Photopolarographic Studies of Some First-row Transition Elements. Part I

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Photopolarographic signals over a range of wavelengths within the near-u.v. and visible portion of the spectrum have been obtained for a number of transition-metal ions. The intensity variation of such signals with wavelength enable characteristic ' spectra ' to be drawn, the intensities being a function of depolarizer concentration. It is suggested that such spectra arise as a result of electronic transitions between levels induced by both photo- and electrode-field excitation of the depolarizer.

INTEREST in the study of photocurrents produced by u.v.-visible irradiation of a mercury electrode has recently been renewed although the photoeffect at a metal-electrolyte interface was discovered some 130 years ago.[1,2] Various interpretations have been suggested and extensive investigations of photocurrents[3,4] have been primarily connected with the use of organic depolarizers. The use of inorganic depolarizers has not been extensively studied. Barker and his co-workers[5-7] and Delahay and Srinavasan[8,9] conclude that the photocurrent is caused primarily by photoemission of electrons from the mercury-electrode surface.

Barker *et al.*[6] suggested that the use of some transition-metal ions (*e.g.* Cd^{2+}, Cu^{2+}, and Zn^{2+}) as depolarizer should be studied in greater detail. Later Durst and Taylor[10] pointed out that aquonickel(II) ion should be used for further investigation.

Attempts to correlate polarographic and spectroscopic parameters have been reported for transition-metal complexes characterized by irreversible reductions. Linear relationships are obtained between the half-wave potentials of the electrode processes and the wavelengths of the corresponding spectral transition.[11-13] Observations of photopolarographic effects[10] with Ni^{II}, Co^{II}, and U^{IV} showed the development of prewaves for the first two cases and a series of postwaves for uranium(IV). Investigations of the effect on photocurrents of the variation of wavelength (or energy of light) have been made.[6,14-17]

We are concerned primarily with the investigations of some first-row transition-metal ions and have studied the influence on the photocurrent of the concentration of depolarizer, nature of the depolarizer, and wavelength of light.

EXPERIMENTAL

Several techniques[4,6,8,16-19] have been developed to measure small photocurrents. We have used a manual type of polarographic set-up; the use of a mercury-pool cathode was abandoned, because of contamination effects and unstable currents obtained due to vibration. Surface contamination could influence potential-dependent photocurrents, i_p.[9,20] Therefore, in all experimental work the dropping mercury electrode (D.M.E.) was used.

The working cell set up (Figure 1a) was similar to that described in ref. 10. The cell consisted of a single-compartment rectangular OGAL cell (4 × 2·5 × 3·5 cm) with optically flat surfaces. A Perspex cover had openings for the two electrodes and a nitrogen inlet tube, arranged so that only the mercury drop was in the light-path. Another OGAL cell (2 × 2·5 × 3·5 cm) filled with distilled water was placed between the lens and the working cell, reducing the i.r. intensity and hence heating effects at the electrode. A shutter was placed between the ' filter-cell ' and the working cell so that the light beam could be cut off.

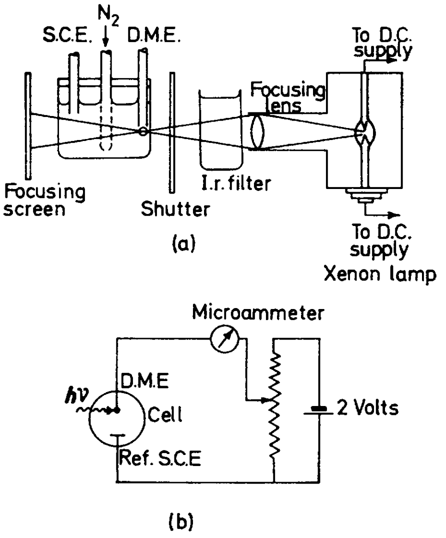

FIGURE 1 Irradiation system and polarographic cell

The excitation source was a D.C. high-pressure Xenon

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lamp (nominal lamp wattage, 150 W) which produced an intense u.v.–visible continuum. The lamp was mounted in a special metal casing. Since the lens had a prefixed position, the mercury drop had to be brought into the correct position. Before adjustment of the D.M.E., the working cell was put into the correct position in the light beam. The capillary was then carefully adjusted so that the light beam was almost completely blocked by the mercury drop at maximum size. This was achieved by observation of the drop image on a focusing screen. Also, the correct position obtained from above could be checked visually. When the drop is in position, it should glow very brightly (*N.B.* prolonged viewing of the illuminated electrode should be avoided!). The solution light-path was *ca.* 4 mm. Measurements were made at room temperature.

