International Journal of Trend in Scientific Research and Development (IJTSRD)
Volume 7 Issue 4, July-August 2023 Available Online: www.ijtsrd.com e-ISSN: 2456 – 6470

Conductometric Investigations on Ni (II)-Thiosemicarbazone Systems

Uma Rathore

GCRC, PG Department of Chemistry, Govt. Dungar College
(NAAC 'A' Grade), MGS University, Bikaner, Rajasthan, India

ABSTRACT

The therapeutic importance of thiosemicarbazone group containing ligands has promoted the selection of this class of ligands and their complexes for the study. This paper describes the conductometric investigations on few Ni (II)- thiosemicarbazone complexes. The conductometric studies have been carried out in doubly distilled water, Triton X-100 and Brij-35 mediums. Association constants and formation constants have been computed and different types of stoichiometry [M : L] have been observed for metal-ligand complexes as; 1: 2, 1: 3, 1: 4 etc.

KEYWORDS: *Ni (II)-Thiosemicarbazone, association constants, formation constants, Triton X-100*

How to cite this paper: Uma Rathore "Conductometric Investigations on Ni (II)-Thiosemicarbazone Systems" Published in International Journal of Trend in Scientific Research and Development (ijtsrd), ISSN: 2456-6470, Volume-7 | Issue-4, August 2023, pp.688-692, URL: www.ijtsrd.com/papers/ijtsrd59751.pdf

IJTSRD59751

INTRODUCTION

Thiosemicarbazone and their metal complexes have a great verity of biological activity. Medicinal study has been done of this class of compounds against tuberculosis, leprosy, psoriasis, rheumatisms, trypanosomiasis and coccidiosis. In chemical and petro-chemical processes thiosemicarbazone worked as pesticides, fungicides and catalysts [1].

Review of literature

Compared to a free ligand, the metal chelates cross the cell membrane by diffusive mechanism instead of active transport mechanism due to the chelation of the metal ion by the polar regions of the ligands. These properties of the ligand binded metal make these complexes attractive drug targets [2].

Aim of study

In this paper we are reporting the association constant, Gibbs Free energies of Ni (II) complexes with thiosemicarbazide based ligand: 2, 6-Dihydroxyacetophenone thiosemicarbazone (2, 6-DHAT).

Materials and methods

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 [3]. Metal-ligand complexes were formed by conductometrically. Conductivity TDS Meter 307 is employed in present study for conductometric investigations.

Procedure

The conductometric titration of the ligand ($1x10^{-3}$) mole/L in doubly distilled water, TX-100 and Brij-35 medium against the $NiCl_2$ ($1x10^{-4}$) mole/L was performed with definite amount of metal ($NiCl_2$) solution [4,5].

The cell was calibrated with standard KCl solution [6].

Results, Findings and Discussion

The values of molar conductance (Λm) for $NiCl_2$ were calculated [7] in water, Brij-35and TX-100 medium at 298.15 K temperature.

$\Lambda m = (Ks - Ksolv.)Kcell \times 1000/C$ -----------(1)

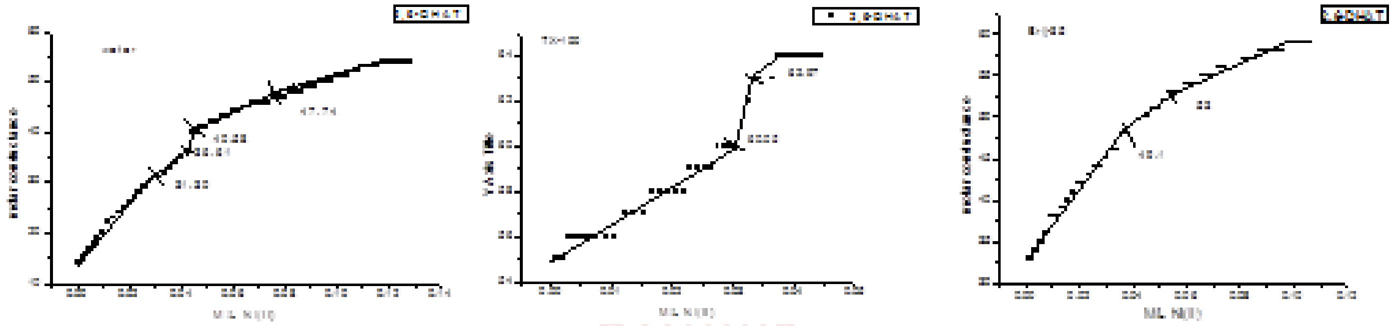
Ks = specific conductance of the solution, Ksolv = specific conductance of the solvent, Kcell = cell constant, C = molar concentration of the metal ion solution.

