EFFECT OF ALKALI HALIDES UPON PHOTOCURRENT DUE TO EMISSION OF ELECTRONS FROM DROPPING MERCURY ELECTRODE INTO WATER

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When dropping mercury electrode (DME) dipped in ultrapure water, thoroughly deaerated with pure hydrogen, is irradiated with UV light, we can observe a cathodic photocurrent in the non-faradaic region of the polarographic curve, in the absence of scavengers of hydrated electrons. Newly we have followed the effect on photocurrent of initial very small additions of alkali metal chlorides to pure water. By repeated experiments, we could show that first additions of the alkali metal halides increase the photocurrent and that the already known suppression of photocurrent by addition of halides begins only after the halide concentration exceeds *ca* 10^{-4} mol l^{-1}. We could show for the first time that in ultrapure water and dilute electrolyte solutions, the photocurrent follows a modified seven-halves law. The extent of the positive effect of small additions of alkali metal halides on photocurrent depends on the nature of each alkali metal cation. The reason for this specificity is discussed.
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The investigation of the photovoltaic phenomena is more than 160 years old. Becquerel[1] was the first to observe appearance of an electric current upon illumination of one of two identical electrodes immersed in dilute acids. Numerous studies were later performed on a variety of systems including both metal–electrolyte and metal–vacuum interfaces. The work of Hertz[2] led to the discovery of photoelectron emission at the metal–vacuum interface, which stimulated the production of numerous and variegated apparates in photocell electronics. Photoelectron emission attracted scientific interest and it has been intensively studied both theoretically and experimentally for decades[3–5]. The results obtained broadened the development of quantum theory of light and the solid state physics.

All photoelectrochemical cells can be divided, according to the nature of the processes involved, into three groups[6].

The first group involves cells in which the photocurrent originates from absorption of light by the solution, resulting in formation of excited molecules and their homogeneous photochemical reactions; the electrode, however, does not directly participate in the photoprocess but plays the role of an "indicator", since excited molecules or radicals can undergo oxidation or reduction on it. The second group of systems is that one for which a photoconduction effect results in a photosignal, as in semiconductor electrodes[7], metals coated with oxide films[8] or dyes[9], and insulators[10]. The third group comprises systems in which a clean metal surface is in contact with an electrolyte, which does not absorb light. These simplest systems will be the object of this paper.

Becquerel observed that the magnitude of the photosignal depended on the characteristics of the illuminating light, the electrode potential, and the electrolyte composition. Audubert[11] remarked on the similarity of the mechanism of the appearance of the photosignals to that of photoemission at the metal–vacuum interface discovered by Hertz. Clark and Garret[12] found that the threshold wavelength above which the Becquerel effect virtually disappeared was almost the same for silver, gold, and copper.

In the early sixties the photosignal at illuminated metal electrodes was a hot subject[13–25]. Berg, M. Heyrovský, and Barker independently proposed views on the nature of the photosignal. Barker and Gardner[25] underlined the important role played by photoelectron emission from the metal into solution, and rationalised the subsequent interactions of emitted electrons with the solvent and solutes. The idea was not new, but Barker and coworkers were the first who gave quantitative evidence of electron photoemission into solutions and who defined clearly the limits of applicability of their concepts[26]. Simultaneously the quantum-mechanical theory of photoemission into electrolytes was developed[27].

The existence of the electric double layer at the metal solution interface[28,29] distinguishes photoemission into electrolyte solutions from emission into vacuum. The magnitude of the potential drop in the diffuse part (the Ψ potential) essentially depends on the bulk concentration of the electrolyte and decreases with increasing electrolyte concentration. The externally applied field results in a change of the electronic work function in electrochemical systems, as opposed to the metal–vacuum interface[30], since the potential drop is confined in a very short space, hence very strong electric fields are produced. Moreover, photoemission into electrolyte solutions, transfers the electron into a condensed medium, which brings about an additional stability gain, due to the solvation, that reduces the work function compared with that one for the metal–vacuum interface. Further-

