Stability Constants and Thermodynamic Functions of Nickel II with Pyrrolidinone-2 : A Polarographic Study

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Pyrrolidinone-2 complexes of nickel were found to be irreversible polarographically. The values of the kinetic parameters, αn and $k^{\circ}_{f,h}$ have been calculated at different temperatures. The effect of temperature has been discussed in terms of the variations in the values of the kinetic parameters. The values of thermodynamic parameters have been calculated. The method of Ringbom and Erikson was used with Cd^{++} as indicator ion to study the nature of complexes.

In continuation of our earlier polarographic studies(1) on the complexation reaction of Cd(II) with pyrrolidinone-2, we report in this paper the results of studies on the behaviour of nickel-pyrrolidinone-2 system at the d.m.e. Nickel showed irreversible behaviour and therefore, Ringbom and Eriksson(2,3) ion indicator method was applied to calculate the stability constants using cadmium as indicator ion. Owing to the weakly basic nature of pyrrolidinone-2, strong complexation is not expected, but the polarographic behaviour of nickel ion in both the absence and presence of pyrrolidinone-2 was sufficiently distinct to indicate complex formation and to allow quantitative assessment of stability constants.

EXPERIMENTAL

Chemicals

All the chemicals used were of analytical grade and their stock solutions were prepared in conductivity water. Ionic strength was maintained constant with potassium nitrate. The pH of all the experimental solutions were maintained at 6.2 ± 0.05. Triton X-100 (Sigma) was used as maximum supressor.

APPARATUS AND PROCEDURES:

Polarograms in all instances were recorded at 20, 30, 40 and 50°C with a manual polarograph (Toshniwal CL02) in conjunction with polyflex galvanometer (Toshniwal PL 50) and pH were measured with an Elico pH meter. A SCE was used as the reference electrode. Purified nitrogen was used for deoxygeration. The dropping mercury electrode had the following characteristics:
m = 2.90 mg/sec, t = 2.9 sec, in open circuit. The number of electrons (n) involved in the reduction process was determined by millicoulometric method of De Vries and Kroon(4).

RESULTS AND DISCUSSION

A single well-defined diffusion-controlled wave appeared in each solution containing 0.05 mM of Ni (II) with varying amounts of ligand. The values of slope from conventional log plots showed the reduction to be irreversible. Hence indicator ion method of Ringbom and Eriksson(3) was applied with Cd^{++} as indicator ion to determine the step wise stability constants.

This technique involved in the determination of the half-wave potentials of the indicator ion over a wide range of ligand concentration in both the absence and the presence of the metal ion whose stability constants were required. Half-wave potential shifts of the indicator ion were smaller in the presence of added nickel ion than in its absence and served for the direct determination of the free ligand concentration. The ligand number, $\bar{n}$, of the metal-ligand system was given, at each value of the free ligand concentration by

$$\bar{n} = \frac{C_x - [X]}{C_m} \qquad \cdots (1)$$

Where C_x = Total ligand concentration
$[X]$ = Free ligand concentration
C_m = Concentration of the metal ion under study

Determination of the stability constants followed from a plot of the formation curve ($\bar{n}$ vs. log [X]) which was integrated graphically to give the Fronaeous(7) relation

$$F_o[x] = \exp \int_0^x \frac{\bar{n}}{x} d[x] \qquad \cdots (2)$$

The shifts in half-wave potential of 5×10^{-4} M Cd(II) in the presence of 0.1 M KNO_3 as a function of pyrrolidinone-2 concentration have been reported previously(1). The procedure was repeated in the presence of 0.05 M Ni (II). The $E_{1/2}$ data obtained are presented in Table 1. From this

data formation curve n vs pL was constructed. The data for this is presented in Table 2. The

TABLE 1

E DATA FOR THE CADMIUM-PYRROLIDINONE-2 SYSTEM IN THE ABSENCE AND PRESENCE OF 0.05 mM Ni (II)

[L]	-E vs. SCE Ni(II) absent volts	ΔE mV	-E vs. SCE Ni(II) present volts	ΔE mV
0.0	0.630	0	0.630	0
0.1	0.638	8	0.636	6
0.2	0.645	15	0.640	10
0.3	0.650	20	0.644	14
0.4	0.655	25	0.648	18
0.5	0.658	28	0.651	21
0.6	0.662	31	0.655	25
0.7	0.667	37	0.658	28
0.8	0.672	41	0.661	31

formation curve indicates the maximum co-ordination number 4 for nickel (II). Graphical integration of the curve was carried out by weighing area under the curve bounded by values of log [L] corresponding to a range of ligand

TABLE 2

FORMATION CURVE DATA OF Ni(II)-PYRROLIDINONE-2 SYSTEM

[L]	[L]	PL	n
0.05	0.035	1.456	0.3
0.1	0.065	1.187	0.7
0.2	0.115	0.939	1.7
0.3	0.180	0.745	2.4
0.4	0.260	0.585	2.8
0.5	0.330	0.482	3.4
0.6	0.415	0.382	3.7
0.7	0.495	0.279	4.1
0.8	0.595	0.237	4.1

concentration values. Values of F [L] were calculated from equation (2) using the fact that the residual integral is given by

$$\lim_{[L]\to 0} F\ [L] = \frac{1}{1-\bar{n}} \qquad \cdots(3)$$

Calculation of stability constants then followed in the normal way by graphical extrapolation. The data are being summarized in Table 3. Distributions of the various species as a function of ligand concentration were presented in Fig. 1.

