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Stability constant and thermodynamic studies of metal complexes with Benzimidazole

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ABSTRACT

Metal- ligand complexation in solutions was studied in water-methanol media by pH-metric titration with the standard glass electrode at ionic strength of 0.1M KNO_3. The titrations were carried out at various temperatures 35°C, 45°C, and 55°C and the pKa values (stability constants) were determined. Copper (II) with benzimidazole gave pKa's of 2.86, 2.52, and 2.46; Stability constant (logK) 338.80, 331.13 and 288.40 while Nickel (II) benzimidazole gave pKa's 2.51, 2.60 and 2.38 and Stability constant (logK) 323.59, 398.11 and 239.85 respectively. It was revealed that the stability constants of the metal complexes decreased as the temperature increases. Formation constants obtained for these complexes showed that metal- ligand ratio were in the range of 1:1 and 1:2. The thermodynamic parameters were also determined at the working temperatures and the results obtained showed negative ΔH and Gibb's free energy (ΔG) indicating exothermic and spontaneous reactions.

Introduction

Recently, considerable attention has been paid to the chemistry of the metal complexes of Schiff bases containing oxygen, nitrogen and other donors (Sigel and Mitekaiti,1992) This may be attributed to their stability, biological activity and potential applications in many fields, such as oxidation catalysis and electrochemistry as Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+}.

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 different temperatures (35°C, 45°Cand 55°C) and ionic strength 0.1 mol L-1 (KNO_3). Calvin-Bjerrum pH titration technique as used by Irving and Rossotti has been applied to determine stability constants of the complexes. Free energy, enthalpy and entropy changes have also been evaluated and the values of n obtained for metal- ligand system indicates the formation of 1:1 and 1:2 complexes. Bjerrum half-integral method (Irving and Rossoti, 1954), interpolation at various n values, graphical method extended to dioxane-water mixture by Van Uitert and Haas, 1953 was used to calculate the log K_1 and log K_2 values. In addition, log K_1 and log K_2 values were also obtained by pointwise calculation(Kumar and Kumar,2007).The ligand forms complexes by giving electrons to cations through donor atoms nitrogen and oxygen. It seems that the ligand behaves as bidentate lig and Chalcones of 4-hydroxy coumarin derivative is known for their biological activities and also acts as a good chelating agent due to their O-O electron donor system (Syamasunder,1984) Proton-monomeric ligand dissociation and metal-monomeric ligand stability constants of 2-(acrylamdosulfacetamide (ASA) with some metal ions were calculated potentometrically in 0.1M.KCl and 40 volume % ethanol-water mixture. The effect of temperature on the dissociation of ASA and the stability of its formed complexes was studied in monomeric. The corresponding thermodynamic functions were derived and the dissociation process is non-spontaneous, endothermic and entropically favourable(Al-Shihri *el ta* ,2002)

The formation constants of binary chelates of d^{10} metal ions Cu (II),Ni (II),Co(II) and Mn (II) with 3-[3(3'-chlorophenyl)-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one have been studied by using Irving-Rossoti method at constant temperature 30 ± °C and ionic strength μ -0.1M dm^{-3} was held constant using sodium nitrate as an electrolyte by potentiometric method. The orders of stability constants of the metal chelates under investigation are Mn(II)< Co(II)< Ni(II)< Cu(II) which in conformity with Irving Williams natural order of stability.It was established that the association of proton is affected by strength of hydrogen bonding between oxygen of hydroxyl group and carboxyl group (Vyas *et al*,2007).

The present paper deals with the stability and thermodynamic studies of cobalt(II) and copper(II) with benzimidazole at different temperatures

Materials And Method

All the chemical used are of good analytical grade and used without further purification. The reagent involved are Benzimidazole(ligand), Copper(11) sulphatepentahydrate, Cobalt (11)chloridehexahydrate, Nitric acid, Sodium hydroxide Methanol, and distilled water, pH meter model 132E ,Thermometer and Magnetic stirrer.

Experimental Complexation in Solutions

The stability constants of the ligands and metal complexes were determined by pH-metric titrations of the samples. The ligands Benzimidazole and the metal salts in 1:2 molar ratio were prepared in 50%v/v methanol/distilled water mixture. All pH-metric measurements were carried out at a constant ionic strength 0.1M KNO_3 and temperature of 298K, 308K and 328K. Measurements were performed with an ATC pH meter model

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132 E equipped with glass calomel electrode assembly. The prepared solutions were titrated against carbonated free sodium hydroxide. The pH readings were stabilized in a few minutes and converted to hydrogen ion concentration according to method of Bjerrum (1941).

