

POTENTIOMETRIC AND THERMODYNAMIC STUDY OF Ni(II) COMPLEXES OF THIOGLYCOLIC ACID IN 40% ETHANOL MEDIUM

Rakhi Methi*
Dr. Priyanka Mathur**

ABSTRACT

Nickel complexes of Thioglycolic acid have been investigated by potentiometric technique in 40% V/V ethanol. It was found that nickel forms colourless 1:2 complexes. The stability constant of the complexes formed have been determined by applying Calvin and Melchior's extension of Bjerrum's method at three different temperature. The values of $\log K_1$, $\log K_2$ at 298 K, 7.52, 4.65 at 303 K, and 8.13, 5.66 and at 308 K 8.26 and 5.78 respectively in 40% ethanol medium. There is no reference in the literature regarding the complexing tendency of thioglycolic acid with nickel ion in 40% aqueous-ethanol medium. Hence the present investigation has been initiated. The composition and stability constant of the complexes have been studied by potentiometric method. The value of thermodynamic parameters ΔG , ΔH , and ΔS have also been calculated. The values of overall changes in ΔG , ΔH and ΔS , at three different temperature accompanying the reaction have also been evaluated in 40% ethanol medium the values are $-47.1668 \text{ KJ mol}^{-1}$, $-32.8369 \text{ KJ mol}^{-1}$, $-0.261392 \text{ KJ mol}^{-1}$, $+154.801 \text{ J/K}$ and $+107.50 \text{ J/K}$ respectively.

Keywords: Thioglycolic Acid, Potentiometric Technique, V/V Ethanol, Thermodynamic Parameters.

Introduction

Methodology Materials

Thioglycolic acid S.D. fine A.R. (B.D.H) reagents $\text{Ni}(\text{NO}_3)_2$, NaOH etc. were used and their solutions were prepared in doubly distilled air free conductivity water. Freshly prepared solutions of the reagents were always used to avoid the effect of ageing.

Equipment's

A Systronics – 335 digital pH meter was used for measurements. A saturated calomel electrode and a wide range glass electrode were used for pH measurements and calibrated by using several buffer solutions of pH 4.0, 7.0 and 9.2. Thus the reading gave immediately concentration and not activities of $[\text{H}^+]$.

Procedure

Potentiometric Studies

The experimental procedure is similar to that described earlier. A series of potentiometric titration of thioglycolic acid with standard NaOH in the absence and presence of Ni^{+2} at various ligands to metal ratios viz, 1:1, 2:1,3:1 etc. were performed. Titrations were also carried out at different temperatures in 40% ethanol. For calculating the values of ΔG , ΔH , and ΔS accompanying the reaction, all the pH titration were performed in 40% V/V acetone. in 0.1M KNO_3 . The results of various titration have been recorded and the relevant curves have been given.

* Research Scholar, Bhagwant University, Ajmer, Rajasthan, India.
** Bhagwant University, Ajmer, Rajasthan, India.

The values of \bar{I} and free ligand concentration [A] calculated from the titrations of ligand in the absence and presence of nickel ion at ratios 5:1 with standard NaOH have also been tabulated together with the other results obtained.

The experimental observation and the results obtained have been tabulated on the following pages.

DETERMINATION OF STOICHIOMETRY POTENTIOMETRIC TITRATION OF TGA IN PRESENCE OF Ni²⁺ AT RATIOS (1) 1:0 (2) 1:1 (3) 2:1 IN 40% V/V ETHANOL MEDIUM WITH 0.1 M NaOH

- **M NaOH V/S 1x10⁻³ M TGA +0.1 M KNO₃ (1:0)**

Table 1

S.No.	Mole of NaOH per mole of ligand	pH
1	0.00	3.60
2	0.20	3.78
3	0.40	4.11
4	0.60	4.45
5	0.80	4.67
6	0.90	4.85
7	1.00	6.87
8	1.05	7.81
9	1.10	8.54
10	1.20	9.51
11	1.40	9.68
12	1.50	10.07
13	1.80	10.35
14	2.00	10.54

