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(72) Inventors KLAUS SOMMER, HERMANN WEBER and WILHELM SPATZ


(19)

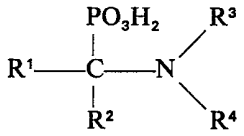

## (54) N-SULPHOALKANE-AMINOALKANE PHOSPHONIC ACIDS, THEIR ALKALI METAL SALTS AND METHOD OF PREPARING THEM

(71) We, BENCKISER-KNAPSACK, GMBH, a German Body Corporate, of Am Hafen 2, 6802 Ladenburg, West Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with N-sulphoalkane-aminophosphonic acids and alkali metal salts thereof, and the preparation of such acids and salts.

It has been found, in accordance with the present invention, that certain new N-sulphoalkane-aminophosphonic acids, as hereinafter defined, possess good complexing properties for multivalent metal ions and also have good water solubility.

Accordingly, the present invention provides, as new compounds, N-sulphoalkane-aminoalkanephosphonic acids of the general formula:




(I)

and alkali metal salts thereof, in which:

$R^1$ is a hydrogen atom,
a lower alkyl group containing from 1 to 6 carbon atoms (especially a methyl or ethyl group),
a phenyl group,
a group of the formula $—R^5—NH_2$ or $—R^5—COOH$ (in which $R^5$ is a lower alkylene group containing from 1 to 6 carbon atoms (especially a methylene group), or
a group of the formula $—R^6—PO_3H_2$ (in which $R^6$ is a lower alkylene group, containing from 1 to 6 carbon atoms, especially an ethylene group);

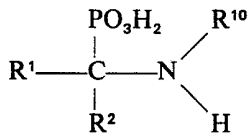
$R^2$ is a hydrogen atom or a group $—PO_3H_2$;

$R^3$ is a group $—R^7—SO_3H$ (in which $R^7$ is an alkylene group containing from 1 to 11 carbon atoms optionally substituted with a phenyl group, hydroxy group or a group $—SO_3H$), or
a group $—R^8—PO_3H_2$ (in which $R^8$ is a lower alkylene group, containing from 1 to 6 carbon atoms, especially a methylene group); and

$R^4$ is a hydrogen atom (if $R^3$ is not a group $—R^8—PO_3H_2$), a methyl group, or a group $—R^7—SO_3H$ (in which $R^7$ has the meaning defined above).

The new aminophosphonic acids of the invention differ from previously known aminophosphonic acids in that one or both of the hydrogen atoms on the nitrogen atoms of the amino group are replaced by alkane-sulphonic acid groups.

The alkali metal salts of the new phosphonic acids of the invention may be prepared by reacting an alkali metal salt of an aminophosphonic acid of the general formula:



(II)

in which $R^1$ and $R^2$ have the meanings defined above, $R^{10}$ is a hydrogen atom, a methyl group or a group $—R^8—PO_3H_2$ (in which $R^8$ has the meaning defined above), with an alkali metal salt of

(a) a chloroalkane-sulphonic acid of the formula:
$Cl—R^7—SO_3H$
(in which $R^7$ has the meaning defined above)

(b) a hydroxyalkane-sulphonic acid of the formula:
$HO—R^7—SO_3H$
(in which $R^7$ has the meaning defined above), or

(c) an alkenyl-sulphonic acid of the formula:
$R^{11}—SO_3H$
(in which $R^{11}$ is an alkenyl group containing from 2 to 6 carbon atoms, optionally substituted with a phenyl group or a group $—SO_3H$).

The reaction is carried out in an alkaline medium, preferably at a pH of at least 9, and at elevated temperature generally in a molar ratio of aminophosphonic acid salt to other reactants of from 1:1 to 1:2.

Any aminophosphonic acid falling within the terms of formula II may be employed in the process of the invention and examples of suitable aminophosphonic acids include aminomethane-diphosphonic acid, N-methylaminomethanediphosphonic acid, imino-bis-methanephosphonic acid, 1-aminoethane-1, 1-diphosphonic acid, 1-aminopropane-1, 1-diphosphonic acid, phenylaminomethane-diphosphonic acid, 2-carboxy-1-aminoethane-1, 1-diphosphonic acid, and 1-aminopropane-1, 1,3-triphosphonic acid.

