Chemistry Research Journal, 2020, 5(2):195-201

Available online www.chemrj.org

Research Article

ISSN: 2455-8990
CODEN(USA): CRJHA5

Potentiometric Study of Ni(II)-Thiosemicarbazone Systems in Micellar Medium

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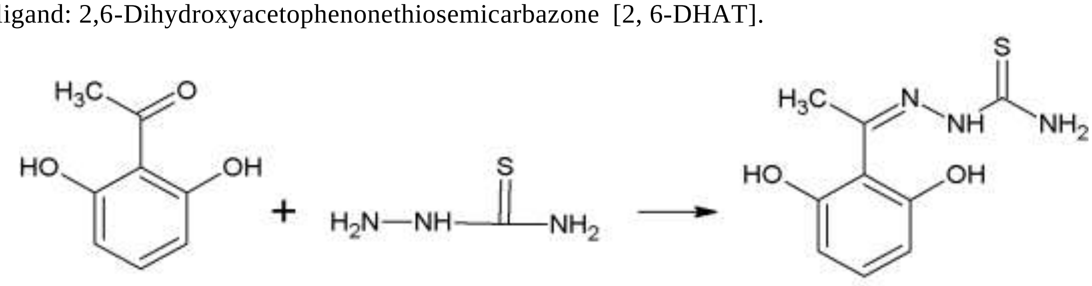
Abstract Ligand 2,6-Dihydroxyacetophenonethiosemicarbazone [2, 6 DHAT] has been synthesized. The present work describes the synthesis, characterization, solution, and biological investigations on Ni (II)-thiosemicarbazone complexes. Solution studies on the complexes have also been carried out in different micellar [HTAB, SDS, TX-100] systems at 25°C and data have been compared with ethanol water mixture. Stability constants and molar ions in 60% ethanol were determined. Proton ligand stability constant and metal-ligand stability have been determined potentiometrically.

Keywords Thiosemicarbazone, stability constant, micellar

1. Introduction

Thiosemicarbazones have been the subject of studies not only for coordination chemistry reasons, but for pharmacological as well, due to their good complexing properties and significant biological activity [1]. Thiosemicarbazones have attracted a crescent interest in recent years due to their biological properties, such as antiviral, antibacterial, anti-malarial, antifungal and antitumoral activities [2]. The research on coordination chemistry and analytical applications of thiosemicarbazones and its metallic derivatives has increased considerably [3].

In this paper we are reporting the synthesis and stability constant of Ni (II) complexes with thiosemicarbazide based ligand: 2,6-Dihydroxyacetophenonethiosemicarbazone [2, 6-DHAT].



2, 6-Dihydroxyacetophenone Thiosemicarbazide 2,6-Dihydroxyacetophenonethiosemicarbazone

Synthesis of ligands

Materials

All the chemicals used were of AR grade and procured from Himedia. Metal salt were purchased from E. Merck and were used as received. All solvent used were of standard/spectroscopic grade. Ligand 2, 6-DHAT was synthesized by condensation reaction of thiosemicarbazide with acetophenone in presence of methanol according to the literature [4].

Metal-ligand complexes were formed by potentiometrically.

All biological activities have been carried out by disc diffusion method under horizontal laminar.

Metal ligand complexes were formed by potentiometric titrations. Ligands and metal complexes were analyzed by TLC method.

Procedure

Potentiometric titration:

pH metric studies has been done with the help of pH meter (pH meter 802). The pH meter was switched on half an hour before begin the titrations. Instrument was calibrated with aqueous standard buffer solution of pH 4.0, 7.0, 9.0 prepared from buffer tablets. The experiment procedure involved the titration of

Solution (i): 1.00 ml HNO_3 *(0.004 M) + 5 ml* KNO_3 *(0.1 M*)

Solution (ii): Solution (i) + 1.25 ml of ligand (0.0005M) and

Solution (iii): Solution (ii) + 0.625 ml of $NiCl_2 . nH_2O$ (0.00025 M)

Volume of all these reaction mixtures was made up to 25 ml using 60% ethanol. For the titration in micellar system, 1.20 ml (5 mmol) of TX-100, 2.25 ml (5 mmol) of SDS and 2.0 ml of HTAB (5 mmol) were added separately in each set of the above reaction mixtures before making up the volume. The reaction mixtures of ethanol and water – ethanol (1:1) solutions were also prepare. The reaction mixtures were titrated individually against standard 0.05 M KOH.

