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Original Research Article

pH – METRIC STUDIES OF METAL COMPLEXES OF TRIAZOLE IN WATER-METHANOL

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Abstract: Ni(II) and Co(II) metal complexes of 1,2,3-triazole have been studied in water –methanol medium by pH –metric titration with the standard glass electrode, ionic strength 0.1M KNO_3 and buffer solution at the pH 7 and 9. The titrations were carried out for the ligand against 0.05M NaOH solution as well as metal-ligand against NaOH at different temperature 35, 45 and 55^oC. The p k_a value (stability constant) were determined at respective Ni(II) 2.51, 2.60, 2.38 and Cu(II) 2.55, 2.30 and 2.20 and the results revealed that metal complex decreases with increasing temperature, the larger the value of the stability constant the further the reaction to the right . This implies that the complex ions with larger stability constant are more stable than the ones with smaller one. Thermodynamics studies result determined at 308k 318k and 323k respectively was calculated as follows: Cobalt (II) ΔH = -52310.86 $KJmol^{-1}$, ΔS = -110.36 and ΔG = -18320.63, - $KJmol^{-1}$17217.05 and - 16113.48 $KJmol^{-1}$, Nickel(II) ΔH = -43457.21 $KJmol^{-1}$, ΔS = -86.32 and ΔG = -16822.41, -16005.14 and -15141.87 $KJmol^{-1}$. Negative values of ΔH, indicated exothermic reaction while negative Gibb's free energy explained the spontaneity of the metal-ligand systems and the feasibility of metal complexes.

Keywords: Metal complexes, pH-metric, stability constants, thermodynamic.

Introduction: Many binary complexes of transition metals have been studied potentiometrically (Braahmbhatt *et al*., 2002). Metal complexes of chalcone have been extensively studied because chalcone possess good synthetic flexibility, selectivity and sensitivity towards the central metal atom. Some coumarin derivatives are reported as an anti-HIV agent (Manwar *et al*., 2007]. Some chalcones of hydroxycoumarin as a ligand and their Fe(II) complexes, bis –(3-[{3-(substituted phenyl)}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one)[Fe(II)]$(H_2O)_2$havebeen investigated and the stability constants of synthesized compounds have been studied pH-metrically by Irving and Rossotti method (Vyas *et al*., 2008).

Potentiometric studies have been carried out on complexes of gabapentin (chemically 2-[1-(aminomethyl) cyclohexyl] ethanoic acid) with Cu(II), Cd(II), Co(II), Ni(II), Pb(II) and Zn(II) in 50% v/v dioxane-water medium at three

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different temperatures (35, 45 and 55^{o}C) and ionic strength 0.1 mol L-1 (KNO_3). Calvin-Bjerrum pH titration technique as used by Irving and Rossotti, (1964) has been applied to determine stability constants of the complexes. Free energy, enthalpy and entropy changes have also been evaluated (Kumar and Kumar, 2007).

The study of Gadolium (III) complex with linear amino carboxylates, stability, dissociation constant and kinetics under a variety of conditions has been carried out. Thestability as measured by complex formation constants, dissociation constant and kinetics are particularly dependent on the solution pH. At low pH values, the coordinating carboxylate groups become protonated, leading to at least partial dissociation of the complex. Within this pH range, resulting hydration number will be relatively high. At sufficiently high pH values, coordination of hydroxide ions can occur. This reduces rapid exchange with solvent water and may allow oligomers to form (Chang *et al*., 1990).

Marques *et al*; (1998) also determined the pK_a for aquacobalamin bound to haptocorrin and found that the pK_a was raised from 8.10 to 8.29 at 25 ºC. They concluded that this small difference meant that the micro-environment of the coordinated water was not significantly different from that of the free aquacobalamin in bulk water.

The chelate effect increases as the number of chelate rings increases 5-membered and 6-membered chelate rings give the most stable complexes 4-membered rings are subject to internal strain because of the small inter-bond angle in the ring .The chelate effect is also reduced with 7-and 8-membered rings, because the larger rings are less rigid, so less entropy is lost in forming them (Lindoy, 1990).