more, the motion of the electron in the electrode vicinity differs from that in the vacuum, where it experiences the presence of external field and image forces which, in solution, are usually screened by ions in the electrical double layer. This leads to a dependence of the photocurrent on the radiation frequency different from that observed for emission into vacuum[27,31–33]. The photoemission current, valid in the near threshold frequency range, is given by the five-halves law, in which the work function depends on the solvent nature[34] and is a linear function of the electrode potential ϕ. As opposed to the classic metal–vacuum work function, this electrochemical work function is the same for all metals[34,35] if the potential is the same. For a given energy of the light quantum, the metal needs a minimum negative potential ("potential red limit") to photoemit electrons. Conversely, for a given metal potential, the light quantum energy should be higher than a minimum energy, which is called "light red limit".

The experimentally observed photocurrent (i) is the result of three components: the emission current (j), the return current of solvated electrons (i_b), and the current of the electrode reaction involving the products of capture of solvated electrons by scavengers (i_s).

"Residual photocurrents" (refs[6,25]) have been observed even in the absence of added electron scavengers. They have usually been associated with the presence of trace impurities, which may act as electron acceptors or with recombination of hydrated electrons[37]. Berg and coworkers[38,39] studied photoresidual currents in nonabsorbing solutions of concentrated electrolytes. This background photocurrent was attributed to the flow of electrons from the electrode to the solution and to the capacitance curent.

However, before the pioneering work of Heyrovský and Pucciarelli[40,41], it was generally accepted that, in the absence of electron scavengers, no net photocurrents should be observed or the resulting stationary photocurrent should be close to zero[42].

A characteristic feature of the photocurrent, which can be observed in aqueous solutions in the absence of scavengers of hydrated electrons, is its strong dependence on the presence and concentration of added inert electrolytes.

The work of Heyrovský and Pucciarelli[40,41], regarding the study of photocurrents in aqueous solutions in the absence of added scavenger of hydrated electrons, could rely on triply distilled water: first normally, then from an alkaline solution of permanganate and finally from a quartz apparatus. However, the authors themselves had to realise that the photocurrent obtainable in the purest water they used, was the same as that of a 10^{-5} mol l^{-1}

KCl solution. Hence, the residual electrolyte concentration of their purest water can be considered higher than that order of magnitude.

The photocurrent was explained by the relatively slow reaction of hydrated electrons with water, which can play the role of a weak electron scavenger.

The authors found that the photocurrent could be decreased by adding 10^{-3} mol l^{-1} monovalent, 10^{-5} mol l^{-1} divalent, or 10^{-6} mol l^{-1} trivalent cation chlorides. They explained the experimental data by the effect of the electric field of the extended double layer on the return of the hydrated electrons generated by photoemission back to the electrode[41].

The possibility of relying on the Milli Q water purification system (Millipore) which can produce ultrapure water (18.2 MΩ cm, UV irradiation), stimulated us to investigate the photopolarographic behaviour of such a pure water and of aqueous electrolyte solutions and thus to extend the earlier work.

Since multivalent cations[41] are more efficient in decreasing the photocurrent than monovalent cations, we selected alkali metal chlorides to study the dependence of photocurrent on dilution. Our aim was to test whether very low electrolyte concentrations, in the absence of scavenger of hydrated electrons, are able to decrease the photocurrent according to the previous given explanation.

EXPERIMENTAL

The water used for measurements was purified by a Milli Q-185 system (Millipore) which can produce ultrapure water (18.2 MΩ cm, UV irradiation)

A quartz cell of about 100-ml volume was used. There were three openings on its top: one for the working electrode (DME), one for the reference electrode (large sheet Pt H_2/H^+ 10^{-7} mol l^{-1}) whose potential was maintained constant by passing gaseous hydrogen through the cell, and one for the inlet-outlet of hydrogen.