Solutions were prepared from chemicals of Analytical Reagent grade. Since quantitative results were not the prime concern, no supporting electrolyte has been used in most experiments, and migration currents were inevitably present. No maximum suppressor was used in case of any interfering side-photoreactions. The introduction of the KCl–Agar bridge from the saturated calomel electrode to the cell was effected just before measurement in order to minimize the amount of KCl diffusing into the working solution. The solution was carefully deoxygenated for 45 min and the nitrogen line was then carefully withdrawn from the solution to a position where the nitrogen was passing over the solution surface, in order to ensure that a nitrogen atmosphere was constantly present.

The currents at the D.M.E. for constant applied potential were measured by a simple circuit; the Pye Universal potentiometer was connected to a simple manual polarograph circuit [21] (Figure 1b). The indicator electrode was a saturated calomel electrode (S.C.E.) and the detecting device was a PYE scalamp DC microammeter 7906/S. Since the currents obtained comprised both reduction and photocurrent components the sensitivity of the microammeter had to be adjusted accordingly. This meant that the resistance of the circuit had to be altered from one set of measurements to another. It is important to note that the sensitivity setting should not be altered during measurement owing to nonlinearity of the scale. All values given are in absolute microamps.

RESULTS

Influence of Potential on Photocurrents.—(i) *Nickel*(II). The hexa-aquonickel(II) ion was studied at a series of concentrations in the range 10^{-5}—0·5M. The dark current, i_D (measured under no illumination), and the 'lighted current', i_l (measured with the electrode irradiated by polychromatic visible light), were both determined at the same potential. The difference between the latter and the former ($i_l - i_D$) is the photocurrent, i_p. When the electrode was illuminated, it was observed that the current required several seconds before it reached a maximum steady value and decreased at a similar rate when the light was cut off by the shutter. This was also observed with other metal ions.

Figure 2 shows the plot of photocurrent *vs.* applied potential for a range of nickel-ion concentrations. Photocurrents increase most rapidly over the range 0·84—0·87 V (*vs.* S.C.E.) producing a photocurrent–potential curve strongly resembling a conventional polarographic wave, particularly at higher depolarizer concentrations. Such similarity extends to the production of maxima of the first and second kind superimposed upon the 'photopolarograms'. While maxima of the first kind appear at depolarizer concentrations in the region of 10^{-4}M, those of the second kind are seen in the region of 10^{-3}M.

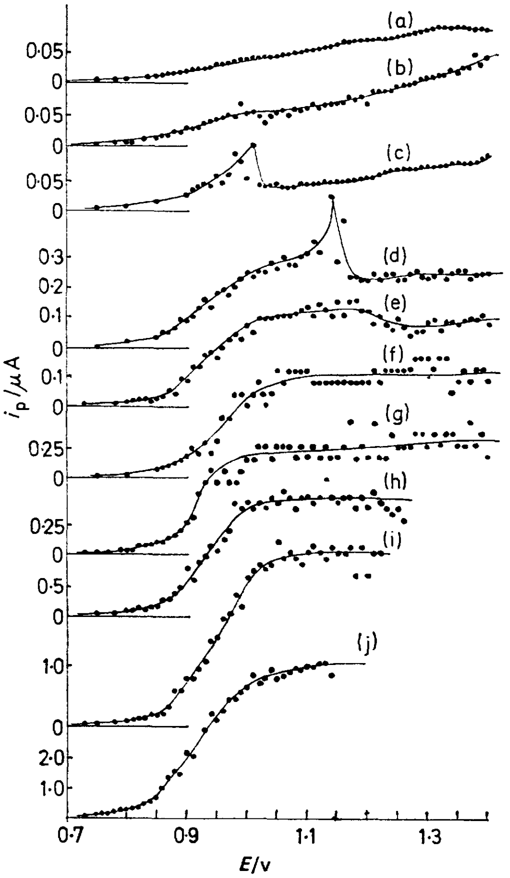

FIGURE 2 Photocurrent *vs.* potential for the hexa-aquo-nickel ion at various concentrations: a, 10^{-5}; b, 5 × 10^{-5}; c, 10^{-4}; d, 5 × 10^{-4}; e, 10^{-3}; f, 5 × 10^{-3}; g, 10^{-2}; h, 5 × 10^{-2}; i, 10^{-1} and j, 5 × 10^{-1}M

