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WO 2007/057235 A2

(54) Title: CELLULOSE SOLUTIONS IN IONIC LIQUIDS

(54) Bezeichnung: LÖSUNGEN VON CELLULOSE IN IONISCHEN FLÜSSIGKEITEN

(57) Abstract: The invention relates to a solution containing cellulose and an ionic liquid containing anions and cations as a solvent, the cations being provided with at least one atom selected among the group comprising nitrogen, oxygen, sulfur, and phosphorus supplied in a protonated form. Also disclosed are methods for the production and use thereof for a physical and chemical treatment.

(57) Zusammenfassung: Die vorliegende Erfindung betrifft eine Lösung enthaltend Cellulose und eine ionische Flüssigkeit enthaltend Anionen und Kationen als Lösemittel, wobei die Kationen mindestens ein Atom ausgewählt aus der Gruppe bestehend aus Stickstoff, Sauerstoff, Schwefel und Phosphor aufweisen, das in protonierter Form vorliegt, sowie Verfahren zu deren Herstellung und Verwendung zur physikalischen und chemischen Behandlung.

As originally filed

Solutions of cellulose in ionic liquids

5 Description

The present invention relates to a solution comprising cellulose and an ionic liquid as solvent, a process for preparing it and its use.

10 Cellulose is a very versatile raw material. In the textile industry, cellulose is, for example, the most important constituent of fiber raw materials, in particular of cotton.

Cellulose can be used unchanged or after physical or chemical treatment. In the latter two cases, it is advantageous for cellulose to be in preferably completely dissolved

15 form in a solvent. However, cellulose is insoluble in most solvents.

Cellulose is soluble as a copper chelate complex in some copper solutions.

Regenerated cellulose can be obtained by precipitation of the cellulose. However, such copper solutions are not very suitable as solvents for cellulose in the case of physical

20 or chemical treatment of the cellulose.

For this reason, the systems known, *inter alia*, as ionic liquids in the literature were proposed very early on as solvents for cellulose.

25 Thus, US-A 1,943,176 describes the dissolution of cellulose in benzylpyridinium chloride.

As an example of an ionic liquid, benzylpyridinium chloride is a salt which is present in molten form and thus as a liquid at comparatively low temperatures.

30

Ionic liquids are becoming increasingly important as solvents, e.g. for carrying out chemical reactions. Peter Wasserscheidt, *Angew. Chem.* 2000, 112, 3926-3945, for example, gives an overview of the use of ionic liquids in transition metal catalysis.

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Ionic liquids which are present in the liquid state even at room temperature are described, for example, by K.N. Marsh et al., *Fluid Phase Equilibria* 219 (2004), 93-98, and J.G. Huddleston et al., *Green Chemistry* 2001, 3, 156-164.

5 DE-A 102 02 838 describes the use of ionic liquids for separating acids from chemical mixtures.

Owing to the good solvent capabilities of ionic liquids, their use for the dissolution of cellulose is also proposed in the more recent international patent application

10 WO-A 03/029329. However, it is emphasized there that the ionic liquids should comprise cations which comprise a quaternary ammonium ion which should be quaternized by alkyl groups, in particular methyl.

Although the characteristics of the cellulose-comprising solution and its preparation

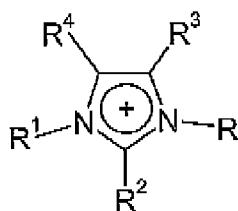
15 described in WO-A 03/029329 have good results, there is a need to provide improved solutions.

It is an object of the present invention to provide a solution of dissolved cellulose which displays improved properties.

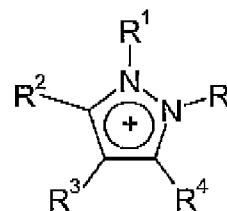
20 It is therefore aimed to address or achieve at least one of the respective prior art disadvantages or objects referred to herein.

The invention, the subject of the present application, is directed to a solution comprising cellulose and an ionic liquid comprising anions and cations as solvent, wherein the cations comprise at least one atom selected from the group consisting of nitrogen, oxygen, sulfur and phosphorus which is present in protonated form, and wherein the ionic liquid comprises at least one cation selected from the group consisting of cations of the formulae (IVe) to (IVt):

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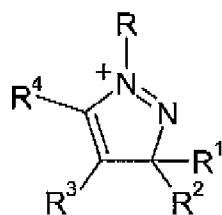
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(IVf)

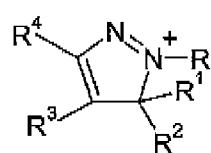
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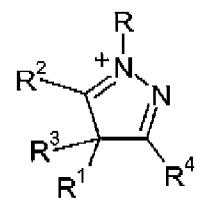


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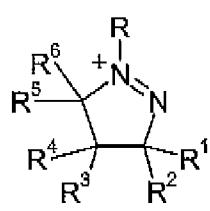
(IVg)



(IVg')

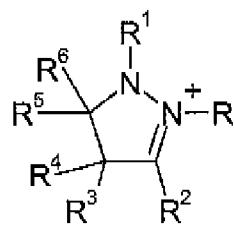


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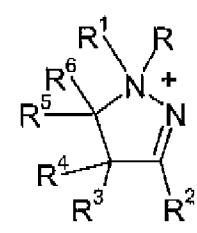


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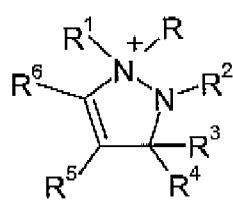
(IVi)



(IVj)

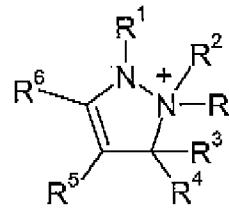


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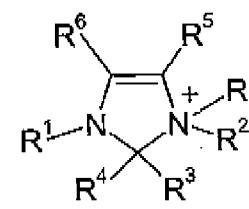


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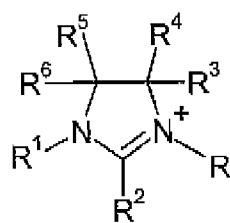
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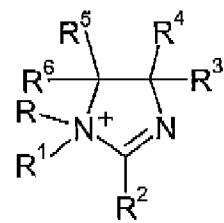


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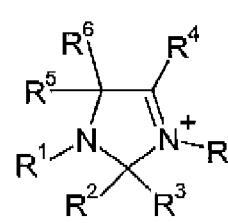


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(IVm)



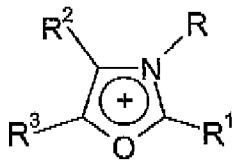
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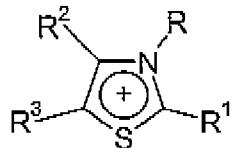
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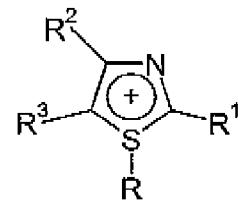
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(IVn')

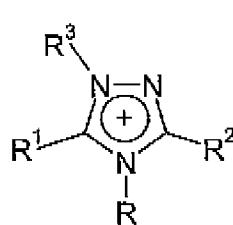


(IVo)

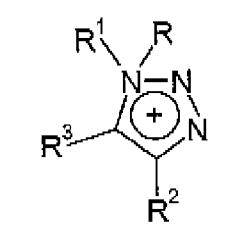


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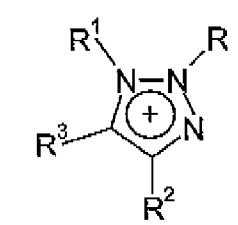
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(IVp)

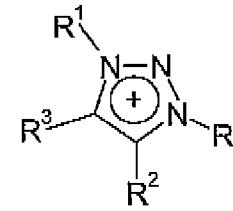


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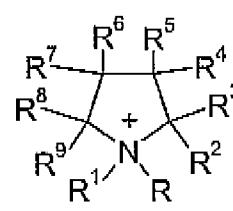


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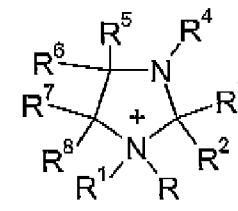
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(IVq'')

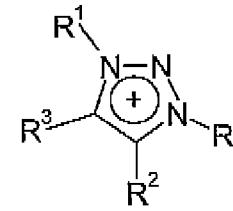


(IVr)

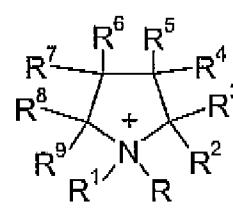


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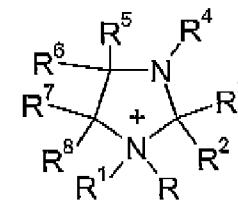
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(IVr'')



(IVs)



(IVt)

and oligomers comprising these structures, where

20 the radical R is hydrogen; and

the radicals R¹ to R⁹ are each, independently of one another, hydrogen, a sulfo group or a carbon-comprising organic, saturated or unsaturated, acyclic or cyclic, aliphatic, aromatic or araliphatic radical which has from 1 to 20 carbon atoms and is unsubstituted or interrupted by from 1 to 5 heteroatoms or functional groups or substituted, with the

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radicals R¹ to R⁹ which are bound to a carbon atom (and not to a heteroatom) in the abovementioned formulae (IV) also being able to be halogen or a functional group; or

two adjacent radicals from the group consisting of R¹ to R⁹ can together also be a 5 divalent, carbon-comprising organic, saturated or unsaturated, acyclic or cyclic, aliphatic, aromatic or araliphatic radical which has from 1 to 30 carbon atoms and is unsubstituted or interrupted by from 1 to 5 heteroatoms or functional groups or substituted.

It has been found that the preparation of cations by means of hydrogen (protonation), in 10 particular by quaternization of the nitrogen, can result in improved properties. In particular, it has been found that solutions comprising ionic liquids are easier to work up. Thus, the ionic liquids can be converted by addition of a base into a distillable form, which makes them easier to separate off.

15 The protonation can be effected at one or more identical or different heteroatoms (N, O, S, P). Apart from generation of a positive charge by protonation, further positive charges can also be present in the cations, for example as a result of alkylation of a nitrogen.

However, the cations preferably have at least one nitrogen atom which is present in protonated form as ammonium cation.

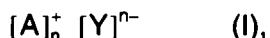
5 The cellulose to be dissolved can originate from, for example, regenerated cellulose, fibrous cellulose, wood fibers, lint, cotton or paper.

