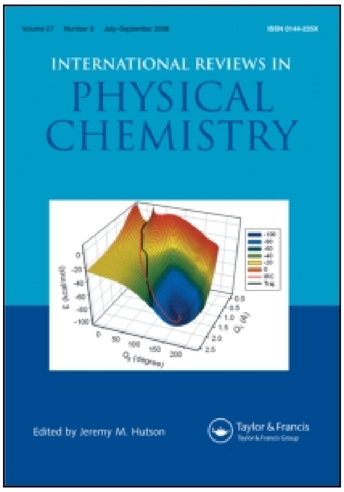

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Back to the hydrated electron—how it is produced and monitored at the dropping mercury electrode in pure water

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Back to the hydrated electron—how it is produced and monitored at the dropping mercury electrode in pure water

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A reproducible current–voltage curve of pure water, obtained with the dropping mercury electrode (DME), contains a 1·2 V wide region where no faradaic processes take place. This region consists of three distinct parts according to different orientations of water molecules and their interactions with the mercury surface. On irradiation of the DME by UV and visible light a cathodic photocurrent is produced in the negative part of the nonfaradaic region, which increases with increasing voltage. The photocurrent appears in water in the absence of scavengers of hydrated electrons, and its magnitude is of the same order as that of the current due to photoemission of electrons into solutions of electrolytes containing scavengers. Additions of electrolytes decrease and ultimately suppress this kind of photocurrent. We explain the photocurrent by the effect of an electric field of the extended electrode double layer on the return of hydrated electrons, generated by photoemission, back to the electrode. Retarded by electrostatic repulsion from the negatively-charged electrode, some of the hydrated electrons undergo a relatively slow reaction with water, which under those conditions acts as a weak electron scavenger.

1. Introduction

Michael Henchman and I met for the first time when he visited the Institute of Physical Chemistry of the then Czechoslovak Academy of Sciences in Prague in 1961. When he heard that early the following year I was going to undertake research at the Department of Physical Chemistry in Cambridge, England, he, a Cambridge graduate, arranged for me to meet some of his friends there, who soon also became my friends and have remained so until the present day.

My research programme in Cambridge, under the supervision of Professor R. G. W. Norrish, concerned fundamental studies in photoelectrochemistry. In the past R. G. W. Norrish, together with E. K. Rideal (Rideal and Norrish 1923), had followed the photodecomposition of permanganate ions in solution by means of potentiometry; that experience provided him with the idea of the basic usefulness of combining photo- with electrochemistry. A reproducibly pure state of an electrode surface was of obvious primary importance in any photoelectrochemical research and hence the dropping mercury electrode (DME) appeared to be an ideal tool for these studies. As I had no experience in photochemistry but knew how to use the DME, we agreed that I would study the effects produced by light at the electrode in solutions which do not absorb the light used. Preliminary experiments had shown that there existed several types of such effects. We were not aware that at the same time Dr G. C. Barker at Harwell was engaged in research along similar lines. In the following years he presented the results of his systematic experiments in a series of papers (Barker and coworkers, 1965, 1966, 1971, 1974a, b) in which he interpreted the phenomenon of cathodic photocurrent as due to the emission of electrons from the DME and to their ensuing fate in the solution and/or at the electrode. Dr H. Berg in Jena touched on the same effects as those we studied when he described the so-called 'photoresidual current' (Berg and Reissmann 1970) as a secondary phenomenon in his field of 'photopolarography' (Berg 1960). A number of researchers then joined in this field of studies (e.g. Delahay and Srinivasan 1966, Korshunov *et al.* 1968, De Levie and Kreuser 1969, Bomchil *et al.* 1970, Brodsky and Pleskov 1972, Bendersky 1977, Perone *et al.* 1978, Pleskov and Rotenberg 1978, Sass 1978, Picq and Vennereau 1979, and others).

From 1961 Mike Henchman was a lecturer at the University of Leeds and was carrying out research in radiation chemistry with Professor F. S. Dainton. The early 1960s was an exciting era in physical chemistry, when many laboratories in the UK, USA, Israel, Germany and other countries were competing in theoretical and experimental studies of a short-lived reactive species of reducing properties and of unit negative charge which could be generated in solutions in various ways and which was finally identified as a solvated electron (for a review see, e.g. Logan 1967, Dainton 1971). During this time specialized radiation chemists, photochemists, electrochemists, solution chemists as well as chemical physicists were waiting impatiently for each new issue of the scientific journals. Mike and I, although working in seemingly different fields, were trying to answer similar questions and were both affected by the unique atmosphere of those years. I found that some results from Professor Dainton's laboratory (Dainton and James 1958) were relevant to mine (Heyrovský 1965); when Mike arranged a memorable visit to Leeds and surroundings I was able to speak to Professor Dainton personally. This visit and numerous references to papers in radiation chemistry provided by Mike were an important inspiration for my research in Cambridge, where at that time nobody was dealing with this type of problem.

One of the conclusions of my work in Cambridge, which ended in spring 1965, was that a cathodic photocurrent could be produced at the DME in aqueous solutions even in the absence of scavengers of hydrated electrons, provided the solution contained only a low concentration of electrolytes. The basic results of my research during that period were published (Heyrovský and Norrish 1963, Heyrovský 1965, 1966a–c, 1967) and it was several years before I returned to photoelectrochemistry, back in my laboratory in Prague; however, it then represented only one of several directions of my interest. In the late seventies, together with Dr Filippo Pucciarelli from the University of Camerino, continuing to work on some of my unsolved problems from Cambridge, we found the positive limit of photoemission of electrons, and later we carried out photocurrent measurements in pure water in the absence of electron scavengers. Results of the first work were published (Heyrovský and Pucciarelli 1977); those of the latter were presented in poster form, partly at the Polarographic Congress in Prague in 1980 (Heyrovský and Pucciarelli 1980) and partly at the 1980 Faraday Discussion No 71 on photoelectrochemistry in Oxford, but they were never published in full. To my knowledge, from the time of our work until now no-one else has carried out electrochemical or photoelectrochemical measurements with the DME in pure water.