The stoichiometric of complexes were decided by association and formation constants. The association constants of complexes were calculated by using equation (2) [8,9] in water, TX-100 and Brij-35 medium.

$KA = [\Lambda_0^2 (\Lambda_0 - \Lambda m)] / [4Cm^2 \gamma\pm^2 \Lambda_m^3 S(z)]$ ---- (2)

KA = association constants, Λm = molar conductance, Λ_0 = limiting molar conductance of metal ion solution, $\gamma\pm$ = activity coefficient, S(Z) = Fuoss-Shedlovsky factor [10]

Association constants (K_A) and gibbs free energy (ΔG_A) of Ni(II) with 2, 6-DHAT were calculated in different medium (water, Triton X-100 and Brij-35)



Plot of molar conductance Vs M/L ratio

The Gibbs free energies were obtained by employing equation (3) [11]
$\Delta GA = -RT \ln K_A$ ----------- (3)

here
R = gas constant (8.314 J), T = absolute temperature

The result of Gibbs free energies were calculated.

$Kf = [\Lambda_M - \Lambda_{obs}]/[(\Lambda_{obs} - \Lambda_{ML})[L]]$ ----------- (4)

The formation constants (K_f) [12,13] of complexes were calculated by applying above eq.

here,
Λ_M = molar conductance of the metal ion solution alone, Λ_{obs} = observed molar conductance of solution, Λ_{ML} = molar conductance of the complex

The calculated values (K_f) for complexes are presented in Tables (i-vii).

Also the Gibbs free energies of complex formation constant were obtained using equation (5) and exhibited in tables(i-vii).

$\Delta G_f = -RT \ln K_f$ ----------- (5)

Table (i): Formation constants and Gibbs free energies of formation for 1:2 (M/L) Ni (II) complexes in water medium

Λobs	[L]	(Λ_M-Λ_{obs})	(Λobs-Λ_{ML})[L]	K_f	ΔG_f (k J/mol)
49	0.000531915	21	1.26	31333.33	-25.62345589
49	0.000526316	21	1.26	31666.67	-25.64964781
49	0.000520833	21	1.26	32000	-25.67556547
50	0.000515464	20	2.26	17168.14	-24.13436079
50	0.000510204	20	2.26	17345.13	-24.15974679
50	0.000505051	20	2.26	17522.12	-24.18487506
51	0.0005	19	3.26	11656.44	-23.17600568
51	0.00049505	19	3.26	11773.01	-23.20063387
51	0.000490196	19	3.26	11889.57	-23.22501942
52	0.000485437	18	4.26	8704.225	-22.4531479
52	0.000480769	18	4.26	8788.732	-22.47706223
53	0.00047619	17	5.26	6787.072	-21.83736715

53	0.000471698	17	5.26	6851.711	-21.86082812
53	0.00046729	17	5.26	6916.35	-21.88406879
53	0.000462963	17	5.26	6980.989	-21.90709326
54	0.000458716	16	6.26	5571.885	-21.34906135
54	0.000454545	16	6.26	5623.003	-21.37166528
54	0.00045045	16	6.26	5674.121	-21.39406465
54	0.000446429	16	6.26	5725.24	-21.41626312
54	0.000442478	16	6.26	5776.358	-21.43826427
54	0.000438596	16	6.26	5827.476	-21.46007158

$\Lambda_{ML} =$ 43.47 $Cm^2Ohm^{-1}mol^{-1}$

Table (ii): Formation constants and Gibbs free energies of formation for 1:3 (M/L) Ni (II) complexes in water medium

Λobs	[L]	(Λ_M-Λ_{obs})	(Λobs-Λ_{ML})[L]	K_f	Δ G_f (k J/mol)
41	0.000675676	29	1.26	31333.33	-22.74075633
41	0.000666667	29	1.26	31666.67	-22.77397983

$\Lambda_{ML} =$ 40.45 $Cm^2Ohm^{-1}mol^{-1}$

Table (iii): Formation constants and Gibbs free energies of formation for 1:34(M/L) Ni (II) complexes in water medium

Λobs	[L]	(Λ_M-Λ_{obs})	(Λobs-Λ_{ML})[L]	K_f	Δ G_f (k J/mol)
33	0.000735294	37	0.00125	29600	-25.48260182
34	0.000724638	36	0.001956522	18400	-24.30587433
35	0.000714286	35	0.002642857	13243.24	-23.4919007
36	0.000704225	34	0.003309859	10272.34	-22.86314127
40	0.000694444	30	0.006041667	4965.517	-21.06388884
40	0.000684932	30	0.005958904	5034.483	-21.09802887