It is preferred that, in the solution of the present invention, more than 1% by weight of cellulose, based on the total weight of the solution, are completely dissolved. More 10 preferably, more than 3% by weight, particularly preferably more than 5% by weight and in particular at least 7% by weight, based on the total weight of the solution, are completely dissolved.

Advantageously, up to 35% by weight of cellulose, based on the total weight of the solution, can be completely dissolved. Furthermore, up to 25% by weight of cellulose, 15 based on the total weight of the solution, can be completely dissolved. Solutions in which up to 15% by weight of cellulose are completely dissolved are especially suitable for particular applications.

For the purposes of the present invention, ionic liquids are preferably salts of the 20 general formula

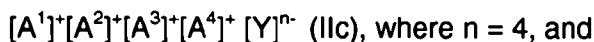
(A) salts of the general formula (I)



25

where n is 1, 2, 3 or 4, $[A]^+$ is a quaternary ammonium cation, an oxonium cation, a sulfonium cation or a phosphonium cation and $[Y]^{n-}$ is a monovalent, divalent, trivalent or tetravalent anion;

30 (B) mixed salts of the general formulae (II)



35 where $[A^1]^+$, $[A^2]^+$, $[A^3]^+$ and $[A^4]^+$ are selected independently from among the groups mentioned for $[A]^+$, and $[Y]^{n-}$ is as defined under (A); or

(C) mixed salts of the general formulae (III)

5 $[A^1]^+[A^2]^+[A^3]^+[M^1]^+ [Y]^{n-}$ (IIIa), where $n = 4$;
 $[A^1]^+[A^2]^+[M^1]^+[M^2]^+ [Y]^{n-}$ (IIIb), where $n = 4$;
 [A¹]⁺[M¹]⁺[M²]⁺[M³]⁺[Y]ⁿ⁻ (IIIc), where $n = 4$;
 [A¹]⁺[A²]⁺[M¹]⁺[Y]ⁿ⁻ (IIId), where $n = 3$;
 [A¹]⁺[M¹]⁺[M²]⁺[Y]ⁿ⁻ (IIIE), where $n = 3$;
 [A¹]⁺[M¹]⁺[Y]ⁿ⁻ (IIIf), where $n = 2$;
 [A¹]⁺[A²]⁺[M⁴]²⁺[Y]ⁿ⁻ (IIIG), where $n = 4$;
 10 [A¹]⁺[M¹]⁺[M⁴]²⁺[Y]ⁿ⁻ (IIIH), where $n = 4$;
 [A¹]⁺[M⁵]³⁺[Y]ⁿ⁻ (IIII), where $n = 4$; or
 [A¹]⁺[M⁴]²⁺[Y]ⁿ⁻ (IIIJ), where $n = 3$, and

15 where $[A^1]^+$, $[A^2]^+$ and $[A^3]^+$ are selected independently from among the groups
 mentioned for $[A]^+$, $[Y]^{n-}$ is as defined under (A) and $[M^1]^+$, $[M^2]^+$, $[M^3]^+$ are monovalent
 metal cations, $[M^4]^{2+}$ is a divalent metal cation and $[M^5]^{3+}$ is a trivalent metal cation.

20 The ionic liquids preferably have a melting point of less than 180°C. The melting point
 is more preferably in the range from -50°C to 150°C, still more preferably in the range
 from -20°C to 120°C and most preferably below 100°C.

25 Compounds which are suitable for forming the cations $[A]^+$ of ionic liquids are, for
 example, known from DE 102 02 838 A1. Thus, such compounds can comprise
 oxygen, phosphorus, sulfur or in particular nitrogen atoms, for example at least one
 nitrogen atom, preferably 1-10 nitrogen atoms, particularly preferably 1-5 nitrogen
 atoms, very particularly preferably 1-3 nitrogen atoms and in particular 1-2 nitrogen
 atoms. If appropriate, further heteroatoms such as oxygen, sulfur or phosphorus atoms
 can also be comprised. The nitrogen atom is a suitable carrier of the positive charge in
 the cation of the ionic liquid, from which a proton or an alkyl radical can then be
 30 transferred in equilibrium to the anion so as to produce an electrically neutral molecule.

35 If the nitrogen atom is the carrier of the positive charge in the cation of the ionic liquid,
 a cation can firstly be produced by quaternization of the nitrogen atom of, for example,
 an amine or nitrogen heterocycle in the synthesis of the ionic liquids. The
 quaternization can be effected by protonation of the nitrogen atom. Depending on the
 protonation reagent used, salts having different anions are obtained. In cases in which

it is not possible to form the desired anion directly in the quaternization, this can be effected in a further step of the synthesis. For example, starting from an ammonium halide, the halide can be reacted with a Lewis acid to form a complex anion from the halide and Lewis acid. As an alternative, it is possible to replace a halide ion by the 5 desired anion. This can be achieved by addition of a metal salt with precipitation of the metal halide formed, by means of an ion exchanger or by displacement of the halide ion by a strong acid (with liberation of the hydrogen halide). Suitable methods are described, for example, in Angew. Chem. 2000, 112, pp. 3926 – 3945, and the references cited therein.

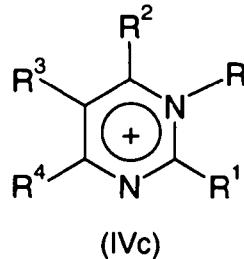
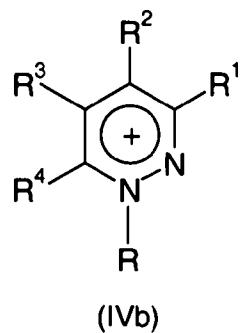
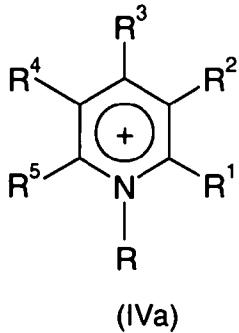
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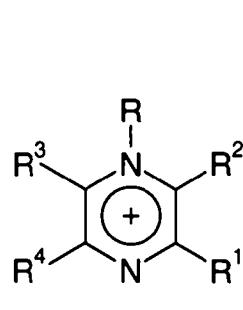
Preference is given to compounds which comprise at least one five- or six-membered heterocycle, in particular a five-membered heterocycle, which has at least one nitrogen atom and, if appropriate, an oxygen or sulfur atom; particular preference is given to compounds which comprise at least one five- or six-membered heterocycle which has 15 one, two or three nitrogen atoms and a sulfur or oxygen atom, very particularly preferably those having two nitrogen atoms. Preference is also given to aromatic heterocycles.

Particularly preferred compounds are ones which have a molecular weight of less than 20 1000 g/mol, very particularly preferably less than 500 g/mol and in particular less than 250 g/mol.

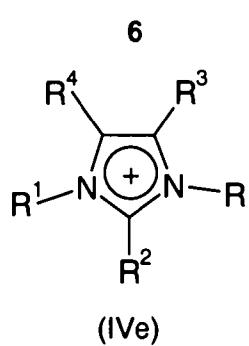
Furthermore, preference is given to cations which are selected from among the compounds of the formulae (IVa) to (IVw),

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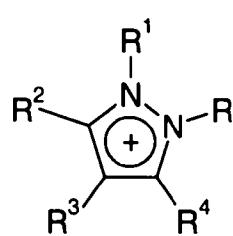




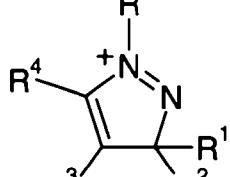
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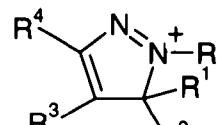
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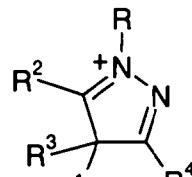
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(IVg)

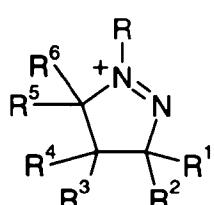


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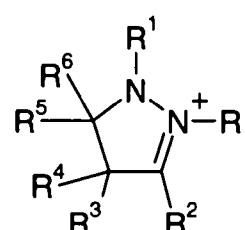


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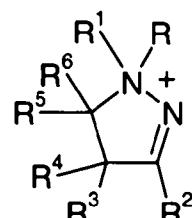
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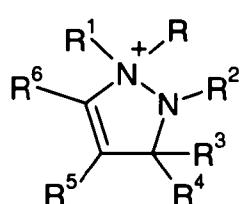


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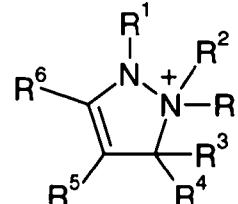


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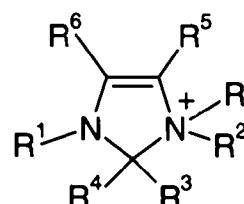
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(IVk)

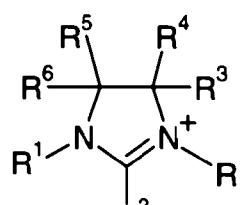


(IVk')

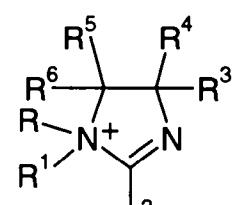


(IVl)

