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METHOD OF PREPARING SULPHO-CARBOXYLIC ESTER SALTS

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This invention is concerned with the preparation of novel chemical compounds and relates particularly to the preparation of compounds having unusual efficacy in various preparations, particularly for use in hair washes, shampoos and the like.

Compounds falling into the category of sulpho-carboxylic esters of higher molecular weight alcohols and of derivatives of polyhydroxy substances are already known and have been disclosed in various publications and patents among which may be cited United States Patents Nos. 1,917,250 and 1,917,255 and British Patent No. 377,249. These compounds are generally prepared and employed in the form of their alkali metal or ammonium salts, as the patents cited above show.

It has been found that compounds of the character indicated, particularly the sulpho-acetates of the straight chain higher aliphatic alcohols, such as lauryl sulpho-acetate, myristyl sulpho-acetate, and the like, in the form of their alkali metal salts, for example, the potassium salt, possess some utility in the preparation of hair washes, shampoos and the like. However, a serious disadvantage of such alkali metal salts, and this is even more true of the free acid derivatives, is their relatively poor solubility in cold water.

It has been found that when the sulpho-carboxylic esters are neutralized with organic nitrogenous bases as, for example, alkylolamines such as mono-, di- and tri-ethanolamine or mixtures thereof such as are present in commercial triethanolamine, compounds result which have greatly enhanced solubility in cold water thereby rendering the compounds admirably suited to the preparation of hair washes, shampoos and the like.

In further investigating this matter, possible methods of preparing the desired compounds were considered and, as a result of careful study and research, novel methods were evolved for preparing the compounds in a relatively simple and inexpensive manner.

It is accordingly one object of the present invention to prepare sulpho-carboxylic esters neutralized with organic nitrogenous bases to markedly increase the water-soluble characteristics of said esters.

Another object is to prepare alkylolamine salts of sulpho-carboxylic esters.

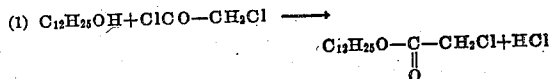
Still another object of the invention is the preparation of hair washes, shampoos and the like containing sulpho-carboxylic esters neutralized with organic nitrogenous bases.

A further and important object of the invention

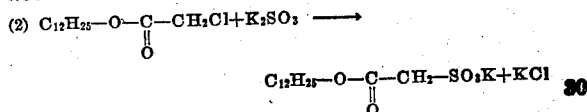
is a novel method of preparing the chemical compounds referred to hereinabove.

Other features will become even more apparent in the light of the following detailed description of the invention.

In the preparation of alkali metal sulpho-carboxylic esters such as sulpho-acetates, it is known, as shown, for example, by the patents referred to hereinabove, to employ a method involving initially reacting a higher molecular weight alcohol, such as lauryl alcohol, with chloracetic or bromoacetic acid or the like to produce the chloroacetic or bromoacetic acid ester of lauryl alcohol in accordance with the following equation:



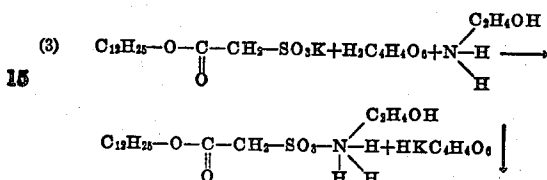
The resulting product, preferably washed free of the formed hydrochloric acid and the unreacted chloroacetic acid, is then treated with an aqueous solution of an alkali metal sulphite, such as K_2SO_3 , in accordance with the so-called Strecker reaction to produce the alkali metal sulphoacetate as indicated in the following equation:



The Strecker reaction appears to operate best when potassium sulphite is employed. Sodium sulphite operates well while ammonium sulphite is not quite so satisfactory as sodium sulphite.

In the course of the investigational work in connection with the present invention, various methods were evolved and employed in an endeavor to produce alkylolamine and similar salts of sulpho-carboxylic esters but without success. It was finally discovered, however, that highly advantageous results could be achieved by reacting an alkali metal or similar salt of a sulpho-carboxylic ester, such as lauryl potassium sulphoacetate, with an organic nitrogenous base such as monoethanolamine, and with a compound which would react with the cationic constituent of the sulpho-acetate salt to produce a compound more insoluble than the sulpho-acetate salt whereby the more insoluble compound would precipitate out and could be removed by filtration or the like, leaving the monoethanolamine salt of the sulphoacetate in solution from which it could, if desired, be recovered by evaporation or drying of the solution.

