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Reductimetric Determination of Nitroso-R-Salt with Iron(II) in Phosphoric Acid Medium

K. VIJAYA RAJU

Department of Engineering Chemistry, College of Engineering, Andhra University, Visakhapatnam-530 003, India

Corresponding author: E-mail: vijayarajukurimella@gmail.com

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Reductimeric titration methods involving potentiometric, visual (10-40 mg) and spectrophotometric (1-3 mg) techniques have been developed for the determination of nitroso-R-salt (NRS) using iron(II) as a reductant in phosphoric acid medium. The reduction of nitroso-R-salt by iron(II) is slow in phosphoric acid medium and found to be catalyzed by resorufin (RSF) which also functions as an excellent redox indicator. In this determination nitroso-R-salt is rapidly and quantitatively reduced to its amino compound by iron(II) in a four electron reduction step. The accuracy and precision of each of the method have been given. The formal redox potentials of [NRS]/[reduced NRS] couple, iron(III)/iron(II) couple, the transition potential of the indicator have been measured at the optimum titration conditions. Based on these potentials data, an explanation for the conditions needed for a satisfactory titration of the nitroso-R-salt has been given. The interference due to diverse ions has been studied.

Key Words: Nitroso-R-salt, Phosphoric acid medium, Iron(II), Resorufin.

INTRODUCTION

Nitriso-R-salt [NRS] is one of the nitroso group of dyes and it finds applications in calico printing as well as in the detection and determination of several metal ions. One of its most interesting and useful applications is the determination of small quantities of cobalt[1,2] and potassium[3] in plant tissues, cobalt in soils[4], glasses[5], steels[6] and carbides[4]. For such an interesting organic compound only a few methods have so far been reported for its determination. The earliest among them is that reported by Clauser[7] in which NRS is reduced by phenylhydrazine and the released nitrogen collected over potash solution to give the nitroso group content. The other methods are based on the reduction of NRS to its corresponding amino compound using suitable reductants like titanium(III)[8,9], chromium(II)[10], iodide[11,12], iron(II)[13] in phosphoric acid medium *etc*. Recently, a new reduction cum cleavage technique to determine the concentration of nitrite and nitroso compounds was proposed[14].

All these methods are not entirely satisfactory. For example, the reductants,both titanium(III)[8,9] and chromium(II)[10] need a special apparatus for their storage as they are highly sensitive to atmospheric oxygen. Further, both direct and indirect methods developed with titanium(III)[8,9] must be carried out at elevated temperature. In the iodometric method involving hydroiodic acid[11] and potassium iodide[12] as reductants, a blank correction must be applied by performing a separate blank titration. Further, the error of the method was stated to be as high as 5 %. In the iron(II)-H_3PO_4 method[13], the concentration of phosphoric acid must be as high as 13.0 M, further, one has to wait for about 0.5 h for completion of the titration, because the reduction of NRS by iron(II) is slow. Moreover, the detection of the end-point (from yellow to colourless) is difficult. The proposed[14] new method needs the use of expensive equipment.

In present report, a convenient reductimetric titration method for the determination of NRS using iron(II) as a reductant in 10 M phosphoric acid medium in presence of small amount of resorufin (RSF) which acts as a catalyst as well as a redox indicator is developed. The end-point of the method can be detected potentiometrically, visually or spectrophotometrically depending on the concentration on the salt. The methods now developed do not suffer from any of the disadvantages associated with the earlier ones.

EXPERIMENTAL

All chemicals were of analytical reagent unless and otherwise stated and all solutions were prepared in distilled water.

Nitroso-R-salt (NRS) solution: About 0.01 M solution of the nitroso-R-salt was prepared by dissolving required amount of AR grade salt in distilled water. Its strength was checked[8] by titrating against a standard solution of titanium(III) chloride solution. The solution (0.01 M) was utilized in the potentiometric and visual end-point (or indicator) methods. From the 0.01 M solution, a 2.5×10^{-3} and 5.0×10^{-5} M solutions

have been prepared by suitable dilution and utilized to record the absorption spectra and in spectrophotometric titrations, respectively.

Iron(II) solution: An approximately 0.05 M solution of iron(II) has been prepared in 0.5 M sulphuric acid medium from an AR grade ammonium iron(II) sulphate hexahydrate and the solution standardized[15] by titrating against a standard solution of dichromate. From this (0.05 M) solution a 0.03 M and a 0.01 M solution was prepared by suitable dilution and utilized in the preparation of reduced NRS and in the spectrophotometric titration, respectively.

