COMPLEXEMETRIC TITRATION OF ZINC

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ABSTRACT

An alkalimetric method for the estimation of Zinc has been described in this paper. It makes use of hexamine to retard the hydrolysis of zinc hydroxide to zincate. The method has been compared with the acidimetric and alkalimetric methods given by other authors.

INTRODUCTION

Various methods have been described in the literature for the estimation of zinc. The volumetric methods are based on (*a*) EDTA and EDTA disodium salt [1—19] (*b*) acidimetry and alkalimetry [20—24] (*c*) Mercurimetry [25] (*d*) Ferrocyanide [26] and (*e*) Iodimetry [27]. Among the gravimetric methods [28—33] mention may be made of phosphate, mercurithiocyanate, bismuthiocyanate, 8-hydroxy quinoline tetra thionine chloride etc. Small quantities of zinc have been determined Polarographically,[34—37] Colorimetrically,[38] Potentiometrically,[39] Photometrically,[40] and Amperometrically,[41]. None of these methods is, however, applicable for the direct estimation of zinc in acidic zinc ammonia flux.

The method described in this paper has been developed with the ultimate object of estimating zinc in zinc flux. It is based on the use of hexamine, to retard the hydrolysis of zinc hydroxide (formed at the end point) to zincate, a difficulty experienced in the direct alkalimetric titrations. The method is also compared with the acidimetric and alkalimetric methods given by others.

SOLUTIONS AND REAGENTS

1. Indicators:—

Thymol violet, BDH 9-13, BDH 10-14, phenolphthalein (8·3—10·0), thymolphthalein (9·3—10·5), orthocresolphthalein (8·2—9·8), thymol blue (8·0—9·6), phenol red (6·8—8·4), methyl red (4·2—6·3) and bromothymol blue (6·0—7·6).

2. Reagents:—

(*a*) Acid hydrochloric 0·5 N, 0·1 N.

(*b*) Sodium hydroxide 0·020 N, 0·5 N.

(*c*) Potassium fluoride 25% w/v (Neutral, freshly prepared).

(*d*) Hexamine—B.P. (German).

(*e*) Sodium gluconate—10% solution.

3. Standard zinc solution:—

Approximately 50 gms of zinc oxide (AR) were heated in a silica basin at 600°—700°C for about 3 hours and cooled in a desiccator.

Solution No. 1

22·01 gm of the dried zinc oxide were accurately weighed and transferred to a beaker. To this hydrochloric acid A.R. (1 : 3) was added slowly with continuous stirring till a clear solution was obtained. The beaker was throughout kept in ice cold water. The volume of the solution was finally made up to 1000 ml.

Solution No. 2

This solution was prepared in a similar manner as solution No. 1, except that only 3·5 gm of the dried zinc oxide accurately weighed were taken for the preparation of the solution.

EXPERIMENTAL

Procedure I—Hexamine Method.—It consists of two steps—

Step I—Titration of Free Acidity/Alkalinity

10 ml of the zinc solution (1) was taken in a 250 ml wax lined conical flask or transparent plastic beaker. To this 20—25 ml water, 25 ml of potassium fluoride solution and 4—6 drops of the phenolphthalein were added. The solution was stirred and titrated slowly with Alkali or acid. The titer (called A) was noted.

Step II—Titration of Free Acidity or Alkalinity plus acidity released from zinc salt

10 ml of zinc solution (1) was taken in a 250 ml conical flask. To this 3-3·5 gms of the hexamine (solid) and 0·2 to 0·4 ml of BDH 10-14 indicator were added and stirred till hexamine dissolved. The solution was titrated to a dirty green colour when a further quantity of about 0·25 ml of the indicator was added. The titration was continued to just pink end point. The titer (called B) was noted.

Calculations:

$$\text{Zinc (as } ZnCl_2\text{), } \% = \frac{(B \pm A) \times N \times 100 \times 0.06815}{W}$$

Where—

(—A) is volume in ml of sodium hydroxide and (+A) volume is ml of hydrochloric acid required for titration of the free acidity or free alkalinity in step I.