1,2,3-triazole is solubility in water with the acidity (p K_a) 1.2,and basicity (pK_b) 9.4 (Gilchrist, 2002).In recent years, there has been some considerable interests in the complexes formed by the oxadiazole, triazole and other related ligands as they are components of some biological molecules.(Agrawal,1999; Mishra *et al*., 1998).

This present work deals with the determination of the stability constants and thermodynamic stability of Co(II) and Ni(II) complexes with 1,2,3-triazole(ligand) using pH metric method in water-methanol medium at three different temperatures.

Experimental: All chemicals used were of analytical grade. The triazole ligand was purchased and used. Ligand solution was prepared in distilled water. Metal salt solutions were prepared by dissolving the corresponding metal salt in distilled water and standardized by standard volumetric methods. pH measurements were done on ATC pH meter model 132E using a standard glass electrode assembly in 50% v/v methanol -water medium at three temperatures (35, 45 and 55^{o}C) and at an ionic strength of 0.1 mol L^{-1} (KNO_3). The pH meter was calibrated with suitable buffers solutions of pH 6 and 9 before use.

The three solutions (total volume 50 mL in each case) were prepared as follows: (A) 2.5mL of 0.01 mol L^{-1}HCl, (B) 2.5 mL of 0.01 mol L^{-1}HCl + 5.0 mL of 0.025 mol L^{-1} ligand, (C) 2.5mL of 0.01 mol L^{-1}HCl + 5.0 mL of 0.025 mol L^{-1} ligand + 2.5 mL of 0.01 mol L^{-1} metal ion solution. An appropriate quantity of potassium nitrate solution (1.0 mol L^{-1}) was added to maintain the desired ionic strength (0.1 mol L^{-1}). The three different solutions were titrated against sodium hydroxide (0.05 mol L^{-1}) prepared in 50% v/v methanol-water.

The pH readings were stabilized in a few minutes and converted to hydrogen ion concentration according to method of Bjerrum (1941).

The stability constants (nH) defined as:

$nH = j+([HCl]–[NaOH])+[OH^-]– [H^+] / [HjA]$

Where j = Total number of ionizable hydrogen in ligand

[HjA] = Calculated amount of ligand added

[NaOH] = Calculated amount of NaOH added

[HCl] = Calculated amount of HCl added

$[H^+]$ = Proton concentration

$[OH^-]$ = Hydroxide ion concentration

The average number of ligands (n_A) bound per metal was calculated using the formular:

$$n_A = \frac{T_A^{\circ} - [T_H - [H]/n_H}{T_M^{\circ}}$$

Where T_H = Total concentration of the Hydrogen ion present

T_A° = *Total concentration of Ligand*

T_M° = *Total concentration of the Metal*

nA = *Average number of ligands bound per metal.*

Table 1:Calculated PKa and stability constant of triazole at different temperatures

Temperature	PKa	nA	STABILITY CONSTANT
35^0C	11.90	1.5	7.94×10^{11}
45^0C	_	_	_
55^0C	_	_	_

At45^0Cand 55^0C, the Ligand (Triazole) is unstable.

Table 2: Determination of number of coordinated ligands in Nickel (II) 1, 2, 3 – triazole complex at different temperatures

