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Determination of the surface charge density of a mercury electrode by extrusion: a new method for correction of the faradaic component

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Abstract

The accurate determination of the surface charge density at the mercury | solution interface by the method of extrusion of mercury drops is impaired by the faradaic current caused by traces of electroactive species. This paper describes a new design of a hanging mercury drop electrode with accurate control of the extruded electrode area, to within 0.1%, together with a new and reliable procedure for correction of the faradaic current. The procedure is based on first obtaining the correction parameters in the presence of increasing amounts of electroactive species and then using these parameters for correction of the faradaic component so as to obtain the surface charge density of the electrode. Implementation of the method with a microcomputer controlled system provides automatic acquisition of corrected electrode charge density values as a function of the electrode potential. The results obtained with this new method are in excellent agreement with those obtained by other methods, as illustrated for aqueous sodium fluoride solution. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Surface charge density; Mercury electrode; Extrusion

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1. Introduction

Adsorption at charged interfaces has been widely studied due to its practical and theoretical importance in electrochemistry, electroanalytical chemistry and bioelectrochemistry. Different techniques were developed with the aim of investigating the effects and quantifying adsorbed species in the electrode | solution interface.

Chronocoulometry has proved to be a powerful technique to measure selectively the adsorption of electroactive molecules and ions [1,2]. In practice, information about adsorption of such species is obtained by examination of the relationship between its activity in bulk solution and its concentration on an electrode surface at a given temperature, pressure and electrical state of the interphase. This dependence can be expressed as an adsorption isotherm. In such investigations, there is some controversy about adoption of the potential [3] or the charge [4] to define the electric state of the interphase. The first assumes that the thickness of the inner layer is independent of the amount of adsorbed substance, while the second considers that the dielectric constant of the inner layer is unchanged. Neither of these assumptions is completely satisfactory [5,6], but the potential has been preferred as the electrical variable in adsorption studies involving neutral species, whereas the charge has gained greater acceptance for charged (ionic) species. Nevertheless, when the electrode charge density is adopted, for most techniques, auxiliary measurements are necessary. This is the case in chronocoulometric studies, where only the changes of the electrode charge density between potential steps are measurable [1,2], as well as for investigations based on differential capacitance measurements by ac methods, which require independent determination of the potential of zero charge (pzc) [1,2,5].

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Traditionally, the surface charge density of an ideally polarized electrode has been obtained from differentiation of electrocapillary curves or from integration of differential capacity curves [1]. Besides the classical (and time-consuming) Lipmann capillary electrometer [7], electrocapillary curves were obtained with dropping electrodes, by relating the surface tension to the weight of the drop at the end of its life, or to the drop-time [1,8]. The pzc values can be obtained from the relatively flat maxima of these curves [9], but are measured frequently with the streaming mercury electrode [10], or a more recent alternative, a rapidly dropping mercury microelectrode [11]. This is advantageous as it can also provide complete charge density curves as a function of the potential, derived from the mean charging current.

Direct charge measurement methods during drop formation of a dropping mercury electrode have also been investigated. They allow longer time periods (some seconds) for adsorption equilibrium than the two methods mentioned above, but are more prone to interference from residual faradaic currents caused by the presence of small amounts (or even traces) of contaminant species, or from minute currents at potentials not sufficiently far from the voltammetric waves of the electroactive substances under study. To circumvent this problem, various strategies have been proposed [12–14], based on the different time dependence of charging and faradaic currents during mercury drop growth.

Shortly after the advent of chronocoulometry, charge density measurements were obtained by manual extrusion with a Kemula type hanging mercury drop electrode [15]. More recently, with the advent of controlled growth mercury electrodes, Osteryoung et al. re-examined the extrusion method, based on the idea that if the newly created electrode area can be modelled accurately and the charge flowing measured precisely, then the surface charge density can be calculated directly [16]. Nevertheless, the results obtained were affected by errors, attributed to the unremoved oxygen.

In this paper, a new method for the precise determination of the surface charge density of a mercury electrode is presented, preliminary data for which have been given already [17,18]. Post-extrusion data, free of capacitive current, are used for the improved correction of the residual faradaic current during drop extrusion. Correction parameters are determined only once in the presence of increasing amounts of electroactive species, and are used afterwards for the automatic correction of the faradaic component. Details of the method and its evaluation will be presented in the following sections.

