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Electrochemical Studies on Sulfonephthaleins IV [1]. Bromopyrogallol Red Self-Assembled Monolayers on a Mercury Electrode

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Summary. The electrochemical reduction behaviour of bromopyrogallol red in aqueous medium at *pH* 2.16 on a hanging mercury drop electrode was studied. The results indicate that in acid medium the reduction process proceeds via an ECEC mechanism. The formation and organization of a self-assembled monolayer of bromopyrogallol red on the hanging mercury drop electrode was studied in $0.1\,M$ $HClO_4$. Cyclic voltammetry and chronocoulometry have been used to characterize the modified electrode. The amount of bromopyrogallol red adsorbed on the HMDE expressed as excess surface coverage (Γ) for both *in situ* and *ex situ* experiments as well as the surface areas occupied by one molecule (σ) were calculated. It was found that the values obtained for Γ and σ utilizing cyclic voltammetric and chronocoulometry are almost identical. Values for *ex situ* experiments are a little lower than those for *in situ* experiments. The effect of the modification time on the organization process and its influence on the rate of electron transfer of the $Cd^{2+/0}$ couple were investigated.

Keywords. Bromopyrogallol; Reduction; Adsorption; Cyclic voltammetry; Chronocoulometry; Self-assembling.

Elektrochemische Studien an Sulfonphthaleinen, 4. Mitt. [1]. Selbstassemblierte Brompyrogallolrot Monoschichten an einer Quecksilberelektrode

Zusammenfassung. Die elektrochemische Reduktion von Brompyrogallolrot wurde in wäßrigem Medium bei *pH* 2.16 an einer hängenden Quecksilbertropfelektrode untersucht. Die Ergebnisse weisen darauf hin, daß in saurem Medium der Reduktionsprozeß über einen ECEC-Mechanismus verläuft. Die Bildung und Organisation einer selbstassemblierten Monoschicht von Brompyrogallolrot an der Elektrode wurde in $0.1\,M$ $HClO_4$ studiert. Diese modifizierte Elektrode wurde mittels cyclischer Voltammetrie und Chronocoulometrie charakterisiert. Die Menge des an die HMDE adsorbierten Brompyrogallolrots wurde in Form der Oberflächenbelegung (Γ) sowohl für *in situ* als auch für *ex situ* Experimente als auch als durch die von einem Molekül eingenommene Oberfläche σ abgeleitet. Es wurde gefunden, daß die Werte für Γ und σ für beide Techniken praktisch identisch sind. Allerdings sind die Γ- und σ-Werte für die *ex situ* Experimente etwas niedriger als jene für die *in situ* Experimente. Die Effekte der Modifizierungszeit auf den Organisationsprozeß und die Art, in der diese Organisation die Elektronentransferrate des $Cd^{2+/0}$-Paares beeinflußt, wurden ebenfalls untersucht.

Introduction

It has been realized for a long time that when certain electrochemically active species are examined using electrochemical techniques, electrosorption of the material onto the electrode surface occurs. Several attempts have been made to use this phenomenon to modify electrode surfaces. The adsorption process is often not fully understood, but in those systems that have been extensively studied it appears that some form of bonding takes place. The spontaneous formation of so-called self-assembled monolayers (SAMs) upon immersing of a surface into a diluted solution of amphifunctional molecules has been the subject of numerous studies [2]. The organization and properties of those SAMs have been investigated by means of spectroscopy, microscopy, electrochemistry, and almost every possible surface technique [3–9]. Recently, SAMs have been used to design a variety of selective sensors [10].

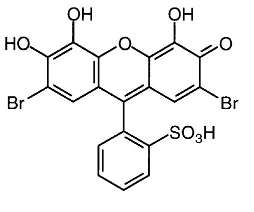
Several dyes and organic reagents which are reducible at the mercury electrode can be used as complexing ligands in which they form adsorptive complex waves of rare earths. It has been found previously that some phenolphthalein dyes, O-crysolphthalexon [11, 12] and thymolphthalexon [13], form adsorptive complex waves with rare earths. Bromopyrogallol red is an important reagent due to its use as a metallochromic indicator [14] in the simultaneous determination of chromium, vanadium, and titanium(IV) [15], in the determination of thallium(III) [16], and in the determination of vanadium(IV) and vanadium(V) [17]. Thus, in continuation of our previous work on sulfonephthaleins [1, 18] it seemed of interest to study the adsorption behaviour of the title compound.

