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THE REDUCTION MECHANISM AT THE MERCURY ELECTRODE IN A 0.9 M NaClO₄ + 0.1 M HClO₄ SUPPORTING ELECTROLYTE OF AN HYDROXYTRIPHENYLMETHANE: ERIOCHROME CYANINE R

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ABSTRACT

The reduction mechanism at a mercury electrode of Eriochrome Cyanine R, in a 0.9 M NaClO₄ + 0.1 M HClO₄ supporting electrolyte, has been investigated by several electrochemical techniques. By means of coulometry at constant potential and cyclic voltammetry it was demonstrated that a radical is formed, which suffers disproportionation, after the first electron transfer. The results of the cyclic voltammetric investigation and the impedance measurements evidenced the intrinsic reversible nature of the electron transfers. Apparent irreversible polarographic behaviour is a consequence of the existence of chemical reactions following the electron transfers. The impedance measurements demonstrated the strong adsorption of the Ox and Red form of Eriochrome Cyanine R as well as of the radical formed. On the basis of the experimental data a reduction mechanism is proposed.

INTRODUCTION

The electrochemistry of the sulphonaphthaleins, quite similar in structure to the acid triphenylmethanes, is now reasonably well understood [1,2]. The general mechanism is of the ECEC type, the first chemical step being a disproportionation reaction of the radical formed after the first electron transfer. Literature data with respect to the reduction of the acid triphenylmethanes are quite scarce [3–6]. Since the triphenylmethanes are an important group of dyes for analytical applications [7,8] and since, as far as we know, no detailed reduction mechanism has been published, we decided to investigate in detail the reduction mechanism at the mercury electrode, beginning with Eriochrome Cyanine R, one of the most important members of the group [9]. In view of the various electrochemical aspects to be expected, we found it worthwhile to apply a number of techniques in combination, viz. dc and ac polarography, controlled potential coulometry and cyclic voltammetry.

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EXPERIMENTAL

Apparatus

All electrochemical measurements were performed with apparatus using the three-electrode configuration. The impedance measurements and some manually constructed polarograms were obtained with a home-made potentiostat.

Polarograms were recorded with the Polarecord E506 (Metrohm) or with the PAR 174 apparatus equipped with a Houston Omnigraphic Model 2000 XY recorder.

Coulometric integrations in the controlled potential coulometric experiments were performed with a voltage-to-frequency converter (HP Model 2212A) as described by Bard and Solon [10]. Pulse counting was performed with a Systron-Donner Model 7014 counter.

Cyclic voltammetry was performed with the PAR 170 Electrochemical System. For scan rates below 200 mV s^{-1} the recorder incorporated in the instrument was used. Oscilloscopic registration was employed with scan rates greater than 200 mV s^{-1} (HP Model 140A oscilloscope). Permanent recording of the i - E curve was obtained with a Polaroid camera attachment (HP Model 196B).

The construction of the impedance bridge is described elsewhere [11]. The analysis of the impedance data was executed with a HP Model 9830A desk calculator equipped with a HP automatic plotter *.

pH was measured with a Radiometer (Model 4) or a Metrohm (digital E500) pH meter equipped with the respective general purpose glass electrodes. The apparatus was calibrated with standard N.B.S. buffers over the pH range investigated.

The three-electrode cell was water-jacketed. For the impedance measurements and polarography a fine tapered siliconized DME was used as working electrode, the auxiliary electrode was a Hg pool and the reference electrode a SCE in which the saturated KCl was substituted by saturated NaCl (SCE(Na)). The SCE(NaCl) was connected to the cell by means of a salt bridge. In case of the cyclic voltammetry experiments the working electrode was a Metrohm Model E410 HMDE ($A = 2.22 \pm 0.07 \text{ mm}^2$) while a Hg pool ($A = 23 \pm 1 \text{ cm}^2$) was used as working electrode in the controlled potential coulometric experiments. Where necessary the drop time of the DME was controlled mechanically and all experiments were executed at $25 \pm 0.1^\circ \text{C}$.