The stability constants defined by:

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

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:

$$n_A = T_A - \left[\frac{(T_H - [H]}{n_H}\right] \Big/ T_M$$

Where T_H = Total concentration of the Hydrogen ion present

T_A = Total concentration of Ligand

T_M = Total concentration of the Metal

n_A = Average number of ligands bound per metal.

Results and discussion

Table 1: Calculated pka and stability constant of benzimidazole at different temperatures

Temperature	pKa	nA	STABILITY CONSTANT
350C	11.98	1.5	9.55 x 1011
450C	1.70	0.5	5.01 x 101
550C	1.69	0.5	4.90 x 101

The protonation constants of Benzimidazole under experimental variables including ionic strength and temperature were obtained. The acid dissociative constant P_{Ka} of Benzimidanole was determined from the resulting $[H^+]$ in 0.025M solution. The activity determined was converted to $[H^+]$ using equations:

$a_{H+} = \gamma\pm[H^+]$ .....(i)

$pH = -\text{Log } a_{H+}$ .....(ii)

Rearranging and substituting into equation (ii) gives

$\text{Log } [H^+] = -\text{pH} - \text{Log } \gamma\pm$ .....(iii)

The constant; $\text{Log}\gamma \pm$ may be obtained from the expression

$$-\text{Log } \gamma\pm = \left[\frac{0.5 Z_1 Z_2 \mu^{1/2}}{1 + \mu^{1/2}}\right] - 0.1\,\mu$$ ..... (vi)

Where Z_1 and Z_2 are the charges +1 or -1 which are H^+ and NO_3^- respectively. The ionic strength, μ of the solution.

$\mu = \frac{1}{2} \Sigma M_1 . Z_1^2$ ..... (vii)

(where M_1 is the molar concentration of I and Z_1 is its charge)..

The expression for the acid dissociation constant for the reaction.

$HA \leftrightarrow H^+ + A^-$ is given by

$$Ka = \frac{[H^+][A^-]}{HA}$$ .....(viii) .

Where (H^+) is from equation (iii) while (HA) and (A^-) are known concentration (Gregory *et al.,* 1977). The calculated P_{Ka} of Benzimidazole at 35^0C is 11.98. Stability constant of the Ligand 9.55 x 10^{11} indicates good stability of the ligand (Table 1).The higher values of stability constants suggest good stable complexes as usual trend of divalent transition metal complex with the ligand such as azoles(Wilkinson ,1998).

The values of n_A obtained for metal – ligand systems represent the average number of coordination number of the ligands to the metal ions .Typically as ligand is added to the solution of the metal ions ML_1 is first formed more rapidly than ML_2 The table2 and 3 show nA results for both metals express the maximum nA values in all cases were found to be approximately 2 indicating that metal-ligand systems coordinate in ratio 1:1 and 1:2 complexes. No precipitate was observed in the titration vessels, showing that the possibility of formation of metal hydroxide can be excluded, The pH metric analysis shows that the complexes have1:2 (metal-ligand) stochiometry, a common feature in the first row transition metals(Holm and O' Connom,1997). Bjerrium half – integral method at various n_A values, graphical method extended to methanol/water mixture by Van Vitert and Hass (1953) was used to calculate the Log K values. The values of n_A calculated for Benzimidazole complexes of Copper, Cobalt, and stability constants are presented as table4 .From these values, the overall orders of stability at 35^oC shows Cu (II) > Co(II) which is in conformity with the Irving Williams natural order of stabilities. Copper(II) shows higher stability than Co(II) as experienced because of its greater lattice and solution energy(Al-Shihri et al,2002).

The determination of stability constant of metal complexes forms is an important factor in the estimation of the thermodynamic functions ΔH, ΔG and ΔS. In order to estimate these factors, a plot of the confirmed stability constants against the reciprocal of temperatures and the slope of the plot gave the values the enthalpy , ΔH .The negative values of ΔH shows that the dissociation constants are accompanying by liberation of heat and the process is exothermic.

The overall changes in energy (ΔG^o) and entropy (ΔS^o) accompanying complexation have been determined using temperature and Gibb's Helmholtz equation and the values obtained presented as table 4. The values of ΔG^o were obtained from the equation $\Delta G^o = -RT\ln K$ or $G = -2.303RT\log K$. The values of ΔS^o were calculated by using the following equation.

