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SOLUBILIZATION OF WATER-INSOLUBLE QUATERNARY AMMONIUM BENZOSULFIMIDES

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This invention relates to the solubilization of normally insoluble compounds, and it particularly relates to the solubilization of insoluble types of quaternary ammonium benzosulfimides (saccharinates).

It has been heretofore discovered that quaternary ammonium benzosulfimides have many desirable properties whereby they act as surface-active agents, germicidal and fungicidal agents, thickening agents and antistatic agents. However, it has also heretofore been found that many of these quaternary ammonium benzosulfimides are substantially water-insoluble. In particular, it has been found that the only water-soluble compounds of this type are those wherein all four substituents in the ammonium radical are aliphatic. When one or more of the substituents are aromatic, whether it be homocyclic or heterocyclic, the compound is, to all intents and purposes, water-insoluble.

In accordance with the present invention, it has now been discovered that the aforesaid water-insoluble quaternary ammonium benzosulfimides can be made water-soluble in the presence of specific proportions of certain salts and certain alcohols. More particularly, it has been found that the salts of such strong mineral acids as hydrochloric and sulfuric acids and strong bases such as sodium and potassium hydroxides are best for the present purposes. Salts of strong bases and such polybasic acids as mono- and di-basic ammonium phosphates have also been found to increase the solubility of these compounds, although somewhat less effectively.

The alcohols suitable for the present purposes include those alcohols which are water-soluble and completely miscible in water and generally comprise the lower alcohols such as methyl, ethyl and isopropyl alcohols.

The fact that salts of the aforesaid type act to increase the water-solubility of quaternary ammonium benzosulfimides is a highly unexpected result because these salts are electrolytes and electrolytes would normally be expected to reduce the water-solubility of organic compounds, in particular surface-active agents such as the quaternary ammonium benzosulfimides, and most especially in the presence of alcohols.

Illustrative of the quaternary ammonium benzosulfimides rendered more water-soluble in accordance with the present invention are alkylaryls such as alkyl dimethyl benzyl ammonium benzosulfimide and lauryl dimethyl benzyl ammonium benzosulfimide, alkylpyridiniums such as N-cetyl pyridinium benzosulfimide and N-lauryl pyridinium benzosulfimide, the picoliniums such as myristyl gamma picolinium benzosulfimide, the quinaldiniums such as decamethylene-bis-4-amino-quinaldinium (dequalinium) benzosulfimide, groupings wherein the molecule contains an ether linkage such as para-octylphenoxyethoxyethyldimethyl benzyl ammonium benzosulfimide, groupings having oxygen in the form of amide or ester linkages such as N-(lauryl colamino formyl methyl)-pyridinium benzosulfimide, those containing a sulfonamide group such as 4-sulfanilamido-benzyl tetradecyl dimethyl ammonium benzosulfimide, these containing a substituted aromatic nucleus such as lauryloxyphenyl trimethyl ammonium benzosulfimide, cetylamino-phenyl trimethyl ammonium benzosulfimide and dodecylbenzyl trimethyl ammonium benzosulfimide, the arylaliphatic isoquinilinium benzosulfimide, the arylaliphatic morpholiniums, such as N-dodecyl-N-methyl morpholinium benzosulfimide, and the arylaliphatic imidazolinium benzosulfimides.

In fact, insofar as applicant is aware, the water-solubility of all relatively water-insoluble quaternary ammonium benzosulfimides, that is those having at least one aromatic group in the quaternary radical, is significantly increased by the addition of the salts and alcohols, in the stated proportions, in accordance with the present invention.

All the quaternary ammonium benzosulfimides are generally prepared in substantially the same manner by mixing, in an aqueous mixture at room temperature, stoichiometric amounts of the selected quaternary ammonium salt, such as a halide or sulfate, and either benzosulfimide or an alkali metal salt of benzosulfimide. Alternatively, an alcoholic solution may be used instead of an aqueous solution. Agitation, although not necessary, is sometimes used to hasten the reaction. Furthermore, the application of heat is also sometimes used to hasten the reaction. The following is an example of the preparation of such type of compounds:

Example 1

36 grams of alkyl dimethyl benzyl ammonium chloride were dissolved in three times its weight of water and to this were added, with stirring, 24 grams of sodium benzosulfimide as a 20% aqueous solution. A flocculent white precipitate was immediately formed and was removed by filtration, yielding 71.4 grams of the wet reaction products. Vacuum-drying over sodium hydroxide yielded 55 grams (92% of theoretical) of the compound alkyl dimethyl benzyl ammonium benzosulfimide.

All other quaternary ammonium benzosulfimides can be prepared in the same manner as in Example 1 merely by substituting the desired quaternary ammonium chloride for the one used in Example 1.

In accordance with the present invention, the water-solubility of any relatively insoluble quaternary ammonium benzosulfimide or of a mixture of any two or more such compounds is achieved by adding to an aqueous mixture thereof a salt selected from the group consisting of sodium and potassium chlorides, sodium and potassium sulfates, and ammonium phosphate, in a proportion of about 0.1–10% by weight of the total mixture, plus an alcohol selected from the group consisting of methyl, ethyl and isopropyl alcohols in a proportion of about 0.95–35% by weight of the total mixture. The most effective and, therefore, the preferable proportion of the salt is about 1.5–3% by weight of the mixture and the preferable proportion of the alcohol is about 5–30% by weight of the mixture.

