Electrochemical Studies of Progressively Alkylated Thiazine Dyes on a Glassy Carbon Electrode (GCE) in Water, Ethanol, and Triton X-100 Media[†]

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Cyclic voltammetric investigations have been performed on the clean glassy carbon electrode (GCE) at (25 ± 0.1) °C on five progressively alkylated thiazine dyes, namely, thionine (Th), methyl thionine (Azure C), dimethyl thionine (Azure A), trimethyl thionine (Azure B), and tetramethyl thionine (methylene blue) in water, water−ethanol, and water−Triton X-100 media. Diffusion coefficient values of the dyes, measured from the electrochemical data in different media, are clearly influenced by the effect of progressive alkylation to the thionine moiety along with the solvent property. In aqueous media the values of diffusion coefficient fall in the range of $(2.66 \cdot 10^6$ to $5.70 \cdot 10^6)$ $cm^2 \cdot s^{-1}$, whereas in presence of ethanol and Triton X-100 the rather lower ranges of $(1.16 \cdot 10^6$ to $3.70 \cdot 10^6)$ $cm^2 \cdot s^{-1}$ and $(0.76 \cdot 10^6$ to $1.80 \cdot 10^6)$ $cm^2 \cdot s^{-1}$ are observed, respectively. At higher pH's the voltammograms display cathodic and anodic post/prepeaks which are the characteristics of the strong adsorption of reactants and/or products. Along with different electrochemical parameters the kinetic parameters of electrode processes have also been determined.

Introduction

Cyclic voltammetry (CV) is perhaps the most powerful electroanalytical technique for the study of electroactive species. Various electrochemical properties of photogalvanic solution have been studied successfully by many workers with the aid of this technique.[1−4] The ease of the measurement has also resulted in extensive use of the technique.[4]

The cyclic voltammetric measurement of chloropromazine (CPZ) at a carbon paste electrode in aqueous 0.1 M HCl showed two anodic waves with peak potentials of (+0.66 and +0.99) V versus SCE, corresponding to the oxidation of CPZ to its cation radical (CPZ^+) and subsequently to its dication (CPZ^{2+}).[5,6] The chemical or electrochemical oxidation of N-substituted phenothiazine in aqueous solution has also been shown to yield the corresponding sulphoxides through the formation of monocations which are prone to facile hydrolysis in a neutral and less acidic medium as compared to that in more acidic media.[7] On the other hand, a linear dependence of voltammetric peak current on the square root of the scan rates suggests that the cyclic voltammetric behavior of thionine, which is attributed to a two-electron reduction of thionine to leucothionine, is of the diffusion type.[8,9] Quickenden and Harrison[10] studied electrochemical properties of thionine by CV at uncoated and thionine-coated photoelectrodes. Examining the cyclic voltammograms obtained during the deposition of thionine on Au and SnO_2 electrodes, they observed that the height of the characteristic thionine oxidation and reduction peaks increased with the number of cycles to asymptotic limits after about 70 cycles in the case of a Au electrode and after 500 cycles in the case of SnO_2. During the cyclic deposition process on Au, the thionine reduction and leucothionine oxidation peaks, which are originally at (0.43 and 0.49) V, respectively, shift in turn to (0.49 and 0.54) V, and a small shoulder appears at about 0.43 V. However, during the deposition on SnO_2, the thionine reduction peak at 0.435 V does not shift. However, the oxidation peak moves from (0.535 to 0.550) V, and the shoulder on the reduction peak appears only temporarily during the middle stage of the deposition. Albery et al.[11] observed that the reduction of thionine on clean Pt-electrode was reversible, whereas on the coated electrode it was nearly reversible. From the measurement of the kinetic parameters for different electrodes, they concluded that the electrochemical rate constant was decreased for electrodes coated at higher voltages and for longer times. In particular, there was a significant reduction in rate constant for electrodes coated at 1.4 V or above for periods longer than 1 h.

The reduction of methylene blue was studied by Wopschall and Shain[12] to test the theory of CV for the case in which the product of the electrode reaction was strongly adsorbed. A brief investigation of the mechanism of two-electron electrode reduction using both aqueous ethanol and aprotic solvent systems, indicated that the reduction probably proceeded through successive one-electron charge transfer, where a rapid reversible protonation interposed between the charge transfers and the intermediate appeared to be more easily reduced than methylene blue.

In a study on the electrochemical aspects of the reaction between leucodye and Fe^{3+} in dye-based photogalvanic systems,[13,14] the authors examined the electrochemical reduction of thionine, methylene blue, and other alkylated thionines in the presence of Fe^{3+} in terms of a catalytic regeneration mechanism. The catalytic current due to the homogeneous chemical reaction between progressively alkylated leucothiazine dyes and Fe^{3+} has been used to estimate the rate constants of the coupled chemical reactions.