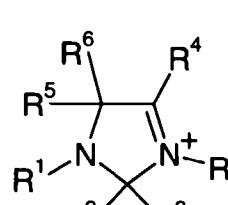
15



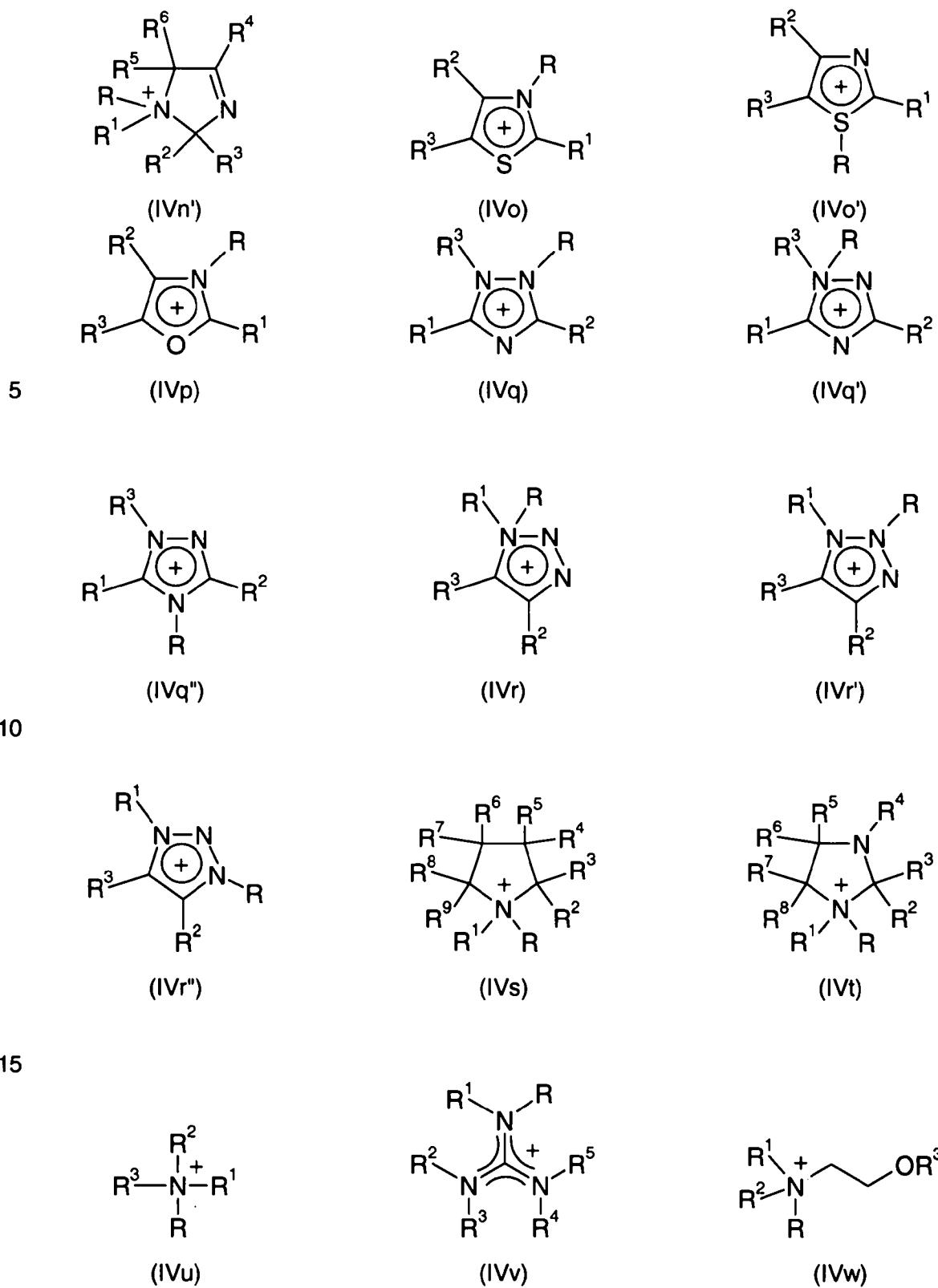
(IVm)



(IVm')

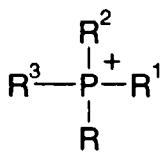


(IVn)

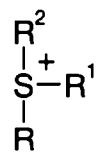


and oligomers comprising these structures.

Further suitable cations are compounds of the general formulae (IVx) and (IVy)



5 (IVx)



(IVy)

and oligomers comprising this structure.

In the abovementioned formulae (IVa) to (IVy),

the radical R is hydrogen; and

10 the radicals R¹ to R⁹ are each, independently of one another, hydrogen, a sulfo group or a carbon-comprising organic, saturated or unsaturated, acyclic or cyclic, aliphatic, aromatic or araliphatic radical which has from 1 to 20 carbon atoms and is unsubstituted or interrupted by from 1 to 5 heteroatoms or functional groups or substituted, with the radicals R¹ to R⁹ which are bound to a carbon atom (and not to a heteroatom) in the abovementioned formulae (IV) also being able to be halogen or a functional group; or

two adjacent radicals from the group consisting of R¹ to R⁹ can together also be a divalent, carbon-comprising organic, saturated or unsaturated, acyclic or cyclic,

20 aliphatic, aromatic or araliphatic radical which has from 1 to 30 carbon atoms and is unsubstituted or interrupted by from 1 to 5 heteroatoms or functional groups or substituted.

In the definition of the radicals R¹ to R⁹, heteroatoms are in principle all heteroatoms

25 which are formally able to replace a -CH₂-, -CH=, -C≡ or =C= group. If the carbon-comprising radical comprises heteroatoms, then preference is given to oxygen, nitrogen, sulfur, phosphorus and silicon. Preferred groups are, in particular, -O-, -S-, -SO-, -SO₂-, -NR⁻, -N=, -PR⁻, -PR'₂ and -SiR'₂-, where the radicals R' are the remaining part of the carbon-comprising radical. The radicals R¹ to R⁹ can in the cases 30 in which they are bound to a carbon atom (and not to a heteroatom) in the abovementioned formula (IV) also be bound directly via the heteroatom.

Possible functional groups are in principle all functional groups which can be bound to a carbon atom or a heteroatom. Examples of suitable functional groups are -OH (hydroxy), =O (in particular as a carbonyl group), -NH₂ (amino), =NH (imino), -COOH (carboxy), -CONH₂ (carboxamide), -SO₃H (sulfo) and -CN (cyano). Functional groups

5 and heteroatoms can also be directly adjacent so that combinations of a plurality of adjacent atoms, for instance -O- (ether), -S- (thioether), -COO- (ester), -CONH- (secondary amide) or -CONR'- (tertiary amide) are also comprised, for example di-(C₁-C₄-alkyl)amino, C₁-C₄-alkyloxycarbonyl or C₁-C₄-alkyloxy.

10 Halogens may be fluorine, chlorine, bromine and iodine.

The radicals R¹ to R⁹ are preferably, independently of one another,

- hydrogen;
- halogen;
- 15 • a functional group;
- C₁-C₁₈-alkyl which is optionally substituted by functional groups, aryl, alkyl, aryloxy, alkyloxy, halogen, heteroatoms and/or heterocycles and/or interrupted by one or more oxygen and/or sulfur atoms and/or one or more substituted or unsubstituted imino groups;
- 20 • C₂-C₁₈-alkenyl which is optionally substituted by functional groups, aryl, alkyl, aryloxy, alkyloxy, halogen, heteroatoms and/or heterocycles and/or interrupted by one or more oxygen and/or sulfur atoms and/or one or more substituted or unsubstituted imino groups;
- 25 • C₆-C₁₂-aryl which is optionally substituted by functional groups, aryl, alkyl, aryloxy, alkyloxy, halogen, heteroatoms and/or heterocycles;
- C₅-C₁₂-cycloalkyl which is optionally substituted by functional groups, aryl, alkyl, aryloxy, alkyloxy, halogen, heteroatoms and/or heterocycles;
- 30 • C₅-C₁₂-cycloalkenyl which is optionally substituted by functional groups, aryl, alkyl, aryl, aryloxy, alkyloxy, halogen, heteroatoms and/or heterocycles; or
- a five- or six-membered, oxygen-, nitrogen- and/or sulfur-comprising heterocycle which is optionally substituted by functional groups, aryl, alkyl, aryloxy, alkyloxy, halogen, heteroatoms and/or heterocycles; or

two adjacent radicals together form

- 35 • an unsaturated, saturated or aromatic ring which is optionally substituted by functional groups, aryl, alkyl, aryloxy, alkyloxy, halogen, heteroatoms and/or

heterocycles and optionally interrupted by one or more oxygen and/or sulfur atoms and/or one or more substituted or unsubstituted imino groups.

C₁-C₁₈-alkyl which is optionally substituted by functional groups, aryl, alkyl, aryloxy, 5 alkyloxy, halogen, heteroatoms and/or heterocycles is preferably methyl, ethyl, 1-propyl, 2-propyl, 1-butyl, 2-butyl, 2-methyl-1-propyl (isobutyl), 2-methyl-2-propyl (tert-butyl), 1-pentyl, 2-pentyl, 3-pentyl, 2-methyl-1-butyl, 3-methyl-1-butyl, 2-methyl-2-butyl, 3-methyl-2-butyl, 2,2-dimethyl-1-propyl, 1-hexyl, 2-hexyl, 3-hexyl, 2-methyl-1-pentyl, 3-methyl-1-pentyl, 4-methyl-1-pentyl, 2-methyl-2-pentyl, 10 3-methyl-2-pentyl, 4-methyl-2-pentyl, 2-methyl-3-pentyl, 3-methyl-3-pentyl, 2,2-dimethyl-1-butyl, 2,3-dimethyl-1-butyl, 3,3-dimethyl-1-butyl, 2-ethyl-1-butyl, 2,3-dimethyl-2-butyl, 3,3-dimethyl-2-butyl, heptyl, octyl, 2-ethylhexyl, 2,4,4-trimethylpentyl, 1,1,3,3-tetramethylbutyl, 1-nonyl, 1-decyl, 1-undecyl, 1-dodecyl, 1-tridecyl, 1-tetradecyl, 1-pentadecyl, 1-hexadecyl, 1-heptadecyl, 1-octadecyl, 15 cyclopentylmethyl, 2-cyclopentylethyl, 3-cyclopentylpropyl, cyclohexylmethyl, 2-cyclohexylethyl, 3-cyclohexylpropyl, benzyl (phenylmethyl), diphenylmethyl (benzhydryl), triphenylmethyl, 1-phenylethyl, 2-phenylethyl, 3-phenylpropyl, α,α -dimethylbenzyl, p-tolylmethyl, 1-(p-butylphenyl)ethyl, p-chlorobenzyl, 2,4-dichlorobenzyl, p-methoxybenzyl, m-ethoxybenzyl, 2-cyanoethyl, 2-cyanopropyl, 2-20 methoxycarbonylethyl, 2-ethoxycarbonylethyl, 2-butoxycarbonylpropyl, 1,2-di(methoxycarbonyl)ethyl, methoxy, ethoxy, formyl, 1,3-dioxolan-2-yl, 1,3-dioxan-2-yl, 2-methyl-1,3-dioxolan-2-yl, 4-methyl-1,3-dioxolan-2-yl, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 4-hydroxybutyl, 6-hydroxyhexyl, 2-aminoethyl, 2-aminopropyl, 3-aminopropyl, 4-aminobutyl, 6-aminohexyl, 2-methylaminoethyl, 2-25 methylaminopropyl, 3-methylaminopropyl, 4-methylaminobutyl, 6-methylaminohexyl, 2-dimethylaminoethyl, 2-dimethylaminopropyl, 3-dimethylaminopropyl, 4-dimethylaminobutyl, 6-dimethylaminohexyl, 2-hydroxy-2,2-dimethylethyl, 2-phenoxyethyl, 2-phenoxypropyl, 3-phenoxypropyl, 4-phenoxybutyl, 6-phenoxyhexyl, 2-methoxyethyl, 2-methoxypropyl, 3-methoxypropyl, 4-methoxybutyl, 6-methoxyhexyl, 2-30 ethoxyethyl, 2-ethoxypropyl, 3-ethoxypropyl, 4-ethoxybutyl, 6-ethoxyhexyl, acetyl, C_nF_{2(n-a)+(1-b)}H_{2a+b} where n is from 1 to 30, 0 ≤ a ≤ n and b = 0 or 1 (for example CF₃, C₂F₅, CH₂CH₂-C_(n-2)F_{2(n-2)+1}, C₆F₁₃, C₈F₁₇, C₁₀F₂₁, C₁₂F₂₅), chloromethyl, 2-chloroethyl, trichloromethyl, 1,1-dimethyl-2-chloroethyl, methoxymethyl, 2-butoxyethyl, diethoxymethyl, diethoxyethyl, 2-isopropoxyethyl, 2-butoxypropyl, 2-octyloxyethyl, 2-35 methoxyisopropyl, 2-(methoxycarbonyl)ethyl, 2-(ethoxycarbonyl)ethyl, 2-(n-butoxycarbonyl)ethyl, butylthiomethyl, 2-dodecythioethyl, 2-phenylthioethyl, 5-hydroxy-

