COADSORPTION OF BULKY IONS BY SURFACTANTS. MONOMOLECULAR LAYERS OF TRIS(2,2'-BIPYRIDYL)RUTHENIUM(II) COMPLEX WITH SODIUM LAURYL SULPHATE ON GLASSY CARBON, PLATINUM, n-SnO$_2$, AND n-Si ELECTRODES

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The electrochemical and photochemical behaviour of tris(2,2'-bipyridyl)ruthenium(II) complex (I) on glassy carbon, platinum, n-SnO$_2$, and n-Si electrodes in the presence of sodium lauryl sulphate (II) was investigated. The surfactant in low concentrations induces self-association of the complex cation and its accumulation in the electrode-solution interface. At the optimum concentrations of sodium lauryl sulphate ($c_{II} \approx 0.6$ mmol l^{-1}) and of the complex ($c_I < 0.1$ mmol l^{-1}), monomolecular layers composed of I, II counterions are formed on the electrodes. The formation of the surface films does not depend on the kind of the electrode and improves the sensitivity of the voltammetric determination of I by as much as an order of magnitude. For the semiconductor electrodes, the surface films enhance the efficiency of conversion of radiant energy into electric energy. The effect under study may participate in the photosynthesis of green plants.

The photochemical and electrochemical properties of tris(2,2'-bipyridyl)ruthenium(II) complex and its derivatives are attracting interest owing to the facts that the complexes are thermally and photochemically stable in aqueous solutions, they exhibit convenient spectral properties, and are frequently used as catalysts and sensitizers of photochemical reactions. Monomolecular layers of the complex containing aliphatic chains of fatty acids bonded *via* ester bonding have been examined and found to decompose water into oxygen and hydrogen on their irradiation[1]. Photolysis of water has been achieved with a relatively high efficiency[2] in cetyltrimethylammonium bromide micellar solutions containing I, a suitable electron acceptor (methylviologen), and colloidal catalysts (RuO$_2$, Pt). In photovoltaic converters containing semiconductor electrodes possessing a very broad forbidden band, the complexes have been employed for increasing the absorption of radiation in the visible region of the spectrum[3−7].

In all cases it was necessary that the complex accumulated in the interface, or that electrochemically and photochemically active layers were formed. The layers were obtained by means of surfactant derivatives[1] or by bonding the modified complex chemically to the surface of the solid (the electrode)[6,7]. However, the preparation

of the layers was rather tedious and the efficiency was low, and moreover, their photochemical stability could not be always ensured.

Ionic surfactants in aqueous solutions in concentrations below the critical micellar concentration induce association of bulky counterions and raise their concentration in the solution–solid phase interface[8–10]. In the present work, electrochemically and photochemically active layers of *I* were obtained with the help of sodium lauryl sulphate.

EXPERIMENTAL

Chemicals and Apparatus

$Ru(bpy)_3(ClO_4)_2$ was prepared by reacting $K_2[RuCl_5(H_2O)]$ with bipyridyl[11], and its purity was checked *via* the molar absorptivity of the first long-wavelength band[4]. Sodium lauryl sulphate was a commercial chemical for tenside investigation (Merck, Darmstadt). The n-SnO_2 (sample resistance $10–500\ \Omega$/square) and n-Si (specific resistance $0.015–0.02\ \Omega$ m) electrodes were prepared as described previously[12]. Anodically polarized in light, the silicon electrode is slowly coated by an insulating layer of oxides of silicon; after $5–15$ measurements the nonconductive layer must be etched off in concentrated HF and the electrode rinsed with distilled water and acetone. The n-SnO_2 electrode has a reasonable service life and requires no special treatment, only cathodic polarization must be avoided in media containing ions which form complex compounds with Sn^{2+} ions. The bright platinum electrode was made of a wire, 0.5 mm in diameter and $0.1\ cm^2$ surface area, sealed up in a glass tube, and purified by cyclic polarization in supporting electrode which was terminated at a potential of 0.2 V. The glassy carbon electrode, of a $1–3\%$ porosity (Radiometer, Copenhagen), was polished by using a diamond paste and polarized at a potential of 0.65 V prior to use. The auxiliary electrode was a large-surface platinum wire. All the potentials were measured against S.C.E. The following instruments were used: a PA 3 polarographic analyzer (Laboratorní přístroje, Prague), a PHM-64 pH-meter (Radiometer, Copenhagen) (± 0.01 pH units), an SP 8-100 spectrophotometer (Pye-Unicam, Cambridge), and a Model 115 spectrofluorimeter (Optica, Milan). For obtaining the c.v. curves at potential ramps exceeding 0.5 V s^{-1}, an instrument consisting of a supply of triangular and reference voltages, summator, potentiostat, and a current-voltage convertorr was employed. The voltammograms were recorded by means of an OPD 280 U oscilloscope (Tesla, Czechoslovakia). The semiconductor electrodes were illuminated by focussed light of a tungsten lamp (colour temperature 2 850 K, illumination 65 000 lx).

