

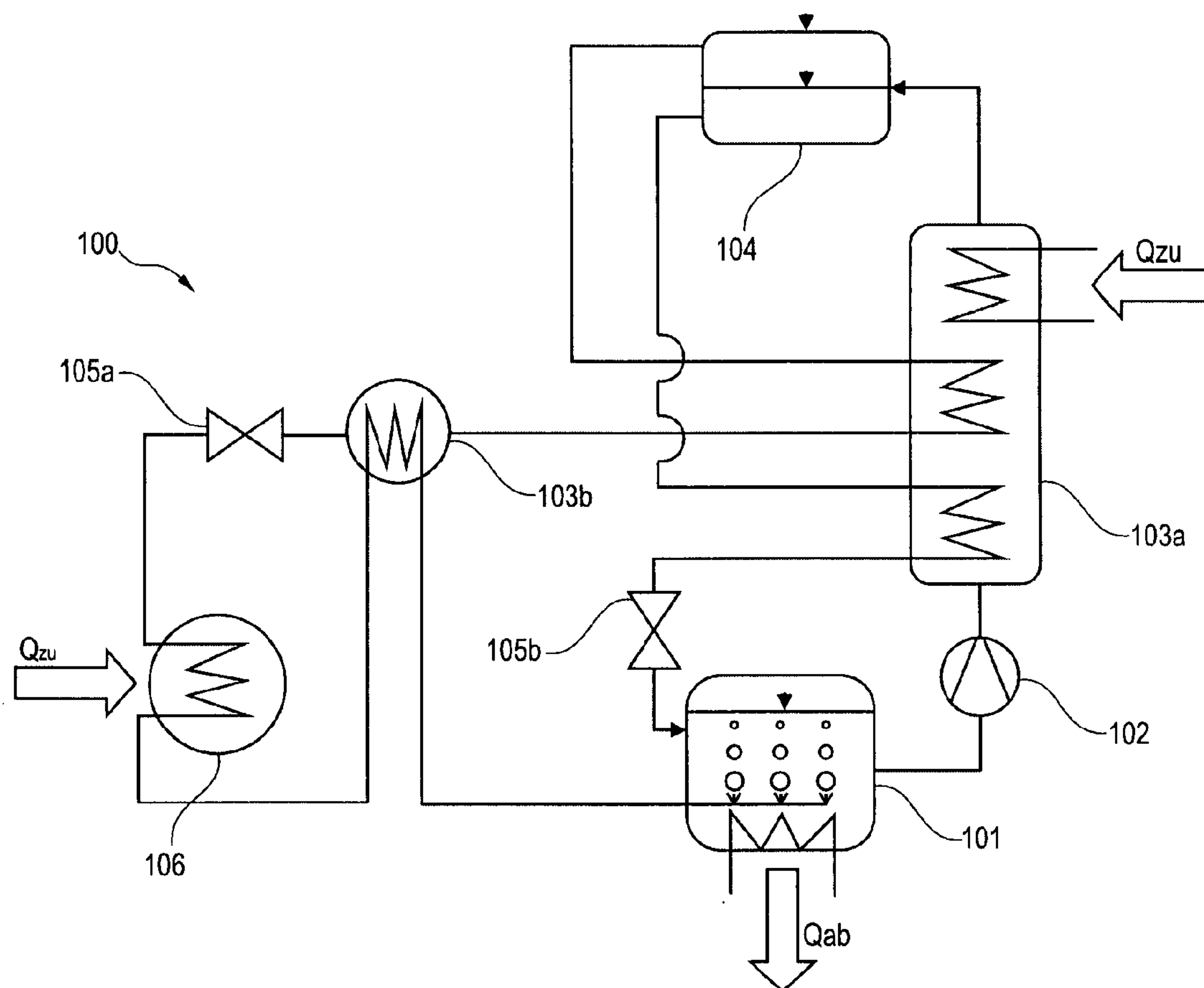
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(19) **United States**(12) **Patent Application Publication**
Kalb(10) **Pub. No.: US 2012/0134905 A1**(43) **Pub. Date: May 31, 2012**(54) **METHOD OF USE OF AN IONIC LIQUID AND
DEVICE FOR SORPTION OF A GAS****Publication Classification**(75) Inventor: **Roland Kalb**, Leoben (AT)(73) Assignee: **VTU HOLDING GMBH**,
Grambach (AT)(21) Appl. No.: **13/380,008**(22) PCT Filed: **Jun. 22, 2010**(86) PCT No.: **PCT/EP10/58856**§ 371 (c)(1),
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261/119.1; 261/157(57) **ABSTRACT**

A method of use of an ionic liquid for sorption of a gas having an electric multipole moment is provided, wherein the ionic liquid comprises an anion and a non-aromatic cation. In particular, the electric multipole moment may be an electric dipole moment and/or an electric quadrupole moment. The sorption may be an adsorption or an absorption. The ionic liquid may be a pure ionic liquid, i.e. a liquid substantially only containing anions and cations, while not containing other components, e.g. water. Alternatively a solution containing the ionic liquid and a solvent or further compound, e.g. water, may be used.