3-oxapentyl, 8-hydroxy-3,6-dioxaoctyl, 11-hydroxy-3,6,9-trioxaundecyl, 7-hydroxy-4-oxaheptyl, 11-hydroxy-4,8-dioxaundecyl, 15-hydroxy-4,8,12-trioxapentadecyl, 9-hydroxy-5-oxanonyl, 14-hydroxy-5,10-dioxatetradecyl, 5-methoxy-3-oxapentyl, 8-methoxy-3,6-dioxaoctyl, 11-methoxy-3,6,9-trioxaundecyl, 7-methoxy-4-oxaheptyl, 11-methoxy-4,8-dioxaundecyl, 15-methoxy-4,8,12-trioxapentadecyl, 9-methoxy-5-oxanonyl, 14-methoxy-5,10-dioxatetradecyl, 5-ethoxy-3-oxapentyl, 8-ethoxy-3,6-dioxaoctyl, 11-ethoxy-3,6,9-trioxaundecyl, 7-ethoxy-4-oxaheptyl, 11-ethoxy-4,8-dioxaundecyl, 15-ethoxy-4,8,12-trioxapentadecyl, 9-ethoxy-5-oxanonyl or 14-ethoxy-5,10-oxatetradecyl.

10 $C_2\text{-}C_{18}\text{-Alkenyl}$ which is optionally substituted by functional groups, aryl, alkyl, aryloxy, alkyloxy, halogen, heteroatoms and/or heterocycles and/or interrupted by one or more oxygen and/or sulfur atoms and/or one or more substituted or unsubstituted imino groups is preferably vinyl, 2-propenyl, 3-but enyl, cis-2-but enyl, trans-2-but enyl or

15 $C_nF_{2(n-a)-(1-b)}H_{2a-b}$ where $n \leq 30$, $0 \leq a \leq n$ and $b = 0$ or 1 .

20 $C_6\text{-}C_{12}\text{-Aryl}$ which is optionally substituted by functional groups, aryl, alkyl, aryloxy, alkyloxy, halogen, heteroatoms and/or heterocycles is preferably phenyl, tolyl, xylol, α -naphthyl, β -naphthyl, 4-diphenyl, chlorophenyl, dichlorophenyl, trichlorophenyl, difluorophenyl, methylphenyl, dimethylphenyl, trimethylphenyl, ethylphenyl, diethylphenyl, isopropylphenyl, tert-butylphenyl, dodecylphenyl, methoxyphenyl, dimethoxyphenyl, ethoxyphenyl, hexyloxyphenyl, methylnaphthyl, isopropynaphthyl, chloronaphthyl, ethoxynaphthyl, 2,6-dimethylphenyl, 2,4,6-trimethylphenyl, 2,6-dimethoxyphenyl, 2,6-dichlorophenyl, 4-bromophenyl, 2-nitrophenyl, 4-nitrophenyl,

25 2,4-dinitrophenyl, 2,6-dinitrophenyl, 4-dimethylaminophenyl, 4-acetylphenyl, ethoxyethylphenyl, ethoxymethylphenyl, methylthiophenyl, isopropylthiophenyl or tert-butylthiophenyl or $C_6F_{(5-a)}H_a$ where $0 \leq a \leq 5$.

30 $C_5\text{-}C_{12}\text{-Cycloalkyl}$ which is optionally substituted by functional groups, aryl, alkyl, aryloxy, alkyloxy, halogen, heteroatoms and/or heterocycles is preferably cyclopentyl, cyclohexyl, cyclooctyl, cyclododecyl, methylcyclopentyl, dimethylcyclopentyl, methylcyclohexyl, dimethylcyclohexyl, diethylcyclohexyl, butylcyclohexyl, methoxycyclohexyl, dimethoxycyclohexyl, diethoxycyclohexyl, butylthiocyclohexyl, chlorocyclohexyl, dichlorocyclohexyl, dichlorocyclopentyl, $C_nF_{2(n-a)-(1-b)}H_{2a-b}$ where

35 $n \leq 30$, $0 \leq a \leq n$ and $b = 0$ or 1 or a saturated or unsaturated bicyclic system such as norbornyl or norbornenyl.

C_5 - C_{12} -Cycloalkenyl which is optionally substituted by functional groups, aryl, alkyl, aryloxy, alkyloxy, halogen, heteroatoms and/or heterocycles is preferably 3-cyclopentenyl, 2-cyclohexenyl, 3-cyclohexenyl, 2,5-cyclohexadienyl or $C_nF_{2(n-a)-3(1-b)}H_{2a-3b}$ where $n \leq 30$, $0 \leq a \leq n$ and $b = 0$ or 1 .

5 A five- or six-membered, oxygen-, nitrogen- and/or sulfur-comprising heterocycle which is optionally substituted by functional groups, aryl, alkyl, aryloxy, alkyloxy, halogen, heteroatoms and/or heterocycles is preferably furyl, thiophenyl, pyrrol, pyridyl, indolyl, 10 benzoxazolyl, dioxolyl, dioxy, benzimidazolyl, benzthiazolyl, dimethylpyridyl, methylquinolyl, dimethylpyrrol, methoxyfuryl, dimethoxypyridyl or difluoropyridyl.

15 If two adjacent radicals together form an unsaturated, saturated or aromatic ring which is optionally substituted by functional groups, aryl, alkyl, aryloxy, alkyloxy, halogen, heteroatoms and/or heterocycles and optionally interrupted by one or more oxygen and/or sulfur atoms and/or one or more substituted or unsubstituted imino groups, the two radicals together are preferably 1,3-propylene, 1,4-butylene, 1,5-pentylene, 2-oxa-1,3-propylene, 1-oxa-1,3-propylene, 2-oxa-1,3-propylene, 1-oxa-1,3-propenylene, 3-oxa-1,5-pentylene, 1-aza-1,3-propenylene, 1- C_1 - C_4 -alkyl-1-aza-1,3-propenylene, 1,4-but-1,3-dienylene, 1-aza-1,4-but-1,3-dienylene or 2-aza-1,4-but-1,3-dienylene.

20 If the abovementioned radicals comprise oxygen and/or sulfur atoms and/or substituted or unsubstituted imino groups, the number of oxygen and/or sulfur atoms and/or imino groups is not subject to any restrictions. In general, there will be no more than 5 in the radical, preferably no more than 4 and very particularly preferably no more than 3.

If the abovementioned radicals comprise heteroatoms, there is generally at least one carbon atom, preferably at least two carbon atoms, between any two heteroatoms.

30 The radicals R^1 to R^9 are particularly preferably, independently of one another,

- hydrogen;
- unbranched or branched C_1 - C_{18} -alkyl which is unsubstituted or substituted by one or more hydroxy, halogen, phenyl, cyano, C_1 - C_6 -alkoxycarbonyl and/or sulfonic acid substituents and has a total of from 1 to 20 carbon atoms, for example methyl, ethyl, 1-propyl, 2-propyl, 1-butyl, 2-butyl, 2-methyl-1-propyl (isobutyl), 2-methyl-2-propyl (tert-butyl), 1-pentyl, 2-pentyl, 3-pentyl, 2-methyl-1-

butyl, 3-methyl-1-butyl, 2-methyl-2-butyl, 3-methyl-2-butyl, 2,2-dimethyl-1-propyl, 1-hexyl, 2-hexyl, 3-hexyl, 2-methyl-1-pentyl, 3-methyl-1-pentyl, 4-methyl-1-pentyl, 2-methyl-2-pentyl, 3-methyl-2-pentyl, 4-methyl-2-pentyl, 2-methyl-3-pentyl, 3-methyl-3-pentyl, 2,2-dimethyl-1-butyl, 2,3-dimethyl-1-butyl, 3,3-dimethyl-1-butyl, 2-ethyl-1-butyl, 2,3-dimethyl-2-butyl, 3,3-dimethyl-2-butyl, 1-heptyl, 1-octyl, 1-nonyl, 1-decyl, 1-undecyl, 1-dodecyl, 1-tetradecyl, 1-hexadecyl, 1-octadecyl, 2-hydroxyethyl, benzyl, 3-phenylpropyl, 2-cyanoethyl, 2-(methoxycarbonyl)ethyl, 2-(ethoxycarbonyl)ethyl, 2-(n-butoxycarbonyl)ethyl, trifluoromethyl, difluoromethyl, fluoromethyl, pentafluoroethyl, heptafluoropropyl, heptafluoroisopropyl, nonafluorobutyl, nonafluoroisobutyl, undecylfluoropentyl, undecylfluoroisopentyl, 6-hydroxyhexyl and propylsulfonic acid;

- glycols, butylene glycols and oligomers thereof having from 1 to 100 units and a hydrogen atom or a C₁-C₈-alkyl group as end group, for example R^AO-(CHR^B-CH₂-O)_n-CHR^B-CH₂- or R^AO-(CH₂CH₂CH₂CH₂O)_n-CH₂CH₂CH₂CH₂O- where R^A and R^B are preferably hydrogen, methyl or ethyl and n is preferably from 0 to 3, in particular 3-oxabutyl, 3-oxapentyl, 3,6-dioxaheptyl, 3,6-dioxaoctyl, 3,6,9-trioxadecyl, 3,6,9-trioxaundecyl, 3,6,9,12-tetraoxatridecyl and 3,6,9,12-tetraoxatetradecyl;
- vinyl; and
- N,N-di-C₁-C₆-alkylamino, for example N,N-dimethylamino and N,N-diethylamino.

