(2.98 B.M.) of the Ni^{II} complex corresponds to an octahedral geometry having two unpaired electrons in the e_g level[16]. The diffuse reflectance spectra of the complex give three bands at 920, 570 and 340 nm corresponding to the transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, respectively, as expected[17] for octahedral Ni^{II} ion which is further confirmed[17] by ν_2/ν_1 ratio of 1.62. The 10Dq value of the complex indicates that TANAH produces a weak field. The Cu^{II} complex has a magnetic moment of 1.96 B.M. corresponding to one unpaired electron[18]. Two bands at 820 and 760 nm corresponding to the transitions, $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ in the diffuse reflectance spectra, point out to the distorted octahedral geometry[18] of the complex. Zn^{II}, Cd^{II} and UO_2^{II} complexes are diamagnetic.

TABLE 2—MAGNETIC MOMENTS AND LIGAND FIELD PARAMETERS OF TANAH (LH) COMPLEXES

Compd.	μ_{eff} B.M.	10Dq cm^{-1}	ν_2/ν_1	B' cm^{-1}	β	$\beta°$
CoL$_2$.2H$_2$O	4.91	11 530	2.13	924	0.951	4.84
NiL$_2$.2H$_2$O	2.98	10 870	1.62	963	0.912	8.78
CuL$_2$.2H$_2$O	1 96	12 840	—	—	—	—

Zn^{II}, Cd^{II} and UO_2^{II} complexes are diamagnetic.

Thermogravimetry : Loss of two moles of water per mole of the complexes in the temperature range 160—320° suggests that they are present in the coordination sphere of the metal ion[19,20]. The complexes are thermally unstable at 280—360° and complete decomposition to metal oxides occurs at 560—720°.

Acknowledgement

The authors are grateful to Prof. Arun K. Dey, for his keen interest in the work, and thankful to U.G.C., New Delhi, for financial support.

References

1. R. C. ELDERFIELD, "Heterocyclic Compounds", Wiley, New York, 1959, p. 565.
2. E. BOYLE, P. C. FREEMAN, A. C. GOULDIE, F. R. MANGON and M THOMSON, *J. Pharm. Pharmacol.*, 1976, 28, 865.
3. R. J. J. SORENSON, U. S. 4 221 785/1980.
4. I. S. AHUJA, R. SINGH and C. P. RAI, *Transition Met. Chem.*, 1977, 2, 257.
5. A. YU TSIVODZE, YU. YA. KHARITONOV, G. V. TSINTSADZE and ZH. D. PETRIASHVILLI, *Koord. Khim.*, 1977, 22, 1164.
6. T. MIYAZAWA, T. SHIMANOUCHI and S. MIZUSHIMA, *J. Chem. Phys.*, 1956, 24, 408 ; 1958, 29, 611.
7. M. MONOYAMA, S. TOMITA and K. YAMASAKI, *Inorg. Chim. Acta*, 1975, 12, 33.
8. D. K. RASTOGI, S. K. SAHNI, V. N. RANA and S.K. DUA, *Transition Met. Chem.*, 1978, 3, 56.
9. M. P. TEOTIA, J. N. GURTU and V. B. RANA, *Indian J. Chem.*, 1980, 19, 133.
10. F. A. FRENCH, E. J. BLANZ, S. C. SADDIX and R. W. BROCKMAN, *J. Med. Chem.*, 1974, 17, 172.
11. K. NAKAMOTO, "Infrared and Raman Spectroscopy of Coordination Compounds", Wiley, New York, 1978, p. 201.
12. F. FUJITA, K. NAKAMOTO and M. KOBAYASHI, *J. Am. Chem. Soc.*, 1956, 78, 3963.
13. R. C. AGGARWAL, N. K. SINGH and L. PRASAD, *Indian J. Chem.*, 1976, 14, 181, 325.
14. R. L. CARLIN, *Transition Met. Chem.*, 1976, 1, 3.
15. F. A. COTTON and G. WILKINSON, "Advanced Inorganic Chemistry". Wiley Eastern, New Delhi, 1984, pp. 877, 882.
16. A. B. P. LEVER and D. ODGEN, *J. Chem. Soc.*, 1967, 2041.
17. L. SACCONI, *Transition Met. Chem.*, 1979, 4, 199.
18. K. C. PATEL and B. E. GOLDBERG, *J. Inorg. Nucl. Chem*, 1972, 34, 637.
19. R. C. AGGARWAL and T. R. RAO, *J. Inorg. Nucl. Chem.*, 1978, 40, 171.
20. P. V. GOGARISHVILI, R. I. MACHKHOSHVILI, N. N. VEKUA, A. E. SHVELASHVILI and Y. Y. KHANTONOV, *Koord. Khim.*, 1976, 21, 750.

