CHAPTER XII

COLLOIDAL SULFUR

The clouding of natural sulfur waters on exposure to the air has been known for a long time. This clouding is due to the formation of colloidal sulfur as a result of the oxidation of hydrogen sulfide by the oxygen of the air. The reaction was referred to by many writers in the latter part of the eighteenth and the early nineteenth centuries, among them being Scheele, Bergman, Le Veillard, Berthollet, Berzelius, and Dobereiner. Thus, in 1808, Berzelius says: 1 "It [H₂S] dissolves in water abundantly; ... if the water contains atmospheric air, some part of the air is destroyed, the hydrogen being oxidized to water, and the sulfur set free, whereupon the water takes on a milky appearance."

FORMATION OF SULFUR SOLS

Oxidation Processes

Oxidation of Hydrogen Sulfide.—Near the middle of the last century, the milky liquid formed by passing hydrogen sulfide into an aqueous solution of sulfur dioxide was investigated in some detail by Wackenroder 2 and by Selmi. 3 At this time the term colloid had not been invented, but Selmi, who recognized quite clearly many of the differences between the milky dispersion and molecular solutions, called the system a pseudo solution.

The reaction between sulfur dioxide and hydrogen sulfide may be represented by the equation:

\[ 2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 3\text{S} + 2\text{H}_2\text{O} \] (1)

The reaction is more complicated than this, however, since it has been found that the so-called Wackenroder's solution contains, in addition to colloidal sulfur, all of the thionic acids from dithionic to

2 Arch. d. Pharm., 47, 272; 48, 140 (1846).
3 Annali del Majochi, 15, 88, 212, 235 (1844); Sobrero and Selmi: Ann. chim. (3) 27, 320 (1850); Ibid. Gazz. 48, 145 (1859).
hexathionic as well as some sulfuric acid. Thus pentathionic and hexathionic acids are formed in accord with the equations:

$$5\text{H}_2\text{S} + 10\text{H}_2\text{SO}_3 \rightarrow 3\text{H}_2\text{S}_8\text{O}_6 + 12\text{H}_2\text{O} \quad (2)$$

$$3\text{H}_2\text{S} + 4\text{H}_2\text{SO}_3 \rightarrow \text{H}_2\text{S}_6\text{O}_6 + 6\text{H}_2\text{O} + \text{S} \quad (3)$$

Odén has shown that the amount of colloidal sulfur produced by the reaction and the degree of dispersity depend on the sulfur dioxide concentration, as shown in Table L. At the higher dilution, 0.225 $N$,

<table>
<thead>
<tr>
<th>SO$_2$ normality</th>
<th>Non-colloidal S in grams</th>
<th>Total</th>
<th>Colloidal S in grams</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Amicroscopic particles</td>
</tr>
<tr>
<td>1.8</td>
<td>0.01</td>
<td>8.33</td>
<td>0.91</td>
</tr>
<tr>
<td>1.44</td>
<td>0.29</td>
<td>9.89</td>
<td>0.16</td>
</tr>
<tr>
<td>0.9</td>
<td>0.40</td>
<td>13.02</td>
<td>0.05</td>
</tr>
<tr>
<td>0.45</td>
<td>14.91</td>
<td>1.94</td>
<td>Traces</td>
</tr>
<tr>
<td>0.225</td>
<td>16.98</td>
<td>Traces</td>
<td>1.94</td>
</tr>
</tbody>
</table>

the yield of sulfur approaches the value 17.3, which is the theoretical value for the simple reaction (1) above; but under these conditions the sulfur is chiefly non-colloidal. With higher concentrations of sulfur dioxide, less sulfur is formed but more of the precipitated particles are colloidal. Moreover, the higher the concentration, the greater the relative amount of amicroscopic particles formed in accord with von Weimarn's theory (see page 1). Another factor in determining the degree of dispersion of the particles is the amount of polythionic acids formed. At the higher concentrations where considerable pentathionic and hexathionic acids result in accord with Equations (2) and (3), most of the sulfur is colloidal, whereas at low concentrations where Equation (1) takes place almost quantitatively, little or no colloidal sulfur is produced.

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5 "Der kolloide Schwefel," 37 (1913).
The sol, which is frequently called Selmi’s sol, may be purified by coagulating the particles with sodium chloride, centrifuging and discarding the supernatant solution, repelting in water, and dialyzing to remove the excess sodium chloride.

The reversibility of the sol is said to be increased by carrying out the reaction around \( 0^\circ \) in the presence of protecting colloids.\(^7\) A finely divided bluish sulfur results on allowing hydrogen sulfide and sulfur dioxide to react above the water in an aspirator bottle.\(^8\)

Sols of sulfur in benzoil, toluol, xylol, kerosene, acetone, and ethyl acetate can be prepared by conducting sulfur dioxide and hydrogen sulfide simultaneously into the respective liquids.\(^9\) A benzol sol formed in this way and containing over 1.5% sulfur has a deep yellow color and is stable indefinitely. Neither electrolytes nor organic non-electrolytes which dissolve in benzol have an appreciable coagulating action. The cause of the marked stability should be investigated.