The radicals R¹ to R⁹ are very particularly preferably, independently of one another, hydrogen or C₁-C₁₈-alkyl, for example methyl, ethyl, 1-butyl, 1-pentyl, 1-hexyl, 1-heptyl, 1-octyl, phenyl, 2-hydroxyethyl, 2-cyanoethyl, 2-(methoxycarbonyl)ethyl, 2-(ethoxycarbonyl)ethyl, 2-(n-butoxycarbonyl)ethyl, N,N-dimethylamino, N,N-diethylamino, chlorine or CH₃O-(CH₂CH₂O)_n-CH₂CH₂- and CH₃CH₂O-(CH₂CH₂O)_n-CH₂CH₂- where n is from 0 to 3.

30 Very particularly preferred pyridinium ions (IVa) are those in which

- one of the radicals R¹ to R⁵ is methyl, ethyl or chlorine and the remaining radicals R¹ to R⁵ are hydrogen;
- R³ is dimethylamino and the remaining radicals R¹, R², R⁴ and R⁵ are hydrogen;
- all radicals R¹ to R⁵ are hydrogen;
- R² is carboxy or carboxamide and the remaining radicals R¹, R², R⁴ and R⁵ are hydrogen; or

- R^1 and R^2 or R^2 and R^3 are together 1,4-buta-1,3-dienylene and the remaining radicals R^1 , R^2 , R^4 and R^5 are hydrogen;

and, in particular, those in which

- R^1 to R^5 are hydrogen; or
- 5 • one of the radicals R^1 to R^5 is methyl or ethyl and the remaining radicals R^1 to R^5 are hydrogen.

Very particularly preferred pyridinium ions (IVa) are pyridinium, 2-methylpyridinium, 2-ethylpyridinium, 5-ethyl-2-methylpyridinium and 2-methyl-3-ethylpyridinium.

10

Very particularly preferred pyridazinium ions (IVb) are those in which

- R^1 to R^4 are hydrogen; or
- one of the radicals R^1 to R^4 is methyl or ethyl and the remaining radicals R^1 to R^4 are hydrogen.

15

Very particularly preferred pyrimidinium ions (IVc) are those in which

- R^1 is hydrogen, methyl or ethyl and R^2 to R^4 are each, independently of one another, hydrogen or methyl; or
- R^1 is hydrogen, methyl or ethyl, R^2 and R^4 are methyl and R^3 is hydrogen.

20

Very particularly preferred pyrazinium ions (IVd) are those in which

- R^1 is hydrogen, methyl or ethyl and R^2 to R^4 are each, independently of one another, hydrogen or methyl;
- R^1 is hydrogen, methyl or ethyl, R^2 and R^4 are methyl and R^3 is hydrogen;
- 25 • R^1 to R^4 are methyl; or
- R^1 to R^4 are methyl or hydrogen.

Very particularly preferred imidazolium ions (IVe) are those in which

- 30 • R^1 is hydrogen, methyl, ethyl, 1-propyl, 1-butyl, 1-pentyl, 1-hexyl, 1-octyl, 2-hydroxyethyl or 2-cyanoethyl and R^2 to R^4 are each, independently of one another, hydrogen, methyl or ethyl.

Very particularly preferred imidazolium ions (IVe) are 1-methylimidazolium, 1-ethylimidazolium, 1-n-butylimidazolium, 1-n-octylimidazolium, 1-n-dodecylimidazolium, 1-n-tetradecylimidazolium, 1-n-hexadecylimidazolium, 1,2-dimethylimidazolium, 1,4-dimethylimidazolium, 2-methylimidazolium, 3-methylimidazolium, 3-ethylimidazolium, 3-n-butylimidazolium, 3-octylimidazolium, 4-methylimidazolium, 2-

ethylimidazolium, 1-vinylimidazolium, 1-n-octyl-4-methylimidazolium and 1,4,5-trimethylimidazolium.

Very particularly preferred pyrazolium ions (IVf), (IVg) or (IVg') are those in which

5 • R^1 is hydrogen, methyl or ethyl and R^2 to R^4 are each, independently of one another, hydrogen or methyl.

Very particularly preferred pyrazolium ions (IVh) are those in which

10 • R^1 to R^4 are each, independently of one another, hydrogen or methyl.

As very particularly preferred pyrazolium ions, mention may be made of pyrazolium and 1,4-dimethylpyrazolium.

In the process of the invention, very particularly preferred 1-pyrazolinium ions (IVi) are

15 those in which

• R^1 to R^6 are each, independently of one another, hydrogen or methyl.

Very particularly preferred 2-pyrazolinium ions (IVj) or (IVj') are those in which

20 • R^1 is hydrogen, methyl, ethyl or phenyl and R^2 to R^6 are each, independently of one another, hydrogen or methyl.

Very particularly preferred 3-pyrazolinium ions (IVk) or (IVk') are those in which

25 • R^1 and R^2 are each, independently of one another, hydrogen, methyl, ethyl or phenyl and R^3 to R^6 are each, independently of one another, hydrogen or methyl.

Very particularly preferred imidazolinium ions (IVl) are those in which

30 • R^1 and R^2 are each, independently of one another, hydrogen, methyl, ethyl, 1-butyl or phenyl, R^3 and R^4 are each, independently of one another, hydrogen, methyl or ethyl and R^5 and R^6 are each, independently of one another, hydrogen or methyl.

Very particularly preferred imidazolinium ions (IVm) or (IVm') are those in which

35 • R^1 and R^2 are each, independently of one another, hydrogen, methyl or ethyl and R^3 to R^6 are each, independently of one another, hydrogen or methyl.

Very particularly preferred imidazolinium ions (IVn) or (IVn') are those in which

- R¹ to R³ are each, independently of one another, hydrogen, methyl or ethyl and R⁴ to R⁶ are each, independently of one another, hydrogen or methyl.

5 Very particularly preferred thiazolium ions (IVo) or (IVo') and oxazolium ions (IVp) are those in which

- R¹ is hydrogen, methyl, ethyl or phenyl and R² and R³ are each, independently of one another, hydrogen or methyl.

10 Very particularly preferred 1,2,4-triazolium ions (IVq), (IVq') or (IVq'') are those in which

- R¹ and R² are each, independently of one another, hydrogen, methyl, ethyl or phenyl and R³ is hydrogen, methyl or phenyl.

Very particularly preferred 1,2,3-triazolium ions (IVr), (IVr') or (IVr'') are those in which

15 • R¹ is hydrogen, methyl or ethyl and R² and R³ are each, independently of one another, hydrogen or methyl, or R² and R³ are together 1,4-buta-1,3-dienylene.

Very particularly preferred pyrrolidinium ions (IVs) are those in which

20 • R¹ is hydrogen, methyl, ethyl or phenyl and R² to R⁹ are each, independently of one another, hydrogen or methyl.

Very particularly preferred imidazolidinium ions (IVt) are those in which

25 • R¹ and R⁴ are each, independently of one another, hydrogen, methyl, ethyl or phenyl and R² and R³ and also R⁵ to R⁸ are each, independently of one another, hydrogen or methyl.

Very particularly preferred ammonium ions (IVu) are those in which

30 • R¹ to R³ are each, independently of one another, C₁-C₁₈-alkyl; or
 • R¹ and R² are together 1,5-pentylene or 3-oxa-1,5-pentylene and R³ is C₁-C₁₈-alkyl, 2-hydroxyethyl or 2-cyanoethyl.

Examples of tertiary amines from which the quaternary ammonium ions of the general formula (IVu) are derived from quaternation by the abovementioned radical R are

35 diethyl-n-butylamine, diethyl-tert-butylamine, diethyl-n-pentylamine, diethylhexylamine, diethyloctylamine, diethyl(2-ethylhexyl)amine, di-n-propylbutylamine, di-n-propyl-n-pentylamine, di-n-propylhexylamine, di-n-propyloctylamine, di-n-propyl(2-ethyl-

hexyl)amine, diisopropylethylamine, diisopropyl-n-propylamine, diisopropylbutylamine, diisopropylpentylamine, diisopropylhexylamine, diisopropyloctylamine, diisopropyl(2-ethylhexyl)amine, di-n-butylethylamine, di-n-butyl-n-propylamine, di-n-butyl-n-pentylamine, di-n-butylhexylamine, di-n-butyloctylamine, di-n-butyl(2-ethylhexyl)amine,

5 N-n-butylpyrrolidine, N-sec-butylpyrrolidine, N-tert-butylpyrrolidine, N-n-pentylpyrrolidine, N,N-dimethylcyclohexylamine, N,N-diethylcyclohexylamine, N,N-di-n-butylcyclohexylamine, N-n-propylpiperidine, N-isopropylpiperidine, N-n-butylpiperidine, N-sec-butylpiperidine, N-tert-butylpiperidine, N-n-pentylpiperidine, N-n-butylmorpholine,

10 N-sec-butylmorpholine, N-tert-butylmorpholine, N-n-pentylmorpholine, N-benzyl-N-ethylaniline, N-benzyl-N-n-propylaniline, N-benzyl-N-isopropylaniline, N-benzyl-N-n-butylaniline, N,N-dimethyl-p-toluidene, N,N-diethyl-p-toluidene, N,N-di-n-butyl-p-toluidene, diethylbenzylamine, di-n-propylbenzylamine, di-n-butylbenzylamine, diethylphenylamine, di-n-propylphenylamine and di-n-butylphenylamine.

15 Preferred tertiary amines (IVu) are diisopropylethylamine, diethyl-tert-butylamine, diisopropylbutylamine, di-n-butyl-n-pentylamine, N,N-di-n-butylcyclohexylamine and tertiary amines derived from pentyl isomers.

Particularly preferred tertiary amines are di-n-butyl-n-pentylamine and tertiary amines derived from pentyl isomers. A further preferred tertiary amine which has three identical radicals is triallylamine.

