SOME PHYSICAL CONSTANTS OF ACETYLSALICYLIC ACID.

BY J. L. HAYMAN, L. R. WAGENER, AND E. F. HOLDEN.

HISTORICAL.

The literature contains many articles upon the melting point of acetylsalicylic acid in which the figure of this physical property is given as low as 118° C. and as high as 139° C. The abstract of the U. S. P. X as published December 1923 THIS JOURNAL[1] states that the melting point of acetylsalicylic acid "when determined in a bath preheated to 120° C. is not below 132° C.," and "that it should contain not less than 99.5 per cent of absolute acetylsalicylic acid." "New and Nonofficial Remedies," 1923, states that it "melts between 130° and 133° C., according to the U. S. P. method, modified by first heating the bath to 120° C. before immersing the melting point tube in the bath."

Strange as it may seem, of all the articles published upon the subject, comparatively few describe the method used in determining the melting point. Several factors are involved in taking the melting point of acetylsalicylic acid, a few of which are: (1) manner of approaching the melting point, (2) temperature of bath upon immersing melting point tube, (3) use of one or two thermometers (one used as auxiliary), (4) employing stirring device for bath, etc., any one of which may alter the final results. Obviously various methods of approach have been employed and this fact alone no doubt accounts for some of the differences obtained in the melting point of acetylsalicylic acid. It is a factor that cannot be overlooked, especially in a substance like acetylsalicylic acid which apparently melts with some decomposition. Since a substance melting with slight decomposition exhibits no sharp melting point, there is a personal error introduced as to what might be considered the correct melting point.

Francois[2] believes that the exact melting point can be determined by using an oil or paraffin bath, employing two thermometers, one inserted in the bath and the oil raised one degree per minute until a temperature of 125° C. is reached, at which time the second thermometer bearing the melting point tube is immersed, and the determination from this point occupying not more than 5 minutes. By this method he obtained 132° C. as the true melting point of acetylsalicylic acid.

Perhaps the best method that has been devised for the determination of the melting point of acetylsalicylic acid is that described by Dahm,[3] in which he uses an oil-bath equipped with a mechanical stirring device, heating the bath to 130° C. before inserting the melting point tube, obtaining by this method a melting point of 133–135° C. (corrected).[4] Since the work of Emery and Wright[5] shows that a depression of 1 degree is made for every 5 minutes heating just below the melting point, Dahm preheats the bath to 130° C. before immersing the melting point tube.

In redetermining the melting point of the acetylsalicylic acid on which Andrews and Herron[6] reported a melting point of 139° C., Leech[7] found it to be 132–132.5°

[1] J. A. PH. A., 12, 102–3 (1923).
[2] *J. Pharm. Chim.*, 15, 213 (1917).
[3] *J. Ind. Eng. Chem.*, 11, 29 (1919).
[4] See U. S. P.
[5] Bureau of Chem., *Dept. of Agr. Bulletin* 162.
[6] *Amer. Drug.*, 67, 85 (1919).
[7] *Reports Chem.*, "Lab. Amer. Med. Assoc.," 12, 63 (1919).

C. when the bath was preheated to 120° C. but on the other hand a melting point of 134.5–135° C. when the bath was preheated to 130° C., confirming the work of Dahm and of Emery and Wright.

There seems to be quite a diversity of opinion as to what really happens at the melting point of acetylsalicylic acid. Tsakalotos[1] claims that 125° C. or even lower is more nearly the correct melting point and that the variation is due to the salicylo-salicylic acid formed by the partial decomposition of the acetylsalicylic acid at the melting point with loss of AcOH. In a more recent paper, Paolini[2] claims that the products of decomposition are AcOH, salicylic acid and a polymolecular salicylide $(C_6H_4CO)_n$.

Capelli[3] in his extensive work upon acetylsalicylic acid while determining the most suitable solvents for crystallization found that this substance when recrystallized from various organic solvents, showed different melting points. In a later paper[4] he ascribes the variation in melting point of acetylsalicylic acid to the water content and not to the presence of any salicylic acid which might be present or formed during melting. The absorbed water supposedly causes partial saponification.

Due to the fact that there is such a diversity of opinion regarding the melting point of acetylsalicylic acid, the apparent melting point of standard commercial samples was determined according to the U. S. P. as modified according to the New and Nonofficial Remedies, to ascertain whether or not we are dealing with a true melting point, and if not, what the products of decomposition may be.

