

It would be desirable therefore to discuss a little further what we mean by 'observer' and the relation of this observer to phenomena. Clearly, by 'observer' we mean something more than a physico-chemical system obeying fixed laws of physics and chemistry, since this is itself a classical or a macroscopic view, hence only relevant for a particular level of perception. For the same reason, it cannot be looked upon as a spatio-temporally bound system. *The observer is an entity which always exists and exists only in the singular.* There is only one observer! It is the same observer that attains these various levels of perception, including the ones in which it sees itself as many observers. The strongest argument in favour of the view is that *an observer is never experienced in the plural.* The inability to visualize such an observer is no more serious than our inability to visualize quantum mechanical objects, for example electrons. This dissociation of the concept of an observer from 'human-being' or from the 'phenomenon of life' is, we believe, important for the resolution of the age-old question: Would there be a Universe if there were no one to observe it? The answer is No, because the existence of the observer is a fundamental truth—the only truth accessible to direct experience. The concept of an external world and laws governing its phenomena are constructs invented by the observer to put order and meaning into his own experience. These constructs are, therefore, subject to change in the observer's perception, for no set of concepts meaningfully describes the entire experience.

An immediate question that arises is, whether these various levels of perception are attainable by a 'human' observer. The following way of looking at the problem may perhaps be helpful. Let us note that if we accept the more general concept of the 'observer' mentioned above, then for this observer, there is no distinction between mental phenomena like thoughts, feelings, emotions, etc., and physical phenomena like burning of wood. Both kinds of phenomena are parts of the observer's experience. The identification is useful, however, in one respect. In the realm of mental phenomena we explicitly recognize the impossibility of observation of a phenomenon without disturbing or changing the phenomenon. It is very difficult to observe thoughts without changing them. Further, mental phenomena are known to be phenomena which themselves change as a result of their understanding. For example, if repeated performance of a habitual act by a person is looked upon as a phenomenon, we do allow for the possibility that the person may get rid of the habit by conscious effort in the form of introspection. Now if there is no qualitative difference between mental and physical phenomena, both taking place in the observer's mind, one must allow for the possibility that the latter may change as a result of conscious effort on the part of the observer. Physical laws could thus be looked upon as habits, only much more deep-rooted, consequently requiring much greater effort to change.

1. Bhandari, R., *Pramāṇa*, 1974, 3, 1.
2. —, *Ibid.*, 1976, 6, 135.

SPECTROPHOTOMETRIC STUDY OF THE REACTION OF OSMIUM WITH ISONIAZID

H. SANKE GOWDA AND B. NARAYANA ACHAR

*Department of Post-Graduate Studies and Research in Chemistry, University of Mysore,
Manasa Gangotri, Mysore 570 006*

ABSTRACT

Isoniazid is proposed as a new reagent for the spectrophotometric determination of microgram amounts of osmium. It forms a yellow complex with Os(VIII) and Os(VI) in the pH range 3.8–4.5 at room temperature. The yellow complex exhibits maximum absorbance at 420 nm. Beer's law is valid over the concentration range 0.1–6.5 ppm for Os(VIII) and 0.4–7.0 ppm for Os(VI). The sensitivities are 0.013 $\mu\text{g}/\text{cm}^2$ for Os(VIII) and 0.026 $\mu\text{g}/\text{cm}^2$ for Os(VI). The effects of time, temperature, order of addition of reagents, reagent concentration and diverse ions are reported.

INTRODUCTION

ISONIAZID, isonicotinic acid hydrazide (INH) is extensively used in the treatment of tuberculosis. It has been proposed for the spectrophotometric determination of vanadium¹ and gold². In the present paper the authors have investigated the

colour reaction between INH and the platinum metals and developed INH as a sensitive reagent for the spectrophotometric determination of osmium. The proposed method offers the advantages of simplicity and good sensitivity without the need for extraction.

TABLE I
Determination of osmium in synthetic mixtures corresponding to syserkite

Osmium (VIII) taken (ppm)	Ir (ppm)	Ru (ppm)	Pt (ppm)	Rh (ppm)	Au (ppm)	Osmium (VIII) found (ppm)
0.8	0.5	0.25	0.20	0.05	0.01	0.85
1.0	0.9	0.40	0.40	0.01	0.05	1.03
1.5	1.2	0.60	0.50	0.03	0.10	1.51
2.4	2.0	0.80	0.60	0.02	0.10	2.42
3.0	2.5	0.50	0.10	0.01	..	3.04
5.0	4.0	0.80	0.20	0.01	..	5.00

EXPERIMENTAL

Standard solution of osmium (VIII) was prepared from osmium tetroxide (M/s. Johnson Matthey Chemicals Ltd., London) in 0.02 M sodium hydroxide. Standard solution of osmium (VI) was prepared from potassium osmate (M/s. JMC) in doubly distilled water. Buffer solutions of the pH range 0.65–5.2 were prepared from 1 M sodium acetate and 1 M hydrochloric acid solutions. A 1% aqueous solution of INH was used. Standard solutions of diverse ions were prepared from analytical grade chemicals. Beckman Model DB spectrophotometer was used for absorbance measurements.

Procedure:—The sample solution containing 20–150 μg of osmium (VIII) or 25–175 μg of osmium (VI) was transferred to a 25 ml volumetric flask. 5 ml of Walpole buffer of pH 3.6 and 5 ml of 1% INH were added and diluted to the mark with doubly distilled water. After 10 minutes, the absorbance was measured at 420 nm against a reagent blank prepared under similar condition. The osmium concentration of the sample solution was then deduced from the standard calibration curve.

