

SPECIFICATION

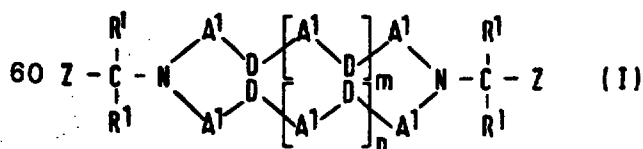
Substituted macrocyclic polyethers

- 5 The present invention relates to novel macrocyclic polyethers, to processes for the preparation of the novel macrocyclic polyethers as well as to complexes formed from the novel macrocyclic polyethers. The present invention
- 10 further relates to compositions, especially aqueous compositions, comprising one or more novel macrocyclic polyethers which can be used as cleaning agents, especially for cleaning a well penetrating an underground
- 15 formation and optionally cleaning formation parts in the vicinity of the said well. Finally, the present invention also relates to cleaning processes using a(n aqueous) composition comprising one or more novel macrocyclic
- 20 polyethers.

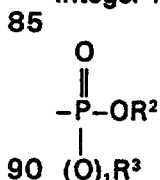
- Synthetic macrocyclic polyethers (often referred to as "crown ethers") are of great interest in that they contain intra-molecular cavities which are fit to accommodate alkali-metal or alkaline-earth metal ions depending on the particular shape of the macro(poly)cyclic polyether applied. Therefore, salts or alkali metals or alkaline-earth metals which are substantially insoluble in water become solubilized in the presence of certain macrocyclic polyethers. It is also possible to dissolve such salts in organic solvents such as benzene or toluene in the presence of certain macrocyclic polyethers. Reference is made in this respect
- 35 to British Patent Specification No. 1,304,367 and to Acc. of Chem. Res., Volume 11 (1978) pages 49-57.

- A novel class of macrocyclic polyethers has now been found which is of great interest, especially because the salts of the novel class of macrocyclic polyethers can be used as cleaning agents, in particular for dissolving water-insoluble inorganic deposits such as barium- and/or calcium deposits. The novel class
- 45 of macrocyclic polyethers according to the present invention is of particular interest in that closely related macrocyclic polyethers virtually lack the ability of dissolving substantially water-insoluble alkali(ne earth) metal salts. The compounds according to the present invention can moreover be prepared under moderate reaction conditions in good yields.

- The present invention therefore relates to
- 55 novel macrocyclic polyethers of the general formula:-

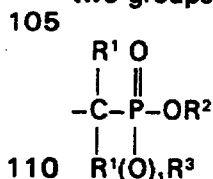


- wherein each A¹ which may be the same or different represents a hydrocarbon radical of up to 12 carbon atoms and each D which may be the same or different represents an
- 70 oxygen or sulphur atom or a hydrocarbon radical having up to 6 carbon atoms or a group N-R (R representing a hydrogen atom or a hydrocarbon radical having up to 12 carbon atoms, a hydrocarbon sulphonyl radical having up to 12 carbon atoms, an alkoxy-carbonyl-methylene radical having up to 4 carbon atoms or a carboxymethylene radical), at least 2 of the said D members representing an oxygen or a sulphur atom or a group N-R,
- 80 and each R¹ which may be the same or different represents a hydrogen atom, an alkyl group having up to 6 carbon atoms or a carboxy group, m and n are each 0 or an integer from 1 to 5 and Z represents a group



- wherein 1 is 0 or 1 and R² and R³ which may be the same or different represent a hydrogen atom or an alkyl group and the corresponding
- 95 salts.

- It has been found that the presence of just one carbon atom between the bridging-nitrogen atoms of the macrocyclic ring and the phosphorus atoms is essential for the performance of the salts of the macrocyclic polyethers according to formula I as cleaning agents. Thus, when a compound according to the general formula I is modified by replacing the two groups



- wherein 1 is 0 or 1 by two 2-phospho-ethyl groups (two carbon atoms being present between the respective phosphorus atom and the bridging nitrogen atom of the macrocyclic ring) or by two -CH₂-SO₃H groups (one carbon atom but a sulphur atom attached thereto rather than a phosphorus atom), the salts of the macrocyclic polyethers thus obtained appear to have insufficient complexing ability to dissolve water-insoluble alkaline-earth metal salts such as barium sulphate (see Comparative Experiments A-C).

- Preferred compounds according to the general formula I are those wherein each A¹ which may be the same or different represents a hydrocarbon radical having in the range of from 2 to 6 carbon atoms including a 1,2-phenylene radical, D represents an oxygen or
- 130 sulphur atom or a group N-R (R representing

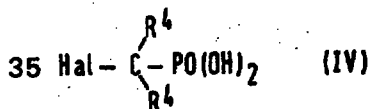


wherein each R¹ which may be the same or different has the meaning as defined hereinbefore, and optionally converting the acid obtained into the corresponding ester or salt.

- 5 This process according to the present invention can be carried out conveniently by dissolving a compound according to the general formula II (e.g. 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane) in water preferably in the presence of a mineral acid such as hydrochloric or hydrobromic acid or sulphuric acid in order to facilitate the reaction followed by the addition of the required amount of (hypo)phosphorous acid in aqueous solution and the required carbonyl-compound if desired a slight excess of the (hypo)phosphorous acid can be used. When using partial alkyl esters such as mono- or dialkyl phosphites or mono-alkylhypophosphites, the reaction should be carried out in the absence of mineral acids.

The above-mentioned process can be carried out conveniently at temperatures in the range of from 10°C to 120°C. Preference is given to temperatures in the range of from 40°C to 110°C.