The reaction between the aminophosphonic acid and chloroalkanesulphonates is suitably carried out at a temperature of about 100°C. Suitable chlorosulphonates include, for example, the sodium and potassium salts of 1-chloroethane-2-sulphonic acid, 1-chloropropane-2-sulphonic acid, 1-chloropropane-3-sulphonic acid, 2-chlorobutane-4-sulphonic acid, 1-chlorobutane-4-sulphonic acid, 1-chlorooctane-2-sulphonic acid and 3-chloroundecane-1-sulphonic acid.

In the case of the reaction of the aminophosphonic acid with a hydroxymethanesulphonate it has been found that hydroxymethanesulphonates react with aminophosphonates to an appreciable extent at temperatures as low as 60°C. the reaction with higher 1-hydroxyalkane-1-sulphonates, such as for example 1-hydroxyethane-1-sulphonate, proceeds more slowly. On the other hand, it has been found that it is necessary to operate at temperatures of between 180° and 240°C and under elevated pressure in the case of 2-hydroxyethane-1-sulphonates.

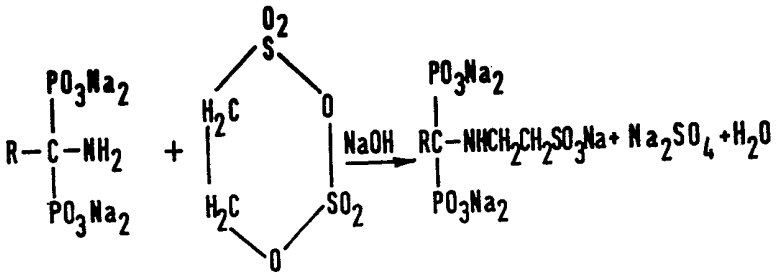
Suitable hydroxyalkanesulphonates for use in the process of the invention include, for example, hydroxymethanesulphonate, 1-hydroxyethane-1-sulphonate, 2-hydroxyethane-1-sulphonate, 1,2-dihydroxyethane-1,2-disulphonate and hydroxycarboxymethanesulphonate.

In the case of reaction of the aminophosphonates with alkali metal salts of chloroalkanesulphonates, mono- or disubstituted sulphoalkane-aminoalkanediphosphonates or sulphoalkane-aminoalkanetriphosphonic acids may be obtained depending on the molar ratios of the reactants. If a 2-hydroxyethane-1-sulphonate is reacted with the aminoalkanephosphonate only a product containing a sulphoalkane group on the nitrogen atom is obtained.

In accordance with a modification of the process of the invention, the hydroxyalkane-sulphonate may be generated *in situ* in the reaction medium.

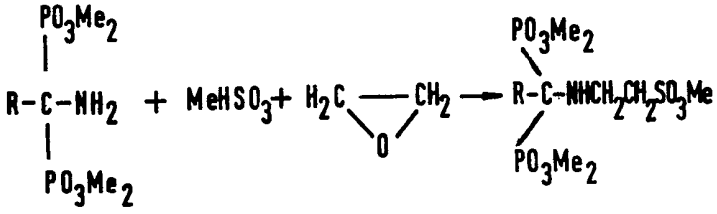
Thus, instead of a 1-hydroxyalkane-1-sulphonate, a corresponding aldehyde or acetyl together with alkali metal bisulphite may be used as reactants.

Instead of a 2-hydroxyethane-1-sulphonate, starting products used in the preparation of the hydroxyethanesulphonic acid may be employed and reacted with the corresponding amino phosphonates. Thus, it is possible to react carbyl sulphate, which has been neutralised with an alkali metal hydroxide or carbonate before the reaction, with the aminoalkanephosphonate in an alkaline medium to give the corresponding N-sulphoalkane-aminoalkanephosphonic acids accoring to the following reaction scheme:




In this case, the actual sulphoalkylation is preferably effected at a temperature of from 180° to 240°C and under elevated pressure.

It is also possible to react ethylene oxide and $NaHSO_3$, from which hydroxyethanesulphonic acid can also be prepared, directly with an aminophosphonate. For this purpose, the aminophosphonate is preferably mixed with the sodium bisulphate solution, following which ethylene oxide is passed in or added dropwise. In this case the sequence in which the reactions are added is of importance, since ethylene oxide can react with sodium bisulphite as well as with the $NH_2$ group of the aminoalkanephosphonate. Thus, if the order of addition is altered, N-hydroxyalkaneaminoalkanephosphonic acids are formed as a major portion of the reaction product. If the specified sequence is adopted, these hydroxyalkane derivatives are formed in only slight amounts. The conversion, which proceeds according to the following reaction scheme, is also preferably carried out at a temperature of from 180° to 240°C when using ethylene oxide and $NaHSO_3$.