2. Experimental

2.1. Reagents

Mercury was purified chemically by a wet process (24 h in 10% KOH, well washed with pure water, followed by 24 h in 1 M HNO_3, both stages with vigorous agitation) followed by triple distillation under vacuum. All solutions were prepared from Milli-Q grade water. Merck Suprapur (NaF) or analytical grade reagents were used without further purification. A calomel electrode saturated with NaCl (SSCE) was employed as a reference electrode. Before each series of experiments, if not otherwise stated, the solutions were placed within a well-sealed cell and purged with high-purity nitrogen for at least 15 min.

2.2. Mercury drop electrode

A hanging mercury drop electrode developed in the laboratory was used as the working electrode, and is illustrated in Fig. 1. It permits the extrusion of drops of any size up to a maximum corresponding to drop fall, over a wide range of flow rates dictated by the mercury column height and glass capillary bore and length. The flow of the mercury is started and interrupted by an innovative, specially-designed valve, consisting of two opposite solenoids acting on a spindle with a finger-like opening or closing action on the top of the capillary bore, as seen in the detail of Fig. 1.

In principle, other electrodes can be adapted for the determination of surface charge density by the method proposed here, such as the simplified and more compact version of this automatic mercury electrode, designed for electroanalysis [19], or commercial mercury electrodes (e.g. from Metrohm, Radiometer, BAS or EG&G-PAR), operated in static mercury drop electrode (SMDE) mode.

Although the construction of the electrode shown in Fig. 1 is somewhat time-consuming, there are advantages which make it particularly suitable for the present measurements:

1. drop generation was very reproducible, with an area RSD below 0.1%, and the opening and closure delays of the valve were short, about 1.5 and 3 ms, respectively, and reproducible to 0.05 ms (values changed somewhat after maintenance and reassembling);
2. the hydrophobic polytetrafluoroethylene (PTFE) tube tip, fixed at the lower extremity of the glass capillary tube, leads to a very long capillary life span, with high immunity to solution infiltration;
3. the electrical resistance between the drop and the external electrical circuit was less than 2 Ω since a platinum contact was glued directly into the junction of the glass and PTFE capillaries;

4. the electrode is controlled entirely by the computer, with every step definable by software, permitting synchronized data acquisition and the freedom to select any extrusion time, instead of a small number of fixed settings available on commercial electrodes, and eventually too fast to ensure equilibrium in the electrical double layer for low adsorbate concentrations;
5. after calibration, drops of any specified area can be generated automatically (upper limit is the drop fall); for example, for generation of a typical drop with size corresponding to an area of 0.033 cm^2 at a mass flow rate of 7.5 mg s^{-1}, the software imposes an extrusion time of close to 1.02 s; the circular area shielded by the neck of the drop is estimated from the internal diameter of the PTFE capillary (60 μm) and included in the calculation;
6. the 120 cm high mercury column (PTFE tubing with external electrical shielding) renders the relative area error caused by small changes of the back pressure with the applied potential and sample composition negligible, although not to the degree attainable with gas pressurisation between 8 and 12 atm [14].