The compounds according to the general formula I wherein 1 = 1 can also be prepared by reacting a compound according to the general formula II with a compound according to the general formula



wherein Hal represents a chlorine, bromine or iodine moiety and each R⁴ which may be the same or different represents a hydrogen atom or an alkyl group of up to 6 carbon atoms, in the presence of a base. Preferably, the reaction should be carried out in the presence of at least two moles of base per mole of compound according to the general formula II. Suitable bases comprise lithium hydroxide, sodium hydroxide, potassium hydroxide, and alkyl-substituted ammonium compounds such as tetra-alkyl-ammonium compounds. 2-Chloromethylphosphonic acid is a suitable starting material for the preparation of 1,10-bis(phosphonomethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane.

It was found convenient to heat the reaction mixture prior to the addition of the compound according to the general formula III. After adding the compound according to the general formula III either in an aqueous solution (when both R¹ represent a hydrogen atom) or as such (e.g. when both R¹ represent a methyl group) the reaction mixture is refluxed for a couple of hours.

The reaction mixture can be worked up by methods known in the art. The acid obtained

can be converted into a corresponding ester by methods known in the art, e.g. by treatment with an ortho ester, a trialkylphosphite or diazomethane. The corresponding salts can be obtained by adding a(n excess of a) base, preferably a base whose cation is not, or hardly compatible with the macrocyclic polyether. Examples of suitable bases comprise lithium hydroxide, sodium hydroxide, potassium hydroxide, ammonia as well as alkyl-substituted ammonium hydroxides. Very good results can be obtained using lithium hydroxide as the lithium salts of the macrocyclic polyethers according to the general formula I are very suitable in aqueous solutions for the dissolution of virtually water-insoluble inorganic salts.

It should be noted that also inner salts of the macrocyclic polyethers according to the general formula I, i.e. quaternary ammonium salts obtained by acidifying the macrocyclic polyethers according to the general formula I, are considered to be within the scope of the present invention.

The present invention also relates to compositions for dissolving salts whose cations are compatible with a macrocyclic polyether according to the general formula I, comprising one or more macrocyclic polyethers according to the general formula I.

The ability of macrocyclic polyethers to dissolve salts whose cations are compatible with the macrocyclic polyethers is well-known and based on their remarkable capability to form complexes with alkali- and alkaline-earth metal ions by holding them entrained within the frame-work formed by the hetero atoms occurring in the ring structure. This is of great interest as the complexes formed are generally readily soluble in polar solvents such as water, lower alkanols, ketones, halogenated alkanes and to a lesser extent in aromatic hydrocarbons such as benzene and toluene. The complexes are normally formed by dissolving the macrocyclic compound and the salt to be dissolved in a suitable solvent such as water, acetone, methanol or dichloromethane, if required under heating. Depending on the solubility of the complex concerned, a dissolved complex will be obtained or the complex will crystallize as such.

Of particular interest are those compositions which are capable of dissolving salts which are substantially insoluble in water such as

barium sulphate, barium carbonate, calcium sulphate and calcium carbonate. The presence of one or more of such salts as deposits on surfaces such as reaction flasks, vessels, pipelines, casings, tubings and bore-heads is undesired in that they tend to increase fouling of the equipment to an unacceptably high level.

Especially in the process of recovering oil from an oil containing sub-terranean formation via a well penetrating the formation, fouling of the tubular equipment in the well with barium

5 sulphate scale may cause undesirable low production rates. Further, precipitation of barium sulphate on the walls of the pore space during the oil-recovery operations will cause permeability decrease in the formation pore space which lowers production rates.

10 Barium sulphate scale can be deposited or formed from pressure and/or temperature changes in the flow of oil, or by the commingling of individually stable waters, of which one is rich in sulphate ions and the other in barium ions. Also fine barite particles that have been included in the drilling mud applied in drilling the well and that have
15 invaded the pay-zone of the formation cause a permanent cleaning of the formation parts.

As the time during which an oil well is being cleaned and out of operation should be as short as possible, the barium sulphate scale
20 must dissolve rapidly into the aqueous composition giving a barium complex which is highly soluble in water. In addition a high loading of the active ingredient is desirable. Aqueous compositions according to the present invention which contain salts of the 1,10-bis(phosphonomethyl)-1,10-diaza-4,7,13,16-tetraoxa-
25 cyclooctadecanes do contribute substantially to the dissolution of barium sulphate solids.

The concentration in which the salt of the macrocyclic polyether according to the general formula I is present in the aqueous solution is not critical. This concentration is suitably taken substantially equivalent to the saturation concentration of the complex of barium with the polyether in the aqueous composition under the prevailing conditions. Suitably, the concentration of the salt of the macrocyclic polyether is at least 0.01 mol/l and preferably higher than 0.05 mol/l, for example 0.3
40 mol/l.

The aqueous composition according to the present invention will normally be alkaline. It will be clear that protonation of the nitrogen bridging atoms in the macrocyclic polyether according to the general formula I will reduce its tendency to form barium complexes. Thus, the higher the pH, the higher the unprotonated portion of the macrocyclic polyether will become and, consequently, the higher the extent to which this macrocyclic polyether can be loaded up with barium ions. In view of this, the aqueous composition preferably has a pH of at least 8, more preferably of at least 10, and particularly a pH in the range of from
55 10 to 11.5. The unprotonated portion of the macrocyclic polyether can be increased by incorporating a base into the aqueous composition, preferably a base whose cation is hardly competitive, if at all, with the barium ion to be complexed by the macrocyclic polyether according to the general formula I; an example of a base that is not, or hardly competitive is lithium hydroxide.

