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Determination of Formation Constant Conductometrically for Cu (II)-Thiosemicarbazone Systems

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ABSTRACT

This paper describes the conductometric investigations on few Cu(II)- thiosemicarbazone complexes. Solution studies on the complexes have also been carried out in different micellar systems at 25° C. 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: *Cu (II)-Thiosemicarbazone, association constants, formation constants, Triton X-100*

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INTRODUCTION

The researchers continuously explored the biopotency of the thiosemicarbazone compounds to uncover their full potential in various applications, including anticancer, antituberculosis, antibacterial and antifungal [1]. The investigation of anticancer and antitumor activities related to the biological effects of thiosemicarbazone complexes is currently a prominent research area [2]. Many studies have been conducted on mono- and bis(thiosemicarbazone) complexes, and it has been determined that Cu(II) complexes effectively show anticarcinogenic activity [3].

In this paper we are reporting the stability constant, association constant, Gibbs Free energies and antimicrobial activityof Cu (II) complexes with thiosemicarbazide based ligand : 4-(Diethylamino) benzaldehyde thiosemicarbazone (4-DEABT).

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 4-DEABT was synthesized by condensation reaction of thiosemicarbazide with 4-(Diethylamino) benzaldehyde in presence of methanol according to the literature [4].

The solid precipitate obtained in both methods, was separated and crystallized. Crystals were purified and recrystalized with ethyl alcohol and dried under vacuum. For green synthesis of ligand microwave has been used.

PROCEDURE

Conductometric Study

The conductometric titration of the ligand ($1x10^{-3}$) mole/L in doubly distilled water, TX-100 and Brij-35 medium against the $CuCl_2$ ($1x10^{-4}$) mole/L was performed with definite amount of metal ($CuCl_2$) solution [5, 6, 7, 8].

The cell was calibrated with standard KCl solution [9].

Results, Findings and Discussion

The values of molar conductance (Λm) for $CuCl_2$ were calculated [10] in water, Brij-35and TX-100 medium at 298.15 K temperature.

$\Lambda m = (K_s\text{-Ksolv.})\text{Kcell} \times 1000/C$ ---------(1)

K_s = specific conductance of the solution, K_{solv} = specific conductance of the solvent, K_{cell} = 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) [11,12] in water, TX-100 and Brij-35 medium.

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

K_A = association constants, Λ_m =molar conductance, Λ_0 = limiting molar conductance of metal ion solution, $\gamma\pm$ = activity coefficient, S(Z) = Fuoss-Shedlovsky factor [13]

Association constants (K_A) and gibbs free energy (ΔG_A) of Cu (II) with [3, 4, 5-TBT] were calculated in different medium (water, Triton X-100 and Brij-35)

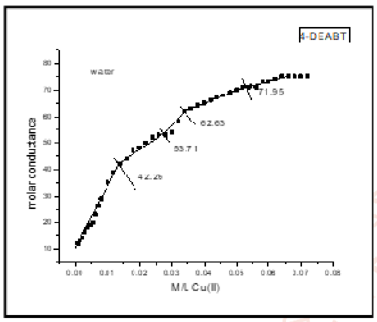

Figure-a

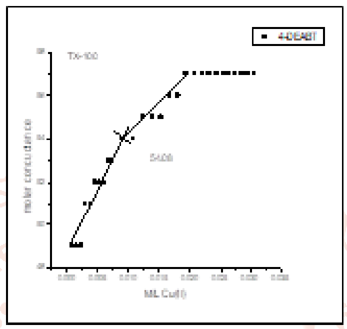

Figure-b

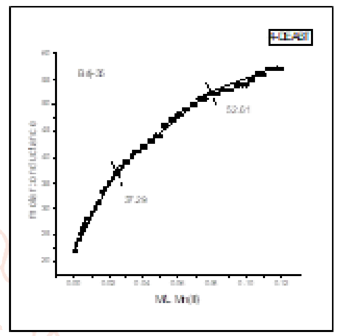

Figure-c

Plot of molar conductance Vs M/L ratio

Graph have been plotted between molar conductance and M/L ratio in water, TX100 and Brij 35 medium (figure a, b and c respectively) .

The Gibbs free energies were obtained by employing equation (3) [14]

$\Delta G_A = - R T \ln K_A$ -------- (3)

here

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

The result of Gibbs free energies were calculated.

