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NOTE

Thermodynamic Stability Constants of Divalent Metals with 3-Ethyl-2,6-Diphenylpiperidin-4-one Ethylenediamine Hydrazone

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The thermodyanmic metal-ligand stability constants of Mn(II), Ni(II), Cu(II) and Zn(II) with 3-ethyl-2,6-diphenylpiperidin-4-one ethylenediamine hydrazone in 70% dioxane-water medium at 30 ± 0.1°C have been determined. The stability constants of the divalent metal follow the order Cu > Ni > Zn > Mn.

Several researchers have reported the medicinal application of hydrazones and their metal complexes[1–5]. The biological activities of these compounds depend mainly on the nature of the functional groups present along with metals associated with them. Literature survey revealed that no work on the study of formation constants of metal complexes of hydrazone derived from 3-ethyl-2,6-diphenyl-piperidin-4-one of ethylenediamine hydrazone was done so far. The present paper deals with the potentiometric determination of stability constants of divalent metals with 3-ethyl-2,6-diphenylpiperidine-4-one ethylenediamine hydrazone (EDPEH).

All the reagents employed were of AnalaR grade. 1,4-dioxane was purified by standard method.[6]

Preparation of 3-ethyl-2,6-diphenylpiperidin-4-one ethylenediamine hydrazone(EDPEH): An equimolar (0.05 mol dm^{-3}) mixture of 3-ethyl-2,6-diphenylpiperidin-4-one[7] and ethylenediamine was treated with 1 g of anhydrous sodium acetate in 150 mL rectified spirit. This mixture was refluxed for 10 h and then poured into a beaker containing deionised water. The pale yellow coloured product was filtered in a Buckner funnel, dried and recrystallised from benzene pet-ether (40–60°C) (yield 50% m.p. 80°C). The purity of the product was checked by co-TLC method. The product was characterised by IR spectrum and microanalysis. IR (cm^{-1}) ($\nu(NH_2)$ 3450; $\nu(CH_2)$ 2950, $\nu(C{=}N)$ 1650, $\nu C{-}N$) 1610, Microanalysis, found (calcd): C = 78.00 (78.50), N = 13.00 (13.08), and H = 8.42 (8.41).

Approximately 0.01 mol dm^{-3} stock solution, of metal ions [manganese nickel, copper and zinc] were prepared from their respective chlorides and standardised by standard procedure.[8] The stock solution of ligand (0.04 mol dm^{-3}) was prepared in dioxane.

The pH metric titrations were carried out at 30 ± 0.1°C at an ionic strength of

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0.1 mol dm^{-3} ($NaClO_4$) under nitrogen atmosphere using an ITL digital pH-meter model DPH-14 (accuracy ±0.01 pH units) having a glass and calomel electrode assembly. The proton-ligand and metal-ligand stability constants have been calculated by Irving-Rossotti techniques[9]. The calculations were restricted to pH values below 8, in order to avoid complications due to the hydrolysis of various species at higher pH.

The metal ligand titrations show that the pH values were sufficiently lower than the corresponding ligand titration under the same conditions. The different metal-ligand concentrations gave almost identical results. Since low concentrations of metal ions were present the possibility of the formation of polynuclear complexes was ruled out.

In the absence of metal ions, the ligand offered two well separated buffered regions 2 and 5–8.5 obviously due to successive protonation of the two nitrogen atoms of the ligand. The proton-ligand stability constants of EDPEH were obtained from the formation curve [n_a *vs.* pH curve] adopting the Bjerrum half-integral method point-wise and the graphical methods, and the values are listed in Table-1.

The pH regions corresponding to metal-ligand equilibria are observed around 6–7.3 for Mn(II), 4.7–6.7 for Ni(II), 3.5 for Cu(II) and 5.5–7.0 for Zn(II).

