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Addition Compounds of Methylene Blue with Bismuth(III), Antimony(III) and Mercury(II)

O. B. SKAAR

Chemical Institute A, University of Oslo, Blindern, Norway

Some new addition compounds of methylene blue with bismuth(III), antimony(III) and mercury(II) were prepared. The composition of the compounds was determined gravimetrically and photometrically. The solubility in different media was also investigated.

Attack [1] and Monnier [2] reported that some inorganic acids and neutral salts form precipitates with methylene blue. Passerini and Michelotti [3] made further study in this field and determined the composition of some of the compounds. During an investigation on the effect of foreign ions on the spectrophotometric determination of boron with methylene blue, the author [4] found some new addition compounds with methylene blue.

The present paper describes the preparation and the determination of the composition of six compounds, one of which has been described before.[2,3] One compound was formed between Bi^{3+}, Cl^- and MB^+ (MB is the radical $C_{16}H_{18}N_3S$ in methylene blue); another between Sb^{3+}, Cl^- and MB^+; two between Hg^{2+}, Cl^- and MB^+; and two between Hg^{2+}, Br^- and MB^+.

EXPERIMENTAL

Instruments. Extinction measurements were made with a Zeiss spectrophotometer PMQ II and 0.500 cm glass cells.

Reagents. Methylene blue from Fluka A.G. (*puriss.*) and from G. T. Gurr Ltd. (vital & fluorchrome) were used. All other reagents were of reagent grade quality.

Water. Ordinary distilled water was employed.

Standard solutions

Methylene blue standard solution (Fluka). 33.650 g of methylene blue (Fluka) was dissolved in water and made up to 6 l. The solution was filtered through a Büchner filter funnel (porosity G 3). The concentration of methylene blue in the filtrate was found by a gravimetric method [5] to be 0.01346 M.

Methylene blue standard solution (Gurr). 19.424 g of methylene blue (Gurr) was dissolved in 5 l of water. The compound was completely dissolved in water. The strength

was determined as above and found to be 0.01048 M. The solution was diluted about 5 % to be just 0.01000 M. This final concentration was controlled by a new determination.

Bismuth standard solution, 0.02000 M Bi^{3+} in 2 N HCl. 5.209 g of bismuth oxychloride (BiOCl, dried at 110°) was dissolved in 400 ml of 5 N hydrochloric acid and made up to 1000 ml with water in a volumetric flask. Another bismuth standard solution being 1 N in hydrochloric acid was prepared in the same way taking the half amount of 5 N hydrochloric acid.

Antimony standard solution, 0.02000 M Sb^{3+} in 2 N HCl. 2.915 g of animony trioxide (Sb_2O_3, dried at 110°C) was dissolved in 400 ml of 5 N hydrochloric acid and made up to 1000 ml with water in a volumetric flask.

Mercury standard solution, 0.02000 M $HgCl_2$. 5.430 g of mercuric chloride was dissolved in water and made up to 1000 ml in a volumetric flask.

Synthesis of the compounds

The slightly soluble compounds were all precipitated from aqueous solutions. A known amount of metal ion was precipitated with a slight excess of methylene blue. From the observed weight of the compound the percentage content of metal ion was calculated on the assumption that all of the metal ions were precipitated as addition compound. The synthesis therefore also include in indirect determination of the metal content in the compounds. The results are given in Table 1.

The compounds were all found to be sparingly soluble in acid solution containing chloride or bromide ions. However, methylene blue itself and its bromide salt are also slightly soluble in these media. Methylene blue should therefore not be added in large excess. A slight excess of methylene blue can be tolerated when the solutions are kept at an elevated temperature.[5]

Preparation 1 a. 50.00 ml of bismuth standard solution (1 N HCl), 40 ml of 5 N hydrochloric acid solution and 50 ml of water were pipetted into a 500 ml Erlenmeyer flask and the solution was heated to 80°C. 160 ml of methylene blue standard solution (Gurr) was added in portions. The mixture was heated to 80°C, then cooled to room temperature and filtered in a previously dried and weighed glass filter crucible (porosity G3). Two portions (about 50 ml) of the filtrate were used to transfer all of the precipitate from the Erlenmeyer flask to the filter crucible. The precipitate was washed with 3 ml of acetone and dried to constant weight at 110°C.

Preparation 1 b. 300.0 ml of bismuth standard solution (2 N HCl) and 165 ml of 5 N hydrochloric acid solution were pipetted into 2 l Erlenmeyer flask and the solution heated to boiling. Then 970 ml of methylene blue standard solution (Gurr) was added. The mixture was again heated to boiling, cooled to 30°C and filtered in a previously dried and weighed glass filter crucible (porosity G3). The precipitate was washed with 3 ml acetone, dried for 12 h at room temperature (weight of precipitate = 4.7740 g) and for 1 h at 110°C (weight = 4.7648 g).

Preparation 2. 50.00 ml of antimony standard solution and 30 ml of 5 N hydrochloric acid solution were pipetted into a 500 ml Erlenmeyer flask and the solution was heated to boiling. 165 ml of methylene blue standard solution (Fluka) were added in portions. The mixture was heated to boiling, cooled to 28°C and further treated as for Preparation 1 a.