Evaluation of Experimental Data

On the cyclic polarization of the electrodes by triangular pulses at voltage ramps $v \geqq 5$ V s^{-1}, diffusion of *I* does not manifest itself electrochemically and the c.v. peaks correspond to adsorption currents solely. The dependences of the charge associated with the electrochemical conversion of the adsorbed depolarizer, Q^{ad}, and of the peak height, I_p^{ad}, on the concentration of *I* (at a constant concentration of *II*) follow the shape of the Langmuir isotherm

$$\Theta = \Gamma/\Gamma_{max} = \omega c_I/(1 + \omega c_I),\qquad(1)$$

where Γ and Γ_{max} are the actual and the saturated-state surface concentrations of depolarizer,

respectively, and ω is the adsorption coefficient of depolarizer; Θ is the degree of coverage of the electrode given by the ratios Q^{ad}/Q^{ad}_{max} or $I^{ad}_p/I^{ad}_{p,max}$. The charge and current in the saturated state were obtained *via* the linear transformation

$$1/Q^{ad} = 1/Q^{ad}_{max} + 1/(\omega Q^{ad}_{max} c_I) \qquad (2a)$$

and

$$1/I^{ad}_p = 1/I^{ad}_{p,max} + 1/(\omega I^{ad}_{p,max} c_I) . \qquad (2b)$$

The adsorption coefficients ω were calculated according to

$$\omega = \Theta/[(1 - \Theta) c_I] \qquad (3)$$

as averages of $6-7$ values obtained over the region of $c_I = 5-35 \ \mu\text{mol l}^{-1}$.

The charge associated with the electrochemical conversion of the adsorbed electroactive material was obtained, independently of the above procedure, by extrapolating the relation

$$Q_T = \text{const.} \ c_I v^{-1/2} + Q^{ad} \qquad (4)$$

to $v \to \infty$ (Q_T is the total, *i.e.* adsorption plus diffusion, faradaic charge).

RESULTS AND DISCUSSION

Polycrystalline n-SnO$_2$ *electrode*. The highly conductive n-SnO$_2$ electrode gives well-developed *c.v.* peaks of I in strongly acid solutions (pH $\leq$ 2). The potentials of the peaks are independent of the potential ramp ($v = 0.002-0.5 \ \text{V s}^{-1}$ for $c_I = 20 \ \mu\text{mol l}^{-1}$), and their difference approaches the theoretical value for a one--electron exchange ($E^C_p = 1.030 \ \text{V}$, $E^A_p = 1.100 \ \text{V}$). The heights of the cathodic peaks are identical and depend linearly on the concentration of I and on the square root of the voltage ramp rate. The extrapolation of relation (4) gave evidence that in pure solutions (free of surfactant) no adsorption of complex I takes place ($Q^{ad} = 0$). It can be thus concluded that, in accordance with published data[6], the Ru(bpy)$_3^{2+}$: : Ru(bpy)$_3^{3+}$ redox couple gives currents controlled by diffusion.