The increased attention paid recently to the structure of water in contact with a metallic surface (Aloisi and Guidelli 1991, Porter and Zinn 1993, Schmickler *et al.* 1993, Booth *et al.* 1994) made us return to the old results which were waiting in the drawers of my desk for their time to come; simple as they are they represent an experimental contribution to the topic of actual interest and they bring back the flavour of the early sixties, a happy time for Mike, for me and, in fact, for science as well.

2. Experimental

The water initially used for measurements was triply distilled: first normally, then from an alkaline solution of permanganate and finally from a quartz apparatus. Later the permanganate stage was omitted, without any detrimental effect on the results. The heavy water was Uvasol min. 99·95% D_2O from Merck. The electrolytes used were of analytical grade purity, and nitrous oxide was taken from a small cylinder manufactured for medical purposes. Mercury for the DME was thoroughly washed with dilute nitric acid and doubly distilled. Pure hydrogen from a gas cylinder was used for expelling air–oxygen from the water and from the cell; before measurement it was bubbled through the sample, during measurement it was passed over it.

In the initial stages of the work a glass cell of about 100 ml volume with a conical bottom leading to a long narrow tube was used; in the tube the mercury dropping from the DME was collected, away from the electrodes and from the bulk of the water sample. Three interconnected bright Pt and one platinized Pt electrodes arranged symmetrically around the DME capillary were introduced to the cell through a large stopper, together with the gas inlet and outlet tubes. The platinized Pt electrode, prepared in the conventional way, was thoroughly washed after preparation and then kept in bidistilled water. The capillaries for the DME were of the spindle type (Novotný and Heyrovský 1987) providing highly reproducible mercury drops of any desirable size and of long drop-times. In further electrochemical and photoelectrochemical research the cylindrical bent capillary was used, and the quartz cell described earlier (Heyrovský and Pucciarelli 1977); the procedure and apparatus used in photocurrent measurements were the same as before.

The voltage was applied to the DME with respect to the potential of a platinized Pt electrode in pure water saturated by hydrogen under atmospheric pressure; to comply with common usage, voltage values have been recalculated and throughout the present paper they are given with respect to the potential of the saturated calomel electrode (SCE).

3. Results and discussion

3.1. *Polarographic study of pure water*

It has been customary right from the start of the polarographic method to add so-called supporting electrolytes to analysed solutions in order to minimize the ohmic drop in the cell. In this way the voltage applied to the electrodes can be equalled to the difference in their electrochemical potentials. After the introduction to electrochemical instrumentation of the potentiostat with the three-electrode system, compensation of the cell resistance became an automatic routine; however, the reference electrode had to have a conducting connection to the working electrode through a salt bridge. Measurements in pure water unpolluted by any electrolyte hence required special experimental conditions; in order to eliminate the salt bridge (plastic conducting membranes impermeable to electrolytes were not known to us at that time) we decided on a two-electrode system.

Firstly, we had to accept that the results would include an error due to the cell resistance R of the order of megohms; with currents i smaller than 0·1 μA the maximum ohmic drop iR would be of the order of 0·1 V. As we were interested mainly in the qualitative picture of the situation at the mercury/water interface in the region of potentials near the point of zero charge, where no faradaic processes take place and hence currents are very small, the given precision was acceptable.

To work with pure water we had to use a reference electrode which would hold a constant potential without any electrolyte—for this purpose we tried a platinized platinum electrode dipping into water in a hydrogen atmosphere, and found that it fitted our needs. For the sake of increasing stability of the electrode potential we connected the platinized electrode in parallel with three bright platinum sheets and placed all four electrodes symmetrically around the working dropping mercury electrode. By comparison of curves obtained with this reference electrode with those recorded with more conventional types of electrodes we estimated the potential of the system H_2/platinized Pt/H_2O at about $-0{\cdot}49$ V versus NHE or $-0{\cdot}74$ V versus SCE.

For the DME we used special capillaries which would produce small drops growing at a slow rate, in order to minimize the currents, faradaic as well as nonfaradaic, and thus keep the *iR* drop in the cell at a low level. With the spindle capillaries at a mercury flow rate under 1 mg s^{-1} the drop-times were up to 50 s.

It was also necessary to minimize the ubiquitous residual current which, according to our experience, is mostly due to the reduction of traces of mercury compounds formed when mercury, collected from the dropping electrode at the bottom of the cell, remains in contact with the electrolysed solution. This heterogeneous chemical reaction of dissolution of metallic mercury is favoured by the passage of bubbles of the inert gas stirring the solution, often together with the liquid metal. In order to prevent this we used a cell with a conical bottom ending in the centre with a long narrow tube in which the mercury, dropped from the capillary, collects during the measurement, far from the electrodes and from the bulk of the measured water.

The DME was introduced into the cell only after preliminary deaeration of the water. The passage of gaseous hydrogen through the liquid around the platinum electrodes so as to maintain constant potential was also useful for removal of the last trace of air–oxygen. After having passed a stream of pure hydrogen through the water for 50 minutes, we let it pass over the water in the cell during the measurement and obtained the polarographic curve shown in figure 1 and the instantaneous current–time curves reproduced in figure 2.

The polarographic current–voltage curve of pure water (showing the mean current flowing through the water and the DME while the polarizing voltage applied to the electrodes is slowly increasing) is limited on the positive side by a large increase in anodic current caused by electrodissolution of mercury, expressed in the net form as

$$Hg - 2\,e^- \rightarrow Hg^{2+}. \tag{1}$$

On the negative side the curve ends by an increase of cathodic current due to electroreduction of water to gaseous hydrogen and hydroxyl ions, in the net formulation

$$2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,HO^-. \tag{2}$$

The curve in the voltage region between the two electrochemical reactions can be divided into three almost linear segments of different slopes—the positive and the middle one extending over some 0·3 V each and the negative one over about 0·6 V. In the positive part of the region the current is anodic, in the negative part it is cathodic and in the middle part it is close to zero.

