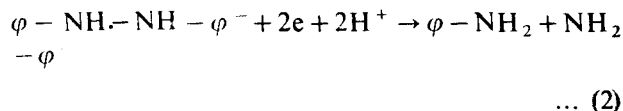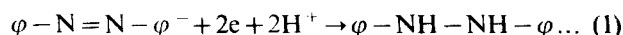
Results and Discussion

Well-defined plateau regions were obtained for the polarograms of all the dyes used under different conditions. A linear dependence of the mean limiting current (i_d) on concentration was established in each instance. In addition, the dependence of the limiting current on the mercury head in the range 20-50 cm was investigated. In each buffer and solvent system, i_d was found to be directly proportional to $\sqrt{h}$. These results show that the limiting currents are diffusion controlled.

For all the investigated dyes, half-wave potential becomes more negative with increasing *p*H, as is expected for the processes that consume protons. In addition, the $E_{1/2}$ values tend to become slightly more negative with increasing concentration and solvent percentage. The logarithmic analysis of the waves in aqueous and non-aqueous media were carried out. The results suggest the participation of 4 electrons/molecule in the reduction process[7,11,16].

Reduction mechanism and diffusion coefficients

The reduction of azo compounds in aqueous medium at DME leads to the formation of the hydrazo compound (Eq. 1) and amines (Eq. 2)[15].

$$\varphi - N = N - \varphi^- + 2e + 2H^+ \rightarrow \varphi - NH - NH - \varphi \dots \text{(1)}$$

$$\varphi - NH - NH - \varphi^- + 2e + 2H^+ \rightarrow \varphi - NH_2 + NH_2 - \varphi$$

$$\dots \text{(2)}$$

In addition, an intermediate step has been described in which electron-transfer (Eq. 1) is followed by disproportionation of the hydrazo compound (Eqs 2, 3).

$$2\varphi - NH - NH - \varphi^- \rightarrow \varphi - NH_2 + \varphi^- - NH_2$$
$$+ \varphi - N = N - \varphi^- \quad \ldots (3)$$
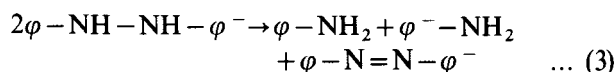
The polarograms of the investigated dyes illustrate that the reduction process takes place in one single wave in acid and slight alkaline media.

The wave is mainly diffusion-controlled with a partial kinetic component as is clear from the plot of $\log i_d$ versus $\log h$. Hence, the disproportionation reaction (Eq. 3) either plays no part in the reduction process or it is a very rapid step.

The polarographic reduction of the acid dyes in this investigation follows the above overall scheme. The values of the diffusion coefficients obtained in the present investigation agree with those given by Powell $(2.4\text{-}2.8 \times 10^{-6})$[15].

Aggregation number from polarographic measurements

By observing the dependence of wave height on the height of the mercury column, it was established that the polarographic waves due to the dyes are diffusion-controlled. Diffusion coefficients were calculated by

Table 1—The Polarographic Data of Acid Dyes at 25°C

Dye Conc. $(M \times 10^4)$	Organic solvent (%, v/v)	$D^{\frac{1}{2}} \times 10^3$ (cm. sec$^{-\frac{1}{2}}$)	Aggregation number (n)	$\log K_D$
	Dye: Acid Red 88			
2.50	50% Dioxane	2.02	1.1	3.00
3.00	(pH 3.3)	1.93	1.2	3.63
4.00		1.74	2.6	3.15
	$(\Delta G = -21.92 \text{ kJ mol}^{-1})$			
5.51	2% Benzyl alcohol		1.0	3.62
5.81	(pH 8.15)	3.15	1.3	3.15
6.50		3.02	1.5	3.02
7.50		2.92	1.7	2.92
	$(\Delta G = -23.8 \text{ kJ mol}^{-1})$			
3.07	5% Butanol	1.89	1.6	4.23
3.78	(pH 3.3)	1.83	2.0	3.41
5.15		1.73	2.6	3.62
	$(\Delta G = -25.73 \text{ kJ mol}^{-1})$			
2.60	5% Butanol	1.78	2.3	4.43
3.07	(pH 8.15)	1.75	2.5	4.09
3.30		1.70	2.9	3.82
	$(\Delta G = -26.48 \text{ kJ mol}^{-1})$			
	Dye: Acid Red 27			
3.23	H₂O,	2.10	0.7	3.57
4.75	(pH 6.55)	2.07	0.7	3.70
5.50		2.00	0.8	4.95
	$(\Delta G = -17.4 \text{ kJ mol}^{-1})$			
4.00	H₂O,	2.00	0.9	3.74
4.75	(pH 8.15)	1.95	1.0	3.48
5.00		1.88	1.2	3.31
	$(\Delta G = -15.86 \text{ kJ mol}^{-1})$			