(in which Me is an alkali metal atom)

The processes described above lead to the preparation of alkali metal salts of the compounds of the invention and these salts may be converted to the corresponding free acids in a conventional manner, e.g. by hydrolysis with an acid or by passage over a cation exchange resin in the acid form.

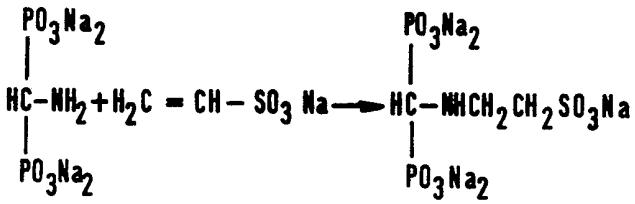
Particularly suitable alkenyl sulphonates for use in the process of the invention are vinyl sulphonate, 1-propene-1-sulphonate, 1-propene-3-sulphonate, 2-phenylethene-1-sulphonate, 2-methyl-2-propene-1-sulphonate, 2-hexene-1-sulphonate, and 2-propene-sulphonate.

Alkenylenedisulphonates, e.g. 2-butene-1,4-disulphonate, 1-butene-3,4-disulphonate and 2-methyl-1-butene-3,4-disulphonate, may also be used.

Whereas the addition of vinyl sulphonate and 1-propene-1-sulphonate takes place sufficiently rapidly even at the boiling point of the aqueous reaction mixture,

in the case of the other mentioned sulphonates reaction temperatures of between 120 and 180°C are required, and accordingly these conversions must be carried out at elevated pressure in pressurised vessels.

The conversion takes place in accordance with the following reaction shceme, illustrating the reaction of aminomethanediphosphonic acid with sodium vinyl sulphonate.



The phosphonic acids of the invention can readily be prepared in good yields and their water solubility is very good for most fields of use. They are good complex-forming agents with respect to divalent and polyvalent metal ions and can be used to advantage in all cases where a good complex-forming ability is required. Their resistance to hydrolysis at high temperatures is particularly noteworthy, and accordingly they can be used in all cases in which temperatures above 100°C are employed. They may also be used in all media in which the hardness constituents in water interfere, or in which the influence of polyvalent metal ions has to be eliminated. The treatment of hard water, textile treatment baths, paper manufacture and tanning may particularly be mentioned.

the new phosphonic acids are also suitable for stabilising water hardness in substoichiometric amounts, i.e. for carrying out the so-called "threshold-treatment".

The extremely good solubility of the free acids in aqueous media, which is lacking in most of the hitherto known aminophosphonic acids, is particularly noteworthy. Thus, the compounds described in the examples dissolve at the very least in an amount of 100 g/100 ml.

In order that the invention may be well understood the following Examples are given by way of illustration only.

## EXAMPLE 1.

47.8 g of aminomethanediphosphonic acid was dissolved together with 50 g of NaOH in 300 ml of water. A solution of 42 g of sodium chloroethanesulphonate in 150 ml of water was added drop-wise to this solution at a temperature of between 30 and 50°C with stirring, and the mixture was boiled for 1 hour with vigorous stirring. After cooling, the mixture was weakly acidified with dilute hydrochloric acid, any aminomethanediphosphonic acid that might have precipitated was filtered off, and the solution was treated with a cation exchange resin to obtain the free sulphophosphonic acid. After the solution had been concentrated by evaporation, the product was crystallised by adding methanol or ethanol. The N-sulphoethane-aminomethanediphosphonic acid obtained has a lime-bonding capacity of 22.8 g Ca/100 g at pH 10.

Yield: 92% of theory.

Analysis:

found:C: 12.4%, N: 4.6%, P: 19.8%, S: 11.1%

calculated:C: 12.04%, N: 4.68%, P: 20.71%, S: 10.72%.

## EXAMPLE 2.

A solution of sodium aminomethanediphosphonate prepared from 47.8 g of aminomethanediphosphonic acid and 60 g of NaOH in 300 ml of water was added with stirring to a solution of 90 g of sodium chloroethanesulphonate in 250 ml of water. After the end of the addition the reaction mixture was boiled for 30 minutes under reflux. After treating the solution with a cation exchange resin and

evaporating the resultant solution to dryness, N,N-bis-sulphoethane-aminomethanediphosphonic acid was obtained as a colourless oil, having the following analysis:

found:N: 3.6%, P: 14.9%, S: 15.8%

calculated:N: 3.44%, P: 15.21%, S: 15.75%

EXAMPLE 3.