Temp.	35^0C				45^0C				55^0C			
Vol. of NaOH	**Ph**	**H^+**	**nH**	**nA**	**pH**	**H^+**	**nH**	**nA**	**pH**	**H^+**	**nH**	**nA**
0	2.21	0.006166	1.153	1.153	1.78	0.016596	0.736165	3.495	1.72	0.019055	0.637816	4.034081
0.2	2.23	0.005888	1.155	1.155	1.87	0.01349	0.850257	3.002	1.76	0.017378	0.694099	3.678149
0.4	2.24	0.005754	1.151	1.151	1.97	0.010715	0.951963	2.660	1.86	0.013804	0.827429	3.06129
0.6	2.26	0.005495	1.153	1.153	1.99	0.010233	0.961771	2.612	1.89	0.012882	0.854517	2.940844
0.8	2.3	0.005012	1.164	1.164	2.02	0.00955	0.979891	2.544	1.94	0.011482	0.90139	2.765727
1	2.33	0.004677	1.169	1.169	2.19	0.006457	1.096573	2.255	1.96	0.010965	0.912637	2.70973
1.2	2.36	0.004365	1.173	1.173	2.21	0.006166	1.099443	2.231	1.99	0.010233	0.932859	2.62955
1.4	2.41	0.00389	1.184	1.184	2.23	0.005888	1.101867	2.208	2.02	0.00955	0.951307	2.557534
1.6	2.45	0.003548	1.189	1.189	2.25	0.005623	1.103866	2.185	2.05	0.008913	0.968092	2.492533
1.8	2.48	0.003311	1.190	1.190	2.26	0.005495	1.10027	2.174	2.07	0.008511	0.975288	2.453633
2	2.5	0.003162	1.188	1.188	2.29	0.005129	1.10665	2.144	2.11	0.007762	0.997081	2.379947
2.2	2.54	0.002884	1.191	1.191	2.35	0.004467	1.125465	2.090	2.19	0.006457	1.042375	2.257345
2.4	2.57	0.002692	1.191	1.191	2.41	0.00389	1.140912	2.044	2	0.01	0.8848	2.636754
2.6	2.62	0.002399	1.195	1.195	2.43	0.003715	1.139658	2.029	2.21	0.006166	1.036537	2.231469
2.8	2.7	0.001995	1.203	1.203	2.47	0.003388	1.144872	2.002	2.22	0.006026	1.033479	2.21872
3	2.76	0.001738	1.206	1.206	2.5	0.003162	1.145919	1.983	2.23	0.005888	1.03033	2.206089
3.2	2.85	0.001413	1.211	1.211	2.51	0.00309	1.140477	1.975	2.25	0.005623	1.032668	2.181728
3.4	2.9	0.001259	1.210	1.210	2.55	0.002818	1.143599	1.952	2.32	0.004786	1.059529	2.10754
3.6	3.04	0.000912	1.216	1.216	2.58	0.00263	1.143214	1.935	2.36	0.004365	1.068822	2.070504
3.8	3.19	0.000646	1.220	1.220	2.63	0.002344	1.147104	1.911	2.37	0.004266	1.0644	2.060315
4	3.51	0.000309	1.226	1.226	2.75	0.001778	1.163178	1.868	2.55	0.002818	1.118246	1.943222
4.2	4	0.0001	1.227	1.227	2.84	0.001445	1.169326	1.841	2.58	0.00263	1.117952	1.925844
4.4	6.5	3.16E-07	1.223	1.223	2.91	0.00123	1.170459	1.822	2.61	0.002455	1.117171	1.909287
4.6	7	1E-07	1.216	1.216	2.99	0.001023	1.171303	1.803	2.64	0.002291	1.115935	1.89348

