

POLAROGRAPHIC BEHAVIOUR OF SOME ACID DYES

Nawal A. A. Alarfaj, Zinat M. EL-Khayate and Eglal A. Moussa*
 Women Student-Medical Studies and Sciences, Department of Chemistry,
 College of Science, King Saud University
 P.O. Box 22452, Riyadh 11495, Saudi Arabia
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يشتمل هذا البحث على دراسة السلوك البولاروجرافي لثلاث صبغات حمضية الكروسين البرتقالية G والاليزارين البنفسجية N والصبغة البرتقالية 10 في محاليل مائية منظمة. وقد أوضحت نتائج البحث أن قيم جهد نصف الموجه ($E_{1/2}$) تنزاح في اتجاه القيم الأكثر سالبية بزيادة الرقم الهيدروجيني لمحلول الصبغة المستخدمة وهو ما يتوقع من العمليات المستهلكة للبروتونات. كما بينت النتائج التي تم الحصول عليها أن البولاروجرام الخاص بكل صبغة يحتوي على موجة واحدة غير عكسية. بالإضافة إلى ما سبق تضمن البحث تعيين معامل الانتشار (D) لكل صبغة من الصبغات الثلاث عند أرقام هيدروجينية مختلفة. وبناءً على افتراض حدوث التوازن التالي: Monomer \rightleftharpoons dimer يمكن حساب ثابت التجمع (K) لكل صبغة من الصبغات المستخدمة.

The polarographic behaviour of three acid dyes Crocein Orange G, Acid Alizarin Violet N and Acid Orange 10 in aqueous buffered solutions is represented. It is clear from the obtained results that the half-wave potential shifts to more negative values as to be expected for processes that consume protons. The results indicate that the process of reduction is irreversible. The polarographic diagrams of the studied dyes gives one difined irreversible wave. The interpretation of the polarographic reduction wave was discussed. The diffusion coefficients of the three dyes were obtained. The aggregation constant in aqueous solution has been calculated in terms of a monomer-dimer equilibrium.

Keywords: Acid dyes, Polarographic behavior.

INTRODUCTION

A number of techniques have been developed to study the behaviour of dyes in different media. The polarographic technique was found to be simpler and faster, thus enabling the behaviour and aggregation of dyes to be studied in a reasonable time [1,2].

Acid dyes constitute an important class of azo dyes used for dyeing fibers [3,4], but little attention has been paid to their polarographic reduction. The polarographic behaviour of three imordant dyes in non aqueous buffered solutions has been studied. The results showed that half-wave potential shifts to more negative values by increasing pH. The results showed more than one wave over the pH range examined [5].

The tendency of many dyes to associate in aqueous solutions has been recognized and it has been suggested that this tendency is universal for dyes. An understanding of the association of dyes in water is of importance in both thermodynamic and kinetic studies of dyeing systems since almost all textile dyes are still applied from aqueous systems [6,7].

Polarography has been used to measure the extent of aggregation of a number of monoazo acid dyes in aqueous solutions. The results obtained showed the effect of increasing the hydrophobic character of the dye and position of the hydrophilic sulphonate groups on aggregation [8].

The diffusion coefficient, and aggregation number of some sulphonated acid dyes were calculated from their diffusion-controlled limiting currents in buffers and mixed solvents [9].

* To whom all correspondence should be addressed

EXPERIMENTAL

Materials and reagents

Three Acid dyes, Crocein Orange G, Acid Alizarin Violet N and Acid Orange 10, were obtained from Aldrich chemical company. They used after purification by recrystallisation from 50% ethanol. Solutions of the dyes in the concentration range of 5×10^{-3} M for Acid Alizarin Violet N and 2.5×10^{-3} M for each Acid orange 10 and Crocein Orange G were prepared. This was done by diluting stock solutions of the dyes with bidistilled water. The required pH was maintained by addition of Britton Robinson buffers [10]. Before recording the polarographic wave the solutions purg by nitrogen for 5 min.

Apparatus

The polarographic measurements were carried out on recording computerized Polarograph model (746 VA Trace Analyzer, Metrohm, Switzerland).