The state of the mercury/water interface in the three voltage regions can be more closely studied from the course of instantaneous current flowing through the DME while the polarizing voltage is kept constant (figure 2). The shape of these *i–t* curves in the positive and in the negative region is similar, except that their directions are of

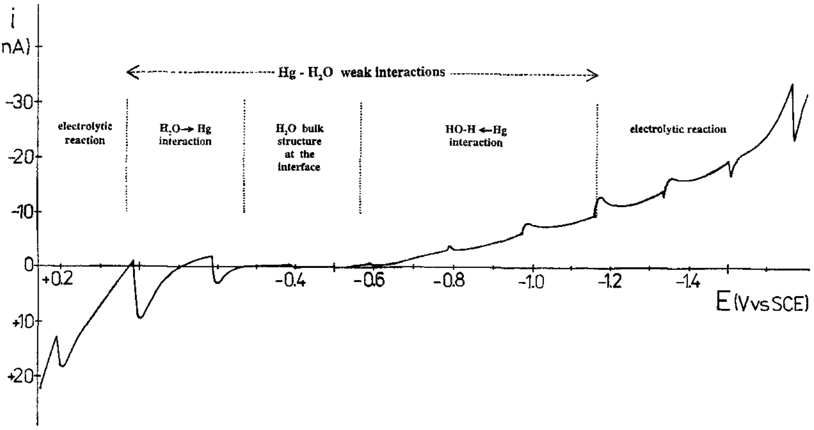

Figure 1. Polarographic current–voltage curve of pure water. Recorded with a very slowly dropping mercury electrode with minimum damping of current oscillations.

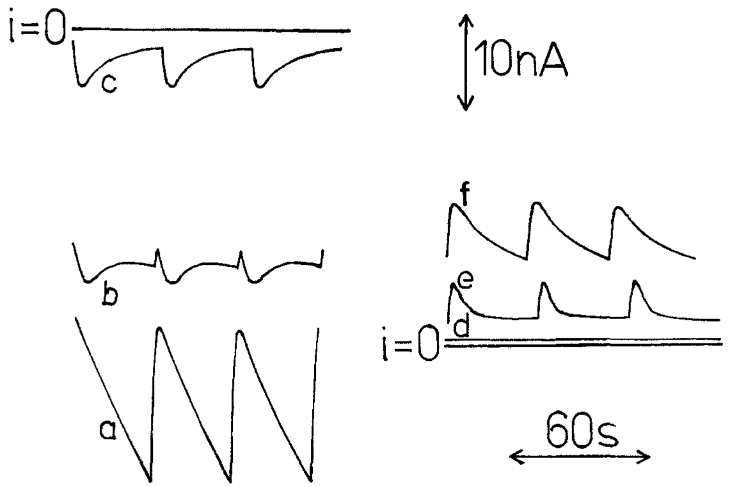

Figure 2. Polarographic current–time curves in pure water. Instantaneous current on three successive drops recorded (with a relatively slow recorder) under conditions as in figure 1 at constant voltage of: (*a*) +0·26 V; (*b*) +0·16 V; (*c*) −0·24 V; (*d*) −0·54 V; (*e*) −0·84 V; (*f*) −1·24 V versus SCE. Curves (*a*)–(*c*) represent anodic currents (in polarographic convention below the zero current line); curves (*d*)–(*f*) show cathodic currents. Curve (*a*) is characteristic for an electrolytic reaction, curves (*b*) and (*f*) for different stages of transition between electrolytic and charging currents, curves (*c*) and (*e*) for charging currents.

opposite sign. At the beginning of drop-life the current increases rapidly to a maximum and then it slowly decreases. This course resembles that of the charging current in conventional polarography (Heyrovský and Kůta 1966), which decreases with time from infinity, according to the relation $i \sim t^{-1/3}$. With pure water the rate of charging of the dropping electrode is retarded because of the high resistance R of the cell, due to the high time constant RC (where C is the differential capacity of the electrode, see below). The important point about the shape of these curves is that in the later stages of the drop-time the current does not increase as the drop size grows. An increase proportional to increasing surface area of the electrode is the sign of a

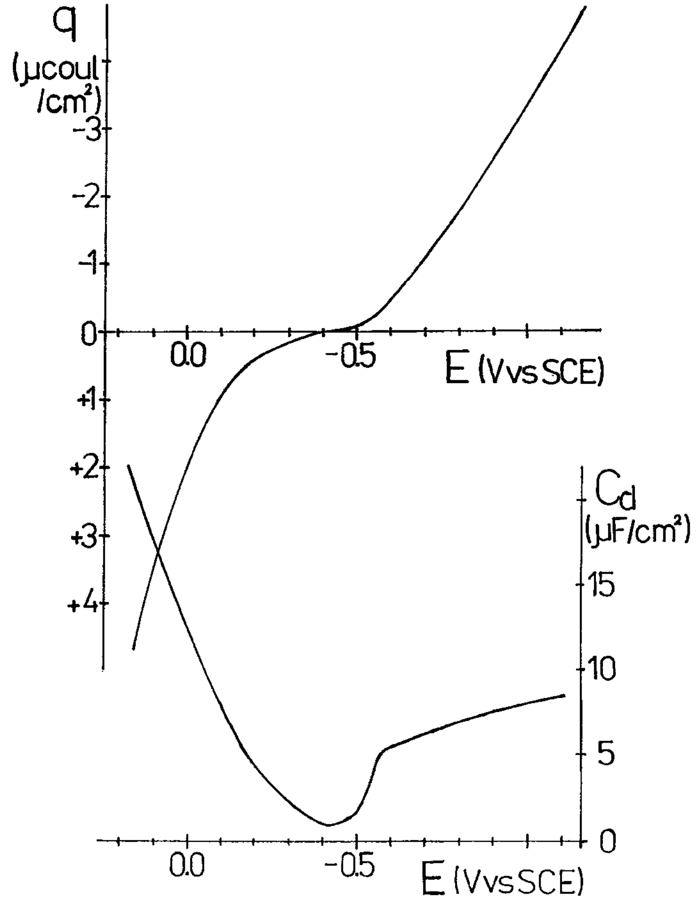

Figure 3. Voltage dependence of charge density (upper curve) and of differential capacity (lower curve) of the DME in pure water. Obtained from data in figures 1 and 2, as described in text.

faradaic current, of the occurrence of electrolysis. This can be observed on the *i–t* curves beyond the threshold voltage range of 1·2 V which indicates where the two above-mentioned electrode reactions, respectively, begin.

