Indian Journal of Chemistry
Vol. 16A, April 1978, pp. 300-305

Electroreduction of 4,5-Diiodofluorescein in Buffer Solution Containing Different Alcohols of Surfactants at Dropping Mercury Electrode*

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Received 3 *January* 1977; *accepted* 1 *November* 1977

The polarographic reduction of 4,5-diiodofluorescein is investigated in buffer solutions (*p*H 2-11) containing different monoprotic alcohols and cationic, anionic or non-charged surfactants. Values of i_l and $E_{\frac{1}{2}}$ of the reduction waves are found to depend on the nature and proportion of alcohol and surfactant. The nature of the waves and the electrode reaction are also investigated. Radius of the reducible species and the kinetic parameters (K°_{fh}, ΔG^* and α) of the electrode reaction have been determined and discussed.

THE polarographic reduction of fluorescein and its di- and tetrahalo derivatives have earlier been shown to proceed according to two main mechanisms[1-4]. In the first mechanism the reduction of furan ring by a two-electron process was envisaged. The reduction may proceed either along a single or two waves depending on the *p*H of the medium and the nature of the reducible species. The second mechanism involved uptake of four electrons, two of which were consumed in the reduction of the furan ring and the other two for the reduction of another electroactive centre in the molecule, such as C-halogen bond[5,6] or the pyrone ring[1-4]. The current due to the reduction of the second electroactive centre increased from fluorescein to dichloro- to dibromo-, to diiodo-derivatives[1,3], i.e. its height increased as the polarity of C-halogen bond decreased. Our experimental data[1-4] are not in favour of the reduction of the halogen atoms. The reduction of the pyrone ring was considered in some cases to be connected with the adsorption of the reduction product at the electrode surface[1,2].

The presence of organic solvent or surfactants largely hindered the adsorption of organic[3] compounds at the electrode surface. Thus it seems of interest to investigate the effect of these substances on the electro-reduction of 4,5-diiodofluorescein with a view to recognizing the second electroactive centre.

Materials and Methods

4,5-Diiodofluorescein (BDH grade) solution, 0·01*M* with respect to this compound and also with respect to NaOH was prepared. Universal buffer solutions of *p*H 2-11·5 were prepared according to Britton and Robinson[7]. Aqueous-alcohol mixtures of different *p*H values between 2·0 and 11·5 were prepared. The alcohols such as methanol, ethanol and *n*-propanol were purified by the recommended methods[8]. Triton X-100, dodecylbenzenesulphonate ($DDBSO_3Na$) and dodecylaminoperchlorate ($DDAClO_4$) solutions (1%) were prepared as given before[9].

The apparatus, electrolysis cell and working procedure were the same as previously given[3]. The characteristics of the dropping mercury electrode were: $m=1{\cdot}973$ mg/sec and $t=4{\cdot}7$ sec/drop (open circuit) at 49 cm Hg.

Results and Discussion

The polarograms of 4,5-diiodofluorescein ($5{\cdot}66 \times 10^{-4}M$) in solutions of *p*H 5·15-9·0 were found to consist of three waves in addition to a prewave at less negative potential[1]. The prewave was attributed to the adsorption of the reduced form of the depolarizer. At *p*H ≥ 9·5 the polarograms consisted of only two reduction waves, the height of the second wave was found to be double that of the first wave at *p*H ≃ 11·0.

The polarograms obtained in the presence of ~35% methanol consisted of three waves within the *p*H range 4-9·5; above *p*H 9·5 only two waves are obtained. The height of the second wave increased at the expense of the first wave till *p*H 11·0.

In the presence of ~35% ethanol the polarograms consisted of two main reduction waves in the *p*H range 2-11·5, in addition to a small wave in between the two waves in acidic or neutral solutions only. At *p*H ~10·0 the height of the second wave became double that of the first then triple at *p*H ≥ 11·0. The same behaviour is observed in presence of ~35% *n*-propanol.

In presence of 25% methanol, 16% ethanol or 12% *n*-propanol, the polarographic maximum observed in pure buffered aqueous solutions[1] was completely eliminated. This revealed that the alcohols act as maxima suppressors and the efficacy of the alcohols which as maxima suppressors followed the: *n*-propanol>ethanol>methanol. This is in accordance with expectations, since the surface activity of alcohols increases as the chain length increases.

