



### Selective Topics in Physical Chemistry for PhD Students

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Answer four questions only of the following:

(80 marks)

- 1) In view of Hammett equation, write an account on the effect of substituents on the polarographic half-wave potential.
- 2) Cyclic voltammetry is considered to be a modern technique in electrochemistry compared with DC-polarography. Write on the importance of this technique in definition and determination of the mechanisms of electrode reactions.
- 3) Answer three only of the following:
  - a- Polarography of complexes.
  - b- Oxygen reduction in polarography.
  - c- Effect of mercury pressure in polarography.
  - d- Analytical determination of a mixture of different cations.
- 4) Write a satisfactory account on types of polarographic current. What is the important of diffusion current in analytical chemistry.
- 5) Sketch and explain the polarographic cell and the current-potential curve (polarogram). Write on the important of using the supporting electrolyte in polarographic measurements.

With my best wishes  
Prof. Dr. El-Sayed Mabrouk

## Model Answer

### Answer of question No. 1

#### Effect of substituents on electrode reaction mechanism

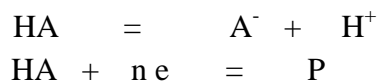
For many organic compounds, the half-wave potential ( $E_{1/2}$ ), the wave height and the wave shape acid-base equilibrium or on the rate of chemical reactions. For polarograms showing a single wave, the effect of pH can be observed in three ways:

- 1-neither the  $E_{1/2}$  nor the  $i_1$  change as the acidity change.
- 2-the  $E_{1/2}$  is shifted to more negative potential but the wave height ( $i_1$ ) remains pH-independent.
- 3-both the  $E_{1/2}$  and the  $i_1$  change with pH.

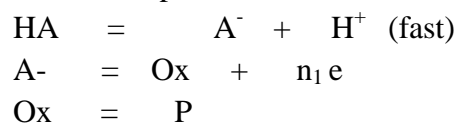
In case of (1), the transported species in solution under goes any transformation prior to the electrode process (electron transfer) and the rate of this reaction is pH-independent. This means that no proton uptake precedes the electron transfer step. The general sequence involved in such case must be electro, proton, electron, proton ( $e, H^+, e, H^+$ ) or electron, electron, proton, proton ( $e, e, H^+, H^+$ ).

For case (2) in which the  $E_{1/2}$  is pH-dependent, but the  $i_1$  is pH-independent. Three possibilities are obtained:

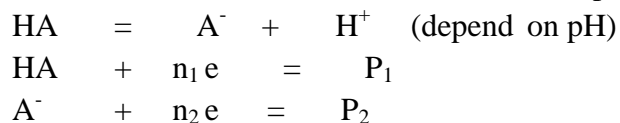
i) A fast proton transfer precedes the electrode process (electron transfer) in which the acidic form is electroinactive:



ii) A fast proton transfer precedes a reversible electrode process in which either the acidic form alone is reduced or the basic form alone is oxidized and this further followed by a chemical reaction. The sequence for the oxidation process is:



iii) proton transfer occur at a rate that depends on pH and both the acidic form and the basic form are electroactive but their half-wave potentials are so close to each other that the two waves merge and a single wave is observed. The electrode mechanism can be represented by the following steps:



in which  $n_1 = n_2, E_1 = E_2$

In all cases the sequence is  $H^+, e, H^+, e$  or  $H^+, e, e, H^+$ .

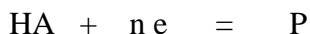
For case 3 in which the  $E_{1/2}$  and the  $i_1$  are pH-dependent, i. e, the  $E_{1/2}$  shifted to more negative potential with rise of pH and the  $i_1$  decreases. This pH-dependent reaction can be either (i) an acid-base reaction or (ii) a chemical reaction such as dehydration or ring opening. A third possibility is that (iii) both forms of the depolarizer are electroactive but differ in the number of electrons transferred.

i)if the change in wave height ( $i_1$ ) is due to an acid-base equilibrium, one wave is observed and its height remains pH-independent as long as the formation of the acidic form from the basic form is fast enough.

As the pH increases and the rate of protonation decreases, the wave height decreases and a plot of the  $i_p$  vs. the pH has the shape of a dissociation curve. The dissociation is given by the equation:



The  $\text{pK}_1$  is the pH at which  $i_{\text{HA}}$  equals half of the original diffusion current as shown in the following figure. The reduction reaction can be represented by the following equation:



ii) the most kind of chemical reaction in this case is a dehydration. In such reaction the hydrated form is electro-inactive and the wave height is controlled by the rate at which it is transformed into the electro-active non-hydrated form. The rate of this dehydration is pH-dependent and therefore the height of this wave is pH-dependent.

iii) processes that involve the electrolysis of two electroactive forms differing in the number of electrons transferred. At sufficient low pH values, the wave height is constant and pH-dependent. As the pH is increased the wave height changes in a way that resembles a dissociation curve. Two types of processes are taken into consideration. These two processes involve the reduction of both the acidic and the basic forms HA and  $\text{A}^-$  which consume different numbers of electrons  $n_1$  and  $n_2$  for HA and  $\text{A}^-$ , respectively. In acid solutions whereas the acidic form is the predominate one, the first process involves the reduction of the acidic form by consuming  $n_1$  electrons is twice that  $n_2$  or  $n_2$  is two-third  $n_1$ . In acid solution (pH 7), the sequence is  $\text{H}^+$ , e, e,  $\text{H}^+$ .