The main object of the present study is to investigate the adsorption of the compound on a mercury electrode in aqueous 0.1 M $HClO_4$ utilizing cyclic voltammetry and double potential step chronoamperometry and chronocoulometry.

Results and Discussion

Bromopyrogallol red (**1**) has the structural formula shown in Scheme 1. Cyclic voltammetry of **1** was performed in aqueous *Britton-Robinson* buffer solutions at different *pH* values. The cyclic voltammogram of $1.0\times10^{-3}\,M$ **1** shows a single cathodic wave with a peak potential of -0.498 V *vs.* Ag/AgCl (sat) at $pH = 2.16$ and a scan rate of 100 mV/s. Since the complete reduction of sulfonephthaleins requires the transfer of two electrons [18–20], as also indicated by the controlled potential coulometric results, the observed CV wave for **1** involves two electrons. Accordingly, the electroreduction of **1** at lower *pH* values will follow the same reduction mechanism as observed for catechol violet and xylenol orange, *i.e.* following an ECEC first-order pathway giving a single two-electron diffusion controlled cyclic voltammetric wave (cf. Scheme 1) [1, 18]. It was concluded that the rate determining step is the protonation of the protonated anion intermediate, leading to the final product.

More attention will be given to the adsorption behaviour of **1** on the mercury electrode which is the key point of the current study in order to modify and characterize the HMDE. The method of choice for this purpose is electrochemical analysis by cyclic voltammetry and chrononamperometry or chronocoulometry.



1

$$\mathbf{1} \xrightleftharpoons[-e^-]{+e^-} \mathbf{1}^{\cdot -}$$

$$\mathbf{1}^{\cdot -} \xrightleftharpoons[-H^+]{+H^+(k_1)} \mathbf{1}^{\cdot} - H$$

$$\mathbf{1}^{\cdot} - H \xrightleftharpoons[-e^-]{+e^-} \mathbf{1}^{-} - H$$

$$\mathbf{1}^{-} - H \xrightleftharpoons[-H^+]{+H^+(k_2)} \mathbf{1} - H_2$$

Scheme 1

Cyclic voltammetry

The cyclic voltammogram of a HMDE recorded in 0.1 *M* $HClO_4$ containing 1×10^{-5} mol · dm^{-3} of bromopyrogallol red after 5 min of modification is shown in Fig. 1a. A cathodic wave is observed at −0.523 V, correspond to a faradaic surface process. Upon scan reversal, an anodic wave of almost the same intensity appears at −0.487 V. This anodic wave presumably indicates that no desorption process of the electroactive species takes place upon reduction. However, the cyclic voltammetric response due to adsorption is asymmetric with unequal anodic and cathodic peak potentials. The cyclic voltammogram obtained in *ex situ* experiments in which the modified HMDE is transferred into a 0.1 *M* perchloric acid solution free of **1** is shown in Fig. 1b. The potential of the reduction peak is shifted to more