Reagents

All solutions were prepared from p.a. grade products with the exception of HClO_4 which was an Ultrex product (J.T. Baker). Stock solutions of the supporting electrolyte were purified by electrolysis at constant potential. The dye was purified according to a method described in the literature [12]. All solutions were prepared with bi-distilled water.

* The computer program for treatment of the experimental data can be obtained from J.H. Sluyters.

RESULTS

Polarography

Polarograms of the Eriochrome Cyanine R (ECR) dye were recorded over the 0.09 to 7.5 pH interval, the pH being controlled with constant ionic strength McIlvaine buffers [13] (μ being fixed at 1.0 M with NaClO_4). All polarograms showed two waves of approximately the same wave height. The second polarographic wave demonstrated a sharp maximum of the first kind which was a function of the dye concentration (depending on the nature of the buffer used, solutions possessing a dye concentration inferior to 6×10^{-5} M did not show the maximum), the pH of the solution, the composition of the buffer and of the concentration of the supporting electrolyte. The maximum can be eliminated by the use of several maximum suppressors e.g. Triton X-100, polyacrylamide and gelatin. Triton X-100 is the most efficient of all (0.0012% already suffices). All of the maximum suppressors investigated, however, caused a severe deformation of the second wave.

A typical manually obtained polarogram of ECR is shown in Fig. 1.

The observed limiting currents of the first and the second wave are $2.49 \mu\text{A}$ and $4.86 \mu\text{A}$, respectively. This suggests that the process responsible for the first wave involves half the amount of electrons necessary for the total reduction. With the aid of the Koutecky equation (including correction for spherical diffu-

Fig. 1. Polarogram of a 1.06×10^{-3} M Eriochrome Cyanine R solution in a 0.9 M NaClO_4 + 0.1 M HClO_4 supporting electrolyte, $t = 2.83$ s, $m = 1.921$ mg s^{-1} .

sion) one calculates $nD_0^{1/2} = 1.70 \times 10^{-3} \text{ cm s}^{-1/2}$ from the first wave, and $nD_0^{1/2} = 1.66 \times 10^{-3} \text{ cm s}^{-1/2}$ from the second wave. The slight discrepancy will be discussed later.

A $\log [i/(i_1 - i)]$ vs. E analysis of the first wave yields a straight line with the reciprocal slope equal to 68 mV, which indicates at first sight a certain irreversibility. Most probably $n = 1$ for this wave, so the total reduction involves two electrons. The variation of the limiting current of the first wave with the square root of the height of the mercury column (corrected for back pressure) is a linear function, which suggests that the first limiting current is diffusion controlled.

When examining the influence of the pH on the half-wave potential of the first wave one can distinguish three intervals.

In the 3.8–4.4 pH region the half-wave potential is independent of pH. In the region where $\text{pH} < 3.8$ the relationship pH vs. $E_{1/2}$ is a straight line with a slope of 65 mV per pH unit. In the $\text{pH} > 4.4$ region the relationship pH vs. $E_{1/2}$ is also a straight line with a slope of 59 mV per pH unit. These results indicate that one proton is involved in the first reduction wave with pH values inferior to 3.8 and superior to 4.4. The fact that one proton is involved in the first reduction wave and that the limiting current is independent of pH over the range investigated suggests the protonation of the oxidized form of ECR is a rapid process and that it is a protonated form which is directly reduced.