Reduced NRS solution: The solution was prepared by taking 5.0 mL of 5.0×10^{-4} M (or 2.0×10^{-3} N) solution of NRS followed by 10 mL of 0.05 M (or N) iron(II) solution (*ca.* 50 fold excess to NRS) and required volume of phosphoric acid (to give an overall strength of 9 M after dilution) in a 50 mL standard flask and diluting to the mark.

Resorufin (RSF) solution: A 0.05 % (w/v) aqueous solution of RSF was prepared.

The potentiometric assembly consists of a digital potentiometer, a bright platinum rod (indicator electrode), a saturated calomel electrode (reference electrode) and a porous glass plate-end salt bridge filled with saturated potassium chloride. A Shimadzu (UV 140) double beam spectrophotometer with optically matched glass cells of 1 cm path length was used to record the absorption spectra. An optical glass cell having dimensions 3 cm × 5 cm × 6 cm (with 3 cm path length) was used to carryout spectrophotometric titrations. As the cell holder for such a glass cell to fit on to the cell compartment is not provided with the spectrophotometer, a few modifications to the cell compartment were made as described by Raju *et al.*[16].

Recommend procedure

Potentiometric method: An aliquot (3-10 mL) of NRS solution is taken into a 50 mL beaker fitted with a four- holed rubber stopper (one for inserting the tip of the burette, the other for accommodating the platinum electrode, the third one for inserting the inlet tube for passing purified nitrogen gas, the fourth one for accommodating the limb of a salt bridge which automatically serves as an out let for nitrogen gas). The solution is treated with enough phosphoric acid to give an overall acid strength of 9 M near the end-point. About 8-10 drops of RSF solution are added (as a catalyst) and the solution titrated against a 0.05 M iron(II) solution potentiometrically under inert atmosphere (by circulating N_2 gas) in the usual way on a magnetic stirrer. The break in potential at the end-point is found to be about 50-60 mV for the addition of 0.05 mL of 0.05 M iron(II) solution. Some of the typical results obtained by the potentiometric method have been shown in Table-1.

Indicator or visual end-poin method: The procedure for the indicator method is the same as that of the potentiometric method excepting that the end-point is detected by the colour transition of the indicator, RSF, from red to blue-green. The colour transition of the indicator is sharp and reversible at the end-point and no indicator correction need be applied. Some of the typical results obtained by the method have been furnished in Table-1.

TABLE-1
DETERMINATION OF NITROSO-R-SALT WITH IRON(II)

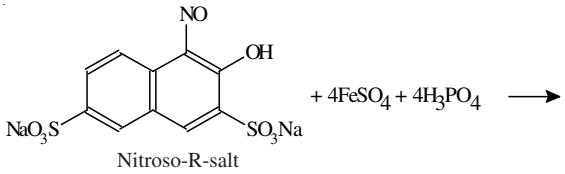
NRS Found* (mg)		Pooled standard deviation (S_g)	$\frac{1.96\times S_g}{\sqrt{n}}$	95 % Confidence limits (mg) $\overline{X} \pm \frac{1.96\times S_g}{\sqrt{n}}$
Standard method	Present method			
Potentiometric method				
11.32	11.37			11.35-11.39
18.86	18.95			18.93-18.97
26.41	26.30	0.03	0.02	26.28-26.32
33.95	33.81			33.79-33.83
37.73	37.87			37.85-37.89
Indicator method				
11.32	11.38			11.35-11.41
18.86	18.95			18.92-18.98
26.41	26.28	0.04	0.03	26.25-26.31
33.95	33.79			33.76-33.82
37.73	37.89			37.86-37.92
Spectophotometric method** (μg)				
943	950			946-954
1320	1311			1307-1315
1698	1687	5.00	4.00	1683-1691
2263	2277			2273-2281
2829	2845			2841-2849

*Average of six determinations. **Micro-gram quantities of NRS determined.