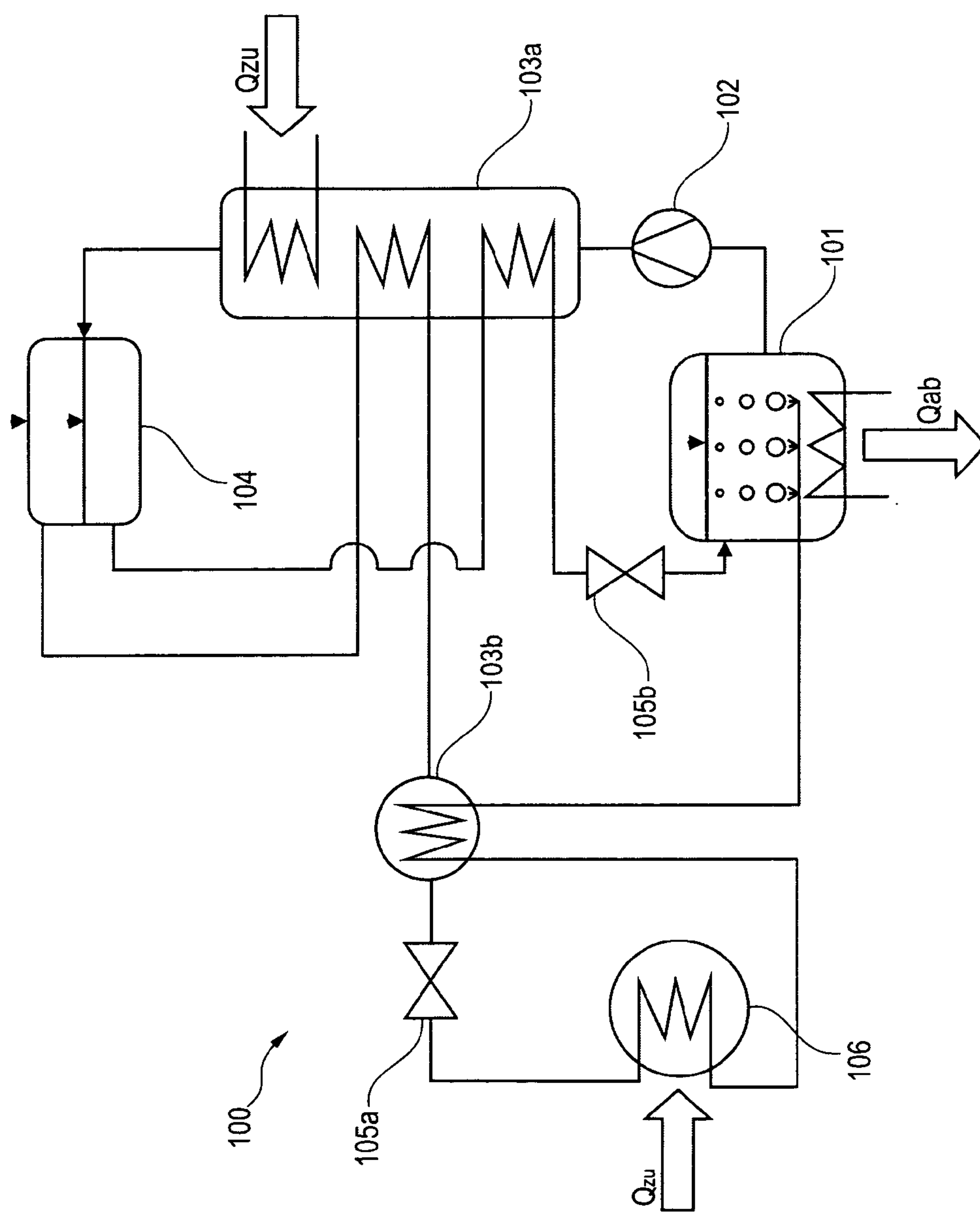


Fig. 1

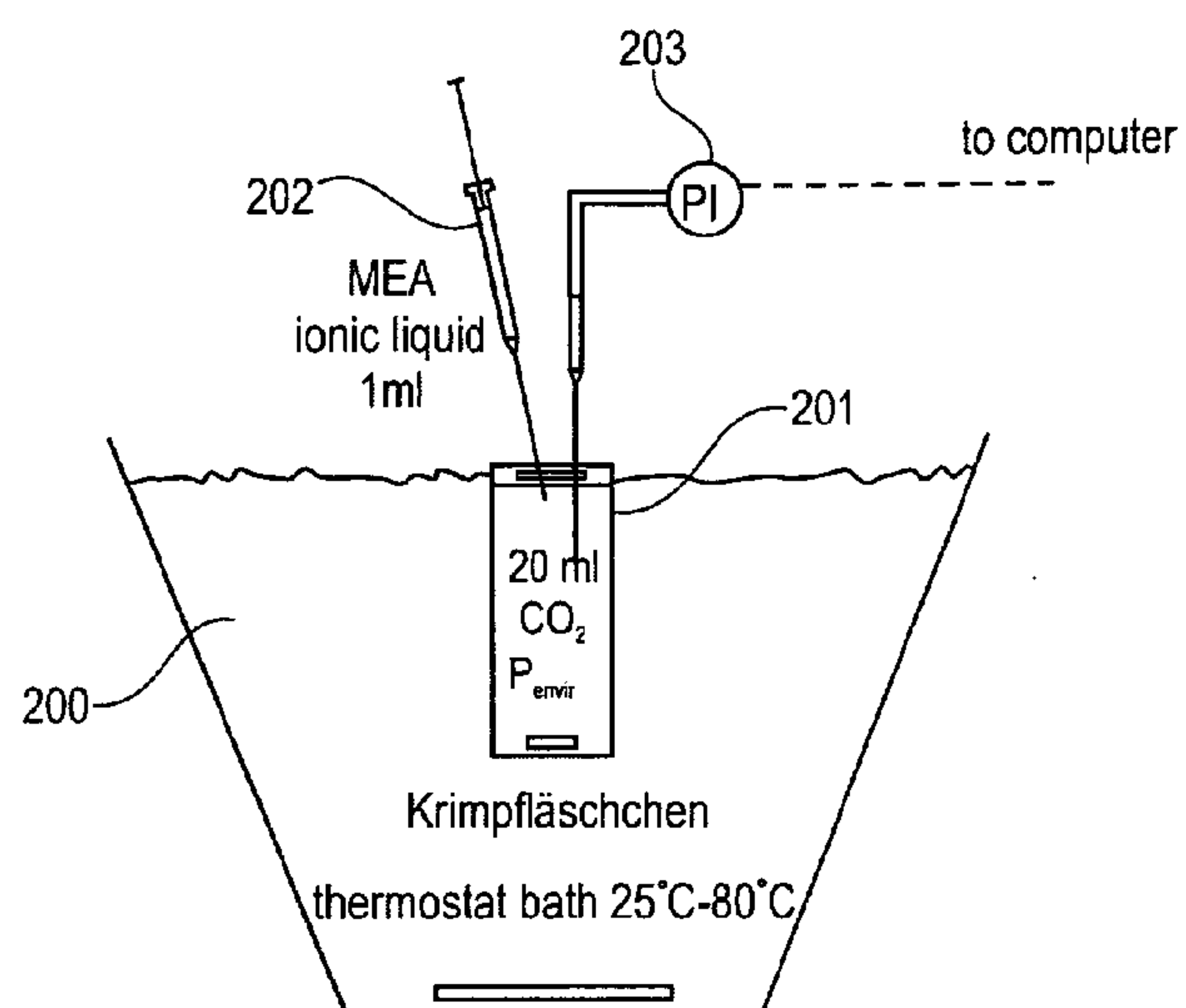


Fig. 2

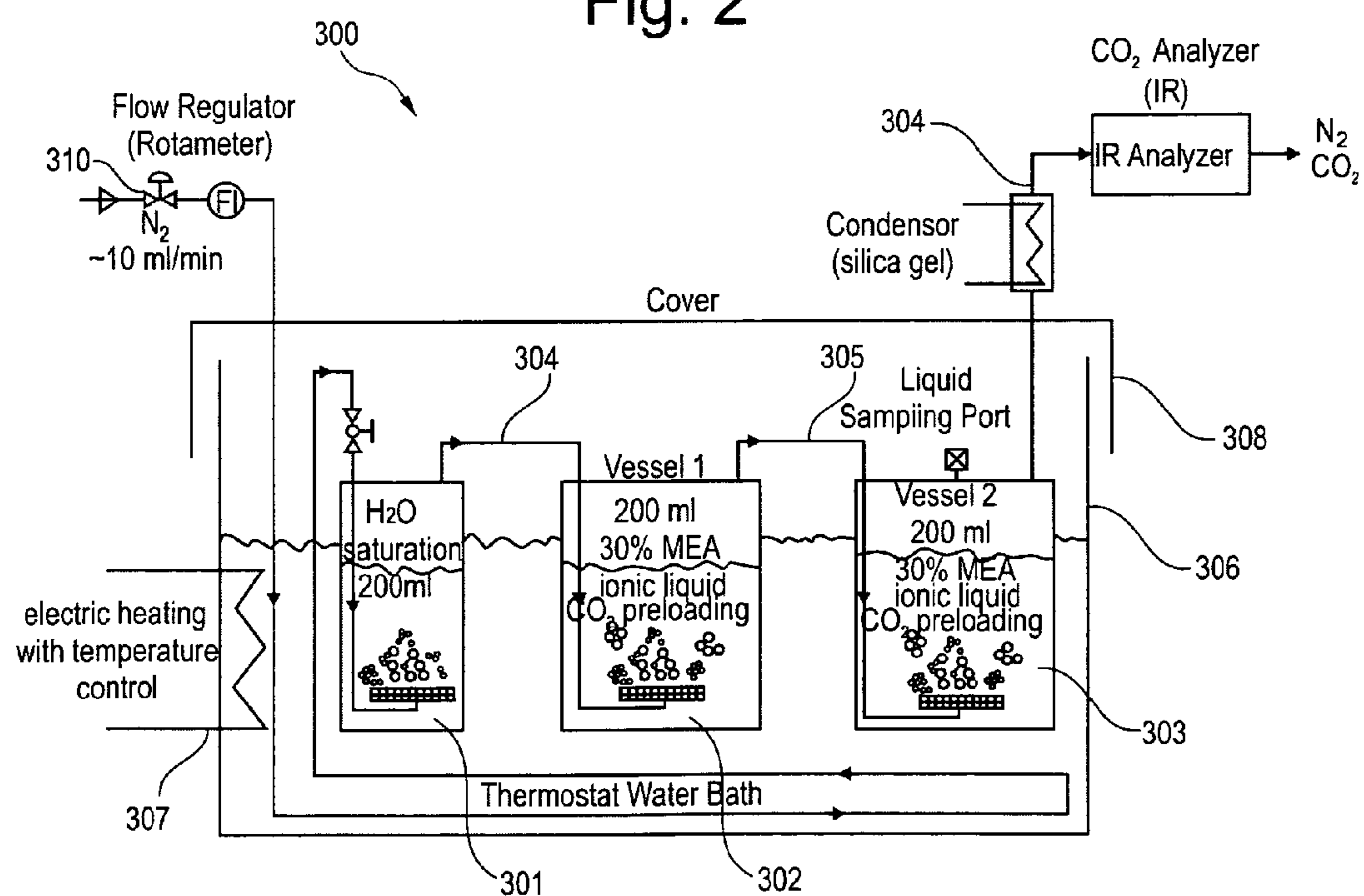


Fig. 3

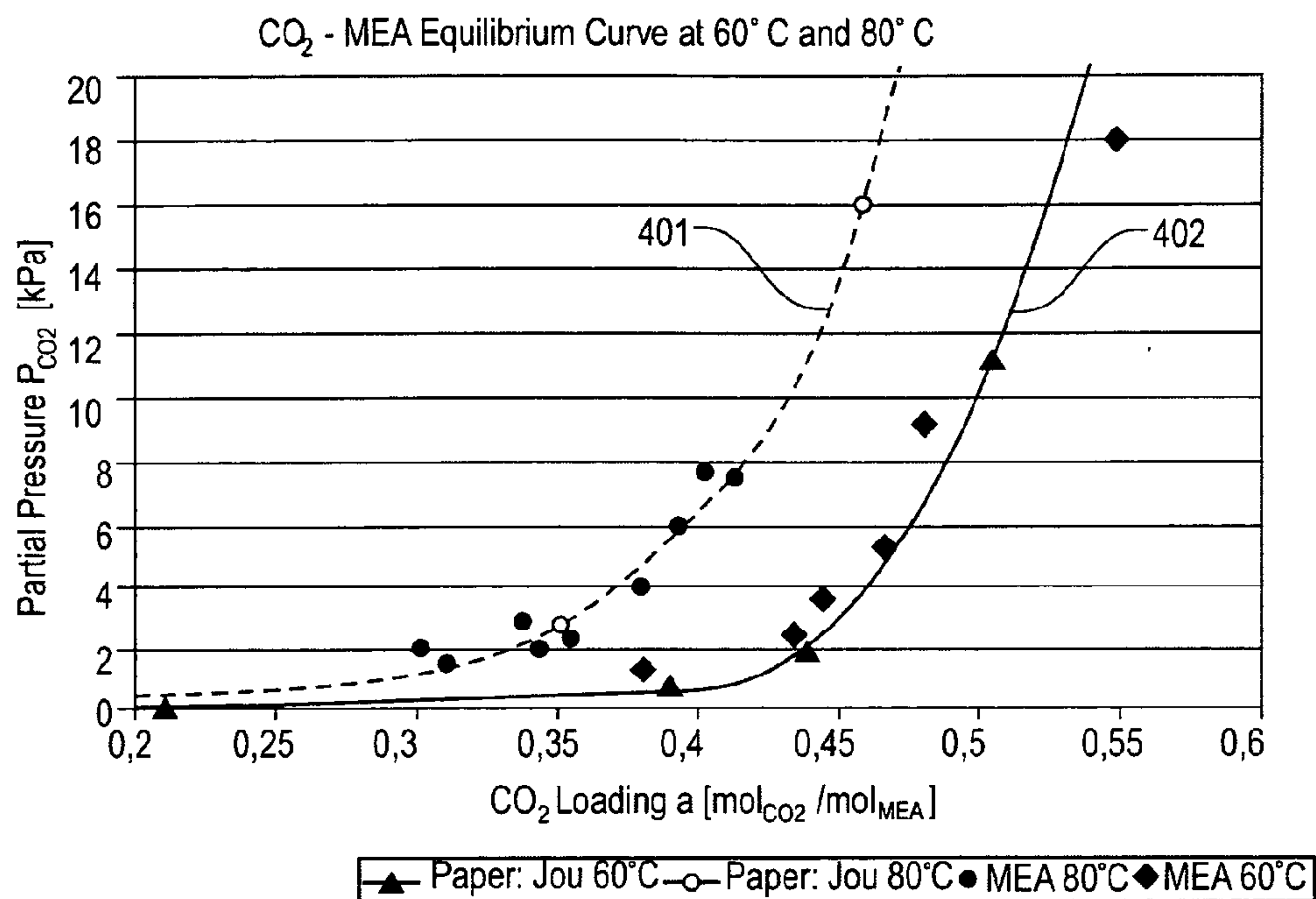


Fig. 4

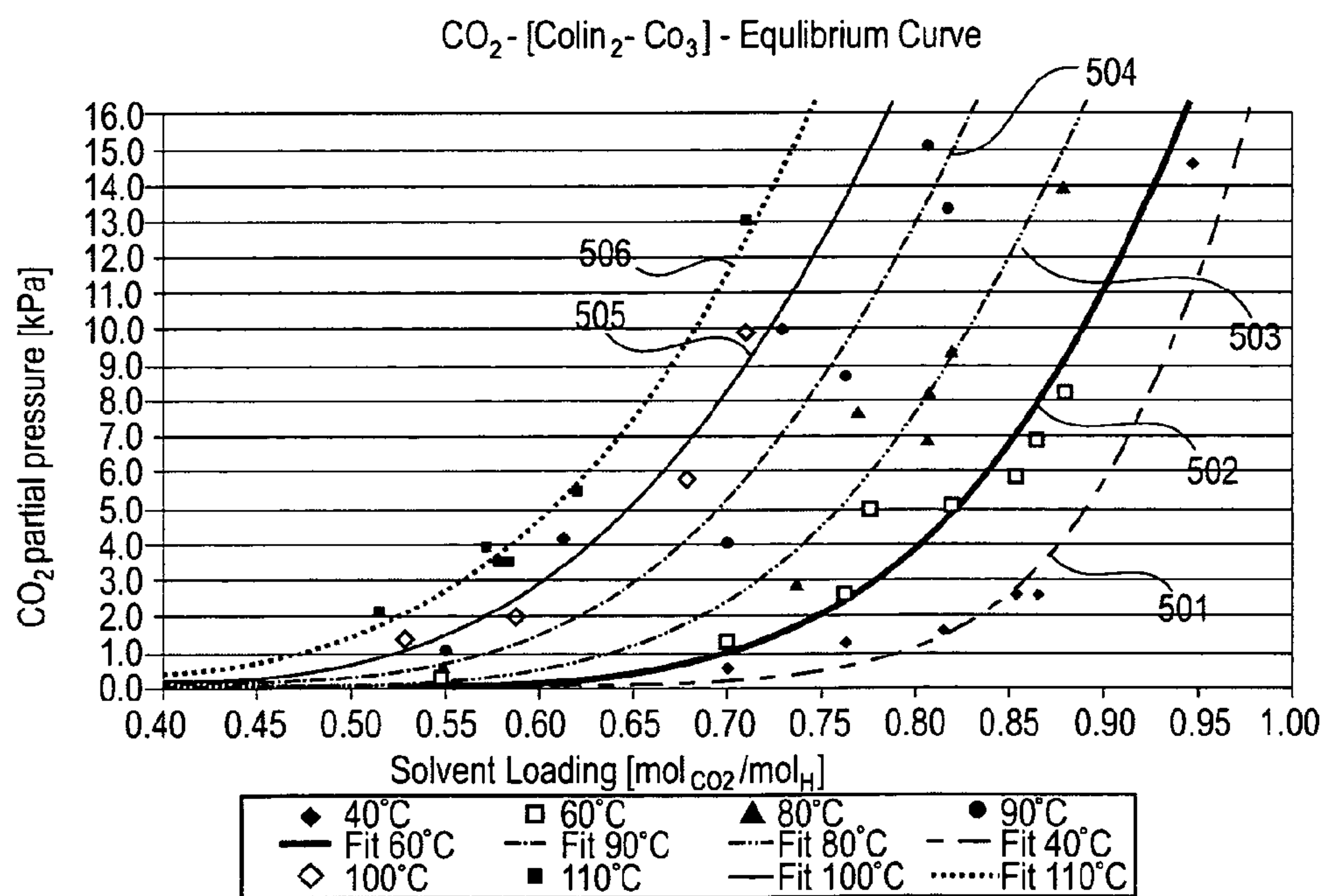


Fig. 5

METHOD OF USE OF AN IONIC LIQUID AND DEVICE FOR SORPTION OF A GAS

FIELD OF THE INVENTION

[0001] The invention relates to a method of use of an ionic liquid, in particular for sorption of a gas or vapor having an electric multipole moment.

[0002] Further, the invention relates to a device for sorption of a gas or vapor.

BACKGROUND OF THE INVENTION

[0003] Carbon dioxide (CO₂) is an undesired diluent that is present in many gas sources. In order to improve the quality of the gases the CO₂ should be removed to acceptable specifications. In gas processing industry, various technologies have been employed for CO₂ removal including chemical solvents, physical solvents, and membranes. By far, chemical solvents that reversibly react with CO₂ are most commonly used for CO₂ removal.

[0004] Furthermore, processes for removal of CO₂ from gaseous streams are known, which comprise the contacting a CO₂ containing gaseous stream with an absorbent comprising from 1 to 20 wt % water and an ionic liquid comprising pyridines or imidazole cations and an anion, wherein said contacting occurs at absorption conditions, to absorb at least a portion of the CO₂ from the CO₂ containing gaseous stream and forming a CO₂-absorbent complex. Afterwards the gaseous product having a reduced CO₂ content is recovered.

[0005] However, the known processes of removal CO₂ may be costly.

OBJECT AND SUMMARY OF THE INVENTION

[0006] It may be an objective of the invention to provide a method of removal of a gaseous or vaporous component and a device for removal of a gaseous or vaporous component which may be save to use or less expensive than known methods.

[0007] This object may be solved by a method of use of an ionic liquid, in particular for sorption of a gas or vapor having an electric multipole moment and a device for sorption of a gas or vapor according to the independent claims. Further exemplary embodiments are described in the dependent claims.

[0008] According to an exemplary aspect of the invention a method of use of an ionic liquid for sorption of a gas having an electric multipole moment is provided, wherein the ionic liquid comprises an anion and a non-aromatic cation. It should be noted that according to this application the terms “gas” and “gaseous” and “vapor” and “vaporous”, respectively may be interchangeably used, i.e. no distinction is made between these two terms.

[0009] In particular, the electric multipole moment may be an electric dipole moment and/or an electric quadrupole moment. The sorption may be an adsorption or an absorption. The ionic liquid may be a pure ionic liquid, i.e. a liquid substantially only containing anions and cations, while not containing other components, e.g. water. Alternatively a solution containing the ionic liquid and a solvent or further compound, e.g. water, may be used. For example, the content of other components than the ionic liquid may be 35% or less by mass, in particular less than 30% by mass, less than 20% by mass, less than 10% by mass, or even less than 5% by mass, wherein for all the above ranges the lower limit may be about