More specifically, it was found that unusually good results were obtained by reacting a sulpho-carboxylic ester such as lauryl potassium sulpho-acetate, tartaric acid, and an organic nitrogenous base such as monoethanolamine. The reaction which takes place results in the formation of potassium acid tartrate which is quite insoluble in cold water and precipitates out, leaving the monoethanolamine salt of lauryl sulphoacetate. The reaction may be illustrated by the following equation:



The reaction takes place when the alkali metal or similar salt of the sulpho-carboxylic acid ester is more soluble or less insoluble than the salt or the like such as potassium acid tartrate which forms during the reaction. Thus, in the specific example referred to above, lauryl potassium sulpho-acetate being more soluble or less insoluble than potassium acid tartrate, the reaction takes place. On the other hand, this particular reaction does not appear to take place when stearyl potassium sulpho-acetate is substituted for lauryl potassium sulpho-acetate, presumably because stearyl potassium sulpho-acetate is less soluble than potassium acid tartrate.

In order to enable those skilled in the art to understand the nature of the invention even more fully, the following examples are given by way of illustration. It will be understood, however, that the specific reactants, the proportions thereof, and the times and temperatures may be varied within limits without departing from the spirit of the invention. The examples, therefore, are to be taken in an illustrative rather than in a limitative sense, the full scope of the invention being pointed out in the claims.

Example I

A. 200 grams of crystalline lauryl potassium sulpho-acetate, prepared from commercial lauryl alcohol, were dissolved in 400 cc. of water at 80 degrees C. to produce a relatively stiff paste.

B. 150 grams of tartaric acid and 141 grams of triethanolamine were dissolved in 400 cc. of water.

C. Compositions A and B were then stirred together at a temperature of about 90 degrees C. A heavy precipitate came down and the previously viscous mixture became quite mobile. The precipitate, which comprises potassium acid tartrate, was filtered off and the filtrate was then neutralized with 50 grams of triethanolamine. The final solution was quite viscous, containing in the neighborhood of 20% of lauryl triethanolamine sulpho-acetate. It possessed unusually good foaming characteristics and made an excellent shampoo.

Example II

133.5 grams of potassium lauryl sulpho-acetate



were dissolved in 700 cc. of boiling water and were then mixed with a previously prepared solution containing 69.4 grams tartaric acid and 28.7 grams of monoethanolamine in 200 cc. of

water. These two solutions were mixed together at a temperature of about 90 degrees C. and the resulting mixture thereof was allowed to cool to room temperature. The liquid was then filtered from the precipitated potassium acid tartrate. The filtrate was a viscous, strongly foaming, substantially odorless and colorless liquid after having been neutralized with 6.7 grams of monoethanolamine to a litmus blue reaction. The solution contained 13.8% of the monoethanolamine salt of lauryl sulpho-acetate and 2.9% of the tartrate of monoethanolamine.

The solution had excellent foaming properties and formed an admirable shampoo.

Example III

133 grams of potassium lauryl sulpho-acetate were dissolved in 700 cc. of boiling water and the resulting solution was then mixed with a previously prepared solution containing 69 grams of tartaric acid, 36.6 grams of pyridine and 200 cc. of water. The two solutions were mixed at a temperature of about 90 degrees C. and were then allowed to cool to room temperature whereupon the resulting solution was filtered from the potassium acid tartrate which had precipitated out. Approximately 780 cc. of a yellow colored limpid solution were obtained which had excellent foaming properties in hard water as well as in the presence of alkalies and acids. The solution contained a substantial proportion of the pyridine salt of the sulpho-acetate of lauryl alcohol.

Example IV

173 grams of lauryl potassium sulpho-acetate were dissolved in 1050 cc. of boiling water and mixed with a solution containing 93 grams of tartaric acid, 51 grams of piperidine and 300 cc. of water. After cooling to approximately room temperature, the solution was filtered off from the precipitated potassium acid tartrate and the solution was then neutralized to a methyl red yellow with 20 grams of piperidine. A water-white viscous liquid was obtained possessing strong foaming properties in alkaline or acid aqueous media as well as in hard water. The solution contained the piperidine salt of lauryl sulpho-acetate and was very suitable for use as a shampoo.

