



SPECTROPHOTOMETRIC, CONDUCTOMETRIC STUDY OF STABILITY CONSTANT OF SUBSTITUTED 1,3-DIARYL CARBAMIDES WITH TRANSITION METAL IONS.

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ABSTRACT

Substituted 1,3-Diaryl carbamides were synthesized by green chemistry technique. Structures were confirmed by spectral & CHN Analysis. These compounds were further implemented for complexometric study with Cu^{2+} , Ni^{2+} , Co^{2+} transition metal ions by Spectrophotometric and conductometric techniques. Conductometric involved modified Job's method for the study. Comparative results obtained by both techniques were used to judge the nature of complexes.

Keywords: 1,3-Diaryl carbamides, Conductometry, Spectrophotometry, Stability Constant.

Introduction

Heterocyclic compounds have wide applications in pharmaceutical chemistry, medicinal chemistry etc. The nitrogen containing heterocyclic compounds exhibit antimicrobial, anticancer, antiviral activity^{1,2} etc. The heterocyclic compounds selected for the study were 1,3-diaryl carbamides. i.e. 1,3-di-o-tolyl carbamide (Ia), 1,3-di-m-tolyl carbamide (IIa) and 1,3-di-p-tolyl carbamide (IIIa). These were synthesized by green chemistry techniques i.e. microwave synthesis³ by known method⁴. Structures were confirmed by spectral analysis and CHN analysis.

The compounds were further implemented for complexometric study by analytical techniques spectrophotometry and conductometry⁵.

Experimental

The metal ions used for study were Co^{2+} , Ni^{2+} , Cu^{2+} . The ligands used were Ia, IIa, IIIa.

Spectrophotometric Study

We work relate comparative study of two techniques. Equimolar solution of Cu^{2+} and ligand 1,3-diaryl carbamide (1×10^{-2}) were mixed in different proportions to prepare Job's solutions. Final volume of each solution was fixed upto 10ml after adjusting appropriate pH and maintaining ionic strength $\mu = 0.1$ M constant. λ_{max} was selected as proposed by Vasburgh and Robert Gold⁶. Job's curves were constructed from which metal ligand stability constant was calculated by Job's method and same procedure was repeated for remaining metal ions.

Conductometric Study

Similar solutions as in spectrophotometric study were prepared. These serve as Job's solution for which conductance was recorded. Corrected conductance may be determined by using the formula
Corrected Conductance = $[(V+v) / V] \times$ observed conductance.

V – Initial volume of ligand
v – Volume of metal. The curves were constructed between metal ligand ratio and corrected conductance. Turner and Anderson's⁷ by modified Job's method for determination of stability constant

$$K = x / ((a - x)(b - x))$$

a, b – initial concentration of metal ion and ligand concentration.

x – concentration of complex can be calculated for Job's curve.

Table 1: Spectrophotometric study

S r. N o.	Compo sition M : Ia	Temperature		Optical Density		Optical Density	
		Cu ²⁺	Ni ²⁺	Co ²⁺			
		a	B	a	b	a	b
1	1 : 9	0.0 99	0.0 91	0.1 08	0.0 58	0.1 86	0.1 38
2	2 : 8	0.0 91	0.0 96	0.1 29	0.0 97	0.2 38	0.2 15
3	3 : 7	0.0 82	0.0 72	0.2 04	0.1 80	0.2 84	0.1 98
4	4 : 6	0.0 62	0.0 52	0.3 57	0.3 09	0.3 71	0.3 31
5	5 : 5	0.3 21	0.2 16	0.4 17	0.3 88	0.4 69	0.4 21
6	6 : 4	0.2 91	0.1 21	0.4 00	0.3 60	0.4 84	0.4 28
7	7 : 3	0.1 21	0.1 42	0.3 41	0.2 87	0.3 89	0.3 43
8	8 : 2	0.1 41	0.1 36	0.2 49	0.1 82	0.2 71	0.2 28
9	9 : 1	0.0 22	0.0 12	0.1 40	0.1 07	0.2 47	0.1 94
M :IIa							
1	1	0.41 2	0.32 1	0.10 6	0.08 4	0.18 8	0.10 9
:	:						
9	9						
2	2	0.51 6	0.14 1	0.18 6	0.13 7	0.25 6	0.21 7
:	:						
8	8						
3	3	0.51 6	0.51 1	0.21 7	0.18 0	0.38 7	0.32 8
:	:						
7	7						
4	4	0.82 1	0.61 2	0.29 7	0.28 0	0.35 2	0.30 1
:	:						
6	6						
5	5	0.91 2	0.82 1	0.35 6	0.34 0	0.46 7	0.40 7
:	:						
5	5						
6	6	0.32 1	0.22 1	0.30 4	0.28 1	0.50 2	0.51 0
:	:						
4	4						
7	7	0.12 1	0.09 9	0.28 5	0.26 3	0.31 4	0.25 8
:	:						

