

A Colloidal Water-soluble Double Sulphide Containing Mercury(II) and Tin(IV)

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If tin(IV), mercury(II) and sodium sulphide are present within certain concentration limits, addition of ammonium chloride yields a red precipitate, which upon washing with water dissolves to a deep red solution. Addition of ethanol to this solution again gives a red precipitate. After the precipitate is completely dried, it becomes almost black, and the compound is no longer water-soluble.

A quantitative analysis of the compound showed a somewhat varying composition, which approximated the formula Hg_2SnS_4 within 10 %.

The red aqueous solution has been the object of different investigations, which all show that a colloidal solution with negatively charged particles is involved. Sedimentation in an ultracentrifuge shows that the particle size varies. The mass of the particles lies in the range 1 300 to 40 000 atomic mass units.

X-Ray investigation of the completely dry double sulphide by the powder method does not show crystallinity.

In inorganic qualitative analysis mercury is often separated from tin, antimony, arsenic and molybdenum by precipitation of mercuric sulphide by the addition of ammonium chloride to a solution containing these metals as thio-ions. When teaching qualitative analysis one of the authors (H-B) has noticed that addition of ammonium chloride to a solution containing thiomercurate, thiostannate and sulphide ions sometimes yields a red precipitate instead of black mercuric sulphide. The red precipitate dissolves readily in water forming a deep red solution.

It is well known that separation of mercury and tin as mentioned above is incomplete. Storch¹ has remarked that mercuric sulphide is soluble to some extent in ammonium thiostannate solution, whereas it is insoluble in ammonium sulphide. He stated that a more detailed investigation would be undertaken, but it evidently has never been published. Wilm² has mentioned that mercuric sulphide can be only partly precipitated by ammonium sulphide when tetravalent tin is present. Feigl³ has observed that mercuric sulphide which is precipitated by the addition of ammonium chloride to a solution of thiomercurate and thiostannate is greatly contaminated with stannic sulphide.

QUALITATIVE EXPERIMENTS

A series of test tube experiments were carried out in order to get an impression of the colour and the amount of impure mercuric sulphide precipitated by the addition of ammonium chloride to a solution containing Sn(IV), Hg(II) and sodium sulphide. The mole ratio of tin to mercury (f), the total molar concentration of tin + mercury (c) and the added amount of ammonium chloride in g/10 ml (m) were varied. The experiments were carried out as follows:

Stock solutions of thiomercurate and thiostannate were made by dissolving mercuric chloride and potassium hexachlorostannate, respectively, in the amount of 2 M sodium sulphide just sufficient to dissolve the primarily formed sulphides, and then diluting with water to the desired concentrations of the metals. In a test tube thiostannate and thiomercurate solutions were carefully mixed so that the total volume was 10 ml; m g ammonium chloride was then added and dissolved by shaking. The progress of the precipitation was observed during the first hour, and after 24 h the colour and amount of the final precipitate and the colour of the clear supernatant solution were judged. Thirty five such experiments were carried out; the values of c were 0.1, 0.2 and 0.5, f varied from 0.4 to 5.7 and m from 0.15 to 2.00.

The results may be summarized as follows:

1. *The progress of the precipitation.* At $f \leq 1.5$ the precipitation takes place immediately upon the addition of ammonium chloride, while at $2.3 \leq f \leq 4.0$ from 2 to 50 min elapse before the precipitation starts. During this period of time the colour of the solution changes from pale yellow to orange. At $f \leq 1$ the precipitate is very dark. At $1.5 \leq f \leq 4.0$ the colour of the precipitate is first yellowish but, as the precipitation is progressing, it gradually changes to orange or orange red. At $m > 1.7$ the precipitate, however, stays yellow.