## Answer of question No. 2:

### Cyclic voltammetry

Cyclic voltammetry (CV) is considered to be very useful modern electrochemical technique. In such technique, simply the potential of the working electrode is varied linearly with time in either the positive or the negative direction until a switching potential is reached. At this time the direction of potential sweep is reversed and the potential is returned to the original value. The current is measured throughout the experiment and the resulting I – E curve is known as a voltammogram. Such technique provides more information about the characteristic of the electrochemical process. The kinetics and thermodynamics of the electrode reaction as well as the electrode reaction mechanism. The characteristics of the voltammogram is the appearance of peak current ( $i_p$ ) at a potential known as peak potential ( $E_p$ ) both of them provide information about the thermodynamics and the kinetics of the electrode reaction taking place. The potential of the working electrode is controlled vs. a reference electrode such as calomel electrode or silver/silver chloride electrode. The controlling potential which is applied across the two electrodes can be considered as an excitation signal. The excitation signal which is a linear potential scan with a triangular waveform. The sweep rates used in the experiments ranging from few mV/s up to several thousands V/s. Up to 500 mV/s an X-Y recorder is most convenient, but above this the slow response of the recorder is insufficient to record the voltammograms, thus an oscilloscope or microcomputer is necessary. The peak current ( $i_p$ ) is related to the scan rate ( $v$ ) by the equation:

$$i_p = 0.446 n F A C (n F/RT)^{1/2} v^{1/2} D^{1/2}$$

in which  $v$  is the sweep rate in V/s,  $A$  is the electrode surface area in  $\text{cm}^2$ ,  $D$  is the diffusion coefficient in  $\text{cm}^2/\text{s}$ ,  $n$  is the total number of electrons,  $F$  is the Faraday's constant (96500 coulombs) and  $C$  is the concentration of the depolarizer. At 25 °C, the equation can be given as:

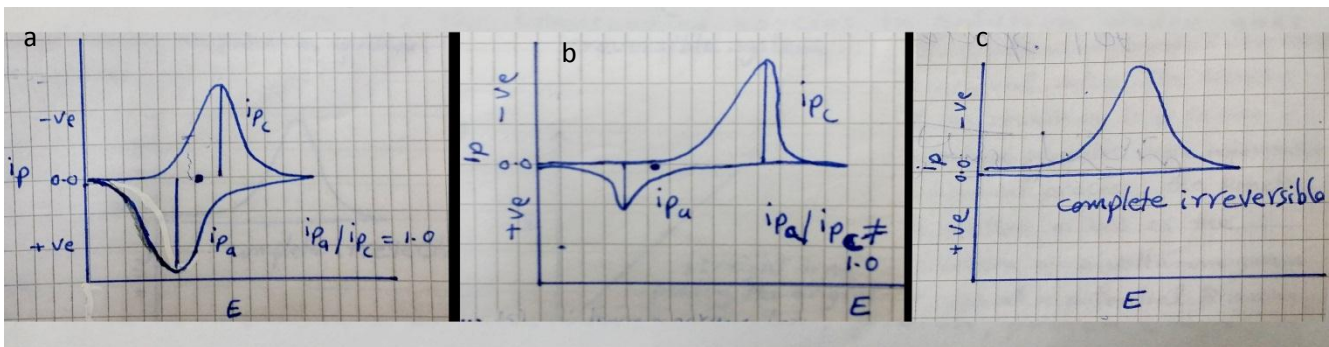
$$i_p = 2.69 \times 10^5 n A D^{1/2} v^{1/2} C$$

For a reversible processes, the peak potential separation  $E_p$  is given by:

$$E_p = E_{pa} - E_{pc} = 59 / n \text{ mV}$$

in which  $E_{pa}$  and  $E_{pc}$  are the anodic and cathodic peak potential, respectively. On the other hand, the ratio of anodic to cathodic current is given by the relation:  $i_{pa} / i_{pc} = 1.0$

Opposite to the reversible reaction, irreversibility means that the rate of electron transfer is sufficient slow with respect to the potential sweep rate. As the sweep rate is increased, the rate of mass transfer increases and the potential of the response in cyclic voltammetry is shifted cathodically for the reduction processes and anodically for the oxidation ones with respect to the standard potential. Also, for a totally irreversible processes, there is no peaks observed in the reverse scan. The following figure shows the cyclic voltammograms of reversible (a), irreversible (b) and totally irreversible (c) processes.



