"Photopolarographic Absorption Spectroscopy" of Nickel(II) Complexes

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Summary A spectrum of photopolarographic current signals, arising in consequence of irradiation of the indicator electrode by light of varying wavelength, is characteristic of certain inorganic complex depolarizers.

SEVERAL reports have recently appeared[1] of attempts to correlate spectroscopic and polarographic parameters for transition-metal complexes characterized by irreversible reductions. In many cases linear correlations exist between half-wave potentials (or activation energies) of electrode processes and the wavelengths of corresponding spectral transitions.

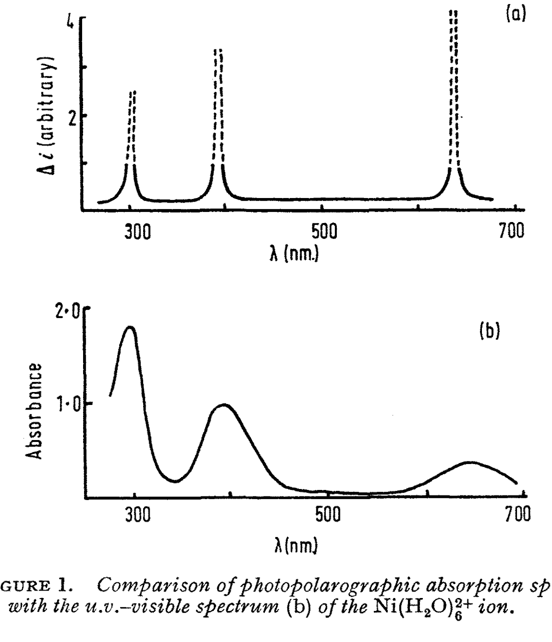

FIGURE 1. *Comparison of photopolarographic absorption spectrum* (a) *with the u.v.–visible spectrum* (b) *of the* $\mathrm{Ni(H_2O)_6^{2+}}$ *ion.*

We report some success with experiments in which radiation of the appropriate wavelength is focused on to a dropping or pool mercury electrode at which resultant polarographic signals are recorded. Reduction of a pre-excited depolarizer occurs at a more positive half-wave potential than that of the unexcited particle as was observed by Durst and Taylor[2] who suggested that the effect of varying wavelength should be investigated. In the case of nickel(II) complexes, a constant applied potential was used corresponding to the foot of the normal polarogram just prior to reduction setting in.

Under the influence of the exciting radiation, an increased current signal over the residual current is expected to occur. For the $\mathrm{Ni(H_2O)_6^{2+}}$ ion it was observed that sharp increases in current occur at wavelengths corresponding almost exactly with those at which absorption maxima appear in the u.v.–visible spectrum of the complex. The peaks, shown in Figure 1, occur over such a narrow wavelength range in this case that it has not so far proved possible to locate exactly the maximum heights.

For other nickel(II) complexes, similar signals are observed at wavelengths characteristic of their absorption maxima. Peaks obtained for the ethylenediamine complex, $\mathrm{Ni(en)_3^{2+}}$, are shown in Figure 2.

Such phenomena lend some support to the hypothesis that, under normal polarographic conditions, low-lying orbitals must be vacated before a transfer of electrons from electrode to depolarizer may occur.[3] In the present case a transition such as:

$$(t_{2g})^6(e_g)^2 \rightarrow (t_{2g})^4(e_g)^4$$
$$({}^3A_{2g}) \rightarrow {}^3T_{1g}(P))$$

occurring at 3950 Å is required for the nickel aquo-complex. Two electrons must vacate the initially filled, lower-energy, nonbonding t_{2g} orbital and be raised to the anti-bonding e_g level. Acceptance of electrode electrons into such vacated orbitals provides a reaction path of overall activation energy considerably lower than one in which electrons are accepted directly into the antibonding orbitals. Such a theory seems preferable to one dependent solely upon the lengthening and weakening of Ni^{2+}–ligand bonds caused by the transition.[2] In cases such as this, where removal of ligand species must occur during the reduction process, bond-weakening may certainly be expected to lower the overall activation energy. However, the *cause* of the weakened structure is the electronic transition and the nonbonding orbitals made available have far more affinity for electrode electrons than the e_g orbitals. In this phenomenon will still lie the greater part of the diminution in activation energy.

Solutions of the complexes were investigated in the absence of supporting electrolyte in order to avoid complications arising from photoresidual currents which tend to flow at all wavelengths even after removal of the excitation source. Avoidance of drop-current oscillations and easier focusing of radiation was possible through the use of a mercury-pool cathode. The radiation source was a xenon lamp used in conjunction with the monochromator from a Stanley Photoelectric Polarimeter.

The technique described, for which the name "Photopolarographic Absorption Spectroscopy" seems to be appropriate, has potentialities as a means of investigating the structural properties of complexed metal ions in solution. Greater resolution between peaks than is found in the conventional absorption spectrum has been observed in many cases. Quantitative significance cannot, at this stage, be given to the ratio of the various peak heights owing to the variation of intensity of the radiation over the wavelength range. The size of some of the peaks, however, gives promise of future analytical exploitation.

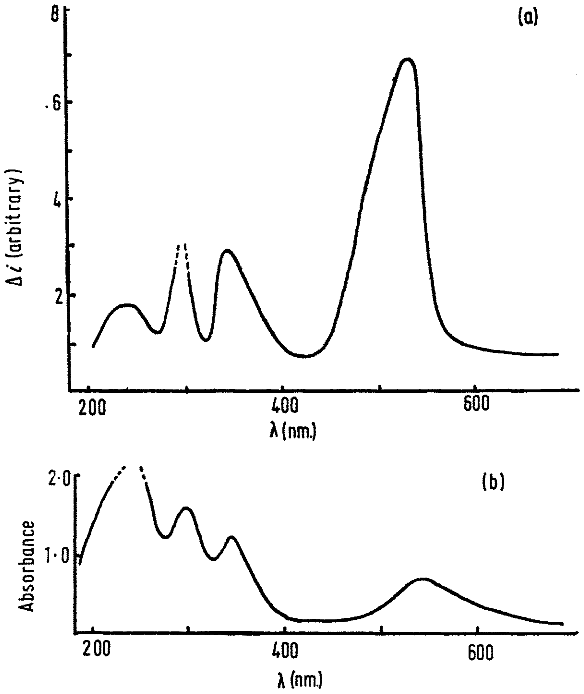

FIGURE 2. *Comparison of photopolarographic absorption spectrum* (a) *with the u.v.–visible spectrum* (b) *of the* Ni(en)$_3^{2+}$ *ion.*

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[3] A. A. Vlček, *Coll. Czech. Chem. Comm.*, 1959, **24**, 181.