The sols in carbon bisulfide, benzol, and carbon tetrachloride are orange at first but turn yellow on standing and the sulfur settles out. If this precipitate is filtered and dried out of contact with air, it is repelthesized by shaking with water, glycerin, and fats.\(^10\)

**Action of Acids on Sodium Thiosulfate.**—Sulfur sols are conveniently formed by the action of hydrochloric acid (Engel\(^11\)) or sulfuric acid (Raffo\(^12\)) on sodium thiosulfate. Since sulfuric acid is most commonly employed the resulting sol is called Raffo’s sol. The equations for a part of the reactions involved are as follows:

\[
3\text{Na}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{SO}_4 \rightarrow 3\text{H}_2\text{S}_2\text{O}_3 + 3\text{Na}_2\text{SO}_4 \quad (1)
\]

\[
\text{H}_2\text{S}_2\text{O}_3 \rightarrow \text{S} + \text{SO}_2 + \text{H}_2\text{O} \quad (2)
\]

\[
2\text{H}_2\text{S}_2\text{O}_3 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{S} + 2\text{H}_2\text{SO}_4 \quad (3)
\]

\[
2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 3\text{S} + 2\text{H}_2\text{O} \quad (4)
\]

\[
3\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{SO}_4 \rightarrow 4\text{S} + 3\text{Na}_2\text{SO}_4 + \text{H}_2\text{O}
\]

To the extent that Equation (2) takes place, sulfur is formed by simple decomposition; but for the most part, it results from an oxida-

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\(^7\) Vogel: Brit. Pats., 202,613; 210,363 (1923).


\(^10\) Sarason: German Pat., 262,467 (1913).

tion process. In addition to sulfur, pentathionic acid\textsuperscript{13} is formed in appreciable amounts in accord with the equation:

\[ 5\text{H}_2\text{S}_2\text{O}_3 \rightarrow 2\text{H}_2\text{S}_5\text{O}_6 + 3\text{H}_2\text{O} \]  

(5)

Odén\textsuperscript{14} worked out the most favorable conditions for sol formation by Raffo's method and found the best results on adding concentrated sulfuric acid slowly to a cold concentrated solution of sodium thiosulfate. The impure dispersion must be coagulated with sodium chloride and repeptized repeatedly to remove the excess sulfuric acid, and finally dialyzed. The time of dialysis may be shortened appreciably by freezing the sol, which gives a reversible precipitate that is almost free from salt. This procedure may be used to advantage also with the Selmi sol.

The stability of sulfur sols is said to be increased to some extent if the sulfur comes out in the presence of protective agents such as gallic acids,\textsuperscript{15} gelatin,\textsuperscript{16} gluten,\textsuperscript{17} and glycerin.\textsuperscript{18} Odén showed, however, that gelatin possesses no such specific protective action on sulfur as it does on colloidal gold. Indeed, Ghosh and Dhar\textsuperscript{19} found that very small amounts of gelatin sensitize sulfur sols toward electrolytes and larger amounts cause coagulation.

\textbf{Sols with Particles of Uniform Size.}—The sols prepared by the methods of both Selmi and Raffo contain particles of widely varying size. Since the coagulum formed on adding sodium chloride is completely reversible, Odén\textsuperscript{20} worked out a method of fractional coagulation which makes it possible to divide the polydisperse sols into fractions containing particles of nearly uniform size. The method is based on the fact that the coarser the particles, the lower the concentration of sodium chloride required for coagulation. By adding gradually increasing concentrations of salt and centrifuging, a series of reversible precipitates, each containing particles of similar size, is obtained. The ultramicroscopic characteristics of a series of sols prepared in this way are given in Table LI.

\textsuperscript{13} Chancel and Diacon: Compt. rend., 56, 710 (1863); Debus: J. Chem. Soc., 53, 278 (1888).
\textsuperscript{14} "Der kolloide Schwefel," 45 (1913).
\textsuperscript{15} German Pat., 381,519 (1923).
\textsuperscript{16} Lobry de Bruyn: Rec. trav. chim., 19, 236 (1900).
\textsuperscript{17} Kelber and Schwarz: German Pat., 245,621 (1912).
\textsuperscript{18} Sarason: German Pats., 216,824–5 (1907); 262,467 (1913).
\textsuperscript{19} Koloid-Z., 44, 218 (1928); Bhatia, Ghosh, and Dhar: J. Indian Chem. Soc., 6,
TABLE LI

CHARACTERISTICS OF MONODISPERSE SULFUR SOLS

<table>
<thead>
<tr>
<th>NaCl in normality</th>
<th>Ultramicroscopic characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sol not coagulated</td>
<td>Sol coagulated</td>
</tr>
<tr>
<td>0.25</td>
<td>$\infty$</td>
</tr>
<tr>
<td>0.20</td>
<td>0.25</td>
</tr>
<tr>
<td>0.16</td>
<td>0.20</td>
</tr>
<tr>
<td>0.13</td>
<td>0.16</td>
</tr>
<tr>
<td>0.10</td>
<td>0.13</td>
</tr>
<tr>
<td>0.07</td>
<td>0.10</td>
</tr>
<tr>
<td>0.00</td>
<td>0.07</td>
</tr>
</tbody>
</table>

**Hydrolysis**

Sulfur monochloride is acted on by water to give sulfur and thiosulfuric acid. Since the latter yields pentathionic acid as previously shown, Freundlich and Scholz$^{21}$ write the gross equation for the reaction as follows:

$$5S_2Cl_2 + 6H_2O \rightarrow 5S + H_2S_6O_6 + 10HCl$$

These investigators prepared a sulfur sol similar in properties to Selmi's and Raffo's sols by vigorous shaking of 10 cc of sulfur monochloride with 70 cc of water at 35°. After a short time a strongly exothermic reaction takes place with the evolution of sulfur dioxide, and the vessel must be immersed in ice water to slow up the process. When the evolution of gas ceases, the resulting sol is purified by coagulating with sodium chloride, centrifuging, and repeptizing as in the case of Selmi's sol. The preparation will be referred to later as Freundlich's sol.

**Replacement of Solvent**

The general method of sol formation, which consists in pouring a solution of the element into a liquid in which the element is insoluble, may be used to advantage in preparing sulfur sols.

**Sulfur in Hydrazine by Water.**—If a solution of sulfur in hydrazine is poured into an excess of water, the sulfur comes out on standing in