The apparatus contains the static mercury drop electrode and reference electrode (Ag/AgCl).

RESULTS AND DISCUSSION

The wave form and limiting current

The typical polarograms I (mA) vs E (-V) for the three acid dyes in pH range (2.44–12.39) are shown in Figs (1-3). From these polarograms it is found that polarograms of the three dyes show only one wave for each dye over the used pH range. The height of the wave also found to be independent of pH.

Effect of pH on the half - wave potential ($E_{1/2}$)

The $E_{1/2}$ values of the three dyes at different pHs are given in Tables (1-3). The results obtained show that the half wave potentials ($E_{1/2}$) for these dyes shift to more negative values by the increase of pH, denoting that electro- reduction process is pH dependant and accompanied by consumption of hydrogen ions.

The Reversibility of the waves

The reversibility of the electro-reduction process was examined by the fundamental equation of logarithmic analysis of the waves [9] obtained at different pH where straight lines are

obtained at different pH and the slopes denoting an irreversible reduction process. Each slope is equal to at 25°C (Table 1-3).

Where n_a is the number of electrons involved in the reduction process and α is the transfer coefficient. The results suggest participation of 4 electrons / molecule of each three acid dyes in the reduction process [8,9].

It is observed from the results that the dyes are reduced irreversibly at all ranges of pH. Similar conclusion was reached by Malik and Gupta [11] using similar dyes using full equation:

$$E = E_{1/2} - \frac{0.0591}{\alpha n_a} \log \frac{1}{I_d - I}$$

the results give the same value for αn_a as the one obtained from the graphical method.

The reduction process must involve the consumption of H^+ ions which can be obtained from the variation of $E_{1/2}$ with pH using the following equation [12], Table (1-3):

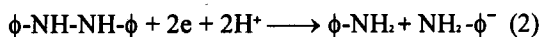
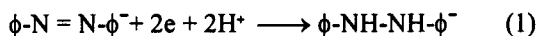
$$\Delta E_{1/2} / \Delta pH = \frac{0.0591}{\alpha n_a} m_H^+$$

where m_H^+ is the number of protons involved in the reduction process.

For the irreversible wave the slope of $E_{1/2}$ vs pH plot is equal to $\frac{0.0591}{\alpha n_a} m_H^+$. The results show

that the ratio $m_H^+ / \alpha n_a$ is always equal to approximately one all over the pH range.

The reduction processes of azo compounds in aqueous media with the dropping mercury electrode (DME) lead to formation of the hydrazo compounds (eq.1) and amines (eq.2), [13]:



In addition, an intermediate step has been described in which electron-transfere step (1) is followed by disprotonation of the hydrazo compound (eq. 2,3)



The polarographic reduction of the acid dyes in this investigation follows the above mechanism.

Table 1: The polarographic Data of Acid Alizarine Violet N ($5 \times 10^{-3} \text{M}$) at different pH at 25°C

pH	i_d	$E_{1/2} (-V)$ (Ag/AgCl)	Slope (S) Analysis	α_{na}	m_H^+
2.44	7.5	0.21	15	0.886	0.788
3.6	8.5	0.3	29.166	1.72	1.53
4.64	-	0.35	20	1.18	1.04
5.25	8.6	0.44	23.9	1.41	1.3
6.61	4.95	0.475	15.38	0.909	0.8
7.68	13	0.52	23.81	1.407	1.24
8.53	9.75	0.535	39.3	2.32	2.08
10.53	10.5	0.55	37.8	2.23	2
11.83	10.27	0.56	20.83	1.23	1.08
12.39	11	0.575	33.3	1.97	1.73

Table 2: The Polarographic Data of Acid Orange10 ($2.5 \times 10^{-3} \text{M}$) at different pH at 25°C

pH	i_d	$E_{1/2} (-V)$ (Ag/AgCl)	Slope (S) Analysis	α_{na}	m_H^+
2.44	9	0.13	10.53	0.62	0.45
3.97	-	-	-	-	-
5.15	20	0.64	24.14 53.6	0.83 3.17	1.05
6.44	19	0.76	17.5	1.03	0.75
7.82	12	6.78	23.08	1.4	1.0
8.49	17	0.83	26.9	1.6	1.16
9.08	17.8	0.85	25	1.5	1.075
10.35	14.2	0.915	11.43	0.7	0.49
11.74	10	0.94	9.5 16.96	0.6 1.00	0.41 0.73
12.25	6.25	0.99	21.4	1.3	0.91

