

The values of $\log K_1$, $\log K_2$ and $\log K_3$ for the complexes of bivalent metal ions studied have been summarised in Table 1. The order of decreasing stabilities of the metal complexes is: $\text{Ni} > \text{Co} > \text{Fe} > \text{Zn} > \text{Pb} > \text{Cd} > \text{Mn} > \text{Mg}$. This order is in agreement with the order found by Mellor and Maley⁵ and Irving and Williams⁶. In the case of Co(II) and Ni(II) , $\log K_1$ and $\log K_2$ values could not be obtained since they form very strong complexes with the ligand as indicated by the values of $\log \beta_2$ and $\log \beta_3$.

The stability constants of Cu(II) complexes could not be determined since Cu(II) is completely complexed at a very low $p\text{H}$ value.

From the values of stability constants at different ionic strengths, it is seen that there is a regular and gradual decrease in the stability constants with the increase in the ionic strength of the medium. A similar behaviour has been observed in the case of dissociation constant of the ligand. These results are in accord with theoretical considerations.

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Potentiometric Investigation on the Complexes of Mn(II) , Co(II) , Ni(II) , Cu(II) & Zn(II) with Quinoline-8-carboxylic Acid & Its 5-Substituted Derivatives in Water-Ethanol Medium†

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The protonation and acid dissociation constants of quinoline-8-carboxylic acid (Q-8-CA) and its 5-substituted derivatives and the formation constants of their chelates with Mn(II) , Co(II) , Ni(II) , Cu(II) and Zn(II) have been studied in water-ethanol medium using Calvin-Bjerrum $p\text{H}$ titration technique as modified by Irving and Rossotti. The metal ions form 1:1 and 1:2 chelates with Q-8-CA and 5- NH_2 -Q-8-CA except Cu(II) , and 1:1 chelates with 5- NO_2 -Q-8-CA. The thermodynamic parameters, ΔG^\ddagger , ΔH^\ddagger and ΔS^\ddagger and their corresponding electrostatic ($\Delta G_{\text{el}}^\ddagger$, $\Delta H_{\text{el}}^\ddagger$) and cratic ($\Delta G_{\text{cr}}^\ddagger$, $\Delta H_{\text{cr}}^\ddagger$) components have been evaluated and discussed. The overall stability constants ($\log \beta_n$) with respect to the metal ions follow the natural order and the order with respect to the ligands is: 5- NO_2 -Q-8-CA < Q-8-CA < 5- NH_2 -Q-8-CA.

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QUINOLINE-8-CARBOXYLIC acid (Q-8-CA) is not only an important analytical reagent^{1,2} but also has a variety of uses due to its antidiuretic, antibacterial, insecticidal and fungitoxicity activities^{3,4}. Lumme⁵ determined the protonation constant $pK(\text{NH}^+)$ and the acid dissociation constant $pK(\text{COOH})$ of Q-8-CA and reported its stability constant with various bivalent transition metal ions at high ionic strengths and at 25°. However, no attention was paid to the nature of complexes formed in the presence of high concentrations of potassium chloride used to maintain the ionic strength constant. Gomez *et al.*⁶ synthesized Co(II) and Ni(II) complexes of 5-nitroquinoline-8-carboxylic acid (5- NO_2 -Q-8-CA) and 5-aminoquinoline-8-carboxylic acid (5- NH_2 -Q-8-CA) and discussed ligand field parameters on the basis of IR and magnetic susceptibility data.

Earlier we reported⁷ the formation constants of Fe(II) complexes with Q-8-CA, 5- NO_2 -Q-8-CA and 5- NH_2 -Q-8-CA in water-ethanol (50%, v/v) medium. In our preliminary investigations with these ligands, it was observed that the formation constants of Co(II) and Ni(II) were abnormally lower than those of Fe(II) under similar conditions. Hence we have undertaken a systematic study to determine the protonation, acid dissociation and metal-ligand formation constants of these ligands with Mn(II) , Co(II) , Ni(II) , Cu(II) and Zn(II) in water-ethanol (50%, v/v) medium at different temperatures and at 0.10 M ionic strength employing Calvin-Bjerrum^{8,9} $p\text{H}$ titration technique as modified by Irving and Rossotti¹⁰.

Thermodynamic parameters, such as ΔG^\ddagger , ΔH^\ddagger and ΔS^\ddagger accompanying the chelate formation have been calculated and discussed. The ΔG^\ddagger and ΔH^\ddagger values have been separated into their corresponding electrostatic and non-electrostatic or cratic components with a view to understanding the nature of bonding between the metal ion and the ligand.