(b) Controlled potential coulometry

Several controlled potential coulometric experiments of an ECR solution containing $2.2 \times 10^{-2} \text{ mmol l}^{-1}$ of dye in a supporting electrolyte of 0.1 M $\text{HClO}_4 + 0.9 \text{ M NaClO}_4$ were executed. The working potential was chosen either at the first plateau (-0.6 V vs. $\text{SCE}(\text{Na})$), or at the second plateau (-0.9 V vs. $\text{SCE}(\text{Na})$) of the polarogram. In both cases it was found that for the reduction of ECR 1.96 electrons were needed. This can only be explained if it is assumed that the product of the first reduction step undergoes a slow reaction in the solution by which the ECR is regenerated via disproportionation. It was also demonstrated that the final product of an exhaustive electrolysis at -0.9 V vs. $\text{SCE}(\text{Na})$ is electroinactive in the -1.3 to 0.2 potential interval since no polarographic wave could be obtained in the mentioned interval. Simultaneously it was observed that the final electrolysis product yields a colorless solution while the Ox form of ECR (at the same pH) forms an orange solution with $\lambda_{\text{max}} = 474 \text{ nm}$. This hypochromic shift of the visible absorption spectrum suggests that the conjugated system, existing in the Ox form, is destroyed on reduction.

(c) Cyclic voltammetry

Two series of cyclic voltammetry experiments were executed: in a first one the potential range covered the interval of the first polarographic wave (0.1 to -0.7 V vs. $\text{SCE}(\text{Na})$) while in the second series the potential range was chosen so as to cover the complete polarogram (0.1 to -1.3 V vs. $\text{SCE}(\text{Na})$). In each case a series of scan rates, chosen between 0.02 and 500 V s^{-1} , were investi-

Fig. 2. Cyclic voltammogram of a $1.1 \times 10^{-3} M$ Eriochrome Cyanine R solution in $0.9 M \text{NaClO}_4 + 0.1 M \text{HClO}_4$ supporting electrolyte covering the first polarographic wave. Scan rate 200 mV s^{-1} .

gated. Typical cyclic voltammograms obtained are shown in Figs. 2 and 3.

With scan rates up to 0.5 V s^{-1} the cathodic and anodic peak potentials of the first electrode process were separated by $59.9 \pm 0.5 \text{ mV}$. However, at the higher scan rates ($V \geq 2 \text{ V s}^{-1}$) the peak separation becomes markedly bigger than 59.5 mV . This finding suggests the first electron transfer to behave reversibly on the polarographic time scale while behaving irreversibly on the cyclic voltammetry time scale. Simultaneously it was observed that at the lowest scan rates ($V = 0.02$ to 0.05 V s^{-1}) the ratio i_a^I/i_c^I was inferior to one, attaining unity when scan rates larger than 0.05 V s^{-1} were used. Evidently the effect of the

Fig. 3. Cyclic voltammogram of a $1.1 \times 10^{-3} M$ Eriochrome Cyanine R solution in a $0.9 M \text{NaClO}_4 + 0.1 M \text{HClO}_4$ supporting electrolyte covering the complete polarogram. Scan rate: 200 mV s^{-1} .

disproportionation reaction shows up at the lower scan rates [14]. Since for scan rates situated in the 0.1 to 0.5 V s⁻¹ range the first wave behaves as a reversible one-electron transfer and is unaffected by the disproportionation reaction, it was possible to determine a thermodynamically meaningful half-wave potential as well as the diffusion coefficient of the Ox form of ECR. The values determined were: $E_{1/2}^I = -0.283$ V vs. SCE(Na) and $D_0^{1/2} = (1.55 \pm 0.02) \times 10^{-3}$ cm s^{-1/2}.

Since at scan rates ≥ 2.0 V s⁻¹ the first electrode process appears to behave as a quasi-reversible electron transfer and the influence of the disproportionation reaction being completely eliminated at these higher scan rates, one can calculate the heterogeneous rate constant, k_{sh} , based on the experimental peak separation values and the theoretical wave function, Ψ vs. ΔE_p , of Nicholson and Shain [15]. A value of $(4.3 \pm 0.2) \times 10^{-2}$ cm s⁻¹, based on scan rates situated between 10 and 200 V s⁻¹, is obtained.

However, when the usual procedure, based on the potential difference between the peak potential E_p and the half-peak potential $E_{p/2}$, for the determination of the transfer coefficient is applied, the result is strongly dependent on the scan rate, as is shown in Table 1. This might mean that the interpretation of the observed behaviour in terms of irreversibility is not correct (see also the Discussion).