Asakawa et al.[15] also successfully applied CV to evaluate the micelle diffusion coefficients of fluorocarbon surfactants using (ferrocenyl methyl)trimethylammonium bromide (FcTAB). The growth behavior of micelles of cetyltrimethylammonium bromide (CTAB) was examined by Hasan and Yakhmi[16] by using CV. The changes in the geometry of the aggregate were examined by monitoring the changes in the self-diffusion

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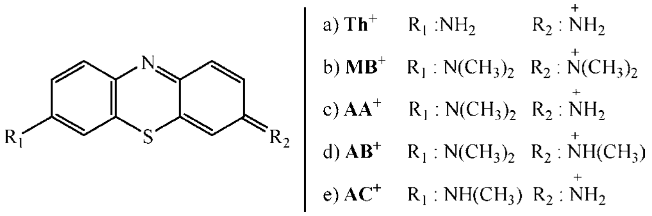

Figure 1. Structures of thiazine dyes: (a) thionine, (b) methylene blue, (c) Azure A, (d) Azure B, and (e) Azure C.

coefficient of micelles. The temperature dependence of the diffusion coefficient of 1,1′-ferrocenedimethylenol [$Fc(MeOH)_2$] and 2,2,6,6-teramethyl-1-piperidinyloxy in aqueous solution and in poly(*n*-isopropyl acryl amide-co-acrylic acid) gels in their swollen state was studied by using steady-state voltammetry and chronoamperometry.[17] Mahajan et al.[18] also studied the effect of monomeric and polymeric glycol additives on the micellar properties of two nonionic surfactants, Tween 20 and Tween 80. They determined the critical micelle concentration of the surfactants by plotting the peak current (I_p) as a function of surfactant concentration.

An understanding of the mechanism of the charge transport, control of the pore dimensions to enhance transport properties, and complete elucidation of the role of the electrolyte in the ion-exchange reaction and charge conduction are absolutely required.

Apart from their potential applications in harvesting solar energy via photochemical and photoelectrochemical means, thiazine dyes have found increasing applications in the field of electrocatalysis of the electrochemical redox process. The electrochemical reactions of progressively alkylated thiazine dyes to corresponding leucodyes at the stationary electrode in the presence of Fe^{3+} ions may be described by what is called the “catalytic regeneration mechanism”,[19,20] according to which an initial electroactive species is regenerated by the homogeneous chemical reaction.

In this paper different electrochemical parameters along with the diffusion coefficient (a kinetic parameter) which results from cyclic votammetric experiments with progressively alkylated thiazine dyes in water, water−alcohol, and nonionic micellar media are reported. The molecular structures of thiazine dyes are given in Figure 1.

Experimental Section

All of the thiazine dyes were supplied by Aldrich Chemical Co. (USA), and the method of purification used for thiazine dyes are reported elsewhere.[19] Cyclic voltammetric experiments are carried out employing a BAS cyclic voltammograph (USA, model CV-27), fitted with a three undivided electrode cell and a Houston X−Y recorder (model 100). The experiments are performed taking 25 mL of dye solution in the presence of 0.1 M H_2SO_4 in the appropriate media as a supporting electrolyte with one working glassy carbon electrode (GCE; MF-2012), one Pt-auxiliary electrode, and a saturated calomel (SCE) reference electrode at (25 ± 1) °C. All solutions are purged with pure nitrogen before the experiment for at least 20 min.

Cyclic voltammograms of the dye solutions ($5 \cdot 10^{-5}$ M) are recorded in water, water−ethanol mixture, and Triton X-100 (0.001 M) as mentioned at various scan rates up to 300 $mV \cdot s^{-1}$. Cyclic voltammograms of the concentrated ($1 \cdot 10^{-4}$ M) dye solutions are also recorded at different scan rates using 0.01 M KCl as supporting electrolyte at various pH. The surface area of the electrode is 0.0804 cm^2. The uncertainties in the measurement of applied voltage and the current are ± 0.2 mV and ± 0.05 μA, respectively.

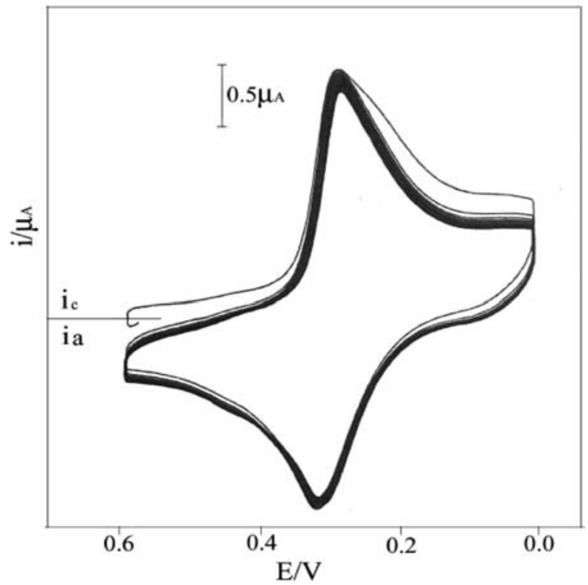

Figure 2. Cyclic voltammograms of thionine ($6.5 \cdot 10^{-5}$ M) with repetitive cycling at a scan rate of 100 $mV \cdot s^{-1}$ in the presence of 0.1 M H_2SO_4.

