

Reaction of Fatty Acids with N-Methyl Taurine¹

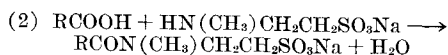
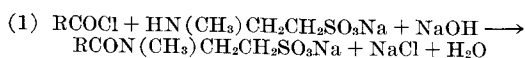
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Abstract

A commercially feasible process has been developed for producing salt-free fatty acyl taurates. The products are especially suited for soap-synthetic bars, contributing most importantly lime-soap dispersing properties.

Introduction

SODIUM acyl N-methyl taurates are made classically and in large quantity by the Schotten-Baumann condensation of fatty acid chlorides with an aqueous solution of the sodium salt of N-methyl taurine (1). However, a mole of salt theoretically—and practically closer to 1.3 moles—is formed per mole of acyl taurate. For many applications this mixture is completely satisfactory and, in fact, further cutting with salt is often practiced. Specifically for soap bar application, however, salt in this proportion is not ordinarily suitable. Although there are attractive ways of desalting the Schotten-Baumann product, inherently the most economically approach is the direct reaction of fatty acids with methyl taurine, avoiding the costly intermediate acid chloride step and splitting off water instead of salt. The comparison of the two methods is shown below.



Although the second reaction has been known for some time, no commercial process existed. It is possible that this was due chiefly to an end-use outlook. The acyl taurates made by the new process are not generally interchangeable in applications with the product from acid chlorides. An important characteristic in the acid chloride derived product is low free fatty acid. A characteristic of the direct condensation reaction is that it occurs to advantage in an excess of fatty acid which is left in the product. Free fatty acid or soap is not desired in many places where the regular acyl taurates are applied, but in mixed soap-synthetic ("combination") bars this is a most natural and acceptable combination.

Following is a description of some of the work which resulted in a commercially feasible product and process and which is, in fact, practiced on a large scale. The process is described in USP 2,880,219.

Experimental

A typical laboratory experiment may be described as follows. In a 250 cc 3 neck flask fitted with a mechanical stirrer, thermometer, and exit to aspirator vacuum are charged 11.8 g dry sodium salt of methyl taurine, 85% purity (.062 moles) and 35.2 g stearic acid (0.124 moles). The flask is then placed in an oil bath controlled at 220C and held for 10 hr under aspirator vacuum with stirring. Wt of product, an off-white brittle mass when cool, is 45.5 g. A typical analysis is 54% acyl taurate or a yield of 93%

TABLE I
Effect of Mole Ratio

Mole ratio fatty acid/MeT	% Yield directly	% Yield based on unreacted MeT	Pet. ether residue %	RCOOH %
1/1	69	82.6	32 (68)*	30.6
1.5/1	90	91.5	42 (87)	37.0
2/1	91.1	94.5	51 (103)	46.8

* Numbers in parentheses are yields calculated from the % residue.

based on methyl taurine. Plant practice is more feasible with methyl taurine solution, added over a short period of time to the molten fatty acid while stripping out the water. For inert atmosphere, important in preventing discoloration, vacuum, nitrogen, steam, and CO₂ are examples of mediums which have been employed successfully.

Products were analyzed to obtain values for the following characteristics:

1. Acyl taurate directly (methylene blue) (2).
2. Unreacted methyl taurine (potentiometric titration of aqueous layer after extracting free fat).
3. Petroleum ether soluble portion (fatty acid and inert fatty matter, by wt).
4. Fatty acid (by titration of pet ether residue).

Comparison of figures derived from the above scheme is shown in Table I, where results using three increasing ratios of fatty acid to methyl taurine are shown.

Obviously, yields calculated from each column would be equal under the most ideal conditions. Absolute values for the last two columns would be equal. Inter-relation of the actual figures gives an insight into what is happening and furnishes a tool for examining various reaction conditions.

The effect of mole ratio is shown in Table I. It is seen from columns 2 and 3 that a principal apparent effect of the excess fatty acid is to conserve the methyl taurine for the desired reaction, or to prevent its decomposition or side reactions. This is important from both a quality and economic standpoint and is the key to successful commercial practice. In Table I, column 2, is considered the true yield. Column 3 is indicative of the methyl taurine used. Actually, it is expressed here as product yield calculated from the methyl taurine remaining. Yield can also be calculated from the amount of fatty acid remaining (column 4). Three yield examples are shown in parentheses in this column and they should be compared with column 2. It is seen that all of the fatty matter is not fatty acid by comparing the last two columns. The difference has been accounted for as fatty ketone, a not unlikely product in high temp fatty acid reactions.

