Reductimetric determination of Nitroso-R-Salt with Iron(II) in buffer medium and in presence of oxalate and the speciation of Iron(III)-oxalate in the medium

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ABSTRACT

Simple, rapid and accurate reductimertric titration methods (potentiometric and visual) have been developed for the detetermination of Nitroso-R-Salt (a high potential chromogenic reagent) using iron(II) as a reducing agent in buffer medium (pH 4.0-5.0) and in presence of sodium oxalate (0.05M) and a small amount of methylene blue which acts as a catalyst as well as a redox indicator. Nitroso-R-Salt (NRS) in the range 15-60mg has been determined with an accuracy of ±0.5% and ±0.7% in the case of potentiometric and visual end-point methods respectivesy. The precision in both the methods has been determined by computing pooled standard deviation and 95% confident limits. In this method NRS is reduced to its corresponding amino compound by iron(II) in a four electron reduction step. The formal redox potentials of the oxidant and reductant systems under the optimum titration conditios have been measured. Based on these potentiials,a satisfactory explanation for the observed redox reaction has been offered. Since oxalate is an iron chelator, a species distribution diagram indicating the extent of formation of various species in iron(III) – oxalate system has been generated using a computer program kown as HYSS.

Key words: Nitroso-R-Salt, Iron(II) reductant, Buffer Medium, Oxalate, Methylene Blue.
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INTRODUCTION

Nitroso-R-Salt [1-Nitroso-2- Naphthal, 3-6 disulfonic acid] is one of the most useful nitroso group of dyes. The salt finds its applications in calico printing as well as in the detection [barium, calcium, cobalt, iron, nickel, silver etc.] and determination of [cobalt, iron, potassium etc.] some metal ions mentioned in parenthesis. It may be emphasized that earlier investigators in the field successfully employed nitoso-R-salt (NRS) for the determination of small quantities of cobalt in plants and animal tissues [1,2], soils [3], carbides[3], glasses[4], steels[5] etc. and potassium in plant tissues[6]. More recently,it

it finds its usefulness as a sensitive chromogenic reagent for the determination of trace quantities of some metal ions [like cobalt(II), copper(II), iron(III)] present in gelatin films[7] and alloys[8]; a few noble metals[9,10] [e.g. osmium(VIII)[9] and palladium(II)[10]]; other subsbances[11,12] [such as thiosulphate[11], thioglycolic acid[11] , vitamin C[12] etc.] and paracetamol content in pharmacutical preparations[13].

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A survey of literature, however, reveals the existence of only a few methods for its assay or determination, though, the comopund has high potential as a choromogenic reagent . The earliest among them is that reported by Clauser[14] in which NRS is reduced by phenylhydrazine and the released nitrogen is collected over potash solution to give the nitroso group content. The other methods so far reported are wet chemical redox procedures in which NRS is reduced to its corresponding amino compound using the conventional reductants like titanium(III)[15,16], chromium(II)[17], iodide[18,19], iron(II) in phosphoric acid medium[20,21] etc. Recently, a new reduction cum cleavage technique to determine the content of nitrite and nitroso compounds was proposed [22].

All these methods so far developed suffer from one disadvantage or the other. For example the conventional reductants such as titanium(III)[15,16], chromium(II)[17] etc. are highly sensitive to atmospheric oxygen and hence they need a special storage appratus to protect them form aerial oxidation. Further, the titrations using the reagents must be carried out at elevated temperatures. In the case of iodometric method [18,19] a blank   correction must be applied by conducting a blank titration and the error involved in the method is stated to be as high as 5.0%. In iron(II)- phosphoric acid methods[20,21] the high concentration of the acid makes the medium viscous and the method expensive; further, the reduction of NRS is found to take about 20 minutes for completion of the reaction and hence an expensive reagent (resorufin) is employed as a catalyst to achieve rapid reduction[21].