50 g of 1-aminoethane-1, 1-diphosphonic acid and 40 g of chloroethanesulphonic acid were suspended in 200 ml of water. 240 g of 30% potassium hydroxide are added dropwise with vigorous stirring. The mixture was then boiled for 1 hour under reflux. To obtain the free N-sulphoethane-1-aminoethane-1,1-diphosphonic acid the reaction solution was treated with a cation exchange resin as in the previous examples, the solution obtained was evaporated, and the oily residue was washed out by forming a suspension in methanol or ethanol. The dried residue had the following analysis:

found:C: 15.2%, N: 4.6%, P: 19.4%, S: 10.9%

calculated:C: 15.34%, N: 4.47%, P: 19.78%, S: 10.22%.

EXAMPLE 4.

50 g of 1-aminoethane-1,1-diphosphonic acid were dissolved with 70 g of KOH in 200 ml of water, and 54 g of potassium chlorobutanesulphonate in 80 ml of water was added dropwise with stirring at a temperature between 40° and 50°C. After the addition, the reaction mixture was boiled for a further 1½ hours, the solution was weakly acidified, and was treated with an acid exchange resin to obtain N-sulphobutane-1-aminoethane-1,1-diphosphonic acid. The dry substance had the following analysis:

found:N: 4.2%, P: 17.8%, S: 9.8%

calculated:N: 4.11%, P: 18.16%, S: 9.39%.

EXAMPLE 5.

From 50 g of 1-aminoethane-1,1-diphosphonic acid (AEDP) and 50 g of NaOH, the tetrasodium salt of AEDP was obtained in the manner previously described, and was reacted as described in the previous examples with the sodium salt of 1-chlorooctane-2-sulphonic acid, N-sulphooctane-1-aminoethane-1,1-diphosphonic acid was obtained after removing the alkali metal ions by means of a cation exchange resin and evaporating the resultant solution under a water jet vacuum.

Analysis:

found: N: 3.6%, P: 15.7%, S: 8.3%

calculated: N: 3.52%, P: 15.61%, S: 8.05%.

Similar results were obtained by reacting the tetrapotassium salt of AEDP with potassium 1-chlorooctane-2-sulphonic acid.

EXAMPLE 6.

66 g of phenylaminomethanediphosphonic acid were suspended together with 48 g of potassium chloroethanesulphonate in 200 ml of water. 70 g of KOH in 100 ml of water was added with stirring. After boiling under reflux for 1 hour the solution obtained was treated as described above with a cation exchange resin to remove alkali metal ions and the potassium chloride formed, and the resultant solution is concentrated by evaporation to give N-sulphoethane phenyl aminomethanediphosphonic acid.

Analysis:

found: N: 3.8%, P: 16.2%, S: 8.9%

calculated: N: 3.74%, P: 16.55%, S: 8.57%.

EXAMPLE 7.

A solution was prepared from 75 g of 1-aminopropane-1, 1,3-triphosphonic acid, 48 g of sodium chloroethanesulphonate and 70 g of NaOH in 350 ml of water. This solution was boiled for 2 hours. After cooling and treating with a cation exchange resin, a solution of N-sulphoethane-1-aminopropane-1,1,3-triphosphonic acid is obtained, which, after evaportaion, gave a product having the following analysis:

found: N: 3.6% P: 22.4%, S: 7.4%

calculated: N: 3.44%, P: 22.82%, S: 7.88%.

EXAMPLE 8.

55 g of 1-aminopropane-1,1-diphosphonic acid were dissolved together with 48 g of sodium chloropropanesulphonate in 400 ml of water and 100 g of 50% caustic soda was added thereto. The reaction mixture was then boiled for 1 hour under reflux and was treated with a cation exchange resin to give N-sulphopropane-1-aminopropane-1,1-diphosphonic acid. The dry residue from the solution had the following analysis:

found: N: 4.4%, P: 18.0%, S: 9.6%

calculated: N: 4.11%, P: 18.16%, S: 9.39%.

EXAMPLE 9.

