Polarographic Reduction of Nickel in Methylene bis thioacetic acid media

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Summary: The reduction of nickel in presence of methylene bis thio acetic acid (referred to herein as MBTAA) has been studied polarographically in the pH range 1-7. The discharge of nickel at the d.m.e. has been found to be irreversible and diffusion controlled at constant ionic strength (1M KNO_3). Hence kinetics of the electrode reaction has been investigated and the values of kinetics parameters (transfer co-efficient   and formal rate constant $k^{\circ}_{f,h}$) have been calculated at 25°, 30°, 35°, 40°, 45° and 50°C by Koutecky's theoretical treatment as extended by Meites and Israel. The values of thermodynamic parameters - $\Delta H^{\#}, \Delta G^{\#}$ and $\Delta S^{\#}$ for the system have also been evaluated at 30°C.

Introduction

In continuation of the earlier work by Saxena and co-workers [1-6] on the polarograhic behaviour of several mercapto compounds and their metal complexes, this communication reports the polarographic behaviour of nickel in presence of methylene bis thioacetic acid, the determination of kinetic parameters under different experimental conditions and the values of thermodynamic parameters for the electrode reaction. The literature is, however, silent on these investigations.

Experimental

Methylene bis thio acetic acid (referred to herein as MBTAA) of 99 percent purity was supplied by Evan's Chemetics Inc., New York. nickel in Nickel sulphate was estimated as nickel dimethyl glyoxinate. All other chemicals used were of Analar grade. The study was made at pH - 4.0 using 0.001 percent triton-X-100 as maximum suppressor and KNO_3 as supporting electrolyte at a constant ionic strength ($\mu = 1M$).

A Cambridge (General purpose) polarograph in conjunction with S.C.E. was used for recording C-V curves by passing oxygen free nitrogen in a thermostated H-cell. The characteristics of the capillary used are

m=1.862 mg/sec, t=3.66 sec, $m^{2/3}t^{1/6}$ = 1.878 at h_{Hg} = 55 cms

To investigate the nature of the cathodic wave produced by Ni^{+2} in MBTAA media, the effects of change in mercury head, temperature and concentration of MBTAA on the wave height were studied with a view to recognise the characteristics of the waves. The conventional log plots of the reduction waves of Ni(II) in different concentrations of MBTAA yielded straight lines with slopes deviating considerably from the theoretical value expected for reversible process and thus revealing the irreversible nature of the waves. Therefore investigations were confined to the kinetic study of the electrode reaction.

The current at the end of drop life was recorded instead of average current, because the determination of kinetic parameters is based on the Koutecky's [7] calculations which are more accurately reproduced by measuring the maximum current [8].

Results and Discussion

Nickel ions in presence of methylene bis thio acetic acid produce single well defined irreversible cathodic waves in 1M KNO_3 as supporting electrolyte and 0.001 percent Triton-X-100 as maximum supressor at pH - 4.0 maintained by Clark's and Lub's buffer, at which subsequent studies were made.

Effect of pH, Hg pressure, temperature and concentration of methylene bis thio acetic acid

Polarograms of Ni^{+2} in MBTAA were recorded at different pH ranging from 1 - 7. It was obs ved that a single well defined cathodic wave was obtained at pH - 4.0. It was also seen that with the increase in pH, the $E_{1/2}$ values shifted towards more negative potentials showing the complex formation. The plots of i_d vs temperature and $h^{1/2}$ and concentrations of MBTAA are shown in Fig.1, curves 1,2 & 3. With increase in the height of Hg column, i_d changed linearly with $h^{1/2}$ (Fig.1, curve 2) and the values of $i_d/h^{1/2}$ were almost constant indicating the diffusion controlled nature of the waves which was further supported by the values of temperature coefficient of i_d.

Solutions of Ni^{2+} containing 0.1M [MBTAA] were polarographed at 25°, 30°, 35°, 40°, 45° and 50°C. It was observed that the $E_{1/2}$ was shifted

to more positive values (Fig.1, curve 1) (Table 2) with the rise in temperature showing the easier reduction of the complexes at elevated temperature which is in accordance with the irreversible nature of the electrode process [9,10].

Polarograms of solutions containing different concentrations of MBTAA (0.02M to 0.10M) showed that with the increase in [MBTAA], $E_{1/2}$ values shifted to more negative potentials (Table 1) revealing complex formation, whereas i_d decreases (Fig.1 curves 3) indicating that the aquo-nickel ions differ in size from their complexes with MBTAA.
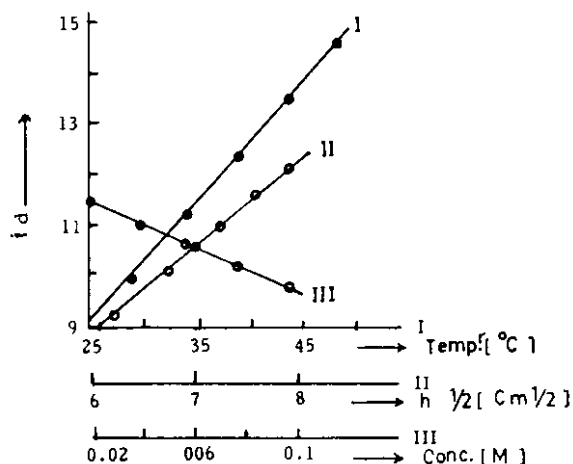

Fig. 1: Plots of i_d vs temperature, $h^{1/2}$ and concentrations of Ni^{+2}-MBTAA system.

Nature of complex

Since the polarographic waves were irreversible in the case of nickel ion, the classical method of Lingane [11] could not be used for studying the complex ion formation. Therefore, the method recommended by Tamamushi and Tanaka [12] and Meites [13] was employed using the following equations for irreversible reduction process.