- **0.1 M NaOH V/S 1x10⁻³ M TGA +0.1 M KNO₃+ 1x10⁻³M (Ni²⁺) (1:1)**

Table 2

S.No.	Mole of NaOH per mole of ligand	pH
1	0.00	3.30
2	0.20	3.35
3	0.40	3.48
4	0.60	3.72
5	0.80	3.98
6	1.00	4.21
7	1.20	4.44
8	1.40	4.67
9	1.60	4.80
10	1.80	4.92
11	1.90	5.10
12	2.00	5.46
13	2.10	6.04
14	2.20	7.11
15	2.40	7.22
16	2.50	7.35
17	2.60	7.55
18	2.80	7.72
19	2.90	8.00
20	3.00	8.95
21	3.10	9.54
22	3.20	9.72
23	3.40	9.99
24	3.50	10.22

- **0.1 M NaOH V/S 1×10^{-3} M TGA + 0.1 M KNO_3 + 5×10^{-3} M (Ni^{2+}) (2:1)**

Table 3

S.No.	Mole of NaOH per mole of ligand	pH
1	0.00	3.35
2	0.20	3.48
3	0.40	3.64
4	0.60	3.85
5	0.80	4.30
6	1.00	4.60
7	1.20	4.90
8	1.40	5.16
9	1.50	5.70
10	1.60	6.05
11	1.80	6.34
12	1.90	6.80
13	2.00	7.10
14	2.10	8.05
15	2.20	8.99
16	2.40	9.45
17	2.50	9.89
18	2.60	10.10
19	2.80	10.34
20	3.00	10.60

- **0.1 M NaOH V/S 1×10^{-3} M TGA + 0.1 M KNO_3 + 5×10^{-4} M (Ni^{2+}) (2:1)**

Table 4

S.No.	Mole of NaOH per mole of ligand	pH
1	0.00	3.45
2	0.20	3.70
3	0.40	3.92
4	0.60	4.31
5	0.80	4.68
6	0.90	4.86
7	1.00	5.07
8	1.10	5.41
9	1.20	6.05
10	1.30	6.94
11	1.40	7.24
12	1.50	7.55
13	1.60	8.06
14	1.70	9.08
15	1.80	9.47
16	1.90	9.82
17	2.00	10.05
18	2.20	10.35
19	2.50	10.60

DETERMINATION OF STABILITY CONSTANT POTENTIOMETRIC TITRATION OF TGA IN THE PRESENCE OF Ni^{2+} AT RATIOS (1) 1:0 (2) 5:1 WITH 0.2 M NaOH IN 40% ETHANOL MEDIUM

Temperature – 25°C

- **0.2 M NaOH V/S 0.1 M KNO_3 + 2×10^{-3} M TGA + 4×10^{-3} M HClO_4 (1:0)**
- **0.2 M NaOH V/S 0.1 M KNO_3 + 2×10^{-3} M TGA + 4×10^{-3} M HClO_4 + 4×10^{-4} M (Ni^{2+}) (5:1)**

Table 5

S.No.	Mole of NaOH per mole of ligand	pH	
		Curve 1 (1:0)	Curve 2 (5:1)
1	0.00	3.26	3.26
2	0.20	3.30	3.30
3	0.40	3.36	3.36
4	0.60	3.40	3.40
5	0.80	3.55	3.55
6	1.00	3.56	3.56
7	1.20	3.68	3.68
8	1.40	3.77	3.77
9	1.60	3.80	3.80
10	1.80	3.99	3.99
11	2.00	4.10	4.10
12	2.20	4.58	4.58
13	2.40	4.87	4.87
14	2.60	4.95	4.95
15	2.80	5.46	5.46
16	2.90	6.30	5.80
17	2.95	7.36	5.92
18	3.00	8.90	6.00
19	3.05	9.45	6.92
20	3.10	9.65	7.47
21	3.20	10.20	8.16
22	3.30	10.46	9.18
23	3.40	10.66	10.16
24	3.50	-	10.70
25	3.60	10.92	10.85
26	3.80	11.40	11.10
27	4.00	-	11.40