Figure 3 shows plots of the ratio $i_p : i_D$ *vs.* depolarizer concentration at various potentials. This was to give some idea of the possible exploitation analytically of enhanced current signals under the influence of light. It is seen that the ratio $i_p : i_D$ is larger for lower concentrations and higher

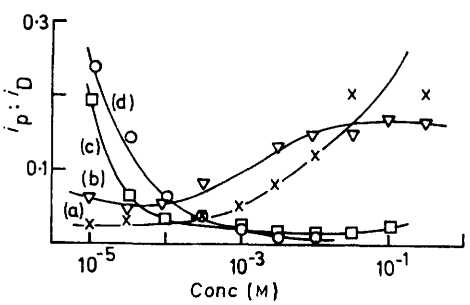

FIGURE 3 Ratio of photocurrent to dark current ($i_p : i_D$) plotted as a function of concentration at various applied potentials: a, 0·80; b, 0·85; c, 1·15 and d, 1·40 V (*vs.* S.C.E.)

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potentials and smaller for higher concentrations and lower potentials.

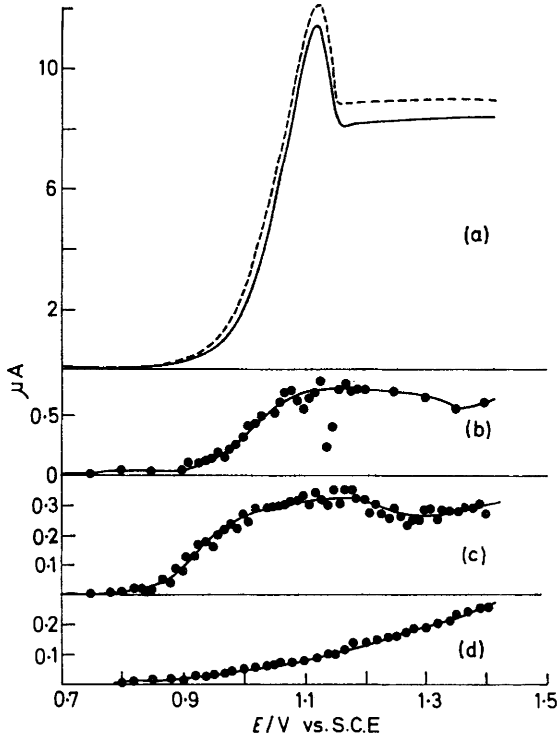

FIGURE 4 Photocurrents of hexa-aquonickel ion in the presence and absence of supporting electrolyte: a, dark (full line) and 'lighted' (dashed line) polarograms for 10^{-3}M-$Ni(H_2O)_6^{2+}$, 0·1M-KNO_3; b, photopolarogram of 10^{-3}M-$Ni(H_2O)_6^{2+}$ in presence of KNO_3; c, photopolarogram of 10^{-3}M-$Ni(H_2O)_6^{2+}$ in absence of KNO_3; and d, photocurrent *vs.* potential for KNO_3 alone

The effect of the presence of a supporting electrolyte was investigated using 0·1M-potassium nitrate and 10^{-3}M-nickel ion. For comparison, the photocurrents of the hexa-aquo nickel(II) ion both with and without supporting electrolyte are plotted in Figure 4 together with the photocurrent for potassium nitrate in the same potential range. The photocurrent obtained with supporting electrolyte is the sum of that for the depolarizer cation without supporting electrolyte and that of potassium nitrate alone.

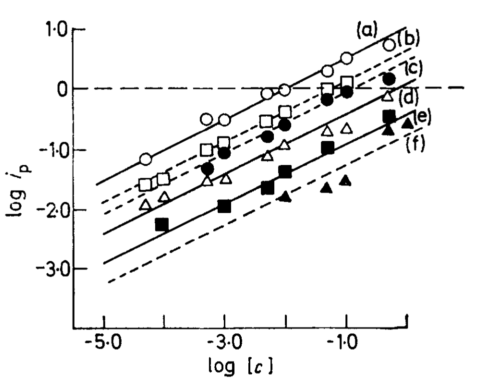

FIGURE 5 Log i_p *vs.* log [depolarizer] for Ni^{2+} and Mn^{2+} for various applied voltages: a, 1·1; b, 1·8; c, 1·45; d, 0·85; e, 0·8; and f, 1·35 V; full line, Ni^{2+}; dashed line, Mn^{2+}

A linear relationship was found in a plot of log i_p and log $[Ni^{2+}]$ (Figure 5), the slope of which shows that i_p is proportional to $[Ni^{2+}]^{\frac{1}{2}}$ for depolarizer concentration $<$0·1M. Similar conclusions were reached by Barker *et al.* for systems such as NaF and KCl saturated with N_2O.