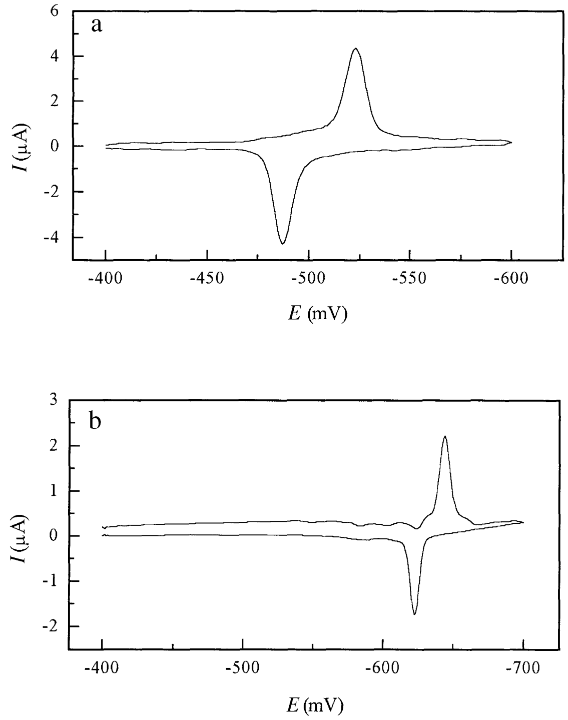


Fig. 1. a: Cyclic voltammetry of a HMDE in 0.1 *M* $HClO_4$ containing 1×10^{-5} mol · dm^{-3} **1** after 5 min of modification at a scan rate of 100 mV/s; b: cyclic voltammetry of the modified HMDE in 0.1 *M* $HClO_4$ (without **1**) at a scan rate 100 mV/s

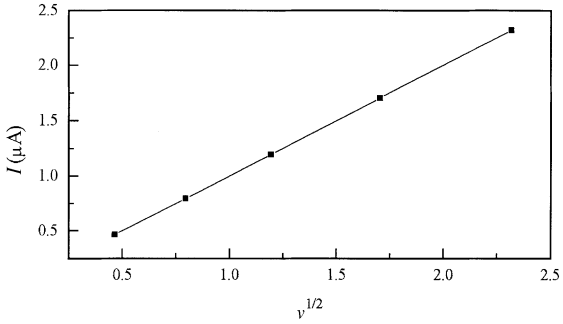


Fig. 2. Dependence of the cathodic peak current on the square root of the scan rate

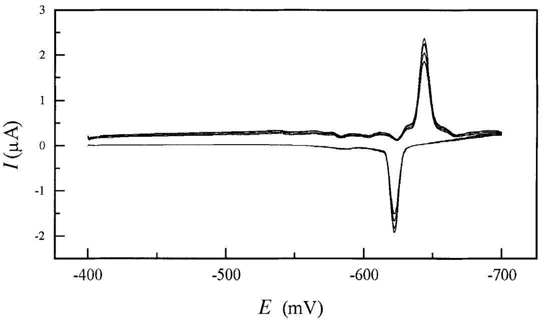


Fig. 3. Cyclic voltammograms of a HMDE in $0.1\,M$ $HClO_4$ containing $1\times10^{-5}\,\mathrm{mol\cdot dm^{-3}}$ **1** after different times of modification at a scan rate of $100\,\mathrm{mV/s}$

negative potential in the *ex situ* voltammogram, indicating a more negative adsorption energy.

From the cyclic voltammetric data, a linear dependence of the peak current of the cathodic wave on the scan rate (Fig. 2) is obtained, indicating a surface confined reaction. It is worth noting the effect of the time for which the HMDE was left in the modification solution prior to running the cyclic voltammograms. Figure 3 shows the cyclic voltammogram of a HMDE in $0.1\,M$ $HClO_4$ containing $1\times10^{-5}\,\mathrm{mol\cdot dm^{-3}}$ of **1** after different times of modification. It is evident that the shape and the total charge of the wave do not change significantly, implying that full coverage is achieved after a short time (less than 5 min) for concentrations of **1** above $1.0\times10^{-5}\,\mathrm{mol\cdot dm^{-3}}$.

The areas of the cathodic waves for both *in situ* and *ex situ* voltammograms were calculated. It was found that the area of the adsorption wave depends on the substrate concentration, reaching a limiting value at higher concentrations. The amount of adsorbed bromopyrogallol red was determined from that area and expressed as surface concentration (Γ, mol/cm^2) which is estimated using Eq. (1) [21] where A(ad) is the area of the adsorption peak, A is the electrode surface area, and Γ is the surface concentration.