Table 1—The Polarographic Data of Acid Dyes at 25°C—*Contd*

Dye Conc. $(M \times 10^4)$	Organic solvent (%, v/v)	$D^{\frac{1}{2}} \times 10^3$ (cm. sec$^{-\frac{1}{2}}$)	Aggregation number (n)	$\log K_D$
2.45	2% Benzyl alcohol,	2.00	0.8	1.70
4.00	(pH 3.3)	2.01	0.8	2.57
4.75		1.99	1.1	2.78
	$(\Delta G = -16.19 \text{ kJ mol}^{-1})$			
1.65	5% Butanol,	2.10	0.7	3.48
4.75	(pH 2.15)	2.04	0.8	3.58
5.49		2.03	0.8	3.64
	$(\Delta G = -16.02 \text{ kJ mol}^{-1})$			
	Dye: Acid Red 141			
2.47	H₂O,	1.97	1.3	4.12
2.75	(pH 3.30)	1.74	2.5	3.55
3.00		1.61	3.0	3.22
	$(\Delta G = -24.84 \text{ kJ mol}^{-1})$			
1.51	H₂O,	1.98	1.3	3.41
1.86	(pH 6.55)	1.86	1.8	3.33
2.17		1.60	2.2	3.12
	$(\Delta G = -27.78 \text{ kJ mol}^{-1})$			
1.86	5% Dioxane	2.17	0.8	3.85
2.47	(pH 4.05)	1.87	1.7	3.28
2.75		1.84	1.9	3.20
	$(\Delta G = -21.330 \text{ kJ mol}^{-1})$			
1.52	5% Butanol	2.24	0.7	5.06
2.47	(pH 3.30)	1.98	1.3	3.87
1.94		1.94	1.4	3.87
	$(\Delta G = -20.17 \text{ kJ mol}^{-1})$			
0.76	5% Butanol	2.05	1.1	4.87
1.52	(pH 6.55)	1.84	1.9	4.57
1.86		1.80	2.1	4.24
	$(\Delta G = -26.36 \text{ kJ mol}^{-1})$			
0.76	25% Ethanol	1.89	1.1	3.12
2.47	(pH 3.30)	1.85	2.7	3.16
2.70		1.81	3.3	3.11
	$(\Delta G = -22.18 \text{ kJ mol}^{-1})$			
0.76	5% Ethanol	2.05	1.6	4.08
2.47	(pH 8.15)	1.72	1.8	3.83
2.75		1.66	2.1	3.60
	$(\Delta G = -21.34 \text{ kJ mol}^{-1})$			
	Dye: Acid Red 13			
4.00	H₂O,	2.21	0.6	3.25
4.84	(pH 2.85)	2.05	0.9	2.99
5.60		1.91	1.3	2.81
	$(\Delta G = -19.66 \text{ kJ mol}^{-1})$			
2.49	25% Dioxane	2.10	0.8	4.24
3.00	(pH 3.3)	1.97	1.1	5.97
3.50		1.92	1.3	4.55
	$(\Delta G = -20.33 \text{ kJ mol}^{-1})$			
3.29	5% Dioxane	2.11	0.8	3.75
4.07	(pH 4.05)	2.10	0.8	3.68
4.50		2.04	0.9	3.50
5.00		1.98	1.1	3.31
	$(\Delta G = -23.26 \text{ kJ mol}^{-1})$			

means of the Ilkovic equation using the number of electrons equal to 4 for this type of dyes[7,11,16]. From the diffusion coefficients (D), the molecular weights (M) were calculated by means of the relationship established by Hillson and McKay[1],

$$\text{Log}\,M = -11.64 - 2.65\log D$$

It is clear from the results in Table 1, that the extent of aggregation increases with increasing concentration of dyes. Also, it is evident that the association to dimer may be the dominant process for the monosulphonic acid dyes. The disulphonic acid dyes are slightly aggregated while the trisulphonic acid dye is molecularly dispersed in aqueous solution.