(ii) *Manganese*(II). The hexa-aquomanganese(II) ion was similarly investigated in the concentration range 10^{-5}—1M (Figure 6). Since in this case photocurrents develop at potentials significantly more negative than is the case for nickel, it was only found possible to obtain limiting photocurrents for the concentrations 5×10^{-2}M, to 10^{-1}M. The foot of the photopolarograms in fact occurs between $-1{\cdot}35$ and $-1{\cdot}45$ V *vs.* S.C.E. Maxima of the first kind were observed for the four highest depolarizer concentrations. The ratio of photocurrent to dark current, $i_p : i_D$, varies with

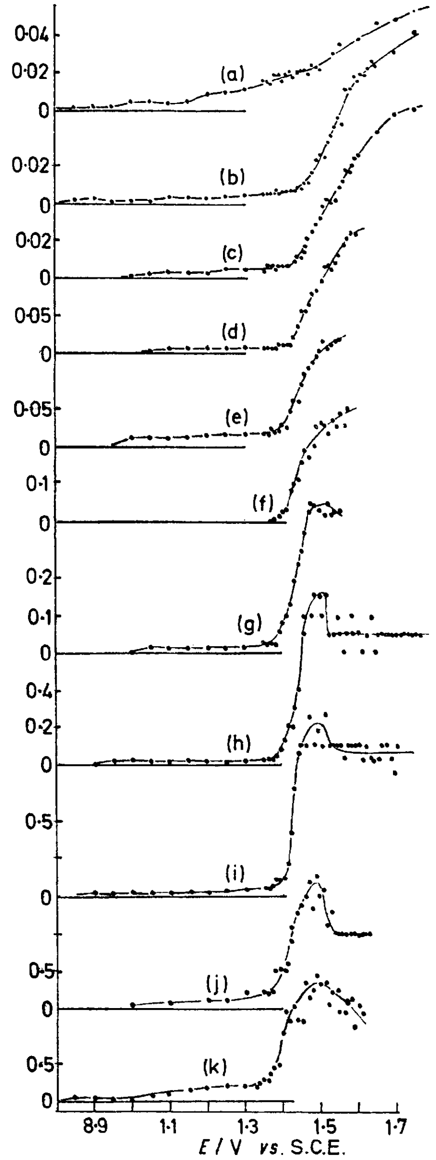

FIGURE 6 Photopolarograms of $Mn(H_2O)_6^{2+}$ ion at various concentrations: a, 10^{-5}; b, 5×10^{-5}; c, 10^{-4}; d, 5×10^{-4}; e, 10^{-3}; f, 5×10^{-3}; g, 10^{-2}; h, 5×10^{-2}; i, 10^{-1}; j, 5×10^{-1}; and k, 1·0M

concentration and applied potential in a very similar manner to that for nickel (Figure 3). Figure 7 shows that the effect of supporting electrolyte is identical to the case of nickel.

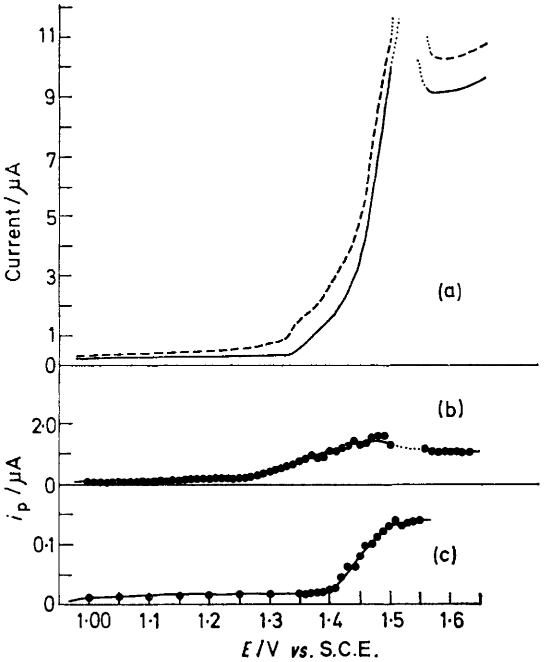

FIGURE 7 Photocurrents of hexa-aquomanganese ion in the presence and absence of supporting electrolyte: a, dark (full line) and 'lighted' (dashed line) polarograms for 10^{-3}M-Mn$(H_2O)_6^{2+}$, 0·1M-KNO$_3$; b, photopolarogram of 10^{-3}M-Mn$(H_2O)_6^{2+}$ in the presence of KNO$_3$; and d, photopolarogram of 10^{-3}M-Mn$(H_2O)_6^{2+}$ in the absence of KNO$_3$

The relationship between i_p and concentration is again suggested to be $i_p \propto [c]^{\frac{1}{2}}$ (Figure 5), although for manganese this is only so up to a concentration of 5×10^{-2}M.