Within the voltage range of 1·2 V the currents are hence nonfaradaic, consisting of charging of the mercury/water interface under corresponding orientation of the water molecules in contact with the mercury surface. In the intermediate region of 0·3 V the current passing through the DME is very small and time independent, which is a sign that the structure of the water touching the metal—presumably identical with the natural structure of water in the bulk of the phase, without any preferred molecular orientation—can respond to the slight variations of the surface charge density of mercury without becoming significantly disturbed. The polarogram of heavy water differs from that described above by a narrower intermediate region—instead of 0·3 V in H_2O it is only about 0·2 V wide in D_2O. This has to be explained by the difference in bulk structure between H_2O and D_2O (Frank 1972).

Figure 3 shows (a) the dependence of the mean charge density at the DME on voltage, obtained by graphical integration of the current–time curves from figure 2 and by dividing the values of charge by the mean surface area of the DME, and (b) the voltage dependence of the mean differential capacity obtained by graphical derivation of the charge density–voltage curve. We can see that from the minimum, which corresponds to the point of zero charge of the mercury/water interface, the capacity increases both in the positive and the negative direction. This means that the orientation of water molecules and their interaction with mercury in the interfacial layer adjusts in both directions to the charge on the metal with the result that the two opposite charges get ever closer together.

On the positive side, where the charging current is anodic and the electrode attracts electrons in the nonfaradaic interaction, the dipole of the water molecule obviously turns with the lone electron pairs on oxygen towards mercury. With increasing positive charge on the electrode the orientation of the dipoles affects the water structure in the interface more strongly and a weak chemical bond is presumably forming between water and mercury, based on charge transfer, where water is electron donor and mercury acceptor; the surface mercury atoms thus undergo a gradual transformation into hydrated mercury ions. These start going into solution when the nonfaradaic current changes into faradaic outside the 1·2 V region, presumably primarily in the form $[H_2O–Hg–Hg–OH_2]^{2+}$ (Johansson 1966).

On the negative side, where the charging current is cathodic in the nonfaradaic region, the trend in orientation of water dipoles in contact with the electrode is with the hydrogen atoms towards mercury. We assume that with increasing negative charge on the electrode a weak interaction similar to a hydrogen bond is gradually established, where this time mercury is the electron donor to one hydrogen atom of the water molecule, of which the HO–H bond becomes ever more polarized. This interaction turns into the electroreduction of water when the voltage region of nonfaradaic interactions is exceeded; once the electrode reaches sufficiently negative potential for the hydrogen of the polarized water molecule in contact with mercury, $[HO–H]_{cont}$, to accept the donated electron e_m^- from the metal and to give up the shared one to the rest of the molecule

$$[HO^{(-)}–H^{(+)}]_{cont} + e_m^- \rightarrow HO^- + H, \tag{3}$$

the possible follow-up reactions

$$2\,(H + HO^-) \rightarrow H_2 + 2\,HO^- \tag{4}$$

or

$$[HO^{(-)}–H^{(+)}]_{cont} + H + HO^- \rightarrow H_2^+ + 2\,HO^- \tag{5}$$

and

$$H_2^+ + e^- \rightarrow H_2 \tag{6}$$

are relatively fast.

The experiment reported above was further repeated with a less sophisticated procedure using a simple cell for photoelectrochemical measurements, less meticulously purified water and a DME of the usual drop-time, 3–6 s. It was ascertained that the results thus obtained were perfectly reproducible and that the characteristic features of polarograms of pure water remained as described. The water samples and the empty cell were first thoroughly deaerated by hydrogen and then the water was introduced by the pressure of hydrogen into the cell with the DME and one platinized Pt electrode. In this way we first followed the dependence of the polarogram of water on temperature. Figure 4 shows what was anticipated, namely that the kinetics of reactions (1) and (3)–(6), corresponding to the faradaic currents, are considerably accelerated by a temperature increase whereas the nonfaradaic currents within the 1·2 V region, corresponding to charging of the mercury/water interface, remain hardly affected by temperature.

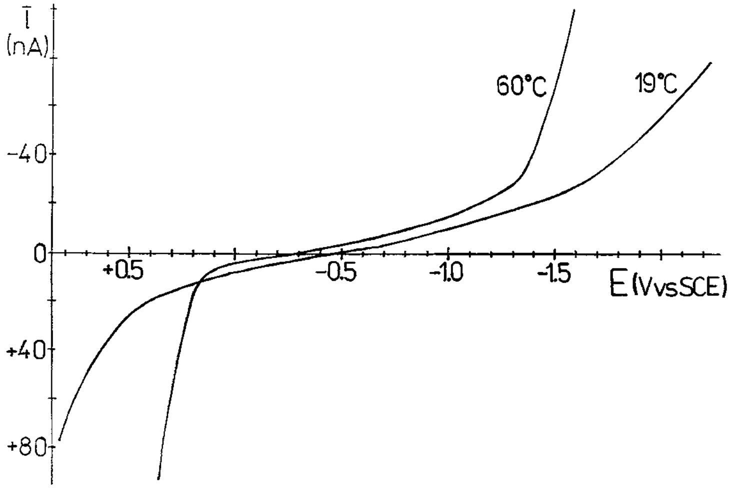

Figure 4. Dependence of the polarographic mean current–voltage curve of pure water on temperature: at 19 °C and at 60 °C.