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*This paper is dedicated to Prof. Issa Mostafa Issa, Head of the Chemistry Department, Assiut University, on his 54th birthday.

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The effect of varying the alcohol content of alcohol-water mixtures was studied at pH values 5·12 and 11·0. At pH 5·12 increasing proportion of alcohol shifted the $E_{1/2}$ of the first main wave to less negative potentials whereas that of the second to more negative values. However, at pH 11·0 the shift of $E_{1/2}$ of the first wave was more towards negative potentials as compared to that of the second wave on increasing the alcohol content. At the same time, the i_l at all pH values decreased in the same direction. This can be explained on the basis of the fact that the adsorption of depolarizer at the electrode surface decreases as the proportion of the alcohol increases, leading to easier reduction at the first wave. At the same time, because the reduction of the pyrone ring is enhanced by adsorption[1,2], the increased proportion of alcohol leads to less easier reduction at the second wave which causes an $E_{1/2}$ shift to more negative potentials in solutions of $p\text{H}<7·0$.

On the other hand, the effect of the surface active agent Triton X-100 (non-charged) and dodecylamineperchlorate (cationic) on the polarograms is almost the same being restricted to: (a) large decrease of i_l at all pH values especially in acidic media, and distortion or elimination of second waves in some cases and (b) the shift of $E_{1/2}$ to more negative values (Fig. 1). Dodecyl benzenesulphonate (anionic) has little effect on i_l and $E_{1/2}$ of the waves. However, in the acidic media and in the presence of 2×10^{-2} % Triton X-100 or 8×10^{-3} % dodecylamineperchlorate the reduction waves become more or less rudimentary. This may be attributed to the complete covering of the electrode surface and hence the transfer of electrons from the electrode surface becomes difficult. This phenomenon is not observed in alkaline media because surface active agent is less adsorbed at the electrode surface.

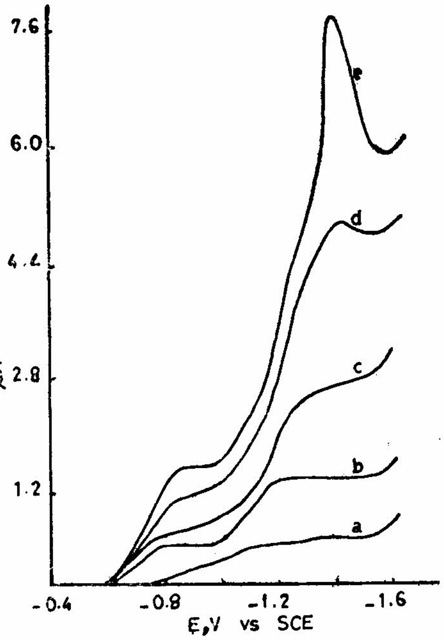

Fig. 1 — Polarograms of 4,5-diiodofluorescein in aqueous medium of pH 5·12 in the presence of different concentrations of dodecylamine perchlorate (DDAClO$_4$) [DDAClO$_4$ $\times 10^3$: (a) 7%; (b) 5%; (c) 3%; (d) 1%; (e) nil]

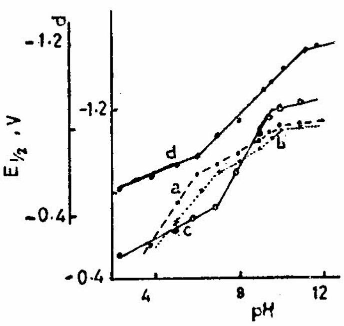

Fig. 2 — $E_{1/2}$ versus pH profile for the first wave in aqueous (curve a) and aqueous-alcohol mixtures containing 35% of methanol (b), propanol (c) or ethanol (d)

In general, the presence of alcohols, and not the surfactant, prevents the adsorption of the depolarizer species at the electrode surface. Hence the electrode reaction becomes more clear and its treatment can be achieved in a more quantitative manner.