Table-1:   Values of i_d, $E_{1/2}$, αn and $k^o_{f,h}$ at different concentrations of MBTAA for Ni^{+2} system at 30°C

[MBTAA]	$i_d(\mu A)$	$-E_{1/2}(V)$	αn	$k^o_{f,h}$ (cm/sec) x 10^{-6}
0.02	11.50	0.840	0.444	3.12
0.04	11.00	0.848	0.437	1.53
0.06	10.70	0.850	0.433	1.06
0.08	10.20	0.854	0.430	0.760
0.10	9.86	0.856	0.420	0.750

$$\frac{\Delta E_{\frac{1}{2}}}{\Delta \log C_X} = -j \cdot \frac{0.06014}{\alpha n} \qquad (1)$$

$$\frac{dE_{\frac{1}{2}}}{d(pH)} = -j \cdot \frac{0.06014}{\alpha n} \qquad (2)$$

where α is the fraction of the total applied potential and 'j' is the number of ligands bound to the metal. The value of $n\alpha$ is given by the equation

$$E_{3/4} - E_{1/4} = -\frac{0.0574}{\alpha n} \qquad (3)$$

The value of $\Delta E_{1/2}/\Delta \log C_X$ is determined from the slope of the plots of $\log C_X$ vs $E_{1/2}$, where C_X is the concentration of MBTAA. The value of 'j' thus obtained at different concentrations and pH's works out to be approximately 1 (in the range 0.95 - 1.12) showing thereby that one mole of MBTAA combines with one mole of nickel ion suggesting the formation of 1:1 complex.

nickel ion is chemically reduced straight to the metal at the d.m.e. [14]

$$Ni^{+2} + 2e^- \qquad\qquad Ni \text{ (metal)}.$$

The formation of 1:1 (M:L) complex may be represented as
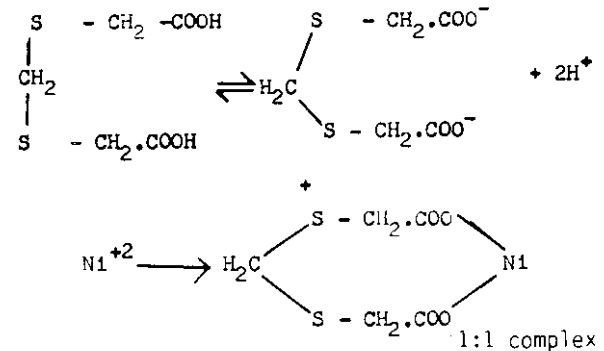
Kinetic Parameters

Since nickel reduces irreversibly at d.m.e. in MBTAA, the values of transfer coefficient (α) and formal rate constant ($k^o_{f,h}$) for the electrode reactions have been determined by Koutecky's method [7] as extended by Meites and Israel [8] using the following standard equations

$$E_{d.e} = E_{\frac{1}{2}} \frac{0.0542}{\alpha n} \quad \log \frac{i}{id - i} \qquad (4)$$

where

Table-2: Values of i_d, $E_{1/2}$, αn and $k^o_{f,h}$ at various temperatures [(MBTAA) = 0.1M]

Temp (°C)	i_d (μ A)	$-E_{1/2}$ (V)	αn	$k^o_{f,h}$(cm/sec) x 10^{-6}
25	9.14	0.860	0.413	0.736
30	9.84	0.856	0.418	0.752
35	11.21	0.852	0.423	0.816
40	12.38	0.846	0.430	0.844
45	13.50	0.840	0.433	0.949
50	14.50	0.836	0.437	0.992

$$E_{\frac{1}{2}} = -0.2412 + \frac{0.05915}{\alpha n} \log \frac{1.349\ k^o_{f,h} t^{\frac{1}{2}}}{D_o^{\frac{1}{2}}} \qquad (5)$$

and are recorded in Tables 1 and 2.

Effect of ligand concentration and temperature on αn *and* $k^o_{f,h}$

With increasing [MBTAA] (Table 1) αn is found to decrease, which implies [15] that transfer of electrons is made increasingly difficult, in other words, the electrode reduction of Nickel is rendered increasingly irreversible with increase in [MBTAA]. The decreasing values of $K_{f,h}$ also

indicate [16] the increased irreversibility of the reduction process.

A perusal of the values of αn and $k^o_{f,h}$ from Table 2 records an increase with the increase in temperature, thereby suggesting that electrode

reaction of Ni(II) tends to become less irreversible as the temperature is raised. The positive shift in $E_{1/2}$ values also lends support to this conclusion.

Thermodynamic functions

The enthalpy of activation (Δ H) for the electrode reaction has been calculated by equating the slope of log $k^o_{f,h}$ vs 1/T plot to $-\Delta H$

The free energy of activation (ΔG) can be determined by expliciting the value of $k^o_{f,h}$ on the basis of general principles of the absolute rate theory according to which

$$ko_{f,h} = \frac{kT}{h} \phi \exp \left[\frac{\Delta G}{RT}\right] \quad (6)$$

Where k = Boltzmann constant, h = Plank's constant, $\phi = 2.0$ x 10^{-8} cm and other terms have their usual meanings.

The entropy of activation (ΔS) calculated from the relation

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

The values of thermodynamic parameters at 30°C are as follows:

ΔG (Kcals/mol)	ΔH (Kcals/mole)	ΔS (cals/deg/mole)
6.75	1.22	-18.25

The positive value of free energy (ΔG) indicates that the reaction is endergonic [17] and the process does not occur spontaneously. The values of enthalpy (ΔH) being positive suggests that the complex formation is endothermic in nature. The negative ΔS values lends support to the irreversible nature of the electrode process.

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