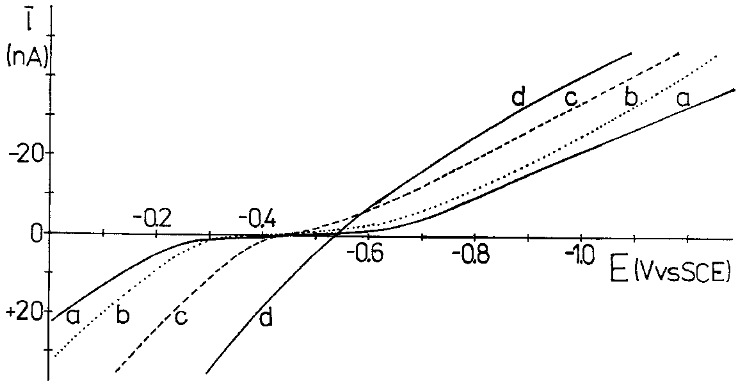

Figure 5. Polarographic mean current–voltage curve of (*a*) pure H_2O; and of aqueous solutions: (*b*) 10^{-5} M KCl; (*c*) 10^{-3} M KCl; (*d*) 10^{-1} M KCl.

The change of the characteristic curve shape on the gradual addition of KCl to water is demonstrated in figure 5: the central part of the curve, where the orientation of water on the electrode surface is least disturbed, becomes narrower as the compact part of the ionic double layer builds up on the solution side. This is to be expected, as the free water molecules in the interface are gradually replaced by the polarized molecules forming part of the hydration spheres of the ions surrounding the electrode. Finally, in 0·1 M KCl the polarogram has the familiar shape of charging current, consisting of two branches of different slopes given by the adsorption of anions on the positive side and of cations on the negative side of the point of zero charge. Using the equation for the mean polarographic charging current (in A) (Heyrovský and Kůta 1966)

$$i_c = 0{\cdot}85\, E_0\, C' m^{2/3} t_1^{-1/3} \tag{7}$$

where E_0 is the potential measured from the point of zero charge of mercury in V, C' the specific integral capacity of the electrode in μF cm^{-2}, m the mercury flow rate through the capillary in g s^{-1} and t_1 the drop-time in s, we have determined the values of C' for the different sections of the current–voltage curves. The polarographic curve of each sample was recorded with three different heights h of mercury reservoir above the tip of the capillary, and the value of the C' (independent of h) was calculated as an average of the three measurements. For H_2O the results were 19 μF cm^{-2} for the positive 0·3 V wide linear segment, 1·7 μF cm^{-2} for the middle 0·3 V wide part and 12 μF cm^{-2} for the negative 0·6 V wide linear section of the curve. These results are in good agreement with the differential capacity curve in pure water given in figure 3. Such values are to be expected, judging by similar data published for dilute aqueous solutions of electrolytes (Grahame 1947, Delahay *et al.* 1966). The corresponding results for D_2O were 31, 3·6 and 19 μF cm^{-2} respectively, i.e. all higher than for H_2O; this difference can be qualitatively accounted for by higher polarizability of the O–D bond as compared with O–H. With 0·1 M KCl in H_2O, from the slope of the two branches of the polarographic curve we obtained for C' the values 37 μF cm^{-2} for the positive and 24 μF cm^{-2} for the negative branch; the results of Ilkovič (1936) for the same solution are 42·2 μF cm^{-2} and 22·3 μF cm^{-2} respectively.

3.2. *Photocurrents on the DME in water and in aqueous solutions in the absence of electron scavengers*

In the abundant literature cited above on photoemission of electrons from metals into solutions of electrolytes the presence of scavengers of solvated electrons is a *conditio sine qua non* for obtaining a net photocurrent. The way in which the electrons, emitted from mercury into 1 M KCl solution on irradiation by a laser pulse, return back to the electrode was experimentally followed (Babenko *et al.* 1977) and in one of the review articles (Pleskov and Rotenberg 1978, p. 8) it is stated: 'If there are no scavengers in the solution, then the solvated electrons return to the electrode at a comparatively rapid rate, and thus the resultant stationary photocurrent in the system will be zero. Solvated electrons can also react with the solvent molecules. The rate of this reaction, however, is usually so small that it cannot give rise to noticeable photocurrents.' At variance with this statement are the experimental results published in the mid-sixties (Heyrovský 1966b, c, 1967) and verified several times since then, and all the figures presented below.

Figure 6 shows the polarogram of pure water recorded in the way described above with the DME in the dark, and then with the electrode irradiated from a high pressure mercury lamp, first by full light and then by light passed through two different edge filters. (The effect of wavelength of the light used on the photocurrent follows the pattern characteristic of electron emission, which has been thoroughly studied in the past and is hence not explicitly discussed in the present paper.) The photocurrent, or the difference between the current recorded under irradiation and in the dark, increases when the water in the cell is saturated under atmospheric pressure by N_2O, an efficient scavenger of hydrated electrons which does not affect the conductivity of water. A comparison of the two photocurrents reproduced in figure 7 demonstrates that the photocurrent in pure water is of the same magnitude as the photocurrent obtained in the solution containing a relatively high concentration of an electron scavenger.

The dependence of the photocurrent in pure water on electrode potential E was tested basically with full emission of the lamp and with drop-time of the DME kept constant by means of an automatic timing device; it could be best fitted over the voltage span of 1 V by the relation $i_p \sim E^{7/2}$, the same as was found valid for similar conditions for the photoemission of electrons into electrolytic solutions containing

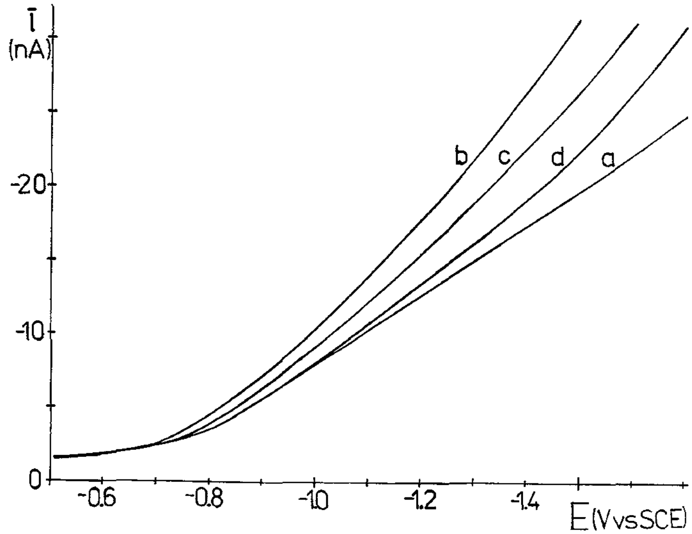

Figure 6. Polarographic mean current–voltage curves in pure water with the DME: (*a*) in the dark; irradiated by high pressure Hg lamp with: (*b*) full light; (*c*) light of wavelength > 298 nm; (*d*) light of wavelength > 336 nm.