RESULTS AND DISCUSSION

Of the six platinum metals only octavalent and sexavalent osmium forms an yellow coloured complex with INH at room temperature (27°C) in the presence of Walpole buffer. Osmium (VI) does not form any coloured complex with INH. Maximum colouration takes place in the pH range 3.8–4.5. All studies are therefore confined to pH 4. The yellow colour is fully developed in 10 minutes after mixing the reagent and is stable for 10 minutes. The order of mixing osmium (M), buffer (B) and INH (L) has some effect on the development and stability of the

colour. If the mixing of the reagents follows the order: MBL, BML or LBM, the maximum colour development takes place in 10 minutes. If the mixing of the reagents follows the order: LMB or MLB the full development of colour takes place in 15 minutes. It is therefore recommended to mix osmium and buffer solutions prior to the addition of INH solution.

The minimum amount of INH required for the maximum development of colour is 5 ml of 1% solution. Higher concentration of the reagent does not alter the colour intensity. The absorbance readings are constant in the temperature range 10–45°C.

Beer's law is obeyed over the concentration range 0.1–6.5 ppm of osmium (VIII) and 0.4–7.0 ppm of osmium (VI). The optimum concentration ranges as evaluated by Ringbom plot are 0.8–6.0 ppm for osmium (VIII) and 1.0–7.0 ppm for osmium (VI). According to Sandell's expression, the sensitivity of the reaction is 0.013 $\mu\text{g}/\text{cm}^2$ for osmium (VIII) and 0.026 $\mu\text{g}/\text{cm}^2$ for osmium (VI). The absorbance of six solutions containing 5 ppm of osmium has a maximum relative deviation of 1.5% and an average deviation of 0.5%.

The sensitivity of the proposed method is more than that of *o*-(β -benzoylthioureido) benzoic acid³, 2-mercaptobenzimidazole⁴, 2-mercaptobenzothiazole⁵, 1-carbamidino-3-methyl-5-pyrazolene⁶, bismuthiol II⁷ and β -benzoyl- α (*o*-tolyl) thiourea⁸ which have been proposed as sensitive spectrophotometric reagents for osmium (VIII).

The yellow colour of the solution is assumed to be the colour of a complex because the solutions of the reagents and the oxidation products of INH are colourless. Job's method of continuous variation^{9,10}, mole ratio method¹¹ and limiting

logarithmic method¹² fail to give the composition of the complex because the yellow colour is not developed even in the presence of 200-fold molar excess of INH. A 925-fold molar excess of INH is necessary for the complete complex formation. The cationic nature of the complex is indicated by the retention of the yellow colour on Dowex 50W-X8 cation exchange resin.

The following amounts ($\mu\text{g/ml}$) of foreign ions are found to give less than 2% error in the determination of $3\mu\text{g/ml}$ osmium: Pd^{2+} (20), Pt^{4+} (1.0), Ru^{3+} (1.0), Rh^{3+} (8.0), Ir^{3+} (8.0), Cu^{2+} (16.0), Ni^{2+} (400), Co^{2+} (44), Au^{3+} (0.2), Fe^{3+} (100), Ag^{+} (0.4), Mn^{2+} (80), F^{-} (1400), Cl^{-} (1600), Br^{-} (600), I^{-} (600), SO_4^{2-} (1000), NO_3^{-} (1600), PO_4^{3-} (400), $\text{S}_2\text{O}_3^{2-}$ (20), EDTA (80), acetate (800), oxalate (12) and citrate (8). Pt^{4+} and Ru^{3+} interfere because of their colour.

Determination of osmium in ores.—Synthetic mixtures corresponding to syserkite were prepared and the osmium content was determined following

the standard procedure. The results are given in Table I.

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PROTON-LIGAND FORMATION CONSTANTS AND FORMATION CONSTANTS OF Tl(I)-3-NITRO SALICYLATES

P. V. KHADIKAR

School of Studies in Chemistry, Vikram University, Ujjain (M.P.) India

AND

P. S. DESHMUKH

Government College, Khargone (M.P.), India

ABSTRACT

Proton-ligand formation constants and formation constants of Tl(I)-complexes with 3-nitro salicylic acid have been determined at 30°C (50% aqueous ethanol, 0.1 M NaClO_4) by various computational methods. The average values of proton-ligand formation constants are found to be $\log pK_1^H = 10.34$ and $\log pK_2^H = 2.30$, the corresponding values for formation constants are 7.87 and 5.05 respectively.

ALTHOUGH the co-ordination chemistry of salicylic acid is well documented, the study of its derivative, 3-nitro salicylic acid (3-NSA), remained neglected until quite recently. Khadikar *et al.*⁵⁻⁷ have reported the complex forming tendency of 3-NSA with number of di- and tri-valent metal ions. The literature does not reveal the complex formation of Tl(I) with 3-NSA. The present study deals with the same. The proton-ligand formation constants of 3-NSA and the formation constants of its complexes with Tl(I) have been determined in the present investigation employing half-integral, point-wise calculation, and linear plot method. Refined values of formation constants are obtained by the method of least-squares.

EXPERIMENTAL

All the chemicals used were of Analar B.D.H. grade.

Polymetron model CL-41 was used for pH titrations conducted at 30° . Measurements were made with an accuracy of ± 0.05 pH units and the reproducibility of the readings was of the same order. The pH-meter was calibrated using Cambridge buffer tablets of pH 4.1 and 9.1.

pH-metric titrations of solutions of (i) free HClO_4 , (ii) free $\text{HClO}_4 + 3\text{-NSA}$ and (iii) free $\text{HClO}_4 + 3\text{-NSA} + \text{Tl(I)}$, were performed in 50% (v/v) aqueous ethanol medium against standard NaOH solution while maintaining the ionic strength at 0.1 M NaClO_4 .