by opening *g* and blowing in at *f*. A fresh supply of water is then added, and the process continued until the extraction is completed.

The flasks are heated on a water-bath, thus having the advantage of reproducing the conditions as they exist in commercial processes.

The suction is secured by means of a filter-pump, and can be regulated so that the solvent passes over the material drop-wise. The time required for the liquid to pass from *b* to *a* in this manner is about fifteen minutes, thus necessitating a minimum amount of attention. The period of extraction is much less than by means of the Soxhlet or other methods in common use, and obviates the danger of decomposition in the tannic acid. It will be seen also that the apparatus is applicable to any form of extraction, and the temperature may be regulated to suit the various conditions.

A REAGENT IN THE CHEMISTRY OF FATS.[1]

BY E. TWITCHELL.

Received December 20, 1905.

(FIRST PAPER.)

IN A previous paper[2] I described a new series of sulphonic acids of the stearic radical combined with various aromatic radicals. These compounds are stable at 100° C. and act as catalytic agents in causing the hydrolysis of fats. At 100° C. less than 1 per cent. of naphthalenestearosulphonic acid added to a mixture of a fat with an excess of water will cause an almost complete separation of the glycerol in eight to ten hours. Of course a continual mixing of the fat and water, as by boiling, is necessary.

Other sulphonic acids containing a higher fatty radical (acid or hydrocarbon) have the power of decomposing fat and water into fatty acid and glycerol at moderate temperatures, but the fatty-aromatic sulphonic acids above referred to are prepared more easily and with better yields. They are therefore used exclusively in my process of separating glycerol from fats on a large scale.

Stearosulphuric acid, prepared by treating oleic acid with a moderate excess of sulphonic acid, has most of the properties

[1] Read before the Cincinnati Section of the American Chemical Society, December 13, 1905.

[2] This Journal, **22**, 22.

of the above sulphonic acids, but it gradually decomposes at ordinary temperatures and quickly on heating to 100° C., and so cannot be used for the hydrolysis of fats.

The special catalytic action of these sulphonic acids, or "sulpho-fatty acids" can be explained as follows: They are soluble in water and their aqueous solutions dissolve fatty bodies, acting like soap solutions. At the same time they are acids which are electrolytically dissociated to a high degree. Therefore, on mixing a glyceride with water and adding a little sulpho-fatty acid, some of the fat will go into solution in the water, and this water will contain hydrogen ions due to the electrolytic decomposition of the sulpho-fatty acid. An ester dissolved in water is rapidly dissociated in the presence of hydrogen ions which can be supplied by adding to the solution a small quantity of a strong mineral acid. A glyceride of a higher fatty acid, being insoluble in water, can not be acted on in this way, but when it is made soluble by the sulpho-fatty acid it behaves just as any soluble ester. The following observations prove this. A soluble glyceride such as triacetin, is rapidly hydrolyzed when boiled with water containing a few drops of a strong mineral acid, while an insoluble glyceride, such as triolein, is not appreciably hydrolyzed at 100°, even when large quantities of strong mineral acids are added to the water (Lewkowitsch has shown that if a very strong solution of hydrochloric acid, sp. gr. 1.16, is employed hydrolysis will take place at a moderate speed, but with this extreme concentration there is probably some other cause for the hydrolysis than the mere presence of hydrogen ions), but on adding a sulpho-fatty acid, thus making the triolein soluble in water, the hydrogen ions become as active as they are with triacetin.

A comparison of the hydrolyzing power of naphthalenestearosulphonic acid and of hydrochloric acid on a soluble glyceride, triacetin, is given in the following table. A half normal aqueous solution of triacetin (8.63 per cent.) was boiled in a flask with a reversed condenser, in one case alone, then with enough hydrochloric acid added to make the solution $^1/_{75}$ normal hydrochloric acid, then with $^1/_{75}$ normal naphthalenestearosulphonic acid. Small measured quantities of the solution were drawn from the flask at intervals and the acetic acid liberated was titrated. The results are expressed in percentages of a complete decomposition.

Time.	Decomposition in H_2O alone. Per cent.	Decomposition in $n/75$ HCl. Per cent.	Decomposition in $n/75$ $C_{10}H_6SO_3HC_{18}H_{35}O_2$. Per cent.
Half hour	.....	31.85	35.02
One hour	0.80	54.12	59.93
One and a half hours	.....	69.64	.....
Two hours	2.24	80.69	83.21
Two and a half hours	.....	.....	.....
Three hours	.....	92.41	92.06
Three and a half hours	2.53	.....	.....
Four hours	.....	98.02	94.59

These experiments were not made with the greatest care but they show plainly enough that both acids are about equally effective, that is, both are about equally dissociated electrolytically and on a soluble ester have the same hydrolyzing power. If in place of triacetin we substitute a glyceride insoluble in water, such as an ordinary fat, then hydrochloric acid of the above concentration has practically no hydrolytic effect, while naphthalenestearosulphonic acid acts with about the same power as it does on the soluble esters.