However, in case of irreversible processes, the peak current can be related to the sweep rate using the following equation:

$$i_p = 3.01 \times 10^5 n (\alpha n_a)^{1/2} A C D^{1/2} v^{1/2}$$

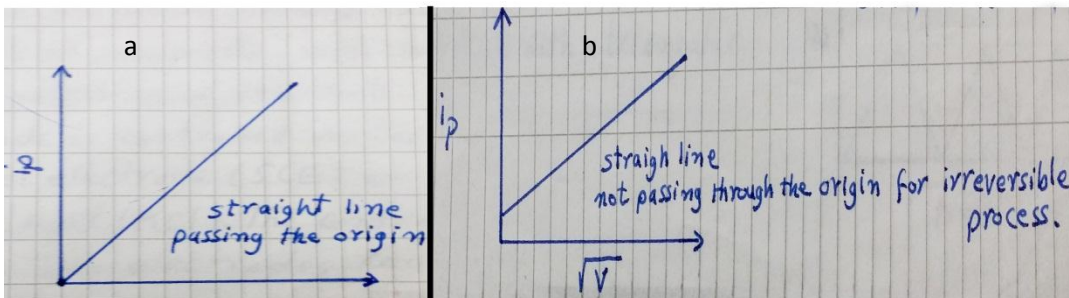
in which  $\alpha$  is the transfer coefficient and  $n_a$  is the number of electrons transferred in the rate-determining step ( the slowest step). The peak potential of an irreversible reaction can be related to the sweep rate using the relation:

$$E_p = -1.14 (RT / \alpha n_a F) + (RT / \alpha n_a F) \ln k_{f,h}^0 / D^{1/2} - RT / 2 \alpha n_a F \ln / \alpha n_a F v$$

The separation of peak potential is given by the equation:

$$E_p - E_p / 2 = 48 \alpha n_a \text{ mV}$$

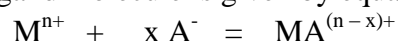
For totally reversible reaction and on plotting  $i_p$  vs. the square root of sweep rate, linear correlation passing through the origin is obtained as shown in the following figure (a), on the other hand, for an irreversible reaction the plotting of  $i_p$  vs. the square root of the sweep rate gives linear correlation not passing from the origin is obtained (Fig. b), Also for irreversible processes, the transfer coefficient can be determined using equation ( ). Thus, on plotting  $E_p$  vs.  $\ln v$ , a linear correlation is obtained with slope equals to  $0.0118 / \alpha n_a$ , from this slope value the transfer coefficient  $\alpha$  can be calculated.



### Answer of question No. 3:

#### a-Polarography of complexes

In polarographic measurements it is important to notice that the half-wave potential ( $E_{1/2}$ ) of metal ion affected by the presence of species that form complex with that ion. This species is known as the ligand (L). In general the  $E_{1/2}$  of the metal complex is more negative than the  $E_{1/2}$  of the simple metal ion. Lingane has shown that the shift in  $E_{1/2}$  to more negative as a function of concentration of the complexing agent (ligand) can be employed to determine the formula and the stability constant of the complex formed in solution n. The reaction between the metal ion and the ligand molecule is given by equation:



Lingane derived the following relation:

$$E_{1/2(C)} - E_{1/2(S)} = E_{1/2} = - (0.0591/n) \log K_f - (0.0591 x/n) \log [A^-]$$

$K_f$  is the formation constant (stability constant) of the complex and  $[A^-]$  is the concentration of the ligand. Thus, a plot of  $E_{1/2}$  against  $\log [A^-]$  gives a straight line of slope equals to  $0.0591 x/n$ . If n is known, the stoichiometry of complex (number of ligand molecules attached to metal ion) can be obtained. Also, from the intercept the formation constant  $K_f$  can be obtained.

#### b- Analysis of the polarographic waves

Analysis of the polarographic waves is very important for testing the thermodynamic reversibility of the reduction wave and the elucidation of the electrode mechanism. The analysis is carried out by employing the fundamental equation concerning the reversible polarographic wave:

$$E_{de} = E_{1/2} - 0.0591/n \log i/i_d - i$$

In which,  $E_{de}$  is the potential of the dropping mercury electrode in volts,  $i_d$  is the diffusion current in microampere.  $E_{1/2}$  is the half-wave potential and n is the total number of electrons involved in the electro-reduction process. The plots of  $E_{de}$  vs.  $\log i/i_d - i$  is straight line of slope ( $S_1$ ) equals to  $-60$  mV for an one-electron, but for 2-electron step it equals to  $30$  mV. For 3-electron step  $S_1$  equals to  $-20$  mV and for 4-electron step it equals to  $-15$  mV. For an irreversible process the values of slope  $S_1$  are

different from these of reversible one. In this case, the fundamental equation of irreversible waves is considered:

$$E_{de} = E_{1/2} - 0.0591/n_a \alpha \log i/i_d - i$$

In which,  $\alpha$  is the transfer coefficient,  $n_a$  is the number of electrons involved in the rate-determining step (slowest step) and the remainder terms have their usual significances.