50 g of imino-bis-methanephosphonic acid and 38 g of chloroethanesulphonic acid were dissolved in 400 ml of water. 62 g of NaOH was added to this solution and the whole was boiled for 45 minutes. The solution was treated with a cation exchange resin and then evaporated to give N-sulphoethane-imino-bis-methanephosphonic acid having the following analysis:

found: C: 15.0%, N: 4.5%, P: 19.9%, S: 10.0%

calculated: C: 15.34%, N: 4.47%, P: 19.78%, S: 10.22%.

EXAMPLE 10.

A solution of 48 g of aminomethanediphosphonic acid, 56 g of KOH and 39 g of potassium hydroxymethanesulphonate was stirred for 3 hours at 70—75°C. Methanol was carefully added to the solution, which was then allowed to stand for some time, in order to obtain a crystallised salt. The crystalline product (crystalline product (potassium N-sulphomethyl-aminomethane-diphosphonate) was dried at 80°C *in vacuo*.

EXAMPLE 11.

27 g of 1,2-diaminoethane-1,1-diphosphonic acid and 38 g of potassium-1,2-dihydroxyethane-1,2-disulphonate were dissolved in 125 ml of 2N KOH, and the resulting solution was heated for 2 hours at 70° to 80°C and evaporated to half its volume *in vacuo*. Methanol was then carefully added thereto. A crystalline product precipitated on standing, which had the following analysis after drying at 50°C *in vacuo*:

found: K: 26.8%, C: 8.8%, N: 5.2, P: 10.5%, S: 11.9%.

EXAMPLE 12.

50 g of 1-aminoethane-1,1-diphosphonic acid was dissolved together with 43 g of KOH in 300 ml of water. 28 g of potassium bisulphite and 8 g of trioxane were added in portions. After this mixture had been heated for 2 hours at 50°C,

aminoethanediphosphonic acid could no longer be detected by thin layer chromatography.

EXAMPLE 13.

53 g of 1-aminopropane-1,1-diphosphonic acid were heated for 30 minutes at 80°C with 30 g of 30% formaldehyde solution and 180 ml of water. After cooling, a solution of 28 g of $K_2S_2O_5$ in 375 ml of 2N KOH was added dropwise and the reaction solution was kept for 1 hour at 65°C.

EXAMPLE 14.

25.6 g of imino-bis-methanephosphonic acid were heated for 2 hours at 60—70°C with 190 ml of 2N NaOH and 20 g of $HOCH_2SO_3Na.H_2O$ in 100 ml of $H_2O$. After cooling, the sodium salt of nitrilosulphomethane-bis-methanephosphonic acid was precipitated by adding methanol.

EXAMPLE 15.

A solution of the tetrapotassium salt of 48 g of aminomethanediphosphonic acid together with 45 g of potassium-2-hydroxyethane-1-sulphonate (potassium isethionate) in 200 ml of water was kept for 5 to 6 hours at a temperature of 190—230°C in a pressurised vessel. After cooling, the resultant solution is slightly acidified with dilute hydrochloric acid, treated with a cation exchange resin and evaporated under a water jet vacuum. After washing the residue with ethanol, N-sulphoethane-aminomethanediphosphonic acid was obtained as a colourless oil having the analysis:

found: C: 12.2%, N: 4.5%, P: 20.0%, S: 11.0%

calculated: C: 12.04%, N: 4.68%, P: 20.71%, S: 10.72%.

EXAMPLE 16.

Following the procedure of Example 15, 64 g of N-sulphoethane-1-aminoethane-1,1-diphosphonic acid was obtained from 51 g of 1-aminoethane-1,1-diphosphonic acid, 40 g of NaOH (or 56 g of KOH), and 40 g of sodium isethionate.

Analysis:

found: C: 15.7%, N: 4.6%, P: 20.0%, S: 10.1%

calculated: C: 15.34:, N: 4.47%, P: 19.78%, S: 10.22%.

EXAMPLE 17.

55 g of 1-aminopropane-1, 1-diphosphonic acid, 40 g of NaOH and 40 g of sodium-2-hydroxyethane-1-sulphonate (sodium isethionate) was reacted at 200°C and the resultant solution treated with a cation exchange resin to give 62 g of N-sulphoethane-1-aminopropane-1,1-diphosphonic acid having the following analysis:

found: N: 4.1%, P: 19.5%, S: 9.4%

calculated: N: 4.28%, P: 18.96%, S: 9.79%

EXAMPLE 18.

N-sulphoethane-phenylaminomethanediphosphonic acid was obtained following the procedure described in Example 15 from 67 g of phenylaminomethanediphosphonic acid, 40 g of NaOH and 40 g of sodium isethionate in 250 ml of water.