Results and Discussion

The aggregation of the dyes in solution is an important phenomenon which must be taken into consideration during the interpretation of the cyclic voltammetric data. Present dyes form dimers and higher aggregates in aqueous solution at high concentrations ($\approx 10^{-4}$ M). Ahmed[21] measured the dimerization constant values of the dyes in water and water−ethanol mixtures at different temperatures from spectroscopic data. In aqueous medium at 30 °C the values are ($1.76 \cdot 10^{-3}$, $2.35 \cdot 10^{-3}$, $3.38 \cdot 10^{-3}$, $6.25 \cdot 10^{-3}$, and $3.68 \cdot 10^{-3}$) $lit \cdot mol^{-1}$ for thionine (Th), Azure C (AzC), Azure A (AzA), Azure B (AzB), and methylene blue (MB) respectively, whereas in 5 % alcohol, these values are ($1.45 \cdot 10^{-3}$, $1.86 \cdot 10^{-3}$, $2.13 \cdot 10^{-3}$, $4.58 \cdot 10^{-3}$, and $2.46 \cdot 10^{-3}$) $lit \cdot mol^{-1}$, respectively. The dimerization process is thus unfavorable in water−alcohol mixtures compared to that in neat water.

Upon electrode reduction, all of these dyes form colorless leucodyes on a forward scan.[8] Some representative voltammograms of thionine are shown in Figures 2 to 4. The systems undergo a reversible electrode reaction on the GCE in 0.1 M H_2SO_4 (supporting electrolyte), up to a scan rate of 100 $mV \cdot s^{-1}$ in water, water−ethanol, and Triton X-100 media. Other electrochemical parameters, namely, the separation of the peak potentials and the half-peak potential values are also in conformity with the reversibility of the system up to the above scan rate. The values of cyclic voltammetric (CV) data in an aqueous medium have already been reported elsewhere.[19] Tables 1 and 2 bear the CV data in the presence of ethanol and Triton X-100, respectively. The values of anodic peak current (i_{pa}) and cathodic peak current (i_{pc}) should be identical for a simple reversible (fast) couple; that is, ideally (i_{pa}/i_{pc}) = 1. But this ratio (shown in Table 1 and 2) deviates from unity even at the slow scan rates in the present systems. However, the deviation becomes less if the calculation is done using the modified equation as suggested by Nicholson.[22]

$$\frac{i_{\mathrm{pa}}}{i_{\mathrm{pc}}} = \frac{(i_{\mathrm{pa}})_0}{(i_{\mathrm{pc}})_0} + \frac{0.485(i_{\lambda})_0}{i_{\mathrm{pc}}} + 0.086 \qquad (1)$$

where $(i_{\mathrm{pc}})_0$ is the peak current for the forward process, $(i_{\lambda})_0$ is the absolute current at the switching potential, and $(i_{\mathrm{pa}})_0$ is the uncorrected return peak current measured from the current axis. The values for $i_{\mathrm{pa}}/i_{\mathrm{pc}} < 1$, which decrease further with increasing scan rates for the thiazine dyes, suggest that the electro-generated leucodyes are involved in the reactions which prevent their reoxidation upon scan reversal.

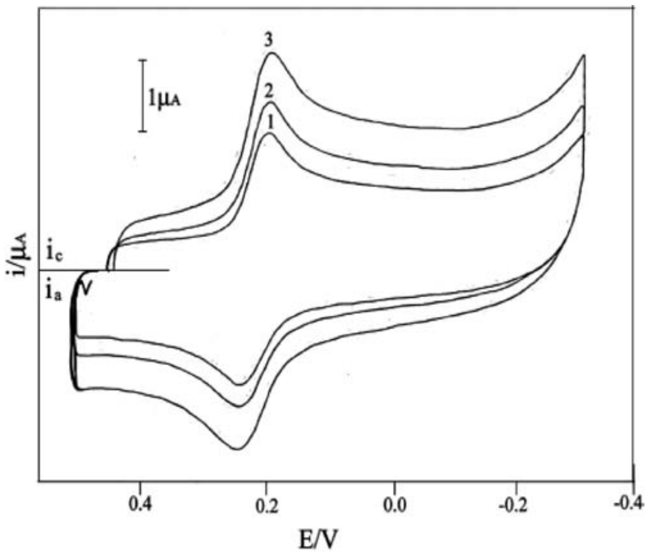

Figure 3. Cyclic voltammograms of thionine ($5.0 \cdot 10^{-5}$ M) in 0.001 M Triton X-100 with scan rates[1−3] of (150, 200, and 300) $\mathrm{mV \cdot s^{-1}}$ in the presence of 0.1 M H_2SO_4.