The present paper describes a convenient reductimetric titration method for the determination of NRS with iron(II) in buffer medium of pH 4 - 5 and in presence of sodium oxalate(0.05M) and a small amount of methylene blue (4-5drops of 0.1% solution) which acts as a catalyst as well as a redox indicator.The end – point in the method can be detected either potentiometrically or following the color change of methylene blue (M.B) at the end-point. The method now developed does not suffer from any of the disadvantages associated with the earlier methods. Further, all the reagents involved in the redox process are common inexpensive reagents which are available in a high state of purity. Moreover, the authors have computed the nature and extent of formation of all the species expected to be formed between iron(III) and oxalate in the reaction medium through a computer program known as HYSS[23], since the formation of such species is responsible for decrease in the redox potential of iron(III)/iron(II) couple and enabling iron(II) to function as a powerful reducing agent in buffer- oxalate medium. Based on the formal redox potentials of oxidant and reductant systems obtained in the reaction medium, a satisfactory explanation for the observed redox reaction has been offered.

MATERIALS AND METHODS

Reagents:-
Iron(II) Solution :- An approximately 0.05M solution of iron(II) in 0.01M sulphuric acid medium has been prepared from an AR grade ammonium iron(II) sulfate hexahydrate and it is standardized[24] by titrating against a standard solution of dichromate.

Nitroso-R-Salt Solution :- About 0.05N (0.0125M) solution of Nitroso-R-Salt has been prepared by dissolving the required quantity of AR grade salt in distilled water. The solution is   standardized[25] by titrating against a standard solution of titanium(III) chloride as described by Knecht and Hibbart.

Acid Solutions :- A 1.0M solution of hydrochloric acid has been prepared in distilled water from an AR grade concentrated sample and the solution is standardized by titration against a standard solution of sodium carbonate in the usual way (in the place of hydrochloric acid, a 1.0M solution of perchloric acid, nitric acid or a 0.5Msolution of sulphuric acid may be used).

Sodium acetate and sodium oxalate solutions:- A 1.0M solution of sodium acetate and a 0.20M solution of sodium oxalate have been prepared in distilled water form their respective AR grade samples.

Buffer solutions :- Various buffers of desired pH in the range1-5 are obtained by mixing suitable volumes of 1.0M hydrochloric acid and 1.0M sodium acetate solutions and diluting the mixture to the desired volume as tabulated in Volgel [26] .

Methylene Blue Solution :- A 0.1% (w/v) solution of the dye is prepared by dissolving 100 mg of a dye sample in 100 ml of distilled water.

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Apparatus:- A digital potentiometer is used for potential measurements. A bright platium rod and a saturated calomel electrode are used as indicator and reference electrodes respectively. The salt bridge consists of a ' U ' tube with porous- end plates and filled with a saturated solution of potassium chloride .

Recommended Procedure :-
[A]. Potentiometric Method
To an aliquot (3-12 ml) of Nitroso- R – Salt solution (0.05 N or 0.0125 M) taken in a 150 ml beaker, 10 ml of sodium acetate (1.0M) and 5-6 ml of hydrochloric acid (1.0 M) are added [to give a desired pH in the range 4.0-5.0 when the solution is diluted to 50 ml], followed by the addition of about 12 ml of sodium oxalate (0.20 M) and 4-5 drops of methylene blue (0.1 %) solutions. The total volume of the solution is diluted to about 50 ml and purified nitrogen gas is passed through the reaction mixture for about 4 minutes to expel any dissolved oxygen. The contents are now titrated against iron(II) solution (0.05 M) following a potentiometric method to detect the end-point, while the solution is being stirred by a magnetic stirrer. A jump in potential of about 150 mV per the addition of 0.05 ml of 0.05 M iron(II) solution has been recorded at the end-point.

[B]. Visual End-Point Method:-
The conditions for the visual end-point method are the same except that the colour transition of M.B., which is blue to coloruless, has been followed to detect the end-point. No inert atmosphere need be maintained during the titration and no indicator correction need be applied to the method.

RESULTS AND DISCUSSION

Some of the typical results obtained by the two methods have been shown in Table-1.