Analysis:

found: N: 3.9%, P: 16.9%, S: 8.3%

calculated: N: 3.74%, P: 16.55%, S: 8.56%.

EXAMPLE 19.

Following the procedure of Example 15, 56 g of N,N-bis-phosponomethaneaminoethanesulphonic acid were obtained from 51 g of imino-bis-methanephosphonic acid, 40 g of NaOH and 40 g of sodium isethionate in 250 ml of water.

Analysis:

found: C: 15.1%, N: 4.4%, P: 19.9%, S: 10.5%

calculated: C: 15.34%, N: 4.47%, P: 19.78%, S: 10.22%.

The analysis and Rf values from thin layer chromatography agree with the product obtained by phosphonomethylating taurine with phosphorous acid and formaldehyde.

EXAMPLE 20.

75 g of 1-aminopropane-1,1,3-triphosphonic acid were dissolved with 84 g of KOH and 46 g of potassium 2-hydroxyethane-1-sulphonate in 250 ml of water and heated at a temperature of about 210°C for 6 to 8 hours in a steel autoclave. To obtain the free N-sulphoethane-1-aminopropane-1,1,3-triphosphonic acid the solution obtained was cooled, slightly acidified with dilute hydrochloric acid, treated with a cation exchange resin and concentrated under a water jet vacuum. After washing the residue with methanol or ethanol, the free acid was obtained as a colourless oil which crystallised on prolonged standing. The product had the following analysis:

found: C: 14.1%, N: 3.5%, P: 23.0%, S: 7.7%

calculated: C: 14.75,% N: 3.44%, P: 22.82%, S: 7.87%.

EXAMPLE 21.

A solution of 47.8 g of aminomethanediphosphonic acid and 40 g of NaOH in 200 ml of water was added dropwise with stirring to a solution of 75 g of sodium vinyl sulphonate in 100 ml of water. After the end of the addition the temperature was gradually raised to the boiling point and the reaction mixture was boiled for 6 hours under reflux. After treating the solution with a cation exchange resin evaporating the solution thereby obtained to dryness, the residue was taken up in 300 ml of methanol and the residue insoluble in methanol was again dried. N,N-bis-sulphoethane-aminomethanediphosphonic acid was obtained, having the following analysis:

found:N: 3.7%, P: 14.9%, S: 15.9%

calculated:N: 3.44%, P: 15.21%, S: 15.75%.

EXAMPLE 22.

47.8 g of aminomethanediphosphonic acid were dissolved with 50 g of NaOH in 150 ml of water. A solution of 35 g of sodium vinyl sulphonate in 90 ml of water was added to the above solution and the mixture was boiled for 4 hours under reflux. After cooling, the mixture was slightly acidified with dilute hydrochloric acid, any aminomethanediphosphonic acid that had possibly precipitated was filtered off, and the solution was treated with a cation exchange resin to obtain the free sulphophosphonic acid. After concentrating the solution thereby obtained, the solution was taken up in methanol whereupon N-sulphoethaneaminomethanediphosphonic acid precipitated as a sparingly soluble residue. After drying, the residue had the following analysis:

found: C: 12.5% N: 4.8%, P: 20.2%, S: 11.0%

calculated:C: 12.04%, N: 4.68%, P: 20.71%, S: 10.72%.

EXAMPLE 23.

50 g of 1-aminoethane-1,1-diphosphonic acid, 40 g of NaOH and 35 g of

sodium vinyl sulphonate were reacted as described in Example 22. After washing with methanol, N-sulphoethane-1-aminoethane-1, 1-diphosphonic acid was obtained as an oily product, having the following analysis:

found:C: 15.0%, N: 4.7%, P: 19.9%, S: 10.0%

calculated:C: 15.34%, N: 4.47%, P: 19.78%, S: 10.24%.

EXAMPLE 24.

50 g of imino-bis-methanephosphonic acid were heated for 6 hours under reflux with 40 g of NaOH and 40 g of sodium-1-propene-1-sulphonate. A thin layer chromatogram of the solution shows only a very slight content of imino-bis-methanephosphonate. To obtain the free sulphoalkanephosphonic acid, the solution was treated with a cation exchange resin and the acid solution was evaporated and washed twice, in each case with 150 ml of methanol. The N-sulphopropane-imino-bis-methanephosphonic acid obtained as oily residue had the following analysis:

found:C: 18.0%, N: 4.4%, P: 18.1%, S: 10.2%

calculated:C: 18.36%, N: 4.28%, P: 18.94%, S: 9.80%

EXAMPLE 25.