Temperature – 30°C

- 0.2 M NaOH V/S 01. M KNO₃+ 4×10⁻³ M HClO₄ + 2×10⁻³ M TGA (1:0)
- 0.2 M NaOH V/S 01. M KNO₃+ 4×10⁻³ M HClO₄ + 2×10⁻³ M TGA + 4×10⁻⁴ M (Ni²⁺) (5:1)

Table 6

S.No.	Mole of NaOH per mole of ligand	pH	
		Curve 1 (1:0)	Curve 2 (5:1)
1	0.00	3.10	3.10
2	0.20	3.16	3.16
3	0.40	3.20	3.20
4	0.60	3.30	3.30
5	0.80	3.36	3.36
6	1.00	3.40	3.40
7	1.20	3.55	3.55
8	1.40	3.60	3.60
9	1.60	3.75	3.75
10	1.80	3.86	3.86
11	2.00	4.00	4.00
12	2.20	4.24	4.24
13	2.40	4.54	4.54
14	2.60	4.90	4.90
15	2.80	5.38	5.25
16	2.90	6.15	5.40
17	3.00	8.86	5.66

18	3.10	9.58	6.57
19	3.20	10.15	7.20
20	3.30	10.42	9.56
21	3.40	10.54	10.17
22	3.50	10.78	10.46
23	3.60	10.90	10.67
24	3.80	11.36	11.00
25	4.00	11.45	11.30

Temperature – 35°C

- 0.2 M NaOH V/S 01. M KNO₃+ 2×10⁻³ M HClO₄ + 2×10⁻³ M TGA (1:0)
- 0.2 M NaOH V/S 01. M KNO₃+ 4×10⁻³ M HClO₄ + 2×10⁻³ M TGA + 4×10⁻⁴ M (Ni²⁺) (5:1)

Table 7

S.No.	Mole of NaOH per mole of ligand	pH	
		Curve 1 (1:0)	Curve 2 (5:1)
1	0.00	3.30	3.20
2	0.20	3.25	3.25
3	0.40	3.30	3.30
4	0.60	3.36	3.36
5	0.80	3.40	3.40
6	1.00	3.56	3.56
7	1.20	3.60	3.60
8	1.40	3.66	3.66
9	1.60	3.75	3.75
10	1.80	3.92	3.92
11	2.00	4.08	4.08
12	2.20	4.20	4.20
13	2.40	4.50	4.50
14	2.60	4.84	4.84
15	2.80	5.32	5.06
16	2.90	6.08	5.20
17	3.00	8.70	5.52
18	3.10	9.50	6.00
19	3.20	10.10	6.96
20	3.30	10.35	9.70
21	3.40	10.48	10.17
22	3.60	10.84	10.55
21	3.80	11.28	10.90
22	4.00	11.45	11.20

DETERMINATION OF DISSOCIATION COSTANT pK_{a1} OF TGA IN AQUEOUS ETHANO FROM FIRST BUFFER REGION**Temperature – 25°C****Table 8**

S. No.	Mole of NaOH per mole of ligand	Stoichiometric Concentration			$\frac{[HA]}{[A]}$	$\frac{\log[HA]}{[A]}$	pK _{a1} = pH + $\log\frac{[HA]}{[A]}$
		pH	[HA]	[A]			
1	0.20	4.25	0.0016	0.0004	4.00	0.6021	4.8521
2	0.40	4.45	0.0012	0.0008	1.50	0.1761	4.6261
3	0.60	4.93	0.0008	0.0012	0.67	-0.1739	4.7561
4	0.80	5.58	0.0004	0.0016	0.25	-0.6021	4.9779

pK_{a1} = 4.8030

K_{a1} = 1.573×10⁻⁵

Temperature – 30°C**Table 9**

S. No.	Mole of NaOH per mole of ligand	Stoichiometric Concentration			$\frac{[HA]}{[A]}$	$\frac{\log[HA]}{[A]}$	$pK_{a_1} = pH + \log\frac{[HA]}{[A]}$
		pH	[HA]	[A]			
1	0.20	4.22	0.0016	0.0004	4.00	0.6021	4.8321
2	0.40	4.39	0.0012	0.0008	1.50	1.1761	4.5661
3	0.60	4.86	0.0008	0.0012	0.67	-0.1739	4.6861
4	0.80	5.50	0.0004	0.0016	0.25	-0.6021	4.8979