Example V

453 grams of lauryl potassium sulpho-acetate, prepared from commercial lauryl alcohol containing about 75% lauryl alcohol, and containing about 40% water were dissolved in 1810 cc. of water previously heated to about 90 degrees C. To the above solution there was then added, at about 90 degrees C., a solution of monoethanolamine acid tartrate prepared by mixing together a solution of 60.9 grams of monoethanolamine (molecular weight 62.6) in 210 cc. of water with a solution of 146 grams of tartaric acid dissolved in 210 cc. of water.

The resulting solution was then allowed to cool for about a day at room temperature and was then decanted and filtered from the precipitate of potassium acid tartrate, the latter then being washed with 50 cc. of water and the wash water being added to the filtrate.

To the approximately 2,660 grams of solution thus obtained, about 20 grams of monoethanolamine were added until methylred gave a yellow color. There was then added to said solution 110 cc. of a solution of monoethanolamine sulphate in order to thicken the solution so as to

render it more suitable as a shampoo preparation for certain classes of trade. The solution of monoethanolamine sulphate was prepared by adding a solution of 325 grams of monoethanolamine dissolved in 250 cc. of water to a solution of a stoichiometrically equivalent amount of 96% sulphuric acid dissolved in 580 cc. of water.

Example VI

10 An aqueous solution of 8.1 parts, by weight, of acid methylpyridinium tartrate in 17 parts, by weight, of water was prepared by mixing one mol of 0.166 normal methylpyridinium hydroxide solution with an aqueous solution of one mol of tartaric acid and evaporating down. This solution was then heated to a temperature of about 90 degrees C. and was then added to a previously heated solution, also at about 90 degrees C., containing 10.4 parts, by weight, of lauryl potassium sulfo-acetate and 50 parts, by weight, of water. The mass was permitted to cool to approximately 25 degrees C. and the acid potassium tartrate which had precipitated out was filtered off. The resulting clear filtrate was neutralized to yellow methylred with 20 volume parts of 0.167 normal methyl-pyridinium hydroxide solution. The resulting solution, containing a substantial proportion of the methylpyridinium salt of lauryl sulfo-acetate, was water-white, viscous, substantially odorless, and had excellent foaming properties in hard water as well as in aqueous acidulated media. It was very suitable for use as a hair wash or shampoo.

Those skilled in the art will readily be able to carry out the invention, make diverse variations all of which, however, are within the spirit of the invention in view of the detailed explanation and guiding principles set out hereinabove.

It will be appreciated, for example, that other organic nitrogenous bases may be employed in place of those described hereinabove. Illustrative of additional bases of this type are propanolamines, butanolamines, hexanolamines, glycerolamines, dibutyl ethanolamine, diethanol ethyl amine, cyclohexyl ethanolamine, alkylol polyamines such as alkylol derivatives of ethylene diamine, quaternary ammonium bases or hydroxides such as tetra-methyl ammonium hydroxide, tetra-ethyl ammonium hydroxide, quaternary ammonium bases with dissimilar alkyl radicals such as methyl-triethyl ammonium hydroxide, propyl-trimethyl ammonium hydroxide, and the like.

Again, it is evident that pure or single sulfo-carboxylic esters need not be employed. Mixtures are, in many cases, at least equally efficacious as, for example, the sulfo-carboxylic esters prepared from the product known as "Lorol Technical" which comprises a mixture of fatty alcohols derived from the hydrogenation of coconut oil or the free fatty acids of coconut oil. Lauryl alcohol comprises about 60% of the total alcohol mixture, the remaining alcohols running from C₆ to C₁₈. Similarly, it is apparent that mixtures of different organic nitrogenous bases, such as mixtures of those referred to hereinabove, may be employed with efficacious results. Indeed, in order to obtain varied solubility and other characteristics mixtures of different organic nitrogenous bases may be employed with mixtures of different sulfo-carboxylic esters.

Instead of employing tartaric acid as described above, oxalic acid and other acids such as perchloric acid or acids of organic character can

be used whose alkali metal or other salts or acid salts are more insoluble than the salt of the sulfo-carboxylic acid employed as one of the reactants at the concentrations and under the conditions of the reaction. Tartaric acid is preferred, however, because of the unusually low cold-water solubility of potassium acid tartrate.