The second electrode process presents quite an interesting situation. With scan rates lower than 50 V s⁻¹ the cyclic voltammogram lacks the anodic counterpart of the cathodic peak. However, when $v \geq 50$ V s⁻¹ the anodic peak starts appearing, being quite pronounced at a scan rate of 500 V s⁻¹. This behaviour furnishes direct experimental evidence of the existence of a chemical step following the electron transfer. The graph $i_{p,c}^{II}/v^{1/2}$ vs. $v^{1/2}$ (Fig. 4) of the peak current of the cathodic part of the second wave, $i_{p,c}^{II}$, is a curve tending towards an horizontal line at the higher scan rates. The general morphology of this curve suggests that the chemical process (the protonation of the Red form of ECR) is irreversible while the faradaic process is reversible.

At the lower scan rates the cathodic peak potential of the second wave is found to be displaced by 35 mV with a tenfold increase in the scan rate. Normally this is an indication of an irreversible faradaic process. However, it may also originate from a reversible electron transfer, followed by a fast chemical reac-

TABLE 1

Apparent transfer coefficient of the first electrode process of Eriochrome Cyanine R

Scan rate v/V s ⁻¹	$(E_p - E_{p/2})/mV$	αn_a^a
50	-92	0.52
100	-103	0.46
200	-114	0.42
500	-134	0.36

^a Since one electron is transferred in the first electrode process the αn_a values are identical with α .

Fig. 4. $i_p/v^{1/2}$ vs. $v^{1/2}$ of the second electrode process. $1.1 \times 10^{-3} M$ Eriochrome Cyanine R in $0.9 M NaClO_4 + 0.1 M HClO_4$. Scan rates between 0.02 and $500 V s^{-1}$.

tion. The observations mentioned above are in favour of the latter interpretation: the Red form of ECR is transformed to an electroinactive species, probably by a fast (irreversible) protonation. From the potential difference between E_p^{II} and $E_{p/2}^{II}$ at the highest scan rates one calculates a value of $219 \pm 20 M^{-1} s^{-1}$ (mean from three scan rates) for the homogeneous rate constant of this reaction.

(d) Impedance measurements

Two series of measurements were performed, viz. (a) with concentrations of ECR varying from $1.06 \times 10^{-3} M$ to $1.38 \times 10^{-4} M$, in the potential region $+0.2 V$ to $-1.3 V$ vs. SCE, at a fixed frequency of $1000 Hz$; (b) with fixed concentrations of $1.03 \times 10^{-3} M$ and $1.06 \times 10^{-4} M$ in the potential region of the first wave ($-0.24 V$ to $-0.32 V$ vs. SCE), and the frequency varied from $70 Hz$ to $30 KHz$. The supporting electrolyte was $0.9 M NaClO_4 + 0.1 M HClO_4$.

In Fig. 5 the measured capacities C_s are represented, together with the double layer capacity of the supporting electrolyte alone. The curves show peaks, two of them in the faradaic regions of the dc polarogram (II and III), the others in the regions situated positively (I) and negatively (IV). From the suppression of the capacities between peaks II and III it can be concluded that anyway the radical formed in the first reduction step is adsorbed at the interface, probably with maximum surface coverage even at the lowest concentration (all C_s values are equal).

Naturally, peaks II and III will correspond to the faradaic processes [16], but influenced by the above-mentioned adsorption of the intermediate. Remarkable is the inversion in the sequence at II and I: increasing peak height with decreasing concentration. This behaviour has been predicted recently as a characteristic feature of electrode reactions with rather strong adsorption of a reactant [17]. In such a case the ac polarogram exhibits two peaks, which explains the occurrence of peak I. It is not quite clear whether we must conclude that the

Fig. 5. Measured capacity curves vs. d.c. potential. ECR concentrations: (○) 0; (●) 138×10^{-4} ; (▽) 2.35×10^{-4} ; (◇) 3.94×10^{-4} ; (□) 7.44×10^{-4} ; (△) 1.06×10^{-3} M.