The average number of ligand molecules attached per metal ion n and the free ligand exponent pL were evaluated according to literature method. The maximum values obtained are almost 3 in all the systems except the Mn-EDPEH system. The stability constant values were calculated by half-integral method and confirmed by point-wise and graphical methods applying the equations (1) to (3).

$$\log \frac{\bar{n}}{(1-\bar{n})} = \log K_{metal}^{metal\ complex} - pL, \quad (1)$$

where $\bar{n}$ values range between 0.2 to 0.8 for pK 1 : 1

$$\log \frac{(2-\bar{n})}{(1-\bar{n})} = \log K_{metal}^{metal\ complex} - pL, \quad (2)$$

where $\bar{n}$ values are selected between 1.2 to 1.8 for pK 1 : 2

$$\log \frac{(3-\bar{n})}{(1-\bar{n})} = \log K_{metal}^{metal\ complex} - pL \quad (3)$$

where $\bar{n}$ values are selected between 2.2 to 2.8 for pK 1 : 3

The stability constants of the 3-ethyl-2,6-diphenylpiperidin-4-one ethylenediamine hydrazone with Mn(II), Ni(II), Cu(II) and Zn(II) in 70% dioxane- water medium at 30 ± 0.1°C are given in Table-1.

Table-1 reveals that the step-wise and overall stability constants increase with increase in the atomic number and atomic radius and obey William's law. The difference between log K_1 and log K_2[log K_1 – log K_2] is positive and lies within 0.09–0.84 log units. This indicates that the ligands attached to the central metal ion are *trans* to each other. This was further confirmed by the ratio of log K_1/log K_2 which is greater than unity. We assume one of the ligand, acts as bidentate neutral ligand while the rest of them act as monodentate.

TABLE-1
PROTON-LIGAND AND METAL-LIGAND STABILITY CONSTANTS OF 3-ETHYL-2,6-DIPHENYLPIPERIDIN-4-ONE-ETHYLENEDIAMINE HYDRAZONE WITH DIVALENT TRANSITION METAL IONS IN AQUEOUS DIOXANE AT 30 ± 0.1°C

System	Bjerrum's method	Pointwise method	Graphical method	Average value
EDPEH				
log K_1^H	7.00	7.10	7.02	7.04
log K_2^H	3.12	3.18	3.00	3.10
log β_2^H	10.12	10.28	10.02	10.14
Mn-EDPEH				
log K_1	3.40	3.35	3.32	3.36
log K_2	2.60	2.60	2.62	2.60
log β_2	6.00	5.95	5.94	5.96
Ni-EDPEH				
log K_1	4.76	5.00	4.79	4.85
log K_2	4.20	4.22	4.24	4.22
log K_3	3.60	3.48	3.64	3.57
log β_3	12.56	12.70	12.67	12.64
Cu-EDPEH				
log K_1	6.46	6.40	6.66	6.50
log K_2	5.62	5.53	5.60	5.58
log K_3	4.83	5.06	4.87	4.91
log β_3	16.90	16.99	17.13	16.99
Zn-EDPEH				
log K_1	3.71	4.00	3.70	3.80
log K_2	3.36	3.48	3.37	3.40
log K_3	3.27	3.27	3.17	3.23
log β_3	10.34	10.75	10.24	10.43

REFERENCES

1. T. Rudolph and J.P. Phillips, *Anal. Chim. Acta*, **34**, 234 (1996).
2. A.G. Skyes and J.A. Well, *Prog. Inorg. Chem.*, **13**, 1 (1970).
3. Q. Albert, *Nature*, **9**, 370 (1973).
4. L.J. Boucher and C.G. Coe, *Inorg. Chem.*, **14**, 1289 (1975).
5. N.S. Biradar, C.S. Potil and W.L. Rudzinski, *Inorg. Chim. Acta*, **78**, 107 (1983).
6. A Weissberger and E.S. Proskauer, Organic Solvents Oxford University Press, London, p. 139 (1935).
7. V. Baliah and C. Noller, *J. Am. Chem, Soc.*, **70**, 3853 (1984).
8. J. Bassett, R.C. Denney, G.H. Jeffery and J. Mandham, A.I. Vogel A Text Book of Inorganic Analysis, Fourth Edition, London, 9a, p.330; 9b, p. 322; 9c, p. 321; 9d, 330 (1978).
9. H.M. Irving and H.S. Rossotti, *J. Chem. Soc.*, 3397 (1953), 2904 (1954).

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