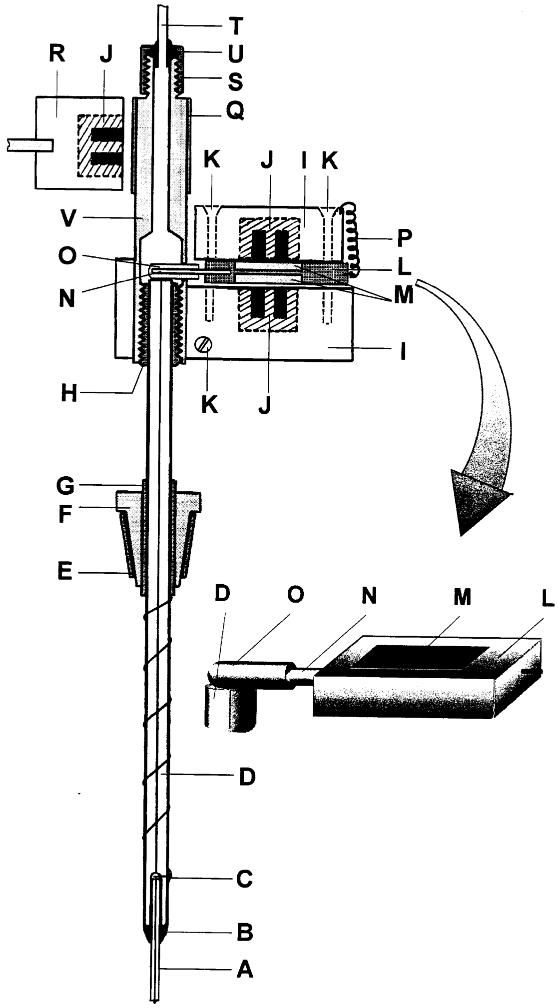

Fig. 1. Schematic drawing of the automatic mercury electrode. A, PTFE capillary tube; B, epoxy glue; C, electrical contact (Pt wire, glued with epoxy); D, glass capillary; E, silicone tube washer; F, Nylon stopper; G, stainless steel tube (with external electrical contact); H, acrylic piece with screw thread glued to glass capillary; I, acrylic support for solenoids; J, solenoids (dashed = core and black = coil); K, fixing screws; L, acrylic moving piece coupled with axis of the valve; M, counter core of the solenoids, embedded in L; N, brass arm, pivoted on V; O, Tygon covering; P, spring to keep valve closed when non energized; Q, iron ring; R, acrylic mounting of drop knocker solenoid; S, stainless steel nut; T, PTFE tube, connected to mercury reservoir; U, PTFE washer; V, main body of the electrode, in acrylic.

2.3. Apparatus

Charge measurements were carried out with the computerised system depicted in Fig. 2. Interfacing was done through two Hewlett Packard HP-IB cards (IEEE-488 standard) plugged into a 16 bit HP-9825 microcomputer. An interface was constructed to control the cell with the mercury electrode and the potentiostat of a PAR 170 electrochemistry system (adapted for external control of the integrator and of the potential applied to the cell). A fast 16 bit digital to analog converter card with sample and hold circuit was developed to generate potentials in the range ±3.3 V with a resolution of 0.1 mV. Data acquisition was performed with a Hewlett Packard model 3437A system voltmeter (12 bits A/D, resolution of 0.025% of full range, with programmable potential ranges, timing of the measurements and number of points). A printer (Grafix MX-80) and a graphic plotter (HP 9872B) completed the system.

3. Fundamentals of operation

The procedure to obtain the surface charge density in extrusion experiments of the studied solutions, which contain small (and unknown) amounts of species electroactive in the potential region where extrusion is performed, consists of two stages. In the first, the correction parameters are obtained (for a given area and mercury flow rate of the electrode capillary) by varying the amount of electroactive material added deliberately to the solution. In the second stage, these parameters are used to perform automatic correction of the faradaic component.

In an ideal solution, the integration of the current that flows to (or from) the mercury electrode during expansion of the drop, under potentiostatic conditions and in the absence of faradaic processes, gives the surface charge, Q_M, of the electrode. In the presence of electroactive species (for example O_2 or other impurities) the measured charge is affected by an error, positive or negative depending on which type of process predominates: anodic or cathodic.