Details of synthesizing ligands and the $p\text{H}$ titration technique are reported in our earlier paper⁷. The metal perchlorate solutions were prepared and standardized complexometrically¹¹. All the titrations were performed in water-ethanol (50%, v/v) medium and an inert atmosphere was maintained by bubbling continuously oxygen-free nitrogen through the reaction-mixtures.

The protonation constants were determined by titrating the following solutions (total vol. 50 ml) against carbonate free sodium hydroxide (1.25 M): (a) HClO_4 ($5 \times 10^{-2} M$); (b) HClO_4 ($5.5 \times 10^{-2} M$) + ligand ($5 \times 10^{-3} M$). The ionic strength was kept constant at 0.10 M by adding requisite quantity of sodium perchlorate and the temperature was maintained at 30°.

For the determination of acid dissociation and chelate formation constants the experimental procedure involved the potentiometric titrations of the following solutions (total vol. 50 ml) against standard sodium hydroxide (0.10 M): (i) HClO_4 ($4.00 \times 10^{-3} M$); (ii) HClO_4 ($4.00 \times 10^{-3} M$) + ligand ($2 \times 10^{-3} M$); (iii) HClO_4 ($4.00 \times 10^{-3} M$) + ligand ($2.00 \times 10^{-3} M$) + metal perchlorate ($4.00 \times 10^{-4} M$).

The $p\text{H}$ correction for the aquo-organic solvent

mixtures was made as suggested by Uitert and Haas¹².

Values of \bar{n}_A , \bar{n} and pL were calculated from Irving and Rossotti formulae¹⁰. From the titration curves of (a) and (b), \bar{n}_A values at different pH meter readings were calculated and the protonation constants were determined from the intercepts of the plots of $\log n/(1-n)$ vs pH . Similarly, acid dissociation constants were calculated from the titration curves (i) and (ii) wherein it was observed that in the initial stage of the titration, the ligand curve shifted to left (or above) the acid curve due to the basic nature of tertiary nitrogen ($C = N$) which accepts a proton from the acid solution. The degrees of formation (\bar{n}) of the metal-ligand system and corresponding pL values at different pH meter readings were evaluated from the titration curves (ii) and (iii). The formation curves thus obtained indicate that Q-8-CA and 5-NH₂-Q-8-CA form 1:1 and 1:2 chelates with all the metal ions studied whereas 5-NO₂-Q-8-CA forms 1:1 chelates except with Cu(II), which gives precipitate. The $\log Kn$ values were computed using (i) half- \bar{n} -method, (ii) successive-approximation method and (iii) least-squares method¹³. The values agree closely and hence the formation constants calculated by the least-squares method are reported.

Thermodynamics of complex formation— Values of $\log Kn$ were determined at 20°, 30°, 40° and 50° and at 0.10 M ionic strength (Table 1). The changes in free energy (ΔG^\ddagger), enthalpy (ΔH^\ddagger) and entropy (ΔS^\ddagger) accompanying the metal-ligand chelate formation have been evaluated by using the van't Hoff isotherm and isochore equations (Table 2). The negative values of ΔG^\ddagger and ΔH^\ddagger reveal the spontaneity and exothermic nature of the reactions.

To get an insight into the extent of ionic and covalent nature of the complex formed, the ΔG^\ddagger and ΔH^\ddagger values were separated into their respective electrostatic (ΔG_e^\ddagger , ΔH_e^\ddagger) and non-electrostatic or cratic (ΔG_c^\ddagger , ΔH_c^\ddagger) components as derived by Degischer and Nancollas¹⁴. Comparison of the electrostatic and cratic parts of the thermodynamic parameters (Table 3) for the equilibrium (1),



TABLE 1 — STEPWISE AND OVERALL STABILITY CONSTANTS OF Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) CHELATES IN WATER-ETHANOL MEDIUM (50% v/v) AT DIFFERENT TEMPERATURES AT 0.10 M IONIC STRENGTH