3	8	0.14 1	0.13 1	0.21 9	0.18 6	0.25 1	0.10 8	
:	:							
2	9	0.10 1	0.06 6	0.21 0	0.13 8	0.26 0	0.30 7	
:	:							
1	1	0.22 0	0.14 0	0.10 8	0.08 7	0.28 4	0.22 7	
:	:							
9	2	0.20 0	0.12 0	0.19 4	0.16 1	0.30 4	0.27 8	
:	:							
8	3	0.19 0	0.11 1	0.28 0	0.23 9	0.38 1	0.32 1	
:	:							
7	4	0.42 0	0.34 0	0.31 6	0.28 1	0.45 7	0.38 9	
:	:							
6	5	0.55 0	0.42 0	0.38 2	0.32 9	0.52 9	0.49 2	
:	:							
5	6	0.37 0	0.38 1	0.38 3	0.33 0	0.48 8	0.42 1	
:	:							
4	7	0.21 0	0.20 1	0.32 6	0.32 1	0.41 7	0.37 4	
:	:							
3	8	0.41 0	0.28 1	0.25 4	0.21 8	0.38 0	0.31 8	
:	:							
2	9	0.32 0	0.26 8	0.11 9	0.10 1	0.30 7	0.25 6	
:	:							
1	1	a = Concentration of M & L = 0.01 N						b =
		Concentration of M & L = 0.005 N						