$$A(\mathrm{ad}) = nFA\Gamma \tag{1}$$

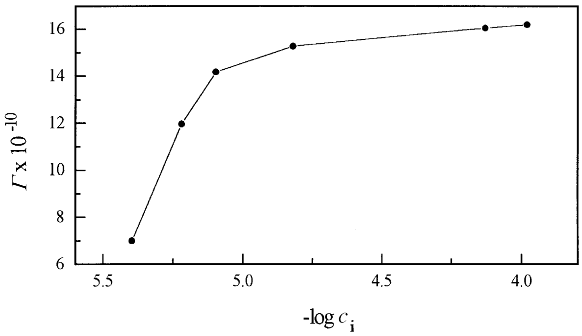


Fig. 4. Cyclic voltammograms of the $Cd^{2+/0}$ couple a) on a bare HMDE and b) on a drop previously modified with **1**

Plotting Γ as a function of the negative logarithm of the substrate concentration yields the graph shown in Fig. 4. It indicates an increase in the surface concentration upon increasing bulk concentration and then levels off at higher values; obviously, coverage and orientation are essentially monolayer and unchanged as the solute concentration is increased by two orders of magnitude [22]. This resistance to reorientation is probably due to interaction of the aromatic rings of **1** with the electrode surface in a flat orientation which would permit only limited interaction. The adsorption isotherm (Fig. 4) shows that the surface coverage reaches saturation at $1\times10^{-5}\,\mathrm{mol}\cdot\mathrm{dm}^{-3}$ **1**. Increasing the concentration of **1** above $1\times10^{-5}\,\mathrm{mol}\cdot\mathrm{dm}^{-3}$ affects the shape of the waves; as the concentration of **1** increases, the wave becomes sharper. Such changes are indicative of organization processes.

It is evident that the relationships are reminiscent of a *Langmuir* isotherm (Eq. (2), [21]; Γ_i: surface concentration of the absorbed species i,Γ_{is}: excess surface coverage, b_i: adsorption coefficient, c_i: bulk concentration) which can be linearized resulting in Eq. (3).

$$\Gamma_i/(\Gamma_{is} - \Gamma_i) = b_i c_i \tag{2}$$

$$c_i/\Gamma_i = 1/\Gamma_{is} b_i + c_i/\Gamma_{is} \tag{3}$$

Plots of c_i/Γ_i against c_i are therefore expected to give straight lines; the linear least-squares fits obtained for *in situ* and *ex situ* experiments are represented by Eqs. (4) and (5).

$$c_i/\Gamma_i = (3.07 \pm 0.02) \times 10^3 + (1.31 \pm 0.01) \times 10^9\, c_i \quad (r = 0.998) \tag{4}$$

$$c_i/\Gamma_i = (3.63 \pm 0.02) \times 10^3 + (1.43 \pm 0.01) \times 10^9\, c_i \quad (r = 0.998) \tag{5}$$

The value obtained for the excess surface coverage Γ_{is} from *ex situ* experiment was always smaller than that from *in situ* measurements, indicating that some loss of the monolayer occured, probably as a result of washing the modified drop. The calculated values of Γ_{is} for *in situ* and *ex situ* experiments were found to be $(7.66\pm0.01)\times10^{-10}$ and $(6.97\pm0.02)\times10^{-10}$ mol/cm^2, respectively. The adsorption

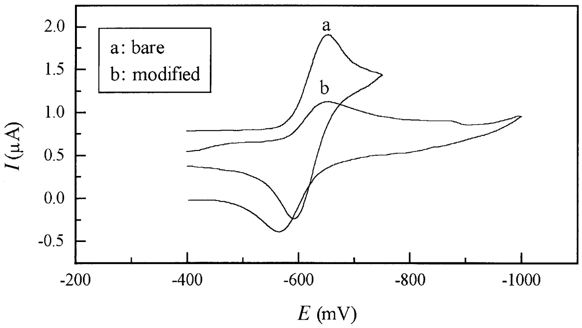


Fig. 5. A plot of surface concentration (Γ_i) against the negative logarithm of bulk concentration c_i

coefficients of the absorbate (b_i) for *in situ* and *ex situ* experiments are estimated to amount to (4.25±0.01) $\times 10^5$ and (3.60±0.03) $\times 10^5\,\mathrm{mol}^{-1}$. The excess of surface coverage calculated under saturation conditions equals (7.66±0.01) $\times 10^{-10}$ mol/cm^2 which corresponds to 21.68 Å per molecule of **1**. This means that a densely packed monolayer is formed on the surface.