Since, according to Capelli, there is a difference in the melting point of acetylsalicylic acid when recrystallized from various solvents, it was thought expedient to recrystallize some of the standard commercial samples from the various solvents and by studying the crystal forms and optical properties, determine whether or not the crystals obtained were similar.

EXPERIMENTAL.

Six standard commercial samples of acetylsalicylic acid were tested for salicylic acid, in accordance with the "New and Nonofficial Remedies," 1923, as follows:

> "If to a solution of 0.1 Gm. of acetylsalicylic acid in 1 cc. of alcohol, 48 cc. of water is added and then 1 cc. of diluted ferric chloride solution (1 volume of ferric chloride solution to 100 volumes of water), no greater violet coloration will be produced within two minutes than is produced in a parallel test using 1 cc. of a standard solution (0.116 Gm. sodium salicylate in 1 liter) in place of the acetylsalicylic acid."

with results as given in Table I. Table II shows the results of obtaining the melting point, congealing, second melting point, congealing, etc. Table III gives the melting points of six commercial samples of acetylsalicylic acid. Table IV shows the melting points of acetylsalicylic acid recrystallized from organic sol-

[1] *J. Pharm. Chim.*, 14, 174 (1916).
[2] *Giorn. Chim. Ind. Applicata*, 3, 403–5 (1921).
[3] *Giorn. Chim. Ind. Applicata*, 6 (1920).
[4] *Ibid.*, 8 (1920).

vents. The results shown in the tables are typical results from a series of determinations.

TABLE I.—COLOR REACTION.

Sample.	Result.
1	Same as standard
2	More pronounced
3	Less pronounced
4	Less pronounced
5	Less pronounced
6	Same as standard

TABLE II.—MELTING POINT ° C.

First	132.5
Second	128.0
Third	126.5

TABLE III.

Sample	Melting point (corrected)*.	Purity.
1	134.0° C.	99.82
2	129.0	99.43
3	133.5	99.80
4	133.0	99.82
5	134.0	99.88
6	134.0	99.84

* See U. S. P.

TABLE IV.

Original m. p.	Solvent.	Melting point.
134.8° C.	Chloroform	134.5° C.
134.8	Benzene	134.3
134.8	Carbon Tetrachloride	133.0
134.8	Acetone	135.8
134.8	Alcohol	135.0

MICROSCOPIC EXAMINATION OF THE MATERIAL CRYSTALLIZED FROM ORGANIC SOLVENTS.

BY EDWARD F. HOLDEN.*

Since there was found to be a slight variation in the melting point of crystals deposited from different organic solvents, as shown in Table IV, a microscopic examination of the crystals was thought advisable. This would determine whether the various crystals are actually identical, or whether the small variation in melting points is due to slight differences in composition. The microscopic examination showed that crystals from all five solvents, chloroform, benzene, carbon tetrachloride, acetone, and alcohol, respectively, were crystallographically and optically identical. They had the following properties:

FORM.

Lath-shaped or tabular crystals, persistently lying on a prominent pinacoid face, designated hereafter as *a*. A few crystals rest on another pinacoidal face, approximately perpendicular to *a*, which will be called *b*. Domes lying in the zone *a* have an interfacial angle very close to 60°. Other less frequently noted faces were: (1) the basal pinacoid at *ca*.89° to the edge between *b* and *a;* (2) another dome in the zone of *a;* and (3) a prism form with two faces. The substance is apparently triclinic, with the axes intersecting approximately at right angles. There are good cleavages parallel to *a* and *b*. Crushed fragments are very flexible shreddy fibers. The figure below shows some of the more common outlines observed under the microscope.

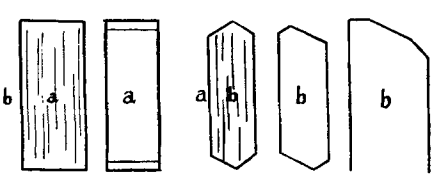

Fig. 1.

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OPTICAL PROPERTIES OF CRYSTALS FROM DIFFERENT SOLVENTS.

The crystals are colorless.

Indices (for yellow light): α 1.505, β 1.645, γ 1.655, all $\pm$.005. n perpendicular to the laths lying on a = *ca.* 1.565. The double refraction, 0.15, is quite high.