Tablel:-1. Determination of Nitroso-R-Salt with Iron(II) in Buffer Oxalate Medium

| Nitroso-R-Salt found*		Pooled standard deviation Sg, mg	$\frac{1.96 \times Sg}{\sqrt{n}}$ mg	95% confidence limits $\overline{X} \pm \dfrac{1.96 \times Sg}{\sqrt{n}}$ mg
Standard method[25] mg	Author's method mg			
Potentiometric Method				
14.15	14.22			14.19 to 14.25
24.99	24.92			24.89 to 24.95
36.31	36.42	0.04	0.03	36.39 to 36.45
47.15	47.06			47.03 to 47.09
56.58	56.69			56.66 to 56.72
Indicator Method				
16.50	16.42			16.38 to 16.46
27.35	27.46			27.42 to 27.50
37.72	37.60	0.05	0.04	37.56 to 37.64
46.21	46.34			46.30 to 46.38
55.64	55.50			55.46 to 55.54

*Average six determinatios

Nitroso-R-Salt in the range 15 – 60 mg has been determined by potentionmetric and visual indicator methods with an accuracy of ±0.5% and ±0.7% respectively. The precision involved in these methods has been found by computing the pooled standard deviation and 95% confidence limits to the mean $\overline{X}$ and incorporated in the same Table. In the present redox reaction, nitroso-R-salt [NRS] is reduced to its corresponding amino compound or reduced nitroso- R-salt [RNRS] by iron(II) in a 4- electron reduction step[20] as shown in Equation-1.

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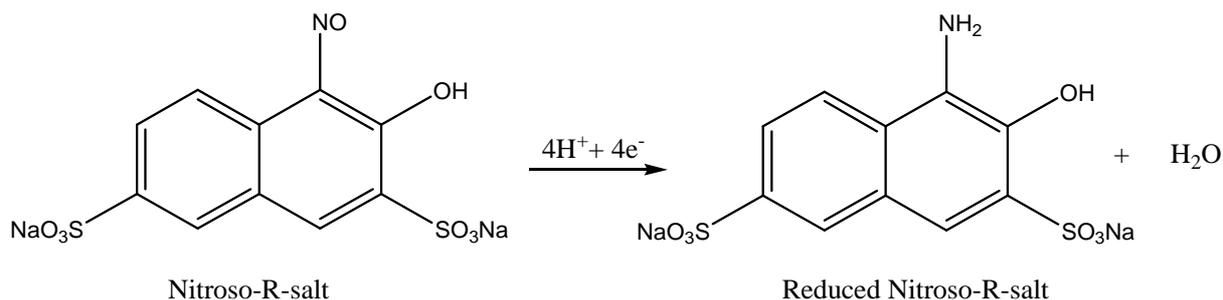
Equation - 1

At the end-point, however, iron(II) reduces methylene blue to its corresponding leuco-base which is colourless in a two electoron reduction step[27] as per the Equation-2.
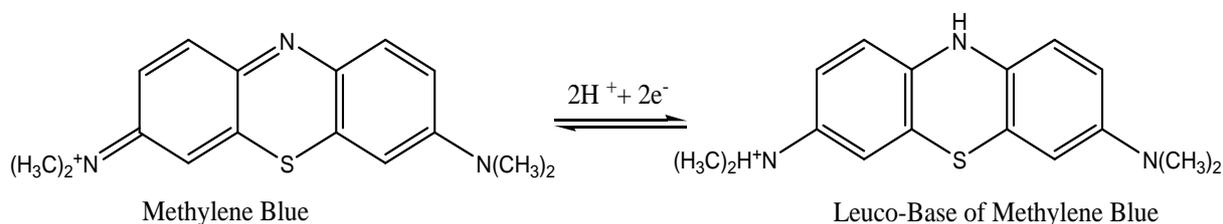
Equaton- 2

In the absence of inert atmosphere, the colourless leuco-base of methylene blue obtained at the end-point is found to undergo aerial oxidation, restoring the blue colour of the dye. However, the short span of time it (leuco-base) exists at the end- point, sustaining the oxditaion by atmosphere oxygen allows the author to detect the end-point avoiding the maintenance of inert atmosphere during the titration.