2. *The amount of the precipitate.* The amounts were only judged visually by comparing the heights of the precipitates in the test tubes after 24 h. The amount of precipitate is not much different at $c = 0.2$ and $c = 0.5$, while it is about half as much at $c = 0.1$. The amount of precipitate rapidly decreases with increasing f ; at $f = 4.5$ the amount is negligible, and at $f = 5.7$ no precipitation at all takes place even after 5 days. At $0.5 \leq m \leq 1.5$ the amount of precipitate is fairly constant, but at $m > 1.5$ it increases somewhat and at $m < 0.5$ it decreases; e.g. at $m = 0.15$ the amount of precipitate is only $1/5$ of the amount at $m = 1$.

3. *The colour of the precipitate.* The colour of the precipitate does not depend upon c , and is fairly independent of f at $1.5 \leq f \leq 4.5$. At $f \leq 1.5$ the precipitate gradually becomes darker with decreasing f , e.g. red brown at $f = 1.0$ and very dark brown at $f = 0.4$. However, the colour is strongly dependent upon m ; at $0.15 \leq m \leq 0.3$ it is dark red, at $m = 0.5$ bright red, at $m = 1.2$ orange, and at $m > 1.5$ yellow.

4. *The colour of the filtrate.* The colour of the clear supernatant solution is nearly independent of c and f and mostly depends upon m . At $0.15 \leq m \leq 0.3$ the filtrate is red, at $m = 0.7$ orange, and at $m > 1.2$ yellowish. The change of colour is accompanied by decreasing intensity of colour.

PREPARATION OF THE RED DOUBLE SULPHIDES

For the sake of analysis and other investigations several preparations were carried out. After some preliminary investigations the following method was found suitable.

Weighed amounts of potassium hexachlorostannate and mercuric chloride are each dissolved in a slight excess of 2 M sodium sulphide. The two solutions are filtered through a hardened filter paper and the flasks and the filter washed with distilled water. Then the solutions are mixed and diluted with water to 250 ml. Finally the ammonium chloride is added while stirring.

After about 20 h the precipitate formed, 0.6–8 g, is filtered off on a medium filter paper. After as much as possible of the filtrate has run off the filter, the precipitate is transferred to an Erlenmeyer flask containing 50 ml of water at 25–30°C. After complete dissolving (a few of the preparations required somewhat more than 50 ml water) 50 ml ethanol are added. This addition causes reprecipitation of the red double sulphide. After 2 h filtration is carried out and the precipitate is washed first with two 30 ml portions of 50 % ethanol in order to remove ionic impurities, then with three 30 ml portions of ethanol and lastly with three 30 ml portions of dry ether. When especially large precipitates are involved, larger volumes of washing liquid are used.

The precipitate is allowed to dry overnight and is then cautiously pulverized and put into a vacuum desiccator over potassium hydroxide pellets. Drying to constant weight requires nearly a month.

Twelve preparations of the type just described were carried out, *cf.* Table 1. Two of them, Nos. 5 and 8, failed, No. 5 because the yield was negligible, and No. 8 because the precipitate could not be quite redissolved in water for the sake of purification.

ANALYSIS OF THE PREPARED DOUBLE SULPHIDES

The percentages of mercury, tin and sulphur in the completely dried double sulphides were determined by slightly modified standard methods.

Table 1. Preparations of water-soluble double sulphides of tin(IV) and mercury(II). The total volume of sodium thiomercurate and thiostannate solution was 250 ml before addition of ammonium chloride. *c* is the total molar concentration of tin + mercury, *f* is the mole ratio tin to mercury, and *m* is the added amount of ammonium chloride in g/10 ml. The yield is given in g of the totally dried product.