The dimerization constant

The present results (Table 1) can be interpreted in terms of a monomer-dimer equilibrium by using the following equation[7],

$$k_D = \frac{\alpha}{2C(1-\alpha)^2}$$

where α is the fraction of dye dimerized and C is the total concentration of dye.

Table 2 shows polarographic data obtained by Coates[16] and Duff[7]. One notices that there is a good agreement between the values of the dimerization constants as well as the diffusion coefficients obtained by three different studies. There is a constant decrease in the value of the diffusion coefficient as the dye concentration increases. The dimerization constant shows only small change with the dye concentration.

Thermodynamics of aggregation

An attempt has been made to investigate the thermodynamic properties (ΔG° for the four acid dyes, and ΔG°, ΔH and ΔS^c for Red 141). The standard free energy change for the formation of dimer is given by $\Delta G_D^\circ = -2.303\,RT\log K_D$. The free energy and heat of formation are related via the entropy of formation by the relation $\Delta G_D^\circ = \Delta H_D^\circ - T\Delta S_D^\circ$.

The values of ΔG° obtained using the above equation are given in Table 1. The free energy change for Acid Red 141 at 3.0°C is found to be -26.23 kJ mol^{-1}. This value at the low temperature indicates the great tendency of the dye to aggregate.

Table 2—Diffusion Coefficients and Dimerization Constants at 25°C for Acid Dyes

Conc. ($M \times 10^4$)	$D^{\frac{1}{2}} \times 10^3$ (cm. sec$^{-\frac{1}{2}}$)	$\log K_D$
Dye: C.I. Acid Orange 12[7]		
0.5	2.15	3.28
1.0	2.12	3.32
2.0	2.01	4.09
3.0	1.97	4.50
5.0	1.94	4.95
Dye: C.I. Mordant Violet 5[14]		
0.80	2.02	2.71
1.66	1.98	3.10
4.15	1.96	2.87
6.22	1.92	3.16
8.30	1.82	4.30

The standard entropy change of dimerization for Red 141 has been also calculated. It is found to be -71.63 J deg^{-1} mol^{-1} at 14°C using the equation $\Delta S^\circ = \dfrac{\Delta H^\circ - \Delta G^\circ}{T}$. This value is comparable with the one obtained by Coates for similar dyes[16] ($\Delta S^\circ = 41.84$-83.68 J deg^{-1} mol^{-1}).

References

1 Hillson P J & McKay R B, *Trans Faraday Soc*, **61** (1965) 374.
2 Iyer S R S & Singh G S, *Dyers Colourist*, **89** (1973) 128.
3 Milicovic B & Eigenmann G, *Helv chim Acta*, **47** (1964) 1039.
4 Iyer S R S & Singh G S, *Kolloid Z Z Polymer*, **242** (1970) 1196.
5 Sivaraja Iyer S R & Singh G S, *Kolloid Z Z Polymer*, **242** (1970) 1196.
6 Malik W U & Gupta P N, *J electroanal Chem Interfacial Electrochem*, **62** (2) (1975) 444.
7 Duff O G, Kirkwood D J & Stevenson D M, *J Soc Dyers Colourists*, **93** (8) (1977) 303.
8 Coward P M & Nursten H E, *American Dyestuff Reporter*, **53** (1964) 325.
9 El-Mariah, Afaf A R & Nursten H F, *J Soc Dyers Colourists*, **82** (1966) 132.
10 Mousa E A, *Ph D Dissertation*, Al-Azhar University for Girls (1980).
11 Valko, E, *J Soc Dyers Colourists*, **55** (1939) 173.
12 Cabral J O & Turner H A, *J Soc Dyers colourists*, **72** (1956) 158.
13 Gemeva I & Jehicka V, *Colln Czech Chem Commun*, **37** (1972) 3994.
14 Islam A M, El-Mariah, Afaf A R, Aboul-Fetouh M S, Salem K M M & Labib A, *Leather Science*, Madras, **21** (1974) 12.
15 Powell E E & Snowden C J, *Analyst*, **100** (1975) 503.
16 Coates E, *J Soc Dyers Colourists*, **85** (1969) 355.