

LETTERS TO THE EDITOR

EXTRACTIVE SPECTROPHOTOMETRIC
METHOD FOR THE DETERMINATION OF
BISMUTH WITH TETRAPHENYL-
ARSONIUM CHLORIDE*Introduction*

THE use of tetraphenylarsonium chloride as an analytical reagent has long been known¹⁻³. The complex halides of many metals and the anions, viz., ClO_4^- , IO_4^- and ReO_4^- form insoluble precipitates with the reagent. The precipitates have been used in the gravimetric analysis. Based on the solubility of some of these precipitates in chloroform, anions like ReO_4^- , TcO_4^- and MnO_4^- have been extracted into chloroform⁴. Similar ion pairs of the reagent with anions such as chloro and thiocyanato complexes of bismuth, cadmium, iridium (IV)⁵, niobium⁶, niobium and titanium⁷, palladium⁸, zinc, tin (IV) and gold⁹ have been used in the extractive spectrophotometric method. A similar reagent, tetraphenylphosphonium bromide has been used in the extractive photometric determination of bismuth¹⁰. Bismuth, in presence of potassium iodide, was found to give a similar precipitate with tetraphenylarsonium chloride having higher solubility in 1,2-dichloroethane than in chloroform. In the present method, the extractive spectrophotometric determination of bismuth as tetraphenylarsonium tetraiodobismuthate in 1,2-dichloroethane was investigated.

Experimental

Absorbance measurements were made with a Beckmann DK-2 spectrophotometer.

Standard solution.—0.2786 g of bismuth oxide (B.P.) was dissolved in minimum volume of concentrated hydrochloric acid. The solution was then boiled to white fumes with 1 ml of concentrated sulphuric acid and a drop or two of concentrated nitric acid. The resulting mass was dissolved in 2N sulphuric acid and was made upto 250 ml and used as the stock solution (0.1 g/100 ml). A 0.01 M solution of tetraphenylarsonium chloride (Fluka A. G., Buchs SG) and freshly prepared (1.6%) solution of potassium iodide (B.D.H.), both in distilled water, were employed as the reagents.

Procedure.—An aliquot of the standard solution containing 10 μg to 100 μg of bismuth was taken in different separating funnels. The volume in each was made upto 5 ml by adding 2N sulphuric

acid. To each of these solutions 1 ml of KI reagent followed by 1 ml of tetraphenylarsonium chloride reagent was added. The resulting mixture having orange yellow precipitate was then shaken for 1 minute with 3 ml of 1,2-dichloroethane. The organic layer was separated and the absorbance was measured at 492 nm against the pure solvent. Alternatively, the orange coloured precipitate formed, after the addition of the reagent was centrifuged and the supernatant liquid was drained off and the precipitate was then dissolved in 3 ml of 1,2-dichloroethane and its absorbance measured at 492 nm. The orange coloured extract was found to obey Beer's law over the concentration range of 3 to 30 $\mu\text{g}/\text{ml}$. The experiments were repeated with varying amounts of bismuth and the amounts of bismuth were calculated from the standard calibration curve. The results of these determinations showed that the error involved was less than 3%.

In a similar manner, 50 μg of bismuth was estimated in presence of the metal ions Fe^{3+} , Cd^{2+} , Sn^{4+} , Hg^{2+} and Sb^{3+} and the anions AuCl_4^- , MoO_4^{2-} , WO_4^{2-} , CrO_4^{2-} , MnO_4^{4-} , CNS^- , $\text{S}_2\text{O}_8^{2-}$, F^- , $\text{C}_2\text{O}_4^{2-}$ and ClO_4^- in amounts equal to and 10 times that of the bismuth added. The recovery of bismuth, in most cases, in presence of equal amounts of interfering ions was good. A 10 fold excess of some of the ions interfered and a few interfered even when present in equal amount.