$E_{1/2}$ and i_l versus pH profiles — The plots of i_l against pH of the medium for the two main reduction waves in the presence of ~35% alcohols, are Z or S-shaped curves, indicating that the electrode reaction is governed by the rate of proton transfer which becomes slower at higher pH values. The descending or ascending part of the i_l versus pH curves shifts to lower pH values in the presence of alcohols. This implies that the rate of proton transfer becomes slower in the presence of alcohols. As the proportion of alcohol increases the H$^+$ ion activity decreases, hence the rate of proton uptake slows down.

The plots of $E_{1/2}$ against pH for the first wave (furan wave) in the presence of different alcohols, consist of three segments (Fig. 2). From the slopes of these curves, the number of H$^+$ ions (Z_{H^+}) involving in the electrode reaction can be calculated using Eq. (1).

$$\Delta E_{1/2}/\Delta p\text{H} = \frac{0·059}{\alpha n_a} \cdot Z_{H^+} \qquad \ldots(1)$$

Substituting the values of αn_a obtained from the slopes of log $(i/i_d - 1)$ versus E plots, values of Z_{H^+} involved in the reduction of furan ring are found to be ~2 (at $p\text{H} \leqslant 9$) and zero (at $p\text{H} \geqslant 10$). Since the electrode reaction involves two protons and two electrons[1,3], the Z_{H^+}/n_a can have the values 2, 1 or 0·5 depending on whether one or two electrons and one or two protons are involved in the rate determining step. The most probable α-values listed in Tables 1 and 2 show that the number of electrons and protons involved in the rate determining step are equal. Accordingly the rate determining step in the main electrode reaction should involve one electron and one proton. The changes in the values of $\Delta E_{1/2}/\Delta$ pH along the first and second segments at $p\text{H} \leqslant 9$ may be attributed to the changes in the values of the transfer coefficient (α). Since at $p\text{H} > 9·5$, $E_{\frac{1}{2}}$ of the first wave is but slightly influenced by pH, it is assumed that H$^+$ ions are not involved in the electrode reaction proper[1,2].

TABLE 1 — KINETIC PARAMETERS OF THE ELECTRO-REDUCTION OF DIIODOFLUORESCEIN IN SOLUTIONS OF pH 5·12 AND 11·0 IN THE PRESENCE OF SURFACTANTS

Surfactants		$(\Delta E/\Delta$ log $(i/i_d - i)$ (V)	α		K°_{fh} cm/sec	$\Delta G^{\ddagger}$ kcal	$K^{\circ}_{fh}D^{-\frac{1}{2}}$	Remark
Type	% w		$n_a = 1$	$n_a = 2$				
			pH = 5·15					
Triton	0·0	0·090	0·65	0·33	$3{\cdot}1 \times 10^{-9}$	78·6	$1{\cdot}3 \times 10^{-6}$	1st wave
		0·250	0·24	0·12	$1{\cdot}0 \times 10^{-7}$	69·9	$4{\cdot}1 \times 10^{-5}$	2nd do
	$2{\cdot}6 \times 10^{-3}$	0·100	0·59	0·30	$3{\cdot}9 \times 10^{-8}$	72·2	$1{\cdot}6 \times 10^{-5}$	1st do
		0·192	0·31	0·15	$1{\cdot}0 \times 10^{-8}$	75·7	$4{\cdot}1 \times 10^{-6}$	2nd do
	$1{\cdot}5 \times 10^{-2}$	0·100	0·59	0·30	$1{\cdot}0 \times 10^{-7}$	69·9	$4{\cdot}1 \times 10^{-4}$	1st do
		0·217	0·27	0·14	$1{\cdot}0 \times 10^{-8}$	75·7	$4{\cdot}1 \times 10^{-6}$	2nd do
$DDAClO_4$	1×10^{-3}	0·147	0·40	0·20	$3{\cdot}9 \times 10^{-7}$	66·5	$1{\cdot}6 \times 10^{-4}$	1st do
		0·143	0·41	0·20	$2{\cdot}5 \times 10^{-8}$	84·9	$1{\cdot}1 \times 10^{-7}$	2nd do
	$7{\cdot}5 \times 10^{-3}$	0·100	0·59	0·30	$3{\cdot}1 \times 10^{-8}$	72·8	$1{\cdot}2 \times 10^{-5}$	1st do
		0·143	0·41	0·20	$1{\cdot}2 \times 10^{-9}$	81·0	$4{\cdot}9 \times 10^{-7}$	2nd do
$DDBSO_3Na$	1×10^{-2}	0·094	0·63	0·31	$5{\cdot}0 \times 10^{-9}$	77·4	$2{\cdot}0 \times 10^{-6}$	1st do
		0·233	0·26	0·13	$5{\cdot}0 \times 10^{-8}$	71·6	$2{\cdot}0 \times 10^{-5}$	2nd do
	$8{\cdot}7 \times 10^{-2}$	0·106	0·55	0·28	$1{\cdot}2 \times 10^{-8}$	75·2	$4{\cdot}9 \times 10^{-6}$	1st do
		0·145	0·41	0·21	$2{\cdot}5 \times 10^{-10}$	84·8	$1{\cdot}0 \times 10^{-7}$	2nd do
			pH = 11·0					
$DDAClO_4$	0·0	0·080	0·74	0·37	$3{\cdot}1 \times 10^{-12}$	95·9	$1{\cdot}3 \times 10^{-9}$	1st do
	$7{\cdot}0 \times 10^{-4}$	0·089	0·67	0·34	$4{\cdot}2 \times 10^{-12}$	95·2	$1{\cdot}7 \times 10^{-9}$	1st do
	$1{\cdot}1 \times 10^{-2}$	0·092	0·64	0·32	$2{\cdot}1 \times 10^{-11}$	91·2	$8{\cdot}5 \times 10^{-9}$	1st do