Very particularly preferred guanidinium ions (IVv) are those in which

25 • R¹ to R⁵ are methyl.

Very particularly preferred cholinium ions (IVw) are those in which

30 • R¹ and R² are each, independently of one another, methyl, ethyl, 1-butyl or 1-octyl and R³ is hydrogen, methyl, ethyl, acetyl, -SO₂OH or -PO(OH)₂;

• R¹ is methyl, ethyl, 1-butyl or 1-octyl, R² is a -CH₂-CH₂-OR⁴ group and R³ and R⁴ are each, independently of one another, hydrogen, methyl, ethyl, acetyl, -SO₂OH or -PO(OH)₂; or

• R¹ is a -CH₂-CH₂-OR⁴ group, R² is a -CH₂-CH₂-OR⁵ group and R³ to R⁵ are each, independently of one another, hydrogen, methyl, ethyl, acetyl, -SO₂OH or -PO(OH)₂.

Particularly preferred cholinium ions (IVw) are those in which R^3 is selected from among hydrogen, methyl, ethyl, acetyl, 5-methoxy-3-oxapentyl, 8-methoxy-3,6-dioxaoctyl, 11-methoxy-3,6,9-trioxaundecyl, 7-methoxy-4-oxaheptyl, 11-methoxy-4,8-dioxaundecyl, 15-methoxy-4,8,12-trioxapentadecyl, 9-methoxy-5-oxanonyl, 14-methoxy-5,10-oxatetradecyl, 5-ethoxy-3-oxapentyl, 8-ethoxy-3,6-dioxaoctyl, 11-ethoxy-3,6,9-trioxaundecyl, 7-ethoxy-4-oxaheptyl, 11-ethoxy-4,8-dioxaundecyl, 15-ethoxy-4,8,12-trioxapentadecyl, 9-ethoxy-5-oxanonyl or 14-ethoxy-5,10-oxatetradecyl.

Very particularly preferred phosphonium ions (IVx) are those in which

10 • R^1 to R^3 are each, independently of one another, C_1 - C_{18} -alkyl, in particular butyl, isobutyl, 1-hexyl or 1-octyl.

Among the abovementioned heterocyclic cations, the pyridinium ions, pyrazolinium ions, pyrazolium ions and imidazolinium ions and also the imidazolium ions are 15 preferred. Preference is likewise given to ammonium ions.

The metal cations $[M^1]^+$, $[M^2]^+$, $[M^3]^+$, $[M^4]^{2+}$ and $[M^5]^{3+}$ mentioned in the formulae (IIIa) to (IIIj) are generally metal cations of groups 1, 2, 6, 7, 8, 9, 10, 11, 12 and 13 of the Periodic Table. Suitable metal cations are, for example, Li^+ , Na^+ , K^+ , Cs^+ , Mg^{2+} , Ca^{2+} , 20 Ba^{2+} , Cr^{3+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Ag^+ , Zn^{2+} and Al^{3+} .

As anions, it is in principle possible to use all anions.

The anion $[Y]^{n-}$ of the ionic liquid is, for example, selected from among

25 the group of halides and halogen compounds of the formulae:
 F^- , Cl^- , Br^- , I^- , BF_4^- , PF_6^- , $AlCl_4^-$, $Al_2Cl_7^-$, $Al_3Cl_{10}^-$, $AlBr_4^-$, $FeCl_4^-$, BCl_4^- , SbF_6^- , AsF_6^- , $ZnCl_3^-$,
 $SnCl_3^-$, $CuCl_2^-$, $CF_3SO_3^-$, $(CF_3SO_3)_2N^-$, $CF_3CO_2^-$, $CCl_3CO_2^-$, CN^- , SCN^- , OCN^-

30 the group of sulfates, sulfites and sulfonates of the general formulae:
 SO_4^{2-} , HSO_4^- , SO_3^{2-} , HSO_3^- , $R^aOSO_3^-$, $R^aSO_3^-$

the group of phosphates of the general formulae
 PO_4^{3-} , HPO_4^{2-} , $H_2PO_4^-$, $R^aPO_4^{2-}$, $HR^aPO_4^-$, $R^aR^bPO_4^-$

35 the group of phosphonates and phosphinates of the general formulae:

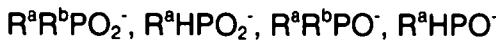


the group of phosphites of the general formulae:



5

the group of phosphonites and phosphinites of the general formulae:



the group of carboxylic acids of the general formula:

10 R^aCOO^-

the group of borates of the general formulae:



15

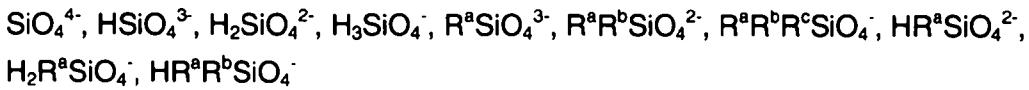
the group of boronates of the general formulae:



the group of carbonates and carbonic esters of the general formulae:

20 $HCO_3^-; CO_3^{2-}; R^aCO_3^-$

the group of silicates and silicic esters of the general formulae:



25

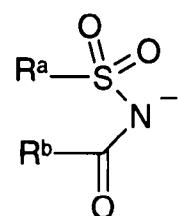
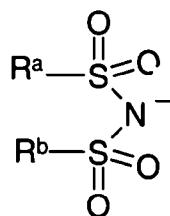
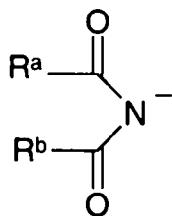
the group of alkyl silane and aryl silane salts of the general formulae:



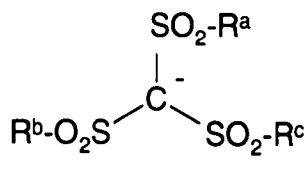
the group of carboximides, bis(sulfonyl)imides and sulfonylimides of the general

30 formulae:

20



the group of methides of the general formula:



5 the group of alkoxides and aryloxides of the general formula



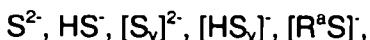
the group of halometalates of the general formula



10 where M is a metal and Hal is fluorine, chlorine, bromine or iodine, q and r are positive integers and indicate the stoichiometry of the complex and s is a positive integer and indicates the charge on the complex;

the group of sulfides, hydrogen sulfides, polysulfides, hydrogen polysulfides and

15 thiolates of the general formulae:



where v is a positive integer from 2 to 10;

the group of complex metal ions such as $\text{Fe}(\text{CN})_6^{3-}$, $\text{Fe}(\text{CN})_6^{4-}$, MnO_4^- , $\text{Fe}(\text{CO})_4^-$.

20

Here, R^a , R^b , R^c and R^d are each, independently of one another, hydrogen, C_1-C_{30} -alkyl, C_2-C_{18} -alkyl which is optionally interrupted by one or more nonadjacent oxygen and/or sulfur atoms and/or one or more substituted or unsubstituted imino groups, C_6-C_{14} -aryl, C_5-C_{12} -cycloalkyl or a five- or six-membered, oxygen-, nitrogen- and/or sulfur-

25 comprising heterocycle, where two of them may together form an unsaturated, saturated or aromatic ring which is optionally interrupted by one or more oxygen and/or sulfur atoms and/or one or more unsubstituted or substituted imino groups, where the radicals mentioned may each be additionally substituted by functional groups, aryl, alkyl, aryloxy, alkyloxy, halogen, heteroatoms and/or heterocycles.

Here, C₁-C₁₈-alkyl which is optionally substituted by functional groups, aryl, alkyl, aryloxy, alkyloxy, halogen, heteroatoms and/or heterocycles is, for example, methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, pentyl, hexyl, heptyl, octyl, 2-ethylhexyl, 2,4,4-trimethylpentyl, decyl, dodecyl, tetradecyl, headecyl, octadecyl, 1,1-dimethylpropyl, 1,1-dimethylbutyl, 1,1,3,3-tetramethylbutyl, benzyl, 1-phenylethyl, α,α -dimethylbenzyl, benzhydryl, p-tolylmethyl, 1-(p-butylphenyl)ethyl, p-chlorobenzyl, 2,4-dichlorobenzyl, p-methoxybenzyl, m-ethoxybenzyl, 2-cyanoethyl, 2-cyanopropyl, 2-methoxycarbonylthyl, 2-ethoxycarbonylethyl, 2-butoxycarbonylpropyl, 1,2-di-(methoxycarbonyl)ethyl, 2-methoxyethyl, 2-ethoxyethyl, 2-butoxyethyl, diethoxymethyl, diethoxyethyl, 1,3-dioxolan-2-yl, 1,3-dioxan-2-yl, 2-methyl-1,3-dioxolan-2-yl, 4-methyl-1,3-dioxolan-2-yl, 2-isopropoxyethyl, 2-butoxypropyl, 2-octyloxyethyl, chloromethyl, trichloromethyl, trifluoromethyl, 1,1-dimethyl-2-chloroethyl, 2-methoxyisopropyl, 2-ethoxyethyl, butylthiomethyl, 2-dodecylthioethyl, 2-phenlythioethyl, 2,2,2-trifluoroethyl, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 4-hydroxybutyl, 6-hydroxyhexyl, 2-aminoethyl, 2-aminopropyl, 4-aminobutyl, 6-aminohexyl, 2-methylaminoethyl, 2-methylaminopropyl, 3-methylaminopropyl, 4-methylaminobutyl, 6-methylaminohexyl, 2-dimethylaminoethyl, 2-dimethylaminopropyl, 3-dimethylaminopropyl, 4-dimethylaminobutyl, 6-dimethylaminohexyl, 2-hydroxy-2,2-dimethylethyl, 2-phenoxyethyl, 2-phenoxypropyl, 3-phenoxypropyl, 4-phenoxybutyl, 6-phenoxyhexyl, 2-methoxyethyl, 2-methoxypropyl, 3-methoxypropyl, 4-methoxybutyl, 6-methoxyhexyl, 2-ethoxyethyl, 2-ethoxypropyl, 3-ethoxypropyl, 4-ethoxybutyl or 6-ethoxyhexyl.