47.8 g of aminomethanediphosphonic acid, 40 g of NaOH and 40 g of sodium-2-propenesulphonate in 300 ml of water was heated for 6 hours at 150°C in a pressurised vessel. After cooling, the reaction mixture was slightly acidified with dilute hydrochloric acid to remove unreacted aminomethanediphosphonic acid, which was filtered off. After treatment with a cation exchange resin concentration by evaporation, and washing with methanol, the product, N-sulphopropane-aminomethanediphosphonic acid, had the following analysis:

found:N: 4.3%, P: 19.2%, S: 11.0%

calculated:N: 4.47%, P: 19.78%, S: 10.22%

Instead of 2-propenesulphonate, 1-propene-3-sulphonate or 2-hexene-1-sulphonate may also be used. When using sodium-2-hexane-1-sulphonate, the product obtained had the following analysis:

found:N: 3.7%, P: 17.1%, S: 9.5%

calculated:N: 3.9%, P: 17.44%, S: 9.03%

EXAMPLE 26.

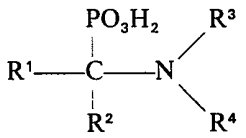
The tetrasodium (or tetrapotassium) salt of 47.8 g of aminomethanediphosphonic acid was heated with 66 g of disodium-2-butene-1,4-disulphonate in 200 ml of water for 6 hours at 150—160°C in a pressurised vessel. After this reaction time a thin layer chromatogram of the solution showed only traces of aminomethanediphosphonic acid. The solution was treated with a cation exchange resin as described in the previous examples, and the evaporation residue was washed with ethanol. The reaction product then had the following analysis.

found:N: 3.6%, P: 15.6%, S: 15.2%

calculated:N: 3.44%, P: 15.21%, S: 15.75%

WHAT WE CLAIM IS:—

1. As new compounds, compounds of the formula:

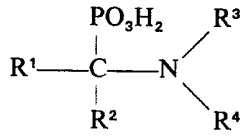


(I)

and alkali metal salts thereof, in which:

$R^1$ is a hydrogen atom,
a lower alkyl group containing from 1 to 6 carbon atoms,
a phenyl group,
a group of the formula $—R^5—NH_2$ or $—R^5—COOH$ (in which $R^5$ is a lower alkylene group containing from 1 to 6 carbon atoms), or a group of the formula $—R^6—PO_3H_2$ (in which $R^6$ is a lower alkylene group containing from 1 to 6 carbon atoms);
$R^2$ is a hydrogen atom or
a group of the formula $—PO_3H_2$;
$R^3$ is a group of the formula $—R^7—SO_3H$ (in which $R^7$ is an alkylene group containing from 1 to 11 carbon atoms optionally substituted with a phenyl group, hydroxy group or a group $—SO_3H$), or
a group of the formula $—R^8—PO_3H_2$ (in which $R^8$ is a lower alkylene group containing from 1 to 6 carbon atoms); and
$R^4$ is a hydrogen atom (if $R^3$ is not a group $—R^8—PO_3H_2$), a methyl group, or a group of the formula $—R^7—SO_3H_2$ (in which $R^7$ has the meaning defined above).

2. As new compounds, compounds of the general formula:

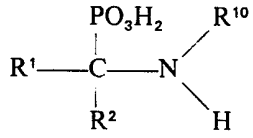


and alkali metal salts thereof, in which:

$R^1$ is a hydrogen atom, or
a methyl, ethyl, phenyl, carboxymethyl or aminomethyl group, or
a group $—C_2H_4PO_3H_2$;
$R^2$ is a hydrogen atom or a group $—PO_3H_2$;
$R^3$ is a group of the formula $—R^7—SO_3H$ (in which $R^7$ is an alkylene group containing from 1 to 11 carbon atoms) or a group $—CH_2PO_3H_2$; and
$R^4$ is a hydrogen atom (if $R^3$ is not a group $—CH_2PO_3H_2$), a methyl group, or a group of the formula $—R^7—SO_3H$ (in which $R^7$ has the meaning defined above).