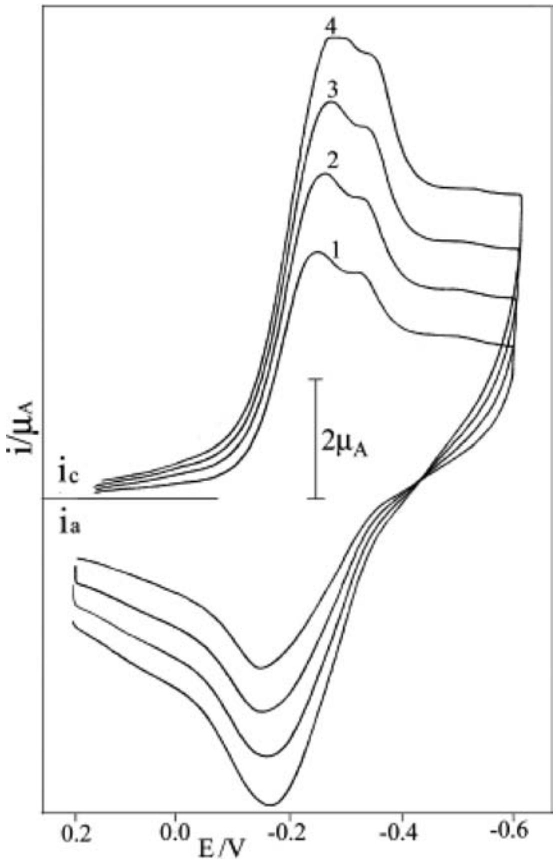

Figure 4. Cyclic voltammograms of thionine ($1.0 \cdot 10^{-4}$ M) at pH 5.8 in the presence of 0.1 M KCl with scan rates[1−4] of (100, 200, 300, and 400) $\mathrm{mV \cdot s^{-1}}$.

Table 1. Electrochemical Data for CV of Dyes ($5 \cdot 10^{-5}$ M) in Ethanol + Water (Volume Fraction 50 %) Media in the Presence of 0.1 M H_2SO_4

dye	V / $\mathrm{s^{-1}}$	E_{pa} / V	E_{pc} / V	ΔE_{p} / V	$i_{\mathrm{pa}}/i_{\mathrm{pc}}$	$E_{\mathrm{pc/2}} - E_{\mathrm{pc}}$	$I_{\mathrm{pc}}\upsilon^{-1/2}$	$0.058/\Delta E_{\mathrm{p}}$ / V
thionine	5	0.190	0.160	0.030	0.87	0.027	3.93	1.93
	10	0.190	0.160	0.030	0.90	0.027	3.88	1.93
	20	0.190	0.158	0.032	0.91	0.028	4.07	1.81
	40	0.192	0.155	0.037	0.91	0.032	4.32	1.57
	60	0.192	0.155	0.037	0.81	0.036	4.61	1.57
	100	0.193	0.152	0.041	0.80	0.038	4.75	1.41
	150	0.193	0.150	0.043	0.79	0.042	4.90	1.35
	200	0.194	0.150	0.044	0.74	0.042	5.15	1.32
	300	0.195	0.148	0.047	0.72	0.045	5.57	1.23
Azure C	5	0.162	0.118	0.044	0.89	0.040	3.21	1.32
	10	0.158	0.116	0.042	0.83	0.041	3.25	1.38
	20	0.156	0.113	0.043	0.87	0.043	3.28	1.35
	40	0.153	0.110	0.043	0.83	0.044	3.50	1.35
	60	0.152	0.108	0.044	0.72	0.045	3.99	1.32
	100	0.151	0.107	0.044	0.69	0.045	4.11	1.32
	150	0.150	0.105	0.045	0.65	0.047	4.39	1.29
	200	0.150	0.103	0.047	0.61	0.049	4.70	1.23
	300	0.150	0.100	0.050	0.57	0.050	5.12	1.16
Azure A	5	0.205	0.175	0.030	0.90	0.030	3.92	1.93
	10	0.206	0.172	0.034	0.84	0.030	4.15	1.70
	20	0.207	0.170	0.037	0.77	0.032	4.60	1.57
	40	0.208	0.168	0.040	0.66	0.035	5.12	1.45
	60	0.210	0.167	0.043	0.62	0.038	5.32	1.35
	100	0.212	0.165	0.047	0.58	0.038	6.01	1.23
	150	0.213	0.160	0.053	0.51	0.040	6.59	1.09
	200	0.214	0.155	0.059	0.48	0.042	6.93	0.98
	300	0.215	0.150	0.065	0.44	0.043	7.49	0.89
Azure B	5	0.165	0.135	0.030	0.80	0.030	3.57	1.93
	10	0.165	0.132	0.033	0.82	0.032	4.25	1.76
	20	0.165	0.130	0.035	0.81	0.034	4.78	1.66
	40	0.160	0.127	0.033	0.78	0.034	5.50	1.76
	60	0.160	0.125	0.035	0.76	0.038	6.04	1.66
	100	0.150	0.120	0.030	0.61	0.042	6.96	1.93
	150	0.148	0.116	0.032	0.59	0.043	7.24	1.81
	200	0.146	0.112	0.034	0.53	0.044	7.49	1.70
methylene blue	5	0.215	0.180	0.035	0.87	0.027	5.71	1.66
	10	0.121	0.178	0.034	0.72	0.028	5.50	1.70
	20	0.210	0.174	0.036	0.60	0.030	5.85	1.61
	40	0.205	0.170	0.035	0.53	0.032	6.75	1.66
	60	0.200	0.160	0.040	0.52	0.032	6.55	1.45
	100	0.195	0.155	0.044	0.52	0.034	7.59	1.45
	150	0.180	0.140	0.040	0.44	0.035	8.27	1.45
	200	0.178	0.135	0.043	0.43	0.036	8.95	1.35
	300	0.175	0.130	0.045	0.41	0.038	9.32	1.29