It is important to study how the presence of a monolayer will affect the rate of electron transfer of outer-sphere redox couples. Whereas *Miller*, *Finklea* and others [9, 23, 24] have used outer-sphere redox couples to study electron transfer across SAMs on gold surfaces, *Lipkowski*, *Guidelli* and coworkers [25–28] have obtained significant structural information about the mercury-film interface. Figure 5 shows the cyclic voltammetry of the $Cd^{2+/0}$ couple with a bare HMDE and a drop previously modified with bromopyrogallol red. It can be seen that a decrease in the rate of electron transfer across the layer of **1** is observed. This again confirms that a densely packed layer is formed.

Chronocoulometry

Double-potential step chronocoulometry is a useful method for the quantitative characterization of an adsorption process, independent of both the relative reduction potentials of the diffusing and adsorbed species and the kinetics of their electrode reactions [21]. In a double-potential step chronocoulometric experiment, the potential is held at an initial value E_i where no electrolysis occurs and is rapidly stepped to a value E_f at which the desired electrode reaction takes place at $t = 0$. At $t = \tau$, the potential is returned to E_i.

In aqueous 0.1 *M* $HClO_4$ solution 0.01 m*M* of **1**, the electrode potential was stepped from an initial value $E_\mathrm{i} = -0.4$ V, where the depolarizer is electrochemically inactive, to a final value $E_\mathrm{f} = -0.6$ V, where the electrode reaction proceeds. The potential was held at E_f for a time τ after which it was stepped back to E_i and maintained there for the same time interval. The charge passing through the electrode during each of the time intervals was measured. Chronocoulometric experiments in the *ex-situ* mode in which the modified HMDE was transferred into 0.1 *M* perchloric acid solution free of **1** following the same procedure from $E_\mathrm{i} = -0.4$ V to $E_\mathrm{f} = -0.7$ V were also carried out. The chronocoulometric data were analysed according to *Anson*'s equations (Eqs. (6) and (7) [29]).

$$Q(t<\tau) = \frac{2nFAD_0^{1/2}C_0}{\pi^{1/2}} t^{1/2} + Q_{\mathrm{dl}} + nFA\Gamma \tag{6}$$

$$Q_r(t) = \frac{2nFAD_0^{1/2}C_0}{\pi^{1/2}} \theta + Q_{\mathrm{dl}} \tag{7}$$

Q($t<\tau$) is the amount of charge that has passed at time t since the application of the potential step, C_0 and D_0 are the concentration and diffusion coefficient of the reactants, respectively, A is the electrode surface, n and F have their usual significance, $Q_{\mathrm{r}}(t) = Q(\tau) - Q(t>\tau)$, Q_{dl} is the charge consumed by the electrode-electrolyte double-layer capacitance, Γ is the excess surface of the adsorbate, and $\theta = (\tau^{1/2} + (t-\tau)^{1/2} - t^{1/2})$.

Plotting $Q_{\mathrm{f}}(t<\tau)$ *vs.* $t^{1/2}$ and $Q_{\mathrm{r}}(t>\tau)$ *vs.* θ affords good straight lines (regression coefficients: 0.998 and 0.996; cf. Fig. 6 as a representative for an *in situ* (study). They have different slopes and intersect each other above the *t*-axis. This demonstrates the adsorption of the subject compound on the electrode surface. The amount of the adsorbate *i.e.* the surface concentration Γ, is determined from the difference between the intercepts of the forward and reverse *Anson* plots (Eqs. (6) and (7)) which is simply $nFA\Gamma$. This difference cancels Q_{dl} and leaves only the net faradaic charge due to the adsorbate. The values of the surface concentration calculated from chronocoulometry are given in Table 1. Again it was found that the value of Γ for *ex situ* studies is a little lower than that calculated for *in situ* experiments.