B=Vol. in ml of sodium hydroxide required for titration of zinc solution in step II.

N=Normality of sodium hydroxide.

W=Weight of the zinc salt in 10 ml of the zinc solution (1).

NOTE—Normality of sodium hydroxide and hydrochloric acid used was the same.

Procedure II—Sodium Zincate Method (For comparison with Procedure I)

This method is based in converting zinc to zincate with a known excess of standard alkali. The excess alkali (*i.e.*, to that required to form zincate) is then titrated with a standard acid. Knowing the free acidity/ alkalinity of the original zinc salt, (as obtained in Procedure I, step I) and the titer of the excess alkali obtained, the quantity of alkali used up by zinc to form zincate is calculated.

Procedure III—Sodium Gluconate Method (For comparison with Procedure I)

The method was the same as procedure I, except that in step II, 30 ml of the sodium gluconate solution was added in place of hexamine.

Procedure IV—Direct Alkalimetric Titration (For comparison with Procedure I)

Free acidity/alkalinity was determined as in procedure I, step I. Zinc was determined in a fresh aliquot of zinc solution by direct titration with alkali using various indicators as mentioned in Table 2.

RESULTS

The accuracy of the procedure (I) was checked by using standard zinc salt solution. The results are given in Table 1. Experiments have also revealed that there are certain critical concentrations of hexamine which are required for different concentrations of the zinc salt to get accurate results (refer Table 1). Further, out of the various indicators listed under "solutions and reagents," only thymol violet, BDH universal and BDH 10-14 have been found to give accurate results with the hexamine method. Even these three indicators have, however, yielded accurate results only under certain limited conditions, which are:—

I. *Thymol violet and BDH universal indicators*

(*a*) Both the indicators give sharp blue end points in the zinc chloride concentration range between 0·0037 gm and 0·1475 gm (when present in suitable dilutions). Below the lower concentration limit the indicator colour change is not sharp, while above the higher limit, it fades away.

(*b*) Approx. 0·5 to 0·75 ml of the indicator is required for each titration. Sharp end point is obtained if half of the indicator is added at the start of the titration and the balance near the end point.

II. *BDH 10-14 Indicator*

(*i*) This indicator gives sharp end point between 0·1088 gm to 0·3656 gm concentration of zinc chloride (when present in suitable dilutions).

Above the higher concentration limit, the end point is unstable while below the lower limit it is not sharp. A sharp end point in higher concentrations can, however, be obtained by suitably diluting the titrant and titrating the solution slowly to a permanent end point.

The results on the potentiometric titrations carried out as per procedure I, are plotted in figure I. Results obtained with procedures III and IV are given in Table 2. A scrutiny of this data shows that these methods do not yield accurate results. This is because the end points in these methods are not sharp.

Efforts were also made to substitute sodium gluconate as a complexing agent in place of hexamine, as the former has been found by the author[42] to retard hydrolysis of aluminium salts. Results in Table 2 however show that sodium gluconate is atleast not effective in retarding the hydrolysis of zinc salts.

DISCUSSION

Role of Hexamine: The *pH* of an aqueous solution of hexamine is between 8-9, showing that it is weakly basic. When added to a neutral zinc chloride solution, it partly precipitates out zinc hydroxide, according to the following equilibrium reaction :—

$$ZnCl_2 + 2H_2O + 2(CH_2)_6N_4 = Zn(OH)_2 + 2(CH_2)_6N_4HCl \qquad (1)$$

No such precipitate is however formed when hexamine is added to an acidic zinc salt solution. This behaviour of hexamine is explained by the fact that hexamine (being basic) requires some free acid to form hexamine hydrochloride. In the case of neutral zinc salt, it extracts the acid from the salt itself, which is partly hydrolysed, while in acidic salt since the free acid is readily available to form hexamine hydrochloride, there is no hydrolysis of the zinc salt itself.