C₂-C₁₈-Alkyl which is optionally substituted by one or more nonadjacent oxygen and/or sulfur atoms and/or one or more substituted or unsubstituted imino groups is, for example, 5-hydroxy-3-oxapentyl, 8-hydroxy-3,6-dioxaoctyl, 11-hydroxy-3,6,9-trioxaundecyl, 7-hydroxy-4-oxaheptyl, 11-hydroxy-4,8-dioxaundecyl, 15-hydroxy-4,8,12-trioxapentadecyl, 9-hydroxy-5-oxanonyl, 14-hydroxy-5,10-oxatetradecyl, 5-methoxy-3-oxapentyl, 8-methoxy-3,6-dioxaoctyl, 11-methoxy-3,6,9-trioxaundecyl, 7-methoxy-4-oxaheptyl, 11-methoxy-4,8-dioxaundecyl, 15-methoxy-4,8,12-trioxapentadecyl, 9-methoxy-5-oxanonyl, 14-methoxy-5,10-oxatetradecyl, 5-ethoxy-3-oxapentyl, 8-ethoxy-3,6-dioxaoctyl, 11-ethoxy-3,6,9-trioxaundecyl, 7-ethoxy-4-oxaheptyl, 11-ethoxy-4,8-dioxaundecyl, 15-ethoxy-4,8,12-trioxapentadecyl, 9-ethoxy-5-oxanonyl or 14-ethoxy-5,10-oxatetradecyl.

If two radicals form a ring, these radicals can together form, for example, 1,3-propylene, 1,4-butylene, 2-oxa-1,3-propylene, 1-oxa-1,3-propylene, 2-oxa-1,3-

propenylene, 1-aza-1,3-propenylene, 1-C₁-C₄-alkyl-1-aza-1,3-propenylene, 1,4-buta-1,3-dienylene, 1-aza-1,4-buta-1,3-dienylene or 2-aza-1,4-buta-1,3-dienylene as fused-on building block.

5 The number of nonadjacent oxygen and/or sulfur atoms and/or imino groups is in principle not subject to any restrictions or is automatically restricted by the size of the radical or the cyclic building block. In general, it will be no more than 5 in the respective radical, preferably no more than 4 and very particularly preferably no more than 3. Furthermore, there is generally at least one carbon atom, preferably at least two 10 carbon atoms, between any two heteroatoms.

Substituted and unsubstituted imino groups can be, for example, imino, methylimino, isopropylimino, n-butyrimino or tert-butyrimino.

15 For the purposes of the present invention, the term "functional groups" refers, for example, to the following: carboxy, carboxamide, hydroxy, di-(C₁-C₄-alkyl)amino, C₁-C₄-alkyloxycarbonyl, cyano or C₁-C₄-alkoxy. Here, C₁C₄-alkyl is methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl or tert-butyl.

20 C₆-C₁₄-Aryl which is optionally substituted by functional groups, aryl, alkyl, aryloxy, alkyloxy, halogen, heteroatoms and/or heterocycles is, for example, phenyl, tolyl, xylyl, α -naphthyl, β -naphthyl, 4-diphenyl, chlorophenyl, dichlorophenyl, trichlorophenyl, difluorophenyl, methylphenyl, dimethylphenyl, trimethylphenyl, ethylphenyl, diethylphenyl, isopropylphenyl, tert-butylphenyl, dodecylphenyl, methoxyphenyl, 25 dimethoxyphenyl, ethoxyphenyl, hexyloxyphenyl, methylnaphthyl, isopropynaphthyl, chloronaphthyl, ethoxynaphthyl, 2,6-dimethylphenyl, 2,4,6-trimethylphenyl, 2,6-dimethoxyphenyl, 2,6-dichlorophenyl, 4-bromophenyl, 2- or 4-nitrophenyl, 2,4- or 2,6-dinitrophenyl, 4-dimethylaminophenyl, 4-acetylphenyl, methoxyethylphenyl or ethoxymethylphenyl.

30 C₅-C₁₂-Cycloalkyl which is optionally substituted by functional groups, aryl, alkyl, aryloxy, halogen, heteroatoms and/or heterocycles is, for example, cyclopentyl, cyclohexyl, cyclooctyl, cyclododecyl, methylcyclopentyl, dimethylcyclopentyl, methylcyclohexyl, dimethylcyclohexyl, diethylcyclohexyl, butylcyclohexyl, 35 methoxycyclohexyl, dimethoxycyclohexyl, diethoxycyclohexyl, butylthiocyclohexyl,

chlorocyclohexyl, dichlorocyclohexyl, dichlorocyclopentyl or a saturated or unsaturated bicyclic system such as norbornyl or norbornenyl.

A five- or six-membered, oxygen-, nitrogen- and/or sulfur-comprising heterocycle is, for 5 example, furyl, thiophenyl, pyranyl, pyridyl, indolyl, benzoxazolyl, dioxolyl, dioxyl, benzimidazolyl, benzthiazolyl, dimethylpyridyl, methylquinolyl, dimethylpyranyl, methoxyfuryl, dimethoxypyridyl, difluoropyridyl, methylthiophenyl, isopropylthiophenyl or tert-butylthiophenyl.

10 Preferred anions are selected from the group of halides and halogen-comprising compounds, the group of carboxylic acids, the group of sulfates, sulfites and sulfonates and the group of phosphates.

Preferred anions are chloride, bromide, iodide, SCN⁻, OCN⁻, CN⁻, acetate, C₁-C₄- 15 alkylsulfates, R^a-COO⁻, R^aSO₃⁻, R^aR^bPO₄⁻, methanesulfonates, tosylate, C₁-C₄ dialkylphosphates, hydrogen sulfate or tetrachloroaluminate.

Particularly preferred anions are Cl⁻, CH₃COO⁻ or CH₃SO₃⁻.

20 Both cations and anions are present in the ionic liquid. Within the ionic liquid, a proton or an alkyl radical is transferred from the cation to the anion. This forms two uncharged molecules. There is thus an equilibrium in which anions, cations and the two uncharged molecules formed therefrom are present.

25 The solution preferably has a temperature of not more than 180°C. The solution of the present invention more preferably has a temperature of not more than 160°C, even more preferably not more than 120°C and particularly preferably not more than 100°C.

30 The present invention further provides a process for preparing a solution according to the invention, which comprises the steps

- a) addition of cellulose to a solution comprising an ionic liquid comprising anions and cations as solvent, wherein the cations comprise at least one nitrogen atom which is present in protonated form as ammonium cation
- 35 b) mixing of the solution until the cellulose is completely dissolved.

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Mixing is preferably carried out by means of stirring, shaking and/or with the aid of microwaves.

5 The dissolution preferably occurs within 3 days, more preferably within one day and particularly preferably within 12 hours.

The present invention further provides for the use of a solution according to the present invention for the physical or chemical treatment of cellulose.

10 The chemical treatment can comprise oxidation, reduction, pyrolysis, hydrolysis, isomerization, esterification, alkoxylation or copolymerization.

The present invention is illustrated by means of the following examples.

15 Comprises/comprising and grammatical variations thereof when used in this specification are to be taken to specify the presence of stated features, integers, steps or components or groups thereof, but do not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof.

Examples

Example 1

0.78 g of newsprint are cut into pieces having a size of about 1 cm², admixed with
5 10.0 g of 1-methylimidazole hydrochloride (1-methylimidazolium chloride) and stirred at
120°C. After 23 hours, the paper has dissolved completely.

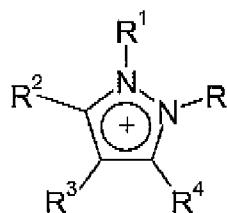
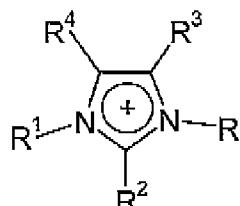
Example 2

7.8 g of filter paper (blue band filter) are cut into pieces having a size of about 1 cm²,
10 admixed with 100 g of 1-methylimidazol hydrochloride and stirred at 95°C. After 72
hours, the paper has dissolved completely.

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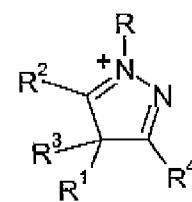
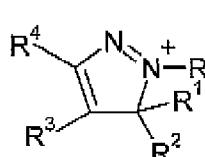
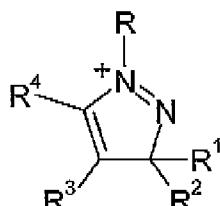
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A solution comprising cellulose and an ionic liquid comprising anions and cations as solvent, wherein the cations comprise at least one atom selected from the group consisting of nitrogen, oxygen, sulfur and phosphorus which is present in protonated form, and wherein the ionic liquid comprises at least one cation selected from the group consisting of cations of the formulae (IVe) to (IVt):



(IVe)

(IVf)

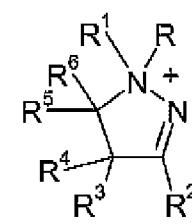
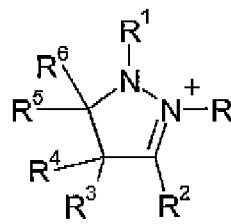
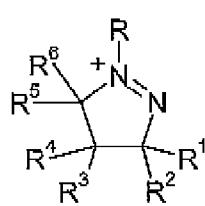


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(IVg)

(IVg')

(IVh)

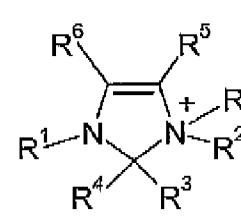
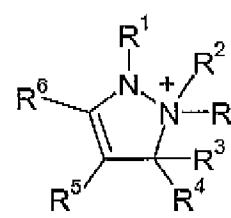
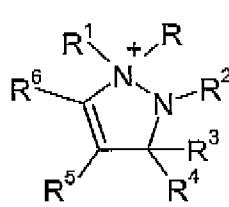


(IVi)

(IVj)

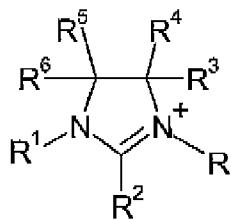
(IVj')

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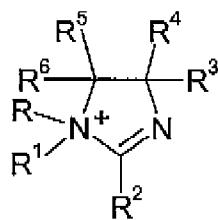


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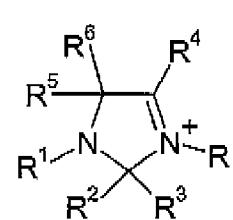
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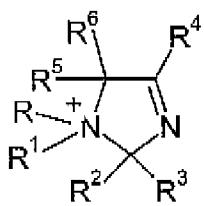
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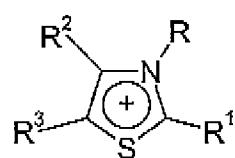
(IVl)