We find through our thorough investigations that the optimum titration conditions (most suitable conditions) for rapid reduction of NRS by iron(II), the pH of the reaction medium must be in the range of 4- 5 and the oxalate ion concentration must be about 0.05M or above. Even under these conditions the above redox reaction is found to be slow at the end-point and requires about 20 minutes for completion of the reaction. However, the reaction is found to be catalysed by methylene blue which incidently funtions as a redox indicator in the method. The catalytic action of methylene blue may be explained as follows: In this reaction both NRS and methylene blue undergo reduction by iron(II), but the reduction of the former is slow while that of latter is rapid. Threfroe, when iron(II) is added to the reaction mixture consisting of NRS and methylene blue in buffer-oxalate medium, it is assumed that iron(II) first of all reacts with methylene blue reducing it to its corresponding colourless leuco-base which being highly susceptible to oxidation (as stated above) tends to transfer its electrons to NRS , thus bringing its rapid reduction to RNRS.

For any redox system of this type, the formal redox potential of the oxidant couple: [NRS]/[RNRS] (or NRS system) and that of the reductant couple: [iron(III)]/[iron(II)] (or iron system) found under the optimum titrations are very helpful to envisage and explain the thermodynamic or theoriticial feasibility of the redox reaction. The potential of the latter couple is avilable from one of our earlier publications [27] and it was found to be about $105\pm5mV$, under the optimum titration conditions [i.e. in a buffer medium of pH about 4.2 and in presence of about 0.05M oxalate ion concentration]. The authors observed that methylene blue solution in the reaction medium has no effect on the formal potential. However, the formal redox potential of the NRS system under the optimum titration conditions has not been reported so far. The authors have therefore determined the potential, as described by Murthy[28], by measuring the potential half way to the equivalence point from the potentiometric titration curve obtained by the method. The value so obtained under the optium titration conditions stated above is found to be 425 ± 5 mV . From

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these potentials of the oxidant (425 mV) and reductant (105 mV) systems it may be seen that there is a different in potential of about 320 mV to expect thermodynamical feasibility for rapid reduction of NRS by iron(II) . The authors however found that kinetically the reduction is slow and catalysed by a small amout of methylene blue. Since methylene blue served as a catalyst as well as a redox indicator in this titration , the authors have measured its transition pontential adopting the method of Belchor et.al[29], and found it to be 255 ± 5 mV . The transition potential of the indicator (255 mV) is found to be intermidiatebetween the formal potentiols of the oxidant (425 mV) and reductant (105 mV) systems, thus explaining the suitability of methylene as a redox indicator in the present redox system.

It is known from a long time that the redox potential of iron system [or iron(III)/iron(II) couple] considerably decreases in presence of certain complexing molecules/ions such as phosphoric acid[30],   triethanomal amine[31,32] , different types of phosphates[33], fluoride[34], oxalate[27] etc. The decrease in potential of iron system causes iron(II) to function as a powerful reducing agent . Thus, iron(II) as a reductant, in presence of these complexing ions finds numerous applications in analytical chemistry and they are beyond the scope of this paper to furnish the details. However, as some of our recent applications ,we, reported reductimetric titration methods for the determination of two nitroso compounds [35], copper(II) [36] (in phohporic acid medium) and vanadium(V) [37] (in buffer oxalate medium) uaing iron(II) as a reductant
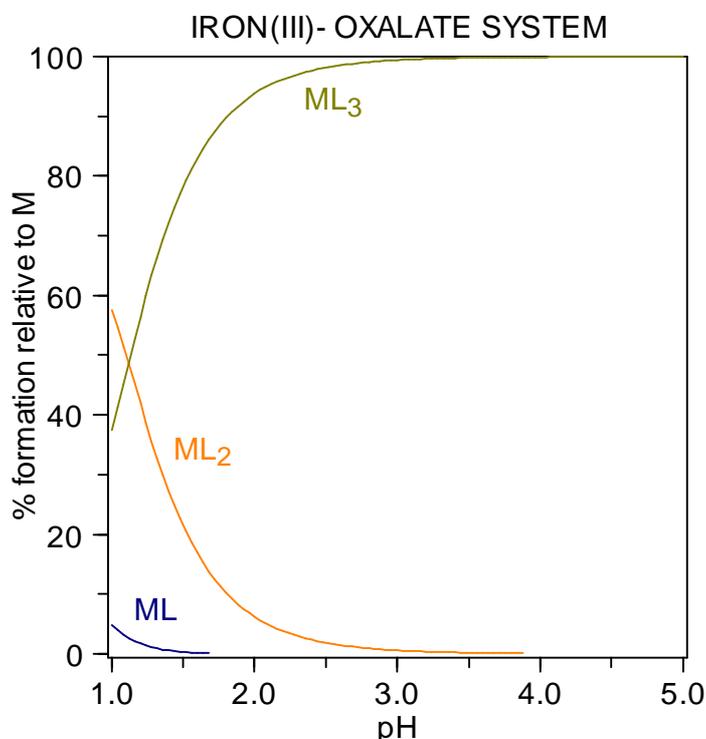