If sodium lauryl sulphate is added, association (at $c_{II} < c_{mc}$) or micellization (at $c_{II} > c_{mc}$) of complex I takes place. This is manifested by the fluorescence spectra (association leads to concentration quenching of fluorescence) (Fig. 1), electronic spectra[8,12], and reactivity of the molecules[10], and also by the dependences of I_p on the concentration of II; the association leads to accumulation of the electroactive material at the electrode surface and increase in I_p, in micellar solutions the surface layers of the depolarizer are washed off, and the decrease in the peak height is also contributed to by the less easy diffusion of the bulky micelles. The maxima on the concentration curves can be attributed to the critical micellar concentration of sodium lauryl sulphate, $c_{mc} \approx 0.6 \ \text{mmol l}^{-1}$ (Fig. 1).

The optimum concentration of sodium lauryl sulphate for the association and accumulation of I is $0.6 \ \text{mmol l}^{-1}$. In comparison with pure solutions the peak

separation diminishes and the potentials vary slightly $\left(E_p^C = 1\cdot065 \text{ V}, E_p^A = 1\cdot090 \text{ V}, \Delta E = 0\cdot025 \text{ V}; v = 0\cdot002 - 1 \text{ V s}^{-1}\right)$ (Fig. 2). In the currentless state the accumulation of the depolarizer takes $20-30$ min. Constant currents can be obtained on a $10-15$ min cycling of the electrode $\left(0\cdot7-1\cdot25 \text{ V}\right)$; the heights of the anodic and cathodic currents are identical. The I_p values depend on the potential ramp rate in a rather complex manner. At low rates, $v = 0\cdot002 - 0\cdot02 \text{ V s}^{-1}$, the $\log I_p$: : $\log v$ quotient is $0\cdot6 - 0\cdot7$, at higher rates, $v = 0\cdot05 - 35 \text{ V s}^{-1}$, it approaches unity. Its concentration dependences also demonstrate that the c.p. peaks involve both adsorption and diffusion currents (Fig. 3). Purely adsorption c.v. peaks can be obtained on the electrode cycling at potential ramps exceeding 5 V s^{-1}; the dependences of Q^{ad} and I_p^{ad} on the concentration of I then continue to follow the Langmuir isotherm shape and the degree of the electrode coverage, the adsorption coefficient, and the amount of adsorbed electroactive material in the saturated state can be evaluated (Table I). The relatively high adsorption coefficient $\left(2\cdot46 . 10^5\right)$ is indicative of a high accumulating efficiency of sodium lauryl sulphate. The average electrode
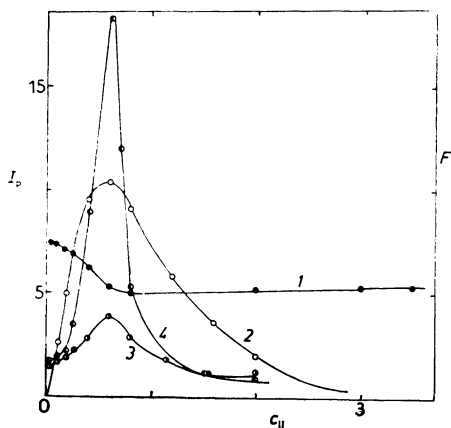

FIG. 1

Dependence of the fluorescence intensity *1* and the height of the cathodic peaks (*2 — 4*) on the concentration of sodium lauryl sulphate; $c_I = 20 \text{ μmol l}^{-1}$, pH 1·14. *2* n-Si electrode, $v = 0\cdot005 \text{ V s}^{-1}$, current in 0·1 μA cm^{-2} units; *3* n-SnO$_2$ electrode, $v = 0\cdot02$ V s^{-1}, current in μA cm^{-2}; *4* n-SnO$_2$ electrode, 20 min accumulation of depolarizer at 1·2 V with stirring, $v = 0\cdot02$ V s^{-1}, current in μA cm^{-2}
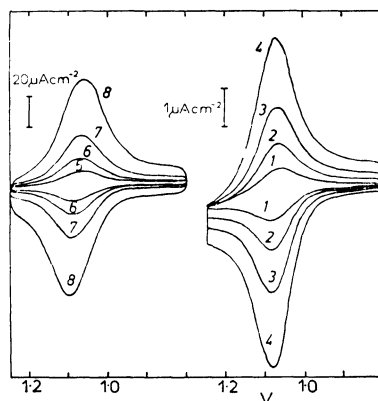
FIG. 2