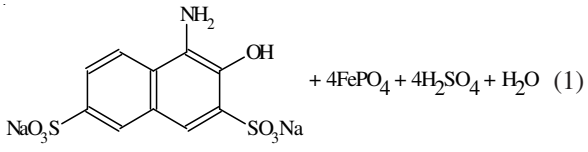
Spectrophotometric titration method: To an aliquot (5-15 mL) of NRS solution (5.0×10^{-5} M or 2.0×10^{-4} N) taken in a titration cell described above (3 cm path length), required amount of phosphoric acid is added to give an overall strength of about 9 M near the end-point and the solution diluted to 50 mL, the titration cell is then placed in the position of the spectrophotometer which was initially set at 410 nm and at zero absorbance with respect to a blank. The reaction mixture is now titrated against a 0.01 M (or N) iron(II) solution by adding it in installments and noting the absorbance after 30 s each addition. Stirring of the solution is provided by circulating the N_2 gas throughout the titration except before noting the absorbance. The titration is continued in this way till the absorbance became almost constant. A plot is drawn between the volume of the titrant and the corresponding absorbance. The resultant curve consists of two straight lines, the point of intersection of which corresponds to the end-point[17]. Some of the typical results obtained by the procedure have been shown in Table-1.

RESULTS AND DISCUSSION

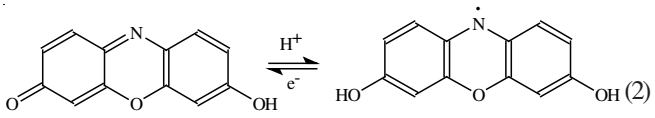
The accuracy of the indicator, ptentiomertic and spectrophotometric methods are found to be ± 0.6, ± 0.5 and ± 0.8 %, respectively. The precision of each method expressed in the form of pooled standard deviation and 95 % confidence limits has also been include in the same table. In the present redox procedure, NRS is reduced to its corresponding amino compound in a four electron reduction step as per eqn. 1. In the visual method, at the end point, the indicator RSF is reduced to its blue-green semiquinone[18,19] form in one electron step as per eqn. 2.



Nitroso-R-salt



Reduced nitroso-R-salt



RSF Semiquinone

It has already been stated in the present paper that the reduction of NRS by iron(II) is slow but, found to be catalyzed by RSF. The mechanism of catalysis may be explained as follows: in phosphoric acid medium, the reduction of NRS by iron(II) is observed to be slow while that of RSF by iron(II) is found fast. So, it is assumed that first of all RSF is reduced by iron(II) to its semiquinone form according to eqn. 2. The free electron present on the semiquinone is likely to be readily transferred to NRS, leading to its rapid reduction. Thus, in presence of RSF the reduction of NRS by iron(II) is found instantaneous.

The spectrophotometric titration of NRS by iron(II) can not be carried out in presence of RSF, because the colours of both RSF(red) and its semiquinone (blue-green) interfere with the determination. However, the rapid reduction of NRS by iron(II) has been achieved by carrying the titration using five fold concentrated iron(II) solution (1.0×10^{-2} N) to that of NRS (2.0×10^{-3} N) solution utilized in spectrophotometric titrations. Spectrophotometic titrations are generally carried out using titrants of higher concentrations[17].

In order to select an appropriate wavelength for the spectrophotometric titration of NRS by iron(II), the author has recorded the absorption spectra of NRS, reduced NRS, iron(II) and iron(III) in 9 M phosphoric acid medium against their corresponding blanks in the visible region (400-700 nm) of the spectrum using glass cells of 1 cm path length. From such spectra it has been found that except NRS, all other solutions have negligible absorbance in the visible region. Therefore, the absorption spectra of NRS (overall concentration 0.5×10^{-3} M or 2.0×10^{-3} N in 9 M phosphoric acid medium) has been recorded and found that it has maximum absorbance at 410 nm. Therefore, the spectrophotometric titration has been carried out at 410 nm.

The author has studied the stability of NRS solution prepared in 9 M phosphoric acid medium spectrophotometrically by measuring its absorbance, at its λ_{max} 410 mm, at definite intervals of time and found no decrease in its absorbance up to one day indicating that NRS solution keeps its stability up to one day in 9 M phosphoric acid medium. The author has also prepared (preparation described under reagents) the reduced NRS solution, in 9 M phosphoric acid medium by reducing NRS with iron(II), but, to prevent the aerial oxidation of reduced NRS, 50 fold excess of iron(II) has been maintained in the reaction medium. The stability of the solution by measuring its absorbance at 410 nm (as in the case of NRS given above) is also studied and found an increase in its absorbance only after 2 h. This study indicates that reduced NRS solution does not keep its stability for more than 2 h towards the oxygen of the air even in the presence of 50 fold excess of iron(II).

