

It is known that the proton chemical shift is an indication of the strength of hydrogen bonding in liquids<sup>5,6</sup>. The initial increase of the proton chemical shift, with concentration of oxalic acid in the present studies shows that the hydrogen bond strength increases with concentration and this is in conformity with our earlier studies by ultrasonic method<sup>1</sup>. The explanation that is usually offered is that solvent dioxane breaks the oxalic acid dihydrate into free water, and hydrogen bonds are formed between the monomer carboxylic acid and dioxane molecules. Since the carboxylic protons are highly electropositive, the formation of O-H...O hydrogen bonds of carboxylic acid monomer with dioxane molecules is favoured more than the hydrated water dioxane hydrogen bonds. The ultrasonic experiments conducted by adding proportionate amount of water (equivalent to water of hydration of oxalic acid) to dioxane support the above view. The proton chemical shift depends only on the strength of the hydrogen bonds but does not have any bearing on the nature of hydrogen bonds in the solution. If dimers were existing in the concentration range mentioned above, the proton chemical shift should be large and independent of the concentration of the oxalic acid. The present high resolution NMR study shows that the dimer carboxylic acid groups are not present to any significant extent as to influence the chemical shift in the concentration ranges 0.06 to 0.09 mole fraction.

The proton chemical shift above the concentration of 0.09 mole fraction of oxalic acid remains constant at the value of 6.74 ppm. with increase of concentration. The proton signal for carboxylic acid usually occurs in the range of 10-13 ppm<sup>7</sup>. In the present study, the chemical shift is in the range of 6.40 to 6.74 ppm. and this may be due to the rapid exchange of carboxylic acid protons with hydroxyl protons of hydrated water released by dioxane. The fact that the proton chemical shift attains the maximum value and remains constant above 0.09 mole fraction shows that dimers carboxylic acid are present in the solution above the critical concentration thereby confirming our earlier observations<sup>1</sup>. Once the formation of these dimers in the solution is favoured, the chemical shift should remain independent of concentration as the dimers are the strongest possible hydrogen bonds that are likely to be present in the solution. However one should observe an increase in the NMR signal strength with the increase of concentration above the critical concentration even though the chemical shift remains the same and such an increase in the NMR signal strength is observed in the present studies.

A comparison of the present high resolution NMR studies and our earlier ultrasonic studies in solution

of oxalic acid in dioxane shows that the observed critical concentration is slightly higher in NMR studies. This difference may be due to the exchange interaction between the carboxylic protons and water protons which does not probably affect the ultrasonic velocity to any significant extent.

The authors wish to express their thanks to the Director, Jawaharlal Institute for providing facilities to carry out the work. They are also thankful to Dr. A. G. Ramachandran Nair for helpful discussion. One of them (T.K.N.) acknowledges the financial assistance given by University Grants Commission, New Delhi.

Department of Physics, T. K. NAMBINARAYANAN,  
Jawaharlal Institute of A. SRINIVASA RAO.

Postgraduate medical  
Education and Research,  
Pondicherry 605 006,  
September 4, 1978.

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#### MORPHOLINE-4-CARBODITHIOATE AS A GRAVIMETRIC REAGENT FOR Zn(II), Cd(II) AND Hg(II)

MORPHOLINE-4-carbodithioate has been found to give white precipitate with Zn(II), Cd(II) and Hg(II) at pH 4.0-11.0. These metals have been estimated from their binary mixtures using ammonical EDTA as the masking agent. The sensitivity of reactions (in  $\mu\text{g/ml}$ ) has been found to follow the order  $\text{Zn} < \text{Cd} < \text{Hg}$ . Physico-chemical methods reveal 1 : 2 metal ligand ratio in all the three cases.

Metal complexes of various carbodithioates<sup>1-3</sup> have been widely studied with respect to their applications in various fields. Morpholine-4-carbodithioate of potassium has not yet been used as a gravimetric reagent for these metals, though Bayer and Ott<sup>4</sup> have reported it as a possible chelating agent. Brown *et al.*<sup>4</sup> have reported the bidentate behaviour

of the ligand in the complexation with Zn(II), Cd(II) and Hg(II). Although numerous complexes of zinc, cadmium and mercury with a variety of coordinating ligands are reported in literature but they suffer from one or more disadvantages.