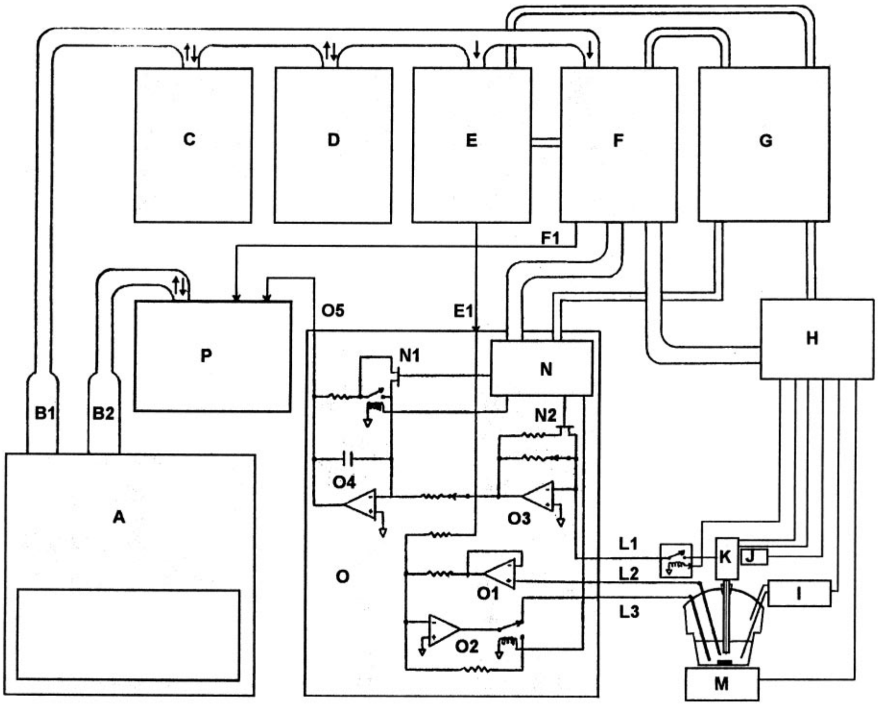

Fig. 2. Block diagram of the automatic system for mercury drop extrusion charge measurements and chronocoulometry. A, microcomputer; B1 and B2, HP-IB interface cards and cabling; C, HP 9872B Graphic Plotter; D, printer; E, 16 bit digital/analog converter; E1, input voltage signal; F, instrumentation control interface; F1, synchronized trigger signal; G, power supply; H, actuator interface; I, nitrogen purge valve; J, drop knocker; K, automatic mercury drop electrode; L1, working electrode connection (mercury drop); L2, reference electrode connection (SSCE); L3, auxiliary electrode connection (platinum gauze); M, magnetic stirrer; N, potentiostat internal interface; N1, integrator reset FET and reed switches; N2, current range selector; O, PAR-170 Electrochemistry System; O1, voltage follower; O2, summing amplifier, with added switch for L3; O3, current to voltage converter; O4, integrator; O5, output signal; P, HP 3837 system voltmeter.

For a dropping mercury electrode, the error in surface charge density, Q_M, can be corrected only by using the equations that describe the different behavior of the faradaic and capacitive currents as a function of time during growth [13,14]. Even so, this is not rigorously correct in many cases owing to non-spherical characteristics of the mercury drops.

At the so-called SMDE (drop growth is interrupted by a valve after a fixed time, leading to a mercury drop with pre-determined area) a simpler correction procedure can be introduced to separate faradaic from capacitive contributions. It can be understood by referring to the illustration in Fig. 3(a), where schematic curves are shown in the absence (B) and in the presence of electroactive material, with predominance of anodic (A) or of cathodic processes (with increasing concentration of electroactive species from C to F).

During extrusion, the charge profile includes two components. One of these is due to the capacitive current from electrode expansion and adsorption processes giving a charge of

$$Q_C = 8.6 \times 10^{-3} Q_0 m^{2/3} t^{2/3} \quad (1)$$

where Q_0 is the charge per unit area (C cm^{-2}) at an applied potential E, and m the mass flow rate (mg s^{-1}). The other is due to the faradaic current, leading to a faradaic charge that, under diffusion limiting conditions, is given by

$$Q_f = \pm 607 n c_\infty D^{1/2} m^{2/3} t^{7/6} \quad (2)$$

where D is the diffusion coefficient (cm^2 s^{-1}) of an electroactive species of concentration c (mol cm^{-3}), the positive sign referring to an oxidation and the negative sign to a reduction. Thus, in the absence of electroactive species, a $t^{2/3}$ dependence of the charge is expected during extrusion. The total charge at the end of extrusion, when $t = t_{ext}$, is given by

$$Q_{ext} = Q_M + Q_{f,ext} \quad (3)$$

where Q_M, the surface charge on the mercury electrode, is the value of Q_C at the end of the extrusion step.

Following extrusion, in the presence of faradaic processes, there will be a further change in electrode charge with time, ΔQ, defined as

$$\Delta Q = Q_{ext} - Q_t \quad (4)$$

where $t > t_{ext}$. This change is proportional to the contributions from the traces of different electroactive species which may be present in solution. If their electrode processes are governed by diffusion, a Cottrellian behavior is to be expected, with ΔQ linearly dependent on $t^{1/2}$, as usual in chronocoulometry [1]. More important, regardless of the exponent of t, for a given set of experimental conditions, at fixed potential and a chosen time t_x at which the charge value is sampled, a linear dependence of $\Delta Q(t=t_x)$ with concentration of electroactive species is obtained.