$$pK_{a_1} = 4.7455$$

$$K_{a_1} = 1.796 \times 10^{-5}$$

Temperature – 35°C**Table 10**

S. No.	Mole of NaOH per mole of ligand	Stoichiometric Concentration			$\frac{[HA]}{[A]}$	$\frac{\log[HA]}{[A]}$	$pK_{a_1} = pH + \log\frac{[HA]}{[A]}$
		pH	[HA]	[A]			
1	0.20	4.17	0.0016	0.0004	4.00	0.6021	4.7721
2	0.40	4.34	0.0012	0.0008	1.50	0.1761	4.5161
3	0.60	4.81	0.0008	0.0012	0.67	-0.1739	4.6361
4	0.80	5.44	0.0004	0.0016	0.25	-0.6021	4.8379

$$pK_{a_1} = 4.69055$$

$$K_{a_1} = 2.039 \times 10^{-5}$$

DETERMINATION OF pK_{a_2} FROM SECOND BUFFER REGION IN AQUEOUS ETHANOL**Temperature – 25°C****Table 11**

S. No.	Mole of NaOH per mole of ligand	Stoichiometric Concentration			$\frac{[HA]}{[A]}$	$\frac{\log[HA]}{[A]}$	$pK_{a_1} = pH + \log\frac{[HA]}{[A]}$
		pH	[HA]	[A]			
1	0.20	10.16	0.0016	0.0004	4.00	0.6021	10.7621
2	0.40	10.62	0.0012	0.0008	1.50	0.1761	10.7961
3	0.60	10.96	0.0008	0.0012	0.67	-0.1739	10.7861
4	0.80	11.36	0.0004	0.0016	0.25	-0.6021	10.7579

$$pK_{a_2} = 10.77555$$

$$K_{a_2} = 1.676 \times 10^{-11}$$

Temperature – 30°C**Table 12**

S. No.	Mole of NaOH per mole of ligand	Stoichiometric Concentration			$\frac{[HA]}{[A]}$	$\frac{\log[HA]}{[A]}$	$pK_{a_1} = pH + \log\frac{[HA]}{[A]}$
		pH	[HA]	[A]			
1	0.20	10.14	0.0016	0.0004	4.00	0.6021	10.7421
2	0.40	10.52	0.0012	0.0008	1.50	0.1761	10.6961
3	0.60	10.89	0.0008	0.0012	0.67	-0.1739	10.7161
4	0.80	11.30	0.0004	0.0016	0.25	-0.6021	10.6979

$$pK_{a_2} = 10.71305$$

$$K_{a_2} = 1.936 \times 10^{-11}$$

Temperature – 35°C

Table 13

S. No.	Mole of NaOH per mole of ligand	Stoichiometric Concentration			$\frac{[HA]}{[A]}$	$\frac{\log[HA]}{[A]}$	$pK_{a1} = pH + \log\frac{[HA]}{[A]}$
		pH	[HA]	[A]			
1	0.20	10.12	0.0016	0.0004	4.00	0.6021	10.7221
2	0.40	10.42	0.0012	0.0008	1.50	0.1761	
3	0.60	10.83	0.0008	0.0012	0.67	-0.1739	10.6561
4	0.80	11.24	0.0004	0.0016	0.25	-0.6021	10.6279

$$pK_{a2} = 10.65055$$

$$K_{a2} = 2.235 \times 10^{-11}$$

SUMMARY OF DISSOCIATION COSTANT OF TGA IN AQUEOUS ETHANOL AT DIFFERENT TEMPERATURE

Table 14

Temperature – 25°C

S. No.	Temperature	Dissociation Constants of TGA	
		K_{a1}	K_{a2}
1	25° C	1.573×10^{-5}	1.676×10^{-11}
2	30° C	1.796×10^{-5}	1.936×10^{-11}
3	35° C	2.039×10^{-5}	2.235×10^{-11}