It will be appreciated that the aqueous composition according to the present inven-

tion can be obtained in various ways. It is possible, for instance, to dissolve the salt of a macrocyclic polyether according to the general formula I in water, whether or not in the presence of an additional base. It is also possible and quite convenient to obtain an aqueous solution of an acid salt of a macrocyclic polyether according to the general formula I—e.g. the mono- or bis-hydrochloric acid salt
70 of 1,10-di(phosphonomethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane—, which solution is then treated with at least an equivalent amount of a base, preferably a base whose cation is hardly compatible, if at all, with the macrocyclic polyether structure. Thus, at least 4 equivalents of base (e.g. lithium hydroxide) should be used to convert a bis-hydrochloric acid salt as referred to hereinabove into a salt of a macrocyclic polyether according to the present invention. Good results have been obtained using up to 16, preferably up to 6 equivalents of base.

An other interesting method of obtaining an aqueous composition according to the present invention comprises the in situ production of the salts of the macrocyclic polyethers by reacting the corresponding macrocyclic polyether with a compound according to the general formula III and (hypo)phosphorous acid or
95 with a compound according to the general formula IV in the presence of an excess of a base. It is also possible to use the crude reaction mixture obtained in the synthesis of the salts of the macrocyclic polyethers according to formula I.

The cation of the salt of the macrocyclic polyether present in the aqueous composition may be any cation, for example, a lithium, sodium, potassium or an ammonium, or alkyl substituted ammonium-ion, for example a tetraalkyl substituted ammonium ion. This cation is preferably not, or hardly competitive with the barium ion to be complexed with the macrocyclic polyether according to formula I.
105 Preference is given to the use of lithium salts.

The aqueous composition used in the process according to the present invention may also contain well-treating or cleaning solution additives which are compatible with the composition. Such additives include, for example, surfactant materials. These surfactant materials may be ionic or nonionic. Examples are alkali metal salts or alkyl aryl sulphonates such as sodium dodecylbenzene sulphonate, alkali metal salts of sulphates of fatty alcohols such as sodium lauryl sulphate and materials having a polyoxyethylene chain. The surfactant material may be present in the composition in a concentration in the range of from,
120 for example, 1 to 3 percent by weight.

The contact time for dissolving a barium sulphate solid with the aqueous composition will vary not only with the conditions but also with the relative proportions of the constituents in the composition and will generally be

in the range of from 1 minute to three hours; for example from 5 minutes to 1.5 hours.

In general, when using an aqueous composition according to the present invention for dissolving a barium sulphate solid, there is no need to adopt temperatures substantially above ambient temperature. Temperatures as low as 10 to 20°C have been found satisfactory. However, the relatively high temperature (say 30–70°C or higher) prevailing in an oil-producing formation into which a production well penetrates, greatly enhances the dissolution of the solid. As discussed hereinbefore, this of great advantage for the in situ preparation of the salts of the macrocyclic polyethers according to formula I.

It will be appreciated that aqueous compositions according to the present invention can also be applied when other types of scale and/or compounds whose ions can be accommodated by the salts of macrocyclic polyethers according to formula I are present in wells and/or formation parts in the vicinity of said wells. The aqueous compositions can be suitably applied when for instance, calcium sulphate solid is also present in the well and/or the formation parts in the vicinity of said well.

It should be noted that the compounds according to the general formula I wherein $1 = 0$ ("phosphinico compounds") may be converted into the corresponding "phosphono compounds" ($1 = 1$) under oxidizing conditions. Such conditions, e.g. the presence of oxygen or air and/or metal ions which can catalyse oxidation reactions may prevail when (aqueous) compositions comprising phosphinico compounds are used as cleaning agents, especially for cleaning wells penetrating underground formations. It is likely that under such conditions a mixture of phosphinico and phosphono compounds will cause the complexation of barium and/or calcium ions. It is also possible that the phosphinico compounds disproportionate to some extent under the prevailing conditions to give a phosphine and a phosphonic acid in a 1:2 ratio.

The present invention is illustrated by means of the following Examples. The experiments described below test the dissolving-capacities of several aqueous compositions were carried out in a cylindrical glass vessel having a height of 2.5 cm and an internal diameter of 0.8 cm and containing five stainless-steel balls with a diameter of 0.32 cm. The vessel was charged with the starting materials and then fixed lengthwise to a horizontal shaft parallel to its central axis. The shaft was rotating at a speed of 180 revolutions per minute. The temperature of the vessel was 20°C unless otherwise indicated.

EXAMPLE 1

(a) 1,10-Bis(phosphonomethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane was pre-

pared as follows. To a solution of 1.31 g (5 mmol) 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane in 4 ml of a mixture of conc.

HCl/H₂O (1:1) was added 2.37 ml of 30% H₃PO₃ (10 mmol). The reaction mixture was heated to 100°C and 1.6 ml of 37% formaldehyde was added after which the reaction mixture obtained was refluxed during 4 hours. Thereafter the reaction mixture was evaporated until dryness and the residue treated with dry ethanol (25 ml) from which 1.4 g mono HCl salt of 1,10-bis(phosphonomethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (2.88 mmol, 58% yield) precipitated. From the mother liquor a further crop of 0.64 g could be isolated giving a total yield of 2.04 g (4.19 mmol, 84% yield).

The mono HCl salt which had precipitated had m.p. 258–260°C

Analysis for the mono HCl salt (C₁₄H₃₃ClN₂O₁₀P₂):

Calculated: C:34.5; H 6.8; N 5.8; O 32.9; Cl:7.3; P 12.8%.

Found: C:33.8; H 6.6; N 5.7; O 33.0; Cl:7.2; P 13.4%.