$\Lambda_{ML} =$ 31.46 $Cm^2Ohm^{-1}mol^{-1}$

Table (iv): Formation constants and Gibbs free energies of formation for 1:3 (M/L) Ni(II) complexes in TX-100 medium

Λobs	[L]	(Λ_M-Λ_{obs})	(Λobs-Λ_{ML})[L]	K_f	Δ G_f (k J/mol)
64	0.000625	10	0.00055625	17977.53	-24.27684387
64	0.000617	10	0.000549383	18202.25	-24.3076271
64	0.00061	10	0.000542683	18426.97	-24.33803262
64	0.000602	10	0.000536145	18651.69	-24.36806957
64	0.000595	10	0.000529762	18876.4	-24.3977468
64	0.000588	10	0.000523529	19101.12	-24.4270728
64	0.000581	10	0.000517442	19325.84	-24.4560558
64	0.000575	10	0.000511494	19550.56	-24.48470373
64	0.000568	10	0.000505682	19775.28	-24.51302425
64	0.000562	10	0.0005	20000	-24.54102476
64	0.000556	10	0.000494444	20224.72	-24.5687124

$\Lambda_{ML} =$ 63.11 $Cm^2Ohm^{-1}mol^{-1}$

Table (v): Formation constants and Gibbs free energies of formation for 1:3 (M/L) Ni(II) complexes in TX-100 medium

Λobs	[L]	(Λ_M-Λ_{obs})	(Λobs-Λ_{ML})[L]	K_f	Δ G_f (k J/mol)
61	0.000685	13	0.000650685	19978.95	-24.52775997
62	0.000676	12	0.001317568	9107.692	-22.58197375
63	0.000667	11	0.001966667	5593.22	-21.3743054
63	0.000658	11	0.001940789	5667.797	-21.40711306
63	0.000649	11	0.001915584	5742.373	-21.43949186
63	0.000641	11	0.001891026	5816.949	-21.47145285
63	0.000633	11	0.001867089	5891.525	-21.50300668

$\Lambda_{ML} =$ 60. 05 $Cm^2Ohm^{-1}mol^{-1}$

Table (vi): Formation constants and Gibbs free energies of formation for 1:3 (M/L) Ni(II) complexes in Brij-35 medium

Λobs	[L]	(Λ_M-Λ_{obs})	(Λobs-Λ_{ML})[L]	K_f	Δ G_f (k J/mol)
54	0.000704	18	0.00070423	25560	-25.11939
54	0.000694	18	0.00069444	25920	-25.154007
54	0.000685	18	0.00068493	26280	-25.188147
55	0.000676	17	0.00135135	12580	-23.364731
56	0.000667	16	0.002	8000	-22.24433
57	0.000658	15	0.00263158	5700	-21.405328
57	0.000649	15	0.0025974	5775	-21.437682
57	0.000641	15	0.0025641	5850	-21.46962
58	0.000633	14	0.00316456	4424	-20.77808
58	0.000625	14	0.003125	4480	-20.809213
58	0.000617	14	0.00308642	4536	-20.839961
59	0.00061	13	0.00365854	3553.333	-20.235638
59	0.000602	13	0.00361446	3596.667	-20.26564
59	0.000595	13	0.00357143	3640	-20.295283
60	0.000588	12	0.00411765	2914.286	-19.744919
60	0.000581	12	0.00406977	2948.571	-19.773868
60	0.000575	12	0.00402299	2982.857	-19.802482
61	0.000568	11	0.00454545	2420	-19.284901
61	0.000562	11	0.00449438	2447.5	-19.312869
61	0.000556	11	0.00444444	2475	-19.340524
61	0.000549	11	0.0043956	2502.5	-19.367874
62	0.000543	10	0.0048913	2044.444	-18.867495
62	0.000538	10	0.00483871	2066.667	-18.894253
62	0.000532	10	0.00478723	2088.889	-18.920725
63	0.000526	9	0.00526316	1710	-18.425358
63	0.000521	9	0.00520833	1728	-18.451276
63	0.000515	9	0.00515464	1746	-18.476925
64	0.00051	8	0.00561224	1425.455	-17.974881
64	0.000505	8	0.00555556	1440	-18.00001
64	0.0005	8	0.0055	1454.545	-18.024885
64	0.000495	8	0.00544554	1469.091	-18.049514
64	0.00049	8	0.00539216	1483.636	-18.073899
64	0.000485	8	0.00533981	1498.182	-18.098047

Λ_{ML} = 53 $Cm^2Ohm^{-1}mol^{-1}$

Table (vii): Formation constants and Gibbs free energies of formation for 1:3 (M/L) Ni(II) complexes in Brij-35 medium

Λobs	[L]	(Λ_M-Λ_{obs})	(Λobs-Λ_{ML})[L]	K_f	Δ G_f (k J/mol)
50	0.000725	22	0.00065217	33733.33	-25.806129
53	0.000714	19	0.00278571	6820.513	-21.849532

Λ_{ML} = 49.1 $Cm^2Ohm^{-1}mol^{-1}$

Conclusion

The negative values of ΔG show the ability of the studied ligand to form stable complexes by conducto metrically.