TABLE 2 — KINETIC PARAMETERS OF THE ELECTRODE REACTION OF DIIODOFLUORESCEIN IN SOLUTIONS OF DIFFERENT pH IN THE PRESENCE OF ALCOHOLS

pH	$\{\Delta E/\Delta \log(i/i_d - i)\}$ V	α		K°_{fh} cm/sec	$\Delta G^{\ddagger}$ kcal	$K^{\circ}_{fh}\ D^{-\frac{1}{2}}$	Remark
		$n_a=1$	$n_a=2$				
		35% METHANOL-AQUEOUS MIXTURE					
4·0	0·132	0·45	0·28	$3{\cdot}9 \times 10^{-5}$	54·9	$1{\cdot}6 \times 10^{-2}$	1st wave
5·12	0·147	0·40	0·20	$2{\cdot}3 \times 10^{-6}$	62·1	$9{\cdot}3 \times 10^{-4}$	1st do
	0·185	0·32	0·16	$8{\cdot}2 \times 10^{-9}$	76·2	$3{\cdot}4 \times 10^{-6}$	2nd do
7·0	0·167	0·35	0·18	$9{\cdot}8 \times 10^{-7}$	64·2	$4{\cdot}1 \times 10^{-4}$	1st do
	0·185	0·35	0·18	$8{\cdot}2 \times 10^{-9}$	76·2	$3{\cdot}4 \times 10^{-6}$	2nd do
9·15	0·111	0·53	0·26	$4{\cdot}9 \times 10^{-10}$	83·2	$2{\cdot}0 \times 10^{-7}$	1st do
	0·270	0·22	0·11	$1{\cdot}9 \times 10^{-7}$	68·3	$7{\cdot}8 \times 10^{-7}$	2nd do
10·0	0·104	0·57	0·28	$2{\cdot}5 \times 10^{-11}$	90·7	$1{\cdot}0 \times 10^{-8}$	1st do
	0·213	0·28	0·14	$2{\cdot}2 \times 10^{-9}$	79·5	$9{\cdot}0 \times 10^{-7}$	2nd do
11·1	0·089	0·66	0·33	$6{\cdot}8 \times 10^{-12}$	93·9	$2{\cdot}7 \times 10^{-9}$	1st do
	0·154	0·38	0·19	$5{\cdot}4 \times 10^{-10}$	83·0	$2{\cdot}2 \times 10^{-7}$	2nd do
		16·5% ETHANOL-AQUEOUS MIXTURE					
2·28	0·222	0·27	0·14	$4{\cdot}6 \times 10^{-5}$	54·5	$1{\cdot}9 \times 10^{-2}$	1st do
5·12	0·170	0·35	0·17	$3{\cdot}0 \times 10^{-6}$	57·9	$1{\cdot}2 \times 10^{-3}$	1st do
	0·256	0·23	0·12	$1{\cdot}0 \times 10^{-7}$	69·9	$4{\cdot}1 \times 10^{-5}$	2nd do
7·5	0·170	0·35	0·17	$9{\cdot}8 \times 10^{-7}$	64·2	$4{\cdot}0 \times 10^{-4}$	1st do
	0·370	0·06	0·03	$1{\cdot}1 \times 10^{-6}$	63·8	$4{\cdot}5 \times 10^{-4}$	2nd do
11·2	0·217	0·27	0·14	$1{\cdot}8 \times 10^{-6}$	62·7	$7{\cdot}4 \times 10^{-4}$	1st do
	0·330	0·06	0·03	$1{\cdot}4 \times 10^{-7}$	69·1	$5{\cdot}8 \times 10^{-5}$	2nd do
		34·5% ETHANOL-AQUEOUS MIXTURE					
2·6	0·110	0·48	0·24	$3{\cdot}1 \times 10^{-5}$	55·7	$1{\cdot}3 \times 10^{-2}$	1st do
5·12	0·098	0·60	0·30	$3{\cdot}0 \times 10^{-8}$	73·0	$1{\cdot}2 \times 10^{-5}$	1st do
	0·189	0·31	0·15	$5{\cdot}3 \times 10^{-9}$	77·3	$2{\cdot}4 \times 10^{-6}$	2nd do
9·55	0·111	0·53	0·27	$5{\cdot}4 \times 10^{-10}$	83·1	$2{\cdot}2 \times 10^{-7}$	1st do
	0·294	0·20	0·10	$1{\cdot}5 \times 10^{-7}$	69·0	$6{\cdot}0 \times 10^{-5}$	2nd do
11·20	0·106	0·56	0·28	$1{\cdot}3 \times 10^{-10}$	86·6	$5{\cdot}3 \times 10^{-8}$	1st do
	0·208	0·28	0·14	$1{\cdot}2 \times 10^{-9}$	82·0	$4{\cdot}9 \times 10^{-7}$	2nd do