Thus, a plot of Q_{ext} versus Q should generate a straight line, with the extrapolation to $\Delta Q=0$ (absence of faradaic interference) indicating the point where $Q_{\text{ext}}=Q_{\text{M}}$, as depicted in Fig. 3(b). The slope f of the straight line depends on the extrusion speed and on the final area of the electrode, but should be independent of species' identity, diffusion coefficient, and of the potential applied to the electrode. Additionally, using different and arbitrary sampling times (such as t_1 and t_2 indicated in Fig. 3) groups of straight lines with different slope are generated, but with coincident extrapolation intercepts at $\Delta Q=0$.

The diffusion limiting conditions required by Eq. (2) are not always fulfilled in practice. At potentials corresponding to the rising portion of the polarographic wave of a reversible system, the same fraction of the diffusion current (or charge) will be observed before and after t_{ext}, with no practical consequence for the method. However, for non-reversible electrode processes, currents can depart significantly from the reversible case, especially at the shortest times. For this reason, the calculations being based on post-extrusion data, some overestimation of the correction can be expected, with its extent depending on the kinetics of the electrode process. Practical results will demonstrate that errors are quite acceptable also for irreversible systems, probably because the faradaic charge involved in the early stage of drop formation is small anyway, irrespective of the kinetics.

The accuracy of the method can also be impaired if adsorption equilibrium has not been reached at the end of the extrusion of the drop. The situation is more favorable than with methods based on streaming or fast dropping mercury electrodes [10,11], since t_{ext} is typically around 1 s. When studying strong adsorbates at low concentrations ($<10^{-4}$ M), it is thus advisable to check the results at higher values of t_{ext}, with the mercury flow rate reduced accordingly in order to attain a similar final drop area.

4. Results

To confirm the theory deduced above and to validate the correction procedure, experiments in well-studied media were performed. Solutions of NaF = 0.100 M were studied extensively, initially by Grahame [20] and more recently, by Foresti et al. [14]. Copper ions and oxygen were chosen as electroactive 'contaminants' in such experiments. O_2 is always present to some extent in aqueous solutions and its reduction kinetics on mercury, especially the second step (reduction of hydrogen peroxide), are highly irreversible. On the other hand, copper ions are reversibly reduced in fluoride medium.

In the evaluation of the procedure, two arbitrary times were chosen, 180 and 480 ms after extrusion. The values of the measured charge, Q_{ext}, when the extrusion step was completed, were plotted against ΔQ, as described above. These experimental points are shown in Figs. 4 and 5. Extrapolation of these points to $\Delta Q=0$, leads to the corrected surface charge density, Q_{M}.

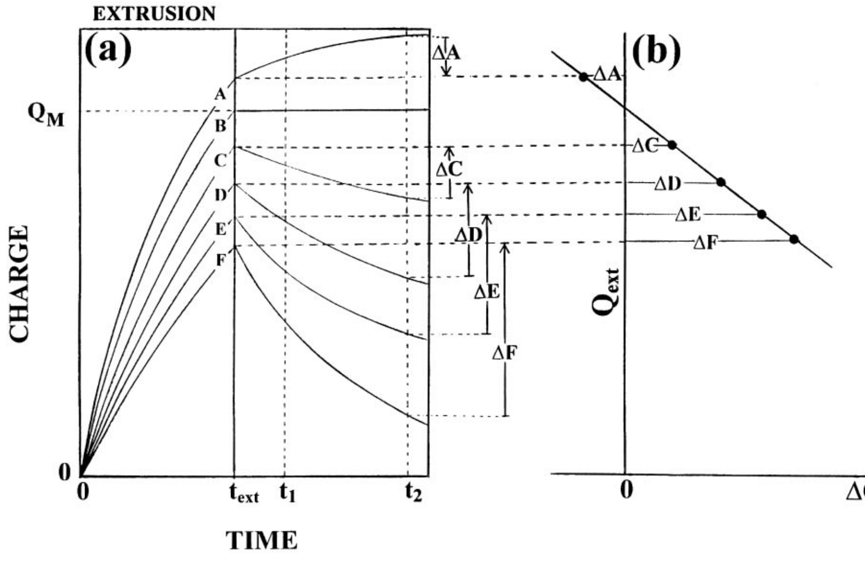

Fig. 3. (a) Scheme of charge variation during and after extrusion: B, in the absence of electroactive species; A, together with oxidation of electroactive species; C–F, together with reduction for increasing concentrations of electroactive species. (b) Schematic plot of Q_{ext} vs. ΔQ showing extrapolation to determine value of Q_{M}.