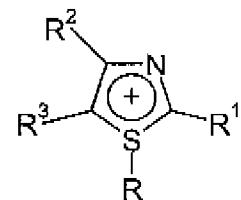
(IVm)



(IVm')

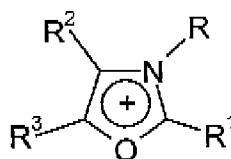


(IVn)

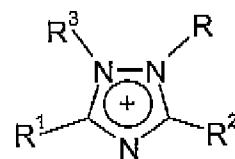


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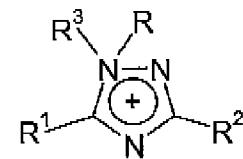
(IVn')



(IVo)

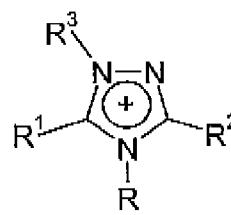


(IVo')

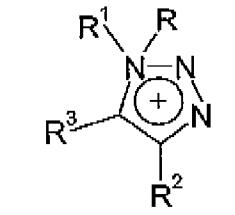


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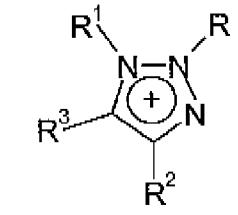
(IVp)



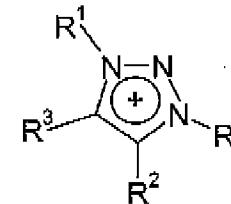
(IVq)



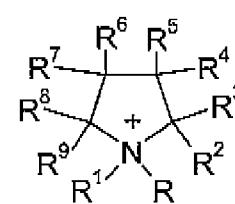
(IVq')



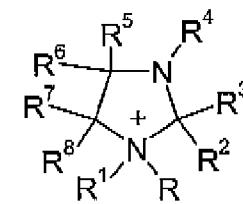
(IVq'')



(IVr)



(IVr')



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(IVrⁿ)

(IVs)

(IVt)

and oligomers comprising these structures, where

5

the radical R is hydrogen; and

10 the radicals R¹ to R⁹ are each, independently of one another, hydrogen, a sulfo group or a carbon-comprising organic, saturated or unsaturated, acyclic or cyclic, aliphatic, aromatic or araliphatic radical which has from 1 to 20 carbon atoms and is unsubstituted or interrupted by from 1 to 5 heteroatoms or functional groups or substituted, with the radicals R¹ to R⁹ which are bound to a carbon atom (and not to a heteroatom) in the abovementioned formulae (IV) also being able to be halogen or a functional group; or

15

20 two adjacent radicals from the group consisting of R¹ to R⁹ can together also be a divalent, carbon-comprising organic, saturated or unsaturated, acyclic or cyclic, aliphatic, aromatic or araliphatic radical which has from 1 to 30 carbon atoms and is unsubstituted or interrupted by from 1 to 5 heteroatoms or functional groups or substituted.

2. The solution according to claim 1, wherein the cations comprise at least one nitrogen atom which is present in protonated form as ammonium cation.

25 3. The solution according to claim 1 or claim 2, wherein more than 1% by weight of cellulose, based on the total weight of the solution, is comprised in the solution.

30 4. The solution according to any one of claims 1 to 3, wherein anions and cations form a salt of the general formula (I)

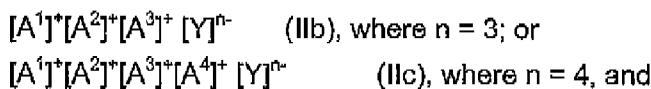


35 where n is 1, 2, 3 or 4, [A]⁺ is a quaternary ammonium cation, an oxonium cation, a sulfonium cation or a phosphonium cation and [Y]ⁿ⁻ is a monovalent, divalent, trivalent or tetravalent anion;

mixed salts of the general formulae (II)

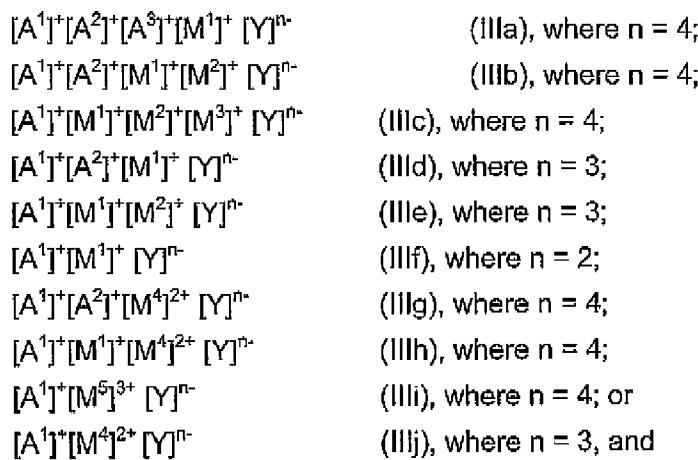


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5 where $[A^1]^+$, $[A^2]^+$, $[A^3]^+$ and $[A^4]^+$ are selected independently from among the groups mentioned for $[A]^+$, and $[Y]^{n-}$ is as defined under (A); or

mixed salts of the general formulae (III)

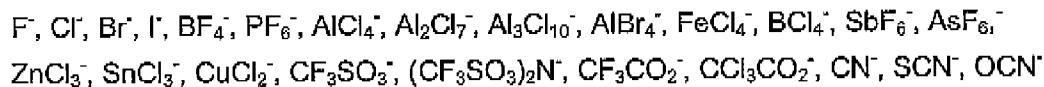


20 where $[A^1]^+$, $[A^2]^+$ and $[A^3]^+$ are selected independently from among the groups mentioned for $[A]^+$, $[Y]^{n-}$ is as defined under (A) and $[M^1]^+$, $[M^2]^+$, $[M^3]^+$ are monovalent metal cations, $[M^4]^{2+}$ is a divalent metal cation and $[M^5]^{3+}$ is a trivalent metal cation.

5. The solution according to any one of claims 1 to 4, wherein the ionic liquid comprises at least one anion selected from the group consisting of:

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the group of halides and halogen compounds of the formulae:



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the group of sulfates, sulfites and sulfonates of the general formulae:

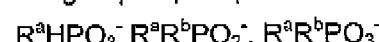


the group of phosphates of the general formulae



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the group of phosphonates and phosphinates of the general formulae:



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the group of phosphites of the general formulae:



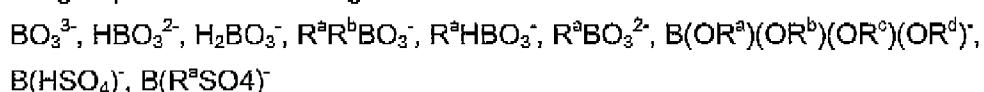
the group of phosphonites and phosphinites of the general formulae:



the group of carboxylic acids of the general formula:



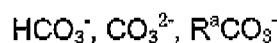
10 the group of borates of the general formulae:



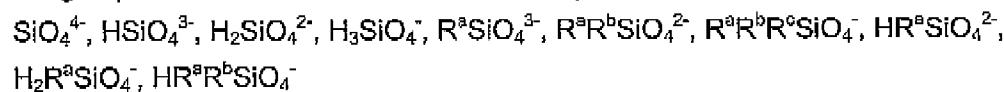
the group of boronates of the general formulae:



the group of carbonates and carbonic esters of the general formulae:



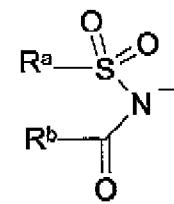
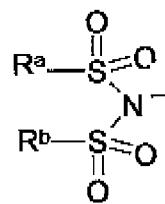
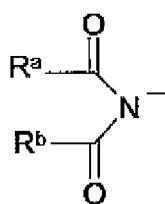
20 the group of silicates and silicic esters of the general formulae:



the group of alkyl silane and aryl silane salts of the general formulae:



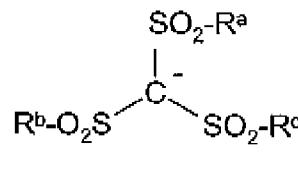
the group of carboximides, bis(sulfonyl)imides and sulfonylimides of the general formulae:



30 the group of methides of the general formula:

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the group of alkoxides and aryloxides of the general formula R^bO^- ;

5

the group of halometalates of the general formula $[\text{M}_q\text{Hal}_r]^{s-}$,

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where M is a metal and Hal is fluorine, chlorine, bromine or iodine, q and r are positive integers and indicate the stoichiometry of the complex and s is a positive integer and indicates the charge on the complex,

15

the group of sulfides, hydrogen sulfides, polysulfides, hydrogen polysulfides and thiolates of the general formulae:

S^{2-} , HS^- , $[\text{S}_v]^{2-}$, $[\text{HS}_v]^-$, $[\text{R}^a\text{S}]^-$, where v is a positive integer from 2 to 10, and

the group of complex metal ions such as $\text{Fe}(\text{CN})_6^{3-}$, $\text{Fe}(\text{CN})_6^{4-}$, MnO_4^- , $\text{Fe}(\text{CO})_4^-$, where

20

R^a , R^b , R^c and R^d are each, independently of one another, hydrogen, $\text{C}_1\text{-C}_{18}$ -alkyl, $\text{C}_2\text{-C}_{18}$ -alkyl which is optionally interrupted by one or more nonadjacent oxygen and/or sulfur atoms and/or one or more substituted or unsubstituted imino groups, $\text{C}_6\text{-C}_{14}$ -aryl, $\text{C}_5\text{-C}_{12}$ -cycloalkyl or a five- or six-membered, oxygen-, nitrogen- and/or sulfur-comprising heterocycle, where two of them may together form an unsaturated, saturated or aromatic ring which is optionally interrupted by one or more oxygen and/or sulfur atoms and/or one or more unsubstituted or substituted imino groups, where the radicals mentioned may each be additionally substituted by functional groups, aryl, alkyl, aryloxy, alkyloxy, halogen, heteroatoms and/or heterocycles.

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6. The solution according to any one of claims 1 to 5 which has a temperature of not more than 180°C .
7. A process for preparing a solution according to any one of claims 1 to 6, which process comprises the steps

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a) addition of cellulose to a solution comprising an ionic liquid comprising anions and cations as solvent, wherein the cations comprise at least one nitrogen atom which is present in protonated form as ammonium cation, and

5 a. mixing of the solution until the cellulose is completely dissolved.

8. The use of a solution according to any one of claims 1 to 6 for the physical or chemical treatment of cellulose.

10 **BASF SE**

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