Discussion

Bismuth, in presence of potassium iodide, forms orange yellow precipitate of tetraphenylarsonium tetraiodobismuthate with tetraphenylarsonium chloride extractable into 1,2-dichloroethane. The orange coloured extract has an absorbance maximum at 492 nm and obeys Beer's law over the concentration range 3 to 30 μg per ml. The maximum error involved in the determination of trace quantities of bismuth in absence of other ions is within 3%.

An examination of the effect of the presence of other metal ions, viz., Fe(III), Cd(II), Sn(IV), Hg(II) and Sb(III) that form halide complexes showed that these metals when present in equal amounts with bismuth did not interfere much (error within 5% in the μg level). However, except Hg(II) and Sn(IV), all the other three in their 10 fold excess interfered. A similar study on the effect of the presence of common anions, viz., AuCl_4^- , MoO_4^{2-} , WO_4^{2-} , CrO_4^{2-} , MnO_4^- , CNS^- ,

$S_2O_8^{2-}$, F^- , $C_2O_4^{2-}$ and ClO_4^- showed that only CrO_4^{2-} and MnO_4^- interfered seriously when present in equal amounts and in 10 fold excess to that of the bismuth. $S_2O_8^{2-}$, $AuCl_4^-$ and CNS^- ions in 10 fold excess interfered, the latter two interfered only slightly. All other anions did not interfere even when present in 10 fold excess.

Interference due to iron (III) could be removed by using oxalic acid and ammonium fluoride as the masking reagents and a good recovery of bismuth (error within 1%) was achieved. These reagents did not interfere in the determination of bismuth. Interference due to chromium (VI) could be removed by prior separation of chromium by extraction with isobutyl methyl ketone from solutions above 1 N with respect to hydrochloric or sulphuric acid, a method that has been used in the determination of chromium^{11,12}. Recovery of bismuth was within 2% error. The application of the common analytical practice of reducing potassium permanganate with oxalic acid in acidic medium proved to be successful in the removal of interference due to MnO_4^- ion. Recovery of bismuth was within 3% error.

Thus the method proved to be a simple and rapid one providing a good recovery of bismuth in presence of equal amounts of most of the common ions. Besides, it also provides simple techniques for the removal of interferences due to these interfering seriously.

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MESOMORPHIC BEHAVIOUR OF SOME SCHIFF BASE COMPOUNDS COMPRISING NAPHTHALENE MOIETY

A NUMBER of homologous series comprising schiff base compounds exhibiting mesomorphism are known. Generally a linear structure favours the development of mesomorphism. It is observed that when molecular structure is varied within a group of suitable compounds the liquid crystalline properties change markedly. The introduction of a 1,4 substituted naphthalene nucleus in place of a 1,4 substituted phenylene ring usually reduces the thermal stabilities of the mesophase.