Preparation 3. 50.000 ml of mercury standard solution was pipetted into a 300 ml Erlenmeyer flask and heated to boiling. 160 ml of methylene blue standard solution (Fluka) was added in portions so that the mixture was still kept at the boiling point. The mixture was cooled to 30°C and further treated as for Preparation 1 a.

Preparation 4 a. 50.000 ml of mercury standard solution and 100 ml of 2.5 M potassium chloride solution were pipetted into a 500 ml Erlenmeyer flask and heated to boiling. The solution was then treated as for Preparation 3. The weight at room temperature and that at 110°C did not differ by more than 0.5 %.

Preparation 4 b. 50.00 ml of mercury standard solution and 50 ml of 5 N hydrochloric acid solution were pipetted into a 300 ml Erlenmeyer flask. The solution was heated and kept at the boiling point while 165 ml of methylene blue standard solution (Fluka) were added in portions. The mixture was cooled to 26°C. The further treatment was as for Preparation 1 a.

Preparation 5 a. 50.000 ml of mercury standard solution and 100 ml of 0.04 M potassium bromide solution were pipetted into a 300 ml Erlenmeyer flask. The solution was heated and kept at the boiling point while 50 ml of methylene blue standard solution (Fluka) were added in portions. The further treatment was as for Preparation 1 b. Air-dried and oven-dried precipitate had the same weight.

Preparation 5 b. 100 ml of mercury standard solution and 10 ml of 2 M potassium bromide solution were pipetted into a 300 ml Erlenmeyer flask. The solution was heated and kept at the boiling point while 100.00 ml of methylene blue standard solution (Fluka) was added in portions. The further treatment was as for Preparation 3.

Preparation 6. 50 ml of mercury standard solution, 50 ml of 2 M potassium bromide solution and 27 ml of 10 N sulphuric acid solution were pipetted into a 500 ml Erlenmeyer flask. The solution were heated and kept at the boiling point while 148.6 ml of methylene blue standard solution (Fluka) was added in portions. The further treatment was as for Preparation 3.

Determination of halide

Chloride and bromide were determined gravimetrically by precipitation with silver nitrate solution. About 1 g of the compound was weighed out accurately and transferred to a 750 ml Erlenmeyer flask containing 500 ml of 1 N nitric acid. The mixture was heated to about 60°C and the halogenides were precipitated by adding a slight excess of 0.1 M silver nitrate solution. The precipitate was filtered in a glass filter crucible, washed with water, dried at 105°C and weighed. The strong nitric acid solution was used to keep antimony and bismuth dissolved. Most of the compounds did not dissolve completely before the silver nitrate solution was added. On prolonged standing a dark blue compound tended to precipitate. It was found possible to remove the dark compound by repeated washing.

Table 1. Composition of addition compounds of methylene blue with bismuth(III), antimony(III) and mercury(II).

Preparation number	Medium	Colour and form	Formula	Observed and calculated content (weight %) of					
				metal ion		halogenide ion		methylene blue	
				found	calc.	found*	calc.	found	calc.
1a	0.8 N HCl	Yellow-brown crystals with bronze lustre	$(C_{16}H_{18}N_3SCl)_3Bi_2Cl_6$	26.28	26.27	20.3	20.1		
1b	1.0 N HCl	»	»	26.24	26.27	19.9	20.1	60.7	60.3
2	1.0 N HCl	Brown needles with bronze lustre	$(C_{16}H_{18}N_3SCl)_2SbCl_3$	13.99	14.03	20.7	20.4	74.3	73.7
3	neutral	Green crystals with lustre	$C_{16}H_{18}N_3SCl{\cdot}HgCl_2$	33.93	33.92	14.6	18.0	56.0	54.1
4a	0.8 N KCl	Red-violet crystals with lustre	$(C_{16}H_{18}N_3SCl)_2HgCl_2$	22.05	22.02	15.7	15.6	70.7	70.2
4b	1.0 N HCl	»	»	22.06	22.02	14.6	15.6	70.6	70.2
5a	0.005 M KBr	Dark-green powder	$C_{16}H_{18}N_3SBr{\cdot}HgBr_2$	27.72	27.68				
5b	0.1 M KBr	»	»	27.67	27.68	29.5	33.1	44.8	44.1
6	1.0 N H_2SO_4 + 0.4 M KBr	Violet crystals with lustre	$(C_{16}H_{18}N_3SBr)_2HgBr_2$	18.41	18.42	31.2	29.4	59.3	58.7

* See comments in the text.

Table 2. Solubility of the addition compounds and of methylene blue in different media.