(iii) *Zinc*(II). Photopolarograms for the hexa-aquozinc-(II) ion showed similar behaviour to that of nickel and manganese except for the appearance of a well defined peaked prewave. This prewave was characteristic only of the photopolarogram and was not a feature of the current–voltage curves without irradiation. The height of the prewave increases as the depolarizer concentration decreases. While the foot of the photopolarogram appears beyond −0·9 V *vs.* S.C.E., the prewave covers the range −0·4 to −0·7 V, attaining a maximum value at *ca.* −0·5 V and decreasing to the photocurrent baseline at −0·7 V. At a concentration of 10^{-5}M the prewave becomes greater than the characteristic zinc photowave.

(iv) *Cadmium*(II). Cadmium ions show photopolarograms starting in the region of −0·45 V *vs.* S.C.E., the most positive observed. Essentially they show no unusual characteristics in relation to the other ions studied although a maximum of the first kind is observed at concentrations $<10^{-4}$M.

Influence of Wavelength on Photocurrents.—It is somewhat unfortunate that photocurrents are often very small so that insertion of a monochromator in the light-path may well render the resultant current too small to measure reliably. Therefore, in place of the monochromator, a series of light filters (Ilford Spectra filters Nos. 601—608 and Kodak colour filters) were introduced individually into the light-path between the working cell and the shutter. Use of such filters gives a good approximation to monochromatic light at a series of wavelengths covering the visible region of the spectrum. Although they decrease the intensity of the radiation, photocurrents are of sufficient magnitude to make detection easy.

Wavelength variation was carried out on the hexa-aquonickel(II) ion for all concentrations cited previously and at various pre-set potentials. Plots of photocurrent *vs.* wavelength took essentially the same form regardless of concentration and applied potential. Figure 8 shows the plot of photocurrent *vs.* wavelength at −1·20 V *vs.* S.C.E. for a depolarizer concentration of 10^{-1}M. No supporting electrolyte was used in these earlier measurements. It would appear that the shape of the plots remains almost unchanged in the presence of excess of potassium nitrate while the peaks appear at wavelengths coincident with those observed in the absence of supporting electrolyte (Figure 9). The influence of wavelength on the photocurrent of potassium is slight, only a single small peak being observed (Figure 8). It is rather surprising that the 'spectra' of ions of all the elements included in Figure 9 take essentially the same form; while there is considerable variation in the relative sizes of the peaks from metal to metal, the wavelengths at which the peaks occur show only slight variation.

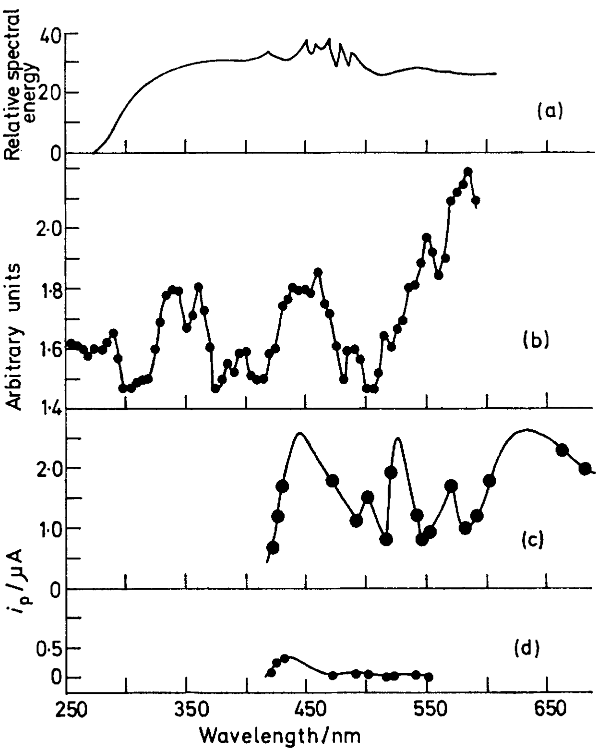

FIGURE 8 a, Relative spectra intensity *vs.* wavelength for Xenon point-source. b, Photopolarographic spectrum of 0·5M-Ni^{II} obtained with monochromator and mercury pool indicator electrode at potential of 0·70 V *vs.* S.C.E. c, Plot of photopolarographic spectrum of 0·1M-Ni^{II} obtained with filters and D.M.E. indicator electrode at potential 1·20 V *vs.* S.C.E. d, Corresponding spectrum of 0·1M-K$^+$ at 1·55 V *vs.* S.C.E. for comparison

