Full Paper

Complexometric Determination Of Ca+2, Mg+2, Ni+2 And Cu+2 With Thiosemicarbazone Derivatives As Complexing Agents

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ABSTRACT

A simple, sensitive and rapid method for the estimation of Ca+2, Mg+2 in hard water, Cu+2 and Ni+2 metal ions in the micro quantities by using tridentate sulfur donor complexing agents.   © 2007 Trade Science Inc. - INDIA

INTRODUCTION

Benzimidazole derivatives possess various analytical applications[1-4]. Sulfur containing thiosemi carbazone metal chelates find wide range of applications in medicine[5-8]. Schiff base metal chelates have broad applications in biological and in industrial fields[9-10]. Thiosemicarbazone and their metal chelates find important applications in the fields like formacology as well as medicine[11-15].

These are known to be biologically important for antibacterial, antifungal, anticarcinogenic, antitumour, antituberculosis properties[14-17]. It is observed that biological activity of ligand increases on complexation with different metalions.

Many benzimidazoles are used as chelating agents, among them 2-mercapto benzimidazole is widely used organic precipitant for metal ions, which is bidentate ligand. But thiosemicarbazones are more sensitive and selective organic precipitants than 2-mercapto benzimidazoles and due to tridentate nature, these are acting as good chelating agents. Here acetyl benzimidazole thiosemicarbazone (ACBZTSC) and N-methyl, acetyl benzimidazole thiosemi carbazone (MACBZTSC) are used as complexing agents to estimate Ca+2, Mg+2 in hard water and Cu+2 and Ni+2 in solution by complexometry.

EXPERIMENTAL

All the chemicals used were of Anala R grade.

2-Acetyl benzimidazole thiosemicarbazone[18]

A mixture of equimolar amount of acetyl benzimidazole and thiosemicarbazide in aqueous methanol containing a few drops of acetic acid was refluxed for 3 h and then cooled. The resulting white solids (80%) were washed and crystallized from dioxane, m.p. 228-230°C.

1-Methyl-2-acetyl benzimidazole thiosemi carbazone

It is prepared by the method reported[18] earlier. Buffer solution is prepared by adopting the standard procedure[19].

The pH measurements were made by using digital pH meter Model DPH 500. Metal solutions are also prepared by using standard procedure[20]. The metal solutions are dissolved in conductivity water. The ligands are prepared in aqueous methanol. The metal and ligands are prepared for 0.1N as stock solutions.

Titration procedure

Pipette out 20ml of the test sample into 250ml conical flask and add 3-4 drops of buffer solution followed with few drops of EBT indicator and titrate the contents against the standard EDTA/ Thiosemicarbazone ligands solution till the colour changes from wine red to blue. Repeat the titration to get concurrent titre values.

RESULTS AND DISCUSSION

In the present work, volumetric estimation of calcium and magnesium was carried out by using ACBZTSC and MACBZTSC as complexone. This was carried out in 2 steps.
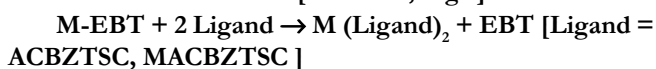
In step1: EDTA was standardised by using $MgSO_4$. The EDTA was used to estimate Ca^{+2} and Mg^{+2} at a pH 9-10 of using EBT as indicator.

Instep2: ACBZTSC and MACBZTSC were used to estimate the Ca^{+2}/ Mg^{+2} under the same conditions as EDTA. The results obtained were in harmony with that of 1st step.

This indicates that ACBZTSC and MACBZTSC can be used in place of EDTA as a complexone. But the results indicate that the metal ligand ratios are 1:

2. Metal ions (10^{-3} M) can be estimated by using 10^{-3} M reagent. In general EDTA forms 1:1 complexes with metal ions.

Similarly the reagents are also useful in the determination of Ca^{+2} and Mg^{+2} in the hardwater. The sharp end point green is observed from intial colour blue. In the place of EDTA, ACBZTSC and MACBZTSC are also can be used.

M + EBT → M-EBT [M = Ca^{+2}, Mg^{+2}]

M-EBT + 2 Ligand → M (Ligand)$_2$ + EBT [Ligand = ACBZTSC, MACBZTSC]

In the estimation of Cu^{+2} and Ni^{+2} by EDTA the proper equivalance point is difficult. This is not sharp and clear, due to this errors are possible.