Medium	The negative logarithm of the molar concentration of methylene blue in saturated solutions of						
	$(MBCl)_3Bi_2Cl_6$ (1b)	$(MBCl)_2SbCl_3$ (2)	$MBCl \cdot HgCl_2$ (3)	$(MBCl)_2HgCl_2$ (4b)	$MBBr \cdot HgBr_2$ (5b)	$(MBBr)_2HgBr_2$ (6)	MBCl
Water	d.	d.	3.5	3.2	4.6	4.5	
0.1 M KCl	3.3	3.0	4.8	4.7	5.3	4.9	
0.1 N HCl	4.7	d.	5.1	4.7	5.2	4.9	3.1
1.0 N »	4.3	4.2	4.3	4.1	4.5	4.1	3.7
2.5 N »	3.9						2.9
5.0 N »	2.8						1.6
0.02 M $KClO_4$	5.8	5.8	5.8	5.8	5.7	5.7	5.5
0.1 M KSCN	5.7	5.7	6.0	5.8	6.1	5.7	5.6
Acetone	5.0			4.5			3.7
Isoamyl alcohol	4.4	4.0	4.6	4.5	5.0	5.2	3.3
Benzene	>7			>7			>7
Carbon tetrachloride	>7			>7			>7
Chloroform	5.7			4.9			<2.3
1,2-Dichloroethane	5.6			4.5			3.6
Ethanol	3.2			3.5			<2.1
Ether	>7			>7			>7
Ethyl acetate	>7			>7			>7
Trichloroethylene r.	>6			>6			>6

r.: A faint red colour was observed in the solutions.
d.: Decomposition of the compound.
MB: $C_{16}H_{18}N_3S$.

After this work had been finished it was noticed that Maurina and Deahl [6] recommend a precipitation of methylene blue as the perchlorate salt before a determination of the chloride content.

Determination of methylene blue

A new photometric method [7] was used for the determination of methylene blue. In strong nitric acid solution methylene blue produces a green-blue solution with absorption maximum at the wavelength 605 mμ. Contrary to methylene blue solutions the green-blue solution obeyed the Beer-Lambert law.

An accurately weighed amount of the compound to be analyzed was transferred to a 250 ml volumetric flask. 200 ml of 3.12 N nitric acid and 12.5 ml of 0.1 M silver nitrate were added and the mixture was made up to the mark with water. After 48 h the mixture was filtered, 5 ml of the filtrate were pipetted into a 250 ml volumetric flask containing 200 ml of 3.12 N nitric acid. The solution was finally made up to the mark with water.

A standard solution was prepared in the same way, starting with 25 ml of methylene blue standard solution (Gurr) instead of the addition compound. The amount of each compound was chosen so that the methylene blue concentration in the last solution should be close to 2×10^{-5} M. The extinction measurements were all made at 605 mμ using 0.500 cm glass cells.

Solubility tests

The solubility of the six different addition compounds and of methylene blue in some aqueous solutions and organic solvents (Table 2) were studied in a semiquantitative way. About 50 mg of a compound was transferred to a bottle containing 20 ml of the tested solution. The bottle was shaken at certain intervals during five days. Then the mixture was filtered and the extinction of the filtrate measured and compared with known concentration of methylene blue in the tested medium.

RESULTS AND DISCUSSION

Composition. The content (in weight per cent) of metal, halide and methylene blue in the compounds is shown in Table 1. From these data simple stoichiometric compositions are suggested for the addition compounds. As seen from the table the agreement between found and calculated percentages are satisfactory, except in some cases for the halide content. These disagreements are, however, never so great that another simple stoichiometric composition could be preferred. Some difficulties (*cf.* Lenz:[8] "Difficulty in the detection of chlorine in methylene blue") in the determination of the halide content made the results less valuable.

From Table 1 the conclusion was drawn that the preparations (1 a—6) consisted of compounds with the composition given by the formulas in the table. Passerini and Michelotti [3] reported that a violet-red compound, $C_{16}H_{18}N_3SCl.HgCl_2$ was formed in neutral solution and in solutions acidified by hydrochloric acid. According to Table 1 this formula belongs to a green compound, and the violet-red addition compound between methylene blue and mercuric chloride contained the two salts in the mole ratio 2:1. The authors mentioned above did not seem to be aware of the presence of two compounds.

A similarity seemed to exist between the compounds containing bromide and those corresponding containing chloride. Compounds 3 and 5 were both

green and compounds 4 and 6 both violet. For compounds 3 and 5 the observed content of methylene blue exhibited the greatest deviation from the calculated value. This may indicate that small amounts of compound 4 and compound 6, respectively, were formed. Contrary to methylene blue, compounds 1, 3, and 5 contain no absorbed water or water of crystallization.

Solubility. The concentrations of methylene blue in different solutions saturated with the compound tested are reported in Table 2. The negative logarithm of the methylene blue concentration is used in the table. This quantity is a inverse measure of the solubility of the compound.

The compounds were nearly insoluble in 0.02 M $KClO_4$ and 0.1 M KSCN. This may be due to the formation of less soluble salts, *e.g.* $MBClO_4$ and MBSCN. The decomposition of compounds 1 and 2 in water and of compound 2 in 0.1 N HCl is due to the protolytic reaction of bismuth and antimony ions.

The addition compounds were less soluble than methylene blue in the media tested. Methylene blue and compounds 1 and 4 were insoluble in benzene, carbon tetrachloride, ether, and ethylacetate. In trichloroethylene these three compounds all gave a faint red colour which became deep red when the solutions were heated.

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