The foregoing results indicate that the reduction of 4,5-diiodofluorescein can be represented as given before[1].

Medium effect on i_l — Plots of total i_l as a function of the concentration of surface active agent indicate a decrease of i_l on increasing the concentration of surface active agent and then attains a constant value at 4×10^{-3} % Triton-X-100. This behaviour inacdites that the reduction current decreases as the electrode surface is gradually covered with adsorption layer of surfactant till complete covering, where i_l attains a minimum value. The adsorbed layer of surface active agent prevents approach of the reducible species to the electrode surface. When the adsorbed film approaches a complete monolayer, reduction of the electroactive species may occur outside this film through electron emitted from the electrode. This opinion finds support from the plots of log i/log h, which are linear with slopes $\approx$0·55 at low concentrations of the surface active agent. At higher concentrations the slope values are $\sim$0·4, indicating partial kinetic contribution for the electrode reaction under these conditions.

The reduction current at constant *p*H is found to decrease with increase in the alcohol content of the medium. This may be attributed to the changes in the effective diffusion coefficient. Decreased diffusion coefficient may result either from increased viscosity (η) or change in the size of the solvated species, and since in different cases these two effects may tend either to reinforce or compensate each other, a quantitative interpretation of the separate influence of each is not a simple matter.

For diffusing particles that are large compared to the solvent molecules the Stokes-Einstein relation[10] predicts that $i_d\eta^{\frac{1}{2}}$=constant where the change of diffusion coefficient (D) is due solely to changes in viscosity. However, if the change of D is also partly due to a change in the size of the solvated species it is evident that the product $i_d\ \eta^{\frac{1}{2}}$ will not be constant. In the present study, the product of $i\ \ \eta^{\frac{1}{2}}$ increases in alkaline medium (pH=11·0), but decreases in acidic medium (pH=5·0) with increasing proportions of alcohols (Fig. 3). Matsuyama[11] attributed the inconstancy of the $i_d\ \eta^{\frac{1}{2}}$ values to changes in the effective size of the diffusing species caused by changes in degree of solvation, and to partial association of the reducible anions with cations which appears to be favoured by increasing alcohol content.