The P.M.R., ¹³C NMR and ³¹P NMR-data (all recorded using D₂O as the solvent) were in accordance with the expected structure.

(b) The vessel was charged with barium sulphate (0.45 mmol), water (1.5 ml), 1,10-bis(phosphonomethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (0.15 mmol) and so much lithium hydroxide that the aqueous solution in the vessel had a pH of 11. After 30 minutes of rotation the suspension was allowed to separate by settling. A sample drawn from the aqueous layer contained dissolved barium sulphate (11.1 g/l). Hence the lithium salt of 1,10-bis(phosphonomethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane had been used with an efficiency of

$$\frac{11.1}{233.2 \times 0.1} \times 100 = 47.8\%$$

After 3 hours of rotation the efficiency had become 54.1% and after 24 hours of rotation the efficiency was 65.2% (15.2 g barium sulphate dissolved per litre) determined by SO₄²⁻-analysis. Within the limits of experimental error the same results were obtained by SO₄²⁻ as well as by Ba²⁺ analysis.

(c) The experiment described under (b) was repeated at a temperature of 70°C. After 24 hours of rotation the efficiency of the lithium salt of 1,10-bis(phosphonomethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (0.37 mmol) was 78% determined by SO₄²⁻ analysis (18.2 g barium sulphate dissolved per litre).

(d) The vessel was charged with water (1.2 ml), natural barite (524 mg, grain size 4 mm) and

1,10-bis(phosphonomethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (0.37 M). Then so much lithium hydroxide was added that the pH of the aqueous liquid had a value of 11. The natural barite contained the following compounds:

Compound	%w	Compound	5W
BaSO ₄	80	Fe ₂ O ₃	3
SiO ₂	13	SrSO ₄	2

Hence, 1.8 mmol of barium sulphate was present in the flask. After 97.5 hours' rotation the liquid contained dissolved barium sulphate in a concentration of 0.088M (20.9g barium sulphate dissolved per litre). Thus the phosphono compound has been used with an efficiency of

$$\frac{0.088}{0.37} \times 100 = 24\%$$

(e) The experiment described under (d) was repeated at a temperature of 70°C. After 96 hours' rotation the efficiency of the lithium salt of the phosphono compound amounted to 53% as determined by SO₄²⁻ analysis.

30 Comparative Experiment A

This experiment differed from that described in Example 1b in that the phosphono compound was replaced by 1,10-bis(2-phosphonoethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (0.1 M). This compound was obtained by reacting 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane with ethylene oxide, heating the 2-hydroxy ethyl compound obtained with thionyl chloride and converting the 2-chloro ethyl compound obtained with the triethyl ester of phosphorous acid followed by acid hydrolysis. The sample drawn after 20 hours' rotation from the aqueous layer contained dissolved sulphate in an amount of 1.5 g/l. No barium ions could be detected in the aqueous layer indicating that most of the complexed barium was present in the vessel as an unwanted solid. This clearly indicates that the presence of an additional carbon atom between the bridging nitrogen atom of the macrocyclic ring and the phosphorous atom virtually destroys the complexing/dissolving ability.

55 Comparative Experiment B

This experiment differed from that described in Example 1b in that the phosphono compound was replaced by 1,10-bis(2-ethylmonophosphate)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (0.1 M). This compound was obtained by reacting the 2-hydroxyethyl compound mentioned in Comparative Experiment A with chlorophosphoric acid diphenyl ester in the presence of sodium hydride in tetrahydrofuran followed by hydrogenolysis

over platinum in acetic acid. The sample drawn after 20 hours' rotation from the aqueous layer contained dissolved barium and dissolved sulphate in amounts of 0.05 and 0.8 g/l, respectively, calculated as barium sulphate, indicating that most of the complexed barium was present in the vessel as an unwanted solid. Hence the 1,10-bis(2-ethylmonophosphate)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane had been used with an efficiency of

$$\frac{0.05}{233.2 \times 0.1} \times 100 = 0.2\%$$

on barium and with an efficiency of

$$\frac{0.8}{233.2 \times 0.1} \times 100 = 3.5\%$$

on sulphate.

90 Comparative Experiment C

This experiment differed from that described in Example 1b in that the phosphono compound was replaced by 1,10-bis(sulphonomethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (0.1 M). This compound was obtained by reacting 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane with sodium sulphite and 37% formaldehyde (see example 2a). The sample drawn after 24 hours' rotation contained dissolved barium in an amount of 0.2 g/l, determined by Ba⁺⁺ analysis. Hence the efficiency of the lithium salt of the sulphonomethyl compound was 0.9%, which clearly indicates that the complexing/dissolving ability is virtually destroyed when the phosphonate is replaced with the sulphonate.

EXAMPLE 2

(a) 1,10-Bis(phosphinicomethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane was prepared by adding to a solution of 1.31 g (5 mmol) 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane in 4 ml conc. HCl/H₂O (1:1) 1.06 ml 50% hypophosphorous acid (10 mmol). The reaction mixture was heated until reflux followed by the addition of 1.6 ml 37% formaldehyde (20 mmol). The reaction mixture obtained was refluxed during 6 hours. After cooling the pH was adjusted with LiOH to pH 6-7. A sample of 1.3 ml was drawn from the reaction mixture (see Example 2b) and the resulting product was then purified over an ion-exchange column (IR 120 (H)). The resultant phosphinico-compound containing fractions were collected and boiled down. This resulted in 1.45 g (2.95 mmol; 74% yield) of the di-HCl salt of 1,10-bis(phosphinicomethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane, a hygroscopic, frothy product.

