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USE OF SURFACE REFLECTION IN SPECTRO-ELECTROCHEMISTRY. VISIBLE SPECTRA OF 9,10-DIPHENYLANTHRACENE RADICAL IONS

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The surface reflection intensity of a tungsten-lamp light source at a platinum electrode changes with the electrolytic formation of colored radical ion; the method serves as a convenient means of obtaining an absorption spectra. An example is shown for the radical cation and anion of 9,10-diphenylanthracene in acetonitrile.

The usefulness of spectrophotometric methods for the studies of electrode processes is well recognized. Several procedures such as the flow method[1)2)], specular reflection method[3)], the internal reflection method[4)], and the use of optically transparent electrode[5)] were devised for the observation of the visible absorption spectra of electrolysis products. However, these methods require rather complex experimental techniques and apparatus.

In this report, a versatile method involving a modification of the specular reflection method[3)] is described. The principal difference in our procedure from theirs lies in the electrode material and in the mode of electrolysis. An electrolysis cell (pyrex glass) of an ordinary type with a three-electrode configuration is sufficient to obtain the spectra. As is illustrated in Fig.1, the collimated light beam of the tungsten lamp falls on the surface of the working electrode (bright platinum plate). After single reflection, the light beam is directed to the entrance slit of a monochromator. Throughout our experiments, the angle of incidence at the electrode was kept costant at about 45 degrees; however, this angle is not important.

In order to show the effectiveness of the procedure, the electrolysis of 9,10-diphenylanthracene was carried out in acetonitrile. The reflected light intensity of the solution before electrolysis is shown in Fig.2(0). The spectrum

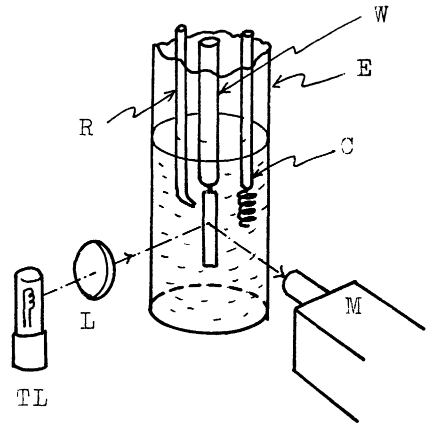

Fig.1 Basic configuration of the apparatus.

E: electrolysis cell (pyrex glass)
W: working electrode (Pt plate; 4 x 10 mm)
C: counter electrode (Pt wire)
R: reference electrode (Ag wire)
TL: tungsten lamp
L: quartz lens
M: monochromator and photomultiplier

has a maximum at about 660 nm, though the spectrum is not corrected for the sensitivity of the photomultiplier (EMI 9558 QB). Before electrolysis the solution was deaerated in the usual way. When the radical ion was produced at the electrode by applying a constant-potential (cation; +1.4 V: anion; -2.2 V) without agitation of the solution, the absorption due to the radical ion occurred and the reflected light intensity changed as shown in Fig.2(1) and (2). The curves in Fig.3 are the corresponding absorption spectra of radical cation and anion of 9,10-diphenylanthracene. In Fig.2, an example of the procedure of calculation is illustrated by the two segments, AB and AC, at 750 nm. The value of log(AB/AC) is plotted as the point D on curve (1) of Fig.3. Similar plotting was done over the whole wavelength region from 450 to 800 nm to draw the complete spectrum. Curve (2) in Fig.3 is also drawn by the same procedure. However, the ordinate scale is in arbitrary units in order to distinguish clearly (1) from (2).

Both curves in Fig.3 have good reproducibility. As is shown in Fig.4, the absorption becomes constant within about one minute after the start of electrolysis. As the measurement was begun after that time, the curves in Fig.3 were reproducible irrespective of the sweep rate of wavelength. The radical ion concentration in the diffusion layer is apparently maintained practically constant fulfilling the steady state condition.

The absorption maxima of these curves in Fig.3 agree well with those obtained by the flow method$^{1)}$, indicating that our procedure is adequate. Besides, the surface reflection at a platinum plate electrode has the very low resistance and a high efficiency of surface reflectance. Moreover, this method does not require the electrolysis of the entire solution. Therefore within few minutes, one can obtain

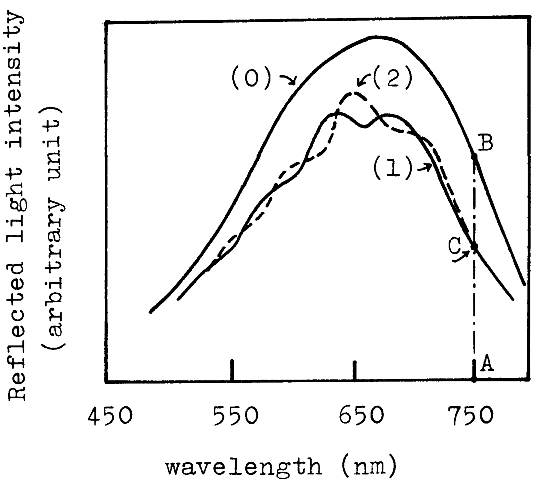

Fig.2 Reflected light intensity of tungsten lamp.

Solvent:acetonitrile
Solute: 1 mM/l 9,10-diphenylanthracene
Supporting electrolyte: 0.1 M-TBAP

(0) before electrolysis
(1) after oxidation
(2) after reduction

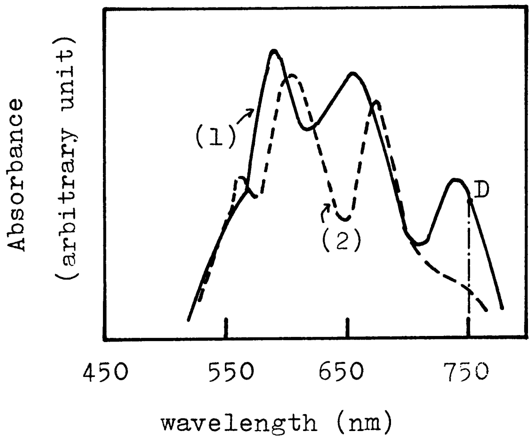

Fig.3 Absorption spectra of radical ions.

(1) cation
(2) anion

(The curves are drawn using the results of Fig.2.)

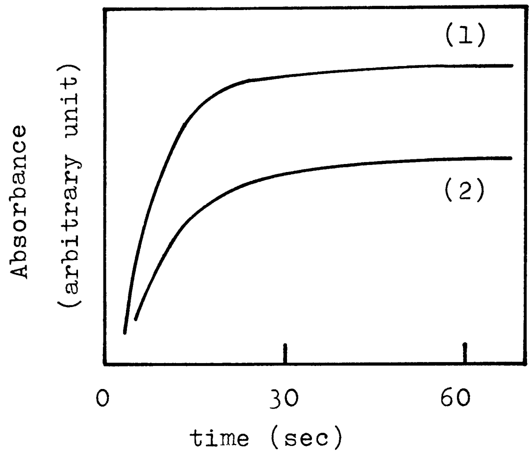

Fig.4 Variation of absorbance with electrolysis time.

(1) cation (680 nm)
(2) anion (670 nm)

the information about the radical ions existing near the electrode surface.

Although the drawing of the whole absorption spectrum requires much time, it is very simple to obtain the wavelength of the absorption maximum of radical ions as far as they have considerable stability. Our procedure is hence useful for the rapid identification of electrogenerated radical ions, especially in the case where the solvent and the original molecule are colorless. The present authors are applying this procedure to studies of electrochemiluminescence of aromatic hydrocarbons.

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