In our investigation, the increase of $i_d\ \eta^{\frac{1}{2}}$ in alkaline medium can be ascribed to increased diffusion coefficient as a result of a decrease in the volume (or radius) of species diffusing to the electrode surface. This may result from the destruction of the aquo-layer surrounding the reducible ion. On the other hand, the decrease of $i_d\ \eta^{\frac{1}{2}}$ in acidic solutions may be due to the increased volume (or radius) of the reducible species due to the solvation of these species by the molecules of the organic solvent. The difference in behaviour can be explained by the fact that the reducible species exist in alkaline media as dianions which are less solvated by alcohol molecules compared to the species in acidic solutions which are the monovalent anions or neutral molecules (pK_1=3·75 and pK_2=4·75)[12].

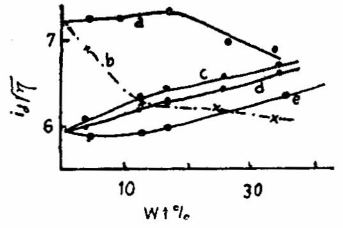

Fig. 3 — Plots of $i_d\ \eta^{\frac{1}{2}}$ versus wt % alcohol (a,b — propanol; b, d — ethanol; e — methanol) for the first wave at different *p*H values [curves (a, b) at *p*H 5; and curves (c-e) at *p*H 11]

The radius of the diffusing species can be calculated from the experimental data using Eq. (2)[3,13].

$$r=K^2/i_d^2\ \eta \qquad \ldots(2)$$

where r is the radius of reducible species (in cm) and $K=n\ \text{cm}^{2/3}t^{1/6}\times2{\cdot}99\times10^{-4}$ and equals $13{\cdot}6\times10^{-5}$ under the experimental conditions. The values thus calculated are given in Table 3. The data indicate that the changes in the radii of the reducible particles depend on the *p*H of the medium, nature and proportion of alcohol in the medium.

Medium effect on $E_{\frac{1}{2}}$ — The observed shift in $E_{\frac{1}{2}}$ of the reduction waves to more or to less negative potentials, on changing the proportions of the organic solvents, was attributed to the changes of dielectric constant of the medium, the interfacial tension and solvation of species[3,6].

The dielectric constant, ϵ, decreases as the proportion of the organic solvent increases. The decrease in ϵ prevents the mobility of the species and favours the formation of associated ion. This in turn leads to a lowering of the negative charge density on the reducible species and hence to an easier reduction, i.e. leads to a shift of $E_{\frac{1}{2}}$ to less negative values. This is a common phenomenon observed in acidic media, while in alkaline media $E_{\frac{1}{2}}$ shifts to more negative values. The variation of $E_{\frac{1}{2}}$ with ϵ is given by Takahashi[14] relation (Eq. 3)

$$E_{\frac{1}{2}(\text{S})}=E_{\frac{1}{2}(\text{W})}-K.\frac{1}{\epsilon(\text{W})}+K.\frac{1}{\epsilon(\text{S})} \qquad \ldots(3)$$

where w = water, and s = solvent. If the dielectric constant is the dominant factor, the shift in $E_{\frac{1}{2}(\text{S})}$ would be a linear function of $1/\epsilon_{(\text{S})}$. This is not the case in the present study (Fig. 4).

The abnormal behaviour in the shift of $E_{\frac{1}{2}}$ of the first wave at $p\text{H} > 10$, which corresponds to the reduction of triphenylcarbonium ion, to more negative values, indicate that the electrode reaction needs higher energy in the presence of organic solvents than in pure aqueous medium. Since the formation of the triphenylcarbonium ion is connected with the existence of the divalent anion[15] and the addition of the organic solvent leads to ions association, it is expected that the participation of the triphenylcarbonium ion in the electrode reaction is lowered.