The present method also involved the measurement of the formal redox potentials of the oxidant system [NRS/reduced NRS] and the reductant system [Fe(III)/Fe(II)] under the optimum titration conditions *i.e.*, in 9 M phosphoric acid medium and in presence of little amount of RSF adopting the procedure of Conant and Fieser[20] in the case of former and that of Rao and Dikshitulu[21] in the case of latter. The potentials are found to be 770 ± 5 mV for the oxidant system and 410 ± 5 mV for reductant system. The difference in potential between the two systems is found to be about 360 mV which is sufficient to bring rapid reduction of NRS by iron(II). Thus, the potentials data satisfactorily account for the conditions needed in the titration.

The transition potential of the indicator RSF was also determined by adopting the procedure of Belcher *et al.*[22] and observed to be 560 ± 5 mV. The potential is found to be intermediate between the oxidant (770 mV) and reductant (410 mV) systems. These potentials data thus support the suitability of RSF as a redox indicator in the determination.

Study of interferences: Chloride, sulphate, acetate, manganese(II), zinc(II) aluminium(III) ions do not interfere in this determination. However, nitrate and nitrite ions interfere at all concentrations.

REFERENCES

1. K.J. McNaught, *Analyst*, **67**, 97 (1942).
2. R.Q. Parks, S.L. Hood, C. Hurwitz and G.H. Ellis, *Ind. Eng. Chem. Anal. Ed.*, **37**, 527 (1943).
3. C.P. Sideris, *Ind. Eng. Chem. Anal. Ed.*, **14**, 765 (1942).
4. H.T. Macpherson and J. Stewart, *Biochem. J.*, **32**, 763 (1938); *Chem. Abstr.*, **32**, 6971 (1938).
5. L.I. Butler and H.O. Allen, *J. Assoc. Off. Agric. Chem.*, **25**, 567(1942); *Chem. Abstr.*, **36**, 6435 (1942).
6. F.W. Haywood and A.A.R. Wood, *J. Soc. Chem. Ind.*, **62**, 37 (1943); *Chem. Abstr.*, **37**, 3691 (1943).
7. R. Clauser, *Ber. Dtsch, Chem. Ges.*, **34**, 891 (1901).
8. E. Knetch and E. Hibbart, *Ber. Dtsch, Chem. Ges.*, **40**, 3819 (1907).
9. S. Musha, *J. Chem. Soc. (Japan)*, **66**, 38 (1945).
10. R.S. Bottle and N.H. Furman, *Anal. Chem.*, **29**, 119 (1978).
11. R. Aldrovandi and F.D. Loronzi, *Ann. Chim. (Rome)*, **42**, 298 (1952).
12. R.D. Tiwari and T.P. Sharma, *Proc. Nat. Acad. Sci. (India)*, **33**, 379 (1963).
13. N. Rukmini and V.S.N.P. Kavita, *J. Indian Chem. Soc.*, **55**, 660 (1978).
14. M.F. Curcio, W.L. Batista, E. Linares, F.D. Nascimento, M.S. Moraes, R.E. Borges, J. Sap, A. Stern and H.P. Monterio, *Antioxid. Redox Signal.*, **13**, 109 (2010).
15. I.M. Kolthoff and R. Belchor, Volumetric Analysis, Interscience Publishers, Vol. 3, p. 177 (1957).
16. K.V. Raju, G.M. Gautam and G.B. Raju, *Microchim. Acta*, **108**, 265 (1992).
17. A.I. Vogels, Text Book of Quantitative Analysis, Longmans, London, edn. 5, p. 722 (1989).
18. E. Ruzika, J. Adamek and J. Andree, *Monatsch Chem.*, **97**, 1558 (1966).
19. K.V. Raju, G.D. Sudhakar and T.B. Patrudu, *Asian J. Chem.*, **19**, 692 (2007).
20. J.B. Conant and L.F. Fieser, *J. Am. Chem. Soc.*, **46**, 1858 (1924).
21. G. Gopal Rao and L.S.A. Dikshitulu, *Talanta*, **10**, 295 (1963).
22. R. Belcher, A. Nutton and I.W. Stephen, *J. Chem. Soc.*, 3857 (1952).