4.8	7.38	4.17E-08	1.208	1.208	5.87	1.35E-06	1.207941	1.732	4.51	3.09E-05	1.206645	1.734561
5	8	1E-08	1.200	1.200	5.99	1.02E-06	1.199955	1.727	4.55	2.82E-05	1.19876	1.729287
5.2	8.36	4.37E-09	1.192	1.192	7.46	3.47E-08	1.192011	1.722	5.96	1.1E-06	1.191952	1.722386
5.4	8.77	1.7E-09	1.184	1.184	7.66	2.19E-08	1.184019	1.717	6.03	9.33E-07	1.183959	1.717121
5.6	9.6	2.51E-10	1.177	1.177	7.78	1.66E-08	1.176026	1.711	6.68	2.09E-07	1.175993	1.71175
5.8	10	1E-10	1.172	1.172	8.66	2.19E-09	1.168204	1.706	7.03	9.33E-08	1.168001	1.706345
6	10.52	3.02E-11	1.174	1.174	8.94	1.15E-09	1.16039	1.701	7.06	8.71E-08	1.160001	1.700871
6.2	10.91	1.23E-11	1.188	1.188	8.96	1.1E-09	1.15241	1.695	7.09	8.13E-08	1.152002	1.695322
6.4	10.99	1.02E-11	1.188	1.188	9.84	1.45E-10	1.147122	1.691	7.77	1.7E-08	1.144026	1.689705
6.6	11.23	5.89E-12	1.212	1.212	10.01	9.77E-11	1.140633	1.687	8.89	1.29E-09	1.136351	1.684231
6.8	11.31	4.9E-12	1.220	1.220	10.08	8.32E-11	1.133463	1.682	9.11	7.76E-10	1.128585	1.678618
7	11.38	4.17E-12	1.229	1.229	10.09	8.13E-11	1.12561	1.676	9.15	7.08E-10	1.120644	1.672797
7.2	11.46	3.47E-12	1.243	1.243	10.11	7.76E-11	1.117895	1.670	9.46	3.47E-10	1.11332	1.667355
7.4	11.5	3.16E-12	1.249	1.249	10.21	6.17E-11	1.111447	1.665	9.6	2.51E-10	1.105828	1.661714
7.6	11.54	2.88E-12	1.255	1.255	10.37	4.27E-11	1.106802	1.662	9.88	1.32E-10	1.099496	1.656886
7.8	11.58	2.63E-12	1.263	1.263	11.17	6.76E-12	1.156394	1.698	10.59	2.57E-11	1.105989	1.661836
8	11.6	2.51E-12	1.264	1.264	11.28	5.25E-12	1.168413	1.706	10.85	1.41E-11	1.112849	1.667003
8.2	11.65	2.24E-12	1.279	1.279	11.37	4.27E-12	1.181147	1.715	10.9	1.26E-11	1.108984	1.6641
8.4	11.67	2.14E-12	1.282	1.282	11.42	3.8E-12	1.186886	1.718	11.07	8.51E-12	1.118891	1.671501
8.6	11.73	1.86E-12	1.307	1.307	11.45	3.55E-12	1.188126	1.719	11.13	7.41E-12	1.119239	1.671759
8.8	11.75	1.78E-12	1.312	1.312	11.48	3.31E-12	1.190059	1.721	11.3	5.01E-12	1.141857	1.688165
9	11.76	1.74E-12	1.311	1.311	11.52	3.02E-12	1.196294	1.725	11.34	4.57E-12	1.143262	1.689162
9.2	11.8	1.58E-12	1.330	1.330	11.58	2.63E-12	1.212058	1.735	11.38	4.17E-12	1.145609	1.690823
9.4	11.83	1.48E-12	1.345	1.345	11.59	2.57E-12	1.208874	1.733	11.41	3.89E-12	1.146145	1.691202
9.6	11.86	1.38E-12	1.361	1.361	11.62	2.4E-12	1.214763	1.736	11.44	3.63E-12	1.147322	1.692031
9.8	11.87	1.35E-12	1.362	1.362	11.63	2.34E-12	1.212076	1.735	11.46	3.47E-12	1.145972	1.69108
10	11.88	1.32E-12	1.364	1.364	11.63	2.34E-12	1.204758	1.730	11.47	3.39E-12	1.141658	1.688023
				1.858				1.939				2.057666

Table 3: Determination of number of coordinated ligands in cobalt (II) 1, 2, 3 - triazole complexes at different temperatures