Equilibrium Study on the Complex Formation of Manganese(ii), Iron(ii), Cobalt(ii), Nickel(ii), Copper(ii) and Zinc(ii) with Catechol and Pyrogallol

S. N. DUBEY* and J. K. NEPAL

Department of Chemistry, Kurukshetra University, Kurukshetra-132 119

THE complex forming tendencies of catechol and pyrogallol have been reported earlier[1-8]. A survey of the literature revealed that no effort appeard to have been made on the determination of the thermodynamic stability constants and thermodynamic parameters of the complexes formed by Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} with catechol and pyrogallol. The present work deals with the potentiometric determination of thermodynamic stability constants and related thermodynamic parameters.

Experimental

The solutions of the metal sulphates (AnalaR) $MnSO_4.H_2O$, $FeSO_4.7H_2O$, $CoSO_4.7H_2O$, $NiSO_4.7H_2O$, $CuSO_4.5H_2O$, $ZnSO_4.7H_2O$, catechol and pyrogallol were prepared in conductivity water. The solutions of the metal sulphates were standardised by known methods. Ferrous sulphate solution was freshly prepared for each set of titration to avoid the possibility of hydrolysis. A Philips PR 9405 M pH meter with glass and calomel electrodes assembly was used to measure the pH. The instrument was calibrated using buffers of pH 4.0 and 9.2.

The titrations were carried out in a specially designed double-walled beaker (250 ml, pyrex) using Calvin-Bjerrum[9,10] titration technique as modified

by Irving and Rossotti[12], and performed in duplicate in order to establish the reproducibility of the measurements. The following three solutions were prepared and titrated against standard alkali $(0.4M)$: (i) $4 \times 10^{-3}M$ perchloric acid, (ii) $4 \times 10^{-3}M$ perchloric acid $+ 3 \times 10^{-3}M$ ligand, and (iii) $4 \times 10^{-3}M$ perchloric acid $+ 3 \times 10^{-3}M$ ligand $+ 5 \times 10^{-4}M$ metal ion solution. The total volume was kept 50 ml and an appropriate amount of sodium perchlorate $(2 M)$ was added to maintain the desired ionic strengths.

Results and Discussion

The pH range investigated for M(II)-catechol and M(II)-pyrogallol systems (M=Mn, Fe, Co, Ni, Cu and Zn) were 6 8—8.8, 4.2—6.8, 7.0—8 8, 7.2—9.0, 6.8—8.6 and 5.0—7.4 ; and 7.0—9.0, 4.0—6.4, 6.4—8 8, 6 8 —9 0, 6 4—8 6 and 4.4—7 0, respectively, at $\mu=0.1$ (30°). The proton—legand stability constants (log K_1^H and log K_2^H) of catechol and pyrogallol,

and stepwise formation constants (log K_n) of their chelates with bivalent metal ions were determined using the method of Irving-Rossotti and the values were further refined by using different computational techniques[11] The final values are given in Table 1. Catechol and pyrogallol behave like weak dibasic acids, the third proton in pyrogallol does not dissociate ($\bar{n}_A$ values remain above 1 even at higher pH). In all the M(II)–catechol and M(II)—pyrogallol systems the values of $\bar{n}$ vary between 0.2 to 1.9, thereby indicating the formation of 1 : 1 and 1 : 2 complexes. A survey of the data (Table 1) revealed that stability constant values decrease with the increase in temperature and thus, lower temperature is favourable for complex formation. The log K_n values also decrease with an increase in the ionic strength of the medium. The thermodynamic stability constant values (log $K_n^{\mu=0}$) were evaluated by extrapolating the concentration stability constants to zero ionic strength (Table 1). The general trend

TABLE 1—STABILITY CONSTANTS AND THERMODYNAMIC PARAMETERS OF SOME DIVALENT TRANSITION METAL COMPLEXES WITH CATECHOL AND PYROGALLOL