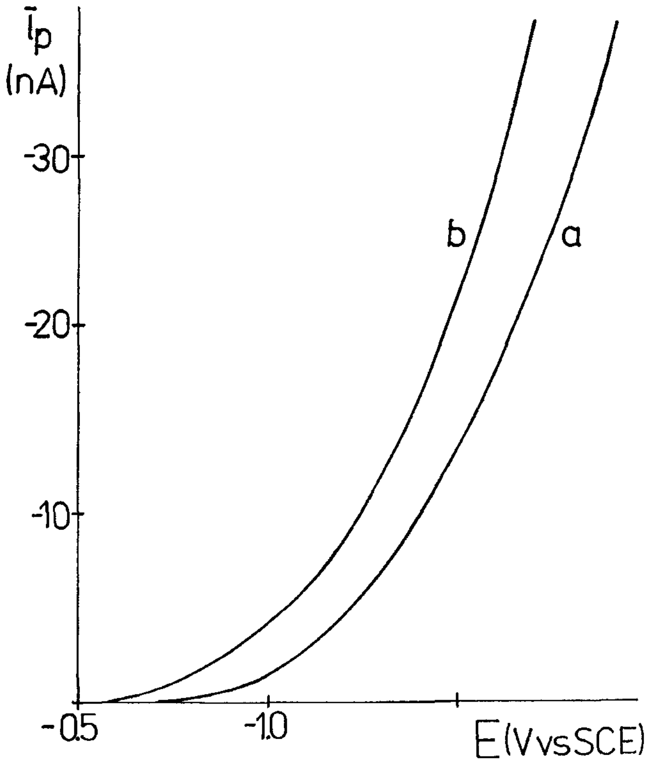

Figure 7. Polarographic mean photocurrent–voltage curve of (*a*) pure water; (*b*) water saturated with N_2O under atmospheric pressure.

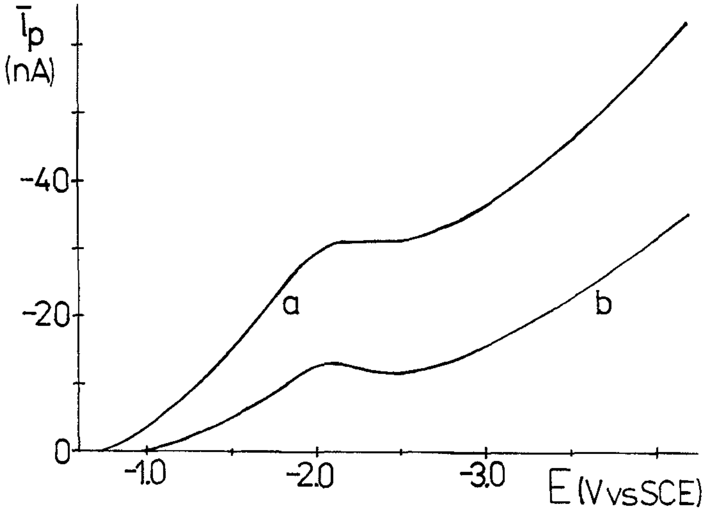

Figure 8. Polarographic mean photocurrent–voltage curve in pure water over a wider voltage range with DME irradiated by high pressure Hg lamp with (*a*) full light; (*b*) light of wavelength > 320 nm.

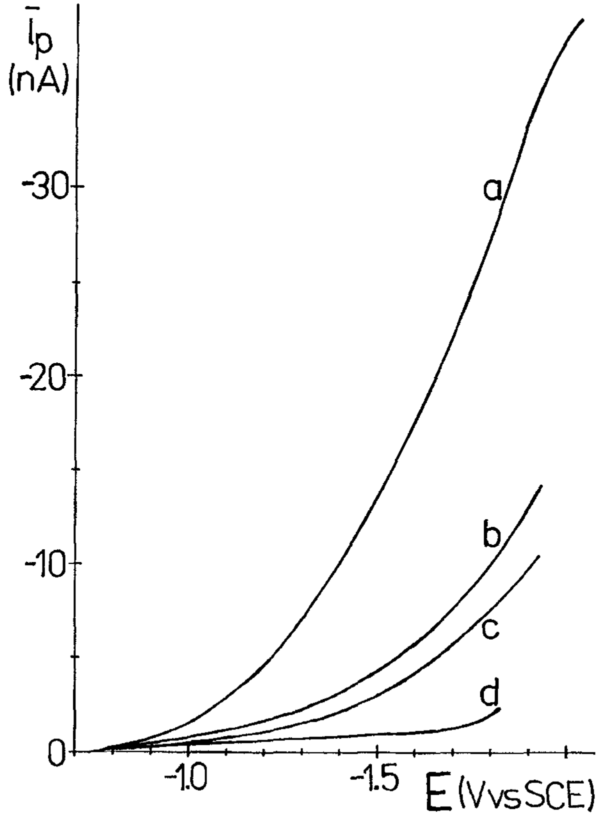

Figure 9. Polarographic mean photocurrent–voltage curve of: (*a*) pure water, ditto 10^{-5} M KCl; (*b*) 10^{-3} M LiCl; (*c*) 10^{-3} M KCl, ditto 10^{-3} M NaOH; (*d*) 10^{-2} M KCl. Full emission of the lamp.