ECR itself is also adsorbed, though the fact that the capacity is still suppressed at potentials positive to peak I may be a strong argument for this.

The peaks corresponding to the second polarographic wave (III) are extremely small. This can be correlated to the idea that the reduction product is involved in an irreversible following reaction, as postulated above. Again the subsequent peaks IV represent most probably the so-called adsorptive post-peaks inherent to strong adsorption of the reduced species [17].

The considerations above are entirely confirmed by the analysis of the data of the second series, in terms of the admittance equations published by Wijnhorst et al. [18]: this analysis is based on the calculation of the quantities Y' and Y'' (in-phase and quadrature components of the interfacial admittance) as a function of frequency. A typical plot of $Y'/\omega^{1/2}$ vs. $\omega^{1/2}$ is shown in Fig. 6. The increasing nature observed is indicative for an electrode reaction complicated by reactant adsorption [19].

The experimental data of the frequency variation series appeared to fit very well the equations of Wijnhorst et al. [18] in terms of the parameters σ (Warburg coefficient), u' (diffusion-adsorption coupling parameter), C_{LF} (low-frequency capacity) and C_{HF} (high-frequency capacity). The results obtained are collected in Table 2 and graphically presented in Figs. 7 and 8.

Fig. 6. $Y'/\omega^{1/2}$ vs. $\omega^{1/2}$. $c_{\text{ECR}} = 1.03 \times 10^{-3} \text{ M}$ in $0.9 \text{ M NaClO}_4 + 0.1 \text{ M HClO}_4$. $E = -0.289 \text{ V}$ vs. SCE(Na). The drawn line represents the theoretical curve calculated with the parameters in Table 2.

From these results the following conclusions can be drawn.

The values of the Warburg coefficient are in very good agreement with the theoretical curve in Fig. 7, which is calculated on the assumption that the reaction is d.c. reversible [19], with $n^2 D_0^{1/2} = 1.65 \times 10^{-3} \text{ cm s}^{-1/2}$. The discrepancy between the measured and the theoretical curve near the half-wave potential, though less than 3%, may well be due to the adsorption of the reactants [18].

Considering the capacity values in Figs. 6 and 8, it is evident that the quantity

Fig. 7. The Warburg parameter σ as a function of potential for $1.03 \times 10^{-3} \text{ M ECR}$. The drawn line represents the theoretical curve with $nD_0^{1/2} = 1.66 \times 10^{-3} \text{ cm s}^{-1/2}$ and $E_{1/2} = 0.285 \text{ V}$.

Fig. 8. Values of the capacitive parameters as a function of potential. ($\circ$) C_{LF} , $1.03 \times 10^{-3} \text{ M ECR}$. ($\bullet$) C_{HF} , $1.03 \times 10^{-3} \text{ M ECR}$. (Δ) C_{LF} , $1.06 \times 10^{-3} \text{ M ECR}$. ($\times$) C_{HF} , $1.06 \times 10^{-3} \text{ M ECR}$.

TABLE 2
Parameters obtained from varied frequency analysis

$E/\text{mV vs. SCE}$	$\sigma/\Omega \text{ cm}^2 \text{ s}^{-1/2}$ 1 mM ECR	$C_{\text{LF}}/\mu\text{F cm}^{-2}$		$C_{\text{HF}}/\mu\text{F cm}^{-2}$		$10^3 u'/\text{s}^{1/2}$	
		1 mM ECR	0.1 mM ECR	1 mM ECR	0.1 mM ECR	1 mM ECR	0.1 mM ECR
-230			111.5		≤ 8		
-240		69	115	27	≤ 8	7-10	3.5-4
-245	732	73		27			
-250	671	75	118	26	≤ 10	7-10	4-5
-255	614	72.5		26			
-260	568	71	117.5	26	5-15	7-10	5-6
-265	530	68.5		25			
-270	501	65.5	116.5	25	20-26	6-9	7-9
-275	479	62		24			
-280	466	57.5	111	23	29	7-10	11-12
-285	458	53		23			
-290	460	48	97	22	29	9-12	13-15
-295	469	43		21			
-300	490	39		18-24		4-11	
-305	518	35		16-22			
-310	546	31		10-20		2-7	
-315	589	27.5		5-18			
-320	636	24		0-15		3-8	