In general the addition of organic solvents to water causes complete destruction of the normal structure of water. The destruction of the associated molecules readily influences the hydration layer surrounding the ions, leading to a shift of $E_{\frac{1}{2}}$ to less

TABLE 3 — VALUES OF $i_d\eta^{1/2}$ AND RADIUS (r) OF THE REDUCIBLE SPECIES AT pH 5·12 AND 11·0 IN AQUEOUS-ALCOHOL MIXTURES

[Depolarizer conc. = 0·56 mM]

Alcohol %	pH	Methanol		Ethanol		n-Propanol	
		$i_d\eta^{1/2}$ (μA)	$10^8 r$ (cm)	$i_d\eta^{1/2}$ (μA)	$10^8 r$ (cm)	$i_d\eta^{1/2}$ (μA)	$10^8 r$ (cm)
Nil	5·12	7·2	3·57	7·2	3·57	7·2	3·57
	11·00	5·9	5·31	5·9	5·31	5·9	5·31
4·0	5·12	7·18	3·59	6·91	3·87	7·3	3·47
	11·00	5·84	5·42	5·97	5·19	6·2	4·81
12·3	5·12	7·24	3·53	—	—	7·66	3·15
	11·00	5·91	5·30	6·28	4·69	6·43	4·47
16·5	5·12	7·33	3·44	6·31	4·65	7·35	3·42
	11·00	5·98	5·18	6·43	4·47	6·61	4·23
25·5	5·12	7·66	3·15	6·24	4·75	6·93	3·85
	11·00	6·28	4·69	6·57	4·29	—	
35·0	5·12	7·91	2·96	6·11	4·95	6·93	3·85
	11·00	6·28	4·69	6·85	3·94	6·93	3·85

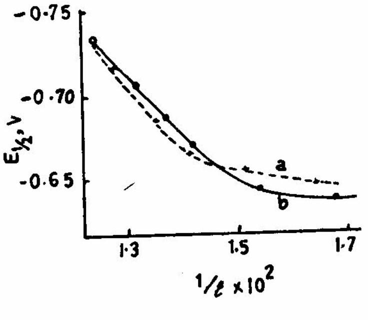

Fig. 4 — Plots of $E_{1/2}$ versus $1/\epsilon_{(s)}$ for the first wave at pH 5 in (a) ethanol and (b) propanol

negative values. Thus, it seems that the destruction of the hydrated layer and solvation of ions through organic solvents, exhibit an important influence on $E_{\frac{1}{2}}$ values. Accordingly, the observed shift in $E_{\frac{1}{2}}$, with increasing proportions of organic solvents, while keeping the pH of the medium constant, is due to the net resultant effect of these two factors.

Electrode reaction — The behaviour of 4,5-diiodofluorescein reveals that it is related to the category of organic compounds where $E_{\frac{1}{2}}$ and i_l are pH-dependent[16]. This pH-dependent reaction can be either a chemical transformation which is not probable for the compound under investigation or an acid-base reaction, which is influenced by pH as shown in Eq. (4)

$$\mathrm{HA} \overset{K_d}{\rightleftharpoons} K_d\mathrm{A}^- + \mathrm{H}^+ \qquad \ldots(4)$$

The ratio of the height i_{HA} of the first wave of the acidic form to i_l could be expressed by the Koutecky equation[16] (5)

$$i_{\mathrm{HA}}/i_l = \frac{0{\cdot}886\sqrt{\dfrac{k_r t_l}{K_1}}\,[\mathrm{H}^+]}{1+0{\cdot}886\sqrt{\dfrac{k_r t_1}{K_1}}[\mathrm{H}^+]} \qquad \ldots(5)$$

which can be modified in the form

$$p\mathrm{H} = \log\left(\frac{i_l - i_{\mathrm{HA}}}{i_{\mathrm{HA}}}\right) + \log\, 0{\cdot}886\sqrt{\frac{k_r t_1}{K_1}}$$

The plot of $\log \dfrac{i_l - i_{\mathrm{HA}}}{i_{\mathrm{HA}}}$ as a function of pH, taking the current of the first wave to represent the reduction of HA is linear, indicating that the electrode reaction involves an acid-base equilibrium.

Considering the informations given by Zuman[16], and the results of the present work, the sequence suggested for the electroreduction of the furan centre of 4,5-diiodofluorescein through the uptake of two electrons would be (,e⁻, H⁺, e⁻, H⁺) which can be represented as shown in Scheme 1.