In order to ensure that the 'spectra' of photopolarographic currents were not caused by light-intensity variations which might have arisen through the use of individual filters, the apparatus was modified slightly. Instead of a dropping electrode, a large area mercury pool was introduced and a monochromator placed in the light-path. The monochromatic light beam was focused vertically upon the mercury surface, with 5 mm of working solution covering it, by means of a parabolic mirror. By use of small intervals of wavelength and a pre-set potential, the ' spectrum ' shown in Figure 8 was obtained. It is seen that many of the peaks closely correspond to those obtained with filters. In fact, those obtained by means of filters appear to be the envelope of those obtained with the monochromator, probably owing to a large band of wavelengths being allowed through the filters. Figure 8 also shows the u.v.–visible spectrum of the xenon point-source from which it is clear that over the range of wavelength used, the intensity was virtually constant.

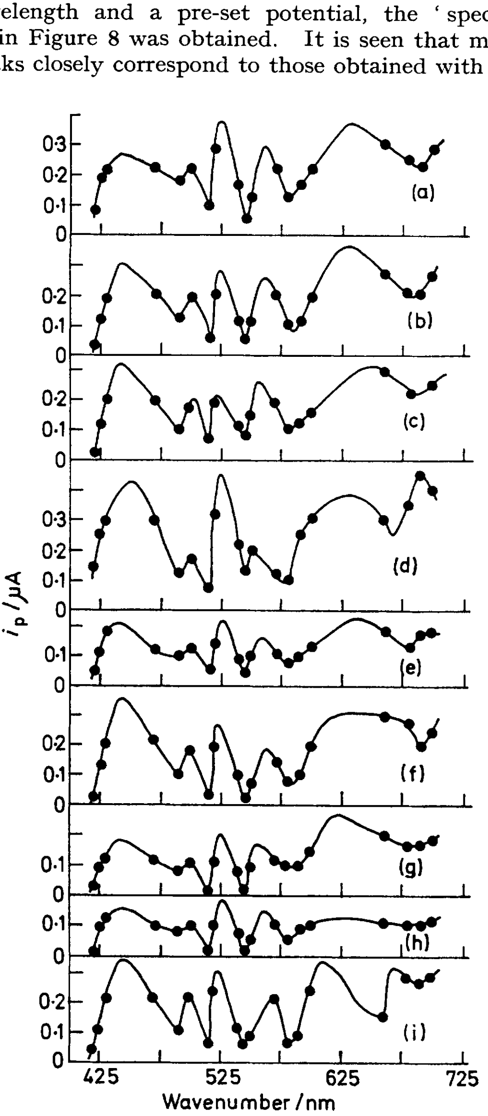

FIGURE 9 Photopolarographic spectra of a range of ions at concentration 10^{-3}M with 0·1M-KNO$_3$ as supporting electrolyte except for calcium, where none was used: a, Zn^{2+}, 1·2 V; b, Cu^{2+}, 1·0 V; c, Ni^{2+}, 1·2 V; d, Co^{2+}, 1·45 V; e, Mn^{2+}, 1·6 V; f, Cr^{3+}, 1·1 V; g, VO^{2+}, 1·1 V; h, Ca^{2+}, 1·5 V; and i, Cd^{2+}, 0·6 V

DISCUSSION

The results reported refer primarily to first-row transition metals with a view to establishing relationships compatible with those obtained by other workers for elements outside the transition block. In order to compare techniques for measuring photocurrents, polychromatic light and 0·1M-potassium nitrate were used. It is found that plots of log i_p, $i_p^{0.5}$, and $i_p^{0.4}$ *vs.* E are similar to those obtained [19] by use of 0·1M-sodium fluoride saturated with nitrous oxide. In the present study it is also found that the plot of $i_p^{0.4}$ *vs.* E is more nearly linear than the other two.