Orientation (Fig. 2). All fragments have apparently parallel extinction, the extinction angle not exceeding 3°. Elongation = Z. X and Y are perpendicular to the elongation and inclined about equally to the prominent face a. α and β are rarely observed, but can be noted on a few of the crushed fibers. The laths generally show γ = 1.655, parallel to their elongation, and n = 1.565, perpendicular to the elongation. The optic axial plane is parallel to the elongation. *Interference Figures:* Laths lying on either a or b show an apparently uniaxial figure, with the optic axis so much inclined as to be entirely out of the field. However, the biaxial character of the figure is shown on very thin laths by the eccentricity of the curves. Fragments showing β and γ give the true biaxial figure, being perpendicular to Bx_a. The optical character is negative, with $2V$ small, and distinct dispersion $\rho < v$.

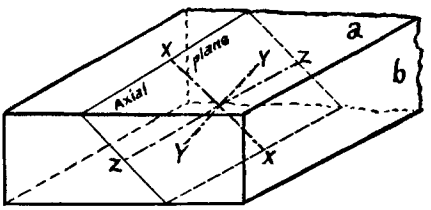

Fig. 2.—Optical orientation.

The assay was carried out according to the directions given in the abstract of the U. S. P. X as follows: "Weigh accurately about 1.5 grams previously dried 3 hours over sulphuric acid, add 50 cc. of $N/2$ NaOH, boil gently for ten minutes, then titrate the excess alkali with $N/2$ H_2SO_4, using 3 drops phenolphthalein T. S. indicator. Each cc. of $N/2$ NaOH corresponds to 0.045027 gram absolute acetylsalicylic acid," modified by using $N/10$ acid instead of $N/2$. The weaker acid was found to give more consistent results, since one drop of $N/2$ alkali introduced quite an appreciable error when dealing with highly pure acetylsalicylic acid. In using the weaker solution the chances for error in this particular case are one-fifth that of the stronger alkali.

DISCUSSION.

It is a well-known fact that with few exceptions, a substance upon melting and congealing should remelt at the same temperature providing decomposition does not take place. With acetylsalicylic acid a gradual decline was found in the melting point as shown in Table I, indicating that decomposition does take place at the melting point, although at the present time the decomposition products have not been conclusively determined. (A later paper may throw more light upon this subject.)

The fact that so many investigators have obtained such varied melting points of acetylsalicylic acid and have not in general stated methods used in obtaining this melting point, would indicate that it is essential to describe the method used in reporting results. This is shown very clearly in the work of Leech in obtaining a difference of from 2 to 2.5 degrees depending upon the temperature of the bath in preheating before immersion of the melting point tube. In determining the melting point of the six commercial samples of acetylsalicylic acid, the U. S. P. X

(abstract) method was followed using the correction of the general directions for melting points. The method gave consistent results in a number of determinations. As can be seen from Tables I and II all samples conform to the standards set by the U. S. P. X (abstract) and "New and Nonofficial Remedies" with the exception of sample 2.

In recrystallizing the acid from chloroform, benzene, carbon tetrachloride, acetone, and alcohol, respectively, it was found that the melting point of the crystals from the various solvents did vary which seems to show that the apparent melting point is not a true melting point. The crystals obtained from chloroform, benzene, and carbon tetrachloride, were small, white, well-defined needle-like crystals, while those from acetone and alcohol formed large, beautiful tabular crystals, many of which were 10 mm. in length. However, the study of their optical properties showed that the crystals from all five solvents were identical in every respect, any difference in appearance of the powders being due to the variation in crystal size which depended upon the rate of crystallization from the solvent.

SUMMARY.

1. Acetylsalicylic acid varies in melting point when crystallized from various solvents.

2. The crystals obtained from various solvents are identical in optical properties and crystal form.

3. Commercial acetylsalicylic acid has a melting point of about 133–134° C. corrected, determined as per U. S. P. X (abstract) method.

4. In reporting melting points of acetylsalicylic acid it is necessary to give methods used.

5. The temperature at which acetylsalicylic acid melts is apparently not a true melting point.

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SOME CRITICAL POINTS OF EMULSIFICATION IN OIL-SOAP EMULSIONS.*[1]

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The following is a continuation of previous work[2] on the emulsification of fixed oils in which the soap as the emulsifying agent is formed simultaneously with the emulsion.

For the determination of the critical points of emulsification in this series we have selected neutral cottonseed (Wesson) oil, to which we have added various percentages of sodium and potassium hydroxides, sodium and potassium carbonates and sodium silicate required to neutralize or saponify the oleic acid added.

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* Scientific Section, A. PH. A., Buffalo meeting, 1924.

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[2] Preliminary report on the Effect of Fatty Acids on Liniments and Emulsions, JOUR. A. PH. A., May, 1924, p. 433.