# The Use of Cyclic Voltammetry in Studying Metal Complex Equilibria

## 금속착물 평형연구를 위한 순환전압 전류법의 이용

위 생 과
전임강사   김    일    광

## 초 록

여러 가지 유기착화제와 금속이온 사이의 가역반응에 대한 순환전압전류법에서의 평형상수
를 다음 식으로 나타내었다.

$F_o[X] =$ anti log $[0.4343 \, nF/RT(\triangle E1/2 + \log (ip)S/(ip)C)]$…

이 제안은 폴라로그래피에서와 비슷한 방법으로 유도하였으며; 이것으로 순환전압전류법의
분석적이용 뿐만 아니라, 착화합물의 크기, 리간드수에 대해서도 비교적 정확한 정보를 얻을
수 있다.

## I. Introduction

It is a basic observation in polarography that the half-wave potential of a simple metal ion is shifted, usually to a more negative value by complex formation. By measuring this shift as a function of the concentration of the complexing agent, both the formation constant and formula of the metal complex may be evaluated. This method is one of the standard techniques of studying metal complex equilibria. Deford and Hume (1) developed a mathematical treatment for the step-equilibria between successively formed complexes in solution. The DeFord and Hume polarographic method for evaluat-ing complex ion systems require a knowledge of reversible half-wave potentials and of the diffusion current. In the presence of polarographic maxima however, calculation of half-wave potential and diffusion current is difficult. It is my proposal that cyclic voltammetric measurements (2) could be used as an alternative to d.c. polarographic measurements with the possible advantage of an improvement in precision of measurements, as the accuracy and reproducibility of cyclic voltammetric measurements are presumably better than can be obtained by conventional d.c. polarography, although no evidence is given in support of these claims.

## II. Theory

It has been shown by DeFord and Hume (1) that the shift in half-wave potential due to complex formation can be expressed as:

$$\triangle E_1/_2 = (E_1/_2)_c - (E_1/_2)_s = 2.303RT/nF \ \log \ fM\frac{I_c}{I_s}\sum_o^N\frac{B_j[X]^j}{fM\bar{X}_j}\cdots\cdots(1)$$

where $(E_1/_2)_c$ and $(E_1/_2)s$ are the half-wave potentials of the complex and simple metal ions respectively, R, T and F have their unusual significance, $n$ denotes the number of electrons involved in the reduction, $I_s$ and $I_c$ are the experimental diffusion currents for the simple and complex ions respectively, $B_j$ is the overall formation constant of the jth complex; $X$ is the activity of the complexing ligand and $fM$ and $fMX_j$ denote the activity coefficients, at the electrode surface, of the metal and complex species respectively. Equation (1) can be rearranged to define a function $F[X]$:

$$F_o[X] = \sum_j^o B_j C_X^j = antilog[0.4343nF/RT(\triangle E_1/_2) + log\frac{I_s}{I_c}]$$

$$= fM\sum_o^N B_j[X]^j/f_{MX_j}$$

$$= B_o + B_1[X]FMfX/fMX + B_2[X]^2fM(fX)^2/f_{MX_2} + \cdots(2)$$

where the symbol $F_o[X]$ is introduced for convenience to represent the experimentally measured quantity on the right-hand side of the eguation. Equation (2) can be written in the form (3) if the ionic strength is kept constant and the activity coefficients are taken as also being constant:

$$F_oX = 1 + B_1[X] + B_2[X]^2 + \ \cdots\cdots\cdots\cdots + BN[X]^N \ \cdots\cdots\cdots\cdots\cdots(3)$$

where $[X]$ denotes the concentration of the complexing ligand, and $f$ the activity coefficient of the species indicated by subscript. $B_1$, $B_2$ and $B_3$ are the overall formation constants for the complexes containia one, two and three ligands respectively. In order to determine $B_1\cdots B_N$, the graphical extrapolation method devised by Leden (3) is applied. It is apparent from equation (3), that a plot of $F_o[X]$ vs. $[X]$ will be a steeply rising

curve. However, as $[X]$ approaches zero, the graph will have a limiting slope of $B_1$ and an intercept, on the $F_o[X]$ axis, of 1. A preliminary value of $B_1$ is thus obtained immediately. A new function $F_1[X]$ is defined by:

$$F_1[X] = [(F_o[X] - 1)/[X]] = B_1 + B_2[X] + \cdots + B_N[X]^{N-1} \cdots (4)$$