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

The formation constants (K_f) [15,16] of complexes were calculated by applying above eq.

here,

Λ_M = molar conductance of the metal ion solution alone,

Λobs = observed molar conductance of solution,

Λ_{ML}= molar conductance of the complex

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

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

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

Table 4.2.4.d.(i)-: Formation constants and Gibbs free energies of formation for 1:3 (M/L) Cu(II) complexes in water medium

Λobs	[L]	(ΛM-Λobs)	(Λobs-ΛML)[L]	Kf	Δ Gf (k J/mol)
74	0.000617284	6	0.001265432	4741.463415	-20.94960879
75	0.000609756	5	0.001859756	2688.52459	-19.54534521
75	0.00060241	5	0.001837349	2721.311475	-19.57534695
75	0.000595238	5	0.001815476	2754.098361	-19.60498938
75	0.000588235	5	0.001794118	2786.885246	-19.634281
75	0.000581395	5	0.001773256	2819.672131	-19.66323003

Λ_{ML} = 71.95 $Cm^2Ohm^{-1}mol^{-1}$

Table 4.2.4.d.(ii)-: Formation constants and Gibbs free energies of formation for 1:4 (M/L) Cu(II) complexes in water medium

Λobs	[L]	(ΛM-Λobs)	(Λobs-ΛML)[L]	Kf	Δ Gf (k J/mol)
64	0.000724638	16	0.000992754	16116.78832	-23.9779486
65	0.000714286	15	0.001692857	8860.759494	-22.49726408
66	0.000704225	14	0.002373239	5899.109792	-21.49031122
67	0.000694444	13	0.003034722	4283.75286	-20.69834429
68	0.000684932	12	0.003678082	3262.569832	-20.0243356
69	0.000675676	11	0.004304054	2555.729984	-19.41996916
70	0.000666667	10	0.004913333	2035.278155	-18.85637252
71	0.000657895	9	0.005506579	1634.408602	-18.3134528
71	0.000649351	9	0.005435065	1655.913978	-18.34580768
71	0.000641026	9	0.005365385	1677.419355	-18.37774507
73	0.000632911	7	0.006563291	1066.538091	-17.2569184
73	0.000625	7	0.00648125	1080.038573	-17.28805231

Λ_{ML} = 62.63 $Cm^2Ohm^{-1}mol^{-1}$

Table 4.2.4.d.(iii)-: Formation constants and Gibbs free energies of formation for 1:5 (M/L) Cu(II) complexes in water medium

Λobs	[L]	(ΛM-Λobs)	(Λobs-ΛML)[L]	Kf	Δ Gf (k J/mol)
62	0.000746269	18	0.006186567	2909.529554	-19.74087629
63	0.000735294	17	0.006830882	2488.697524	-19.35418461

Λ_{ML} = 53.71 $Cm^2Ohm^{-1}mol^{-1}$

Table 4.2.4.d.(vi)-: Formation constants and Gibbs free energies of formation for 1:7 (M/L) Cu(II) complexes in water medium

Λobs	[L]	(ΛM-Λobs)	(Λobs-ΛML)[L]	Kf	Δ Gf (k J/mol)
47	0.000847458	33	0.004016949	8215.189873	-22.31002766
48	0.000833333	32	0.004783333	6689.89547	-21.80167252
50	0.000819672	30	0.006344262	4728.682171	-20.94292778
52	0.000806452	28	0.007854839	3564.681725	-20.24353062
53	0.000793651	27	0.00852381	3167.597765	-19.9512166
53	0.00078125	27	0.008390625	3217.877095	-19.99019556
54	0.000769231	26	0.009030769	2879.045997	-19.71480737

Λ_{ML} = 42.26 $Cm^2Ohm^{-1}mol^{-1}$

Table 4.2.4.d.(v)-: Formation constants and Gibbs free energies of formation for 1:7 (M/L) Cu(II) complexes in TX-100 medium

Λobs	[L]	(ΛM-Λobs)	(Λobs-ΛML)[L]	Kf	Δ Gf (k J/mol)
55	0.000877193	8	0.000807018	9913.043478	-22.80175104
55	0.000862069	8	0.000793103	10086.95652	-22.8448481
55	0.000847458	8	0.000779661	10260.86957	-22.88720842
56	0.000833333	7	0.0016	4375	-20.77486852
56	0.000819672	7	0.00157377	4447.916667	-20.81582843
57	0.000806452	6	0.002354839	2547.945205	-19.43520396

57	0.000793651	6	0.00231746	2589.041096	-19.4748531
57	0.00078125	6	0.00228125	2630.136986	-19.51387782
57	0.000769231	6	0.002246154	2671.232877	-19.55229748
57	0.000757576	6	0.002212121	2712.328767	-19.59013055
57	0.000746269	6	0.002179104	2753.424658	-19.62739469
57	0.000735294	6	0.002147059	2794.520548	-19.66410675
57	0.000724638	6	0.002115942	2835.616438	-19.70028284
57	0.000714286	6	0.002085714	2876.712329	-19.7359384
57	0.000704225	6	0.002056338	2917.808219	-19.77108818
57	0.000694444	6	0.002027778	2958.90411	-19.80574635

Λ_{ML} = 54.08 Cm^{2}Ohm^{-1}mol^{-1}

Table 4.2.4.d.(vi)-: Formation constants and Gibbs free energies of formation for 1:2 (M/L) Cu(II) complexes in Brij-35 medium