10 ppm. However, in case of water as the other component the ranges may be between about 10 ppm and 50% by mass, in particular between about 10 ppm and 35% by mass, between about 10 ppm and 20% by mass, between about 10 ppm and 10% by mass, or even between about 10 ppm and 5% by mass. In this context it should be noted that according to specific embodiments the sorption may be performed by the ionic liquid itself, e.g. may particularly be a physical sorption. In general, the ionic liquid may also perform a chemical sorption, a physical sorption or a combined chemical-physical sorption. This process has to be distinguished from a process in which the ionic liquid only forms a solvent for a compound or component, e.g. a polymer, which then acts as the sorbent for the gas having an electric multipole moment. That is, according to specific embodiments of the invention the ionic liquid may form the sorbent which sorbs the gas having an electric multipole moment. Consequently a method according to an exemplary embodiment may comprise the step of sorbing a gas having an electric multipole moment by an ionic liquid, wherein the ionic liquid may be a pure or substantially pure ionic liquid or may include some additives having only few, e.g. less than 35% by mass, further components. In the most generic form the ionic liquids may be represented by [Q⁺]_n[Z^{m-}], wherein Q represents a non-aromatic cation and which may be produced by a process as described for example in WO 2005/021484 which is hereby herein incorporated by reference.

[0010] According to an exemplary aspect of the invention a device for sorption of a gas having an electric multipole moment is provided, wherein the device comprises a reservoir of an ionic liquid comprising an anion and a non-aromatic cation.

[0011] In particular, the device may comprise an inlet, a container including the ionic liquid, and optionally an outlet. The device may be used to sorb gas having an electric multipole moment, e.g. CO₂, from a medium which is selected out of the group consisting of recovery gas, synthesis gas, water gas, natural gas, inhaled air, and exhaled air. In particular, the device may be a heat pump. The heat pump may comprise a circuit including CO₂ and the ionic liquid which comprises an anion and a non-aromatic cation as working media. In particular, the usage of a pair of working media containing CO₂ and an ionic liquid in a heat pump may be advantageous since CO₂ is not toxic is of less concern with respect to environmental effect compared to other vaporizable working substances.

[0012] According to an exemplary aspect of the invention a method of use of an ionic liquid for sorption of a gas having an electric multipole moment is provided, wherein the ionic liquid comprises a carbanion and a cation.

[0013] The use of non-aromatic cations of the ionic liquid may provide for an ionic liquid which may be cheaper and more secure than the use of aromatic cations. Such ionic liquids may be a suitable medium to sorb specific gases, e.g. CO₂, or vapor out of a mixture of gases and may also be suitable to release these specific gases or vapor again. The specific gases and the ionic liquid may form a complex, i.e. the specific gases may be complex bound. According to some exemplary embodiments it may even be possible to remove the complex bound in the form of a solid compound. The uses of such ionic liquids for sorption of gases may be advantageous since ionic liquids may be used showing no or at least substantially no vapor pressure, e.g. a non measureable vapor pressure or even a vapor pressure in the same magnitude of

order of steel. Thus, the gases or mixture of gases may not be contaminated by vapor of the ionic liquid. Furthermore, the use of non-aromatic ionic liquids may increase the performance of the sorption process compared to the case in which aromatic ionic liquids are used. For example, the removal of CO₂ by using non-aromatic ionic liquids may exhibit an improved performance even in cases where the vapor pressure of CO₂ is low.

[0014] However, alternatively it may also be possible to use an ionic liquid having aromatic cation in case the ionic liquid comprises a carbanion. That is, when using an ionic liquid comprising a carbanion the cation may be an aromatic or a non-aromatic anion.