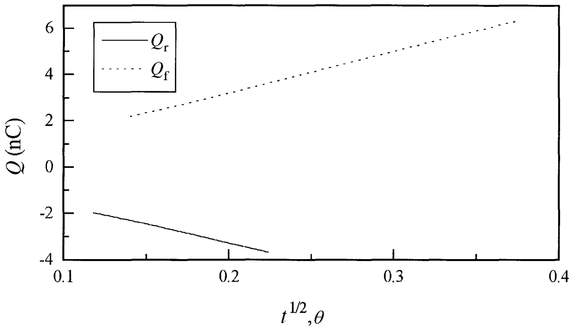


Fig. 6. *Anson* plots of Q_{f} *vs.* $t^{1/2}$ and Q_{r} *vs.* θ for 1.0×10^{-5} *M* of **1**

Table 1. Values of Γ and σ for *in situ* and *ex situ* experiments calculated from cyclic voltammetric and chronocoulometric investigations of **1**

	Cyclic voltammetry		Chronocoulometry	
	in situ	*ex situ*	*in situ*	*ex situ*
$\Gamma\times10^{-10}$ (mol/cm^2)	7.66	6.97	7.11	6.23
σ(Å)	21.68	23.84	23.36	26.66

Finally, the surface area of the electrode occupied by one molecule, σ, can be estimated from $\sigma = 1/N_A\Gamma$ where N_A is *Avogadro*'s number and Γ is the surface concentration in mol/Å. Examination of Fig. 5 shows that the limiting coverage value is attained at bulk concentration of $1 \times 10^{-5}\,\mathrm{mol \cdot dm^{-3}}$ **1**. Thus, the surface areas occupied by the adsorbed substrate molecules (Table 1) are calculated from the values of surface concentration at $1 \times 10^{-5}\,\mathrm{mol \cdot dm^{-3}}$ utilizing cyclic voltammetric and chronocoulometric techniques.

Experimental

Reagents and solutions

Bromopyrogallol red and perchloric acid of analytical grade purity were used. A stock solution of fresh 5.0 m*M* bromopyrogallol red in triply distilled water was prepared, kept in an inert nitrogen atmosphere, and diluted as required.

Apparatus and procedures

All measurements were made at 298 K. Electrochemical experiments were carried out on an EG&G PAR Potentiostate/Galvanostate model 363 A. An EG&G three electrodes electrolysis cell system model SMDE 303 A was used. A hanging mercury drop electrode (HMDE) in the medium hanging drop mode was used as the working electrode. The electrode area was $1.26 \times 10^{-4}\,\mathrm{cm^2}$. Platinum wire and silver/silver chloride/aqueous potassium chloride electrodes were used as counter and reference electrodes, respectively. The electrochemical system was interfaced with an IBM Value Point 433 DX/DP Computer. The data were acquired, stored, and manipulated employing EG&G M270/500 software which controls the potentiostate *via* IEEE488 GPIB. Positive feedback was used for compensation of the solution resistance. All solutions were freshly prepared and kept in an inert nitrogen atmosphere. Solutions were purged with pure nitrogen before the measurements, and an atmosphere of nitrogen was maintained above the working solution. The cyclic voltammograms and chronoamperograms were recorded in equally spaced time intervals both for the pure supporting electrolyte solution and in the presence of the substrate. The background data were subtracted digitally implying the assumption of a simple additivity of *Faradaic* and *non-Faradaic* currents, minimizing effects such as double layer charging currents.

The HMDE was cleaned by washing thoroughly with 30% HNO_3, followed by 30% $HClO_4$ and water. Cyclic voltammetry was performed in the electrolyte solution through a relevant potential window until a satisfactory background was obtained. A fresh mercury drop was then modified in a stirred dyestuff solution (10^{-7} to 10^{-3} of bromopyrogallol red in 0.1 *M* $HClO_4$ solution) for a measured period of time. *In situ* electrochemical measurements were carried out in the modification solution under a nitrogen atmosphere. Cyclic voltammetry was recorded in different potential windows at $0.2\,\mathrm{V \cdot s^{-1}}$. *Ex situ* experiments were conducted in deaerated solutions of 0.1 *M* $HClO_4$ after the modified drop had carefully been washed with $HClO_4$ and water several times.

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