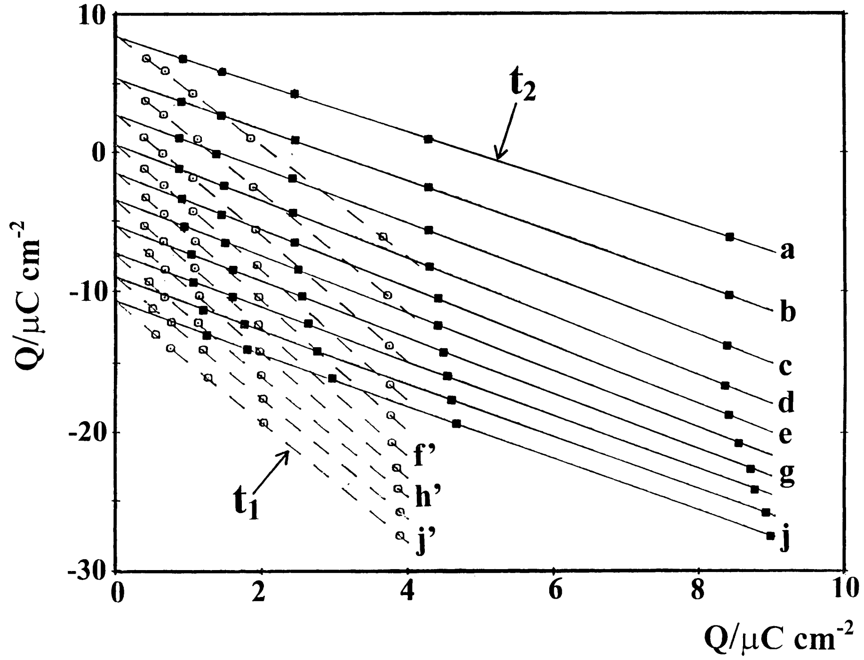

Fig. 4. Plots of Q_{ext} vs. ΔQ in 0.100 M NaF solution for increasing concentrations of Cu^{2+} (0.02, 0.04, 0.08, 0.15 and 0.30 mM) and traces of O_2, in the potential range − 0.100 to − 1.000 V vs. SSCE. Measurements obtained (---) 180 ms and (—) 480 ms after drop extrusion.

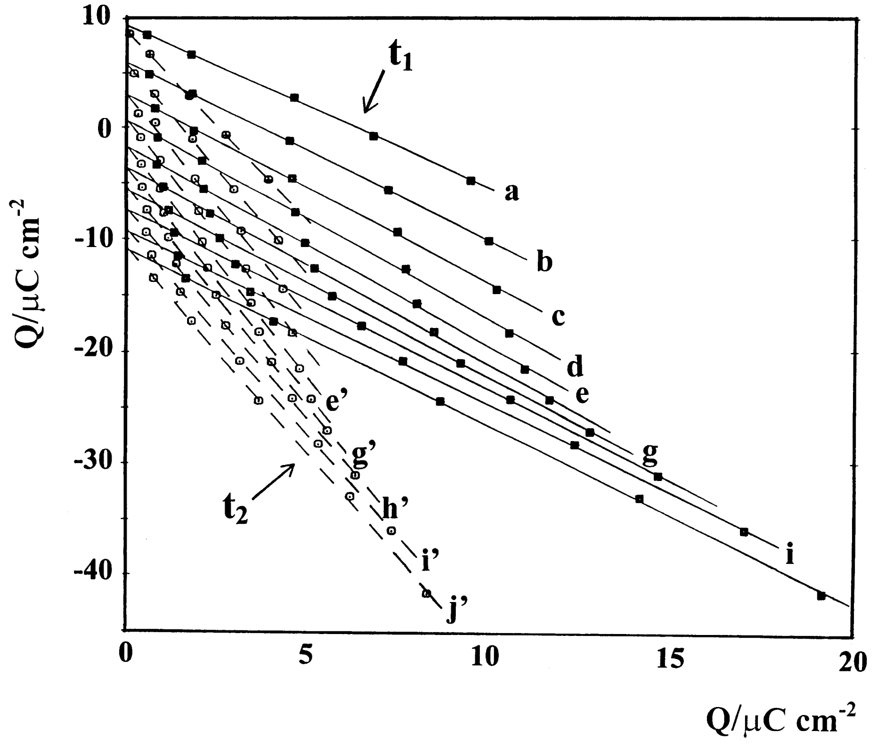

Fig. 5. Plots of Q_{ext} vs. ΔQ in 0.100 M NaF solution for increasing concentrations of O_2 (up to 0.26 mM) in the potential range − 0.100 to − 1.000 V vs. SSCE. Measurements obtained (---) 180 ms and (—) 480 ms after drop extrusion.

