Electrometric Estimation of Bismuth

By V. D. Anand, B. N. Prasad and Aqil Ahmed Amani

(Received June 8, 1959)

Thiourea and its derivatives, which are good sulfur coordinators[1], have been used for the detection and determination of a number of ions. Bismuth ion forms a yellow compound on the addition of thiourea[2]. Recently an electrometric study of the bismuth complexes with thiourea and substituted thioureas employing the bimetallic electrode system has been communicated by the anthors' laboratories[3]. During the course of this work it was observed that the method can be easily adopted for the quantitative determination of bismuth. The present communication reports in detail the application of the bimetallic electrode system to the estimation of bismuth with thiourea, substituted thioureas and urea.

B.D.H. reagent grade bismuth trichloride was recrystallized twice from acetone and its solutions of varying concentrations in anhydrous methanol, ethanol and acetone were prepared. The strength of these solutions was determined by the oxychloride method[4]. Thiourea solutions were standardized by the Volhard procedure[5] as modified by Cuthil and Atkins[6].

The bimetallic electrode system was used, employing the Pt : W bimetallic couple, first proposed by Furman and Wilson[7]. The Bi : W electrode system was also used. An aliquot of the bismuth chloride solution was taken in a pyrex cell fitted with the platinum and tungsten (or the bismuth and tungsten) electrodes. The electrical circuit was similar to that used by Gay[8], and consisted of a 1.5 V. cell with its negative pole connected to the tungsten electrode, a 1 kΩ fixed resistance, a 200 Ω variable rheostat and a suitably shunted galvanometer, all connected in series. Galvanometer deflections were noted after successive additions, from the burette, of small amounts of standard thiourea solution and thorough stirring.

The addition of the titrant near the end point was dropwise. Maxima in the galvanometric deflection mark the equivalence points, corresponding to the formation of different complexes.

A representative curve from an actual determination of bismuth against thiourea in acetone medium, using the Pt : W bimetallic electrode system, is shown in Fig. 1. The curve shows two peaks corresponding to the two complexes of bismuth with thiourea reported in the earlier communication[3].

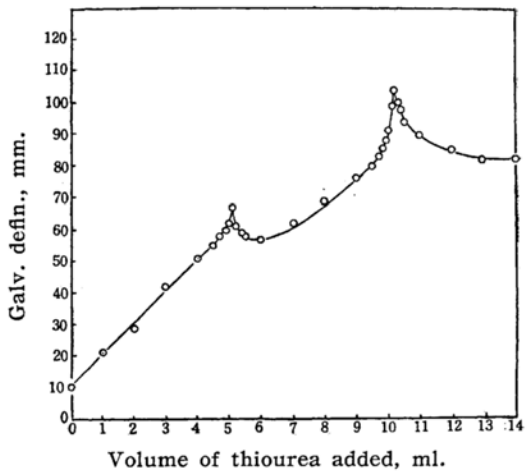

Fig. 1. Titration of bismuth against thiourea in acetone medium, using Pt: W bimetallic electrode system.

Table I shows the results of determination of bismuth against thiourea, phenyl thiourea, *p*-toluyl thiourea and urea in different non-aquous media using the Pt : W bimetallic system.

The estimation of bismuth against the same ligands was also done with the Bi : W bimetallic electrode couple. The results are recorded in Table II. The titrations with urea had to be restricted to methanol and ethanol medium only because of the low solubility of urea in acetone.