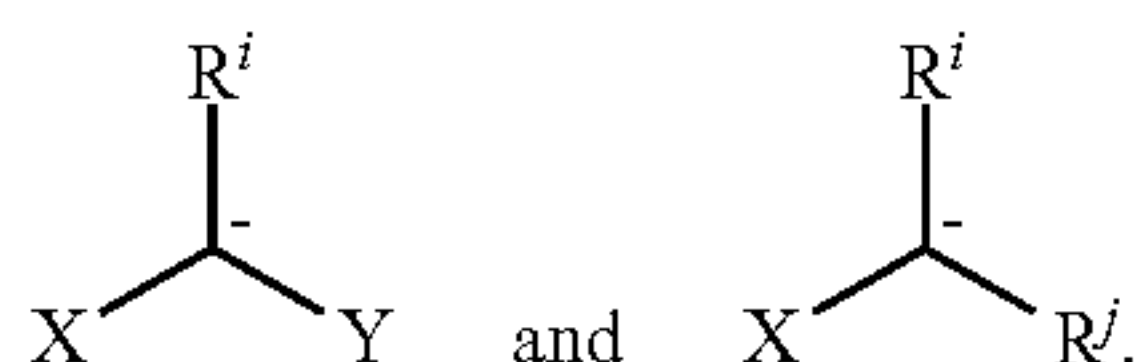
[0015] Next, further aspects of exemplary embodiments of the method of use of an ionic liquid for sorption of a gas are described. However, these embodiments also apply for the device for sorption of a gas.

[0016] According to an exemplary embodiment of the method of use of an ionic liquid the non-aromatic cation is an aliphatic cation. The term "aliphatic cation" may also include cations having aliphatic side chains.

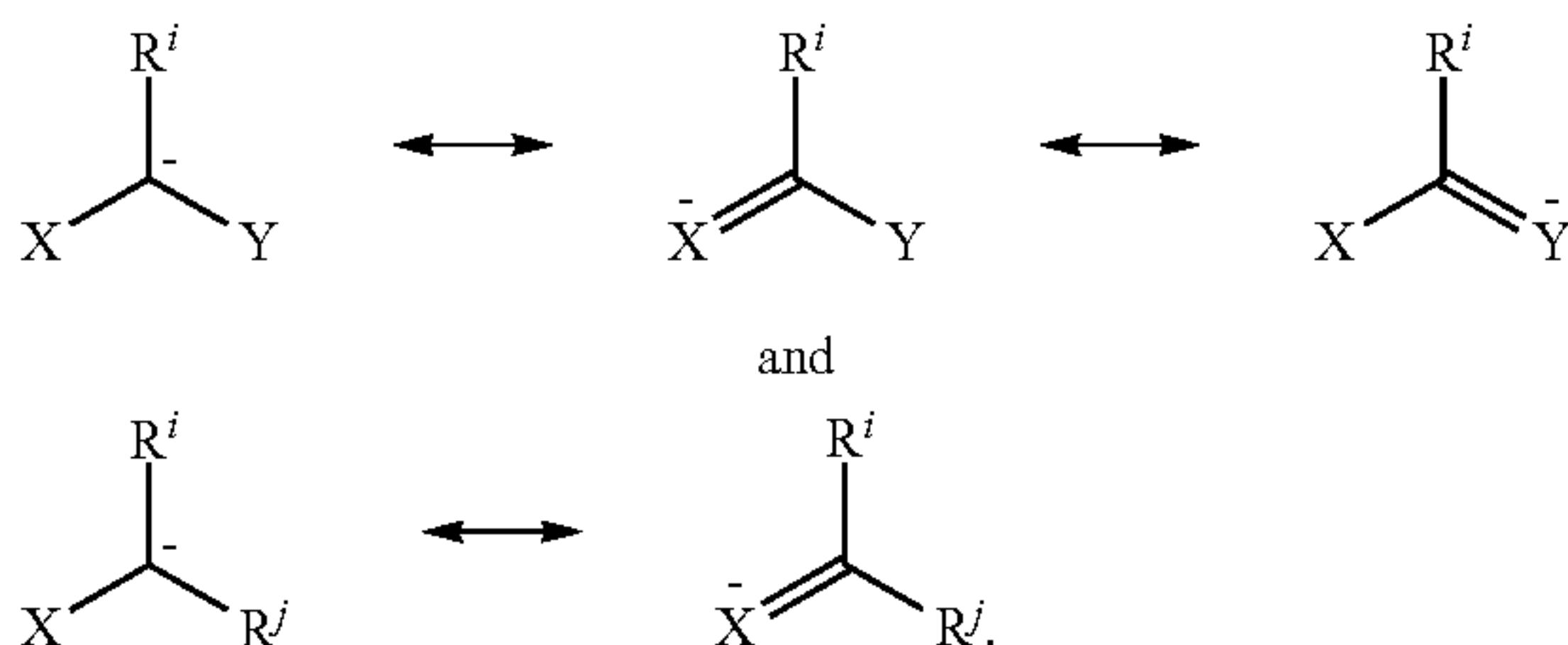
[0017] Aliphatic cations may be suitable non-aromatic cations for an ionic liquid which are less expensive and/or less toxic than typical aromatic cations.

[0018] According to an exemplary embodiment of the method of use of an ionic liquid the ionic liquid satisfy the generic formula [Q⁺][A⁻],

[0019] wherein the anion can be described by one of the following structures:

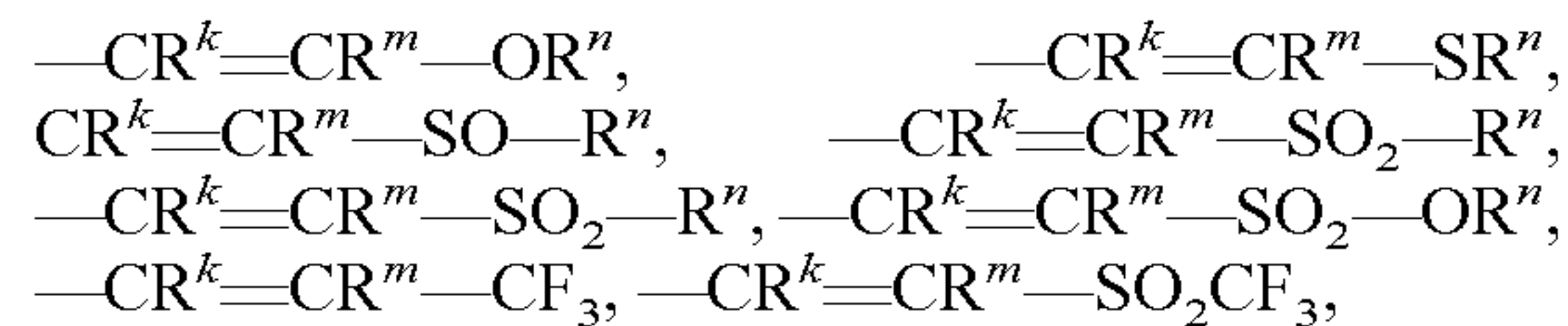


[0020] In particular, the anion may be describable by the resonant or mesomeric states:



wherein X and Y may indicate, independently from each other, groups which may attract electrons due to the inductive effect or the mesomeric effect and/or which may delocalize and/or stabilize (localize) electrons. Examples for such groups may be:

[0021] —CN, —NO₂, —NO₃, —CO—R^k, —COOR^k, —C=N—R^k, —CO—NR^kR^m, —NR^kR^m, —OH, —OR^k, —SH, —SR^k, —SO—R^k, —SO₂—R^k, —SO₂—OR^k, —PO—OR^kOR^m (phosphonate), —I, —Cl, —Br, —F, —CCl₃, —CCl₂R^k, —CClR^kR^m, —CF₃, —CF₂R^k, —CFR^kR^m, —SO₂CF₃, —COOCF₃, —C₆H₅, —CR^k=CR^mRⁿ, —C≡CR^m, CR^k=CR^m—CN, —CR^k=CR^m—NO₂, —CR^k=CR^m—CO—R^k, —CR^k=CR^m—COOR^k, —CR^k=CR^m—C=N—Rⁿ, —CR^k=CR^m—CO—NRⁿR^o, —CR^k=CR^m—NRⁿR^o,



wherein R^k, R^m, Rⁿ, R^o may, independently from each other, denote hydrogen, C₁- to C₃₀-alkyl and their aryl-, heteroaryl-, cycloalkyl-, halogen-, hydroxy-, amino-, carboxy-, formyl-, —O—, —CO—, —CO—O— or —CO—N< substituted components, like 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, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, icosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, phenylmethyl (benzyl), diphenylmethyl, triphenylmethyl, 2-phenylethyl, 3-phenylpropyl, cyclopentylmethyl, 2-cyclopentylethyl, 3-cyclopentylpropyl, cyclohexylmethyl, 2-cyclohexylethyl, 3-cyclohexylpropyl, methoxy, ethoxy, formyl, acetyl or C_nF_{2(n-a)+(1-b)}H_{2a+b} wherein n≤30, 0≤a≤n and b=0 or 1 (e.g. CF₃, C₂F₅, CH₂CH₂—C_(n-2)F_{2(n-2)+1}, C₆F₁₃, C₈F₁₇, C₁₀F₂₁, C₁₂F₂₅);

[0022] C₃- to C₁₂-cycloalkyl and their aryl-, heteroaryl-, cycloalkyl-, halogen-, hydroxy-, amino-, carboxy-, formyl-, —O—, —CO— or —CO—O-substituted components, e.g. cyclopentyl, 2-methyl-1-cyclopentyl, 3-methyl-1-cyclopentyl, cyclohexyl, 2-methyl-1-cyclohexyl, 3-methyl-1-cyclohexyl, 4-methyl-1-cyclohexyl or C_nF_{2(n-a)-(1-b)}H_{2a-b} wherein n≤0, 0≤a≤n and b=0 or 1;

[0023] C₂- to C₃₀-alkenyl and their aryl-, heteroaryl-, cycloalkyl-, halogen-, hydroxy-, amino-, carboxy-, formyl-, —O—, —CO— or —CO—O-substituted components, e.g. 2-propenyl, 3-butenyl, cis-2-butenyl, trans-2-butenyl or C_nF_{2(n-a)-(1-b)}H_{2a-b} wherein n≤30, 0≤a≤n and b=0 or 1;