	35^{O}C				45^{O}C				55^{O}C			
Vol of NaOH	**pH**	**[H^{+}]**	**nH**	**nA**	**pH**	**[H+]**	**nH**	**nA**	**pH**	**[H+]**	**nH**	**nA**
0	2.34	0.004571	1.217	2.113	1.89	0.012882	0.884	2.908	1.85	0.014125	0.834985	3.081493
0.2	2.39	0.004074	1.228	2.078	1.93	0.011749	0.920	2.774	1.87	0.01349	0.850257	3.002623
0.4	2.41	0.00389	1.227	2.064	1.98	0.010471	0.961	2.633	1.87	0.01349	0.840098	3.015124
0.6	2.42	0.003802	1.222	2.056	1.99	0.010233	0.961	2.612	1.89	0.012882	0.854517	2.940844
0.8	2.44	0.003631	1.220	2.042	2.2	0.00631	1.111	2.242	1.9	0.012589	0.856373	2.911116
1	2.47	0.003388	1.221	2.024	2.2	0.00631	1.057	2.243	1.93	0.011749	0.880642	2.808179
1.2	2.48	0.003311	1.216	2.016	2.22	0.006026	1.105	2.219	2.06	0.00871	0.995253	2.464699
1.4	2.52	0.00302	1.219	1.994	2.24	0.005754	1.107	2.197	2.11	0.007762	1.024807	2.374105
1.6	2.56	0.002754	1.222	1.974	2.25	0.005623	1.103	2.185	2.13	0.007413	1.029987	2.342748
1.8	2.58	0.00263	1.219	1.963	2.31	0.004898	1.125	2.127	2.16	0.006918	1.041305	2.298077
2	2.63	0.002344	1.222	1.941	2.39	0.004074	1.150	2.062	2.19	0.006457	1.051408	2.256974
2.2	2.71	0.00195	1.230	1.912	2.43	0.003715	1.156	2.033	2.29	0.005129	1.097829	2.143321
2.4	2.73	0.001862	1.225	1.903	2.52	0.00302	1.177	1.981	2.36	0.004365	1.121013	2.081154
2.6	2.79	0.001622	1.227	1.883	2.61	0.002455	1.192	1.939	2.46	0.003467	1.150093	2.011141
2.8	2.87	0.001349	1.231	1.862	2.67	0.002138	1.197	1.914	2.51	0.00309	1.157466	1.981052
3	2.88	0.001318	1.224	1.856	2.72	0.001905	1.199	1.895	2.57	0.002692	1.165879	1.949602
3.2	2.94	0.001148	1.223	1.841	2.84	0.001445	1.210	1.861	2.66	0.002188	1.178889	1.911122
3.4	3.03	0.000933	1.224	1.824	2.94	0.001148	1.214	1.837	2.72	0.001905	1.182599	1.888214
3.6	3.12	0.000759	1.223	1.808	3.03	0.000933	1.215	1.819	2.81	0.001549	1.189587	1.86031
3.8	3.23	0.000589	1.22	1.793	3.07	0.000851	1.211	1.810	2.85	0.001413	1.187204	1.847197
4	3.38	0.000417	1.221	1.778	3.52	0.000302	1.226	1.771	2.91	0.00123	1.186852	1.830893
4.2	3.65	0.000224	1.222	1.761	4.01	9.77E-05	1.227	1.753	3.48	0.000331	1.217642	1.768171
4.4	4.21	6.17E-05	1.221	1.746	4.96	1.1E-05	1.223	1.743	4.23	5.89E-05	1.221437	1.746303
4.6	5.62	2.4E-06	1.215	1.737	5.09	8.13E-06	1.215	1.738	4.39	4.07E-05	1.214221	1.740211
4.8	6.97	1.07E-07	1.207	1.732	7.24	5.75E-08	1.208	1.732	4.6	2.51E-05	1.206899	1.734197
5	7.03	9.33E-08	1.200	1.727	7.47	3.39E-08	1.200	1.727	6.06	8.71E-07	1.199962	1.727555
5.2	7.77	1.7E-08	1.192	1.722	7.61	2.45E-08	1.192	1.722	6.31	4.9E-07	1.191979	1.722347
5.4	8.02	9.55E-09	1.184	1.717	7.92	1.2E-08	1.184	1.717	6.64	2.29E-07	1.183992	1.717077
5.6	8.29	5.13E-09	1.176	1.711	8.31	4.9E-09	1.176	1.711	7.02	9.55E-08	1.176	1.711744