Measurements in ultrapure water required special experimental conditions. In order to avoid contamination by electrolytes different from those we added and to accurately control the electrolyte concentration, we used a two-electrode system and had to accept an error due to the cell resistance.

The capillary for the DME was of the "spindle" type[43], providing highly reproducible mercury drops. The DME was introduced into the cell only after preliminary deaeration of the sample. The experiments were usually carried out at room temperature, except for those regarding the influence of temperature on the photocurent which were carried out at 60 °C. Light from a Leitz Xenon 150 W lamp (irradiance 1–10 mW m^{-2} nm^{-1} at a distance of 0.5 m) was focused by quartz lenses on the capillary tip in order to make the drop grow in a highly illuminated region. A cylindrical cell (1.5 cm diameter, 5.0 cm length), filled with ultrapure water was settled in the optical path as IR filter in order to reduce a thermal effect on the electrode.

The current-applied voltage curves were obtained with an EG&G Princeton Applied Research (273 Model) potentiostat with external computer control. For each sample, the current-applied voltage without, with and again without irradiation were recorded to be sure that no permanent modifications occurred in the sample after irradiation. The difference between the current recorded under irradiation and in the dark gave the photocurrent.

The reported data are the average of duplicate measurements. Photocurrent calculations were performed using the Kaleidagraph™ software (Version 3.0.1, Adelbeck© Software). The experimental conditions to obtain the current-applied voltage curves (sampled polarography) were: purge time 1 h, equilibration time 20 s, scan rate 5 mV s^{-1}, scan increment 20 mV, step time 4 s, initial applied voltage +0.8 V, final applied voltage –3.2 V for Milli Q water, –2.7 V for electrolyte concentration up to 10^{-4} mol l^{-1} and –2 V for electrolyte concentration up to 10^{-2} mol l^{-1}.

The electrolytes were of the best available quality (99.99%) and were purchased from Aldrich. 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 from water and from the cell: before measurement, it was bubbled through the sample for one hour and during measurement it was passed over it.

RESULTS AND DISCUSSION

In the photopolarographic study of ultrapure water, we noticed the presence of polarographic maxima of the first kind, caused by oxygen traces present in the hydrogen bubbled through the cell. Maxima appear in the region of the first reduction step of molecular oxygen. Their position and height are not fully reproducible and depend on the purge time. Hence we decided to use always the same long purge time (1 h). Maxima progressively decrease as the electrolytic concentration is increased and they cannot be observed any longer if alkali metal chlorides are present at a concentration of 10^{-5} mol l^{-1}. The hypothesis that adsorbable traces from the water purification system columns can be responsible for the ill reproducibility of the polarographic maxima can obviously not be ruled out.

The photopolarographic behaviour of ultrapure water is shown in Fig. 1. We found that only a slight increase in photocurrent can be provided by alkali metal chlorides in concentration up to 10^{-6} mol l^{-1}; hence, we did not try to differentiate the cation aptitude to increase the photocurrent. As added electrolytes have to cope with 10^{-7} mol l^{-1} H$_3$O$^+$, which are always in equilibrium with water and which are characterised by very high mobility, the full efficiency of added electrolytes in increasing the photocurrent shows when the electrolyte concentration is at least two orders of magnitude higher.

As it is clear from Fig. 2, we were able to demonstrate, for the first time, that the photocurrent increases when alkali metal chlorides, in concentrations up to 10^{-4} mol l^{-1}, are added to ultrapure water. Further increase in