No.	<i>c</i>	<i>f</i>	<i>m</i>	yield
1	0.2	1.0	0.5	5.69
2	0.2	1.5	0.5	3.60
3	0.2	2.2	0.5	1.70
4	0.2	3.0	0.5	0.61
5	0.2	4.0	0.5	nil
6	0.2	2.2	0.25	1.43
7	0.2	2.2	1.0	1.82
8	0.2	2.2	2.0	—
9	0.2	1.8	0.5	2.33
10	0.2	1.8	0.5	1.79
11	0.2	1.8	1.0	1.69
12	0.2	0.5	0.5	7.71

Determination of mercury. The double sulphide is dissolved in 2 M sodium sulphide, after which mercury and tin are separated according to the method of Hiltner and Gittel ⁴. Hydrogen peroxide is added dropwise to the sulphide solution with the result that the free sulphide ions and the sulphide in the thiostannate ions are oxidized to sulphate, and mercuric sulphide separates quantitatively. Tartrate ions are present in order to keep the tin in solution. According to our experience no greater excess of 30 % hydrogen peroxide than 0.5 ml should be added. The precipitated mercuric sulphide is filtered off on filter paper, washed and dissolved (both filter and sulphide) in conc. sulphuric acid plus nitric acid. After complete oxidation of the filter the sulphuric acid is diluted with water to twice its volume and boiled again in order to hydrolyze the nitrosyl sulphuric acid formed. After the solution is diluted with water and cooled down to below 15°C the mercury is titrated with standard thiocyanate solution. The thiocyanate solution is standardized against mercuric oxide (Merck, rubrum, p.a.). Experiments show that titration of mercury in sulphuric acid solution yields practically the same results as the usual titration in nitric acid solution. The method has been tested on known mixtures of mercury and tin with good results.

Determination of tin. The determination of tin is simply carried out by roasting the double sulphide, whereby the sulphur is oxidized to sulphur dioxide and the mercury evaporates while the tin is transformed to stannic oxide, which can be weighed. In order to determine the amount of impurities in the stannic oxide, the last compound is volatilized by heating with ammonium iodide according to Caley and Burford ⁵. The method has been tested with good results on sulphide precipitates containing known amounts of mercury and tin.

Determination of sulphur. The determination of sulphur is carried out by oxidation of the sulphide to sulphate by means of bromine, the same method as often used for sulphur determination in pyrite ⁶. The sulphate formed is precipitated with barium chloride according to Hintz and Weber ⁷. The method yields excellent results when no tin is present, but too high results with tin present (coprecipitation of tin). This difficulty can be overcome by allowing the boiling with hydrochloric acid to proceed only to near dryness so that no stannic acid is formed, and further by precipitating the barium sulphate in 0.4 M hydrochloric acid, which at the same time is 0.2 M with respect to sodium chloride.

The results of the analyses carried out are given in Tables 2a and 2b. The estimations of mercury and sulphur were carried out without complications and the results are assumed to be rather accurate. The tin estimations, however, were rather tedious and inaccurate. It appeared that complete volatilization of stannic oxide with ammonium iodide required several heatings with ammonium iodide because of the impurities in the stannic oxide. These impurities turned out to be mainly silica. This silica must come from the

Table 2a. Analysis of the prepared double sulphides. The preparation numbers refer to the nos. in Table 1. The figures marked with * are not measured but calculated from the equation: % HgS + % SnS₂ = 94.0.

Preparation No.	% Hg	% Sn	% S	% Hg + Sn + S
1	58.49	17.70	19.87	96.06
2	57.35	18.43	19.48	95.26
3	57.30	17.92	20.10	95.32
4	56.63	18.5 *	19.67	—
6	57.53	17.46	19.35	94.34
7	56.78	18.84	20.35	95.97
9	57.43	18.74	19.76	95.93
10	57.72	—	19.71	—
11	56.94	18.72	20.48	96.14
12	59.0 *	16.42	—	—

Table 2b. "% S calculated" is calculated from the found (Table 2a) Hg and Sn percentages assuming that Hg is found as HgS and Sn as SnS₂. The atomic ratios are calculated from the analysis given in Table 2a.