Shape of the *c.v.* peaks of tris(2,2′-bipyridyl)-ruthenium(II) complex on n-SnO$_2$ electrode. $c_I = 20 \text{ μmol l}^{-1}$, $c_{II} = 0\cdot6 \text{ mmol l}^{-1}$, pH 1·13. Potential ramp (V s^{-1}): *1* 0·002, *2* 0·005, *3* 0·01, *4* 0·02, *5* 0·05, *6* 0·1, *7* 0·2, *8* 0·5

area per molecule of the electroactive material, $1\cdot8$ nm^2, as well as the very occurrence of the saturated state indicates that monomolecular films are probably formed.

The formation of surface films results in a substantial increase in the sensitivity of the voltammetric determination of I. The relative increase in the peak heights as compared with pure solutions is particularly marked at low concentrations of depolarizer, where the adsorption currents play a major role. Under optimum conditions $\left(c_{II} = 0\cdot6 \text{ mmol l}^{-1}, v = 0\cdot1-2 \text{ V s}^{-1}\right)$, I can be determined reliably at concentrations as low as $0\cdot05 \mu\text{mol l}^{-1}$ which represents a $20-30$ fold increase in the sensitivity of the analytical determination.

In micellar solutions $\left(c_{II} = 4 \text{ mmol l}^{-1}\right)$, the $Ru(bpy)_3^{2+}/Ru(bpy)_3^{3+}$ redox couple behaves similarly as in aqueous solutions. The peak heights depend linearly on the

TABLE I

Adsorption isotherms of tris(2,2'-bipyridyl) ruthenium(II) complex

Electrode	Adsorption coefficient $\omega \cdot 10^{-5}$	$c_s^{sat\,a}$ $10^{-10} \text{ mol cm}^{-2}$	A^b nm^2
n-SnO$_2$	2·46	0·93	1·8
n-Si	3·78	1·49	1·1
Pt	1·68	0·88	1·9
C	3·83	1·40	1·2

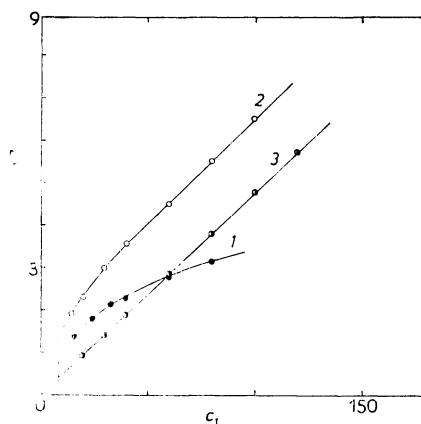^{a} Surface concentration for the saturated state; ^{b} average electrode surface area per molecule of complex.

FIG. 3

Dependence of the height of the cathodic peaks on the concentration of tris(2,2'-bipyridyl)ruthenium(II) complex. $c_{II} = 0\cdot6$ mmol l^{-1}, pH $1\cdot14$, $v = 0\cdot02$ V s^{-1}; c_I in μmol l^{-1}, current in μA cm^{-2}. 1 n-Si electrode, 2 n-SnO$_2$ electrode, 3 n-SnO$_2$ electrode, solution free of surfactant

depolarizer concentration and on the square root of the potential ramp rate, $v =$ $= 0.002 - 0.5$ V s^{-1}, which points to an electrode process controlled by diffusion solely. In comparison with pure solutions the potentials of the peaks are shifted slightly to higher values $\left(E_p^C = 1.070 \text{ V}, E_p^A = 1.140 \text{ V} \right)$, and the peak heights are about a third lower due to the less easy diffusion of the bulky micelles.