$C_{LF} - C_{HF}$ attains a maximum twice, viz. at a potential ca. 40 mV positive to the half-wave potential and at a potential far positive to the faradaic region. In view of the available theoretical equations [17,18] this must mean that (a) both the Ox component (ECR) and the Red component (the radical) are adsorbed, (b) the Red component is adsorbed more strongly than the Ox component, (c) for both species the adsorption coefficient is potential-dependent, probably quadratically. The latter follows also from the fact that outside the faradaic region the measured capacity in the presence of ECR is lower than the capacity of the supporting electrolyte. The evidence for these postulae is given in more detail in the Appendix.

DISCUSSION

The dissociation sequence of ECR can be represented as follows:

The pH intervals where only a single form of ECR exists in solution are [19]: $[H^+] > 1.0 M$ (H_4L : red [L represents the completely ionized form of ECR]); 0.5–1.4 (H_3L^- : orange); 3.1–4.1 (H_2L^{2-} : red); 7.0–9.0 (H_3L^{3-} : yellow) and $pH > 13.3$ (L^{4-} : violet).

So in a 0.9 M $NaClO_4$ + 0.1 M $HClO_4$ supporting electrolyte form Ia is the only ECR species present in solution.

This would induce one to think the first reduction step to be:

The real structure [20] of ECR, however, is an hybrid of the contributing structures like I and II (system 1):

This, together with the experimental observation that the limiting current of the first polarographic wave is pH independent strongly suggests it is form II (or its hybrid I), and not form Ia, which is directly reduced, the electron transfer being preceded by a fast proton acceptance. We therefore propose the next reduction mechanism for ECR at pH = 1.0, essentially identical to the Phenol Red mechanism proposed by Senne and Marple [20], [1]:

In the mechanism proposed steps (2a) and (2c) represent the first and the second polarographic wave, respectively. Step (2b) is the disproportionation reaction of the neutral radical Y' , formed by the first reduction step, and (2d) the (irreversible) protonation following the final reduction. About the relative kinetic influences of the various processes the following conclusions can be drawn from our experiments:

The very slight difference between the two polarographic currents must mean that step (2b) hardly influences the first wave. This is confirmed by the excellent agreement between the values of $D_0^{1/2}$ obtained from the d.c. and the a.c. experiments (taking $n = 1$).

The a.c. measurements show in addition that the first step is reversible on the a.c. time scale and thus on the d.c. time scale. Therefore the apparent irreversible behaviour observed in the polarogram and in the cyclic voltammograms must have a different meaning.

The most plausible explanation is based on the adsorptive behaviour of both the ECR and the radical which also becomes evident from the a.c. measurements. It is known from the work of Wopschall and Shain [21] that the cyclic voltammogram is sensitive to reactant adsorption, especially at higher scan rates, while also the d.c. polarogram attains a decreased slope if the adsorption is rather strong [22].

The second reduction process is always found to be irreversible because of the fast protonation step (2d). However, from the cyclic voltammetry experiments it follows that the electron transfer itself is fast. Another consequence of the large rate of step (2d) is that it also displaces the equilibrium of (2b) to the right, thus making this process irreversible too.

The proposed mechanism also explains, in a satisfactory way, the fact that the completely reduced form of ECR is colorless. In fact, examining the structure of the (IVa) form of ECR one observes the conjugated system, present in the (Ia) form, has broken down completely, explaining the hypochromic shift observed in the adsorption spectrum.

It can be concluded that the experimental results presented in this paper provide satisfactory evidence for the proposed reaction mechanism.