### c- Effect of mercury pressure

The effect of mercury height (mercury pressure) on the limiting current ( $i_l$ ) may throw light on the factors controlling the reduction process such as diffusion, rate of chemical reaction or adsorption phenomenon. The relation between the limiting current ( $i_l$ ) and the mercury height ( $h$ ) is given by the relation:  $i_l = K h^x_{corr}$  or  $\log i_l = \log K + x \log h$  where  $K$  is a constant

$\log i_l$  as a function of  $h$  is a straight line of slope equals to  $x$ . The value of the exponent  $x$  reveals the electrode reaction nature. For diffusion-controlled current,  $x = 0.5$ , for adsorption current,  $x = 1.0$ . mentioned ones if the electrode process is governed by combination of two kinds of these processes.

### d- Amperometric titration

Polarographic methods can be employed to estimate the equivalence point of titrations provided that at least one of the reactants or the products is oxidized or reduced. In this technique, the current is measured as a function of the reagent volume at a fixed potential. The cell used in these measurements is shown in the following figure (FIG. 1a). An example of amperometric titration is the titration of  $Pb^{2+}$  ions with sodium sulfate or sodium oxalate in which sulfate ions are electro-inactive whereas lead ions are electro-active. The potential is that applied should be sufficient to give a diffusion current should be more than 0.7 V because the  $E_{1/2}$  of lead is 0.62 V in these solutions. On adding the reagent ( $Na_2SO_4$ ), lead sulfate or lead oxalate will be precipitated and a linear decrease of current is observed (Fig. 1b) as  $Pb^{2+}$  ions are removed from the solution. The end point is obtained by extrapolation of the linear portion as shown in Fig. 1a. Another example is the titration of lead ions with chromate ions in which both the reagent and the analyte are electro-active. The potential is adjusted at  $-1.0$  V. As shown in Fig. 1c both lead ions and chromate ions give diffusion currents and a minimum is obtained which corresponding to the end point.

### Answer of question No. 4:

#### Polarographic currents

Polarographic currents are classified to various types according to the process that govern the value of the limiting current. The most common types of polarographic limiting currents are: i) diffusion current, ii) kinetic current, iii) catalytic current and iv) adsorption current. Diffusion current ( $i_d$ ) is limited by the rate of diffusion of the electroactive species to toward the electrode surface. Kinetic current ( $i_k$ ) is limited by the rate of chemical reaction accompanied the electrode process and taking place at or near the electrode surface. Catalytic current ( $i_c$ ) is also limited by the rate of chemical reaction, but in this

case in this case the reaction can be classified as catalytic. Adsorption current ( $i_a$ ) is limited by the coverage of the electrode surface either by the original compound being electrolyzed. By the electrolysis products or by an intermediate. The latter processes may either enhance the rate of electrode process, retarded it or completely blocked it through the adsorbed layer which is formed at the electrode surface. (h) on the limiting current ( $i_l$ ) or by studying the effect of concentration of the original compound (depolarizer) on the limiting current. According to Ilkovic equation:

$$i_d = 607 n D^{1/2} m^{2/3} t^{1/6} C$$

in which  $i_d$  is the diffusion current in microampere,  $n$  is the total number of electrons involved in the reduction process,  $D$  is the diffusion coefficient in  $\text{cm}^2/\text{sec}$ ,  $m$  is the rate of mercury flow in  $\text{mg}/\text{sec}$ ,  $t$  is the drop time in sec and  $C$  is the concentration of the depolarizer in mM. From this equation the plot of  $i_d$  vs.  $C$  is linear correlation passing through the origin as shown in (1/2) the following figure (Fig. a), indicating that  $i_d$  increases linearly with concentration. The same result is obtained for first order kinetic current. For adsorption current, the current increases with increasing the concentration of the depolarizer until a limit value at which the electrode surface becomes completely covered and the current reaches constant value (Fig. b). for catalytic current, the current increases gradually with increasing the concentration but not linearly as in case of diffusion the most common types  $n$  current (Fig. c). Polarographic currents are also affected by temperature. Increase of temperature increases the diffusion current by  $2\% / ^\circ\text{C}$  whereas the kinetic current increases by  $5-10\% / ^\circ\text{C}$ . Adsorption current may increase or decrease with increasing temperature. In cases adsorption current does not affect by temperature