Cyclic voltammetric measurements of $5 \cdot 10^{-5}$ M dye solution in the presence of 0.1 M H_2SO_4 are consistent with two-electron reversible redox couples of dye/leucodye pairs up to the scan rate of 100 $\mathrm{mV \cdot s^{-1}}$. The formal potential values for the two-electron dye/leucodye couples are found to be (0.205, 0.175, 0.207, 0.281, and 0.196) V [average values for a scan rate between (5 and 100) $\mathrm{mV \cdot s^{-1}}$] for Th, AzC, AzA, AzB, and MB, respectively, in an aqueous medium.[19] But, the value of $0.058/\Delta E$ is rather low for all dyes. This deviation is more prominent in water−alcohol and micellar media than that in neat water. Some early examination of Wopschall and Shain[12] also found a low value (1.66) of this parameter contrary to the coulometric value of 2 for methylene blue and interpreted it as being due to the result of two successive one-electron reversible charge transfer, with fast protonation of the intermediate to form a species which is more easily reduced than methylene blue.

Separation between the peak potentials (ΔE_{p}) increases slowly with the increase in scan rate because the dye/leucodye couple deviates more and more from the reversibility. The quasi-reversibility of the electrode processes in the present system is also apparent from the difference between the peak potentials (ΔE_{p}) and the half-peak potential ($\Delta E_{\mathrm{pc}} - \Delta E_{\mathrm{p/2}}$), whereas in

Table 2. Electrochemical Data for CV of Dyes ($5 \cdot 10^{-5}$ M) in 0.001 M Triton X-100 in the Presence of 0.1 M H_2SO_4

	V	E_{pa}	E_{pc}	ΔE_p				$0.058/\Delta E_p$
dye	s^{-1}	V	V	V	i_{pa}/i_{pc}	$E_{pc/2} - E_{pc}$	$I_{pc}\upsilon^{-1/2}$	V
thionine	5	0.235	0.205	0.030	0.94	0.030	3.02	1.93
	10	0.235	0.204	0.031	0.80	0.030	3.10	1.87
	20	0.236	0.203	0.033	0.89	0.032	3.19	1.75
	40	0.237	0.202	0.035	0.85	0.033	3.25	1.65
	60	0.238	0.200	0.038	0.82	0.035	3.38	1.53
	100	0.240	0.198	0.042	0.75	0.036	3.48	1.38
	150	0.242	0.197	0.045	0.79	0.040	3.61	1.29
	200	0.243	0.197	0.046	0.78	0.045	3.60	1.26
	300	0.245	0.196	0.049	0.79	0.048	3.47	1.18
Azure C	5	0.195	0.160	0.035	0.80	0.035	2.85	1.66
	10	0.196	0.158	0.038	0.80	0.037	2.50	1.55
	20	0.197	0.157	0.040	0.80	0.038	2.84	1.45
	40	0.198	0.156	0.042	0.72	0.039	3.13	1.38
	60	0.199	0.155	0.044	0.81	0.040	3.28	1.32
	100	0.200	0.154	0.046	0.74	0.041	3.32	1.26
	150	0.202	0.153	0.049	0.69	0.041	3.36	1.18
	200	0.203	0.152	0.051	0.69	0.043	3.58	1.14
	300	0.204	0.150	0.054	0.63	0.045	3.47	1.07
Azure A	5	0.200	0.170	0.030	0.80	0.032	3.57	1.93
	10	0.202	0.168	0.034	0.86	0.032	3.50	1.70
	20	0.204	0.166	0.038	0.80	0.034	3.54	1.53
	40	0.206	0.164	0.042	0.71	0.035	3.50	1.38
	60	0.208	0.162	0.046	0.74	0.037	3.89	1.26
	100	0.210	0.160	0.050	0.62	0.040	4.11	1.16
	150	0.212	0.158	0.054	0.65	0.043	4.39	1.07
	200	0.214	0.156	0.058	0.63	0.046	4.25	1.00
	300	0.215	0.155	0.060	0.61	0.050	4.20	0.96
Azure B	5	0.205	0.175	0.030	0.85	0.032	2.50	1.93
	10	0.203	0.173	0.030	0.81	0.032	2.75	1.93
	20	0.201	0.170	0.031	0.80	0.035	2.66	1.87
	40	0.200	0.168	0.032	0.78	0.036	2.88	1.81
	60	0.198	0.163	0.035	0.68	0.038	2.97	1.66
	100	0.196	0.159	0.037	0.66	0.042	3.08	1.57
	150	0.196	0.159	0.037	0.65	0.044	3.36	1.57
	200	0.194	0.154	0.040	0.66	0.047	3.36	1.45
	300	0.194	0.152	0.042	0.61	0.048	3.29	1.38
methylene blue	5	0.210	0.180	0.030	0.75	0.025	4.29	1.93
	10	0.212	0.180	0.032	0.75	0.028	4.00	1.81
	20	0.214	0.178	0.036	0.73	0.029	4.07	1.61
	40	0.215	0.178	0.037	0.72	0.030	4.13	1.57
	60	0.216	0.176	0.040	0.71	0.031	4.61	1.45
	100	0.216	0.175	0.041	0.60	0.033	4.90	1.41
	150	0.218	0.174	0.044	0.55	0.035	5.17	1.32
	200	0.218	0.173	0.045	0.52	0.038	5.15	1.29
	300	0.220	0.172	0.048	0.51	0.040	5.30	1.21