Table 3: The polarographic Data of Crocein Orang G ($2.5 \times 10^{-3} \text{M}$) at different pH at 25°C

pH	i_d	$E_{1/2} (-V)$ (Ag/AgCl)	Slope (S) Analysis	α_{na}	m_H^+
2.44	13	0.22	25	1.48	2.125
4.62	12	0.405	9.26	0.55	0.79
5.45	13.4	0.52	5.88	0.35	0.5
6.44	1375	0.652	11.9 30.95	0.70 1.83	1.01 2.66
7.68	14	0.69	18.2 56.7	1.08 3.35	1.5
8.73	14.5	0.75	16.25 84.37	0.96	1.39
9.86	13.5	0.808	34.2 141.67	2.02	2.9
10.53	-	-	-	-	-
11.47	14.5	0.812	39	2.30	3.3
12.23	-	-	-	-	-

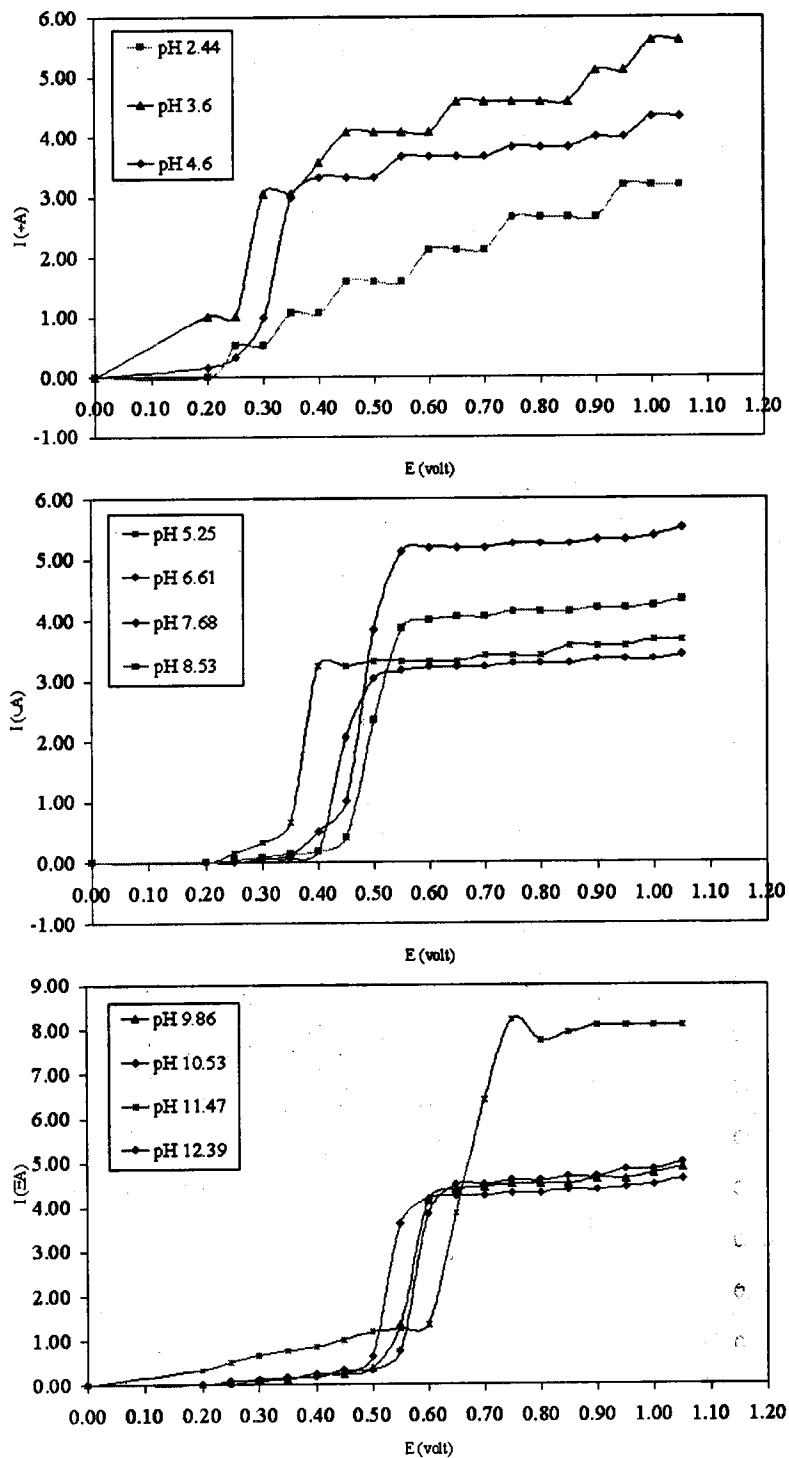


Fig. 1: Polarograms of Acid Alizarin Violer N (5×10^{-3} M) at different pH (a) 2.44–4.6, (b) 5.25–8.53, and (c) 9.86–12.39.