On the basis of these figures, the following deductions can be made:

1. the pairs of experimental values, corresponding to a broad variation in concentration of electroactive material, define a straight line;
2. the straight lines obtained at different potentials or in the presence of different (added deliberately) electroactive species have quite similar slopes for the

Table 1
Regression analysis of data from Figs. 4 (spiking with copper ions) and 5 (variable amounts of O_2) in 0.100 M NaF electrolyte solution[a]

E/V vs. SSCE	Variable copper ion concentrations					Variable oxygen concentrations				
	$t_1 = 180$ ms		$t_2 = 480$ ms		Mean value	$t_1 = 180$ ms		$t_2 = 480$ ms		Mean value
	Q_M /μC cm^{-2}	f	Q_M /μC cm^{-2}	f	Q_M /μC cm^{-2}	Q_M /μC cm^{-2}	f	Q_M /μC cm^{-2}	f	Q_M /μC cm^{-2}
−0.100	8.28	−3.79	8.23	−1.62	8.26	8.91	−3.60	9.36	−1.54	9.14
−0.200	5.28	−3.95	5.21	−1.70	5.25	6.05	−3.94	6.13	−1.68	6.09
−0.300	2.61	−4.07	2.54	−1.76	2.58	3.13	−4.05	3.10	−1.72	3.12
−0.400	0.48	−4.33	0.34	−1.88	0.41	0.56	−4.15	0.61	−1.80	0.59
−0.500	−1.63	−4.47	−1.67	−1.97	−1.65	−1.53	−4.23	−1.68	−1.83	−1.61
−0.600	−3.65	−4.39	−3.64	−1.94	−3.65	−3.56	−4.15	−3.62	−1.80	−3.59
−0.700	−5.38	−4.40	−5.42	−1.92	−5.40	−5.30	−4.02	−5.59	−1.71	−5.45
−0.800	−7.38	−4.24	−7.30	−1.86	−7.34	−7.24	−3.88	−7.42	−1.65	−7.33
−0.900	−9.05	−4.20	−9.02	−1.82	−9.04	−9.02	−3.78	−9.20	−1.59	−9.11
−1.000	−10.71	−4.16	−10.67	−1.80	−10.69	−10.58	−3.80	−10.83	−1.61	−10.71

[a] Values of Q_M as a function of applied potential for current sampling times t_1 and t_2.

same time delay after the finishing of the extrusion process;

3. the intersections of the straight lines obtained with different time delays converge to the same charge value;
4. the charge density values obtained from measurements performed in the presence of O_2 or of Cu^{2+} are in very good agreement.

Table 1 contains the surface charge density values determined in this way 180 and 480 ms after drop extrusion, with increasing concentration of oxygen or copper ions. In the same table are also included, next to each value of Q_M, the respective slopes of the extrapolated lines. The close agreement between these slopes (RSD = 5.5%) over a wide potential range (−0.1 to −1.0 V) is worthy of note, as is the excellent linearity over the considered concentration range of electroactive species.

Fig. 6 is a plot of the results obtained from Table 1 on which are also shown lines corresponding to surface charge densities measured by previous researchers. As can be seen, the agreement between the new proposed procedure and these other values is excellent for all but the less negative potentials obtained in the presence of oxygen, where departures approach 1 μC cm^{-2}. This is acceptable for most applications and confirms the validity of the proposed method.