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

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 copper (II) Benzimidazole complex is more spontaneous. However, as the temperature increases, from 35^0C to 55^0C, the stability of Cobalt and Copper –Benzimidazole complex decreases. This also confirms the irreversibility of the metal complexes. The negative value of ΔS is due to the increased order as a result of salvation process.

Conclusion

The results of the pH-metric studies on complexes of Benzimidazole of Cu(II)and Co(II)in water- methanol medium. The order of stability is Cu(II) and Co(II) and the stability constants for the formation of the coordination complexes were determined and found to decrease with increasing temperature and the number of metal per ligand in the complexes found to be approximately 2 , showing thatML_1 and ML_2 complexes were feasible.

The results of thermodynamic studies reveal that metal complexes were irreversible, spontaneous and exothermic.

Table2: Determination of number of coordinated ligands in Cobalt (II) benzimidazole complex at 35^0C

Temp. ^{0}C	35^0C			45^0C			55^0C		
Vol of NaOH	pH	nH	nA	pH	Nh	nA	pH	nH	nA
0	1.9	0.89643	2.870275	1.73	0.655165	3.927254	1.54	0.246387	10.4429
0.2	1.92	0.909171	2.808054	1.75	0.677843	3.766359	1.55	0.260137	9.814044
0.4	1.94	0.921064	2.750079	1.76	0.683319	3.706909	1.57	0.298773	8.478004
0.6	1.96	0.932146	2.695931	1.78	0.704199	3.568592	1.59	0.335504	7.490228
0.8	1.97	0.932535	2.673359	1.8	0.723899	3.443849	1.65	0.458184	5.441049
1	1.99	0.942496	2.623883	1.81	0.728083	3.396592	1.59	0.311279	7.944654
1.2	2.01	0.951724	2.577429	1.84	0.759948	3.227853	1.61	0.346551	7.078319
1.4	2.04	0.968981	2.510885	1.86	0.776386	3.133751	1.62	0.3576	6.803693
1.6	2.07	0.98465	2.450616	1.89	0.804211	3.000458	1.66	0.432892	5.574139
1.8	2.11	1.006323	2.377964	1.94	0.852205	2.808009	1.68	0.462196	5.177461
2	2.15	1.025495	2.314005	1.96	0.863865	2.746957	1.7	0.489971	4.843145
2.2	2.16	1.023091	2.299892	1.99	0.884673	2.65974	1.77	0.602813	3.903363
2.4	2.18	1.027037	2.271583	2.05	0.930388	2.507557	1.82	0.669515	3.484611
2.6	2.23	1.048215	2.206609	2.11	0.969355	2.386122	1.86	0.715134	3.234358
2.8	2.26	1.055874	2.171661	2.14	0.981998	2.335035	1.91	0.768334	2.984377
3	2.32	1.077061	2.110373	2.21	1.018564	2.231574	1.97	0.825676	2.752896
3.2	2.37	1.090448	2.066124	2.3	1.058695	2.128092	2.02	0.865555	2.602954
3.4	2.42	1.101583	2.027083	2.35	1.073177	2.080738	2.08	0.908671	2.457436