[0024] C₃- to C₁₂-cycloalkenyl and their aryl-, heteroaryl-, cycloalkyl-, halogen-, hydroxy-, amino-, carboxy-, formyl-, —O—, —CO— or —CO—O-substituted components, e.g. 3-cyclopentenyl, 2-cyclohexenyl, 3-cyclohexenyl, 2,5-cyclohexadienyl or C_nF_{2(n-a)-3(1-b)}H_{2a-3b} wherein n≤0, 0≤a≤n and b=0 or 1; and

[0025] aryl or heteroaryl having 2 to 30 carbon atoms and their alkyl-, aryl-, heteroaryl-, cycloalkyl-, halogen-, hydroxy-, amino-, carboxy-, formyl-, —O—, —CO— or —CO—O-substituted components, e.g. phenyl, 2-methyl-phenyl (2-tolyl), 3-methyl-phenyl (3-tolyl), 4-methyl-phenyl, 2-ethyl-phenyl, 3-ethyl-phenyl, 4-ethyl-phenyl, 2,3-dimethyl-phenyl, 2,4-dimethyl-phenyl, 2,5-dimethyl-phenyl, 2,6-dimethyl-phenyl, 3,4-dimethyl-phenyl, 3,5-dimethyl-phenyl, 4-phenyl-phenyl, 1-naphthyl, 2-naphthyl, 1-pyrrolyl, 2-pyrrolyl, 3-pyrrolyl, 2-pyridinyl, 3-pyridinyl, 4-pyridinyl or C₆F_(5-a)H_a wherein 0≤a≤5,

wherein pairs of the R^k, R^m, Rⁿ, R^o may be bonded directly to each other or via C₁-C₄, which may be substituted if necessary, so that a saturated, unsaturated, or conjugated unsaturated ring may be formed.

[0026] According to an exemplary embodiment of the method of use of an ionic liquid the ionic liquid satisfy the

generic formula $[Q^+]_a[A^{a-}]$, wherein $[A^{a-}]$ with the charge a is selected out of the group consisting of:

[0027] dialkyl ketones, dialkyl-1,3-diketones, alkyl- β -keto esters, terminal alkynes, linear or cyclic 1,3-thioethers, dialkyl phosphonates, dialkyl malonic acid esters, β -cyano carbonic acids and their respective alkylesters, β -alkoxy carbonic acids and their respective alkylesters, β -cyano nitriles, cyclopentadiene (substituted if necessary), trialkylimines, dialkylimines, diaryl ketones, alkyl-aryl-ketones, diaryl-1,3-diketones, alkyl-aryl-1,3-diketones, β -aryloxy carbonic acids and their respective alkylesters, β -aryloxy carbonic acids and their respective arylestes, aryl- β -ketoesters, diarylphosphonates, alkyl-aryl-phosphonates, diaryl malonic acid esters, alkyl-aryl-malonic acid esters, β -cyano carbonic acids arylestes and arylimines.

[0028] According to an exemplary embodiment of the method of use of an ionic liquid the ionic liquid satisfy the generic formula $[Q^+]_a[A^{a-}]$, wherein $[A^{a-}]$ is a carbanion formed by deprotonating a chemical compound out of the group consisting of:

[0029] acetoacetic ester, malonic mononitrile, malonic acid dimethylester, malonic acid diethylester, acetylacetone, malonic acid dinitrile, acetone, diethylketone, methlethylketone, dibutylketone, 1,3-dithian, acetaldehyde, benzaldehyde, crotonaldehyde and butyraldehyde.

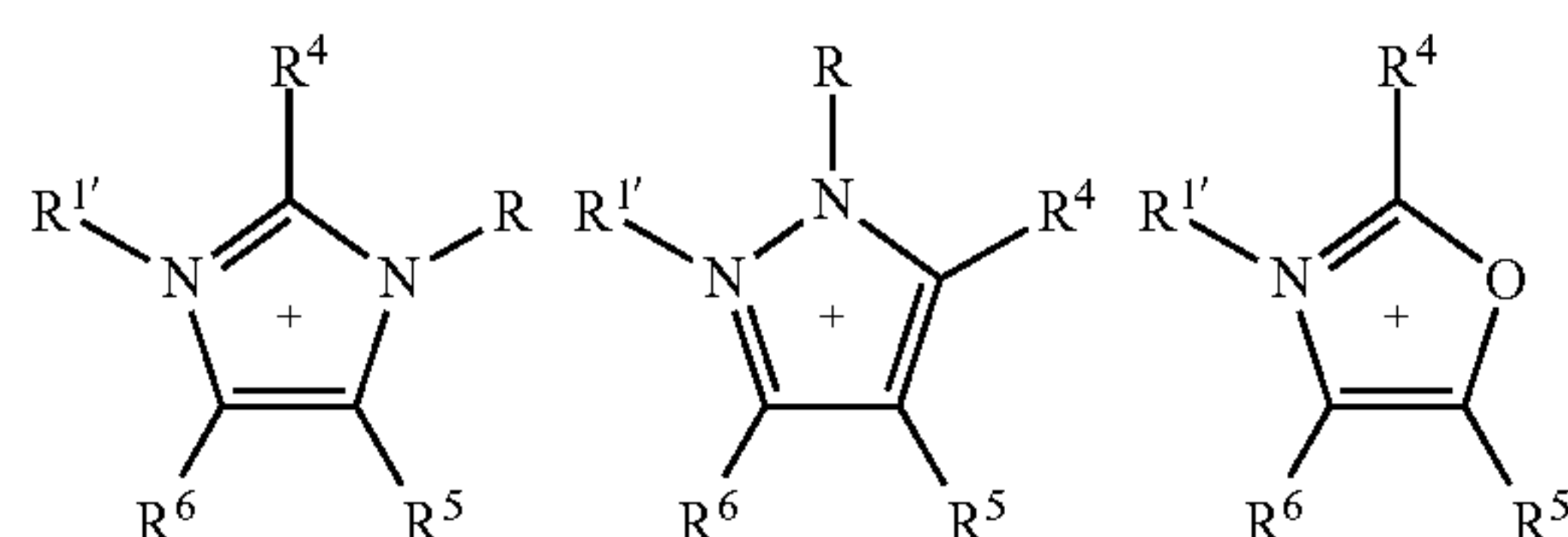
[0030] According to an exemplary embodiment of the method of use of an ionic liquid the ionic liquid satisfy the generic formula $[Q^+]_a[A^{a-}]$, wherein $[A^{a-}]$ is a carbanion and wherein $[C]^+$ is one out of the group consisting of quaternary ammonium cation $[R^1R^1R^2R^3N]^+$, phosphonium $[R^1R^1R^2R^3P]^+$, sulfonium $[R^1R^1R^2S]^+$ and a hetero aromatic cation. In particular, the carbanion may be formed by deprotonating a chemical compound out of the group consisting of: acetoacetic ester, malonic mononitrile, malonic acid dimethylester, malonic acid diethylester, acetylacetone, malonic acid dinitrile, acetone, diethylketone, methlethylketone, dibutylketone, 1,3-dithian, acetaldehyde, benzaldehyde, crotonaldehyde and butyraldehyde.

[0031] In particular:

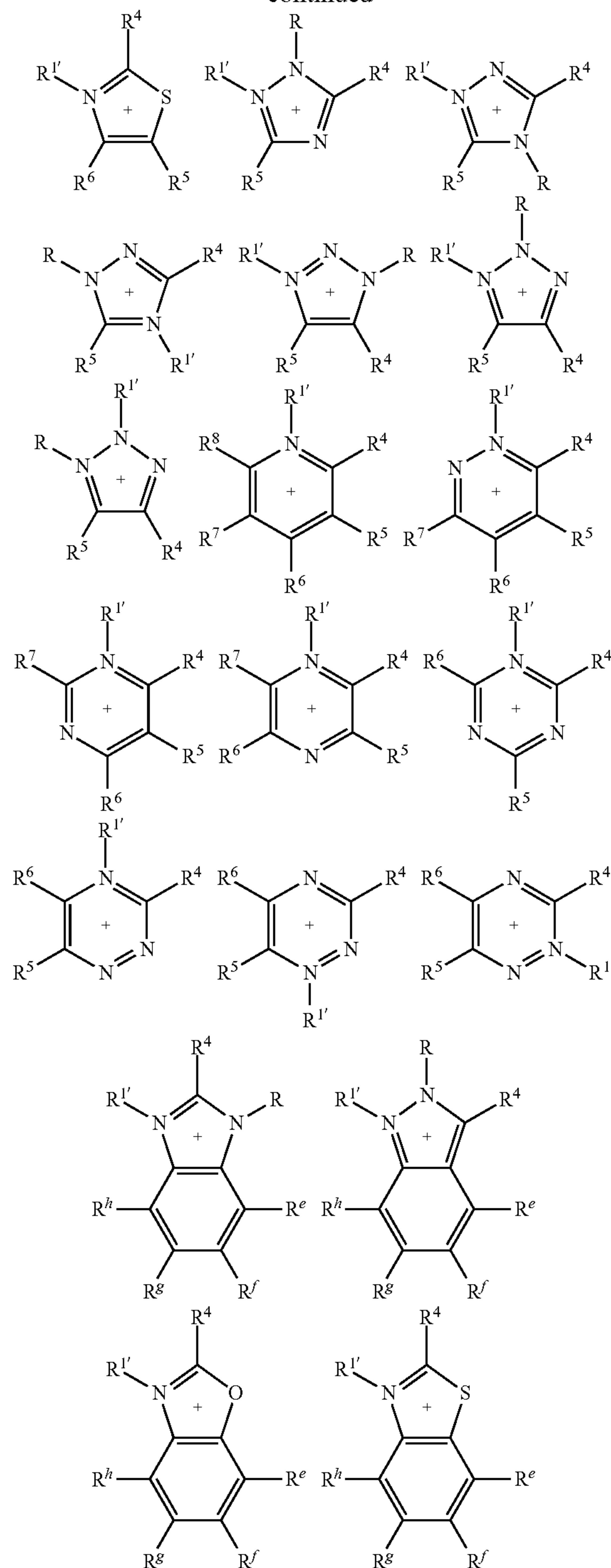
[0032] R^1 , $R^{1'}$, R^2 , R^3 may be alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl or heteroaryl which may be independently substituted, or

[0033] two of the moieties R^1 , $R^{1'}$, R^2 , R^3 may form a ring together with a hetero-atom to which they are bound. The ring may be saturated, unsaturated, substituted or unsubstituted. The chain may be interrupted by one or more hetero-atoms out of the group consisting of O, S, NH or N—C₁-C₄-alkyl.