an ideal reversible reaction these values should be 30 mV.[23] However, an appreciable deviation of ΔE_p from the ideal reversible value is apparent only at very high scan rates, which suggests that the electrodic processes involved are very fast.

The plots of i_{pc} as a function of $\upsilon^{1/2}$ (i_{pc} measured for forward scan of the first cycle) indicate that the variation of the current is linear with $\upsilon^{1/2}$ upon a scan rate of $\approx$ 100 $mV \cdot s^{-1}$, and the line drawn through the experimental points at slow scan rates passes through the origin. The representative plot for the thionine system is shown at Figure 5. At higher scan rates the points deviate from the straight line in all of the systems studied here. The foregoing observation also indicates that the electrode process is diffusion-controlled at slow scan rates.

The effective diffusion coefficient values of the dyes in water, water−alcohol, and water−Triton X-100 are summarized in Table 3. The diffusion coefficient values are calculated using Randles Seveik equation.[24] For the one-electron reversible process

$$i_p = 2.69 \cdot 10^5 n^{3/2} A D^{1/2} \upsilon^{1/2} C_0 \qquad (2)$$

where i_p is the peak current (in amperes), A is the area of the electrode (in cm^2), D is the diffusion coefficient (in $cm^2 \cdot s^{-1}$), C_0 is the concentration (in $mol \cdot cm^{-3}$), υ is the potential scan rate (in $mV \cdot s$), and n is the number of electrons transferred in the redox process. The diffusion coefficients are measured from the slope of the plot of i_{pc} versus $\upsilon^{1/2}$ up to the scan rate of 20 $mV \cdot s^{-1}$. The values for MB and Th are $5.70 \cdot 10^6$ $cm^2 \cdot s^{-1}$ and $3.05 \cdot 10^6$ $cm^2 \cdot s^{-1}$, respectively, on GCE. A value of $7.60 \cdot 10^6$ $cm^2 \cdot s^{-1}$ for MB and $2.28 \cdot 10^6$ $cm^2 \cdot s^{-1}$ for Th was reported by previous workers, measured at a Pt-wire type “hanging mercury drop electrode” (HMDE) and indium-doped SnO_2 electrode.[12,13] AzC has the lowest value of diffusion coefficient ($2.66 \cdot 10^6$ $cm^2 \cdot s^{-1}$ in water), but no systematic variation is observed with alkylation of the dye. However, the preliminary study shows the diffusion coefficient values in water−alcohol and micellar media are interestingly much smaller compared to neat water. It is interesting to note that a slight increase of solution viscosity results in the considerable decrease in the diffusion coefficient values for both 50 % volume fraction of water−ethanol and water−Triton X-100 mixtures.

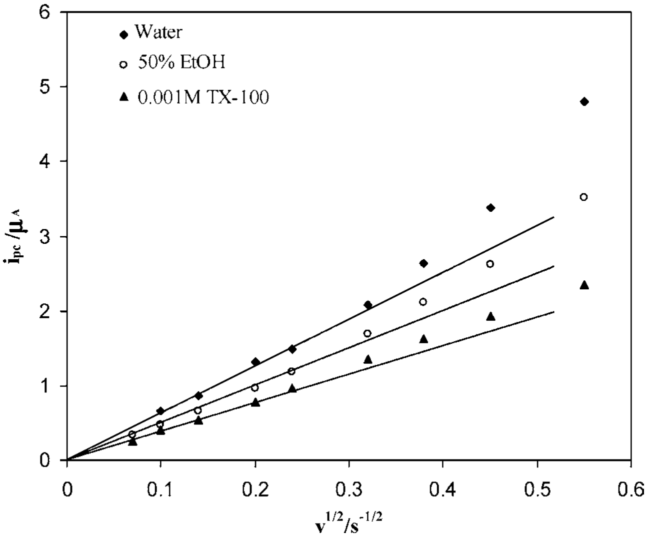

Figure 5. Plot of cathodic peak currents as a function of (scan rates)$^{1/2}$ for thionine ($5 \cdot 10^{-5}$ M) in different solvents at GCE.