Metal ion	Stability constant	Temperature			
		20°	30°	40°	50°
QUINOLINE-8-CARBOXYLIC ACID					
H ⁺	pK^a	6.60	6.50	6.42	6.33
Mn(II)	$\log K_1$	3.10	3.05	2.99	2.93
	$\log K_2$	2.66	2.60	2.55	2.48
	$\log \beta_2$	5.76	5.65	5.54	5.41
Co(II)	$\log K_1$	4.51	4.40	4.32	4.25
	$\log K_2$	3.59	3.50	3.43	3.38
	$\log \beta_2$	8.10	7.90	7.75	7.63
Ni(II)	$\log K_1$	5.18	5.07	4.97	4.88
	$\log K_2$	4.36	4.26	4.17	4.09
	$\log \beta_2$	9.54	9.33	9.14	8.97
Cu(II)	$\log K_1$	6.41	6.28	6.15	6.05
	$\log K_2$	5.63	5.51	5.39	5.28
	$\log \beta_2$	12.04	11.79	11.54	11.33
Zn(II)	$\log K_1$	3.96	3.85	3.76	3.67
	$\log K_2$	3.24	3.15	3.07	3.00
	$\log \beta_2$	7.20	7.00	6.83	6.67
5-AMINOQUINOLINE-8-CARBOXYLIC ACID					
H ⁺	pK^a	8.54	8.44	8.36	8.29
Mn(II)	$\log K_1$	3.90	3.84	3.77	3.69
	$\log K_2$	3.02	2.94	2.89	2.81
	$\log \beta_2$	6.92	6.78	6.66	6.50
Co(II)	$\log K_1$	5.41	5.29	5.18	5.08
	$\log K_2$	4.71	4.61	4.52	4.44
	$\log \beta_2$	10.12	9.90	9.70	9.52
Ni(II)	$\log K_1$	6.13	6.00	5.88	5.77
	$\log K_2$	5.35	5.23	5.12	5.02
	$\log \beta_2$	11.48	11.23	11.00	10.79
Cu(II)	$\log K_1$	7.79	7.65	7.51	7.39
	$\log K_2$	7.04	6.90	6.76	6.64
	$\log \beta_2$	14.83	14.55	14.27	14.03
Zn(II)	$\log K_1$	5.16	5.04	4.93	4.82
	$\log K_2$	4.57	4.46	4.37	4.27
	$\log \beta_2$	9.73	9.50	9.30	9.09
5-NITROQUINOLINE-8-CARBOXYLIC ACID					
H ⁺	pK^a	4.56	4.51	4.47	4.43
Mn(II)	$\log \beta_1$	3.15	3.10	3.04	2.97
Co(II)	$\log \beta_1$	3.58	3.50	3.42	3.35
Ni(II)	$\log \beta_1$	3.89	3.80	3.70	3.58
Zn(II)	$\log \beta_1$	3.24	3.15	3.05	2.97

TABLE 2 — THERMODYNAMIC PARAMETERS OF 1:1 AND 1:2 METAL CHELATES AT 30° AND $\mu = 0.10 M$.

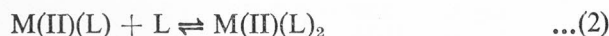
System	1:1 Complex			1:2 Complex		
	$-\Delta G^\ddagger$ (kcal mol ⁻¹)	$-\Delta H^\ddagger$ (kcal mol ⁻¹)	ΔS^\ddagger (e.u.)	$-\Delta G^\ddagger$ (kcal mol ⁻¹)	$-\Delta H^\ddagger$ (kcal mol ⁻¹)	ΔS^\ddagger (e.u.)
Mn(II) + Q-8-CA	4.23	2.54	5.58	3.61	2.68	3.07
Co(II) + Q-8-CA	6.10	3.41	8.88	4.85	3.02	6.06
Ni(II) + Q-8-CA	7.03	3.92	10.26	5.91	3.80	6.96
Cu(II) + Q-8-CA	8.71	5.11	11.88	7.64	4.81	9.34
Zn(II) + Q-8-CA	5.34	4.06	4.23	4.37	3.48	2.94
Mn(II) + 5-NH ₂ -Q-8-CA	5.33	3.18	7.10	4.08	3.12	3.17
Co(II) + 5-NH ₂ -Q-8-CA	7.34	4.30	10.01	6.40	3.87	8.34
Ni(II) + 5-NH ₂ -Q-8-CA	8.32	4.86	11.42	7.25	4.48	9.15
Cu(II) + 5-NH ₂ -Q-8-CA	10.61	5.63	16.44	9.57	5.53	13.33
Zn(II) + 5-NH ₂ -Q-8-CA	6.99	4.50	8.22	6.18	4.40	5.86
Mn(II) + 5-NO ₂ -Q-8-CA	4.30	2.66	5.41	—	—	—
Co(II) + 5-NO ₂ -Q-8-CA	4.85	3.23	5.34	—	—	—
Ni(II) + 5-NO ₂ -Q-8-CA	5.27	4.12	3.80	—	—	—
Zn(II) + 5-NO ₂ -Q-8-CA	4.37	3.95	1.39	—	—	—