the electrolyte concentration up to 10^{-3} mol l^{-1} decreases the photocurrent as already shown and explained[41] and ultimately suppresses it when the concentration reaches 10^{-2} mol l^{-1}. Figure 3 details the behaviour of a classic electron scavenger (H_3O^+, 10^{-4} mol l^{-1}) in the absence of supporting
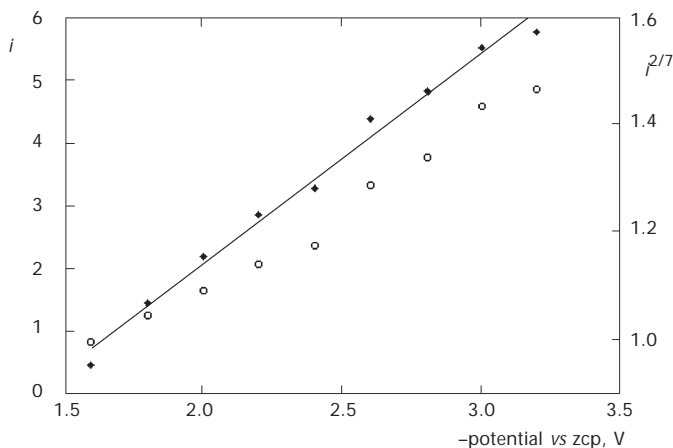

F$_{IG.}$ 1

Dependence of the photocurrent i (○) and $i^{2/7}$ (◆) on applied voltage, measured with respect to the zero charge potential (zcp) for Mili Q water. —— $y = 0.3667 + 0.38845x$, $R = 0.99369$
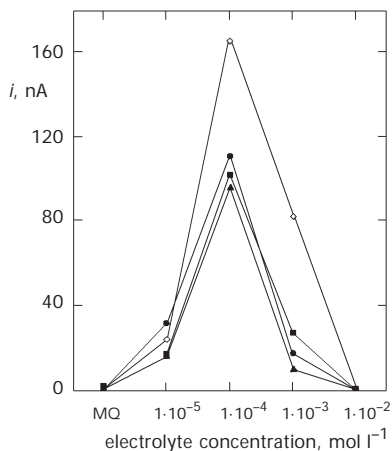

F$_{IG.}$ 2

Comparison of the photocurrent obtained for Milli Q water and for alkali metal chlorides, in the concentration range 10^{-5}–10^{-2} mol l^{-1} at –2.2 V (measured with respect to the zcp): ◇ LiCl, ■ NaCl, ▲ KCl, ● CsCl

electrolyte. Figures 4–7 demonstrate that 10^{-4} mol l^{-1} alkali metal chlorides produce a photocurrent that depends on the cation nature.

We want now to analyse the parameters that can be influenced by progressive addition of electrolytes to ultrapure water for cathodic polarisation of the DME in order to explain the increase in photocurrent, which can be obtained by adding electrolytes to ultrapure water up to 10^{-4} mol l^{-1}.
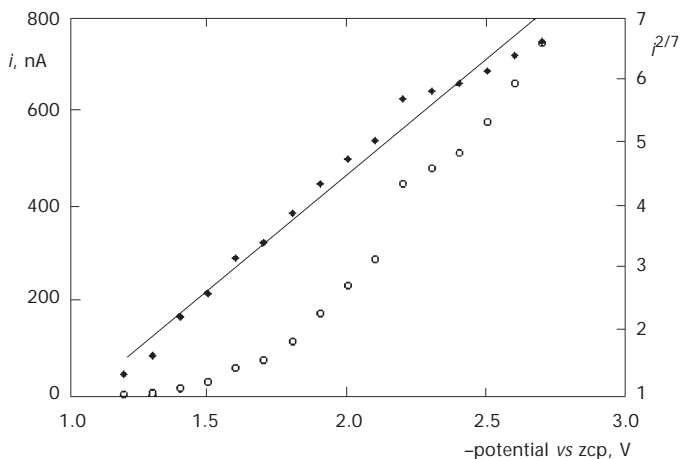