The kinetic parameters were calculated by Koutechy's theoretical treatment as extended by Isreal and Meites(5). The value of αn was obtained by equating the slope of $E_{d,e}$ vs. $\log(i/i_d - i)$ plot to $-0.0542/\alpha n$ and intercept of the same plot giving $E_{1/2}$ was used to calculate $K^{\circ}_{f,h}$.

TABLE 3

DERIVED FUNCTIONS FOR NICKEL-PYRROLIDINONE SYSTEM

[Pyrrolidinone -2]	F	F [X]	F [X]	F [X]	F [X]
0.000	1.00	-	-	-	-
0.040	1.12	3.00	-	-	-
0.063	1.49	7.78	107	-	-
0.100	2.55	15.5	145	-	-
0.159	5.64	29.2	117	731	-
0.251	17.8	67.0	262	1043	-
0.398	80.5	199	499	1252	3145
0.501	196	380	774	1543	3079
0.631	501	793	1254	1986	3147
0.764	1288	1621	2049	2568	3233
	B = 1.5	B = 87.5	B = 685.0		B = 3180.0

The values of $k^{\circ}_{f,h}$ increases with temperature (Table 4). Shift in half-wave potential towards more positive value shows the easier reduction of the complex at higher temperature (Table 4) and is in accordance with the irreversible nature of the processes.

The enthalpy of activation $(\Delta H)^{\neq}$ for the electrode reaction has been calculated(6) by equating the slope of log $K^{\circ}_{f,h}$ vs. 1/T plot to $(-\Delta H^{\neq}/2.303\ R)$.

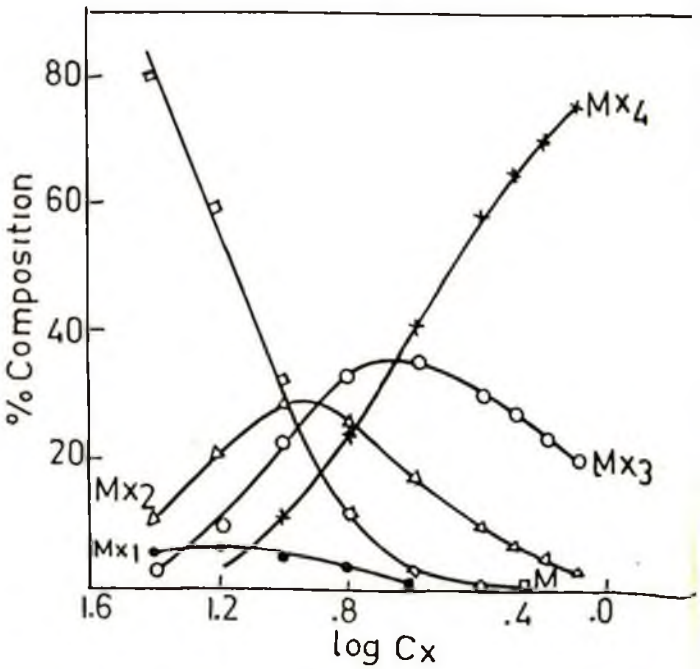


Fig. 1 Distribution diagram for nickel (II) - pyrrolidinone-2 system.

TABLE 4

KINETIC PARAMETERS AND THERMODYNAMIC FUNCTION

Temp °C	i (uA)	E vs SCE (V)	n	k° x 10 Cm/sec
20	8.60	1.165	0.417	0.335
30	9.01	1.008	0.437	2.40
40	10.0	0.970	0.452	3.41
50	10.71	0.962	0.459	42.8

The free energy of activation $(\Delta G)^{\neq}$ could be determined from following equation(7).

$$k^{\circ}_{f.h} = \frac{kT}{h}\,\phi\,/\exp\,\frac{(\Delta G^{\neq})}{RT}$$

Where k = Boltzman constant: h = plank's constant: $\phi = 2.0 \times 10^{-8}$ cm and other terms have their usual meaning. The entropy of activation $(\Delta S)^{\neq}$ was calculated from the relation

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

Entropy change is negative as must be the case with common ligands.

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