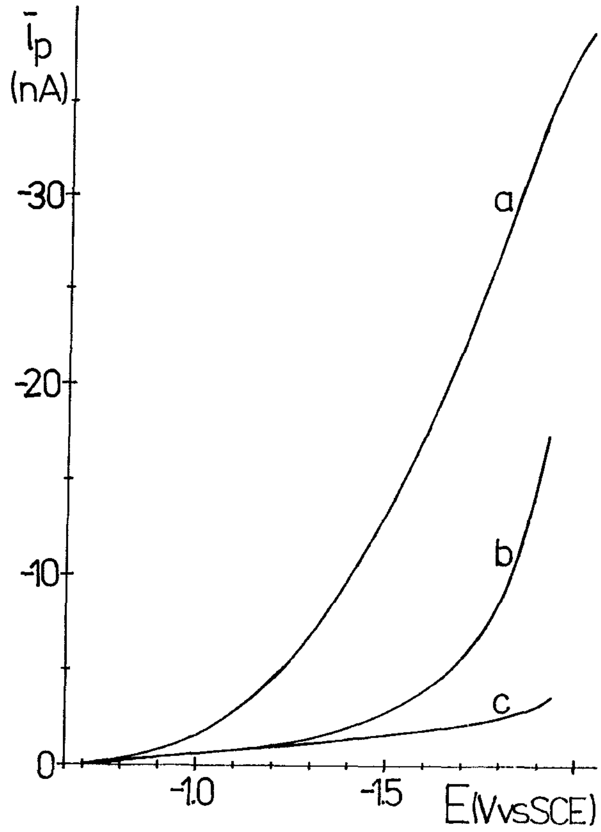

Figure 10. Polarographic mean photocurrent–voltage curve of: (*a*) pure water; (*b*) 10^{-5} M $BaCl_2$; (*c*) 10^{-4} M $BaCl_2$. Full emission of the lamp.

scavengers (Heyrovský and Pucciarelli 1977). (Within the potential range concerned, where the absolute value of currents did not exceed 50 nA, the applied voltage was taken as a measure of electrode potential *E*.)

The photocurrent in pure water appears in the 0·6 V wide voltage range of the hydrogen bond type interaction of water molecules with the electrode surface outlined above. At the negative end of this range, where in the absence of irradiation the electroreduction of water begins, a step appears on the photocurrent–voltage curve, i.e. a region about 0·4 V wide, where the photocurrent is independent of voltage (figure 8). This photocurrent step shows an unusual dependence on the height *h* of the mercury reservoir: while the mean photocurrent due to emission of electrons into solutions of electrolytes containing electron scavengers is known to be independent of *h*, the height of the photocurrent step in pure water decreases linearly with increasing *h*. Beyond the step in the negative direction the photocurrent resumes a steep increase with the applied voltage (figure 8).

A characteristic feature of the photocurrent in pure water is its strong dependence on the presence and concentration of added electrolytes, in particular on the charge of the cations. This dependence is demonstrated in figures 9–11. Obviously, the mechanism of the photocurrent in pure water is determined by the state of the electrode double layer.

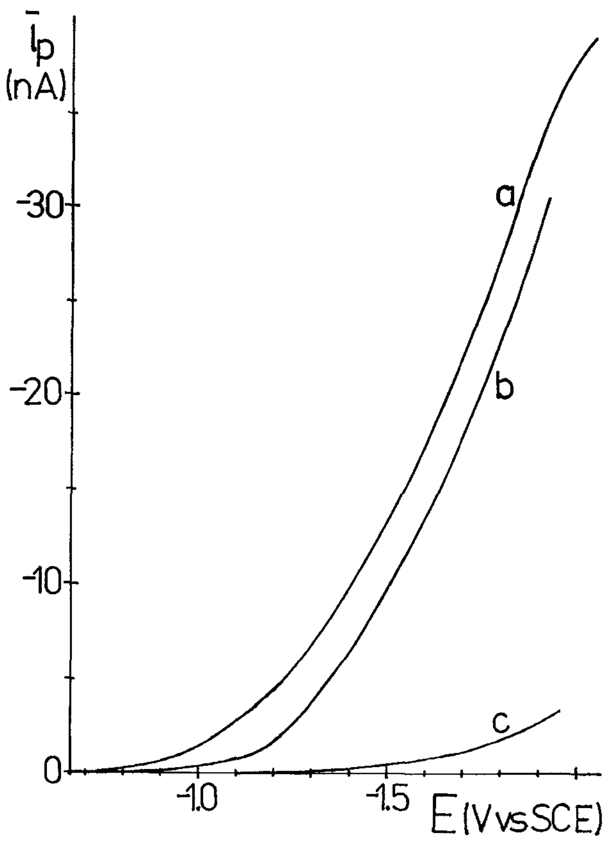

Figure 11. Polarographic mean photocurrent–voltage curve of: (*a*) pure water; (*b*) 2 × 10^{-6} M $LaCl_3$; (*c*) 10^{-5} M $LaCl_3$. Full emission of the lamp.

In sufficiently concentrated electrolytic solutions and in the absence of electron scavengers the electrons photoemitted from the electrode and hydrated in the solution return to the electrode by diffusion before they can be consumed by the relatively slow reaction with the solvent

