METHYL SALICYLATE II.[1]—SOLUBILITY IN WATER AT 30°.

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In the studies of the hydrolysis of methyl salicylate, the results of which will be published later, it became advisable to determine with some degree of accuracy, the solubility of the ester in water and in some other solutions in which the rate of hydrolysis was being measured.

No accurate measurements have been found in the literature. Cahours[2] records that the oil is scarcely soluble in water. The United States Pharmacopœia[3] and the National Standard Dispensatory[4] say that it is sparingly soluble and the Chemiker-Kalender[5] "wenig löslich;" statements evidently originating from the observations of Cahours made sixty-five years ago.

The method of analysis employed is essentially the same as that described in the first paper. The solution in which the methyl salicylate is to be determined is filtered to remove any undissolved ester (the first few drops passing through the filter being discarded), made strongly alkaline with sodium hydrogen carbonate to unite with and hold back any free salicylic acid, extracted repeatedly, not less than three times, with chloroform and the chloroform extracts run into about 20 cubic centimeters of a 10 per cent solution of sodium hydroxide and saponified in a steam bath. After evaporation of the chloroform the salicylic acid is extracted and made to a definite volume with water for the color comparisons.

When the comparison is made with standard solutions prepared with salicylic acid, the color shades are different, owing to the formation of small quantities of other phenolic compounds besides salicylic acid in the hydrolysis of the ester, and are quite difficult to match in the wedge colorimeter. Some eyes read the percentage very much too low, while

[1] The first article on the occurrence and determination of salicylic acid in methyl salicylate, the separation and determination of the two substances in foods and drugs, and the hydrolysis of the ester with sodium carbonate and sodium hydroxide appeared in *This Journal, Sec. A.* (1908), 3, 101, and *J. Am. Chem. Soc.* (1908), 30, 1465.

[2] *Ann. d. Chem. u. Pharm.* (1843), 48, 61.

[3] 8th ed. (1900), 290.

[4] (1905), 970.

[5] (1907), 1, 104.

others have the opposite tendency. Very satisfactory standards are prepared by dissolving a weighed quantity of pure methyl salicylate in chloroform and carrying through the saponification in the same manner as the determinations. Standards, representing from 1 to 2 milligrams of methyl salicylate in 50 cubic centimeters of solution, have been found to be most satisfactory for comparison with the wedge colorimeter.

The solutions for analysis were prepared by agitating a large excess of pure methyl salicylate in water varying in purity from that of the usual laboratory distilled product to a conductivity of 2.8×10^{-6} at 30°.[6] As the rate of hydrolysis of the ester in $\frac{N}{10}$ sulphuric acid is under investigation, the solubility in this strength of acid has been determined from time to time as the hydrolysis proceeds.

In the following tables, No. is the number of the determinations, T is the time expressed in hours during which the solutions were agitated, S is the quantity of substance used in the determination, expressed in cubic centimeters, and Q is the methyl salicylate found in solution and expressed as grams of solute in 100 cubic centimeters of solvent.

TABLE I.—*Solubility of methyl salicylate in water (temperature, 30°).*

No.	T	S	Q
1	18	5	0.063
2	66	10	.069
3	139	10	.076
4	354	10	.076
5	834	10	.071
6	978	5	.074
7	2,160	5	.093
8	336	5	.074

Determinations Nos. 1 to 6, inclusive, were made upon different portions of the same solution, prepared by constantly agitating in a bottle 10 cubic centimeters of methyl salicylate and 500 cubic centimeters distilled water at 30°±1°. No. 7 is the analysis of a mixture of 15 cubic centimeters of distilled water and 0.5 cubic centimeter of methyl salicylate which had been agitated in a sealed glass tube for three months, at temperatures varying from 30° to 100°. The system had approached an equilibrium and the amount of methyl salicylate hydrolized was found to be 0.0125 gram.[7] No. 8 is the analysis of a mixture of 10

[6] In standardizing cells at 30°, I have used the temperature coefficients found by Jones and West, *Am. Chem. Jour.* (1905), 34, 381.

[7] This determination is not to be taken as an accurate measure of the equilibrium or the rate of hydrolysis for the reason that the action of the solutions on the glass was found to be considerable. A portion of the salicylic acid was found to be present in the form of the sodium salt.

cubic centimeters of water, conductivity 2.8×10^{-6} at 30°, and 0.6 cubic centimeter of methyl salicylate which was agitated in a sealed tube at $30° \pm 1°$. This determination is probably as reliable as any that have been made and represents a fairly accurate average. Electrodes were sealed into this cell and measurements of the conductivity of the aqueous phase showed that it had changed but little during the last seven days of the ten days' agitation.

TABLE II.—*Solubility of methyl salicylate in $\frac{N}{10}$ sulphuric acid solution (temperature, 30°).*

No.	T	S	Q
1	66	10	0.077
2	139	10	.077
3	354	10	.076
4	978	5	.078

It is to be expected that the solvents will show a constantly increasing capacity for dissolving the ester as the hydrolysis proceeds, owing to the slowly increasing concentration of the methyl alcohol, one of the products of the hydrolysis. The rate of the increase in the concentration of the ester is very slow as shown from the tube of distilled water which had been agitated for three months with the solute. The concentration of the methyl salicylate had increased to 0.093, and from the determination of the salicylic acid the concentration of the methyl alcohol in the aqueous solution was found to be approximately 0.02 gram per 100 cubic centimeters. Since the rate of hydrolysis in acid solutions is more rapid than in water, it is probable that the increase in the concentration of the ester will be more rapid in the former than in the latter.

SUMMARY.

The solubilities of methyl salicylate in pure water and in $\frac{N}{10}$ sulphuric acid solution at 30° have been determined. The average of a number of determinations is 0.074 gram per 100 cubic centimeters for the former solvent and 0.077 for the latter.

Slight improvements in the colorimetric method for determining methyl salicylate as given in the first paper are described.