The reagents employed for the gravimetric estimation of zinc and cadmium are oxine, 8-hydroxy quinaldine and quinaldinic acid. The mercury is estimated as cyclopentanone-2-carboxy anilide and thioanilide.

The oxinates and quinaldinates of zinc and cadmium are volatile above 130° C and not selective for Zn(II) and Cd(II) while anthranilates suffer from the disadvantage that they decompose in basic medium. Cyclopentanone-2-carboxyanilide Hg(II) complex loses its weight above 110° C. In the estimation of Hg(II) as thioanilide, chloride ions interfere very much.

The main advantage of morpholine-4-carbodithioate over the well known method is that Zn(II), Cd(II) and Hg(II) chelates can be precipitated over a wide pH range; they are thermally more stable and can be weighed directly after drying at 120–130° C and the separation and determination are quite fast. The interference due to several ions can be overcome by controlling the pH or by using EDTA as the masking agent. This paper describes the use of morpholine-4-carbo-dithioate for the gravimetric estimations of Zn(II), Cd(II) and Hg(II) and their separations in binary mixtures using ammoniacal EDTA as masking agent.

#### Experimental

Potassium salt of the reagent was prepared by mixing morpholine, carbon disulphide and potassium hydroxide in ether at 0° C in 1 : 1 : 1 molar ratio. The standard solutions of Zn(II), Cd(II) and Hg(II) were obtained by dissolving zinc sulphate, cadmium sulphate and mercuric chloride respectively of A.R. quality in distilled water. The strengths of the solutions were ascertained by using oxine [for Zn(II) and Cd(II)] and thioanilide [for Hg(II)].

#### Gravimetric Estimations of Zn(II), Cd(II) and Hg(II)

An aliquot of Zn(II) solution taken in a 250 ml. beaker, was diluted to about 100 ml. It was warmed gently and an excess (two fold) of the 1% (w/v) reagent solution was added with constant stirring. The pH of the solution was adjusted by adding acetate buffer (pH 5.0–5.6). The white precipitate formed was digested on a waterbath for 30 minutes and filtered through a G-4 sintered glass crucible. The precipitate was washed repeatedly with distilled water dried at 110–120° C and weighed as  $Zn(C_5H_8ONS_2)_2$ .

Similar procedures were adopted in case of Cd(II) and Hg(II).

The conversion factor  $Zn/Zn\text{-chelate} = 0.1676$ .  $Cd/Cd\text{-chelate} = 0.2572$  and  $Hg/Hg\text{-chelate} = 0.3820$ . The precipitation of Zn(II), Cd(II) and Hg(II) is quantitative in pH range 4.5–9.0. The results of 30 estimations reveal that the metals can be estimated with an average error better than  $\pm 0.3\%$ .

#### Effect of Foreign Ions

Phosphate, oxalate, fluoride, borate, iodide, bromide, nitrate, acetate did not interfere in these estimations in the pH range 4.5–6.0; at higher pH values phosphate, oxalate, fluoride and borate ions interfere.

#### Sensitivity of reactions

The sensitivity of the reagent for Zn(II), Cd(II) and Hg(II) was found 6  $\mu$ g/ml, 3  $\mu$ g/ml and 2  $\mu$ g/ml respectively. It is in the order  $Zn < Cd < Hg$ .

#### Separation and Determination of Zn(II) and Hg(II) from their Binary Mixture

When Zn(II) and Hg(II) were present in the solution, the carbodithioate of Hg(II) was precipitated first by masking Zn(II) with ammoniacal EDTA. The solution containing the two ions was taken in a 500 ml beaker and diluted to 200 ml. The ammoniacal solution of EDTA (0.1 M) was then added to mask Zn(II) ions, and Hg(II) estimated according to the procedure given earlier.

The filtrate containing the Zn-EDTA complex was concentrated, and after cooling, 2 ml conc.  $H_2SO_4$  and potassium bromate were added to it. The mixture was evaporated to dryness and diluted with 50 ml. distilled water. Excess of bromate was removed by adding potassium bromide and heated till the solution became colourless. It was just neutralised with ammonia (1 : 1). The 1% (w/v) reagent was then added; the white precipitate so formed was digested at 60–70° C for about 30 minutes. It was filtered through sintered crucible (G-4), washed several times with distilled water, dried at 110–120° C and weighed as  $Zn(C_5H_8ONS_2)_2$ . The results are tabulated in Table I.