For the study of adsorption phenomena, where electroactive species may be unwanted contaminants, it is neither practical nor necessary to make several additions of electroactive material (contaminant) to each solution under study, since a simplified procedure was developed. As noted above, the slope f of the straight lines is rather constant if the mercury flow rate during extrusion, the final drop area and the sampling time (t_1 or t_2) are maintained invariant, and its value needs to be determined only once during a calibration experiment (like Table 1). Subsequently, it is sufficient to measure sets of Q_{ext} and ΔQ as a function of the

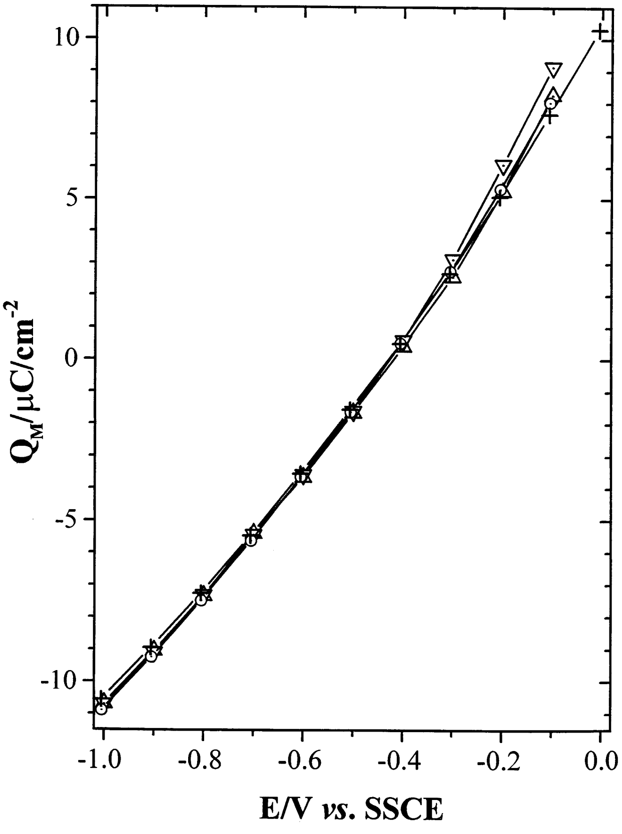

Fig. 6. Comparison of the values of the surface charge density on mercury electrodes as a function of potential in 0.100 M NaF solution obtained in this work; (▽) in the presence of oxygen and (△) in the presence of Cu^{2+}, and those determined by (○) Foresti et al. [18] and (+) Grahame [19].

potential. To find Q_M at each potential, the effect of unknown traces of electroactive material present in each solution is corrected through the relationship:

$$Q_M = Q_{ext} - f\Delta Q \quad (5)$$

In practice, with the computer data acquisition and analysis system presented in Fig. 2, this is done automatically for waiting times t_1 and t_2 after completion of the extrusion.

In any case, for routine automatic application, the lower the concentration of electroactive impurities, the better are the results; if their concentration becomes too high, the correction cannot be accurate enough, because a slight change in the slope f produces an appreciable change in the value of Q_M from extrapolation. Thus, obtaining the same value of Q_M by extrapolation of Q_{ext} values for t_1 and t_2 constitutes a valuable internal consistency test for the method. Any difference between these Q_M values (for t_1 and t_2) could be due to too high a concentration of impurities as well as unexpected difficulties, for example, the appearance of pre- or post-adsorption waves of electroactive species.

5. Conclusions

The novel procedure for correction of the faradaic component, implemented with a new hanging mercury drop electrode in a system comprising computer control of all relevant experimental parameters, data acquisition and analysis, permits fast and automatic gathering of corrected electrode charge values as a function of the electrode potential. The accurate experimental results obtained in 0.1 M NaF are in agreement with those from the literature obtained by different methods, demonstrating the validity of the proposed approach. Similar measurements in 0.1 M NaCl lead to the same conclusion [18].

The ability of the new method to overcome automatically the interference of the residual faradaic current from electroactive species is an attractive feature for adsorption studies at the interface of the mercury electrode. Going further, to recognise the adsorption of electroactive species selectively, an association of this method with double potential step chronocoulometry is of great advantage because it makes it ultimately possible to plot their surface concentration directly as a function of the charge at the electrode (instead of the potential). Since exactly the same instrumentation is required, this demanded solely appropriate linking of the software for both methods, as will be demonstrated in a forthcoming paper, devoted to the investigation of the induced adsorption of mixed electroactive metal complexes. In principle, the proposed method can be implemented with any commercial instrumentation including a static mercury drop electrode and embracing chronocoulometry in its experimental repertoire, by appropriate modification of the software.

Acknowledgements

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