Table 3. Values of the Diffusion Coefficient of the Dyes in Different Media

	$10^{-6} \cdot D/cm^2 \cdot s^{-1}$		
dye	water	EtOH	Triton X-100
thionine	3.05	1.80	1.10
Azure C	2.66	1.16	0.87
Azure A	4.40	2.29	1.36
Azure B	4.13	2.47	0.76
methylene blue	5.70	3.70	1.80

Previous workers deposited dye layers on the metal electrode by maintaining the electrode at some empirically selected potential while it was immersed in a solution of the dye.[3,25,26] Quickenden and Harrison,[10] on the other hand, developed a method of deposition of dye layers by repetitive cycling of the potential scan. The comparison of CV’s obtained when the thionine-coated electrodes are immersed in background and thionine-containing electrolyte that the thionine and leucothionine peaks observed with the coated electrodes originates almost entirely from the dye coating, rather than for any thionine solution.

In Figure 2 the results of the repetitive cycles of a voltage scan on a GCE for the thionine is shown. The behavior of the thionine and four other dyes at $6.5 \cdot 10^{-5}$ M (in 0.1 M H_2SO_4) on a GCE is substantially different from the study of thionine on the Au-electrode reported previously.[2,10] Instead of a progressive increase of anodic and cathodic currents on cycling, the peak currents in the present systems decrease. The peak

Table 4. Effect of pH on the Cyclic Voltammograms of the Dye Solutions

dye	pH	changes/observations	adsorption
thionine ($1 \cdot 10^{-4}$ M) in 0.1 M KCl	3.6	pre-cathodic and post-anodic peaks	product strongly adsorbed
	4.2	pre-cathodic and post-anodic peaks	product strongly adsorbed
	5.3	post-cathodic and pre-anodic peaks	reactant strongly adsorbed
	5.8	post-cathodic and pre-anodic peaks	reactant strongly adsorbed
Azure C ($2 \cdot 10^{-4}$ M) in 0.1 M KCl	4.1	pre-cathodic and post-anodic peaks	product strongly adsorbed
	5.1	post-cathodic and pre-anodic peaks	reactant strongly adsorbed
	6.0	post-anodic peaks	product strongly adsorbed
	7.0	pre-cathodic and pre and post-anodic peaks	product strongly adsorbed
Azure A ($2 \cdot 10^{-4}$ M) in 0.1 M KCl	5.2	pre-cathodic and post-anodic peaks	product strongly adsorbed
	5.4	pre-cathodic and post-anodic peaks	product strongly adsorbed
	5.7	pre-cathodic and post-anodic peaks	product strongly adsorbed
	6.2	anodic peak current is greater than cathodic	product weakly adsorbed
Azure B ($2 \cdot 10^{-4}$ M) in 0.1 M KCl	4.8	post-cathodic and pre-anodic peaks	reactant strongly adsorbed
	5.3	post-cathodic and pre-anodic peaks	reactant strongly adsorbed
	5.7	post-anodic peaks	product strongly adsorbed
	6.2	anodic peak currents high	product weakly adsorbed
methylene blue ($2 \cdot 10^{-4}$ M) in 0.1 M KCl	4.6	post-cathodic and pre-anodic peaks	reactant strongly adsorbed
	4.8	post-cathodic and pre-anodic peaks	reactant strongly adsorbed
	6.0	anodic peak currents increases sharply	product weakly adsorbed
	8.4	slight cathodic postpeak and anodic peak currents increases sharply	both reactant and product adsorbed

Table 5. Heterogeneous Rate Constants

dye	υ / V·s^{-1}	$\Delta E_p \cdot n$ / V	Ψ	$k \cdot 10^{-3}$ / cm·s^{-1}
thionine	1.0	0.140	0.24	6.55
	0.8	0.130	0.29	7.08
	0.6	0.120	0.35	7.61
	0.5	0.110	0.46	8.88
	0.4	0.100	0.58	10.02
	0.3	0.80	1.14	17.05
Azure C	1.0	0.130	0.29	7.39
	0.8	0.120	0.35	7.98
	0.6	0.100	0.58	11.46
	0.5	0.900	0.78	14.07
	0.4	0.800	1.14	18.39
	0.3	0.700		
Azure A	1.0	0.120	0.36	11.81
	0.8	0.110	0.46	13.49
	0.6	0.100	0.58	14.74
	0.5	0.900	0.78	18.09
	0.4	0.800	1.14	23.65
	0.3			
Azure B	1.0	0.130	0.29	10.04
	0.8	0.120	0.36	11.14
	0.6	0.100	0.58	15.55
	0.5	0.900	0.78	19.09
	0.4	0.800	1.14	24.96
	0.3			
methylene blue	1.0	0.140	0.24	8.96
	0.8	0.120	0.36	12.02
	0.6	0.110	0.46	13.30
	0.5	0.100	0.58	15.31
	0.4	0.900	0.78	18.42
	0.3			

