

Short Communication

Pakistan J. Sci. Ind. Res., Vol. 18, Nos. 3-4, June-August 1975

ANALYTICAL APPLICATION OF LINEAR SCAN AND/OR CYCLIC VOLTAMMETRY PEAK CURRENT

MAHBOOB MOHAMMAD* and M. ALIMUDDIN

Department of Chemistry, University of Islamabad, Islamabad

(Received October 31, 1974)

The relationship between the peak current (I_p) and the concentration (C^b) of electroactive species O (in the bulk) for a reversible process.

is given by^{1,2}

$$O + ne \rightleftharpoons R \quad (1)$$

$$I_p = 602 n^{\frac{3}{2}} A D^{\frac{1}{2}} C^b V^{\frac{1}{2}} \quad (2)$$

Where D is the diffusion coefficient, n is the number of electrons, A is area of electrode and V is the sweep rate. Thus for the same species with constant V and A

$$I_p \propto C^b \quad (3)$$

Which is the basis of analytical application of peak current in linear scan and cyclic voltammetry. In other words from a calibration curve of I_p vs C^b (of known concentrations) for O , the unknown concentration of O in a given sample is determined.

For two different electroactive species, undergoing the same electrode process, as given in equation 1 (with n remaining constant), the I_p will differ by the ratios of their $D^{\frac{1}{2}}$, provided their concentration remain the same (sweep rate and electrode area also remain the same). It is, however, well known that the diffusion coefficient of similar species, e.g. anthracene and naphthalene, differ very little² hence a calibration curve for anthracene is expected to be almost valid for naphthalene (within 5% error).

The validity of the above relationship was tested in the present work with 3-nitroaniline-4-nitroaniline system in acetonitrile on a hanging mercury drop electrode.

Figure 1 shows a calibration curve for 3-nitroaniline which is known to give one electron reversible wave (first reduction potential).³ The broken lines

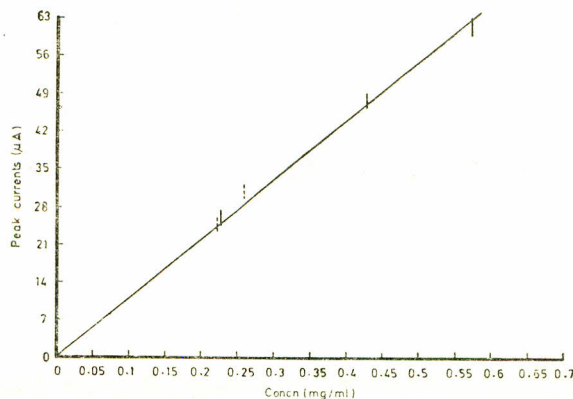


Fig. 1 Calibration curve for 3-nitroaniline. The line shows the error in peak current (3-5 runs). The broken lines are for 4-nitroaniline.

show the peak current for two different concentrations of 4-nitroaniline which is also known to give one electron reversible wave (first reduction potential).³ The concentration of 4-nitroaniline determined from the calibration curve for 3-nitroaniline are 0.225 ± 0.010 mg/ml and 0.280 ± 0.010 mg/ml while actual concentration are 0.220 and 0.260 mg/ml, which are within experimental error.

Thus the present work has shown the utility of equation 1 in analytical chemistry for two different species but undergoing the same electrode process. The investigation for irreversible case is under investigation.

Experimental

Heath EU 401 polarographic module was used with Mosley X-Y recorder. The peak current was recorded at 2V/min scan rate. Nitrogen gas from cylinder was passed through acetonitrile to saturate it before using it for deaeration. Acetonitrile was purified by twice distilling from phosphorus pentoxide. Tetrabutylammonium perchlorate (Matheson, Coleman and Bell) was used directly. Nitroanilines were purified as described earlier.³

References

1. M. Mohammad, *Introductory Linear Scan and Cyclic Voltammetry for Organic Chemists* (submitted to Islamabad University Press, Islamabad). See also R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).
2. R.N. Adams, *Electrochemistry at Solid Electrode*, (Marcel Dekker, New York, 1969), p. 221.
3. M. Mohammad, A.Y. Khan, M. Afzal, A. Nisa and R. Ahmed, *Aust. J. Chem.*, **27**, 2495 (1974).

*Now at the Department of Chemistry, State University of New York, College of Forestry, Syracuse, New York, 13210, U.S.A.