Preparation No.	% S calculated	Atomic ratios		Yields in the preparations	
		Sn/Hg	S/Hg	% Hg	% Sn
1	18.91	0.511	2.124	66.7	33.2
2	19.12	0.543	2.125	51.6	18.7
3	18.83	0.529	2.195	31.2	7.5
4	—	0.55	2.173	13.8	2.5
6	18.63	0.514	2.104	26.2	6.1
7	19.25	0.560	2.242	34.0	8.6
9	19.30	0.551	2.153	38.1	11.6
10	—	—	2.136	28.9	—
11	19.21	0.555	2.250	26.9	8.3
12	—	0.47	—	68.2	64.1

action of sodium sulphide solution upon the glass containers, and then be coprecipitated when precipitating the double sulphides. We assume the tin determinations to be correct within 2 % and we assume them generally to be too low. The general features shown by Tables 2a and 2b are:

a. The sum of the three principal components is somewhat less than 100 %. The sulphur percentages, which correspond to the amounts found for mercury and tin, are somewhat smaller than the experimentally found percentages. The reason for this is partly that the tin determinations are a little too low and partly a considerable impurity of ammonium sulphide. In four of the preparations ammonia was determined. The content calculated as ammonium hydrogen sulphide was between 0.8 and 1.2 %. As will be evident from investigations later mentioned, the red double sulphides are colloidal and the particles negatively charged. The negative charge is presumably caused by adsorbed sulphide ions, which in the solid double sulphide must be accompanied by positive ions, *viz.* ammonium ions. All the solid double sulphides showed a considerable content of ammonia, while no chloride and no sodium could be detected.

b. The atomic ratios show that the composition of the double sulphides is not far from SnS₂·2HgS. However, the deviations from this formula are so considerable that they can hardly be due to analytical errors, and besides the composition is not constant. The atomic ratios Sn/Hg and S/Hg seem to increase with increasing *f* (the ratio between tin and mercury concentrations in the solution used for preparation). The atomic ratios Sn/Hg and S/Hg increase with increasing *m* (quantity of ammonium chloride added when precipitating the double sulphides).

c. The yields of both tin and mercury in the precipitates rapidly decrease with increasing *f*. In all the preparations the yield of mercury is greater than the yield of tin.

PROPERTIES OF THE DRIED DOUBLE SULPHIDES

After complete drying the double sulphides are black powders, some of them with a red tinge. They are nearly insoluble in water. In order to see

whether the substances are crystalline or not, X-ray powder photographs were taken of two of the preparations. The result was entirely negative, there being no indication at all of lines on the film.

PROPERTIES OF THE RED SOLUTION

Right after precipitation the double sulphides are, as mentioned above, readily soluble in water, and even after reprecipitation with ethanol and washing they are still water-soluble. The solution is deep red and of colloidal character.

A double sulphide was prepared as before (Table 1, expt. No. 2). After the ether used for the final washing had been allowed to evaporate, the double sulphide was dissolved in 100 ml water. This solution had a content of dry double sulphide of 3.6 g (solution A).

1. *Ultracentrifuge investigation* *. The measurements were carried out in a Svedberg-type oil-turbine ultracentrifuge at a speed of 1 000 r.p.s. at 27°C. A mixture of 1 volume "solution A" and 1 volume 0.2 M sodium chloride was used. The sedimentation was followed by the Schlieren-method. The colloidal particles had sedimentation constants between 2×10^{-13} and 20×10^{-13} c.g.s. units. Assuming that the particles are spherical and introducing Stokes's law, and assuming the density of the particles in water to be the same as that measured pycnometrically on the completely dried solid, namely 4, it is found that the mass of the particles lies in the range 1 300 to 40 000 atomic mass units, and their diameter in the range 10 to 30 Å.