Analysis for the di-HCl-salt ($C_{14}H_{34}Cl_2N_2O_8P_2$):
 Calculated: C:34.2; H:7.0; N:5.7; O:26.0;
 P:12.6; Cl:14.4%
 5 Found: C:31.0; H:6.2; N:4.7; O:27.3;
 P:10.6; Cl:15.3%

(metal containing residue of 7.6% was found, likely from entrained LiCl). The PMR, ^{13}C

10 NMR and ^{31}P NMR-data (all recorded using D_2O as the solvent) were in accordance with the expected structure.

(b) The vessel was charged with barium sulphate (0.3 mmol/ml) and the sample referred to in Example 2a (1.3 ml) which had been made alkaline with lithium hydroxide to pH = 11 and diluted to 10 ml. The concentration of the phosphinico compound was 0.1 M. After 24 hours of rotation the suspension

20 was allowed to separate by settling. A sample drawn from the aqueous layer contained dissolved barium sulphate (4.4 g/l) Hence, the lithium salt of the phosphinico compound had been used with an efficiency of

$$\frac{4.4}{233.2 \times 0.1} \times 100 = 18.9\%$$

30 EXAMPLE 3

(a) 1,10-Bis(phosphinico(alpha-methyl)methyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane was prepared in the manner described

35 in Example 2a using acetaldehyde (0.6ml, about 10 mmol in 1.5 ml water) instead of formaldehyde. The conversion, followed by NMR-analysis was about 35%. The product was directly treated with lithium hydroxide

40 (see Example 3b).

The compound was characterized by ^1H , ^{13}C and ^{31}P NMR in D_2O .

The following signals were assigned:

^1H NMR in D_2O/HCl (H_2O as 0 ppm):

45 δ : -0.98 (t); -1.08 (m) and -3.44 (m).

^{13}C NMR in D_2O :

δ = 73.2 (ethylene carbon atoms between oxygen atoms);

66.6 (carbon atoms of an ethylene group next to the oxygen atom and between an oxygen and a nitrogen atom); 54.6 (carbon atoms of an ethylene group next to the nitrogen atom and between an oxygen and a nitrogen atom); and 10.7 (carbon atom of the alpha methyl group). Also a coupling constant of 10Hz (C-P) was recorded.

55 ^{31}P NMR in D_2O : δ - 36.8ppm (ext. reference 85% H_3PO_4).

(b) The reaction mixture obtained in the experiment described in example 3a (8 ml) was made alkaline with lithium hydroxide to pH = 11 and diluted to 16.5 ml (thus obtaining the alpha-methyl phosphinico-compound in a concentration of 0.1 M). After 24 hours

65 of rotation with 0.3 mmol/ml barium sul-

phate the suspension was allowed to separate by settling. A sample drawn from the aqueous layer contained dissolved barium sulphate (2.1 g/l). Hence, the lithium salt of the alpha-methyl phosphinico compound had been used with an efficiency of 8.9%. It should be noted that unreacted starting material (1,10-diaza-4,7,13,16-tetraoxacyclooctadecane) has also some ability to complex barium-ions under the prevailing conditions. It was found that the unreacted starting material could dissolve no more than 0.2 g barium sulphate per litre under these conditions.

(c) The experiment described in Example 3a

80 was repeated using phosphorous acid (30%) rather than hypophosphorous acid. The reaction was rather slow as followed by NMR-analysis and at 10% conversion (NMR-analysis) lithium hydroxide was added until the pH of the reaction mixture was 11. The total (diluted) reaction mixture was 8 ml which did not contain more than 0.5 mmol of 1,10-bis(phosphono(alpha-methyl)methyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane. This

85 mixture was used in the manner described hereinbefore to dissolve barium sulphate. After 24 hours' rotation and working up, 0.66 g of barium sulphate had dissolved per litre (uncorrected for starting material) amounting

90 to an efficiency of about 4.5%.

(d) The experiment described in Example 2a was repeated using acetone (1.2g, 20 mmol) in 1.5 ml H_2O instead of formaldehyde. The reaction was followed with NMR-analysis and a conversion of 10% of the starting material into 1,10-bis(phosphinico(alpha,alpha-dimethyl)methyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane was calculated based on the following ^1H , ^{13}C , and ^{31}P

105 NMR signals:

^1H NMR in D_2O/HCl (H_2O as 0 ppm):

δ = -1.02; -1.12 (ring protons); -3.54 (d, alpha methyl groups).

^{13}C NMR in D_2O : in addition to signals attributed to the ring also δ = 25.3 (alpha methyl groups, d). A coupling constant of 10Hz (C-C-P) was recorded. ^{31}P NMR in $H_2O/D_2O/HCl$: -40.5 ppm (ext. reference 85% H_3PO_4). The reaction mixture was used

110 for testing in the manner described in example 3c. After 24 hours' rotation and working up, 0.55 g of barium sulphate had dissolved per litre (uncorrected for starting material) amounting to an efficiency of about

115 3.2%.

Example 4

To a solution of 100 mg 1,10-bis(phosphono-methyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (0.2 mmol) in 2ml water was added so much LiOH that the pH reached the value 11. Then calcium sulphate (15 mg, 0.11 mmol) was added at room temperature under stirring. The calcium sulphate solid dissolved

125 almost instantaneously. Thereafter a further

130

amount of calcium sulphate solid (13 mg, 0.096 mmol) was added. The resultant mixture was stirred but no clear solution was obtained. Upon the addition of a further amount of 16 mg, 1,10-bis(phosphonomethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (0.04 mmol) the mixture became clear almost immediately. Thus the phosphono compound had been loaded up to 87%.