Figure -1. Percentage Distribution of Iron(III) oxalate complexes as a function of pH

The reagent described in the present paper namely iron(II) as a reductant in buffer medium and in presence of oxalate was introduced by Murthy and co-workers in late seventies[38] and the reagent finds a handful of applications in analytical chemistry[27, 39-41]. Raju and co-workers measured [27] the formal redox potentials of iron(III)/ iron(II) couple in media of varying pH (1-5) and oxalate ion concentrations (upto a maxium of 0.12 M) . They reported [27] that at a fixed pH (about 4.0) the potential decrease from 475 mV to 75 mV with increase in oxalate ion concentration from 0.0 M to 0.12 M ; and at fixed oxalate ion concentration(0.06 M) the value decreases from 375 mV to 85 mV with increase in pH from 1 to 5 . From these data it is evident that the redox potential of iron system decreases with increase in pH and oxalate ion concentration. Thus, both pH and concentration of oxalate ion have profound influence on the redox potential of iron system. In general, under normal experimental conditions the reactions using iron(II) as a reductant are carried out in dilute sulphuric acid (1-2N) medium wherein the redox

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potential of iron system is reported[42]to be about 680 mV . Thus, the potential of iron system decreases from about 680 mV in 1-2 M sulphuric acid medium to about 75 mV in buffer(pH 4.0) oxalate (about 0.12 M) medium.

The lowering in potential of iron system is attributed to the formation of different types complexes between iron(III) and oxalate ion depending on the pH of the medium. The decrease in potential of iron system thus enhances the reducing ability of iron(II) enabling it to function as a powerful reducing agent. It is quite interesting to obtain Information on the nature and extent of formation of various species of iron(III)-oxalate system because the information is necessary to understand its effect on the formal potential of the system. Though Bobtlesky et.al[43] made a partial study in this direction , no detailed data have so far been reported . Hence, the authors obtained a species distribution diagram for iron(III) oxalate system using the fromation costants of various species reported in literature. A computer program HYSS [23] is used to generate species distribution diagram shown in Figure-1, which gives the extent of formation of all the species in solution as a function of pH The species distribution diagram indicates that ML_3 [trisoxalatoferrate(III)] is the major species in the pH region 1.4 to 5.0 and reaches 99% of the total metal at a pH of 3.2 and above. The concentration of ML [monooxalatoferrate(III)] and ML_2 [bisoxalatoferrate(III)] monotonously decreases with increase in pH . These species exists only below a pH of 3.0.

CONCLUSION

Nitroso-R-Salt, which finds numerous applications as a chromogenic reagent In analytical chemistry, can be determined (in the range 15- 60mg) accurately by either a potentiometric or a visual method using iron(II) as a reducing agent in buffer medium (pH 4-5) and in presence of sodium oxalate (0.05M) & methylene blue which acts as a catalyst as well as a redox indicator. The proposed analytical method not only involves the use of inexpensive, highly pure common laboratory reagents but also offers several advantages over the existing methods. The species distribution diagram generated using a computer program known as HYSS reveals the formation of trisoxalatoferrate(III) as the predominent species between iron(III) and oxalate in the reaction medium. The formation of the coordination species seems to be responsible for decimating the formal redox potential of iron(III)/ iron(II) couple and boosting the reducing ability of iron(II) in buffer oxalate medium

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