Cathodic photocurrent can be obtained on the irradiation of a highly doped electrode in acid solutions of I saturated by air oxygen[5]. The photochemical oxidation of I with the participation of oxygen and of hydrogen ions leads to the formation of $Ru(bpy)_3^{3+}$. The oxidized product diffuses to the electrode and is electrochemically reduced on it by electrons from the conduction band, tunelling through the narrow region of the spatial charge of the highly doped SnO_2 electrode. If, on the other hand, a low-doped electrode or an electrode anodically polarized in deaerated solutions are exposed to radiation, excitation of molecules of I on its surface takes place, electrons are transferred to the conduction band of SnO_2, and anodic photo-current results[5]. It a suitable amount of sodium lauryl sulphate is added, the cathodic and anodic photocurrents obtained are $3 - 5$ times higher than in pure solutions. In the three-electrode connexion $\left(\text{n-}SnO_2/\text{s.c.e}/\text{Pt} \right)$ the cathodic photocurrent in $0.1\text{M-}H_2SO_4$ at $c_I = 20$ µmol l^{-1} (0.0 V) in the absence of sodium lauryl sulphate and in its presence in a concentration of about 0.6 mmol l^{-1} is 0.03 and 0.14 µA cm^{-2}, respectively. The anodic photocurrent, at the same concentrations (1.1 V), is 0.02 and 0.061 µA cm^{-2}, respectively.

Single-crystal n-Si *electrode.* No c.v. peaks can be obtained by polarization of the n-Si electrode $(-1$ to 2.25 V$)$ in pure solutions of I. If a small amount of sodium lauryl sulphate is added, the complex is converted into an electroactive form capable of electron exchange with the electrode (Fig. 4). Similarly as for the n-SnO_2 electrode, the dependence of I_p on the concentration of II has a characteristic shape showing accumulation and, at higher concentrations of II, micellization of the depolarizer (Fig. 1). Micellization is a competitive process with respect to the adsorption, and the *c.v.* peaks vanish on its quantitative occurrence. The complex accumulates to the highest extent at surfactant concentrations of $0.4 - 0.8$ mmol l^{-1}. The semiconductor nature and the uncompensated resistance of the electrode are manifested by the irreversible course of the electrode process. The potentials of the peaks depend on the voltage ramp, and their difference exceeds greatly the theoretical value and increases with increasing potential ramp rate (Fig. 4, Table II). The dependences of Q and I_p on the concentration of I do not attain the saturated state, thus indicating that both adsorption and diffusion currents are involved. The same is deduced from the analysis of the dependence of the peak heights on the rate of the potential ramp. The $\log I_p/\log v$ quotient does not attain the value of unity, it only lies within the region of $0.64 - 0.84$. No peaks being observed in the absence of surfactant, the surface film of I with the surfactant clearly possesses electrocatalytic properties and enables also diffusion currents to show up.

Since for the n-Si electrode, high potential ramp rates cannot be used or the adsorption currents measured due to the irreversible nature of the electrode process involved, the calculation of the adsorption coefficient was only approximate. The degree of coverage of the electrode was approximated by

$$\Theta = \left(Q - Q^{d}\right)/\left(Q - Q^{d}\right)_{max} \qquad (5a)$$

$$\Theta = \left(I_{p} - I_{p}^{d}\right)/\left(I_{p} - I_{p}^{d}\right)_{max} , \qquad (5b)$$

TABLE II

Potentials of the peaks of tris(2,2'-bipyridyl)ruthenium(II) complex on n-Si electrode; $c_{I} = 20\ \mu mol\ l^{-1}$, $c_{II} = 0.6\ mmol\ l^{-1}$, $0.1\text{M-}H_2SO_4$

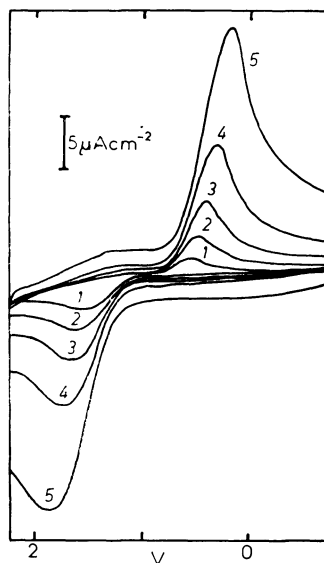| Peak	Potential, V, for the potential ramp (V s^{-1})						
	0.005	0.01	0.02	0.05	0.1	0.2	0.5
Cathodic	0.720	0.660	0.570	0.465	0.405	0.320	0.150
Anodic	1.425	1.486	1.535	1.620	1.659	1.745	1.850