References

[1] Demertzi, D.K., Domopoulou, A., Demertzis, M. A., Valle, G., Papageorgiou, A. J. (1997). Palladium(II) complexes of 2-acetylpyridine N(4)-methyl, N(4)-ethyl and N(4)-phenyl-thiosemicarbazones Crystal structure of chloro(2 acetylpyridine N(4)-methylthiosemicarbazonato) palladium(II). Synthesis, spectral studies, in vitro and in vivo antitumor activity, J. Inorg. Biochem., 68, 147-155.

[2] Khana, T., Razab, S., Lawrenceb, A. J.,(2022). Medicinal Utility of Thiosemicarbazones with Special Reference to Mixed Ligand and Mixed Metal Complexes: A Review, Russian journal of coordination chemistry, 48(12) 877-895.

[3] Latika, D., Singh, R. V., (2011). Synthesis, Spectroscopic Characterization, Antimicrobial, Pesticidal and Nematicidal Activity of Some Nitrogen-Oxygen and Nitrogen-Sulfur donor Coumarins based Ligands and their Organotin(IV) Complexes, Appl. Organomet. Chem., 25, 643-652.

[4] Lobana, T. S., Sanchez, A., Casas, J. S., (1997). Synthesis, Characterization, and In vitro Cytotoxic Activities of Benzaldehyde Thiosemicarbazone Derivatives and Their Palladium (II) and Platinum (II) Complexes Against Various Human Tumor Cell Lines, Journal of the Chemical Society, 22, 4289-4300.

[5] Rathore, U., Gupta, R., Soni, M., Bhojak, N., (2016). Conductometric and pH Metric Investigations on Thiosemicarbazone Co(II) Systems, International Journal of New Technologies in Science and Engineering, 3(3): 1-10.

[6] Gomaa, E. A., Jahdali, B. M. A., (2011). Association of Cu(NO3)2 With Kryptofix-221 in Mixed (MeOH-DMF) Solvents at Different Temperatures, American Journal of Fluid Dynamics, 1(1): 4-8.

[7] Biswas, R., Brahman, D., (2009). Thermodynamics of the Complexation between Salicylaldehyde Thiosemicarbazone with Cu(II) Ions in Methanol–1,4-Dioxane Binary Solutions, Indian Journal of Chemistry, A(48): 1145.

[8] Gryzybkowski, W., Pilarczyk, M., (1989). Electrical Conductance and Apparent Molar Volumes of Al(ClO4)2, $Be(ClO_4)_2$ and $Cu(ClO_4)_2$ in N, N-Dimethylformamide Solutions at 25^{o}C, Electrochimica Acta, 32, 1601-1605.

[9] Shishtawi, N. A. E., Hamada, M. A., (2010). EAGomaa, Influence of Permanent Magnet on the Association Constants of $FeCl_3$ in 50% Ethanol-H_2O Solutions (conductometrically) at 298.15 K Using a new Equation for 1:3 Asymmetric Electrolytes, Journal Chemical engineering data, 55, 5422-5424.

[10] Hamada, M. A., Shishtawiand, N. A. E., Gomaa, E. A., (2009). Conductometric Evaluation of Association Constants for Aqueous Solutions of $CoCl_2$ in the Absence and Presence of a Magnetic Field, Southern Brazilian Journal of Chemistry, 17: 33-40.

[11] Gomaa, E. A., (1987). Solute-Solvent Interactions of Some Univalent-Univalent Salts with Various Organic Solvents at 25^{o}C, Thermochimica Acta, 120: 183-189.

[12] Gomaa, E. A., (1988). Theoretical Contribution of Solvation of AgBr in Some Organic Solvents at 25^{o}." Thermochimica Acta, 128, 99-120.

[13] Dossoki, F. I. E., (2008). Electric Conductance and Semi-Emperical Studies on Two Thiophene Derivatives/Metal Cation Complexation, Journal of Molecular Liquids, 142, 53-56.

[14] Nasrabadi, M.R., Ahmedi, F., Tazari, S. M. P., Ganjal, M. P., Alizadeh, K., (2009). Conductometric Study of Complex Formation between Some Substituted Pyrimidines and Some Metal Ions in Acetonitrile and the Determination of Thermodynamic Parameters, Journal of Molecular Liquids, 144, 97-101.