Λobs	[L]	(Λ_M-Λ_{obs})	(Λobs-Λ_{ML})[L]	K_f	Δ G_f (k J/mol)
79	0.000526316	2	0.000705263	2835.820896	-19.70046151
79	0.000520833	2	0.000697917	2865.671642	-19.72640958
80	0.000515464	1	0.001206186	829.0598291	-16.65300829
80	0.000510204	1	0.001193878	837.6068376	-16.67842408
80	0.000505051	1	0.001181818	846.1538462	-16.70358185
80	0.0005	1	0.00117	854.7008547	-16.72848676
80	0.00049505	1	0.001158416	863.2478632	-16.75314387
80	0.000490196	1	0.001147059	871.7948718	-16.77755804

Λ_{ML} = 77.66 Cm^{2}Ohm^{-1}mol^{-1}

Table 4.2.4.d.(vii)-: Formation constants and Gibbs free energies of formation for 1:3(M/L) Cu(II) complexes in Brij-35 medium

Λobs	[L]	(Λ_M-Λ_{obs})	(Λobs-Λ_{ML})[L]	K_f	Δ G_f (k J/mol)
66	0.000657895	15	0.000934211	16056.33803	-23.99678101
67	0.000649351	14	0.001571429	8909.090909	-22.5371502
68	0.000641026	13	0.002192308	5929.824561	-21.52840446
69	0.000632911	12	0.002797468	4289.59276	-20.72601508
70	0.000625	11	0.0033875	3247.232472	-20.03616271
71	0.000617284	10	0.003962963	2523.364486	-19.41118178
72	0.000609756	9	0.00452439	1989.218329	-18.82178171
72	0.00060241	9	0.00446988	2013.477089	-18.85181867
73	0.000595238	8	0.005011905	1596.199525	-18.27632958
74	0.000588235	7	0.005541176	1263.269639	-17.69666606
74	0.000581395	7	0.005476744	1278.131635	-17.72564907
75	0.000574713	6	0.005988506	1001.919386	-17.12229666
76	0.000568182	5	0.006488636	770.5779335	-16.47173745
76	0.000561798	5	0.00641573	779.3345009	-16.49973796
77	0.000555556	4	0.0069	579.7101449	-15.76646226
77	0.000549451	4	0.006824176	586.1513688	-15.79384396
78	0.000543478	3	0.007293478	411.3263785	-14.91615199
78	0.000537634	3	0.007494624	400.286944	-14.84873661
78	0.000531915	3	0.007414894	404.5911047	-14.87523974

Λ_{ML} = 64.58 Cm^{2}Ohm^{-1}mol^{-1}

Table 4.2.4.d.(viii)-: Formation constants and Gibbs free energies of formation for 1:3 (M/L) Cu(II) complexes in Brij-35 medium

Λobs	[L]	(Λ_M-Λ_{obs})	(Λobs-Λ_{ML})[L]	K_f	Δ G_f (k J/mol)
65	0.000666667	16	0.003386667	4724.409449	-20.96526966

Λ_{ML} = 59.92 Cm^{2}Ohm^{-1}mol^{-1}

Table- 4.2.4.d.(ix)-: Formation constants and Gibbs free energies of formation for 1:5 (M/L) Cu(II) complexes in Brij-35 medium

Λobs	[L]	(Λ_M-Λ_{obs})	(Λobs-Λ_{ML})[L]	K_f	ΔG_f (k J/mol)
47	0.000769231	34	0.002646154	12848.83721	-23.44455375
49	0.000757576	32	0.004121212	7764.705882	-22.19646324
51	0.000746269	30	0.005552239	5403.225806	-21.2979525
53	0.000735294	28	0.006941176	4033.898305	-20.57371961
54	0.000724638	27	0.007565217	3568.965517	-20.2702678
56	0.000714286	25	0.008885714	2813.504823	-19.68088398
58	0.000704225	23	0.010169014	2261.772853	-19.1399771
59	0.000694444	22	0.010722222	2051.813472	-18.89855633

Λ_{ML} = **43.56 Cm^{2}Ohm^{-1}mol^{-1}**

Table 4.2.4.d.(x)-: Formation constants and Gibbs free energies of formation for 1:9 (M/L) Cu(II) complexes in Brij-35 medium

Λobs	[L]	(Λ_M-Λ_{obs})	(Λobs-Λ_{ML})[L]	K_f	ΔG_f (k J/mol)
35	0.000862069	46	0.002275862	20212.12121	-24.56716837
36	0.000847458	45	0.003084746	14587.91209	-23.75911323
38	0.000833333	43	0.0047	9148.93617	-22.60297975
39	0.000819672	42	0.005442623	7716.86747	-22.18114892
41	0.000806452	40	0.006967742	5740.740741	-21.44810086
43	0.000793651	38	0.008444444	4500	-20.84467647
46	0.00078125	35	0.01065625	3284.457478	-20.06440816

Λ_{ML} = **32.36 Cm^{2}Ohm^{-1}mol^{-1}**

Conclusion

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

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