FIG. 4

Shape of the c.v. peaks of tris(2,2'-bipyridyl)ruthenium(II) complex on n-Si electrode. $c_{I} = 20\ \mu mol\ l^{-1}$, $c_{II} = 0.6\ mmol\ l^{-1}$, pH 1.14, potential ramp (V s^{-1}): 1 0.02, 2 0.05, 3 0.1, 4 0.2, 5 0.5

where Q^d and I_p^d refer to the diffusion current solely; the values were estimated based on the slopes of the linear segments of the concentration dependences $Q = Q(c_I)$ and $I_p = I_p(c_I)$ at $c_I > 70\ \mu\text{mol l}^{-1}$. The ω value was calculated for the concentration of $20-40\ \mu\text{mol l}^{-1}$, in which a complete electrocatalytic efficiency of the surface film is assumed. Although approximate, the value agrees well with the results obtained for other electrodes (Table I). The charge corresponding to the complete coverage of the electrode by the electroactive material was obtained by extrapolation from Eq. (4); the value is also consistent with the results obtained for other electrodes and gives evidence of the formation of a monomolecular surface layer (Table I).

Due to the anodic polarization of the n-Si electrode the boundaries of the valence and conduction bands are bent and the concentration of holes beneath the surface is increased. As a result of excitation of the electrode modified by the surface film of I, electrons from the $Ru(bpy)_3^{2+}$ ions are injected into the valence band of n-Si and anodic photocurrent appears. Immediately after the irradiation the current rises rapidly and then dies away exponentially with time. The charge estimated from the current vs time dependence corresponds roughly to a complete reaction of the monomolecular layer of the depolarizer. A steady photocurrent whose dependence on the potential corresponds with the anodic peak of I (Fig. 5) persists for several hours. This indicates an exchange of the oxidized molecules in the surface film or their reduction restoration by molecules of water.

Platinum and glassy carbon electrodes. The behaviour of I on platinum and glassy carbon electrodes is identical. In pure solutions, free of surfactant, reversible c.v. peaks are observed ($E_p^C = 1 \cdot 030$ V, $E_p^A = 1 \cdot 090$ V, $v = 0 \cdot 002 - 0 \cdot 5$ V s^{-1}). The heights of the cathodic and anodic peaks are comparable and depend linearly on the concentration of I on the square root of the potential ramp rate.
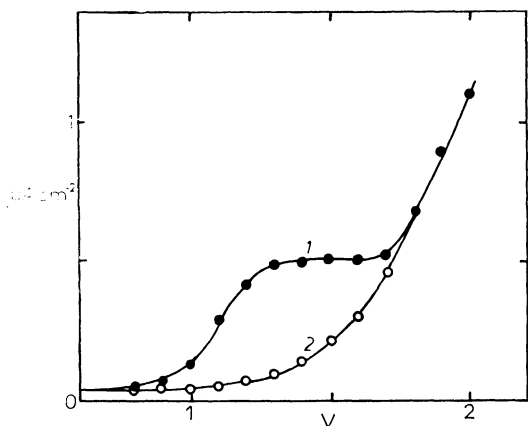

FIG. 5

Dependence of the anodic photocurrent on the potential of the n-Si electrode in the presence 1 and in the absence 2 of sodium lauryl sulphate. $c_I = 20\ \mu\text{mol l}^{-1}$, $c_{II} = 0 \cdot 6$ mmol l^{-1}, pH $1 \cdot 13$