$$(\mathrm{Oxidized})^{x-} + \mathrm{e}^- \xrightarrow{E_1} \mathrm{P}^{(x+1)}$$

$$\mathrm{P}_1^{(x+1)-} + \mathrm{H}^+ \overset{K_1}{\rightleftharpoons} (\mathrm{P}_1\mathrm{H})^{x-} \quad (p\mathrm{H\text{-}dependent})$$

$$\mathrm{P}_1\mathrm{H}^{x-} + \mathrm{e}^- \xrightarrow{E_2} \mathrm{P}_2^{(x+1)-}$$

$$(\mathrm{P}_2\mathrm{H})^{(x+1)-} + \mathrm{H}^+ \overset{K_2}{\rightleftharpoons} (\mathrm{Red.})^{x-}$$

Scheme 1

In media containing sufficiently high [H⁺] the rate of protonation (K_1) is high leading to a low stability of the intermediate ($\mathrm{P}_1^{(x+1)-}$). Thus the two steps involving the electron transfer would proceed at the same rate and accordingly E_1 will not differ much from E_2. The reduction of furan ring under such conditions will comprise one wave with a height corresponding to two electrons (at $pH \leqslant 9$).

If the $[H^+]$ is not sufficient to achieve the protonation of the intermediate ($P_1^{(x+1)-}$), the second reduction step is only achieved at higher energies, i.e. at more negative potentials. This leads to the reduction of furan ring through two waves each corresponding to one electron. The retarded wave overlaps the pyrone wave at $pH > 9{\cdot}5$. The decrease in the height of original furan wave is due to slower rate of protonation of the intermediate radical anion[3] ($P_1^{(x+1)-}$). This is substantiated by the fact that the i_l versus pH plots are typical dissociation or association curves either Z or S-shaped. The lowering of i_l of the first wave, as is obvious from i_l versus pH curves, starts at lower pH values with increasing proportion of the alcohols in the medium. An increase in alcohol content causes a decrease in the activity of the protons. In other words the proton exchange with the reducible species becomes slower as the polarity of the medium is decreased by the addition of a high proportion of the alcohol[17]. Thus the dissociation of the protonated intermediate will be easier in the presence of alcohols. The lowering of i_l of the furan wave is ascribed to the increased stability of the $P_1^{(x+1)-}$ species. Accordingly, it is possible to calculate the equilibrium constant (termed protonation constant K_p) of the reaction (Eq. 6) using Eq. (7) and analysing the i_l versus pH curves as given previously[3]. The values obtained in aqueous medium 35% methanol, ethanol and *n*-propanol amount to 10·2, 10·0, 9·75 and 9·6 respectively. These results indicate that pK_d values are dependent on the nature and proportion of the alcohol in the medium. These values were found to decrease on increasing the proportion of the alcohol due to decreased H^+ ion activity

$$P_1^{(x+1)-} + H^+ \overset{K_p}{\leftrightharpoons} P_1H^{x-} \qquad \ldots(6)$$

$$K_p = \frac{[P_1H^x]}{[P_1^{(x+1)-}][H^{x-}]} \qquad \ldots(7)$$

Kinetic parameters of the electrode reaction — Values of some kinetic parameters of the electrode reaction were calculated at different pH values and in the presence of varying proportions of alcohols or surfactants. Values of rate constant (K°_{fh}) and activation energy (ΔG^*) were calculated using the equations[9,18] (8) and (9) respectively.

$$\log K^{\circ}_{fh} = \log\,(i/i_d - i)_{E=0(\mathrm{NHE})} + \log\,(D^{1/2}/0{\cdot}87\ t^{1/2}) \qquad \ldots(8)$$

and

$$\Delta G^* = 5778{\cdot}8\ (5{\cdot}097 - \log K^{\circ}_{fh})_{E=0(\mathrm{NHE})} \qquad \ldots(9)$$

Representative results are given in Tables 1 and 2. These values indicate that the different kinetic parameters (K°_{fh}, ΔG^* $K^{\circ}_{fh}\,D^{-1/2}$) are influenced by pH of the medium, nature and proportion of the alcohol and surfactant. The values of $K^{\circ}_{fh}\ D^{-1/2}$ reveal that the electrode reaction is mainly governed by the rate of electron transfer, i.e. it is essentially kinetic. Values of K°_{fh} and ΔG^* indicate that as the pH or alcohol and surfactant proportion increases, the reduction process becomes more difficult. At the same time, values of transfer coefficient (α) indicate that the electrode reaction proceeds irreversibly. The degree of irreversibility depends on pH of the medium, nature and proportion of organic solvent and surfactant.

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