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Example 5

(a) The vessel was charged with barium sulphate (0.45 mmol) and a solution of 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (0.1 M), sodiumphosphite (0.2 M) and 37% formaldehyde (0.2 M) in 1.5 ml water. The reaction mixture was kept under stirring at ambient temperature during 24 hours. A sample drawn after settling of the suspension contained equal amounts of dissolved barium and dissolved sulphate. The efficiency of the in situ prepared sodium salt of 1,10-bis(phosphonomethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (calculated as the amount of BaSO₄ (mole) dissolved per mole of 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane charged) was 3.1%. It should be noted that the efficiency of 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane under the same conditions amounts to 0.4%.

The experiment was repeated at a temperature of about 70°C. The efficiency of the in situ prepared sodium salt had increased to 5.7%, calculated on the amount of BaSO₄ (mole) dissolved per mole of 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane.

(b) A crude reaction mixture obtained by reacting 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (0.1 M), phosphorous acid (0.2 M) and formaldehyde (0.4 M) in acidic medium (6N HCl) to pH = 11 was used after the addition of an excess of lithium hydroxide as the "macrocylic polyether". The efficiency on dissolving solid barium sulphate (0.3 mole per litre) at 20°C after 24 hours under standard conditions as described in Example 1b was 49% (calculated on 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane charged, indicating a yield of 75%).

In the cleaning method according to the invention, the (aqueous) cleaning compositions adapted for dissolving solids, especially barium sulphate are contacted with the surfaces to be cleaned for a period of time sufficiently long to remove at least a portion of the solid (barium sulphate scale) on said surfaces. Hereby, the composition may be circulated over the surfaces to be cleaned. Thus, when cleaning equipment in a well, the composition may be circulated through the tubular goods in the well, such as by being pumped down through the production tube and being returned to the surface through the annular space between the production tubes and the casing (or vice versa). Also, the com-

position may be pumped down through the production tubing and into the formation, thereby cleaning the well and the formation pore space by dissolving barium sulphate present therein whilst flowing along the surfaces that need cleaning. The spent composition of such once-through-dynamic was procedure is later on returned to the surface by the fluids that are produced through the well after the cleaning operation. In an alternative manner, the cleaning composition may be applied batchwise. The composition is then pumped down in the well and optionally in the pore space of the formation parts to be cleaned and kept in contact in non-flowing condition with the surfaces that are covered with barium sulphate scale, over a period of time sufficiently long to dissolve at least a considerable part of said scale. It is also possible to pump down through the production tubing and into the formation the reactants (the macrocyclic polyether according to formula I, the (hypo)-phosphorous acid and the compound according to formula III, in particular 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane, phosphorous acid and an aqueous solution of formaldehyde) which cause in situ formation of the salt of the macrocyclic polyether according to formula I which will then exert its cleaning activities under the prevailing conditions. Also crude reaction mixtures can be pumped down through the production tubing and into the formation. If desired, the cleaning composition, or portions thereof, in which barium sulphate has been dissolved can be acidified to obtain the macrocyclic polyether according to formula I so that it can be recovered and reused.

105 CLAIMS

1. Macrocylic polyethers according to the general formula:-

110



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wherein each A¹ which may be the same or different represents a hydrocarbon radical of up to 12 carbon atoms and each D which may be the same or different represents an oxygen or sulphur atom or a hydrocarbon radical having up to 6 carbon atoms or a group N-R (R representing a hydrogen atom or a hydrocarbon radical having up to 12 carbon atoms, a hydrocarbon sulphonyl radical having up to 12 carbon atoms, an alkoxy-carbonyl-methylene radical having up to 4 carbon atoms or a carboxymethylene radical), at least 2 of said D members representing an oxygen or a sulphur atom or a group N-R, and



amount of calcium sulphate solid (13 mg, 0.096 mmol) was added. The resultant mixture was stirred but no clear solution was obtained. Upon the addition of a further amount of 16 mg, 1,10-bis(phosphonomethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (0.04 mmol) the mixture became clear almost immediately. Thus the phosphono compound had been loaded up to 87%.

Example 5

(a) The vessel was charged with barium sulphate (0.45 mmol) and a solution of 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (0.1 M), sodiumphosphite (0.2 M) and 37% formaldehyde (0.2 M) in 1.5 ml water. The reaction mixture was kept under stirring at ambient temperature during 24 hours. A sample drawn after settling of the suspension contained equal amounts of dissolved barium and dissolved sulphate. The efficiency of the in situ prepared sodium salt of 1,10-bis(phosphonomethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (calculated as the amount of BaSO_4 (mole) dissolved per mole of 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane charged) was 3.1%. It should be noted that the efficiency of 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane under the same conditions amounts to 0.4%.

The experiment was repeated at a temperature of about 70°C. The efficiency of the in situ prepared sodium salt had increased to 5.7%, calculated on the amount of BaSO_4 (mole) dissolved per mole of 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane.

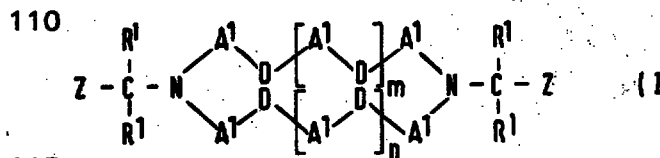
(b) A crude reaction mixture obtained by reacting 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (0.1 M), phosphorous acid (0.2 M) and formaldehyde (0.4 M) in acidic medium (6N HCl) to pH = 11 was used after the addition of an excess of lithium hydroxide as the "macrocylic polyether". The efficiency on dissolving solid barium sulphate (0.3 mole per litre) at 20°C after 24 hours under standard conditions as described in Example 1b was 49% (calculated on 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane charged, indicating a yield of 75%).