As indicated in Example V, the solution of the organic nitrogenous base salt of the sulfo-carboxylic ester may be thickened, if desired, by the addition thereto of monoethanolamine sulphate. In place of the latter, organic nitrogenous bases other than monoethanolamine, such as those disclosed above, may be neutralized with acids other than sulphuric acid as, for example, phosphoric acids, nitric acid, acetic acid and the like, and employed for thickening purposes. In general, the thickening material may be a neutral water-soluble salt the cation of which does not precipitate out the sulfo-carboxylic ester.

If it is desired to still further decrease the solubility of the salt, such as potassium acid tartrate, methyl alcohol, ethyl alcohol or other organic solvents may be added to the reaction mixture to provide an environment in which the potassium acid tartrate or the like is even still more insoluble than it is in cold water alone.

The term "higher", as employed herein in connection with the alcohol sulfo-carboxylic esters, is intended to mean not less than eight carbon atoms and, concomitantly, the term "lower" will be understood to mean less than eight.

What we claim as new and desire to protect by Letters Patent of the United States is:

1. The method of preparing esters of alcohols containing at least 8 carbon atoms and sulfo-carboxylic acids containing less than 8 carbon atoms, the hydrogen of the sulphonic groups of which is replaced by an organic nitrogenous base, which includes the steps of reacting an organic nitrogenous base, an ester of an alcohol containing at least 8 carbon atoms and a sulfo-carboxylic acid containing less than 8 carbon atoms, the hydrogen of the sulphonic group of which is replaced by a metal cation, an acid which reacts with the metal salt of the sulfo-carboxylic acid ester to produce a salt of said acid and the metal cation of said sulfo-carboxylic acid ester which is more insoluble than the sulfo-carboxylic acid ester metal salt constituting one of the reactants whereby a precipitate is formed, and then separating said precipitate from the solution.

2. The method of claim 1 wherein said metal cation is potassium.

3. The method of preparing sulfo-acetates of alcohols containing at least eight carbon atoms, the hydrogen of the sulphonic group of which is replaced by an organic nitrogenous base, which comprises providing an aqueous material containing a substantial proportion of the potassium salt of a sulfo-acetate of an alcohol having at least eight carbon atoms, adding an aqueous solution containing tartaric acid and an organic nitrogenous base, stirring the mixture, and removing the resulting precipitate of potassium acid tartrate.

4. The method of preparing alkylolamine sulfo-acetates of aliphatic alcohols having at least eight carbon atoms which includes the steps of reacting, in aqueous media, an aliphatic alcohol potassium sulfo-acetate, the alcohol radical of which contains at least eight carbon atoms, an alkylolamine, and an acid whose potassium salt

is less water-soluble than the aliphatic alcohol potassium sulpho-acetate whereby said salt is precipitated, and then separating the precipitate from the solution.

5. The method of preparing lauryl monoethanolamine sulpho-acetate which includes the steps of reacting lauryl potassium sulpho-acetate, tartaric acid, and monoethanolamine and separating the resulting precipitate of potassium acid tartrate.

6. The method of preparing lauryl monoethanolamine sulpho-acetate which comprises providing an aqueous material containing a substantial proportion of lauryl potassium sulpho-acetate, adding an aqueous solution containing tartaric acid and monoethanolamine, stirring the mixture at a temperature of about 90 degrees C., and removing the resulting precipitate of potassium acid tartrate after cooling said mixture.

7. The method of preparing lauryl alkylolamine sulpho-acetate which includes the steps of re-

acting, in aqueous media, lauryl potassium sulpho-acetate, tartaric acid, and alkylolamine and separating the resulting precipitate of potassium acid tartrate.

8. The method of preparing lauryl alkylolamine sulpho-acetate which comprises providing an aqueous material containing a substantial proportion of lauryl potassium sulpho-acetate, adding an aqueous solution containing tartaric acid and alkylolamine, stirring the mixture at a temperature of about 90 degrees C., and removing the resulting precipitate of potassium acid tartrate after cooling said mixture.

9. The method of preparing lauryl sulpho-acetate the hydrogen of the sulphonic acid radical of which is replaced by an organic nitrogenous base which includes the steps of reacting lauryl potassium sulpho-acetate, tartaric acid, and an organic nitrogenous base, and separating the resulting precipitate of potassium acid tartrate.

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