VALUE OF \bar{n} AND $-\log[A]$ AT DIFFERENT pH VALUE CORRESPONDING TO (FIG – II – 2) IN 40% ETHANOL

Temperature – 25°C

Table 15

S. No.	pH	Concentration of Ligand Bound $\times 10^{-3}$	\bar{n}	$-\log[A]$
1	5.7	0.10	0.250	7.86
2	5.8	0.15	0.375	7.73
3	6.0	0.20	0.500	7.56
4	6.2	0.25	0.625	7.37
5	6.4	0.30	0.750	7.17
6	6.5	0.35	0.875	6.88
7	7.2	0.40	1.000	6.39
8	8.2	0.45	1.125	5.48
9	8.4	0.50	1.250	5.22
10	8.6	0.55	1.375	5.03
11	9.0	0.60	1.500	4.65

VALUE OF \bar{n} AND $-\log[A]$ AT DIFFERENT pH VALUE CORRESPONDING TO IN 40% ETHANOL
Temperature – 30°C

Table 16

S. No.	pH	Concentration of Ligand Bound $\times 10^{-3}$	\bar{n}	$-\log[A]$
1	5.2	0.10	0.250	8.39
2	5.4	0.20	0.500	8.17
3	5.5	0.25	0.625	8.06
4	5.8	0.30	0.750	7.74
5	6.2	0.35	0.875	7.33
6	6.5	0.40	1.000	7.04

7	6.8	0.45	1.125	6.75
8	7.0	0.50	1.250	6.56
9	7.5	0.55	1.375	6.07
10	8.0	0.60	1.500	5.59

VALUE OF \bar{n} AND $-\log[A]$ AT DIFFERENT pH VALUE CORRESPONDING TO (FIG – II – 4), IN 40% ETHANOL

Temperature – 35°C

Table 17

S.No.	pH	Concentration of Ligand Bound $\times 10^{-3}$	\bar{n}	$-\log[A]$
1	5.00	0.10	0.250	8.57
2	5.20	0.20	0.500	8.34
3	5.40	0.25	0.625	8.11
4	5.70	0.30	0.750	7.76
5	6.20	0.35	0.875	7.27
6	6.40	0.40	1.000	7.06
7	6.50	0.45	1.125	6.99
8	6.80	0.50	1.250	6.76
9	7.50	0.55	1.375	6.01
10	7.80	0.60	1.500	5.73

SUMMARY OF $\log K_1$, $\log K_2$, K_1 , K_2 & $[A]_{\bar{n}-1/2}$, $[A]_{\bar{n}-3/2}$ IN 40% ETHANOL MEDIUM AT DIFFERENT TEMPERATURE

Table 18

S. N.	Temp.	$\log K_1$	$\log K_2$	K_1	K_2	$[A]_{\bar{n}-1/2}$	$[A]_{\bar{n}-3/2}$
1	25°C	7.56	4.65	3.630×10^7	4.46×10^4	2.705×10^{-8}	2.206×10^{-5}
2	30°C	8.17	5.59	5.011×10^8	3.89×10^5	0.6705×10^{-8}	2.551×10^{-6}
3	35°C	8.34	5.73	2.187×10^8	5.37×10^5	0.45×10^{-8}	1.8599×10^{-6}

DETERMINATION OF STABILITY CONSTANT BY LEAST SQUARE METHOD IN 40% ETHANOL AT DIFFERENT TEMPERATURE

Temperature – 25°C

Table 19

S. No.	pH	\bar{n}	$[A]$	$Y = \frac{\bar{n}}{(\bar{n}-1)[A]}$	$X = \frac{(2-\bar{n})[A]}{(\bar{n}-1)}$	$X^2 \times 10^{-16}$	XY
1	5.7	0.25	1.350×10^{-8}	-0.2475×10^8	-3.140×10^{-8}	9.850	0.777
2	5.8	0.375	1.690×10^{-8}	-0.355×10^8	-4.3936×10^{-8}	19.303	1.560
3	6.0	0.50	2.70×10^{-8}	-0.3703×10^8	-8.10×10^{-8}	65.610	2.99
4	6.2	0.625	0.426×10^{-7}	-3.9086×10^7	-1.563×10^{-7}	244.00	6.109
5	6.4	0.75	0.664×10^{-7}	-4.6873×10^7	-3.32×10^{-7}	1102.00	15.56
6	6.5	0.875	0.818×10^{-6}	-8.561×10^6	-7.362×10^{-6}	541900.00	63.02
7	8.2	1.125	0.3922×10^{-5}	22.959×10^5	2.744×10^{-5}	7529000.00	62.99
8	8.4	1.25	0.6005×10^{-5}	8.327×10^5	1.80×10^{-5}	3240000.00	14.98
9	8.6	1.375	0.918×10^{-5}	3.9970×10^5	1.528×10^{-5}	2334000.00	6.107
10	9.0	1.50	2.20×10^{-5}	1.36×10^5	2.220×10^{-5}	4840000.00	2.992