FIG. 3
Dependence of the photocurrent i (○) and $i^{2/7}$ (◆) on the applied voltage, measured with respect to the zcp for 10^{-4} mol l^{-1} HCl. —— $y = -2.762 + 3.6343x$, $R = 0.98987$
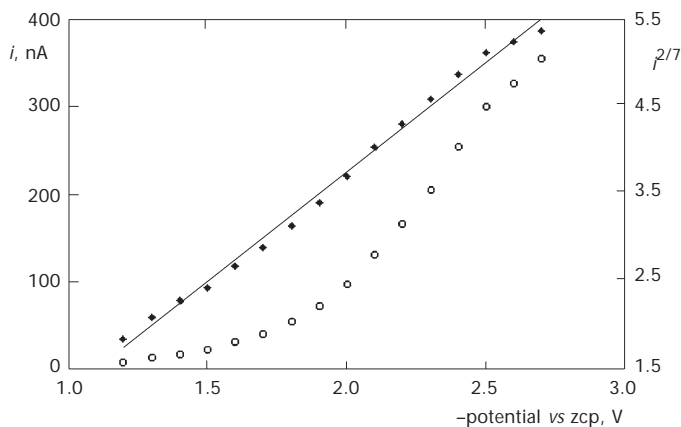

FIG. 4
Dependence of the photocurrent i (○) and $i^{2/7}$ (◆) on the applied voltage, measured with respect to the zcp for 10^{-4} mol l^{-1} LiCl. —— $y = -1.2299 + 2.4849x$, $R = 0.99704$

Ionic Strength Increase

According to the kinetic salt effect, a decrease in the rate constant has to be expected for reactions between species with opposite charges, and a constancy of it for reactions between a charged species and a neutral molecule.

Since the possible reactions in which the hydrated electron can be involved in the vicinity of the electrode are
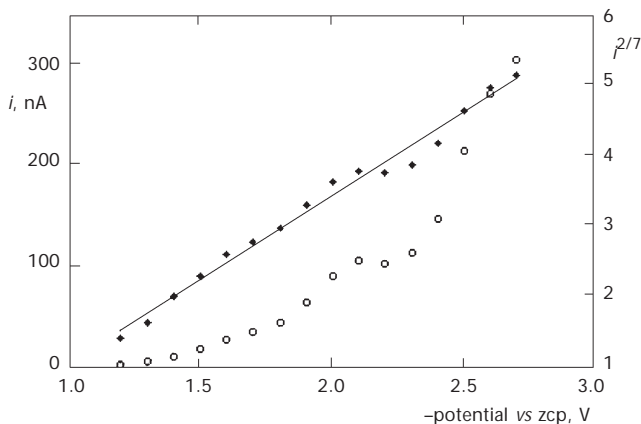

FIG. 5
Dependence of the photocurrent i (○) and $i^{2/7}$ (◆) on the applied voltage, measured with respect to the zcp for 10^{-4} mol l^{-1} NaCl. —— $y = -1.3185 + 2.3695x$, $R = 0.9931$
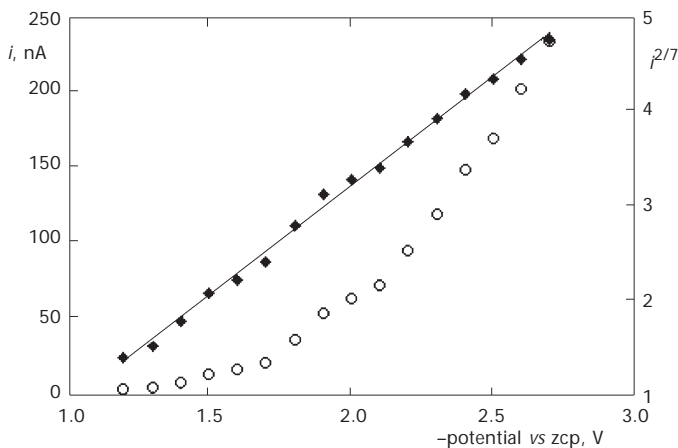