The peculiar properties of sulpho-fatty acids can be applied in other ways in the chemical treatment of fats. Their property of dissolving in both fatty acid and water and rendering these two mutually soluble can be used to cause the separation of solid and liquid fatty acids.

When a melted mass of mixed fatty acids is allowed to cool the solid constituent crystallizes out, forming a porous mass holding the liquid fatty acid in its pores. If to the melted fatty acid a small quantity of a sulpho-fatty acid has been added, this will remain dissolved in the liquid after the solid has crystallized out pure. The liquid fatty acid will thus become slightly soluble and by simply treating with water can be washed out of the mixture, partly in solution but mainly as an emulsion. In both forms it passes through an ordinary filter-paper while the solid fatty acid is retained.

I have used this process in the laboratory in the following way for the separation of stearic and palmitic from oleic and linolic acids in tallow and other fats.

To 5 grams of the crystallized fatty acid is added about $^1/_{10}$ gram of naphthalenestearosulphonic acid, which is conveniently kept and used in the form of a 10 per cent. aqueous solution. A little dilute sulphuric acid (containing about $1^1/_4$ per cent.

H_2SO_4) is added and the mass is thoroughly ground up with a pestle. Twenty to 30 cc. in all of the dilute sulphuric acid are then added and the mixture allowed to settle. In a little while a copious layer of oil will rise to the surface. The mixture is then filtered through an ordinary filter-paper with the help of a filter-pump, pouring off the oil first and allowing it to be drawn through before the rest is brought on the filter. The mass on the filter-paper is then washed with the same dilute sulphuric acid solution until the filtrate is no longer cloudy. Eighty to 90 per cent. of the liquid fatty acid contained in the mixture will have been removed by this treatment. To extract the remainder the impure solid fatty acids must be removed from the filter and treated again with naphthalenestearosulphonic acid and dilute sulphuric acid as before. It requires several such treatments to extract the last few percentages of liquid fatty acid.

The crystalline mass on the filter-paper is finally washed with pure water, then collected and dried in any convenient manner, weighed and otherwise examined.

The object of the sulphuric acid in this process is to reduce the solubility of the sulpho-fatty acid in water and cause it to nearly all dissolve in the oil and not in the water as it would if pure water were used. If the proper amount of sulphuric acid is used, the acid water has still a strong tendency to emulsify with the oil containing the sulpho-fatty acid and will wash it out of the solid fatty acid mechanically, while pure water would dissolve out the sulpho-fatty acid before all the oil was washed out. The success of this method of separation depends largely on this equilibrium between the fatty and aqueous solutions of the sulpho-fatty acid. Instead of sulphuric acid any strong mineral acid may be used or, if instead of the sulpho fatty acid one of its soluble salts, which has the same property of dissolving in both fatty acid and water, has been made use of, then the same salt of a strong acid should be added to the water.

At ordinary temperatures the liquid fatty acids extracted from the mixture are not quite free from solid fatty acids. The amount thus lost corresponds to the solubility of the solid in the liquid fatty acids at the temperature of the operation. This error can be reduced to a minimum by conducting the operation at a temperature a little above the melting-point of oleic acid.

Stearosulphuric acid can be used for this separation, as at the

temperature of the work it decomposes only very slowly. However, I have found the mono-sodium or potassium salt of this acid just as efficient and much more stable.

Within the last few months a French patent has been issued to F. Lanza for the separation of solid and liquid fatty acids. Stearosulphuric acid, called in the specifications sulpho-oleic acid, is the reagent used in his process, which is very similar to the one described in this paper.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE, DIVISION OF FOODS. SENT BY H. W. WILEY.]

STUDY OF APPLE MARC.[1]

BY W. D. BIGELOW AND H. C. GORE.

Received December 19, 1905.

GENERAL DISCUSSION.

APPLE marc, or the insoluble matter of the flesh of the apple, is composed mainly of parenchymous tissue, containing besides this only the somewhat lignified vascular bundles in small quantity, and a little albuminoid matter. For this reason apple marc affords a convenient material for study of parenchymous tissue, such tissue being, of course, much easier of study in the nearly pure form in which it occurs in the apple, than in the grains and grasses in which it occurs together with more complex tissue. Parenchymatous tissue has been very little worked with *per se*, notwithstanding the fact that it is the first tissue formed in plant growth, and therefore of extreme importance physiologically.

In our work with apple marc[2] we found that about 40 per cent. of the product was rendered soluble by boiling with water. This method of treatment, which has been used by Weisburg[3] and Wohl and Van Niessen[4] in their work with beet marc, is well adapted to the study of such products, because after the treatment not only the undissolved tissues, but the dissolved portions, can be readily recovered nearly unchanged and further examined. Acid or alkali treatment of course alters the composition of the dissolved material to a very much greater extent than water.

[1] Read before the Agricultural Section of the American Chemica Society, June 23, 1905.

[2] U. S. Dept. Agr., Bur. Chem., Bull. 94, p. 87.

[3] Neue Z. Rübenz, 21, 325 (1888).

[4] Z. Ver. Zucker-Ind. 39, 924 (1889).