[0034] The hetero aromatic cation may be a 5 or 6 membered ring comprising at least one N and if necessary one O and/or one S. The hetero aromatic cation may be substituted or unsubstituted and/or annelated. Preferably, the hetero aromatic cation is selected from the group consisting of:



-continued



[0035] wherein the moieties R may be one of the following:

[0036] R hydrogen, C₁-C₃₀-alkyl, C₃-C₁₂-cycloalkyl, C₂-C₃₀-alkenyl, C₃-C₁₂-cycloalkenyl, C₂-C₃₀-alkynyl, aryl or heteroaryl, wherein the latter 7 moieties may have one or more halogenic moiety and/or 1 to 3 moieties selected from the group consisting of C₁-C₆-alkyl, aryl, heteroaryl, C₃-C₇-cycloalkyl, halogen, OR^c, SR^c, NR^cR^d, COR^c, COOR^c,

CO—NR^cR^d, wherein R^c and R^d may be hydrogen, C₁-C₆-alkyl, C₁-C₆-halogenalkyl, cyclopentyl, cyclohexyl, phenyl, tolyl or benzyl;

[0037] R¹, R^{1'}, R², R³ may be hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl or heteroaryl which may be independently substituted; or

[0038] two of the moieties R¹, R^{1'}, R², R³ may form a ring together with a hetero-atom to which they are bound. The ring may be saturated, unsaturated, substituted or unsubstituted. The chain may be interrupted by one or more hetero-atoms out of the group consisting of O, S, NH or N—C₁-C₄-alkyl;

[0039] R⁴, R⁵, R⁶, R⁷, R⁸ may be, independently of each other, hydrogen, halogen, nitro, cyano, OR^c, SR^c, NR^cR^d, COR^c, COOR^c, CO—NR^cR^d, C₁-C₃₀-alkyl, C₃-C₁₂-cycloalkyl, C₂-C₃₀-alkenyl, C₃-C₁₂-cycloalkenyl, aryl or heteroaryl, wherein the latter 6 moieties may comprise one or more halogenic moiety and/or 1 to 3 moieties selected out of the group consisting of C₁-C₆-alkyl, aryl, heteroaryl, C₃-C₇-cycloalkyl, halogen, OR^c, SR^c, NR^cR^d, COR^c, COOR^c, CO—NR^cR^d, wherein R^c and R^d may be, independently of each other, hydrogen, C₁-C₆-alkyl, C₁-C₆-halogenalkyl, cyclopentyl, cyclohexyl, phenyl, tolyl or benzyl; or

[0040] two neighboring moieties of the moieties R, R⁴, R⁵, R⁶, R⁷, R⁸, may form, together with an atom they are bound, a ring which may be unsaturated or aromatic, unsaturated or saturated, wherein the chain formed by the respective moieties may be interrupted by one or more hetero-atoms out of the group consisting of O, S, NH or N—C₁-C₄-alkyl;

[0041] R^e, R^f, R^g, R^h may be, independently of each other, hydrogen, C₁-C₆-alkyl, aryl-, heteroaryl-, C₃-C₇-cycloalkyl, halogen, OR^c, SR^c, NR^cR^d, COOR^c, CO—NR^cR^d or COR^c, wherein R^c, R^d, may be, independently of each other, hydrogen, C₁-C₆-alkyl, C₁-C₆-halogenalkyl, cyclopentyl, cyclohexyl, phenyl, tolyl or benzyl; preferably for hydrogen, halogen, C₁-C₆-alkyl, in particular, hydrogen or C₁-C₆-alkyl.

[0042] According to an exemplary embodiment of the method of use of an ionic liquid the non-aromatic cation is a quaternary material. In particular, the quaternary material may be a quaternary salt. Alternatively, the non aromatic cation may comprise or may consist of protonated bases.

[0043] According to an exemplary embodiment of the method of use of an ionic liquid the gas is one out of the group consisting of: H₂O, HCN, H₂S, H₂Se, H₂Te, CO₂, CO, CS₂, COS, CF₂O, CF₂S, O₃, NO, NO₂, N₂O, N₂O₃, NOCl, NF₃, HNO₂, HNO₃, RCOR', RCOH, RCOOH, CF₃SO₃H, CF₃COOH, RCOOR', ROH, ROR (including cyclic ethers like tetrahydrofuran), RSH, RSR (including cyclic thioethers like tetrahydrothiophen), ROCl, ROBr, RONH₂, RONHR', RONR'R'', RSO₂Cl, RSO₂Br, ROCN, RCON, RCN, HF, HCl, HBr, HI, SO₂, SO₃, NH₃, NH₂R, NHR'R'', NR'R''R''', PH₃, PH₂R, PHR'R'', PR'R''R''', BF₃, BCl₃, BBr₃, B₂H₆, BrF₃, ClF₃, ClF₅, ClCN, IF₅, AsH₃, CH₃F, CH₃Cl, CH₃Br, CH₃I, POCl₂, PSCl₂, PF₅, SF₄, SF₆, SO₂F₂, SO₂Cl₂, SOCl₂, H₂C=CHBr, H₂C=CHCl and ethylene oxide. In general, every gas or vapor having a multipole moment and which may be classified as an harmful substance, irritant, or toxic substance, e.g. (strong) acids, (strong) bases, may be sorbed by using a method according to an exemplary embodiment of the invention. In particular, the sorption process may be used to remove these gases or vapors from air which is inhaled or exhaled.

[0044] According to an exemplary embodiment of the method of use of an ionic liquid at least one of R, R', R'' and/or R''' is a moiety out of the group consisting of: C₁-C₈-alkyl,

alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl and heteroaryl. In particular, R, R', R'' and/or R''' may denote a moiety or radical which may be partially and/or independently substituted. For clarity reasons it should be mentioned that in this application the term C₁-C₈-alkyl or similar terms is an abbreviatory notation for C1-alkyl, C2-alkyl, . . . , up to C8-alkyl or similar terms.

[0045] According to an exemplary embodiment of the method of use of an ionic liquid the anion comprises a carbonate, an alkylcarbonate, an arylcarbonate, alkylcarbonate, carboxylate, a carbanion, and/or an aromatic compound. In particular, the carbonates may be alkaline metal carbonates, alkaline earth metal carbonates, quaternary tetraalkylammonium carbonates, quaternary tetraalkylphosphonium carbonates, hydrogencarbonate, and/or arylcarbonate, for example. In particular, the arylcarbonate may be phenylcarbonate or benzylcarbonate, for example.

[0046] According to an exemplary embodiment of the method of use of an ionic liquid the anion comprises at least one polar group.

[0047] In particular, the polar group may be formed by an acetate, a sulfonate, a sulfate, a carbonate, and/or a malonate compound. Furthermore, it should be noted that the anion may be polar. In particular, the anion may be formed by a small ion having a high charge density or by an ion, carrying a functional group with a heteroatom with a high charge density e.g. O, N, F.

[0048] According to an exemplary embodiment of the method of use of an ionic liquid the cation is a quaternary or protonated cation out of the group consisting of ammonium, phosphonium, sulfonium, piperidinium, pyrrolidinium and morpholinium.

[0049] According to an exemplary embodiment of the method of use of an ionic liquid the cation is one out of the group consisting of trialkylmethylammonium, tetramethylammonium, triethylmethylammonium, tributylmethylammonium, and trioctylmethylammonium, trialkylammonium, trimethylammonium, triethylammonium, tributylammonium, and trioctylammonium. In particular, the trialkylmethylammonium may be a C₁-C₁₀-trialkylmethylammonium.

[0050] According to an exemplary embodiment of the method of use of an ionic liquid the cation is one out of the group consisting of tetramethylammonium, triethylmethylammonium, tributylmethylammonium, and trioctylmethylammonium.

[0051] According to an exemplary embodiment of the method of use of an ionic liquid the anion can be written in the form [RCO₂⁻], wherein [RCO₂⁻] is one out of the group consisting of carboxylate, formiate, acetate, propionate, butyrate, benzoate, and salicylate.

[0052] According to an exemplary embodiment of the method of use of an ionic liquid the anion can be written in the form [RCO₂⁻], wherein [RCO₂⁻] is a carboxylate and wherein R is a radical out of the group consisting of C₁-C₃₀-alkyl, C₃-C₁₂-cycloalkyl, C₂-C₃₀-alkenyl, C₃-C₁₂-cycloalkenyl, C₂-C₃₀-alkynyl, aryl and heteroaryl. In particular, the moiety or radical R may comprise or include one or more halogen radicals.

[0053] According to an exemplary embodiment of the method of use of an ionic liquid the anion can be written in the form [RCO₂⁻], wherein [RCO₂⁻] is a carboxylate wherein R represents one to three radicals out of the group consisting of, C₁-C₆-alkyl, aryl, heteroaryl, C₃-C₇-cycloalkyl, halogen, cyanide, ORc, SRc, NRcRd, CORc, COORc, CO—NRcRd,

wherein Rc and/or Rd, is one of the group consisting of hydrogen, C₁-C₆-alkyl, C₁-C₆-halogenalkyl, cyclopentyl, cyclohexyl, phenyl, tolyl, and benzyl.

[0054] According to an exemplary embodiment of the method of use of an ionic liquid the gas is CO₂.