We see that the plot of $F_1[X]$ against $[X]$ will have a limiting slope, as $[X]$ tends to zero, of $B_2$ and an intercept, on the $F_1[X]$ axis of $B_1$. A function of $F_2[X]$ is defined similary, viz:

$$F_2[X] = [(F_1[X] - B_1)/[X]] = B_2 + B_3[X] + \cdots + B_N[X]^{N-2} \cdots (5)$$

The procedure is continued in this maner until all $n$ complexes have been accounted for. For the penultimate complex, $MX_{N-1}$, the $F_{N-1}[X]$ function is given by:

$$F_{N-1}[X] = [(F_{N-2}[X] - B_{N-2})/[X]] = B_{N-1} + B_N[X] \cdots \cdots (6)$$

Here the $F_{N-1}[X]$ vs. $[X]$ plot is a straight line and indicates directly that the penultimate function has been reached. The final function, $F_N[X]$, will be independent of ligand concentration thus,

$$F_N[X] = [(F_{N-1}[X] - B_{N-1})/[X] = B_N \cdots \cdots (7)$$

so that a straight line, parallel to the $[X]$ axis and an intercept $B_N$, is obtained, thus giving the stability constant and composition of the highest complex.

## III. Discussion

It can be seen, therefore that the reliability of the results obtained depends on the precision with which changes in half-wave potential can be measured. For large changes in $\triangle E_{1/2}$, small errors in the measurement of the half-wave potentials are not especially significant. However, when $\triangle E_{1/2}$ is small, then the relative errors produces in $F_o[X]$ are rather large, and subsequent calculations of formation constants are subject to very large errors. Thus, there is the possibility of large errors in $F_o[X]$ which are greatly magnified in subsequent calculations, obtain $F_1[X]$, $F_2[X]$, etc; and stability

constants of the higher complexes may contain very large errors.

For reversible electrode reaction the half-wave potential for the reversible systems the equation to the polarographic wave is given by

$$E_{d.e} = E_1/_2 - 2.303 \ RT/nF \ \log \ (i/i_d - i) \quad \cdots\cdots\cdots\cdots\cdots\cdots (8)$$

where all symbols are those conventionally used in polarography. Consequently, $E_1/_2$ may be directly measured by plotting $E_{d.e}$ vs. $\log \ (i/i_d - i)$ as this plot should be a straight line of slope 2.303 $RT/nF$ and intercept $E_1/_2$. In the presence of polarographic maxima however, this theoretical relationship will not be observed even though the electrode reaction may in fact be reversible. Thus calculation of $E_1/_2$ and also $i_d$ in the presence of maxima is difficult. To overcome the problem, maximum suppressors such as gelatin can be added. In their presence the current/voltage curve may then be observed to follow the theoretical shape. However, maximum suppressors can often alter the kinetics of the electrode reaction, or themselves form metal-ion complexes, and the half-wave potential observed in their presence may not be that due to the complex formation of the ligand being studied. Half-wave potentials obtained from polarogram require a knowledge of $i_d$, $i$ and $E_{d.e}$ to be defined for each value of $i$. Thus, the precision of $E_1/_2$-values depends on the accuracy with which the current as well as the potential can be measured from the polarogram.