A different way of expressing columns 1 and 2 is shown in Table II, where the marked improvement in utilization of methyl taurine is shown more directly. It is seen that somewhere between mole ratios of 1.2/1 and 1.5/1 of fatty acid to methyl taurine, the

TABLE II
Effect of Mole Ratio on Side Reactions of Methyl Taurine

Mole ratio	% of used MeT not in acyl taurate
1:1	20
1.2:1	11.5
1.5:1	2
2:1	0

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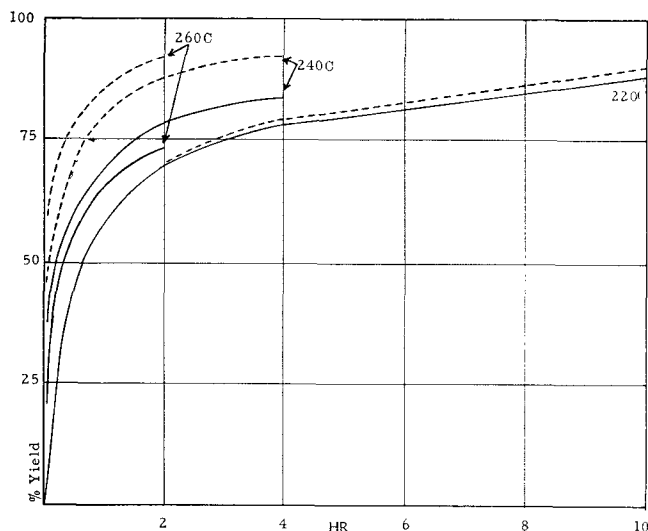


Fig. 1. Comparison of reaction rates at three temp. Mole ratio of stearic acid to methyl taurine is 1.5/1. Solid line indicates yield; broken line indicates methyl taurine used.

reaction becomes quite efficient.

The effect of temp is shown in Table III where three temp are compared at two mole ratios. It is difficult generally to consider temp independently of time and, in this case, separately from methyl taurine decomposition as well. The following conclusions can be drawn from the data in Table III: that higher temp speed up the reaction, as expected; that more methyl taurine is decomposed at higher temp; and (confirming), that higher mole ratios reduce the methyl taurine side reactions.

• Letters to the Editor

Some Alleged Errors in the Azelaoglyceride Technique

IT HAS recently been alleged (1,2) that acetone permanganate (Proc. I) (3) and acetic acid acetone permanganate (Proc. II) (4a, 5) oxidation procedures for analysis of fats are liable to error due to production of incompletely oxidized products (I.O.P) stated to be ketohydroxy (acetoxy) derivatives which break down completely on saponification with alcoholic KOH to products giving water-soluble Mg. salts. The actual production of any ketoderivatives has not however been demonstrated by specific ketogroup reactions (quantitatively or qualitatively) in any instance. Further, some earlier results (6,7) showed that no such compounds are produced in detectable amounts during either of these oxidation procedures. These results are as follows: (a) When known mixtures of methyl oleate and methyl stearate were oxidized by either of these procedures and the acidic products of oxidation were separated by washing in ether solution with aqueous carbonate, the same yields of neutral material (after correcting for residual iodine value) agreeing well with the known proportions of methyl stearate were obtained (6). The process used for isolation of neutral material cannot bring about the hydrolysis of I.O.P. and the results hence prove absence of production of I.O.P. in both procedures. (b) It was found that the higher saturated acid content of fats could be determined [in addition to the usual procedure of oxidizing the fat by Proc. I or II and submitting the oxidation products to Bertram

TABLE III
Effect of Temp at Mole Ratios of 1.5/1 and 2/1

Temp C	Time, hr	% Yield		% of used MeT not in acyl taurate	
		1.5/1	2/1	1.5/1	2/1
220	10	90	93.1	2	0
240	4	81	92.5	6	5
260	2	79	87.3	15	7.5

By analysis at intervals during the reaction period, data such as are plotted in Figure I are obtained. The rate of product formed (solid line) versus the methyl taurine used (broken line) is shown for three temp. Although the final amount of methyl taurine consumed is about the same in each of the three cases shown, the amount ending up as product varies. Products at the higher temp were increasingly darker. A plot of similar data for a mole ratio of 2/1 would show, as indicated in Table III, that the difference between methyl taurine consumed and product formed would be much less at the higher temp.

Considerable work has been done and is continuing in the application of these products in detergent bars. Characteristics such as hardness and other physical features of the bar, limesoap dispersing ability, and foaming may be varied depending on the fatty acid used. They are finding particular utility in combination bars. Amounts in the range of 15-20% have been found optimum for limesoap dispersing ability.

REFERENCES

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separation after hydrolysis with alcoholic KOH (4a)], by oxidizing the mixed fatty acids by Proc. II and submitting the products of oxidation directly to Bertram separation (7). The new procedure avoids treatment of the oxidation products with alcoholic KOH and cannot produce breakdown of I.O.P. if any is formed. The yields of saturated acids for a number of representative fats by this new procedure were the same as by the usual procedure (7) confirming absence of production of I.O.P. in both oxidation procedures.

Eshelman & Hammond (1) based their suggestion on an increase in ester groups in the oxidation products from methyl undecylenate, oleate and linoleate in Proc. II. This increase was probably due to some esterification of free carboxyl by ethanol generated from the di-ethyl ether during prolonged continuous extraction from an aqueous medium containing excess of strong mineral acid since the latter is known to produce splitting of ethers to alcohols (8). The larger increase for methyl linoleate was due to leaving out of consideration malonic acid from its oxidation products which will also get extracted and partially esterified. The lower than theoretical values in Proc. I was due to complete disruption of some of the oxidation products in this procedure as reported elsewhere (7).

Laxminarayana & Rebello (2) based their suggestion on the proportions of neutral derivatives (N.D.) obtained on passing di- and mono-saturated glycer-