Figure 5 demonstrates quite clearly that, for transition metals, the linear relationship between photocurrent and square root of depolarizer concentration holds at low concentrations as suggested by Barker.[5-7]

By use of the relationships suggested by Barker,[6] the ' square law ' of ref. 9, the ' five halves law ',[22-24] and finally the dependence of the logarithm of photocurrent on potential,[16,25] we find that no linear relationships are obtained for most of our concentrations. This suggests that a new relationship has to be found for use with transition elements. Plots of log $i_p/(i_{p,\mathrm{Lim}} - i_p)$ *vs.* E so far give the best linear plots for the present investigations. This might not come as a surprise, since the photocurrent *vs.* potential curves (Figures 2 and 6) resemble conventional polarograms. Before any discussion of the shape of such ' photopolarograms ', it is necessary to investigate the origin of the photocurrents from which they are obtained. So far there are three hypotheses for the origin of photocurrents at an indicator electrode. Barker [5-7] has described his photocurrents in terms of photoemission of electrons from the metal by tunnelling through the potential barrier at the interface, followed by thermalization and hydration. These electrons are then captured by hydrogen ions or other reducible ions or molecules (so called scavengers) in solution at some distance from the electrode surface. On the other hand, Heyrovsky [15,16,25] envisaged a charge-transfer interaction between adsorbed solvent molecules and the electrode surface whereby, on irradiation, electron transfer from the electrode to solvent molecules occurs. Finally, Berg [4,26] has suggested that photocurrents occur only within regions of short wavelengths whereby electrons are ejected and captured directly by protons.

However, none of these three accounts completely for the present experimental observations of ' photopolarograms ' and ' photopolarographic spectra '. It is clear that the photocurrents do not originate entirely from photoemission or charge-transfer processes. Further processes occur simultaneously. The ' photowaves ' for nickel, obtained by Durst and Taylor,[10] did not extend beyond a potential of −0·8 V *vs.* S.C.E. and those of Barker [6] extended to −1·1 V in only one

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[22] Yu. Ya Gurevich, A. M. Brodskii, and V. G. Levich, *Electrokhimiya*, 1967, **3**, 1302.

[23] A. M. Brodskii and Yu. Ya Gurevich, *Zhur. eksp. teor. Fiz.*, 1968, **54**, 213.

[24] Z. A. Rotenberg, Yu.M. Pleskov, and V. I. Lekomov, *Electrokhimiya*, 1968, **4**, 1022.

[25] M. Heyrovsky, D.Phil. Thesis, Cambridge University, 1966.

[26] H. Berg, *Electrochim. Acta*, 1968, **13**, 1249.

instance. Comparison of these waves with the present ' photopolarograms ', shows them to be situated around the foot of the ' photopolarogram '. Thus, equations suggested for these waves should not necessarily be applicable to the present data.

We suggest a further mechanism, based on the linear relationship between half-wave potentials of electroreductions and wavelengths of corresponding spectral transitions.[11-13] It has been suggested [10,14] that, according to ligand-field theory, electrons within ions in an octahedral field absorb energy from the light irradiation. A transition from the t_{2g} to antibonding e_g orbitals occurs allowing acceptance of electrode electrons into vacated t_{2g} orbitals. An electron-transfer path is thus provided of lower energy to that in which electrons are accepted directly into antibonding orbitals. Similar excitation processes have been postulated as occurring within the electrode field in the absence of irradiation.[27] Since, with no irradiation, a reduction current is controlled primarily by the number of reducible ions around the electrode being reduced, any increase of current, at the same applied potential, must relate to an increment of ion reduction. Under irradiation, the number of ions in a suitable state for direct electron transfer is increased.

Intensities of photocurrents for Ni^{2+} are much higher than those for Mn^{2+} at all concentrations. It is clear from the electronic configuration of Ni^{2+} $[{}^3A_{2g}, (t_{2g})^6(e_g)^2]$ and of Mn^{2+} $[{}^6A_{1g}, (t_{2g})^3(e_g)^2]$, that the orbitals of the latter have the stable half-filled configuration. Transition of electrons between bonding and anti-bonding orbitals will off-balance the stability of the Mn^{2+} ion. This will result in fewer ions becoming excited than is the case for Ni^{2+}, and will consequently give rise to decreased photocurrents. Further, in the case of Ni^{2+}, the ' photopolarograms ' occur at a lower potential than those of Mn^{2+}. Figure 3 shows some evidence for the suggested mechanism. The value of the ratio $i_P : i_D$ increases with decreasing concentration of the depolarizer at high potential settings. This suggests that, while the normal reduction current has declined owing to lowering of depolarizer concentration, the same number of quanta of light energy still excite the same number of ions. Inspection of this Figure shows that development of a new analytical technique may be a future possibility. Measurement of photocurrents might be possible at very low concentration (10^{-6}—10^{-8}M).

