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The Formation Constants and Thermodynamic Parameters of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} Chelates Formed with Dithiodiglycolic Acid

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pH-Measurements have been made for determination of formation constants of the Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} chelates with dithiodiglycolic acid (DTDGA) at different temperatures 20°, 30° and 40°C and varying ionic strengths 0.1, 0.2, 0.5 and 1M KNO_3 by employing Calvin-Melchior's extension of Bjerrum's method in aqueous media. Thermodynamic parameters for chelation processes have also been calculated. The formation constants are discussed in relation with atomic properties.

INTRODUCTION

Transition metal complexes using sulphur donor ligands are quite important as insecticide and fungicide and are used in analytical chemistry. They are also finding use in vulcanization of rubber, froth flotation process for concentration of ore[1]. Metal complexes formed with sulphur compounds have been the subject of investigations by Saxena and coworkers[2–5]. Comparatively less is known about the transition metal complexes of dithiodiglycolic acid[6] (DTDGA). In view of the significant role of sulphur compounds, the present investigation deals with the study of formation constants and thermodynamics of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} complexes with dithiodiglycolic acid at 20°, 30° and 40°C and varying ionic strengths 0.1, 0.2, 0.5 and 1 M KNO_3 by employing Calvin-Melchior's extension of Bjerrum's method[7,8] in aqueous media.

EXPERIMENTAL

Dithiodiglycolic acid (DTDGA) was supplied by Evan's Chemetics Inc. New York. All other chemicals were of analaR grade. EC digital pH meter (accuracy ± 0.01 pH) equipped with a glass-calomel electrode assembly was used to measure the pH. The temperature of the cell was maintained constant by the thermostat.

RESULTS AND DISCUSSION

Proton-ligand systems: The values of ionization constants of dithiodiglycolic acid at different temperatures and varying ionic strengths in aqueous and aqua-organic media were evaluated earlier[9] and are used here in calculations. *Binary Systems:* From titration curves, the formation function $\bar{n}$ and free ligand exponent pl_{ML} was calculated at different pH values. The $\bar{n}$ values were plotted against pl_{ML} to get the formation curves. From these formation curves, the values of formation constants log K_1 were calculated which corresponds to pl_{ML} values at $\bar{n} = 0.5$ and are reported in Table 1 which follow the sequence

$$Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Mn^{2+}$$

which is in conformity with the Irving-Williams order[10]

TABLE 1
VALUES OF FORMATION CONSTANTS OF METAL COMPLEXES OF DTDGA

Metal complexes	20°C		30°C			40°C	
	$\mu = 0.1$	0.0	0.1	0.2	0.5	1.0	0.1M
Mn^{2+}	2.55	2.61	2.60	2.59	2.57	2.53	2.66
Co^{2+}	2.72	2.78	2.77	2.76	2.73	2.70	2.84
Ni^{2+}	2.77	2.81	2.80	2.78	2.75	2.73	2.86
Cu^{2+}	2.81	2.88	2.87	2.86	2.84	2.80	2.93
Zn^{2+}	2.69	2.75	2.74	2.71	2.69	2.64	2.80

The plot of formation constants against atomic number of these metals reveals that there is a monotonic rise to a maximum of copper followed by a lower value of zinc. Similarly, plot of log β against reciprocal of ionic radii of metal ions shows that the ligand forms a least stable complex with Mn^{2+} and more stable complex with Cu^{2+} in comparison to other metal ions. A correlation between second ionization potential and formation constants of complexes was pointed out by Irving-Williams[11], Schwarzenbach, Ackermann and Prue[12] and Calvin-Melchoir[7]. A similar correlation was observed in the present case of the plot of log K against second ionisation potential.

The plot of electronegativity against log K shows that stability of these metal complexes increases with increasing electronegativity which suggest that the metal-ligand bond would be covalent[13,14].

Thermodynamic functions such as free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) accompanying complexation are determined at 30°C with the help of standard equations[15] and are summarised in Table 2. The negative values of $\Delta G°$ show that reaction tends to proceed spontaneously. The positive value of enthalpy indicates the endothermic nature of the reaction suggesting that higher

temperature favours the chelation process in fair agreement with increasing stability with temperature. The positive entropy changes strongly favours the chelation process. The very large entropy change is also justified by considering the greater availbility of coordination sites of these metal ions[16].

TABLE 2
VALUES OF THERMODYNAMIC PARAMETERS OF METAL COMPLEXES OF DTDGA AT 30°C.

Metal complexes	$-\Delta G°$ K Cal/mole	$\Delta H°$ KCal/mole	$\Delta S°$ Cal/deg/mole
Mn^{2+}	3.61	2.72	20.89
Co^{2+}	3.85	2.63	21.38
Ni^{2+}	3.89	2.10	19.76
Cu^{2+}	3.99	2.61	21.78
Zn^{2+}	3.81	2.42	20.56

REFERENCES

1. R.K. Patel and R.N. Patel, *J. Indian Chem. Soc.*, **67**, 638 (1990).
2. M.C. Saxena and R.S. Saxena, *J. Indian Chem. Soc.*, **56**, 149 (1979).
3. R.D. Parikh and R.S. Saxena, *J. Electrochem. Soc. (India)*, **33**, 67 (1984).
4. _____, *Anales De Quimica*, **80**, 536 (1984).
5. G.L. Khandelwal and R.S. Saxena, *J. Indian Chem Soc.*, **58**, 1059 (1981).
6. K. Suzuki, C. Karaki, S. Mori and K. Yamaskii, *J. Inorg. Nucl. Chem.*, **30**, 167 (1968).
7. M. Calvin and M.C. Melchior, *J. Am. Chem. Soc.*, **70**, 3270 (1948).
8. J. Bjerrum, Metal Amine Formation in Aqueous Solutions, P. Haase and Sons, Copenhagen (1941).
9. S. Sharma, K.K. Saxena and R.S. Saxena, *J. Chem. Soc. (Pak.)*, 10, **159** (1988).
10. H. Irving and R.J.P. Williams, *J. Chem. Soc.*, 3192 (1953).
11. _____, *Nature*, **162**, 146 (1948).
12. G. Schwarzenback, H. Ackermann and J. E. Prue, *Nature* **163**, 723 (1949).
13. L.G. Van Uitert, W. C. Fernetius and B.E. Douglas, *J. Am. Chem. Soc.*, **75**, 2736 (1953).
14. M.C. Dey and J. Selbin, Theoretical Inorganic Chemistry, Reinhold, New York, p. 114 (1957).
15. K.B. Yatsimirskii and V.P. Vasilev, Instability Constants of Complex Compounds, Pergamon Press, Oxford p. 63 (1960).
16. A. E. Martell and S. Chaberek, Organic Sequestering Agents, Chapman and Hall, London, p. 140 (1959).

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