$$\begin{aligned} \Sigma xy &= 177.085 a & &= 279.77 \times 10^5 \\ \Sigma y &= -1.881.47 \times 10^5 & b &= 122.64 \times 10^{10} \\ \Sigma x &= 7.471 \times 10^{-5} & \log K_1 &= 7.44 \\ \Sigma x^2 &= 18.486 \times 10^{-10} & \log K_2 &= 4.64 \\ n &= 10 & \log \beta &= 12.08 \end{aligned}$$

DETERMINATION OF STABILITY CONSTANT BY LEAST SQUARE METHOD IN 40% ETHANOLAT DIFFERENT TEMPERATURE

Temperature – 30°C

Table 20

S. No.	pH	\bar{n}	[A]	$Y = \frac{\bar{n}}{(\bar{n}-1)[A]}$	$X = \frac{(2-\bar{n})[A]}{(\bar{n}-1)}$	$X^2 \times 10^{-16}$	XY
1	5.2	0.25	0.402×10^{-8}	-0.830×10^8	-0.938×10^{-8}	879.00	0.778
2	5.4	0.50	0.670×10^{-8}	-1.490×10^8	-2.01×10^{-8}	4.04	2.99
3	5.5	0.625	0.854×10^{-8}	-1.951×10^8	-3.13×10^{-8}	9.29	6.10
4	5.8	0.75	1.793×10^{-8}	-1.674×10^8	-8.96×10^{-8}	80.28	14.99
5	6.2	0.875	0.460×10^{-7}	-15.21×10^7	-4.14×10^{-7}	1713.00	62.96
6	6.8	1.125	1.770×10^{-7}	5.090×10^7	12.38×10^{-7}	15326.00	63.01
7	7.0	1.25	2.720×10^{-7}	1.838×10^7	8.16×10^{-7}	6658.00	14.99
8	7.5	1.375	0.8358×10^{-6}	4.387×10^6	1.392×10^{-6}	19370.00	6.166
9	8.0	1.50	2.551×10^{-6}	1.176×10^6	2.551×10^{-6}	65070.00	2.999

$\Sigma xy = 174.914 a = 1.190 \times 10^8$
 $\Sigma x = 534.82 \times 10^{-8} \quad b = 0.00750 \times 10^{16}$
 $\Sigma y = -6.7165 \times 10^8 \quad \log K_1 = 8.07$
 $\Sigma x^2 = 108231.98 \times 10^{-16} \quad \log K_2 = 5.80$
 $n = 9 \quad \log \beta = 13.87$