In the cleaning method according to the invention, the (aqueous) cleaning compositions adapted for dissolving solids, especially barium sulphate are contacted with the surfaces to be cleaned for a period of time sufficiently long to remove at least a portion of the solid (barium sulphate scale) on said surfaces. Hereby, the composition may be circulated over the surfaces to be cleaned. Thus, when cleaning equipment in a well, the composition may be circulated through the tubular goods in the well, such as by being pumped down through the production tube and being returned to the surface through the annular space between the production tubes and the casing (or vice versa). Also, the com-

position may be pumped down through the production tubing and into the formation, thereby cleaning the well and the formation pore space by dissolving barium sulphate present therein whilst flowing along the surfaces that need cleaning. The spent composition of such once-through-dynamic was procedure is later on returned to the surface by the fluids that are produced through the well after the cleaning operation. In an alternative manner, the cleaning composition may be applied batchwise. The composition is then pumped down in the well and optionally in the pore space of the formation parts to be cleaned and kept in contact in non-flowing condition with the surfaces that are covered with barium sulphate scale, over a period of time sufficiently long to dissolve at least a considerable part of said scale. It is also possible to pump down through the production tubing and into the formation the reactants (the macrocyclic polyether according to formula I, the (hypo)-phosphorous acid and the compound according to formula III, in particular 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane, phosphorous acid and an aqueous solution of formaldehyde) which cause in situ formation of the salt of the macrocyclic polyether according to formula I which will then exert its cleaning activities under the prevailing conditions. Also crude reaction mixtures can be pumped down through the production tubing and into the formation. If desired, the cleaning composition, or portions thereof, in which barium sulphate has been dissolved can be acidified to obtain the macrocyclic polyether according to formula I so that it can be recovered and reused.

CLAIMS

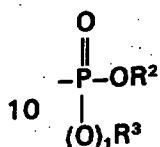
1. Macrocyclic polyethers according to the general formula:-



wherein each A^1 which may be the same or different represents a hydrocarbon radical of up to 12 carbon atoms and each D which may be the same or different represents an oxygen or sulphur atom or a hydrocarbon radical having up to 6 carbon atoms or a group N-R (R representing a hydrogen atom or a hydrocarbon radical having up to 12 carbon atoms, a hydrocarbon sulphonyl radical having up to 12 carbon atoms, an alkoxy-carbonyl-methylene radical having up to 4 carbon atoms or a carboxymethylene radical), at least 2 of said D members representing an oxygen or a sulphur atom or a group N-R, and

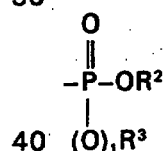


each R^1 which may be the same or different represents a hydrogen atom, an alkyl group having up to 6 carbon atoms or a carboxy group, m and n are each 0 or an integer from 1 to 5 and Z represents a group



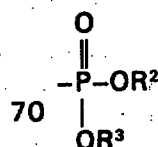
wherein 1 is 0 or 1 and R^2 and R^3 which may be the same or different represents a hydrogen atom or an alkyl group, and the corresponding salts.

2. Compounds according to claim 1, wherein each A^1 which may be the same or different represents a hydrocarbon radical having in the range of from 2 to 6 carbon atoms including a 1,2-phenylene radical, D represents an oxygen or a sulphur atom or a group N-R (R representing a hydrogen atom, an alkyl group of up to 6 carbon atoms, a hydrocarbon sulphonyl radical of up to 6 carbon atoms or an alkoxy-carbonyl-methylene radical having up to 4 carbon atoms or a carboxymethylene radical); at least 4 of the said D members representing oxygen atoms and/or groups N-R; and each R^1 which may be the same or different represents a hydrogen atom, an alkyl group having up to 4 carbon atoms or a carboxy group; m and n are 1 or 2; and Z represents a group



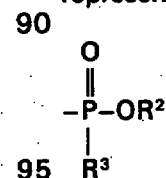
wherein 1 is 0 or 1 and R^2 and R^3 which may be the same or different represent a hydrogen atom or an alkyl group of up to 6 carbon atoms, and the corresponding salts.

3. Compounds according to claim 1, wherein each A^1 which may be the same or different represents an ethylene, diethylene, triethylene or tetraethylene radical, particularly an ethylene radical; D represents an oxygen atom or a group N-R (R representing an alkyl group of up to 4 carbon atoms, particularly a methyl group, a hydrocarbon sulphonyl radical of up to 4 carbon atoms or a methoxy- or ethoxycarbonyl radical); at least 4 of the said D members representing an oxygen atom; and each R^1 which may be the same or different represents a hydrogen atom or a methyl or ethyl group; m and n are 1 or 2; and Z represents a group



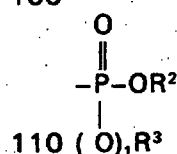
wherein R^2 and R^3 both represent a hydrogen atom, and the corresponding salts.

4. Compounds according to claim 1, wherein each A^1 may be the same or different represents an ethylene, diethylene, triethylene or tetraethylene radical, particularly an ethylene radical; D represents an oxygen atom or a group N-R (R representing an alkyl group of up to 4 carbon atoms, particularly a methyl group, a hydrocarbon sulphonyl radical of up to 4 carbon atoms or a methoxy- or ethoxy carbonyl radical); at least 4 of the said D members representing an oxygen atom; and each R^1 which may be the same or different represents a hydrogen atom or a methyl or ethyl group; m and n are 1 or 2; and Z represents a group



wherein R^2 and R^3 both represent a hydrogen atom, and the corresponding salts.