Typical adsorption phenomena appear in solutions containing sodium lauryl-sulphate in low concentrations $\left(c_{II} = 0{\cdot}2 - 1 \text{ mmol } l^{-1}\right)$; the peaks increase, their separation diminishes $\left(E_p^C = 1{\cdot}065 \text{ V}, E_p^A = 1{\cdot}095 \text{ V}; \Delta E_p = 0{\cdot}03 \text{ V}\right)$, the $\log I_p/\log v$ quotient depends on the potential ramp rate and approaches unity at high rates $\left(v = 5 - 35 \text{ V s}^{-1}\right)$. The anodic and cathodic peaks are increased by the adsorption of depolarizer to the same extent $\left(I_p = 8{\cdot}7 \text{ and } 77{\cdot}5 \text{ }\mu\text{A cm}^{-2}\right.$ in the absence and in the presence of II, $c_{II} = 0{\cdot}6 \text{ mmol } l^{-1}$, respectively; $c_I = 20 \text{ }\mu\text{mol } l^{-1}$, $0{\cdot}1\text{M-}$ $\left.\text{-H}_2\text{SO}_4, v = 0{\cdot}5 \text{ V s}^{-1}\right)$. The dependences of the charge and the peak height on concentration of I follow the shape of the Langmuir isotherm. The adsorption coefficients and the surface concentrations corresponding to the complete coverage of the electrode are given in Table I.

In micellar solutions $\left(c_{II} = 4 \text{ mmol } l^{-1}\right)$ only diffusion currents were observed on the two electrodes, the peak heights being 40% lower than in aqueous solutions. The potentials of the peaks are virtually the same as in aqueous solutions $\left(E_p^C = \right.$ $= 1{\cdot}060 \text{ V}, E_p^A = 1{\cdot}120 \text{ V}, v = 0{\cdot}002 - 0{\cdot}01 \text{ V s}^{-1}\right)$, the peak separation, however, increases with increasing potential ramp. Clearly, a diffusion-controlled irreversible process is involved.

The accumulating effect of sodium lauryl sulphate is little dependent on the electrode nature. The adsorption coefficients and surface concentrations (for the saturated state) are commensurable, and in all cases the formation of monomolecular layers can be assumed (Table I).

For achieving the accumulating effect, the depolarizer must in general be combined with a tenside which acts as its counterion. As long as this rule is adhered to, the accumulating effect of surfactants is universal. Sodium lauryl sulphate can be used to form electroactive surface layers of other cationoid depolarizers such as Fe(bpy)_3^{2+} : : Fe(bpy)_3^{3+} or methylene blue[12,14]. Cationoid tensides, on the other hand, can be used for the accumulation of anionic depolarizers (luminol, cytidylic acid[8,14]).

The surface films are formed as a result of weak interactions, particularly electrostatic and hydrophobic, which do not exhibit a state of saturation, and the adsorbate cannot be expected to have a uniform composition. Simultaneous adsorption of I and II on polycrystalline SnO_2 powder $\left(c_I = 50 \text{ }\mu\text{mol } l^{-1}, c_{II} = 0{\cdot}8 \text{ mmol } l^{-1}, \right.$ $0{\cdot}1\text{M-H}_2\text{SO}_4\right)$ was evaluated and the adsorbate was found to contain I and II in amounts of 0·4 and 1·14 $\mu\text{mol g}^{-1}$, respectively. Thus, while in the solution before the adsorption the I-to-II ratio was 0·06, in the adsorbate it was as high as 0·36, hence, a relative accumulation of I took place at the surface of the solid.

The structures of the counterions in the solution–electrode interface display a dense arrangement of the molecules. This is borne out by the appreciable decrease in the fluorescence quantum yield and chemiluminescence intensity observed if the surface layers are formed[8].

The surface layers improve the efficiency of the radiant energy conversion. Favourable effects arise from the accumulating action of the surfactant and from the cata-

lytic properties of the surface layers of the depolarizers and sensitizers. With the n-Si electrode the c.v. peaks were observed only in the presence of sodium lauryl sulphate. The formation of the surface films on the $n-SnO_2$ electrode resulted in a multiple increase in the cathodic as well as anodic photocurrents, although the electron transfer mechanism in the two cases is different. The results bear out the assumption that anionic surfactants in general have a favourable effect on the electrochemical and photochemical behaviour of cationic substrate. Since the phase boundary and surfactant sensitizer concepts form important links in the current theories of photosynthesis[15], it can be assumed that the effects studied also take part in the processes of photosynthesis of green plants.

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