DETERMINATION OF STABILITY CONSTANT BY LEAST SQUARE METHOD IN 40% ETHANOLAT DIFFERENT TEMPERATURE

Temperature – 35°C

Table 21

S. No.	pH	\bar{n}	[A]	$Y = \frac{\bar{n}}{(\bar{n}-1)[A]}$	$X = \frac{(2-\bar{n})[A]}{(\bar{n}-1)}$	$X^2 \times 10^{-16}$	XY
1	5.0	0.25	2.60×10^{-9}	-0.1282×10^9	-6.06×10^{-9}	0.3672	0.777
2	5.2	0.50	0.453×10^{-8}	-2.210×10^8	-1.358×10^{-8}	1.844	3.001
3	5.4	0.625	0.768×10^{-8}	-2.170×10^8	-2.816×10^{-8}	7.929	6.110
4	5.7	0.75	1.629×10^{-8}	-1.842×10^8	-8.144×10^{-8}	66.324	15.00
5	6.2	0.875	0.534×10^{-7}	-13.11×10^7	-4.806×10^{-7}	239.76	63.00
6	6.5	1.125	1.017×10^{-7}	8.851×10^7	7.118×10^{-7}	5066.59	63.00
7	6.8	1.25	1.98×10^{-7}	2.525×10^7	5.94×10^{-7}	3528.00	14.99
8	7.5	1.375	0.965×10^{-6}	3.808×10^6	1.608×10^{-6}	25850.00	6.123
9	7.8	1.50	1.8599×10^{-6}	1.614×10^6	1.859×10^{-6}	34558.00	3.000

$\Sigma xy = 175.00 \quad a = 1.3287 \times 10^8$
 $\Sigma x = 416.296 \times 10^{-8} \quad b = 0.01012 \times 10^{16}$
 $\Sigma y = -7.623 \times 10^8 \quad \log K_1 = 8.12$
 $\Sigma x^2 = 71388.91 \times 10^{-16} \quad \log K_2 = 5.88$
 $n = 9 \quad \log \beta = 14.00$

SUMMARY OF STABILITY CONSTANT CALCULATED BY LEAST SQUARE METHOD IN 40% ETHANOLAT DIFFERENT TEMPERATURE

Table 22

S. No.	Temp.	log K ₁	log K ₂	Log β
1	25° C	7.44	4.64	12.08
2	30° C	8.07	5.80	13.87
3	35° C	8.12	5.88	14.00

**SUMMARY OF STABILITY CONSTANT CALCULATED BY SCHRODER'S COVERGENCE
FORMULAS METHOD IN 40% ETHANOL**

Table 23

S. No.	Temp.	log K ₁	log K ₂	Log β
1	25° C	7.56	4.66	12.22
2	30° C	8.17	5.60	13.77
3	35° C	8.34	5.74	14.08

**SUMMARY OF STABILITY CONSTANT CALCULATED BY DIFFERENT METHODS IN 40%
ETHANOLAT DIFFERENT TEMPERATURE**

Table 24

S. No.	Method	25° C			30° C			35° C		
		log K ₁	log K ₂	log β	log K ₁	log K ₂	log β	log K ₁	log K ₂	log β
1	Extension of Bjerrum's	7.56	4.65	12.21	8.17	5.59	13.76	8.34	5.73	14.07
2	Least Square	7.44	4.64	12.08	8.07	5.80	13.87	8.12	5.88	14.00
3	Schroder's Convergence formula	7.56	4.66	12.22	8.17	5.60	13.77	8.34	5.74	14.08
	Mean Value	7.52	4.65	12.17	8.13	5.66	13.80	8.26	5.78	14.05

VALUE OF 1/T AND LOG β IN 40% ETHANOL CORRESPONDING

Table 25

S. No.	Temperature K	1/T × 10 ⁻³	Log β
1	298	3.356	12.17
2	303	3.300	13.80
3	308	3.247	14.05

Summary

Nickel complexes of thioglycolic acid have been investigated by potentiometric technique in aqueous 40% V/V ethanol. It was found that Nickel ions form colourless 1:2 complexes. The stability constants of the complexes formed have been determined by applying Calvin and Melchior's extension of Bjerrum's method at three different temperature and were further refined by alternative methods (least square treatment: convergence formula of successive approximation). The values of log K₁, and log K₂ computed by alternative method at 25°C, 30°C, and 35°C have been found to be 7.31, 4.48, 7.43, 4.62, 7.57, 4.87, and in 40% the values are 7.52, 4.65, (at 25°C), 8.13, 5.56 (at 30°C), 8.26, 5.78, (at 35°C).

The value of the overall changes in ΔG_1 , ΔG_2 , ΔH , ΔS_1 , ΔS_2 accompanying the reaction have also been evaluated at 30° C. The values are -47.1668 KJ mol⁻¹, -32.8369 KJ mol⁻¹ -0.26139 KJ mol⁻¹ +154.801 J/K and +107.50 J/K in 40% ethanol medium.

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