5. Compounds according to claim 3 or 4, wherein A^1 represents an ethylene radical; D represents an oxygen atom; and each R^1 which may be the same or different represents a hydrogen atom or a methyl or ethyl group; m and n are both 1; and Z represents a group



wherein 1 is 0 or 1, and R^2 and R^3 both represent a hydrogen atom and the corresponding salts.

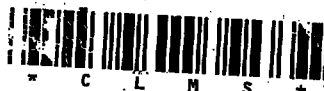
6. 1,10-Bis(phosphonomethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane and alkyl esters and salts thereof.

7. 1,10-Bis(phosphono(alpha-methyl)methyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane and alkyl esters and salts thereof.

8. 1,10-Bis(phosphinicomethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane and alkyl esters and salts thereof.

9. 1,10-Bis(phosphinico(alpha-methyl)methyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane and alkyl esters and salts thereof.

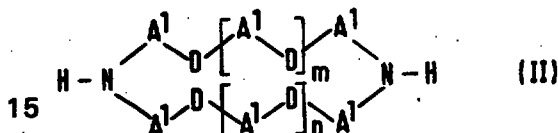
10. 1,10-Bis(phosphinico(alpha,alpha-dimethyl)methyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane and alkyl esters and salts thereof.



11. A complex formed from a compound as defined in any one of claims 1-10 with a cation being compatible (as hereinbefore defined) with such compound.

- 5 12. Process for the preparation of macrocyclic polyethers according to the general formula I or esters or salts thereof which comprises reacting a macrocyclic polyether according to the general formula:-

10



- 20 wherein A¹, D, m and n have the meanings as defined in claim 1 with (hypo)phosphorous acid or partial alkyl esters thereof in the presence of a compound according to the general formula

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- wherein each R¹ which may be the same or different has the meaning as defined in claim 1, and optionally converting the acid obtained
- 35 into the corresponding ester or salt.

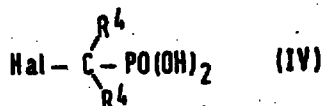
13. Process according to claim 12 wherein the reaction between a macrocyclic polyether according to formula II and (hypo)phosphorous acid is carried out in the presence of a compound according to the general formula III at a temperature in the range of from 10°C to 120°C, preferably in the range of from 40°C to 110°C.

14. Process according to claim 12 or 13, wherein a macrocyclic polyether according to formula II and (hypo)phosphorous acid are heated in the presence of aqueous formaldehyde.

15. Process according to any one of claims 12-14 and substantially as hereinbefore described with reference to the Examples.

16. Process for the preparation of macrocyclic polyethers according to the general formula I wherein I = 1, which comprises reacting a compound according to the general formula II with a compound according to the general formula

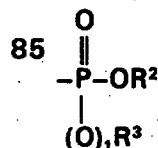
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wherein Hal represents a chlorine, bromine or iodine moiety and each R⁴ which may be the same or different represents a hydrogen atom or an alkyl group of up to 6 carbon atoms, in the presence of a base.

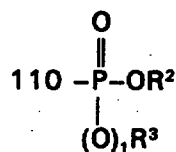
17. A composition for dissolving salts whose cations are compatible (as hereinbefore defined) with a macrocyclic polyether according to the general formula I comprising one or more macrocyclic polyethers according to the general formula I.

18. A composition according to claim 17 comprising water as the solvent and a salt of a macrocyclic polyether according to the general formula I, wherein A¹, D, R, R¹, m and n are as defined hereinbefore and Z represents a group



- 90 wherein I is 0 or 1 and R² and R³ which may be the same or different represent a hydrogen atom or an alkyl group provided that at least one of R² and R³ represents a cation which is not, or hardly competitive with the cation of the salt to be dissolved.

19. An aqueous composition according to claim 18, especially for dissolving barium sulphate solid comprising a salt of a macrocyclic polyether according to the general formula I, wherein A¹ represents an ethylene, diethylene, triethylene or tetraethylene radical particularly an ethylene radical, D represents an oxygen atom; each R¹ which may be the same or different represents a hydrogen atom or a methyl- or ethyl group; m and n are 1 or 2; and Z represents a group



- wherein I is 0 or 1 and R² and R³ which may be the same or different represent a hydrogen atom or an alkyl group of up to 6 carbon atoms provided that at least one of R² and R³ represents a cation which is not, or hardly competitive with the cation of the salt to be dissolved.

20. An aqueous composition according to claim 19, comprising a lithium or sodium salt of 1,10-bis(phosphonomethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane.

21. A composition according to any one of claims 17-20, substantially as hereinbefore described with reference to the Examples.

22. Process for cleaning surfaces covered with substantially insoluble salts whose cations are compatible with a macrocyclic poly-



ether according to the general formula I by contacting the surfaces with a (an aqueous) composition as claimed in any one of claims 17-21.

- 5 23. Process according to claim 22, especially for cleaning a well penetrating an underground formation and optionally formation parts in the vicinity of the said well by contacting the well and/or said formation parts with an aqueous composition as claimed in any one of claims 17-21.

- 10 24. Process according to claim 22 or 23, in which the aqueous composition has a pH of at least 8, preferably in the range of from 10 to 11.5.

- 15 25. Process according to any one of claims 22-24, in which the aqueous composition also contains a base whose cation is not, or hardly competitive with the cation to be complexed with the macrocyclic polyether according to formula I.

- 20 26. Process according to any one of claims 22-25, in which an aqueous composition is used in which the salt of the macrocyclic polyether according to the general formula I is formed in situ.

- 25 27. Process according to claim 26, in which an aqueous composition is used which comprises a crude reaction mixture obtained by a process as claimed in any one of claims 12-16 and a (an excess of a) base.

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