The two peaks in the titration curve correspond to the two end points in these titrations. This agrees with the formation of the two complexes viz., $2BiCl_3 \cdot 3X$ and

1) J. H. Yoe and L. G. Overholser, *Ind. Eng. Chem., Anal. Ed.*, **14**, 435 (1942).
2) C. Mahr, *Z. anal. Chem.*, **94**, 161 (1933); **97**, 96 (1934).
3) V. D. Anand and B. N. Prasad, communicated to *Z. anorg. u. allgem. Chem.* (accepted for publication).
4) "Scotts Standard Methods of Chemical Analysis", 5th Ed., D. Van Nostrand Co., Inc., New York (1944), p. 153.
5) J. Volhard, *Ber.*, **7**, 100 (1847).
6) R. Cuthil and C. Atkins, *J. Soc. Chem. Ind.*, **56**, 5T (1937).
7) N. H. Furman and E. B. Wilson, *J. Am. Chem. Soc.*, **50**, 277 (1928).
8) J. R. Gay, *Ind. Eng. Chem., Anal. Ed.*, **11**, 383 (1939); cf. A. Findlay, "Practical Physical Chemistry", Longman Green and Co., Inc., London (1949), p. 240.

TABLE I. ELECTROMETRIC DETERMINATION OF BISMUTH
(Pt : W Bimetallic electrode system)

Solvent medium	Weight of the bismuth complex					
	$2BiCl_3 \cdot 3X$*			$BiCl_3 \cdot 3X$*		
	Calculated g.	Found g.	Error mg.	Calculated g.	Found g.	Error mg.
			Thiourea			
Acetone	0.1428	0.1430	+0.2	0.1809	0.1811	+0.2
	0.0142	0.0142	—	0.0180	0.0181	+0.1
	0.0072	0.0072	—	0.0091	0.0090	−0.1
Methanol	0.0812	0.0815	+0.3	0.1028	0.1026	−0.2
	0.0162	0.0164	+0.2	0.0205	0.0204	−0.1
	0.0041	0.0040	−0.1	0.0052	0.0052	—
Ethanol	0.1290	0.1293	+0.3	0.1631	0.1635	+0.4
	0.0257	0.0258	+0.1	0.0325	0.0327	+0.2
	0.0129	0.0129	—	0.0163	0.0162	−0.1
			Phenyl thiourea			
Acetone	0.0180	0.0184	+0.4	0.0255	0.0252	−0.3
	0.0091	0.0092	+0.1	0.0129	0.0128	−0.1
	0.0044	0.0046	+0.2	0.0063	0.0064	+0.1
Methanol	0.0689	0.0685	−0.4	0.0979	0.0972	−0.7
	0.0346	0.0344	−0.2	0.0491	0.0488	−0.3
	0.0138	0.0137	−0.1	0.0196	0.0194	−0.2
Ethanol	0.0359	0.0357	−0.2	0.0510	0.0514	+0.4
	0.0180	0.0180	—	0.0255	0.0256	+0.1
	0.0073	0.0073	—	0.0103	0.0102	−0.1
			p-Toluyl thiourea			
Acetone	0.0426	0.0423	−0.3	0.0614	0.0609	−0.5
	0.0212	0.0212	—	0.0305	0.0302	−0.3
	0.0084	0.0083	−0.1	0.0121	0.0121	—
Methanol	0.0513	0.0508	−0.5	0.0739	0.0745	+0.6
	0.0258	0.0255	−0.3	0.0371	0.0372	+0.1
	0.0103	0.0102	−0.1	0.0149	0.0149	—
Ethanol	0.0253	0.0250	−0.3	0.0365	0.0363	−0.2
	0.0128	0.0128	—	0.0184	0.0185	+0.1
	0.0052	0.0052	—	0.0074	0.0074	—
			Urea			
Methanol	0.0764	0.0768	+0.4	0.0934	0.0939	+0.5
	0.0382	0.0383	+0.1	0.0467	0.0465	−0.2
	0.0192	0.0192	—	0.0234	0.0233	−0.1
Ethanol	0.1125	0.1133	+0.8	0.1375	0.1364	+1.1
	0.0225	0.0227	+0.2	0.0275	0.0272	−0.3
	0.0112	0.0111	−0.1	0.0137	0.0137	—

* X denotes the complexing ligand.