current attains a constant value in each case after (10 to 20) cycles. This behavior is to some extent similar to that of Rhodamine B on the SnO_2 glass electrode.[1] Of course in the later case the currents were found to decrease continuously on every repetitive cycle and ultimately merged with the background currents. Present results suggest that, under the experimental conditions, although the previously assumed tendency of the thionine dye adsorption on a GCE surface is rather weak in the presence of 0.1 M H_2SO_4, partial electrode poisoning toward the process of oxidation and reduction of the adsorbed dyes may take place. However, it is also reported by the previous workers that the cyclic voltammogram does not change with repeated cycling unless a certain potential is exceeded during a sweep.[1] It has been shown that for concentrations below $\approx 0.2 \cdot 10^{-3}$ M the methylene blue system fits the simple theory of CV in which the adsorption of the reactant is ignored.[12] It was argued that, above $0.2 \cdot 10^{-3}$ M concentrations, the adsorption of methylene blue must be considered. In Figure 4 representative cyclic voltammograms of the dye ($1 \cdot 10^{-4}$ M) in the presence of 0.1 M KCl at pH 5.8 are shown. It has been observed that the presence of 0.1 M KCl and, at comparatively higher pH's, both anodic and cathodic peak potentials are shifted toward more negative potentials than those observed in the presence of 0.1 M H_2SO_4. Moreover, the voltammograms display cathodic and anodic post/prepeaks which are the characteristics of strong adsorption of the reactant and/or products. The observed natures of the voltammograms vis-à-vis the adsorption characteristics of various dyes are summarized in Table 4. At a concentration of $1 \cdot 10^{-4}$ M, thionine gives voltammograms with small cathodic prepeaks as well as anodic postpeaks at pH 3.6 to 4.2, indicating that the products are strongly adsorbed. At pH 5.3 and above, cathodic postpeaks and anodic prepeaks are observed which indicate a strong adsorption of the reactant dye. Similarly, AzC exhibits a cathodic prepeak and anodic postpeak at pH 4.1, indicating that the products are strongly adsorbed. At pH 5.1 a cathodic postpeak and an anodic prepeak appear which indicates that the reactant dye is also adsorbed strongly. However, at pH 6.0 and above cyclic voltammograms are suggestive of strong adsorption of products only. While voltammograms of AzA show evidence of strong product adsorption within the pH range of 5.2 and 6.2, AzB exhibits evidence of reactant adsorption at low pH and product adsorption at high pH values. MB, on the other hand, gives cathodic postpeaks and anodic prepeaks up to pH of 4.8 indicating strong reactant adsorption, while at high pH both the reactant and the product are adsorbed.

Sackett et al.[6] have also observed the pH dependency of the initial oxidation of promethiazine, whereas similar processes for CPZ were completely independent of pH above the value of zero. Apparently, the proximity of the highly charged ring system in the oxidized form lowers the pK_a of the side-chain amine to cause the deprotonation. The pH dependency of the oxidation potential of promethiazine has been noted even before and was attributed to the electronic interaction between the ring system and the amine.[27] Results indicated that oxidation of the ring lowers the pK_a of the side-chain amine by at least 5 units, resulting in the deprotonation of the amine in the oxidized form. Similarly, in the case of thiazine dyes, it can be argued that, although amino nitrogen are very weakly basic, the same groups which could be protonated along the bridging nitrogen at low pH in leucodyes are deprotonated at high pH. While the effects of pH on the voltammograms of the present dyes are similar, enhanced irreversibility of the redox processes is also accompanied by certain changes in the shapes of the voltammogram at high pH values.

It has been shown that for quasi-reversible electrode processes, the separation between corresponding oxidation and reduction peaks in the cyclic voltammogram is a function of the corresponding electrodic rate constants. Nicholson[22] had provided a table of the computed relationship between the peak separation and a kinetic factor Ψ. The latter is related to the rate constant k for a quasi-reversible oxidation by

$$\psi = (D_0/D_r)^{\alpha/2} k\{D_0 \pi \nu (nF/RT)\}^{-1/2} \qquad (3)$$

where the subscripts 0 and r designate oxidation and reduction processes, respectively, and α is the transfer coefficient and all other symbols have their usual meanings. It is assumed that the diffusion coefficient of dyes and leucodyes are not very different; the quantity $(D_o/D_r)^{\alpha/2}$ is very close to unity regardless of the α value, and the rate constant for the electrodic oxidation of dyes at a GCE can be obtained. Table 5 gives the values of Ψ at various scan rates for the electrodic process of the present cationic dyes. Kinetic factors at the various scan rates are measured from the curve of the variation of peak potential separation with Ψ. When Ψ′s are sufficiently large, the results become identical to one where the electron transfer is assumed to be Nernstian. On the other hand, for very small Ψ, the back reaction for electron transfer is unimportant, and the processes for oxidation and reduction can be treated separately as the totally irreversible case. At lower scan rates, all of the thiazine dyes displayed reversible electrode reactions. Quasi-reversibilities are prominent above 300 $\mathrm{mV \cdot s^{-1}}$ scan rates. As such, kinetic measurements are made within the range of (300 to 1000) $\mathrm{mV \cdot s^{-1}}$ scan rates. The heterogeneous rate constants of the electron transfer of the five thiazine dyes are given in Table 5. The table shows that the order of the kinetic parameter is same for all of the dyes. However, the values of the parameter increase slightly with alkylation in dye molecule from thionine to AzB, while MB gives a little lower value than AzB.

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