2. *Conductance measurements*. The conductance was measured by a commercial instrument with dipping electrodes. The specific conductance of solution A was found to be $2.20 \text{ mohms}^{-1} \text{ cm}^{-1}$. After 10 times dilution with water the specific conductance decreased to $295 \text{ } \mu\text{ohms}^{-1} \text{ cm}^{-1}$ and after 100 times dilution to $47 \text{ } \mu\text{ohms}^{-1} \text{ cm}^{-1}$. The corresponding conductance per gram-atom mercury per cm^3 is calculated to 21, 29 and $45 \text{ ohms}^{-1} \text{ cm}^2$, respectively. These values are rather high for a colloidal solution. However, the conductance is not only due to the charged colloidal particles and their "gegenions", but at least two thirds of the measured conductance is due to ionic impurities. Solution A diluted 10 times with water was dialysed 5 days; hereby the conductance decreased from 295 to $70 \text{ } \mu\text{ohms}^{-1} \text{ cm}^{-1}$.

3. *Dialysis*. The red constituent of the solution turned out not to be able to penetrate an ordinary dialysis membrane, (Visking cellulose casing), which fact showed that a colloidal solution was involved.

4. *Coagulation by the addition of electrolytes*. In the recorded experiments solution A was used 10 times diluted with water. To 4 ml of this solution was added 1 ml of a solution of an electrolyte. In Table 3 are recorded the electrolyte concentrations which cause half of the red double sulphide to coagulate. It is seen that the ratio of the concentrations of tri-, bi-, and uni-valent cations is 1:3:600. Magnesium does not seem, for some obscure reason, to fit into the scheme. The coagulating effect of electrolytes shows that the red double

* The authors are much indebted to the Research Laboratory of the Carlsberg Breweries, Copenhagen, for running the sedimentation measurements.

Table 3. Coagulation of the red water-soluble double sulphide by addition of different electrolytes. The given concentrations are the concentrations of electrolyte which are able to coagulate half of the red double sulphide.

Electrolyte	Molar conc.
NaCl	0.6
KCl	0.8
NaNO ₃	0.8
MgCl ₂	0.03
ZnCl ₂	0.004
BaCl ₂	0.003
MgSO ₄	0.5
ZnSO ₄	0.003
AlCl ₃	0.0009
CeCl ₃	0.0015

sulphide is a negatively charged colloid. The negative charge of the colloid was confirmed by paper electrophoresis.

5. *The action of acids and bases.* Diluted acid coagulated the colloidal particles. Diluted sodium carbonate solution had no influence on the colloidal solution. On the other hand a black precipitate of mercuric sulphide was formed and the supernatant liquid became colourless when the colloidal solution was made 0.1 M with respect to sodium hydroxide.

6. *Absorption spectrum in visible and ultraviolet light.* The absorption spectrum of solution A was measured by means of a recording spectrophotometer (Cary Model 11). In the range 800—700 m μ the absorption coefficient was very small (order of magnitude 0.1) but with decreasing wavelength it increased continuously in the range down to 200 m μ , *e.g.*, it is 3 at 650 m μ and 530 at 400 m μ . The laws of Lambert and Beer were found to be valid. The absorption spectrum is consistent with assuming the solution to be colloidal.

DISCUSSION

The investigated phenomena are consistent with many complications met when precipitating sulphides.

Some of the properties of the colloidal double sulphide can be explained by assuming a mixture of mercuric and stannic sulphide, *e.g.* the behaviour upon dry heating and the action of strong base, whereas other properties indicate a chemical compound, *e.g.* the colour of the substance and the pronounced tendency to form colloidal solutions.

The X-ray powder photographs of the dried double sulphide show that it is either built up of small colloidal crystallites or has a random or almost random structure.

The precipitation of the colloidal double sulphide proceeds rather slowly, and only part of the mercury is precipitated. The solution changes colour before the precipitation has become visible; this indicates that the first stage involves the mercury becoming bound in some way to the tin, possibly by formation of polynuclear sulphide complexes containing sulphide ions in excess to give a negative charge. These polynuclear complexes grow until they reach colloidal dimensions, and may then be precipitated by electrolytes.

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