Thus, any technique which enables $\triangle E_1/_2$ values to be measured more accurately than by conventional d.c. polarography will lead to improved calculations of the stability of complexes. The use of a.c. summit potentials, $E_s$ which are known to coincide with d.c. half-wave potentials (4), is a plausible technique, because $E_s$-values can be obtained simply from the point of maximum current without the need of any further interpretation (5). The application of cyclic voltammetry(stationary electrode polarography) seemed to be a promising technique at first sight, because of the simplicity with which $E_1/_2$-values can be obtained directly from cyclic voltammogram. In cyclic voltammetry instead of producing currentpotential steps as in polarography, a peaked currentpotential curve is formed. Qualitatively, the peak current $i_p$ is analogous to polarographic step height, and peak potential $E_p$ is analogous to half-wave potential. The relationships for reversible case are given in Equations (9) and (10) (6):

$$i_P = 2.72 \times 10^5 n^{3/2} A \ C^0 \ D^{\frac{1}{2}} V^{\frac{1}{2}} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (9)$$

$$E_p = E_{1/2} - (1.109 \pm 0.002) \ (KT/nF) \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (10)$$

Here V is the micro electrode potential sweep rate and A is the electrode area. Other terms have the same significance as before. The peak potential differs from half-wave potential by a constant factor, and is 28.5/n mv more cathodic than the half-wave potential at 25℃.

It is a little difficult to measure the peak potentials precisely from a recorded curve, because the variation of current is not very great in the vicinity of the peak(peak may be broad), and therefore Mueller and Adams (7) recommended the measurement of the half-peak potential, $E_{p/2}$ because $E_{p/2}$ can be determined more precisely than $E_p$. This is defined as the potential where the current, after correction for the residual current, is half as large as at the peak. The half-peak potential precedes $E_{1/2}$ by 28.0/n mv (6), or

$$E_{p/2} = E_{1/2} + (0.0280/n) \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (11)$$

Thus, $E_{1/2}$-values obtained from cyclic voltammogram should be more reproducible, because $E_{1/2}$ is obtained directly from the value of peak potential or half-peak potential.

In many cases, the polarograms made with the stationary electrode or hanging drop electrode showed maxima (8). These maxima are ususally observed just cathodic of the normal peak potential due to an increased supply of reducible material at the electrode surface at potential where the maxima are observed, however, the magnitude of the spike decreases as increasing the rate of voltage scan. This illustrates the problems due to maxima in the cyclic voltammetry are not so critical for the measurement of peak potential or half-peak potential.

The possible use of cyclic voltammetry will be therefore the aim of overcome the problems of maxima without the undesirable use of maximum suppressors and for the advantage of accuracy in half-wave potential measurement. Furthermore, the reversibility of the system can be checked by cyclic voltammogram, where the difference in potential between cathodic and anodic peaks must close to the value of $2 \times 0.028/n$ volt for a reversible system (9).

The expression on the right handside of the Equation (2) can be alternatively expressed as

$$F_o[X] = antilog \ [0.4343 \ nF/RT \ (\triangle E_{1/2}) + log \ (i_d)_s/(i_d)_c] \cdots (12)$$

where $(i_d)_s$ and $(i_d)_c$ are the diffusion currents of the simple metal and complex ions respectively. If cyclic voltammetry is used this expression becomes

$$F_o[X] = antilog \ [0.4343 \ nF/RT \ (\triangle E_{1/2}) + log \ (i_p)_s/(i_p)_c] \cdots (13)$$

where $(i_p)_s$ and $(i_p)_c$ are the peak currents of the simple metal and the complex ions respectively. The function $F_1[X] = [F_o[X] - B_o)/[X]]$ is now introduced by Deford and hume method, where $B_o$ is the formation constant of the zero compelex and is of course, unity. If $F_1[X]$ is plotted against $[X]$ and is extrapolated to $[X] = 0$, then the value of $F_1[X]$ at the intercept equals $B_1$. The formation constant of higher complexes (if present) may be determined in a similar manner.


# VI. Conclusion


The proposions contained in this proposal are somewhat novel in concept and purpose, but the foregoing methods are applicable only when the electrode process of both simple and complexed species occur reversibly. An analytical application of the use of cyclic voltammetric measurements in the evaluation of complex equilibria was undertaken with a view of to obtaining accurate and reliable information as to the number and magnitude of complexes.


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