FIG. 6
Dependence of the photocurrent i (○) and $i^{2/7}$ (◆) on the applied voltage, measured with respect to the zcp for 10^{-4} mol l^{-1} KCl. —— $y = -1.4324 + 2.3152x$, $R = 0.99822$

$$e_{aq} + H_2O = H^\bullet + OH_{aq}^- \tag{1}$$

$$e_{aq} + H_3O_{aq}^+ = H^\bullet + H_2O \tag{2}$$

it follows that the rate constant (k) for reaction (*1*) ($k = 16 \pm 1$ M^{-1} s^{-1}, ref.[44]) should remain almost constant and the rate constant for reaction (*2*) ($k = 1.4 \cdot 10^{10}$ M^{-1} s^{-1}, ref.[26]) should decrease with increasing electrolyte concen-
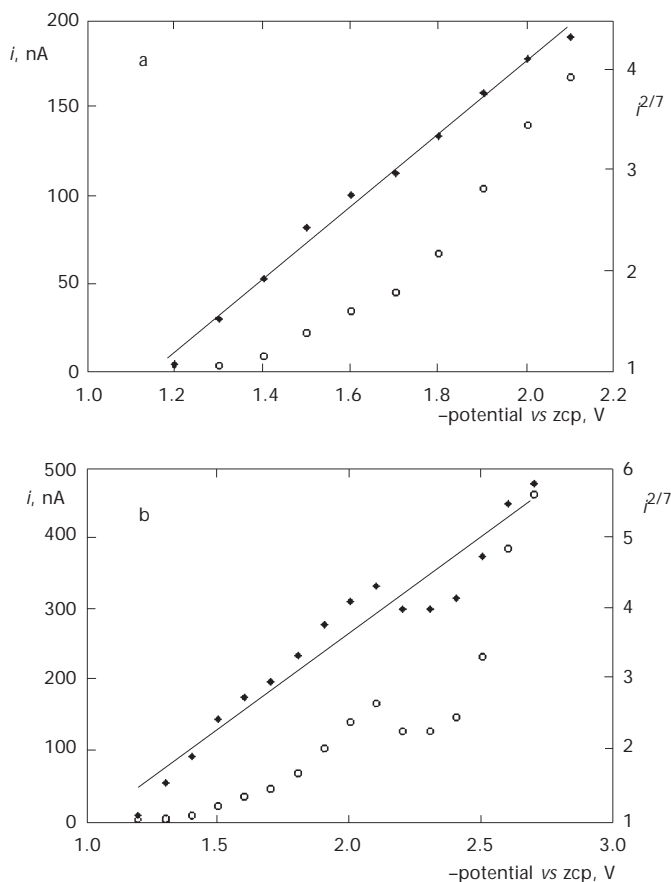

FIG. 7
Dependence of the photocurrent i (○) and $i^{2/7}$ (◆) on the applied voltage, measured with respect to the zcp for 10^{-4} M CsCl. —— $y = -3.0839 + 3.5795x$, $R = 0.99672$ (a). The same for a wider voltage window. —— $y = -1.7777 + 2.7169x$, $R = 0.96935$ (b)

tration. This can further support the decrease in the photocurrent for concentrations higher than 10^{-3} mol l^{-1}, but it cannot explain the increase in photocurrent when electrolyte concentration increases up to 10^{-4} mol l^{-1}.

Ionic strength increase results in a decrease in the resistence of the investigated solutions. The potential of the polarizable electrode E is $E = V - iR$, where V is the applied voltage, R is the electrical resistance of the medium, and i is the current. Under constant V, the decrease in R, with increasing electrolyte concentration, results in a higher actual electrode potential, which, in turn, increases electron emission. However, this phenomenon is not able to explain the specific increase of photocurrent on fist addition of different electrolytes to pure water. Actually, for the alkali cations series, at a given electrolyte concentration, the cation Li$^+$ should give the highest resistence, since the mobility of this highly hydrated, and hard cation is the lowest. One would expect to observe for Li$^+$ the lowest photocurrent, that is not so.

Decrease in the Mean Hydration Length

The effect of the decrease in the mean hydration length with increasing electrolyte concentration, which leads to a photocurrent decrease[35], was proved to vanish for[42] concentrations lower than 10^{-3} mol l^{-1}; hence it will not be further discussed here.