5.8	8.71	1.95E-09	1.168	1.706	8.33	4.68E-09	1.168	1.706	7.06	8.71E-08	1.168001	1.706345
6	9.56	2.75E-10	1.161	1.701	8.52	3.02E-09	1.160	1.700	7.25	5.62E-08	1.160005	1.700871
6.2	10.29	5.13E-11	1.160	1.701	9.16	6.92E-10	1.152	1.695	7.9	1.26E-08	1.152035	1.695338
6.4	10.51	3.09E-11	1.158	1.699	10.17	6.76E-11	1.150	1.694	8.41	3.89E-09	1.144116	1.689768
6.6	10.71	1.95E-11	1.159	1.700	10.49	3.24E-11	1.149	1.693	9.33	4.68E-10	1.136968	1.684674
6.8	10.84	1.45E-11	1.159	1.700	10.83	1.48E-11	1.158	1.699	9.7	2E-10	1.130277	1.679847
7	10.92	1.2E-11	1.157	1.699	10.91	1.23E-11	1.157	1.698	9.82	1.51E-10	1.123013	1.674542
7.2	11.05	8.91E-12	1.163	1.703	11.02	9.55E-12	1.159	1.700	10.03	9.33E-11	1.116903	1.670027
7.4	11.09	8.13E-12	1.160	1.701	11.09	8.13E-12	1.160	1.701	10.11	7.76E-11	1.109916	1.664801
7.6	11.16	6.92E-12	1.162	1.702	11.18	6.61E-12	1.165	1.708	10.19	6.46E-11	1.103137	1.659669
7.8	11.2	6.31E-12	1.161	1.701	11.24	5.75E-12	1.168	1.706	10.27	5.37E-11	1.09661	1.654668
8	11.25	5.62E-12	1.162	1.702	11.3	5.01E-12	1.172	1.709	10.33	4.68E-11	1.08992	1.649479
8.2	11.27	5.37E-12	1.158	1.699	11.35	4.47E-12	1.176	1.711	10.38	4.17E-11	1.083169	1.644178
8.4	11.33	4.68E-12	1.163	1.703	11.41	3.89E-12	1.184	1.717	10.46	3.47E-11	1.077474	1.639655
8.6	11.36	4.37E-12	1.163	1.703	11.44	3.63E-12	1.185	1.717	10.49	3.24E-11	1.070487	1.634039
8.8	11.38	4.17E-12	1.160	1.701	11.47	3.39E-12	1.186	1.718	10.68	2.09E-11	1.070515	1.634061
9	11.41	3.89E-12	1.161	1.701	11.5	3.16E-12	1.189	1.720	10.75	1.78E-11	1.066543	1.630836
9.2	11.44	3.63E-12	1.162	1.702	11.54	2.88E-12	1.196	1.725	10.81	1.55E-11	1.062578	1.627594
9.4	11.48	3.31E-12	1.167	1.706	11.56	2.75E-12	1.196	1.725	10.84	1.45E-11	1.056876	1.622887
9.6	11.51	3.09E-12	1.170	1.707	11.57	2.69E-12	1.193	1.723	10.87	1.35E-11	1.051346	1.618273
9.8	11.54	2.88E-12	1.173	1.710	11.61	2.45E-12	1.202	1.729	10.88	1.32E-11	1.04429	1.612316
10	11.56	2.75E-12	1.174	1.710	11.64	2.29E-12	1.209	1.733	10.88	1.32E-11	1.04429	1.612316
				1.805				1.893				1.693

Table 4. : Determination of stability constant and thermodynamic properties of 1, 2, 3 – triazole metal complexes at three temperatures