Potentiometric titration (Fig. I refers) show (1) negligible initial change and (2) a rapid final change in the *pH* of the solution, accompanied by precipitation of zinc hydroxide near the end point. This behaviour is typical of a buffer solution. It is at the end point that hexamine has proved to be effective, inasmuch as it combines with zinc hydroxide in such a way so as to prevent its further hydrolysis to zincate. But for hexamine the end point is not sharp.

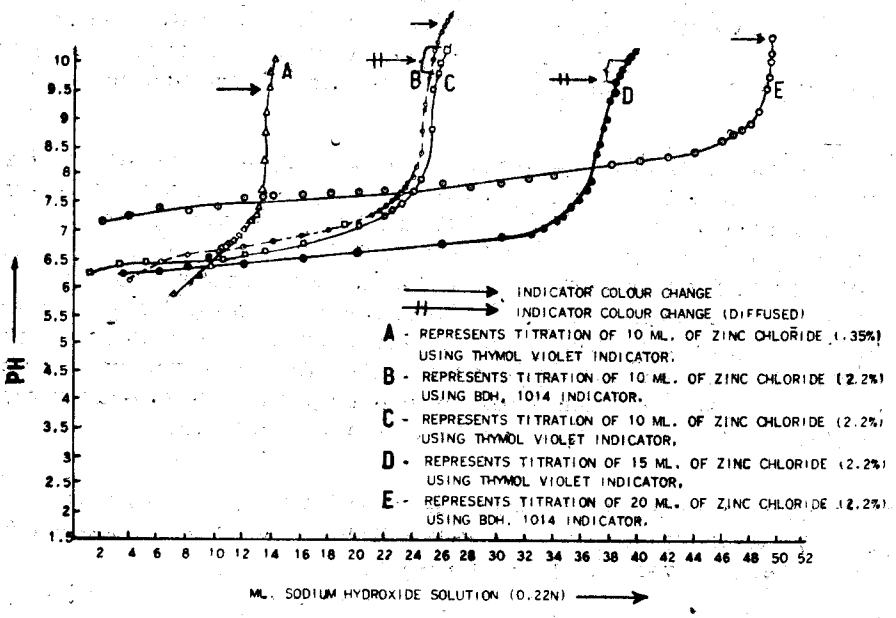

Fig. 1—Potentiometric determination of Zinc in Zinc Chloride.

The acid (i.e., produced as a result of hydrolysis of the zinc salt) in combination with hexamine, is a measure of the zinc concentration of the solution. It can be titrated with alkali according to the following reaction:—

$$(CH_2)_6 N_4HCl + N_a OH = N_a Cl + (CH_2)_6 N_4 + H_2O$$

For a given concentration of the zinc salt in the solution there is a minimum concentration of hexamine (refer Table 1) which must be added for accurate results. The quantity of hexamine required is however, not in stiochometric ratio to zinc salt. Excess hexamine does not affect the accuracy of the method, on the other hand it gives sharper end point.

Indicator—As stated above the choice of the indicators in the method developed is very much limited. The fact that different indicators are required (Table 1 refers) for the titration of low and high concentration of zinc salts, show that probably the zinc and or hexamine ions modify the character of the indicators. Titration must, therefore, be carried out strictly under the conditions described in this paper to avoid errors.

Effect of zinc concentration on detection of the end point

In high concentration of the zinc salt, the end point is not stable. This is attributed to the occlusion (and or sorption) of a part of the zinc salt in zinc hydroxide precipitate formed in situ towards the end point. On keeping, the precipitate slowly orient itself thereby releasing the occluded zinc salt, which in turn hydrolyses simultaneously liberating acid. The error due to this can be avoided by either (1) appropriately diluting the solution prior to titration or (2) carrying out the titration slowly to a permanent end point. It is, however, best not to attempt to titrate concentrated zinc solutions.