[0055] Summarizing, according to an exemplary aspect of the invention, a method of use is provided which uses an ionic liquid having a non-aromatic cation to sorb gases having an electric multipole moment. The gas may in particular be CO₂ while the ionic liquid may be an organic salt having a melting temperature of below 200° C., preferably below 100° C. The organic salts may be quaternary salts having a generic formula of: [K⁺][RCO₂]. The described method of use may be in particular useful for all processes in which CO₂ shall be removed as pure substance or from a gas or vapor mixture independent of whether CO₂ is a main or secondary component, a process gas, or a working medium. Some exemplary applications may be the use in a heat pump or refrigerator based on ionic liquid/CO₂ as working media, or removing of CO₂ out of recovery gas, synthesis gas, water gas, inhaled air, and exhaled air. The removing out of inhaled/exhaled air may be in particular useful in the field of aerospace, submarines, or building services engineering wherein the very low vapor pressure if the ionic liquid may be advantageous since the ionic liquid may not evaporate into the air. Furthermore, it may be possible to use ionic liquids which selectively remove CO₂ while do not remove water or water vapor, i.e. hydrophobic ionic liquids may be used. Another possible application may be the purification of CO₂ and/or non-pressurized storing of CO₂, since the ionic liquid forms a complex bound with the quadrupolar CO₂ which complex bound may be broken by heating, microwave, ultrasonic wave, or by adding bipolar solvents, e.g. water, alcohol, etc. In general, every gas or vapor having a multipole moment and which may be classified as an harmful substance, irritant, or toxic substance, e.g. (strong) acids, (strong) bases, may be sorbed by using a method according to an exemplary embodiment of the invention. In particular, the sorption process may be used to remove these gases or vapor from air which is inhaled or exhaled, e.g. for purifying breathable air.

[0056] The aspects defined above and further aspects of the invention are apparent from the examples of embodiment to be described hereinafter and are explained with reference to these examples of embodiment. It should be noted that features described in connection with one exemplary embodiment or exemplary aspect may be combined with other exemplary embodiments and other exemplary aspects.

BRIEF DESCRIPTION OF THE DRAWINGS

[0057] The invention will be described in more detail hereinafter with reference to examples of embodiment but to which the invention is not limited.

[0058] FIG. 1 schematically illustrates a heat pump.

[0059] FIG. 2 schematically illustrates a test arrangement for measuring a gas sorption.

[0060] FIG. 3 schematically illustrates a test arrangement for measuring equilibrium curves.

[0061] FIG. 4 illustrates equilibrium curves for monoethanolamine.

[0062] FIG. 5 illustrates equilibrium curves for choline carbonate.

DESCRIPTION OF EMBODIMENTS

[0063] The illustration in the drawing is schematically.

[0064] FIG. 1 schematically shows a heat pump which may use a process according to an exemplary embodiment, i.e. a process which may be based on pair of working media comprising CO₂ and an ionic liquid comprising a non-aromatic ionic liquid.

[0065] In particular, FIG. 1 shows a heat pump **100** having an absorber **101**, including the pair of working media, e.g. CO₂ and the ionic liquid, wherein the ionic liquid acts as a sorbent and CO₂ is the sorbat. The mixture is transmitted via a pump **102** to a heat exchanger **103a** in which the mixture absorbs heat or releases heat. After the heat exchanger the mixture is transmitted to a settler **104** in which at least a partial separation of the mixture into a sorbent rich phase and a sorbat rich phase is performed. The sorbent rich phase is transferred to a second heat exchanger **103b** and a restrictor **105a** into an evaporizer **106**. In the evaporizer **106** the sorbat at least partially evaporates out of the sorbat rich phase which is then introduced back into the absorber **101**. Optionally, the sorbat rich phase may be passed through another heat exchanger, e.g. heat exchanger **103b**, before it is introduced into the absorber. The sorbent rich phase is transferred from the settler **104** to the absorber **101** via a second restrictor **105b** in which it is brought back to the pressure level of the absorber **100**. Optionally the sorbent rich phase may be passed through another heat exchanger, e.g. heat exchanger **103a**, before it is introduced into the second restrictor **105b**.

[0066] The described heat exchanger is only an example for a device using a method of use according to an exemplary embodiment of the invention. A plurality of embodiments may become apparent for a person skilled in the art. For example, a ionic liquid having a non-aromatic cation may be used in an open device, i.e. a device which does not include the ionic liquid in a closed loop, in order to enable the sorption of a gas having an electric multipole moment.

[0067] In the following some experimental results are described showing the ability of ionic liquid to absorb CO₂.

[0068] FIG. 2 schematically shows a fluid tank **200** used as a heat reservoir in order to provide a constant temperature selectable in the range between 25° C. and 80° C. A vessel or vial **201** having a volume of about 20 ml is placed in the tank, wherein the vial is filled with CO₂ at a partial pressure of the environmental pressure, e.g. atmospheric pressure of about 1000 hPa. Additionally, a CO₂ sorbing fluid is injected **202** into the vial. The sorption of the CO₂ is determined by measuring the decrease of the pressure in the vial by a digital manometer **203** which is connected to a computer. The speed of the pressure decrease is an indicator of the reaction kinetics and the total decrease of the pressure is an indicator for the total CO₂ sorption. The tests were performed at two temperatures 25° C. and 80° C., wherein at the higher temperature a smaller amount of CO₂ may be desirable since this may be an indicator for an estimation of the ability of the fluid to release the CO₂. For testing several ionic liquids are injected and compared to a reference sample, wherein an aqueous solution (30%) of monoethanolamine is used. In particular, the resulting parameter was the equilibrium concentration at constant reduced pressure, i.e. the pressure reached in the vial, and at the set temperature, wherein the result was calculated in mol-

$_{gas}$ per mol $_{IL}$, wherein the index gas denotes CO₂ and the index IL denotes ionic liquid. The equilibrium concentration were calculated by the following formular:

$$\frac{\text{pressure decrease [hPa]} \cdot 0.02145 [l]}{83.145 \cdot \text{temp[K]}} \bigg/ \frac{\text{mass of CO}_2 [\text{g}]}{\text{molar mass} [\text{g/mol}]}$$

wherein 0.02145 is the volume of the vial and 83.145 is the gas constant in the used units.

[0069] The following results were achieved:

name	solvent	conc. [%]	T [° C.]	pressure decrease [hPa]	time [min]	charging [mol _{CO2} /mol _{IL}]
TBMP-acetate		100	25	332	4000	0.08
TBMP-acetate		100	80	342	3160	0.08
TEMA-acetate	H ₂ O	70	25	495	2400-5000	0.1
TEMA-acetate	H ₂ O	70	80	130	2400	0.03
TOMA-acetate		100	25	448	2500	0.19
TOMA-acetate		100	80	122	1000	0.05
MEA	H ₂ O	30	25	679	250	0.12
MEA	H ₂ O	30	80	440	130	0.08

wherein:

TBMP denotes tributyl methyl phosphonium,
TEMA denotes triethyl methyl ammonium,
TOMA denotes trioctyl methyl ammonium, and
MEA denotes monoethanolamine.

[0070] As can be seen the acetate anion may be responsible for a high CO₂ sorption, while similar sorption amounts may be achievable by cations having different structures.

[0071] FIG. 3 schematically illustrates a test arrangement 300 for measuring equilibrium curves. In particular, FIG. 3 shows an equilibrium cell comprising three vessels 301, 302 and 303 each closed by a respective frit in order to ensure a good mass transfer between the gas, e.g. CO₂ and the sorbing fluid. The vessels are interconnected by flexible plastic tubes 304 and 305 having non-return valves. The vessels are placed in a heat reservoir 306 to ensure a constant temperature which can be controlled by using an electric heating 307. The heat reservoir is covered by a cover or lid 308 in order to ease the temperature control. A container or condenser 309 including silica gel is implemented downstream of the equilibrium cell wherein the silica gel is used to dry the generated gas which is then analyzed. Additionally, an input amount or volume to the equilibrium cell is controlled or regulated by using a rotameter 310.

[0072] FIG. 4 illustrates equilibrium curves for monoethanolamine. In particular, FIG. 4 shows the partial pressure p_{CO2} versus the CO₂ loading for 60° C. and 80° C. for an aqueous solution (30%) of monoethanolamine. For each temperature a respective curve is approximated based on measurements, wherein a first curve 401 approximates the equilibrium curve for 80° C. while a second curve 402 approximates the equilibrium curve for 60° C. The values generated for MEA are comparable with the data published in literature, known to the expert.

[0073] FIG. 5 illustrates equilibrium curves for choline carbonate. In particular, FIG. 5 shows values for the partial pressure p_{CO2} versus the CO₂ loading for six different temperatures 40° C., 60° C., 80° C., 90° C., 100° C., and 110° C. for an aqueous solution (60%) of choline carbonate. Additionally, to the measured values fits for the different temperatures are shown in FIG. 5 as well. In particular, graph 501 shows the fit for 40° C., graph 502 shows the fit for 60° C., graph 503 shows the fit for 80° C., graph 504 shows the fit for 90° C., graph 505 shows the fit for 100° C., and graph 506 shows the fit for 110° C.

[0074] Furthermore, an experiment concerning the influence of water on the CO₂ sorption was performed. TEMA acetate having a water amount of 10% was used as an ionic liquid. TEMA acetate was introduced for four days into a CO₂ atmosphere having a pressure of 600 hPa at a temperature of 80° C. In one case the TEMA acetate comprised included a surplus of water while in the other case no water was added. The water content of the sample including water increased from 10% to 35% while the sample without water increased only from 10% to 15%. After the four days acid was added to the two samples which lead to a clear generation of foam or gas in the sample without water, while the reaction of the probe with water was less intense. Thus, the water may lead to a reduced CO₂ sorption of the ionic liquid.

[0075] In the following two examples will be described wherein trioctylmethylammonium (TOMA)-acetylacetonate or -acetate is used to sorp a gas having an electric multipole moment.

Example 1

Sorption of Hydrogen Sulphide

[0076] The experiment was performed at room temperature and a vapor pressure equilibrium of 338 hPa. A beaded bottle is flushed with 120 ml of hydrogen sulphide by using two needles. One of the needles is connected to a manometer having a resolution of 1 hPa. Subsequently 1 ml of TOMA-acetate is injected into the bottle by using one of the needles, wherein the TOMA-acetate was preheated by a hairdryer in order to reduce the viscosity. After 30 minutes of stirring by using a magnetic stir bar a constant reduction of the pressure of 622 hPa was observed. This pressure reduction corresponds to a molar ratio of 0.26 mol_{H2S}/mol_{IL} at an equilibrium pressure of 338 hPa. For comparison, a 30% aqueous solution of monoethanolamine provides, under the same conditions, a pressure reduction of 651 hPa which corresponds to a molar ratio of 0.11 mol_{H2S}/mol_L at an equilibrium pressure of 309 hPa.