Metal ion	**(^{0}C) Temperature**	**Stability Constant**	**ΔG KJmol^{-1}**	**ΔH KJmol^{-1}**	**ΔS Jmol^{-1}deg^{-1}**
CoII	35	logK= 1318.25	-18.32063	-52.31080	-11.036
	45	logK=630.95	-17.21705	-5231080	-11036
	55	logK=380.18	-16.11348	-52.31086	-11036
Ni(II)	35	logK=707.9	-16.86841	-43.45721	-86.32
	45	logK=446.68	-16.00514	-43.45721	-86.32
	55	logK=251.18	-15.14187	-43.45721	-86.32

Discussion: pH results of the titrations of 1,2,3-triazole against sodium hydroxide in methanol-water medium for metal complexes of Co(II) and Ni(II) in table2 and 3 has revealed that the reaction mixture tends towards alkaline medium as pH values decrease as the temperature increases from 35^0C to 55^oC. This effect shown on the $[H^+]$which also decreases, showing that more ligands occupy or found in the coordination sphere of the metal complexes due to monomeric nature of the ligand with only one replaceable or dissociable hydrogen atom an indicative of decrease ligand acidity (Al-shihri,2002).

The stability constants or dissociation constants (nH) of the metal complexes calculated by Bjerrum method decrease with increasing temperatures. The protonation constant of 1, 2, 3-triazole under experimental variables including ionic strength and temperatures, At 35^oC, nA is 1.5 and pKa calculated as 11.90 and the stability constant was found to be 7.94 x 10^{11}, indicate a good stability of the ligand while at 45^oC and 55^oC, the ligand is very unstable and could not be detected at that temperatures as shown in table1.

Co (II) metal complexes are more stable than corresponding Ni (II) complexes. This is attributed to the size of the metal ions. The order of stability constants of the metal chelates according to Irving William is Mn (II) <Co (II<) Ni (II) < Cu (II).The result obtained is in conformity with that order. The greater stability of Co (II) than Ni (II) may be attributed to the additional stabilization due to Jahn Taller distortion present in the case of Co (II). It may also be due to partial oxidation of Co (II) (Kumar *et al*., 2007).

The results of pK_a values determined at different temperatures 35^oC, 45^oC , 55^oC for Co(II) are 3.12,2.80 and 2.58 and the log K calculated as 1318.25, 630.95 and 380.18 respectively while Ni(II) have the pK_a values of 2.85, 2.65 and 2.40 and their log K calculated as 707.9, 446.68 and 251.18 respectively. The results of pK_a and log K decrease as the temperatures increase, indicating that metal complexes of Co (II) and Ni (II) become less stable as the temperature increase. This shows that the metal complexes will be better formed with 1, 2, 3-triazole at 35^oC. However, Co (II) complexes in solution are more stable and best formed at that temperature than Ni (II).

Thermodynamic studies of the metal complexes with 1,2,3-triazole at different temperatures were calculated for the overall changes in energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) accompanying complication using temperature and Gibb's Helmholtz equation and the values obtained presented in table 4. The values of ΔG^o were obtained from the equation:

ΔG^o = -Trunk.

The values of ΔS^o were calculated using the following equation.

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

The free energies of formation ΔG of metal complexes all have negative values indicating spontaneity of the reaction process. The values of ΔG obtained show that at 35^oC, the formation of Co (II) triazole complex is more spontaneous. However, as the temperature increases, from 35^oC to 55^oC, the stability of Cobalt and Nickel-triazole complex decreases. The results of the entropy change indicate that the degree of disorderness of the metal complexes is high with Co (II) than Ni (II). The negative values of ΔH showed that the reactions are exothermic.

Conclusion: The results of pH-metric studies on complexes of triazole of Co (II) and Ni (II) in water- methanol medium have revealed than the order of stability is Co (II) and Ni (II). The stability constants for the formation of the coordination complexes were determined and found to decrease with increasing temperature. The coordination number of metal per ligand in the complexes calculated to be approximately 2, confirming that ML_1 and ML_2 complexes were feasible.

The results of thermodynamic studies show that metal complexes were irreversible, spontaneous and exothermic in characters.

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