3.6	2.46	1.107319	1.99852	2.38	1.077246	2.054312	2.15	0.952433	2.323523
3.8	2.53	1.12098	1.956324	2.52	1.118021	1.961501	2.3	1.032289	2.124405
4	2.74	1.161389	1.871036	2.69	1.151797	1.886617	2.42	1.075758	2.019971
4.2	2.85	1.170752	1.838988	2.8	1.163279	1.850803	2.62	1.127987	1.908711
4.4	2.91	1.170459	1.822362	3.03	1.183385	1.802457	2.82	1.15813	1.841762
4.6	3.15	1.185077	1.783007	3.3	1.194108	1.769521	3.04	1.176163	1.796519
4.8	3.38	1.189724	1.759231	3.53	1.195062	1.751374	3.31	1.186528	1.76397
5	3.49	1.185762	1.748243	3.91	1.194587	1.735328	3.55	1.187599	1.745539
5.2	3.7	1.183189	1.735141	4.13	1.188726	1.727059	3.79	1.184838	1.732726
5.4	3.96	1.17914	1.724137	4.29	1.181727	1.720364	3.99	1.179465	1.723663
5.6	4.17	1.172993	1.716123	4.51	1.174625	1.713738	4.15	1.172851	1.71633
5.8	4.34	1.16596	1.709322	4.64	1.166977	1.707831	4.33	1.165912	1.709391
6	4.46	1.158447	1.703143	4.78	1.159257	1.701953	4.53	1.158678	1.702803
6.2	4.59	1.150844	1.697015	4.92	1.151459	1.696108	4.75	1.151201	1.69649
6.4	4.72	1.14314	1.690956	5.2	1.143715	1.690106	4.86	1.143377	1.690606
6.6	4.81	1.135299	1.685019	5.48	1.13585	1.684201	4.99	1.135537	1.684666
6.8	4.92	1.127454	1.679005	5.74	1.127918	1.678315	5.26	1.12775	1.678563
7	5.08	1.119621	1.672888	6.14	1.119968	1.672371	5.54	1.119869	1.672518
7.2	5.2	1.111711	1.6668	7.15	1.112003	1.666377	5.8	1.111928	1.666476
7.4	5.38	1.103809	1.660614	7.75	1.104025	1.660347	6.12	1.103966	1.660379
7.6	5.54	1.095867	1.654398	8.03	1.096049	1.654236	7.11	1.096002	1.654207
7.8	5.9	1.087942	1.648066	8.28	1.088088	1.648047	7.71	1.088023	1.647998
8	6.36	1.079981	1.641698	8.48	1.08014	1.641778	7.97	1.080043	1.641702
8.2	7.08	1.072002	1.635272	8.89	1.072361	1.635553	8.16	1.072067	1.635316
8.4	7.54	1.064015	1.628775	9.91	1.067798	1.631858	8.19	1.064072	1.628819
8.6	7.76	1.056026	1.622183	10.48	1.070158	1.633772	8.38	1.056112	1.622253
8.8	7.88	1.048035	1.615489	10.53	1.063939	1.62871	8.48	1.048142	1.615578
9	7.93	1.04004	1.608689	11.15	1.106672	1.662353	8.9	1.040375	1.608975
9.2	8.04	1.032051	1.60179	11.33	1.133254	1.682001	10.28	1.041024	1.609531
9.4	8.14	1.024065	1.594785	11.42	1.14899	1.693205	10.61	1.043359	1.611523
9.6	8.22	1.016079	1.58767	11.48	1.159991	1.700856	10.84	1.048987	1.61629
9.8	8.38	1.008115	1.580462	11.53	1.170103	1.707762	11.02	1.058095	1.623897
10	8.58	1.000182	1.573169	11.6	1.191091	1.721722	11.15	1.067802	1.631861
			1.940917			2.118014			2.241434