TABLE 3 — ELECTROSTATIC AND CRATIC COMPONENTS OF THERMODYNAMIC PARAMETERS OF EQUILIBRIA (1) AND (2)

(Values in kcal mol⁻¹)

System	1 : 1 Complex				1 : 2 Complex			
	Electrostatic		Cratic		Electrostatic		Cratic	
	-ΔGc‡	ΔHe‡	-ΔGc‡	-ΔHc‡	-ΔGc‡	ΔHe‡	-ΔGc‡	-ΔHc‡
Mn(II) + Q-8-CA	2.97	1.14	3.68	3.70	2.42	0.93	3.61	3.61
Co(II) + Q-8-CA	3.69	1.42	4.83	4.83	3.08	1.18	4.19	4.20
Ni(II) + Q-8-CA	4.00	1.53	5.45	5.45	3.27	1.26	5.05	5.06
Cu(II) + Q-8-CA	4.35	1.67	6.78	6.78	3.79	1.45	6.27	6.26
Zn(II) + Q-8-CA	2.67	1.03	5.08	5.09	2.39	0.92	4.40	4.40
Mn(II) + 5-NH ₂ -Q-8-CA	3.30	1.27	4.45	4.45	2.44	0.94	4.06	4.06
Co(II) + 5-NH ₂ -Q-8-CA	3.94	1.51	5.82	5.81	3.57	1.37	5.24	5.24
Ni(II) + 5-NH ₂ -Q-8-CA	4.25	1.63	6.49	6.49	3.75	1.44	5.92	5.92
Cu(II) + 5-NH ₂ -Q-8-CA	5.35	2.05	7.68	7.68	4.67	1.79	7.32	7.32
Zn(II) + 5-NH ₂ -Q-8-CA	3.55	1.36	5.85	5.86	3.03	1.16	5.57	5.56
Mn(II) + 5-NO ₂ -Q-8-CA	2.93	1.12	3.79	3.78	—	—	—	—
Co(II) + 5-NO ₂ -Q-8-CA	2.92	1.12	4.35	4.35	—	—	—	—
Ni(II) + 5-NO ₂ -Q-8-CA	2.58	0.99	5.11	5.11	—	—	—	—
Zn(II) + 5-NO ₂ -Q-8-CA	2.05	0.79	4.74	4.74	—	—	—	—

indicates that ΔGc‡ values are significantly more negative than ΔGe‡ values suggesting that cratic forces are stronger than the electrostatic forces in 1 : 1 chelates. The difference between the two components decreases in the order : Cu(II) > Ni(II) > Co(II) > Mn(II). This indicates that ionic character and number of unpaired electrons increase in the reverse order: Cu(II) < Ni(II) < Co(II) < Mn(II). Thermodynamic data (Table 3) computed for the equilibrium (2),



show a decrease in the ionic and covalent characteristics indicating that bis complexes are less stable than the mono complexes.

The overall stability constants (log β_n) with respect to the metal ions follow the order: Mn(II) < Co(II) < Ni(II) < Cu(II) > Zn(II). The order with respect to the ligands is : 5-NO₂-Q-8-CA < Q-8-CA < 5-NH₂-Q-8-CA. This sequence is in accordance with the electron-withdrawing and electron-donating properties of the nitro and amino groups respectively.

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Complexes of Gallium(III) with Pyrocatechol, Pyrogallol & Protocatechuic, α-Resorcylic, Gallic & 2,3-Dihydroxynaphthalene-6-sulphonic Acids in Aqueous Medium

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Calvin-Bjerrum pH titration technique as modified by Irving and Rossotti, has been applied for determining the step-wise formation constants of the complexes of Ga(III) with pyrocatechol (PYC), protocatechuic acid (PCA), α-resorcylic acid (RCA), pyrogallol (PGL), gallic acid (GLA) and 2,3-dihydroxynaphthalene-6-sulphonic acid (DHNSA). Log K values and overall changes in ΔG, ΔH and ΔS accompanying the complex formation have been evaluated at 25°, 35° and 45°C and at an ionic strength 0.2M (NaClO₄). Stoichiometries of the various complexes have also been discussed.

IN continuation of our earlier work^{1,2} on Ga(III) complexes, we report in this note the proton-ligand stability constants of pyrocatechol (PYC),