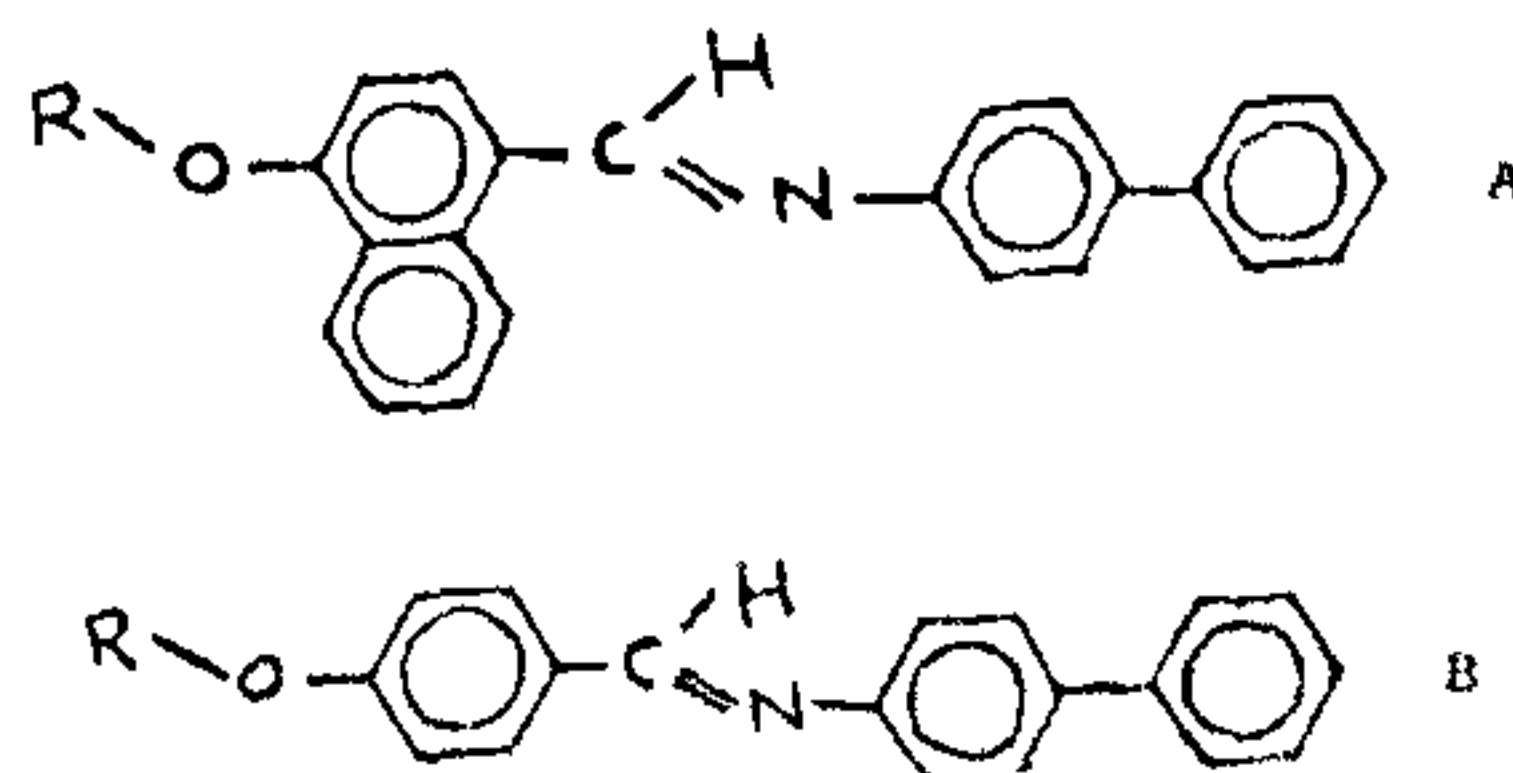
Dave *et al.*¹⁻⁵, have studied a number of schiff base series comprising a naphthalene moiety. As a part of our programme of the study of the effect of breadth on mesomorphism we describe here the mesomorphic behaviour of the four compounds of the series 4-*n*-alkoxy-1-naphthalidene-4'-aminobiphenyls. The melting points and transition temperatures are summarized in Table I.

TABLE I
4-*n*-Alkoxy-1-naphthylidene-4'-aminobiphenyls
 $RO.C_{10}H_6CH : N.C_6H_4.C_6H_5$

R	Transition temperatures (°C)		
	Smectic	Nematic	Isotropic
1. CH_3	201.5
2. $C_{12}H_{25}$..	(103.0)	107.5
3. $C_{16}H_{33}$..	92.0	97.0
4. $C_{18}H_{37}$	(69.0)	83.5	93.0

Values in parenthesis indicate monotropy.

The methyl derivative is non-mesomorphic; the dodecyl derivative exhibits a monotropic nematic mesophase and the last two members, *i.e.*, hexadecyl and octadecyl derivatives exhibit enantiotropic nematic mesophases. The octadecyl derivative exhibits a monotropic smectic mesophase also.



The nematic mesophase exhibited by these compounds has the threaded texture and the smectic mesophase has the broken fan shaped texture.