The following examples are illustrative of aqueous solutions of normally water-insoluble quaternary ammonium benzosulfimides:

Example 2

An aqueous mixture was prepared at room temperature consisting of 0.023 gram cetyl pyridinium chloride, 0.010 gram decamethylene-bis - 4 - aminoquinaldinium chloride (dequalinium chloride), 0.028 gram benzosulfimide, 15 grams ethyl alcohol and 83.439 grams water. A precipitate was immediately formed which, when analyzed, proved to be a mixture of cetyl pyridinium benzosulfimide and dequalinium benzosulfimide which had been formed in situ. There was then added to the mixture 1.5 grams sodium sulfate. Almost immediately the precipitate disappeared indicating that the benzosulfimides had gone into solution.

The solution was then cooled until at 34° F., some precipitation or crystallization of the benzosulfimides became apparent. The solution was then brought back to

room temperature. As the temperature of the solution increased above 34° F., the precipitate quickly began to disappear and none whatever was apparent at room temperature.

The solution was then subjected to a 3-cycle freeze-thaw test wherein it was alternately brought down to 34° F. and raised to room temperature three times. At the end of this 3-cycle test, when the solution was brought back to room temperature, no precipitate was apparent. The solution was then allowed to stand for two weeks and, when observed at the end of this period, there was still no precipitate apparent.

Example 3

The same mixture was prepared at room temperature as in Example 2. However, in place of the sodium sulfate, 2 grams of ammonium phosphate $(NH_4)H_2PO_4$ was added to the mixture. Immediately the precipitate began to disappear.

Example 4

An aqueous mixture was prepared at room temperature which consisted of 0.1 gram alkyl dimethyl benzyl ammonium benzosulfimide, 20 grams ethyl alcohol, 2 grams potassium chloride and 79.9 grams water. The alkyl dimethyl benzyl ammonium benzosulfimide, which is normally completely insoluble in water at room temperature, immediately went into total solution.

The temperature of the solution was then lowered until a precipitate was observed at 35° F. The temperature was then raised to room temperature and as the temperature increased the precipitate began to disappear. At room temperature no precipitate was apparent. The solution was then subjected to the same 3 cycle freeze-thaw test as in Example 1 and no precipitate was observed either immediately after the test or after the solution had been permitted to stand for two weeks.

Example 5

An aqueous mixture was prepared at room temperature which consisted of 0.2 gram p-octyl phenoxy ethyl dimethyl benzyl ammonium benzosulfimide, 15 grams methyl alcohol and about 83.5 grams water. A precipitate identified as p-octyl phenoxy ethyl dimethyl benzyl ammonium benzosulfimide immediately formed. 1 gram of sodium chloride was then added and the precipitate almost immediately disappeared.

Example 6

The same procedure was used as in Example 5 except that lauryl isoquinolinium benzosulfimide was used as the quaternary compound, sodium chloride was used as the salt and the alcohol was isopropyl. A precipitate formed and then disappeared upon the addition of the sodium chloride.

Example 7

Three aqueous mixtures were prepared at room temperature, each containing 0.01 gram of dequalinium benzosulfimide and 15 grams of alcohol. The alcohol in the first was ethyl, in the second isopropyl and in the third methyl. Each had a precipitate of dequalinium benzosulfimide. Then 1 gram of sodium sulfate was added to each mixture. The precipitate in each mixture almost immediately disappeared.

Example 8

The same procedure was used to prepare three separate mixtures as in Example 7 except that cetyl pyridinium benzosulfimide was used as the quaternary compound and the quantity thereof used was 0.1 gram. The salt used was potassium sulfate but the quantities of alcohol and potassium sulfate were the same as in Example 7. In each case the precipitate disappeared when the potassium sulfate was added.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is, therefore, to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

The invention claimed is:

1. A method of increasing the water-solubility of a substantially water-insoluble quaternary ammonium benzosulfimide which comprises admixing with said benzosulfimide in aqueous mixture about 0.1–10% by weight of the mixture of a salt selected from the group consisting of sodium and potassium chlorides, sodium and potassium sulfates and ammonium phosphate and about 0.95–35% by weight of the mixture of a member of the group consisting of methyl alcohol, ethyl alcohol and isopropyl alcohol.

2. The method of claim **1** wherein the proportion of the salt is about 1.5–3% by weight of the mixture and the proportion of the alcohol is about 5–30% by weight of the mixture.

3. The method of claim **1** wherein the quaternary ammonium benzosulfimide is formed in situ in the mixture.

4. An aqueous solution consisting essentially of water, a quaternary ammonium benzosulfimide which is normally insoluble in water at room temperature, about 0.1–10% by weight of the composition of a salt selected from the group consisting of sodium and potassium chlorides, sodium and potassium sulfates and ammonium phosphate, and about 0.95–35% by weight of the composition of an alcohol selected from the group consisting of methyl, ethyl and isopropyl alcohols.

5. The solution of claim **4** wherein the salt is present in a proportion of about 1.5–3% by weight of the composition and the alcohol is present in a proportion of about 5–30% by weight of the composition.

6. The solution of claim **4** wherein the benzosulfimide is formed in situ in the solution.

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