After each addition of a certain amount of alkali to the the reaction mixture the change in the pH of the solution is measured. The graphs were plotted against values of pH and volume of alkali added. Using Irving and Rossotti stability constants of the metal ligand complexes were calculated from the titration curves.

Result and Discussion

Potentiometric titration:

Proton-ligand stability constants (pK)

The proton–ligand formation curves were estimated by plotting graphs between the values $(\bar{n}_A)$ Vs pH readings. The pK values were obtained from formation curve by noting the pH at which $(\bar{n}_A)$ = 0.5 and $(\bar{n}_A)$= 1.5. The proton-ligand formation number $(\bar{n}_A)$ were calculated by Irving and Rossotti expression [5]. The result indicated that the ligand was mono dissociable.

$$\bar{n}_A = Y - \frac{(V_L - V_a)(N + E^0)}{(V_0 + V_a)T_L} \quad (1)$$

Where, V^0 = Initial volume of solution (25 ml), E^0 = Initial concentration of free acid (HNO_3), Y= Number of dissociable protons from ligand, T_L is concerntration of ligand in solution, (V_L–V_a) = Volume of alkali (KOH) consumed by acid and ligand on the same pH [6].

Metal ligand stability constant (logK):

The average number of metal ions associated with the ligand $(\bar{n})$ at different pH values was estimated from the curve plotted between n- and pH. Metal ligand stability constant (logK) were obtained by the half integral method by plotting graph between $(\bar{n})$ vs. pL.

$$\bar{n} = \frac{(V_M - V_L)(N + E^0)}{(V_0 + V_L)\bar{n}_A T_m} \quad (2)$$

$$pL = \log_{10}\left[\frac{\sum_{n=0}^{n=J} \beta_n^H (\text{antilog}\, pH)}{T_L - \bar{n} T_M} \cdot \frac{V_0 + V_M}{V_0}\right] \quad (3)$$

Where N, E^0, V^0 and V_L have same significance as in equation (1), V_M is the volume of KOH added in the metal ions titration to attain the given pH reading and T_M total concentration of metal present in solution. log $K_1$and logK_2 were calculated from the formation curve by the known value of pL at which ($\bar{n}$) =0.5 and ($\bar{n}$) =1.5 corresponding to the values of logK_1 and logK_2, respectively. The value of logK_1 and logK_2 also determine in different miceller systems [7 -11].

Table 1: The $\bar{n}_A$ and pH values of Ligand 2,6 DHAT in Alc. + water and Alcohol

Sr. No.	pH	Alcohol $\bar{n}_A$	**Sr. No.**	pH	Alcohol $\bar{n}_A$
1	4.4	1.0647974	1	4.4	1.095021
2	4.65	1.0604655	2	4.65	1.056102
3	4.9	1.0388613	3	4.9	1.099281
4	5.15	1.0129507	4	5.15	1.090633
5	5.4	1.0172662	5	5.4	1.077667
6	5.65	1.0129486	6	5.65	1.07334
7	5.9	1.0086317	7	5.9	1.064699
8	6.15	1.0086314	8	6.15	1.069007
9	6.4	1.0043153	9	6.4	1.073314
10	6.65	1.0086303	10	6.65	1.073311
11	6.9	1.00863	11	6.9	1.068993
12	7.15	1.0043146	12	7.15	1.068988
13	7.4	1.0043145	13	7.4	1.068985
14	7.65	1.0086286	14	7.65	1.064668
15	7.9	1.0043138	15	7.9	1.064663
16	8.15	1.0043136	16	8.15	1.06466
17	8.4	1.0043134	17	8.4	1.060345
18	8.65	1.0043131	18	8.65	1.060342
19	8.9	1.0043126	19	8.9	1.060338
20	9.15	1.0129357	20	9.15	1.060333
21	9.4	1.0129341	21	9.4	1.056019
22	9.65	1.0129326	22	9.65	1.047395
23	9.9	1.0129305	23	9.9	1.051701
24	10.15	1.0301676	24	10.15	1.043078
25	10.4	1.034469	25	10.4	1.064611
26	10.65	1.0473816	26	10.65	1.090449
27	10.9	1.0602919	27	10.9	1.129197
28	11.15	1.0387282	28	11.15	1.180847
29	11.4	0.9785211	29	11.4	1.197999
			30	11.65	1.344223
			31	11.9	1.399889
			32	12.15	1.502505