In the determination of free acidity, a similar difficulty as in the case of titration of concentrated zinc salts has been experienced, more so when the titration is carried out quickly. It is probably due to the fact that during neutralisation of free acidity, a part of the alkali is also simultaneously sorbed on the zinc fluoride. At the end point, therefore, the titrant consumed will be more than that required for neutralising free acidity. This sorbed alkali however, desorbs when the solution is allowed to stand after neutralisation. It is, therefore, suggested that the titration be carried out slowly so that there is negligible sorption of the titrant, alternately the solution after titrating in the normal manner, be allowed to stand till the desorption of alkali is complete. The released alkali be then titrated back with an acid and this titer substracted from the total titer.

After completion of this work, author has tried several other indicators for the direct titration of free alkalinity/acidity of zinc salts without the addition of potassium fluoride. This work is being written up for publication.

Acknowledgement—The author is thankful to the Director, Defence Research Laboratory (Material), Kanpur, Ministry of Defence, Government of India, for his kind permission to publish this paper.

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TABLE 1

RESULT SHOWING THE % RECOVERY OF ZINC CHLORIDE (AS PER PROCEDURE I)

Sl. No.	Amount of zinc chloride taken (gm)	Normality of alkali 'N'	Hexamine added (gm)	% recovery of zinc chloride using indicators			Remarks	
				BDH 10—14	Thymol violet	BDH Universal	Thymol violet/BDH Universal	BDH 10—14
1	2	3	4	5	6	7	8	9
1	0·01843	0·20	1·25	129·8	98·64	101·0	End point sharp	End point not sharp but can be detected with some difficulty. The colour slowly changes from greenish to yellowish green but not to pink.
2	0·03686	0·20	1·25	106·66	101·2	98·5	End point sharp	End point not very sharp but can be detected with difficulty. The colour slowly changes from greenish to yellowish green but not to pink at the end point.
3	0·05529	0·20	1·25	101·5	100·5	99·5	do.	End point improves but still detectable with some difficulty.
4	0·0925	0·20	1·25	102·8	97·9	98·5	do.	do.
5	0·1088	0·20	1·25	98·9	99·8	100·0	do.	End point sharp.
6	0·1290	0·20	1·25	101·1	98·55	100·5	do.	do.
7	0·1475	0·20	1·25	100·0	98·8	97·8	End point fades away on keeping and becomes permanent on further addition of 0·1 to 0·15 ml of alkali. The results recorded represent titration to a permanent end point.	do.
8	0·1843	0·20	1·25	101·3	98·0	"	Difficult to get permanent end point.	do.
9	0·3686	0·20	2·5	100·0	"	"	do.	do.
10	0·5529	0·20	3·5	100·0	"	"	do.	End point diffused. The titration carried to a permanent end point.
11	0·7372	0·20	4·6	96·2 99·5	diffused end point permanent end point	"	do.	

NOTE—10 ml of zinc solution (Prepared by suitably diluting solution No. 1) was taken for all titrations except Nos. 10 and 11 where 15 and 20 ml respectively of solution No. 1 was used.

TABLE 2

RESULTS WITH PROCEDURE II, III AND IV

Sl. No.	Procedure adopted for titration.	Volume of zinc chloride solution taken (ml.)	% Recovery of zinc chloride with									Remarks
			Phenolphthalein.	Thymolphthalein.	Orthocresolphthalein.	Thymol Blue.	Phenol Red.	Methyl Red.	Bromothymol Blue.	BDH 10—14	Naphthol benzene.	
1	2	3	4	5	6	7	8	9	10	11	12	13
1	II	10 ml. (Solution No. I)	92·0	106·2	113·0	112·5	136·0	End point not sharp	End point not sharp	..	..	..
2	III	10 ml. (Solution No. I)	75·2–90	74·9 80·75	..	..	..	..	..	End point not traceable.	84·0	Indicator colour change at the end point was slow and diffused.
3	IV	100 ml. (Solution No. 2)	93·8	92·0	131·0	..	..	..	..	..	..	There was lot of precipitation of zinc hydroxide and the end point was not sharp.