$BiCl_3 \cdot 3X$ (Where X stands for the complexing group). The two end points afford a convenint internal check on the accuracy of the procedure. The titration may, however, be stopped at either stage, since both equivalence points give accurate values within the limits of experimental error and results are easily reproducible.

It is evident from an examination of Tables I and II that the error is generally small and far less than is usually met with in the ordinary estimations. This is indicative of the fact that the electrometric determination is a simple, convenient and rapid procedure, easily applicable to the quantitative determination of bismuth.

TABLE II. ELECTROMETRIC DETERMINATION OF BISMUTH
(Bi : W Bimetallic electrode system)

Solvent medium	Weight of the bismuth complex					
	$2BiCl_3 \cdot 3X$*			$BiCl_3 \cdot 3X$*		
	Calculated g.	Found g.	Error mg.	Calculated g.	Found g.	Error mg.
			Thiourea			
Acetone	0.1428	0.1437	+0.9	0.1809	0.1823	+1.4
	0.0142	0.0143	+0.1	0.0180	0.0182	+0.2
	0.0072	0.0072	—	0.0091	0.0090	−0.1
Methanol	0.0812	0.0806	−0.6	0.1028	0.1020	−0.8
	0.0162	0.0163	+0.1	0.0205	0.0208	+0.3
	0.0041	0.0041	—	0.0052	0.0052	—
Ethanol	0.1290	0.1298	+0.8	0.1631	0.1640	+0.9
	0.0257	0.0259	+0.2	0.0325	0.0328	+0.3
	0.0129	0.0128	−0.1	0.0163	0.0164	+0.1
			Phenyl thiourea			
Acetone	0.0180	0.0182	+0.2	0.0255	0.0258	+0.3
	0.0091	0.0091	—	0.0129	0.0131	+0.2
	0.0044	0.0045	+0.1	0.0063	0.0063	—
Methanol	0.0689	0.0684	−0.5	0.0979	0.0983	+0.4
	0.0346	0.0344	−0.2	0.0491	0.0493	+0.2
	0.0138	0.0138	—	0.0196	0.0195	−0.1
Ethanol	0.0359	0.0362	+0.3	0.0510	0.0506	−0.4
	0.0180	0.0180	—	0.0255	0.0254	−0.1
	0.0073	0.0072	−0.1	0.0103	0.0103	—
			p-Toluyl thiourea			
Acetone	0.0426	0.0429	+0.3	0.0614	0.0618	+0.4
	0.0212	0.0214	+0.2	0.0305	0.0303	−0.2
	0.0084	0.0084	—	0.0121	0.0122	+0.1
Methanol	0.0513	0.0508	−0.5	0.0739	0.0733	−0.6
	0.0258	0.0256	−0.2	0.0371	0.0368	−0.3
	0.0103	0.0104	+0.1	0.0149	0.0149	—
Ethanol	0.0253	0.0255	+0.2	0.0365	0.0361	−0.4
	0.0128	0.0126	−0.2	0.0184	0.0182	−0.2
	0.0052	0.0052	—	0.0074	0.0073	−0.1
			Urea			
Methanol	0.0764	0.0769	+0.5	0.0934	0.0944	+1.0
	0.0382	0.0384	+0.2	0.0467	0.0470	+0.3
	0.0192	0.0193	+0.1	0.0234	0.0236	+0.2
Ethanol	0.1125	0.1136	+1.1	0.1375	0.1361	−1.4
	0.0226	0.0228	+0.2	0.0275	0.0272	−0.3
	0.0112	0.0113	+0.1	0.0137	0.0136	−0.1

* X denotes the complexing ligand.

Sincere thanks of the authors are due to Professor S. S. Joshi, D. Sc. (London), Head of Chemistry Department for facilities and keen interest and the Ministry of Scientific Research and Cultural Affairs for the award of a scholarship to one of them (V. D. A.).

Chemical Laboratories
Banaras Hindu University
Banaras-5, India