Table 2: The $\overline{n}_A$ and pH values of Ligand 2,6 DHAT in HTAB, SDS and TX-100 medium

Sr. No.	HTAB		Sr. No.	SDS		Sr. No.	TX-100	
	pH	$\overline{n}_A$		**pH**	$\overline{n}_A$		**pH**	$\overline{n}_A$
1	pH	$\overline{n}_A$	1	4.4	1.0950362	1	4.15	1.1856857
2	4.4	1.1814037	2	4.65	1.0950096	2	4.4	1.1553708
3	4.65	1.1683722	3	4.9	1.0993004	3	4.65	1.1466981
4	4.9	1.1640157	4	5.15	1.0733696	4	4.9	1.1294033
5	5.15	1.1510369	5	5.4	1.0215681	5	5.15	1.1423266
6	5.4	1.1380633	6	5.65	1.0129393	6	5.4	1.1380026
7	5.65	1.1250949	7	5.9	1.017251	7	5.65	1.1423039
8	5.9	1.120762	8	6.15	1.017251	8	5.9	1.1466044
9	6.15	1.1207523	9	6.4	1.0172496	9	6.15	1.155222
10	6.4	1.1250599	10	6.65	1.0215621	10	6.4	1.1552096
11	6.65	1.1250499	11	6.9	1.0215603	11	6.65	1.1595082
12	6.9	1.1293568	12	7.15	1.0301845	12	6.9	1.1638127
13	7.15	1.1336634	13	7.4	1.0215586	13	7.15	1.1637931
14	7.4	1.1250249	14	7.65	1.0301821	14	7.4	1.16378
15	7.65	1.129331	15	7.9	1.0344924	15	7.65	1.1723932
16	7.9	1.1293207	16	8.15	1.034491	16	7.9	1.1766889
17	8.15	1.133626	17	8.4	1.0388008	17	8.15	1.1766748
18	8.4	1.1336154	18	8.65	1.0387977	18	8.4	1.1852857
19	8.65	1.1292949	19	8.9	1.0474195	19	8.65	1.1852635
20	8.9	1.1292845	20	9.15	1.0517283	20	8.9	1.1852487
21	9.15	1.1292742	21	9.4	1.0560367	21	9.15	1.1938572
22	9.4	1.1249501	22	9.65	1.0560322	22	9.4	1.1981493
23	9.65	1.1249402	23	9.9	1.0689628	23	9.65	1.2196698
24	9.9	1.1206223	24	10.15	1.0689573	24	9.9	1.2584144
25	10.15	1.1162958	25	10.4	1.0775769	25	10.15	1.3272988
26	10.4	1.137832	26	10.65	1.0603208	26	10.4	1.4177033
27	10.65	1.146429	27	10.9	1.0602991	27	10.65	1.8866571
28	10.9	1.1593429	28	11.15	1.0731999			
29	11.15	1.1593111	29	11.4	1.142043			
30	11.4	1.249711	30	11.65	1.4346163			
31	11.65	1.3614919						

Table 3: The $\overline{n}$ And pL values of Ligand 2,6 DHAT with Ni (II) in Alc.+water

Sr. No.	pH	pL	$\overline{n}$
1	4.4	4.317904	0.0486834
2	4.65	4.0754792	0.0651633
3	4.9	3.8490238	0.1163793
4	5.15	3.6245388	0.170468
5	5.4	3.382455	0.1867044
6	5.65	3.1494938	0.2215734
7	5.9	2.9170122	0.2567353
8	6.15	2.6800324	0.2823977
9	6.4	2.4573701	0.3351502
10	6.65	2.2294504	0.3764855
11	6.9	2.0028448	0.4192513
12	7.15	1.7634256	0.4382036
13	7.4	1.5182767	0.446778
14	7.65	1.2720936	0.4534041
15	7.9	1.0281056	0.463888
16	8.15	0.7879683	0.4810499
17	8.4	0.5429524	0.4896206
18	8.65	0.3030037	0.50676