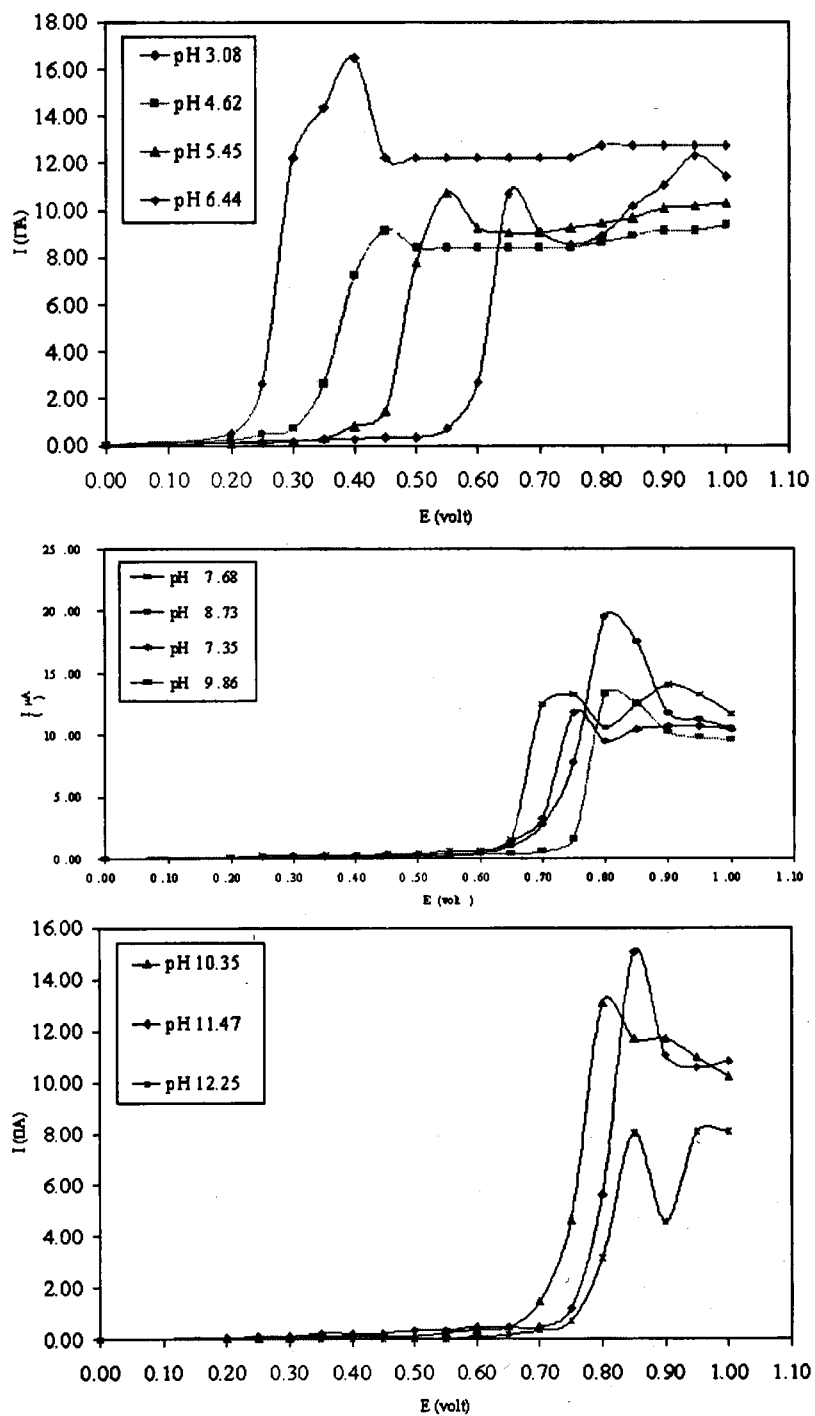


Fig. 2: Polarograms of Crocin Orange G (5×10^{-3} M) at different pH (a) 3.08–6.44, (b) 7.68–9.86 and (c) 10.35–12.25.