3. Compounds as claimed in claim 1 specifically disclosed in any of the examples herein.

4. A process for the preparation of an alkali metal salt as claimed in claim 1 which comprises reacting an alkali metal salt of an aminophosphonic acid of the general formula:



in which $R^1$ and $R^2$ have the meanings defined in claim 1 and $R^{10}$ is a hydrogen atom, a methyl group, or a group $—R^8—PO_3H_2$ (in which $R^8$ has the meaning

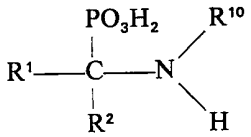
defined in claim 1); with a chloroalkane-sulphonic acid of the formula:

$$Cl—R^7—SO_3H$$

(in which $R^7$ has the meaning defined in claim 1); at an elevated temperature in an alkaline medium and in a molar ratio of aminosulphonic acid to chloroalkane sulphonic acid of from 1:1 to 1:2.

5. A process as claimed in claim 4 in which the reaction is carried out at a temperature of about 100°C.

6. A process for the preparation of an alkali metal salt as claimed in claim 1 which comprises reacting alkali metal salt of an aminophosphonic acid of the general formula:



in which $R^1$ and $R^2$ have the meanings defined in claim 1 and $R^{10}$ is a hydrogen atom, a methyl group or a group $—R^8—PO_3H_2$ (in which $R^8$ has the meaning defined in claim 1); with a hydroxyalkane-sulphonic acid of the formula:

$$HO—R^7—SO_3H$$

(in which $R^7$ has the meaning defined in claim 1), at an elevated temperature in an alkaline medium and in a molar ratio of aminophosphonic acid to hydroxyalkane-sulphonic acid of from 1:1 to 1:2.

7. A process as claimed in claim 6 in which the reaction is carried out at a temperature of from 180° to 240°C under elevated pressure.

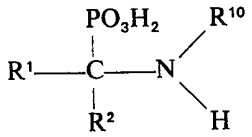
8. A modification of the process as claimed in claim 6 or claim 7 in which the hydroxyalkane-sulphonic acid is generated *in situ* in the reaction medium.

9. A process as claimed in claim 8 in which the hydroxyalkane-sulphonates is a 1-hydroxyalkane-1-sulphonate and is generated by the reaction of a corresponding aldehyde or acetyl with an alkali metal bisulphite.

10. A process as claimed in claim 8 in which the hydroxyalkane-sulphonic acid is 2-hydroxyethane-1-sulphonic acid and is generated *in situ* by reacting carbyl sulphate with the aminophosphonic acid to form the desired final product defined in claim 1.

11. A process as claimed in claim 8 in which the hydroxyalkane-sulphonic acid is 2-hydroxy-ethane-1-sulphonic acid and is prepared by the reaction of an alkali metal bisulphite and ethylene oxide, the alkali metal bisulphite being first added to the aminophosphonic acid, followed by the ethylene oxide.

12. A process for the preparation of an alkali metal salt compound as claimed in claim 1 which comprises reacting an alkali metal salt of an aminophosphonic acid of the general formula:—



in which $R^1$ and $R^2$ have the meanings defined in claim 1 and $R^{10}$ is a hydrogen atom or a group $—R^8—PO_3H$ (in which $R^8$ has the meaning defined in claim 1); with an alkenyl-sulphonic acid of the formula:

$$R^{11}—SO_3H$$

in which $R^{11}$ is an alkenyl group containing from 2 to 6 carbon atoms, optionally substituted with a phenyl group or a group $—SO_3H$; at elevated temperature in an alkaline medium and in a molar ratio of aminophosphonic acid to alkenesulphonic acid of from 1:1 to 1:2.

13. A process as claimed in claim 12 in which the reaction is carried out at a temperature of from 120 to 180°C.

14. A process as claimed in any one of claims 4—13 in which the reaction is carried out in an alkaline medium maintained at a pH of at least 9.

15. A process as claimed in any one of claims 4—14 in which the alkali metal salt obtained is subsequently converted to the free acid.

16. A process as claimed in claim 4 substantially as hereinbefore described with reference to Examples 1 to 9.

17. A process as claimed in claim 6 substantially as hereinbefore described with reference to Examples 10—11 and 14—19.

18. A process as claimed in claim 8 substantially as hereinbefore described with reference to Examples 12 and 13.

19. A process as claimed in claim 12 substantially as hereinbefore described with reference to Examples 21—26.

20. Compounds as claimed in claim 1 when obtained by a process as claimed in any one of claims 4—19.

MARKS & CLERK,
Chartered Patent Agents,
57—60 Lincoln's Inn Fields,
London, WC2A 3LS.
Agents for the Applicants.

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