#### Determination and Separation of Cd(II) and Hg(II) in their Binary Mixture

The known volumes of Cd(II) and Hg(II) were taken in a 500 ml beaker. It was diluted to 150 ml and then added 0.1 M solution of ammoniacal EDTA to mask Cd(II) ions. The Hg(II)-carbodithioate was precipitated first and determined according to the procedure given earlier.

The filtrate containing the Cd(II) complex of EDTA was concentrated to about 50 ml. It was acidified with hydrochloric acid (50%) to demask Cd(II) ions and then 1% (w/v) reagent solution was added with constant stirring till the precipitation is completed. During the process of precipitation pH was main-

TABLE I  
Determination and separation of Zn(II) and Hg(II)

Sl. No.	Metal taken in mg		Complex mg		Metal found mg		Error %	
	Hg	Zn	Hg	Zn	Hg	Zn	Hg	Zn
1.	20.04	13.04	52.4	77.6	20.01	13.0	-0.15	-0.30
2.	20.04	26.08	52.4	155.2	20.01	26.01	-0.15	-0.26
3.	20.04	39.12	52.4	232.6	20.01	38.98	-0.15	-0.35
4.	40.08	26.08	104.8	155.2	40.08	26.01	-0.12	-0.26
5.	60.13	32.60	157.2	193.8	60.05	32.50	-0.13	-0.36

TABLE II  
Determination and separation of Cd(II) and Hg(II)

Sl. No.	Metal ions taken mg		Wt. of complex		Metal ion found		Error %	
	Hg	Cd	Hg	Cd	Hg	Cd	Hg	Cd
1.	20.04	16.84	52.4	65.2	20.01	16.77	-0.15	-0.4
2.	20.04	33.68	52.4	130.6	20.01	33.59	-0.15	-0.26
3.	40.08	33.68	104.8	130.6	40.03	33.59	-0.12	-0.26
4.	40.08	67.37	104.7	261.2	40.03	67.18	-0.12	-0.28
5.	80.17	67.37	209.6	261.2	80.06	67.18	-0.13	-0.28

tained 5.0-5.5. The contents were heated over a water bath for about 30 minutes. The white precipitate, after keeping for about two hours, was filtered in a sintered crucible (G-4), washed with water, dried at 110-120° C and then weighed as Cd(C<sub>5</sub>H<sub>8</sub>ONS)<sub>2</sub>.

The observations of some trials are given in Table II.

We wish to record our sincere thanks to Dr. R. N. Gupta, Principal, Hindu College, Moradabad, for providing all necessary facilities. Thanks are also due to Dr. M. S. Mehra, Principal, Bareilly College, Bareilly and Dr. B. D. Kansal, Hindu College, Moradabad for helpful discussions.

Hindu College,  
Moradabad,

NEPAL SINGH.  
S. K. KULSHRESTHA.  
A. K. AGARWAL.

and

Lucknow University,  
Lucknow, May 11, 1978.

T. N. SRIVASTAVA.

#### RECOGNITION OF A SEDIMENTOLOGICAL BREAK BETWEEN QUARTZITE AND LIMESTONE MEMBERS OF THE TAL FORMATION, LESSER HIMALAYA, INDIA

THE Tal Formation is the topmost lithological unit of the Krol belt sediments and is assigned a traditional Cretaceous age<sup>1,2</sup>, though recently some workers have given a Permian<sup>3</sup> or Precambrian age<sup>4,5</sup>. The age of Tal Formation is mainly given on the basis of the fossil contents in the locally developed shell limestone (Limestone Member)<sup>6</sup>, as the entire Tal succession is unfossiliferous. Here, some petrological data are presented indicating a sedimentological break between shell limestone (Limestone Member) and the underlying Quartzite Member in the Nilkanth section.

The Tal Formation in Nilkanth section is very thin, made up of about 70-80 m thick sequence of unfossiliferous quartzites and shales, capped by a 20-30 m thick shell limestone band<sup>7</sup>. The sediments just below the shell limestone are essentially medium-grained quartzites and correspond to the Quartzite Member of the Tal Formation<sup>8</sup>. The Quartzite Member and the sediments below are unfossiliferous. The shell limestone (Limestone Member) is full of broken fossils and overlies the Quartzite Member with an irregular contact. Normally, such a situation where a thick unfossiliferous succession is followed by a fossiliferous

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