Example 2

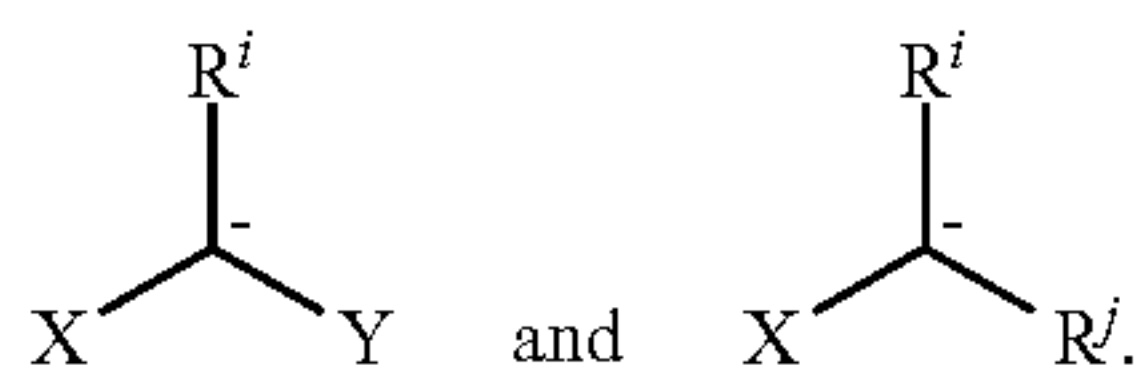
Sorption of Carbon Dioxide

[0077] The experiment was performed at room temperature and a vapor pressure equilibrium of 523 hPa. A beaded bottle is flushed with 120 ml of carbon dioxide by using two needles. One of the needles is connected to a manometer having a resolution of 1 hPa. Subsequently 1 ml of TOMA-acetylacetonate is injected into the bottle by using one of the needles, wherein the TOMA-acetylacetonate was preheated by a hairdryer in order to reduce the viscosity. After 30 minutes of stirring by using a magnetic stir bar a constant reduction of the pressure of 437 hPa was observed. This pressure reduction corresponds to a molar ratio of 0.18 mol_{CO2}/mol_{IL} at an equi-

librium pressure of 523 hPa. For comparison, a 30% aqueous solution of monoethanolamine provides, under the same conditions, a pressure reduction of 670 hPa which corresponds to a molar ratio of $0.12 \text{ mol}_{\text{CO}_2}/\text{mol}_L$ at an equilibrium pressure of 290 hPa.

[0078] Finally, it should be noted that the above-mentioned embodiments illustrate rather than limit the invention, and that those skilled in the art will be capable of designing many alternative embodiments without departing from the scope of the invention as defined by the appended claims. In the claims, any reference signs placed in parentheses shall not be construed as limiting the claims. The word “comprising” and “comprises”, and the like, does not exclude the presence of elements or steps other than those listed in any claim or the specification as a whole. The singular reference of an element does not exclude the plural reference of such elements and vice-versa. In a device claim enumerating several means, several of these means may be embodied by one and the same item of software or hardware. The mere fact that certain measures are recited in mutually different dependent claims does not indicate that a combination of these measures cannot be used to advantage.

1. A method comprising:
using an ionic liquid for sorption of a gas having an electric multipole moment, wherein the ionic liquid comprises an anion and a non-aromatic cation.
2. The method according to claim 1, wherein the non-aromatic cation is an aliphatic cation.
3. The method according to claim 1, wherein the non-aromatic cation is a quaternary material.
4. The method according to claim 1, wherein the gas is one out of the group consisting of:
 H_2O , HCN , H_2S , H_2Se , H_2Te , CO_2 , CO , CS_2 , COS , CF_2O , CF_2S , O_3 , NO , NO_2 , N_2O , N_2O_3 , NOCl , NF_3 , HNO_2 , HNO_3 , RCOR' , RCOH , RCOOH , $\text{CF}_3\text{SO}_3\text{H}$, CF_3COOH , RCOOR' , ROH , ROR , RSH , RSR , ROCl , ROBr , RONH_2 , RONHR' , $\text{RONR}'\text{R}''$, RSO_2Cl , RSO_2Br , ROCN , RCN , RCN , HF , HCl , HBr , HI , SO_2 , SO_3 , NH_3 , NH_2R , $\text{NHR}'\text{R}''$, $\text{NR}'\text{R}''\text{R}'''$, PH_3 , PH_2R , $\text{PHR}'\text{R}''$, $\text{PR}'\text{R}''\text{R}'''$, BF_3 , BCl_3 , BBR_3 , B_2H_6 , BrF_3 , ClF_3 , ClF_5 , ClCN , IF_5 , AsH_3 , CH_3F , CH_3Cl , CH_3Br , CH_3I , POCl_2 , PSCl_2 , PF_5 , SF_4 , SF_6 , SO_2F_2 , SO_2Cl_2 , SOCl_2 , $\text{H}_2\text{C}=\text{CHBr}$, $\text{H}_2\text{C}=\text{CHCl}$ and ethylene oxide.
5. The method according to claim 4, wherein at least one of R , R' , R'' and/or R''' is a moiety out of the group consisting of:
 C_1 - C_8 -alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl and heteroaryl.
6. The method according to claim 1, wherein the anion comprises a carbonate, an alkylcarbonate, an arylcarbonate a carboxylate, a carbanion, and/or an aromatic compound.
7. The method according to claim 1: wherein the ionic liquid satisfies the generic formula $[\text{Q}^+][\text{A}^-]$, wherein the anion is described by one of the following structures:



8. The method according to claim 1, wherein the ionic liquid satisfies the generic formula $[\text{Q}^+][\text{A}^{a-}]$, wherein $[\text{A}^{a-}]$ with the charge a -, is selected out of the group consisting of:

dialkyl ketones, dialkyl-1,3-diketones, alkyl- β -keto esters, terminal alkynes, linear or cyclic 1,3-thioethers, dialkyl phosphonates, dialkyl malonic acid esters, β -cyano carbonic acids and their respective alkylesters, β -alkoxy carbonic acids and their respective alkylesters, β -cyano nitriles, cyclopentadiene (substituted if necessary), trialkylimines, dialkylimines, diaryl ketones, alkyl-aryl ketones, diaryl-1,3-diketones, alkyl-aryl-1,3-diketones, β -aryloxy carbonic acids and their respective alkylesters, β -aryloxy carbonic acids and their respective arylesters, aryl- β -ketoesters, diarylphosphonates, alkyl-aryl-phosphonates, diaryl malonic acid esters, alkyl-aryl-malonic acid esters, β -cyano carbonic acids arylesters and arylimines.

9. The method according to claim 1, wherein the ionic liquid satisfies the generic formula $[\text{Q}^+][\text{A}^{a-}]$, wherein $[\text{A}^{a-}]$ is a carbanion formed by deprotonating a chemical compound out of the group consisting of:

acetoacetic ester, malonic mononitrile, malonic acid dimethylester, malonic acid diethylester, acetylacetone, malonic acid dinitrile, acetone, diethylketone, methylethylketone, dibutylketone, 1,3-dithian, acetaldehyde, benzaldehyde, crotonaldehyde and butyraldehyde.

10. The method according to claim 1, wherein the anion comprises at least one polar group.

11. The method according to claim 1, wherein the cation is a quaternary or protonated cation out of the group consisting of:

ammonium, phosphonium, sulfonium, piperidinium, pyrrolidinium, and morpholinium.

12. The method according to claim 1, wherein the cation is one out of the group consisting of:

trialkylmethylammonium, tetramethylammonium, triethylmethylammonium, tributylmethylammonium, trioctylmethylammonium, trialkylammonium, trimethylammonium, triethylammonium, tributylammonium, and trioctylammonium.

13. The method according to claim 1, wherein the cation is one out of the group consisting of:

tetramethylammonium, triethylmethylammonium, tributylmethylammonium, and trioctylmethylammonium.

14. The method according to claim 1, wherein the anion is written in the form $[\text{RCO}_2^-]$, wherein $[\text{RCO}_2^-]$ is one out of the group consisting of:

carboxylate, formate, acetate, propionate, butyrate, benzoate, and salicylate.

15. The method according to claim 1, wherein the anion is written in the form $[\text{RCO}_2^-]$, wherein $[\text{RCO}_2^-]$ is a carboxylate wherein R is a radical out of the group consisting of:

C_1 - C_{30} -alkyl, C_3 - C_{12} -cycloalkyl, C_2 - C_{30} -alkenyl, C_3 - C_{12} -cycloalkenyl, C_2 - C_{30} -alkynyl, aryl and heteroaryl.

16. The method according to claim 1, wherein the anion is written in the form $[\text{RCO}_2^-]$, wherein $[\text{RCO}_2^-]$ is a carboxylate wherein R represents one to three radicals out of the group consisting of:

C_1 - C_6 -alkyl, aryl, heteroaryl, C_3 - C_7 -cycloalkyl, halogen, cyanide, ORc , SRc , NRcRd , CORc , COORc , $\text{CO}-\text{NRcRd}$,

wherein Rc and/or Rd , is one of the group consisting of:

hydrogen, C_1 - C_6 -alkyl, C_1 - C_6 -halogenalkyl, cyclopentyl, cyclohexyl, phenyl, tolyl, and benzyl.

17. The method according to claim 1, wherein the gas is CO_2 .

18. The method according to claim **17**, wherein CO₂ is sorbed from a medium which is selected out of the group consisting of:

recovery gas, synthesis gas, water gas, inhaled air, and exhaled air.

19. A device for sorption of a gas having an electric multipole moment, the device comprising:

a reservoir of an ionic liquid comprising an anion and a non-aromatic cation.

20. The device according to claim **19**, wherein the device is a heat pump, and wherein the heat pump comprises a circuit including CO₂ and the ionic liquid comprises an anion and a non-aromatic cation as working media.

21. A method comprising:

using an ionic liquid for sorption of a gas having an electric multipole moment, wherein the ionic liquid comprises a carbanion and a cation.

22. The method according to claim **21**, wherein the ionic liquid satisfies the generic formula $[Q^+][A^{a-}]$,

wherein $[Q]^+$ is one out of the group consisting of quaternary ammonium cation $[R^1R^1R^2R^3N]^+$, phosphonium $[R^1R^1R^2R^3P]^+$, sulfonium $[R^1R^1R^2S]^+$ and a hetero aromatic cation.

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