Table 3: Determination of number of coordinated ligands in copper (ii) Benzimidazole complex at different temperatures

Temp. ^{0}C	35^{0}C			45^{0}C			55^{0}C		
Vol of NaOH	pH	nH	nA	pH	nH	nA	pH	nH	nA
0	2.01	1.009105	2.549784	1.73	0.655165	3.927254	1.54	0.246387	10.4429
0.2	2.06	1.042221	2.449576	1.75	0.677843	3.766359	1.55	0.260137	9.814044
0.4	2.08	1.048633	2.415526	1.76	0.683319	3.706909	1.57	0.298773	8.478004
0.6	2.11	1.061775	2.366791	1.78	0.704199	3.568592	1.59	0.335504	7.490228
0.8	2.14	1.073589	2.322117	1.8	0.723899	3.443849	1.65	0.458184	5.441049
1	2.18	1.090437	2.267898	1.81	0.728083	3.396592	1.59	0.311279	7.944654
1.2	2.21	1.099443	2.23113	1.84	0.759948	3.227853	1.61	0.346551	7.078319
1.4	2.24	1.107379	2.19708	1.86	0.776386	3.133751	1.62	0.3576	6.803693
1.6	2.27	1.114313	2.165459	1.89	0.804211	3.000458	1.66	0.432892	5.574139
1.8	2.3	1.120308	2.13602	1.94	0.852205	2.808009	1.68	0.462196	5.177461
2	2.34	1.129851	2.100276	1.96	0.863865	2.746957	1.7	0.489971	4.843145
2.2	2.38	1.137915	2.067816	1.99	0.884673	2.65974	1.77	0.602813	3.903363
2.4	2.43	1.148252	2.031783	2.05	0.930388	2.507557	1.82	0.669515	3.484611
2.6	2.49	1.159832	1.994255	2.11	0.969355	2.386122	1.86	0.715134	3.234358
2.8	2.55	1.168952	1.961587	2.14	0.981998	2.335035	1.91	0.768334	2.984377
3	2.6	1.173496	1.936947	2.21	1.018564	2.231574	1.97	0.825676	2.752896
3.2	2.63	1.17223	1.921978	2.3	1.058695	2.128092	2.02	0.865555	2.602954
3.4	2.69	1.176777	1.897556	2.35	1.073177	2.080738	2.08	0.908671	2.457436
3.6	2.78	1.184837	1.867768	2.38	1.077246	2.054312	2.15	0.952433	2.323523
3.8	2.86	1.188588	1.845046	2.52	1.118021	1.961501	2.3	1.032289	2.124405
4	2.99	1.195794	1.817203	2.69	1.151797	1.886617	2.42	1.075758	2.019971
4.2	3.11	1.198342	1.796649	2.8	1.163279	1.850803	2.62	1.127987	1.908711
4.4	3.24	1.198957	1.779047	3.03	1.183385	1.802457	2.82	1.15813	1.841762
4.6	3.48	1.201536	1.758582	3.3	1.194108	1.769521	3.04	1.176163	1.796519
4.8	3.63	1.197723	1.747483	3.53	1.195062	1.751374	3.31	1.186528	1.76397
5	3.79	1.192864	1.737834	3.91	1.194587	1.735328	3.55	1.187599	1.745539
5.2	3.98	1.187376	1.729023	4.13	1.188726	1.727059	3.79	1.184838	1.732726
5.4	4.14	1.180789	1.72173	4.29	1.181727	1.720364	3.99	1.179465	1.723663
5.6	4.36	1.174058	1.714566	4.51	1.174625	1.713738	4.15	1.172851	1.71633
5.8	4.52	1.166652	1.708307	4.64	1.166977	1.707831	4.33	1.165912	1.709391
6	4.61	1.1589	1.702476	4.78	1.159257	1.701953	4.53	1.158678	1.702803
6.2	4.75	1.151201	1.69649	4.92	1.151459	1.696108	4.75	1.151201	1.69649
6.4	4.89	1.143419	1.690544	5.2	1.143715	1.690106	4.86	1.143377	1.690606
6.6	5.08	1.135623	1.684537	5.48	1.13585	1.684201	4.99	1.135537	1.684666
6.8	5.26	1.12775	1.678563	5.74	1.127918	1.678315	5.26	1.12775	1.678563
7	5.46	1.119842	1.672558	6.14	1.119968	1.672371	5.54	1.119869	1.672518
7.2	5.74	1.111917	1.666492	7.15	1.112003	1.666377	5.8	1.111928	1.666476
7.4	5.92	1.103945	1.660409	7.75	1.104025	1.660347	6.12	1.103966	1.660379
7.6	6.04	1.095958	1.654261	8.03	1.096049	1.654236	7.11	1.096002	1.654207
7.8	6.12	1.087966	1.648032	8.28	1.088088	1.648047	7.71	1.088023	1.647998
8	6.2	1.079971	1.641712	8.48	1.08014	1.641778	7.97	1.080043	1.641702
8.2	6.31	1.071978	1.635297	8.89	1.072361	1.635553	8.16	1.072067	1.635316
8.4	6.44	1.063984	1.628786	9.91	1.067798	1.631858	8.19	1.064072	1.628819
8.6	6.71	1.055993	1.622175	10.48	1.070158	1.633772	8.38	1.056112	1.622253
8.8	6.99	1.048	1.615469	10.53	1.063939	1.62871	8.48	1.048142	1.615578
9	8.43	1.040127	1.608763	11.15	1.106672	1.662353	8.9	1.040375	1.608975
9.2	10.25	1.040422	1.609015	11.33	1.133254	1.682001	10.28	1.041024	1.609531
9.4	10.91	1.062626	1.627633	11.42	1.14899	1.693205	10.61	1.043359	1.611523
9.6	11.19	1.089848	1.649422	11.48	1.159991	1.700856	10.84	1.048987	1.61629
9.8	11.34	1.112663	1.666863	11.53	1.170103	1.707762	11.02	1.058095	1.623897
10	11.57	1.178337	1.713298	11.6	1.191091	1.721722	11.15	1.067802	1.631861
			2.118014			2.01434			1.162429

Table 4: Determination stability constant and thermodynamic properties of benzimidazole 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=338.84	-14806.38	-32037.53	-55.94
	45	logK=199.52	-14246.93	-32037.53	-55.94
	55	logK=158.49	-13687.47	-32037.53	-55.94
CuII	35	logK=338.84	-1611.84	-38957	-72.55
	45	logK=331.13	-15886.33	-38957	-72.55
	55	logK=288.40	-15160.82	-38959	-72.55

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