Metal ion	Ligand		30±0.5°				40+0 5°	50±0 5°	30±0 5°		40±0 5°
		$\mu=0.05$	$\mu=0.10$	$\mu=0.15$	$\mu=0.20$	$\mu=0.0$	$\mu=0.1$	$\mu=0.1$	$-\Delta G$ kcal mol⁻¹	$-\Delta H$ kcal mol⁻¹	ΔS cal K⁻¹ mol⁻¹
H⁺	CAT log K_1^H	11.72	11 59	11.~4	11 24	11.92	11.22]]	11 08¹			
	log K_2^H	9.32	9.21	9.14	9.03	9 41	9.05	8.92			
	PYR log K_1^H	10 95	10.85	10.70	10 67	11.02	10.67	10 65			
	log K_2^H	8.82	8 76	8.66	8 64	8 87	8 66	8.60			
Mn²⁺	CAT log K_1	7.38	7.27	7.18	7 12	7.45	7 40	7 31	10.08	2.61	23.85
	log β_2	13.43	13 20	12.98	12 57	13.70	13 38	12.89			
	PYR log K_1	6.47	6.41	6 30	5.50	6.55	5.73	5.70	8.89	7.62	4.05
	log β_2	11.17	10.82	10 65	9.65	11 47	9 93	9.86			
Fe²⁺	CAT log K_1	14 33	13 89	13 73	13.66	14.50	13.50	13.15	19.27	8.30	35.03
	log β_2	26.46	25 80	25.55	24 99	26.83	24.50	23 94			
	PYR log K_1	12.93	12.88	12.70	12.33	13.01	12 54	12.36	17.87	7.03	34 62
	log β_2	23.89	23.66	23.47	22.93	24 25	23.01	22.77			
Co²⁺	CAT log K_1	7.97	7 81	7.49	7.35	8 45	7.58	7.48	10.83	3.66	22.91
	log β_2	14 65	13.99	13.55	13 13	15.05	13.76	13.62			
	PYR log K_1	8.16	8.10	7.76	7.63	8.55	7.89	7.82	11.24	3.39	25.07
	log β_2	14 25	13.86	13.40	13.13	15.10	12.60	12.52			
Ni²⁺	CAT log K_1	7.60	7.59	7 40	7.32	7.70	7.48	7.40	10.53	3.04	23.92
	log β_2	13.74	13 63	13 35	12.90	14.06	13.52	13.05			
	PYR log K_1	7.85	7.40	7.15	7.10	8.03	7.23	7.17	10 27	2.77	23.95
	log β_2	13.27	12 75	12.32	12 20	13.45	11.99	11.77			
Cu²⁺	CAT log K_1	13.06	12.96	12 68	12 35	13.32	12.54	11.90	17.98	13 05	15.74
	log β_2	23.46	23.30	21 92	22.20	23.70	22.54	21.11			
	PYR log K_1	12 70	12.54	12 40	12.23	12 89	12.30	12.27	17.39	4.57	40 28
	log β_2	23.23	23.01	22 85	22.51	23.44	22.35	22.27			
Zn²⁺	CAT log K_1	8 73	8 48	8.38	7.89	8.96	8.38	8.02	11 76	6.09	18.10
	log β_2	15.87	15.51	15.32	14.46	16.10	15.32	14.64			
	PYR log K_1	8.67	8.41	8.37	7.95	8.94	8.42	8.23	11.67	2.03	30.78
	log β_2	15.47	14.87	14.67	14.18	15.89	14.51	13.94			

in the values of log $K_1{}^{\mu=0}$ and log $\beta_2{}^{\mu=0}$ (30°) indicate that the stability of Co^{II} complexes are somewhat higher than Ni^{II} complexes. In the above systems, the values of log $\beta_2{}^{\mu n}$ ($n=0.05$, 0.10, 0.15 and 0 20) were plotted against inverse ionic radii (r^{-1}) at different temperatures. The points corresponding to Mn^{II}, Ni^{II}, Cu^{II} and Zn^{II} complexes lie on linear curves and those of Fe^{II} and Co^{II} complexes lie above. Similar trend was observed by plotting the values of log $\beta_2{}^{\mu n}$ ($n=0.05$, 0.10, 0.15 and 0.20) vs second ionisation potential of metal ions. The stability constants of the metal chelates follow the order, $Mn^{II} < Fe^{II} > Co^{II} > Ni^{II} < Cu^{II} > Zn^{II}$, which agrees with the Irving—William's[14] natural order, except Co^{II}. The greater stability of Co^{II} complex as compared to Ni^{II} complex may be due to the additional stabilisation acquired by Co^{II} complex due to Jahn-Teller distortion, and the higher oxidation state in the complex[15]. A number of workers reported higher stability for cobalt complexes[16-19] as compared to that of nickel. Abnormally high stability in case of ferrous complex may be as a result of the orbital stabilisation and additional resonance energy stabilisation introduced through the ligands carrying an aromatic ring system[14], and the higher oxidation state in the complex. In general, catechol complexes are more stable than pyrogallol complexes, which can be justified on the basis of basicity of the ligand.