Decrease in the Thickness of the Diffuse Part of the Double Layer

With increasing electrolyte concentration, a subsequent decrease in the absolute value of the potential difference $|\Psi|$ between the outer Helmholtz plane (OHP) and the solution bulk has to be expected. This decrease causes:

a) A decrease in the concentration at the interface of a positively charged acceptor and, hence, a decrease in the photocurrent produced by the reaction between hydrated electrons and hydrogen ions (Eq. (*2*)). Again, this further supports the decrease in the photocurrent for concentrations higher than 10^{-3} mol l^{-1}, but it cannot shed light on the increase in photocurrent when the electrolyte concentration increases up to 10^{-4} mol l^{-1}.

b) An increase in the return of hydrated electrons to the electrode. When the diffuse layer thickness decreases, its retarding effect on the motion of the negative hydrated electrons is reduced because the negative charge on the electrode surface is better shielded. This gives a rationale for the photocurrent decrease for electrolyte concentrations higher than 10^{-4} mol l^{-1} (ref.[41]), but it must be negligible for lower concentrations.

c) An increase in the photoemission current, *j*.

The photoemission current can be described, under the threshold approximation by the seven-halves[45] law for a polychromatic radiation whose highest energy is *h*ν:

$$j = A[h\nu - (h\nu_0(0) + e\Phi)]^{7/2} , \tag{3}$$

where Φ is the electrode potential. When the solution is too dilute, this law has to be modified, in analogy with the modified five-halves law[46,47] for a monochromatic radiation in order to take into account the double layer effect on the photoemission step. It is suggested that Eq. (*3*) must be replaced by

$$j = A\{h\nu - [h\nu_0(0) + e(\Phi - \Psi)]\}^{7/2} . \tag{4}$$

The absolute value of Ψ decreases with increasing electrolyte concentration. Since Ψ is negative for cathodic polarisation, it follows that electrolyte addition makes the photoemission step easier. At concentration up to 10^{-4} mol l^{-1}, the increase in the photoemission current, caused by the decrease in the absolute value of Ψ, is the only phenomenon that can explain the observed increase in photocurrent.

We want to stress that, even if Eq. (*4*) gives the photoemission current and not the observed photocurrent *j*, it fits experimental results, as can be seen from Figs 1, 3–7, because in dilute solution the observed photocurrent is proportional to the emission current[42]. It has also to be argued that within certain limits there is a linear relationship between the electrode potential and the applied voltage and the Ψ potential is directly proportional to the Φ potential. Figures 4–7 demonstrate that in the absence of hydrated electron scavengers, the photocurrent is not equal to zero as stated by Pleskov and Rotenberg[48].

A decrease in photocurrent was observed at higher temperature (60 °C). This was unexpected since the rate of the scavenging process should increase. Probably, the effect of an increased rate of the return of hydrated electrons to the electrode due to higher thermal motion, overcomes the effect of the enhanced scavenging process. A decreased density of water could also explain this experimental evidence.

A decrease in photocurrent was also observed with increasing the mercury reservoir height and hence with increasing dropping frequency. It was

hypothesised that, since the capacitive current is linearly dependent on that height, photocurrents could be partly overlapped.

A photocurrent step can be observed with increasing voltage applied to the electrode. This is particularly evindent for the case of caesium in Fig. 7. The reduction of water leads to a local alkalinisation of the solution near the electrode. At higher potentials, the electron gains further kinetic energy, which allows it to escape in the bulk. This allows the photocurrent to increase again[42]. Newly we can add that the more negative the potential is, the stronger is its compacting power of the diffuse layer; hence, at a higher applied voltage, the diffuse layer is not able to exert its delaying power on hydrated electrons. Again, if the applied voltage is further increased, the increase in the kinetic energy of the electrons can easily explain the new increase in photocurrent.