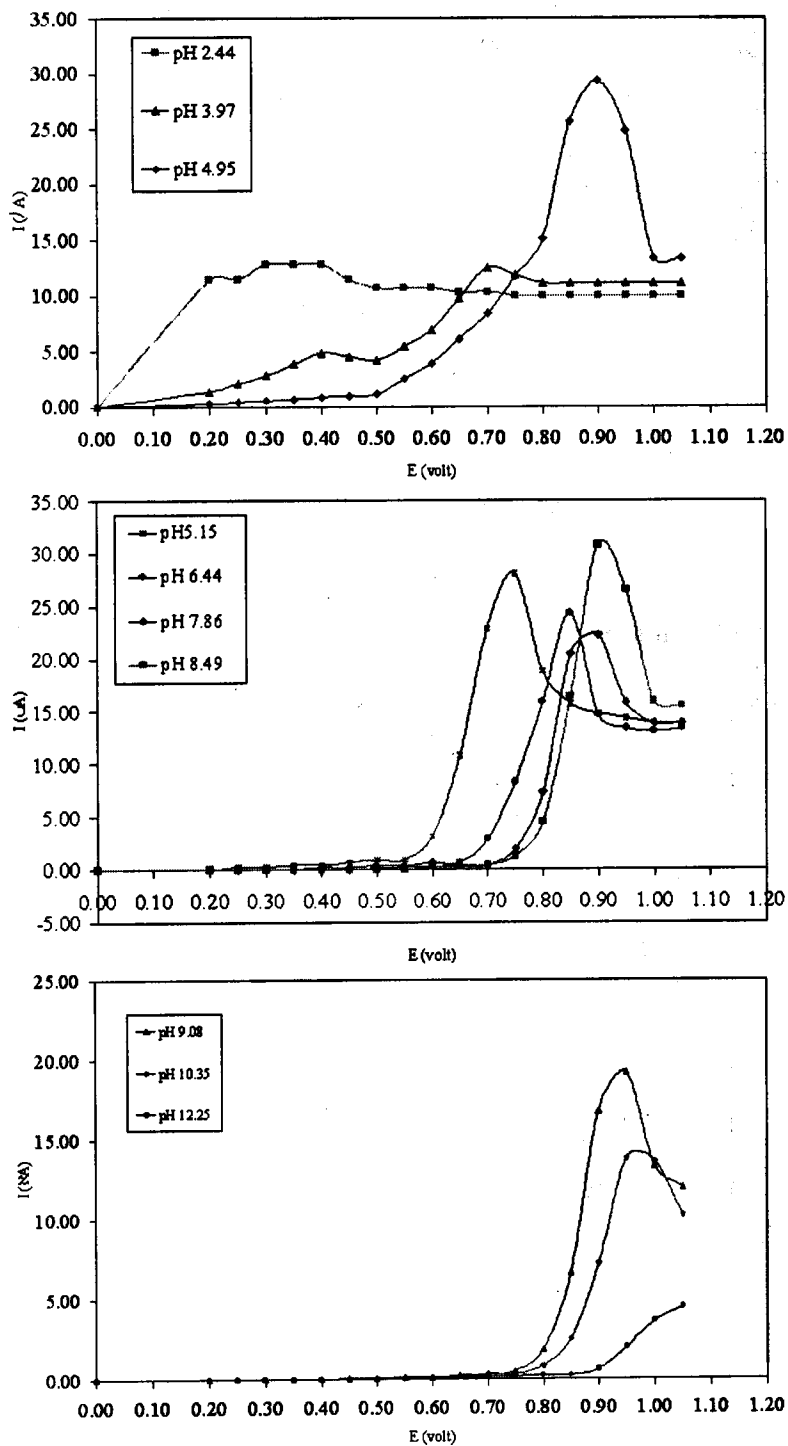


Fig. 3: Polarograms of Acid Orange 10 (5×10^{-3} M) at different pH (a) 2.44–4.95, (b) 5.15–8.49 and (c) 9.08–12.25.

The diffusion coefficients were calculated by means of the Ilkovic equation using the number of electrons equal to 4 for this type of dyes [8].

The values of the diffusion coefficients obtained in the present investigation for the three acid dyes agree with those given by Powell [13] and El. Mariah [9], (Table 4).

Aggregation constant from polarographic measurements

It is of interest to consider how the present results can be interpreted in terms of a monomer-dimer equilibrium using the following equation:-

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

Where (K_D) is the dimerization constant, (C) is the total concentration of dye and (α) is the fraction of dye dimerized which equals:

$$\alpha = \frac{D_1^{1/2} - D^{1/2}}{D_1^{1/2} - D_2^{1/2}}$$

The diffusion coefficient $D_2^{1/2}$, cannot be obtained from the diffusion current at high dye concentrations, as the aggregate is greater than dimers [8]. However, an estimation of D_2 may be obtained by using Hillson and McKay equation [14], which gives:

$$D_2^{1/2} = 0.877 D_1^{1/2}$$

The $D_1^{1/2}$ values are obtained by extrapolating the measured diffusion coefficients (D) of zero concentration. The results for the investigated dyes are given in Table (4).

Table 4: Diffusion coefficient's and Aggregation constant's for the studied Acid dyes .

1. Crocein Orange G

Dye conc. ($M \times 10^{-3}$)	$D^{1/2} \times 10^{-3}$ (cm. sec $^{-1/2}$)	$D_1^{1/2} \times 10^{-3}$ (cm. sec $^{-1/2}$)	$D_2^{1/2} \times 10^{-3}$ (cm. sec $^{-1/2}$)	$K_D \times 10^3$
pH = 1.5	1.28			
2.5	0.77			
3.5	0.55	1.65	1.447	0.427
4.5	0.43			
5.0	0.38			

2. Acid Alizarin violet N

Dye conc. ($M \times 10^{-3}$)	$D^{1/2} \times 10^{-3}$ (cm. sec $^{-1/2}$)	$D_1^{1/2} \times 10^{-3}$ (cm. sec $^{-1/2}$)	$D_2^{1/2} \times 10^{-3}$ (cm. sec $^{-1/2}$)	$K_D \times 10^3$
pH = 2.5	0.19			
3.5	0.43			
4.5	0.33	0.72	0.631	0.108
5.0	0.30			

3. Acid Orange 10

Dye conc. ($M \times 10^{-3}$)	$D^{1/2} \times 10^{-3}$ (cm. sec $^{-1/2}$)	$D_1^{1/2} \times 10^{-3}$ (cm. sec $^{-1/2}$)	$D_2^{1/2} \times 10^{-3}$ (cm. sec $^{-1/2}$)	$K_D \times 10^3$
pH = 2.5	0.66			
3.5	0.47			
4.5	0.37	0.795	0.697	1.038
5.0	0.33			

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