The thermodynamic functions $\triangle G$, $\triangle H$ and $\triangle S$ were calculated using the standard equations[18]. The $\triangle H$ values were calculated by plotting the values of log K_n at different temperatures as a function of $(1/T)$ and equating the gradient of this plot with $-\triangle H/4.57$. The values of $\triangle G$, $\triangle H$ and $\triangle S$ are given in Table 1. Chelates of Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} are formed spontaneously as is obvious by the negative values of $\triangle G$. The negative values of $\triangle H$ ensure that the reaction is exothermic. Positive values of $\triangle S$ indicate that entropy is the principal driving force for complex formation.

Acknowledgement

References

1. S. K. Lee, E. O. Price and J. E. Land, *J. Am. Chem. Soc.*, 1956, 78, 1325.
2. S. N. Dubey and R. C. Mehrotra, *J. Indian Chem. Soc.*, 1966. 43 73.
3. I. P. Mavani, C. R Jejurkar and P. K. Bhattacharya, *J. Indian Chem. Soc.*, 1972, 49, 469.
4. V. P. Koryukovo, A. M. Andrianov and L. K. Olenik, *J. Inorg. Chem.*, 1974, 19, 194, 358.
5. D. C. Patel and P. K. Bhattacharya, *J. Inorg. Nucl. Chem.*, 1971, 33, 529.
6. S. N. Dubey and R. C. Mehrotra, *J. Inorg. Nucl. Chem.*, 1964, 26, 1543.
7. S. N. Dubey and R. C. Mehrotra, *J. Indian Chem. Soc.*, 1965, 42, 685.
8. S. N. Dubey and R. C. Mehrotra, *Indian J. Chem.*, 1967, 5, 327.
9. M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, 1945, 67, 2003.
10. J. Bjerrum, "Metal Amine Formation in Aqueous Solution", Haase and Son, Copenhagen, 1941.
11. H. Irving and H. S. Rossotti, *J. Chem. Soc.*, 1953, 3397.
12. H. M. Irving and H. S. Rossotti, *J. Chem. Soc.*, 1954, 2904.
13. K. B. Yatsimirskii and V. P. Vasil'ev, "Instability Constants of Complex Compounds", Pergamon, London, 1960, p. 59.
14. H. Irving and R J. P. Williams, *J. Chem. Soc.*, 1953, 3192.
15. P. C. Shrivastava, S. K. Adheja and B. K. Banerjee, *J. Indian Chem. Soc.*, 1980, 57, 985.
16. G. Vartak and N. G. Menon, *J. Inorg. Nucl. Chem.*, 1966, 28, 2911.
17. W. D. Johnston and H. Freiser, *J. Am. Chem. Soc.*, 1952, 74, 5239.
18. S. N. Kakkar, N. S. Ponia and P. V· Khadikar, *J. Indian Chem. Soc.*, 1972, 49, 1189.
19. Y. K. Agrawal and S. G. Tandon, *J. Indian. Chem. Soc.*, 1972, 49, 719.

Thermodynamics of Complexation of 2,5-Dihydroxy-deoxybenzoin with some Common Cations

N. PRIYOKUMAR and N. R. BANNERJEE*

Chemistry Department, University of Delhi, Delhi-110 007

IN continuation of our work on complexes of 2-hydroxydeoxybenzoin[1] with Fe^{III}, Cu^{II}, Zn^{II} and Cd^{II} ions, the present study describes the sequestering efficiency of 2,5-dihydroxydeoxy-benzoin with the same metal ions The Calvin—Bjerrum's titration technique as modified by Irving and Rossotti[2] has been adopted.

The proton—ligand and metal—ligand thermodynamic stability constants have been calculated from the results of titration of the following solutions against standardised carbonate-free NaOH solution (0.214 3 mol dm^{-3} ; dioxan—water medium 1 : 1 by volume): (i) $HClO_4$ (4.5 mol m^{-3}) + Na_2SO_4 (0 20 mol m^{-3}), (ii) $HClO_4$ (4.5 mol m^{-3})+Na_2SO_4 (0.20 mol m^{-3}) + ligand (2.00 mol m^{-3}), and (iii) metal sulphate (0.20 mol m^{-3}) in $HClO_4$ (4.5 $mol^{-3}m^{-3}$) + ligand (2.00 mol m^{-3}) each in 20 ml of dioxan—water (1 : 1 by volume) containing $NaClO_4$ (0.05, 0.10, 0.15 and 0.20 mol dm^{-3}, respectively) at 298 K. The changes of the thermodynamic parameters, $\triangle G$, $\triangle H$ and $\triangle S$ associated with the complexation reaction have been evaluated using the temperature coefficient of stability constant and Gibbs—Helmholtz equation from the results at three