The observed photocurrents as well as the slope of the fitting line (see Figs 1, 3–7), correlate well with the acidity of the specific cation[49] which can polarise the coordinated water molecules and make them more easily reducible by the hydrated electron. The behaviour of the classic electron scavenger H_3O^+ in the absence of supporting electrolyte, fits in the acidity series of the first group of elements of the Periodic table. The low photo-
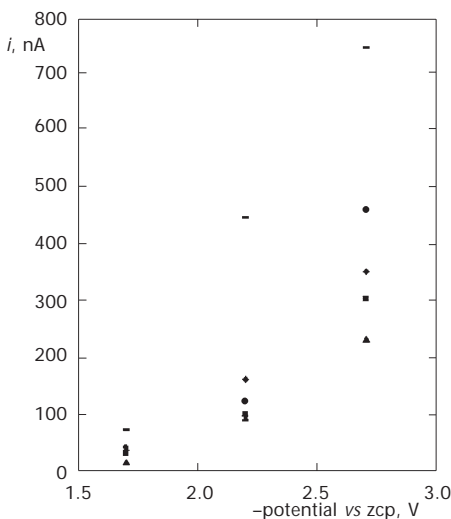

F<small>IG</small>. 8

Comparison of the photocurrent obtained for hydrogen chloride and alkali metal chlorides, at a concentration of 10^{-4} mol l^{-1}, at different applied voltages (measured with respect to the zcp): – HCl ♦ LiCl, ■ NaCl, ▲ KCl, ● CsCl

current that can be observed in ultrapure water is suggested to be related to the presence of 10^{-7} mol l^{-1} H_3O^+.

The different aptitudes of metal chlorides to produce a photocurrent were also independently confirmed by measurements of the currents in the dark and under illumination at a fixed applied voltage.

It has to be taken into account that discreteness of charge at the electrode–solution interface[26] greatly enhances emission, compared with the ideal case of a smoothed-out charge in the plane of closest approach because of preferential emission near the cation. The harder the cation is, the higher the magnitude of this effect.

Another physical phenomenon, which has to be considered to explain the ion specificity in producing a photocurrent, is the dielectric saturation. The dielectric saturation of water at the electrode–solution interface is lower in the case of soft ions of large radii, and higher with the hard ions[50]. Hence, the dielectric permittivity (ε) follows the order $\varepsilon_H < \varepsilon_{Li} < \varepsilon_{Na} < \varepsilon_K < \varepsilon_{Cs}$. As the electric field (E) is inversely proportional to the permittivity of the medium, it follows that $E_H > E_{Li} > E_{Na} > E_K > E_{Cs}$ and hence $|\Psi_H| < |\Psi_{Li}| < |\Psi_{Na}| < |\Psi_K| < |\Psi_{Cs}|$. Since for cathodic polarisation, Ψ is negative, the photoemission current should follow the order $j_H > j_{Li} > j_{Na} > j_K > j_{Cs}$. In Fig. 8 we can observe that this is experimentally confirmed: the anomalous behaviour of caesium can easily be explained by taking into account the specific adsorption on this large and ill-hydrated cation on the electrode surface[51].

CONCLUSIONS

For the first time, it has been demonstrated that the photocurrent in the cathodic part of the non-faradaic region of the current-applied voltage curve that is produced upon illumination of the electrode in the absence of scavengers of hydrated electrons, first increases and then decreases with increasing electrolyte concentration. It passes through a maximum when the electrolyte concentration is 10^{-4} mol l^{-1}. The dependence of the photocurrent on electrolyte concentration can be explained by the coexistence of two opposite trends: increase in the photoemission step *vs* increase in the rate of hydrated electrons returning to the electrode. The maximum shows when they balance each other.

It has been demonstrated that the photocurrent follows a seven-halves dependence on the electrode-applied voltage for pure water and for dilute electrolytes, as well as for the classic electron scavenger H_3O^+ without supporting electrolyte. This kind of dependence is typical of photocurrents ob-

tained in the presence of added electron scavengers and supporting electrolyte. The dependence occurs even in absence of both. Different alkali metal cations show their different aptitude to affect the primary photocurrent and this was explained in terms of their diffuse layer potential and their acidity.

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