Table 2: Conductometric study

S	r.	Compo sition M : Ia	Temperature		Correcte d Conduct ance Cu ²⁺		Correcte d Conduct ance Ni ²⁺		Correct ed Conduc tance Co ²⁺		8	8	0.217	0.11	0.957	0.397	1.80	1.27
			a	B	a	b	a	b										
1	1	9	0.1	0.0	0.0	0.0	1.0	0.7	8	8	0.217	0.11	0.957	0.397	1.80	1.27	8	
			551	814	924	682	01	81										
2	2	8	0.1	0.1	0.1	0.9	0.9	1.0										
			224	224	200	84	72	68										
3	3	7	0.1	0.1	0.2	0.1	0.9	0.8										
			703	573	496	963	88	06										
4	4	6	0.4	0.2	0.2	0.2	0.7	0.6										
			774	828	548	072	14	72										
5	5	5	0.1	0.7	0.4	0.6	1.0	0.4										
			830	890	815	315	8	65										
6	6	4	0.8	0.6	1.1	0.8	0.3	0.3										
			512	112	424	336	36	36										
7	7	3	0.6	0.4	0.5	0.6	1.9	1.6										
			465	097	797	987	72	83										
8	8	2	0.5	0.4	0.7	0.5	0.7	0.8										
			156	878	416	778	38	10										
9	9	1	0.3	0.3	0.2	0.3	0.4	0.0										
			629	439	204	059	18	38										
M :IIa																		
1	1	0.199	0.11	0.155	0.141	1.33	1.08											
			2	1	9	1	9											
2	2	0.238	0.16	0.145	0.118	1.66	0.74											
			9	2	8	8	4											
3	3	0.405	0.26	0.257	0.184	1.84	0.66											
			1	4	6	6	3											
4	4	1.247	0.89	0.337	0.207	2.08	0.68											
			7	4	2	6	6											
5	5	0.931	0.80	1.141	0.793	2.58	0.48											
			5	8	5	5	0											
6	6	0.657	0.38	1.293	0.854	3.07	2.06											
			7	2	4	2	4											
7	7	0.409	0.15	1.040	0.695	1.73	1.66											
			9	4	7	4	6											
M :IIIa																		
1	1	0.17	0.16	0.529	0.309	1.12	1.10											
			7	7	1	1	2											
2	2	0.21	0.18	0.385	0.256	2.30	2.05											
			4	1	2	8	4	2										
3	3	0.16	0.22	0.287	0.248	2.61	2.45											
			6	2	3	3	3	7										
4	4	0.19	0.28	0.348	0.208	2.68	2.53											
			8	2	6	6	8	4										
5	5	0.48	0.41	1.228	1.143	2.16	1.83											
			0	7	5	0	0											
6	6	0.35	0.20	1.217	0.691	3.53	3.20											
			5	6	6	2	6	0										
7	7	0.21	0.17	1.052	0.870	2.90	2.57											
			4	1	3	4	7	4										
8	8	0.23	0.21	0.754	0.579	2.89	2.77											
			7	7	2	6	8	2										
9	9	0.27	0.24	1.959	1.179	3.26	2.85											
			7	8	9	9	8	0										

a = Concentration of M & L = 0.01 N b = Concentration of M & L = 0.005 N

Table: 3 Comparative results of Spectrophotometric & Conductometric techniques

Sr	Na K (K	me Spectrophotome (Conductomet	N of trically) rically)
1	Cu ²⁺ -IIIa	3.552836	3.914672
2	Cu ²⁺ -IIIb	3.650884	3.707479
3	Cu ²⁺ -IIIc	3.511124	4.121786
4	Ni ²⁺ -IIIa	4.396321	4.425126
5	Ni ²⁺ -IIIb	3.702002	2.947378
6	Ni ²⁺ -IIIc	3.415491	2.899086
7	Co ²⁺ -IIIa	4.121786	2.728824
8	Co ²⁺ -IIIb	0.540394	2.441148
9	Co ²⁺ -IIIc	3.665822	4.1633761

Results & Discussion

The spectrophotometric technique using the formula of $K = \frac{[ML]}{[M][L]}$ The conditional stability constant log K was determined by Job's variation method. By considering the concept of ionic changes occurring during complex formation, the conductance of solution may be used as a basis for the Conductometric study and applied modified Job's method for determination of stability constant. By considering same aspect, Conductometric determination of stability constant of 1,3-di-o-tolyl carbamides, 1,3-di-m-tolyl carbamides, 1,3-di-p-tolyl carbamide with transition metal ions Cu,Co,Ni was carried out.

The transition metal ions shows variables oxidation states and 2+ oxidation state is common for them. These metal ions great tendency to form complexes with several ligands like neutral molecules like NH₃, H₂O, CN⁻, Cl⁻ etc. These ligands possess lone pair of e⁻ which they donate to transition

metal ion in the formation of complex compound. These metal ions have small size and high positive charge density which makes them easy to accept lone pair of electrons from ligands. They form stable complexes with N, O and F donors and have strong metal ligand orbital interaction. The values of stability constant by spectrophotometry and conductometry are presented in table 3. The data reveals that the values of conditional stability constants obtained by both techniques represents good agreement with each other which reflects the stable complex formation between transition metal ions and ligands

Conclusion

Results obtained from Spectrophotometric and conductometric techniques are in good agreement with each other indicating 1:1 complex formation.

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