$$e_{aq}^{-} + H_2O \rightarrow H + {}^{-}OH \qquad (8)$$

with rate constant $k = 16 \pm 1$ M^{-1} s^{-1} which limits the half-life of e_{aq}^{-} in pure water to about 780 μs (Hart *et al.* 1966). In water not especially treated, as it was in our case, the parallel reactions with the low concentration of protons and with traces of impurities reduce the lifetime of the hydrated electron. Without added electrolyte the electrode diffuse double layer, formed by the H^+ and ^-OH ions of bulk concentration of the order of 10^{-7} M, extends to the solution over a distance of about 1 μm from the electrode surface, i.e. far beyond the distance of less than 10 nm to which the electrons are emitted (Barker *et al.* 1966). The H^+ ions are distributed in the double layer according to the potential gradient, their local concentration close to the negatively-charged electrode is higher than 10^{-7} M, and some of the emitted electrons are scavenged by them. However, the value of the observed photocurrent approaches that obtained in a 0·1 M solution of a strong acid, and hence its origin must be due to another reason. The movement of the majority of the emitted and subsequently hydrated electrons back towards the negatively-charged electrode occurs in the electrostatic field which repels the negative particles; their diffusion is then retarded by the coulombic force acting in the opposite direction, and before they reach the electrode the majority of them disappear in the course of the slow motion by way of reaction (8). Under such conditions water plays the part of a weak electron scavenger. With increasing concentration of electrolytes added to the water the compact part of the electrode double layer builds up and the thickness of the diffuse part decreases, particularly with salts of multivalent cations. The retarding effect of the diffuse part of the double layer on the motion of the negative entities is thus reduced and more hydrated electrons reach the electrode before they decompose. The effective thicknesses of the double layer estimated for different solutions according to the Gouy–Chapman theory correlate well with the photocurrents shown in figures 9–11.

The step on the polarographic photocurrent–voltage curve of water (figure 8) appears in the voltage region where the electroreduction of water begins at the electrode surface. According to reaction (2) the immediate surroundings of the electrode are thereby rendered alkaline. The photoelectrons of the lowest energy emitted from the electrode into this medium find it impoverished of protons which in water of $\mathrm{pH} < 8$ represent efficient scavengers. Fewer of the hydrated electrons are therefore scavenged in the electrode vicinity, more of them return to the electrode and the increase of photocurrent with applied voltage slows down; as a result a plateau is formed on the curve. Only in a higher-voltage region do the photoemitted electrons have enough energy to penetrate the reaction layer where pH is high and reach the layers of water where the scavenging efficiency is unaffected by the electrolytic reaction. With a higher mercury reservoir, i.e. with a higher rate of drop formation, the pH of the water surrounding the tip of the capillary becomes higher than with the slowly growing drop, as a result of greater accumulation of OH^- ions, products of reaction (2), while the photoemission proceeds at a constant rate; there are less H^+ ions, scavengers of the hydrated electrons, around the fast dropping electrode and hence the net effect is a decrease in the photocurrent with an increase in h.

The effect of surfactants on the photocurrent in solutions without electron scavengers, shown in figure 12, completes the qualitative picture outlined above. In a 10^{-4} M solution of tetrabutyl ammonium chloride a DME of 5 s drop-time polarized to negative potentials is, from the beginning of its growth, completely covered by a layer of $N(C_4H_9)_4^+$ cations (Novotný *et al.* 1982). Due to the high surface concentration of the adsorbed cations the diffuse part of the double layer in the dilute solution is contracted and all the emitted electrons return to the electrode as in a 0·1 M solution of KCl; the steep increase in photocurrent at the negative end of the curve is caused by desorption of the quaternary cation from the mercury surface. On the other hand, complete coverage of the DME by sodium octyl sulphonate in its 10^{-4} M solution leads to a considerable increase in the photocurrent. The photoemitted electrons become hydrated at the minimum distance of about 1 nm from the electrode (cf. Grossweiner and Baugher 1977), i.e. just outside the perpendicularly oriented long octyl chains terminated by the negatively-charged $-SO_3^-$ group turned towards the aqueous phase. The layer of negative charge along the surface strongly delays the return of the hydrated electrons and prevents their tunnelling back to the electrode; thus the efficiency of the scavenging reaction (8) is increased above the level observed in pure water.

In cases where the concentrations of scavengers and electrolytes in aqueous solutions are low, the mechanism outlined above of the 'water' photocurrent has to be taken into account when interpreting results of electrochemical experiments with photoemission. This could help to solve some of the problems with data obtained in

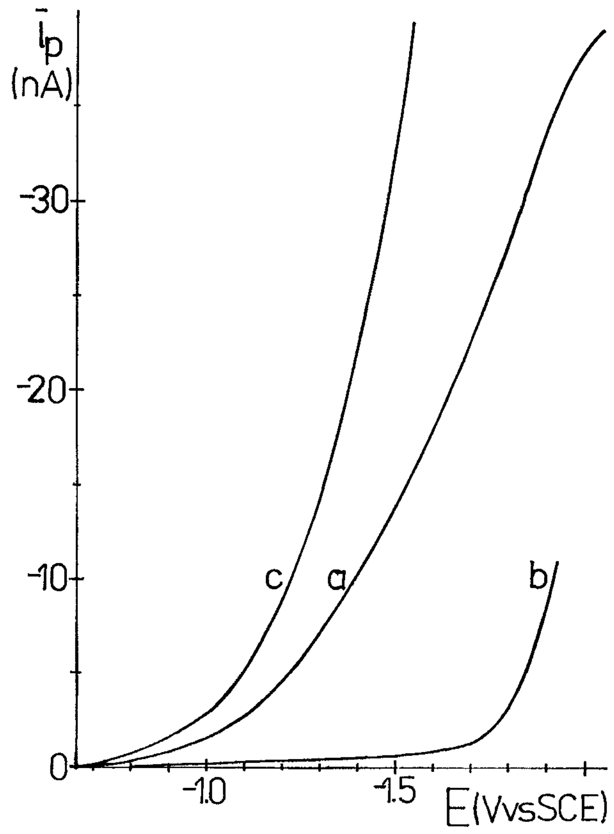

Figure 12. Polarographic mean photocurrent–voltage curve of: (*a*) pure water; (*b*) 10^{-4} M $N(C_4H_9)_4Cl$; (*c*) 10^{-4} M $C_8H_{17}SO_3Na$. Full emission of the lamp.

dilute media (e.g. Barker *et al.* 1966, Bomchil *et al.* 1970, Brodsky and Pleskov 1972). Heyrovský has shown (1966b) that with a 10^{-5} M solution of $HClO_4$ the 'scavenger' photocurrent, observed when the electrode is irradiated by visible light, gets engulfed in the much higher 'water' photocurrent if UV light is included in the irradiation.

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