APPENDIX

The equations used for analysing the electrode admittance are [18]:

$$Y'_{el} = \frac{\omega^{1/2}}{2\sigma} + \omega(C_{LF} - C_{HF}) \frac{u^2}{z^2 + (z + u)^2} \quad (A1)$$

$$Y''_{el} = \frac{\omega^{1/2}}{2\sigma} + \omega(C_{LF} - C_{HF}) \frac{u + 2z}{z^2 + (z + u)^2} + \omega C_{HF} \quad (A2)$$

$$u = u' \omega^{1/2} \quad (A3)$$

$$z = 1 - u'(7\pi/24t_m)^{1/2} \quad (A4)$$

Expressions for the parameters C_{HF} , C_{LF} and u' in terms of $j = (nF/RT)(E - E_{1/2}^r)$ and bulk concentration c_0^* for supposed Langmuirian adsorption [17]:

$$C_{HF} - C_d = \left\{ \frac{s \exp(j)}{[\exp(j) + s]} [(nF/RT) - a_0 + a_R]^2 - [b_0 \exp(j) + b_R s] \right\} \frac{RT\beta_0 c_0^* \Gamma_M}{1 + \exp(j) + \beta_0 c_0^* [\exp(j) + s]} \quad (A5)$$

$$C_{LF} - C_{HF} = \frac{\{(nF/RT)(1 - s) \exp(j) - [a_0 \exp(j) + a_R s][\exp(j) + 1]\}^2}{[\exp(j) + s][\exp(j) + 1]\{1 + \exp(j) + \beta_0 c_0^* [\exp(j) + s]\}^2} \times RT\beta_0 c_0^* \Gamma_M \quad (A6)$$

$$u' = \frac{[\exp(j) + s][\exp(j) + 1]}{\{1 + \exp(j) + \beta_0 c_0^* [\exp(j) + s]\}^2} \beta_0 \Gamma_M D_0^{-1/2} \quad (A7)$$

with the following definitions of symbols:

C_d = double layer capacity in the supporting electrolyte

β_0, β_R = adsorption coefficients

Γ_M = maximum surface excess

$$s = (D_O/D_R)^{1/2} \beta_R/\beta_0 \quad (A8)$$

$$a_O, a_R = -d(\ln \beta_O)/dE, \quad -d(\ln \beta_R)/dE \quad (A9)$$

$$b_O, b_R = -d^2(\ln \beta_O)/dE, \quad -d^2(\ln \beta_R)/dE \quad (A10)$$

N.B. In eqns. (A5) to (A7) a possible drop time dependence, which is most probably negligible [18], is left out of consideration.

For the redox couple $ECRH^+/ECRH$ it is plausible to assume $a_O \approx a_R$ and $b_O \approx b_R$.

From eqn. (A6) it can be deduced that $C_{LF} - C_{HF}$ is always positive, and attains a maximum at $E - E_{1/2}^r > 0$, if $s > 1$. This is what is found experimentally.

From eqn. (A5) it follows that $C_{HF} - C_d$ can become negative if b_O and b_R have a substantial positive value. At extreme potentials ($E \gg E_{1/2}$ and $E \ll E_{1/2}$) the measured capacity (Fig. 6) can be identified with C_{HF} , since $C_{LF} - C_{HF}$ tends to zero.

The limiting expressions for C_{HF} are:

$$\exp(j) \rightarrow \infty \quad C_{HF} = -b_O RT \frac{\beta_0 c_0^* \Gamma_M}{1 + \beta_0 c_0^* \Gamma_M} \quad (A11)$$

$$\exp(j) \rightarrow 0 \quad C_{HF} = -s b_R RT \frac{\beta_0 c_0^* \Gamma_M}{1 + s \beta_0 c_0^* \Gamma_M} \quad (A12)$$

This means that the observed behaviour, $C_s < C_d$, indicates that both b_O, b_R as

well as s must be different from zero, in other words, both the Ox and Red component are adsorbed and the adsorption coefficients depend at least quadratically on potential.

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