M + FSB → M-FSB [M = Cu^{+2} and Ni^{+2}]

M-FSB + ACBZTSC → M (ACBZTSC)$_2$ + FSB (Fast Sulfone Black)
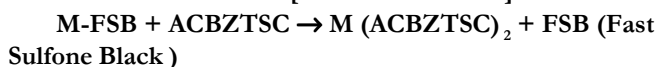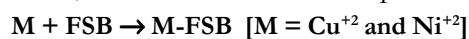
But by using these complexones the end point is sharp and clear green colour is obtained. This is due to the two tridentate ligands are occupying the 6 corners of the octahedron easily.

The advantages of these methods are:

Selective, sensitive and specific.

Endpoint is clear and sharp.

More accurate results.

Endpoint colour is constant for several hours.

By using EDTA upto 10^{-3} M of metal can be estimated. But 5×10^{-4} M of metal also can be estimated by using these new reagents volumetrically.

Based on the results presented above octahedral structure is assigned to Ca, Mg, Cu and Ni complexes. The metal complex composition is assigned as 1:2 in solution state.
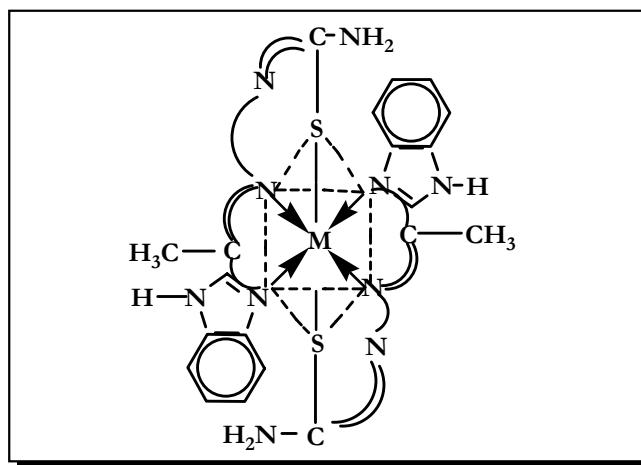
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REFERENCES

[1] F.J.Welcher; Organic Analytical Reagents, Newyork, Van Nostrand, **4**, 127 **(1948)**.

[2] R.B.Singh, B.S.Garg, R.P.Singh; Talanta, **25**, 619 **(1978)**.

[3] A.V.Reddy, Y.K.Reddy; Talanta, **33**, 617 **(1986)**.

[4] K.H.Reddy, D.V.Reddy; Indian J.Chem., **22**, 824 **(1983)**.

[5] K.Butler, U.S.Patent; No.3, **382**, 266 **(1968)**.

[6] A.V.Reddy, B.K.Reddy, C.Jaya Kumar, L.S.Sharma; Asian. J. of Chem., **9**, 487 **(1997)**.

[7] M.Ali, S.E.Livingstone; Coordination Chem.Rev., **13**, 126 **(1973)**.

[8] R.Willam; J.Med.Chem., **15**, 655 **(1972)**.

[9] Z.M.Zaki, S.S.Haggag, M.Shabasy; Spectrosc.Lett., **28**, 489 **(1995)**.

[10] B.Singh, B.H.Misra; J.Indian Chem.Soc., **63**, 1069 **(1986)**.

[11] M.Ali, M.Nizamuddin, F.Smith, G.Hynes; polyhedron, **15**, 975 **(1996)**.

[12] K.Palat, M.Bazilova; Ceska Slov Farm., **43**, 279 **(1994)**.

[13] R.William; J.Med.Chem., **15**, 655 **(1972)**.

[14] M.J.M.Campbell; Co ord.Chem.Rev., **15**, 279 **(1975)**.

[15] M.Z.Geary; Coord.Chem.Rev., **16**, 81 **(1981)**.

[16] B.L.Feedlander, A.Frust; J.Am.Chem.Soc., **81**, 638 **(1952)**.

[17] A.M.Badawey, K.Thomas; Farmaco, **50**, 537 **(1995)**.

[18] K.Syamasundar, M.Adharvana Chary; J.Indian Chem.Soc., **78**, 32 and references Cited in, **(2001)**.

[19] A.I.Vogel; 'Text Book of Quantitative Chemical Analysis', Longman 2nd.ed. ELBS, London, 868-872.

[20] A.I.Vogel; 'Text Book of Quantitative Inorganic Analysis', Longman, p. 258, 309,329, 389, 479 **(1962)**.