Table 4: The $\overline{n}$ And pL values of Ligand 2,6 DHAT with Ni (II) in Alcohol

Sr. No.	pH	pL	$\overline{n}$
1	4.4	4.6317035	0.5127643
2	4.65	4.4277109	0.5884222
3	4.9	4.2130719	0.6439791
4	5.15	4.0083186	0.7122966
5	5.4	3.7751166	0.7367094
6	5.65	3.5216264	0.7315221
7	5.9	3.2701133	0.7292096
8	6.15	3.0071669	0.7100751
9	6.4	2.7445155	0.6910971
10	6.65	2.494533	0.6910714
11	6.9	2.2518008	0.701875
12	7.15	2.0018349	0.7018225
13	7.4	1.7518519	0.7017963
14	7.65	1.5037544	0.7045855
15	7.9	1.2537881	0.7045327
16	8.15	1.0038051	0.7045063
17	8.4	0.7612408	0.7154472
18	8.65	0.5168062	0.72355

Table 5: The $\overline{n}$ And pL values of Ligand 2,6 DHAT with Ni (II) in HTAB

Sr. No.	pH	pL	$\overline{n}$
1	4.4	4.3838283	0.2475556
2	4.65	4.1364091	0.2523364
3	4.9	3.9036165	0.2860717
4	5.15	3.6811452	0.3390768
5	5.4	3.445646	0.3661844
6	5.65	3.2106207	0.3937265
7	5.9	2.9760698	0.4217296
8	6.15	2.7456823	0.4566596
9	6.4	2.4973005	0.4592255
10	6.65	2.2661777	0.49199
11	6.9	2.0245945	0.5062947
12	7.15	1.7878444	0.5286145
13	7.4	1.5551936	0.5574828
14	7.65	1.3188355	0.5796795
15	7.9	1.0789897	0.5959634
16	8.15	0.8480056	0.6260398
17	8.4	0.6137049	0.650382
18	8.65	0.3850631	0.6828497

Table 6: The $\overline{n}$ And pL values of Ligand 2,6 DHAT with Ni (II) in SDS

Sr. No.	pH	pL	$\overline{n}$
1	4.4	4.3799495	0.1814662
2	4.65	4.1416504	0.2050833
3	4.9	3.8876871	0.1963708
4	5.15	3.6518748	0.2251675
5	5.4	3.4286781	0.2786879
6	5.65	3.1974183	0.3150923
7	5.9	2.964608	0.3476486
8	6.15	2.7373584	0.3900448
9	6.4	2.5107617	0.432407
10	6.65	2.2740215	0.4559099
11	6.9	2.0336896	0.4727585
12	7.15	1.7863074	0.4771723
13	7.4	1.5582528	0.5149289
14	7.65	1.3107344	0.5189893
15	7.9	1.0743974	0.541813
16	8.15	0.8446482	0.5751331
17	8.4	0.603481	0.5893248
18	8.65	0.3690934	0.6141787
	8.9	0.2202647	0.7655196

Table 7: The $\overline{n}$ And pL values of Ligand 2,6 DHAT with Ni (II) in TX-100

Sr. No.	pH	pL	$\overline{n}$
1	4.15	4.413658	0.28734
2	4.4	4.137231	0.234151
3	4.65	3.902025	0.263626
4	4.9	3.653779	0.266852
5	5.15	3.408091	0.275159
6	5.4	3.153406	0.265693
7	5.65	2.90295	0.264574
8	5.9	2.648356	0.255232
9	6.15	2.402023	0.262375
10	6.4	2.156225	0.270553
11	6.65	1.910989	0.279878
12	6.9	1.677944	0.312793
13	7.15	1.450388	0.355372
14	7.4	1.22812	0.406608
15	7.65	1.005926	0.456379
16	7.9	0.770199	0.481235
17	8.15	0.540794	0.516527
18	8.4	0.309358	0.54755
19	8.65	0.124914	0.652442

Conclusion

The values of log K are greater than zero, which exhibits the formation of metal ligand complexes by potentiometrically.

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