The shape of the ' photopolarograms ' can be explained by the mechanism outlined. There should be two paths by means of which the ' limiting photocurrent ' could be obtained. First, if we assume that a number of reducible ions around the electrode are excited by the radiation, these excited species have to diffuse through the solution to the electrode surface. Hence, indirectly, the dissolved depolarizer acts as a ' self-generated supporting electrolyte ' for the excited ions. In most cases, however, the excited life of ions is short while the irradiation time is long compared with the rate of diffusion. Preliminary investigation shows that very little variation of the magnitude of photocurrents occurs with variation of the mercury reservoir height as was also observed by Heyrovsky.[16] It appears more appropriate to suggest that limiting photocurrents are kinetically controlled although diffusion processes might well play some part. Second, we assume that the limiting photocurrent is controlled primarily by the rate with which ions are excited by irradiation. We assume further that, at lower applied potentials, the rate with which excited ions are reduced is slow compared to the rate of excitation. As the applied potential increases, the rate of reduction becomes faster than the rate of excitation as is outlined in the Scheme.

$$\begin{array}{rcll} nM^{2+} & \xrightarrow{2ne} & nM & \text{No irradiation} \\ mM^{2+} & \xrightarrow{h\nu} & (mM^{2+})^* & \multirow{2}{*}{$\left.\begin{array}{l} \\ \\ \end{array}\right\}$ With irradiation} \\ nM^{2+} + (mM^{2+})^* & \xrightarrow{2(n+m)e} & (m+n)M & \end{array}$$

SCHEME

The presence of two types of maxima in the photopolarograms can be readily explained as though they were conventional types of polarograms.[28] Maxima of the first kind usually occur in dilute, those of the second kind in more concentrated solution.

It is quite surprising to observe that the ' spectrum ' of photopolarographic currents produce similar patterns for nickel, manganese, and other metal ions studied, except for some shifts of wavelength for certain peaks. Ions in the close vicinity of the electrode before reduction, experience a very large field-force generated within the double layer. The partially lifted degeneracy of d orbitals into t_{2g} and e_g orbitals may be still further lifted within the electrode field to produce further subshells. Electron transfer between such sub-shells may be imagined by analogy with the Stark effect. Since the ions, including Zn^{II} ions, are in an octahedral environment in our experiments, similar photopolarographic spectra may be expected on this basis.

The spectra obtained for calcium(II) and cadmium(II) have similar patterns to those of the other ions while that of potassium has a quite different character, showing only one small peak in the short wavelength region. In the case of cadmium the large electric field-force in the vicinity of the electrode could produce such f-orbital splitting that sub-shells of similar energy to those of the filled d orbitals might arise. Similarly, in the case of calcium with stable filled p orbitals, neighbouring d orbitals may become available for electronic transition. The intensities of the calcium peaks are substantially smaller than those for most of the other metals but are comparable with those of manganese(II) with the stable d^5 configuration. In the case of potassium, with its single small peak, only p orbitals are presumably available for transition.

Figure 8 clearly demonstrates that the similarities in spectral patterns do not derive from the filter-intensity effect or from the intensity variation of the xenon

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[27] A. A. Vlcek, *Coll. Czech. Chem. Comm.*, 1959, **24**, 181.

[28] J. Heyrovsky and J. Kuta, ' Principles of Polarography,' Academic Press, New York, 1966, p. 429.

source. A constant factor throughout the work was the use of mercury as indicator electrode material and it might be considered possible that mercury acted as an intermediate absorber of radiation and that this produced the similarities. It is known, however, that mercury absorbs at 253·7 nm in the u.v. region while these spectra were obtained in the near-u.v. and visible regions. If mercury were acting in this way the spectrum of potassium would be expected to be similar to the others. It would be interesting to conduct experiments using other electrodes, such as carbon paste, to prove conclusively that mercury plays no part.

Impurities are unlikely to have been an influencing factor since the same impurities would have had to be present in comparable concentrations with all the ions in order to obtain a reasonable photocurrent intensity.

What is fairly conclusively proved is that the ' spectra ' observed with the transition-metal ions do not, as was at first thought, correlate with their u.v.-visible spectra, but are more likely to be functions of their *d* orbital configurations induced during both photo- and electrode-field excitation.

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