

**Method for absorbing a volatile substance in a liquid
absorption agent**

5 The invention relates to a process for the absorption of a volatile substance from a gas phase in a liquid absorbent which comprises an ionic liquid and a wetting-promoting additive, where the gas phase is brought into contact with a film of the absorbent.

10 In numerous technical processes, volatile substances are absorbed from a gas phase in a liquid absorbent. Such an absorption is carried out in many separation processes, such as, for example, in extractive distillations, in which the extraction takes place in a
15 rectification column, or in gas purification processes, such as, for example, the removal of carbon dioxide from combustion waste gases, during which the absorption takes place in a gas scrubber. Moreover, such an absorption is also used in absorption
20 refrigerating machines.

In such absorption processes, it is advantageous if the absorbent has only a low vapour pressure and virtually does not pass into the gas phase. Consequently, it has
25 already been proposed to use an ionic liquid as absorbent since ionic liquids have a negligibly low vapour pressure.

WO 02/074718 describes the use of ionic liquids as
30 extractive solvents for extractive distillations.

The use of ionic liquids as absorbents for carbon dioxide is known from J.F. Brennecke and E.J. Maginn, AIChE Journal 47 (2001) 2384-2389.

35 WO 2005/113702, WO 2006/084262 and WO 2006/134015 describe the use of ionic liquids as absorbents in absorption refrigerating machines.

The inventors of the present invention have now found that the absorption processes known from the prior art which use an ionic liquid as absorbent produce only an inadequate and often also at times fluctuating mass transfer if the absorption takes place in an apparatus in which the gas phase is brought, for the absorption, into contact with a film of the absorbent.

Summary of Invention

In one aspect, there is provided a process for the absorption of a volatile substance from a gas phase in a liquid absorbent, where the gas phase is brought into contact with a film of the absorbent, characterized in that the absorbent comprises a wetting-promoting additive from the group of nonionic surfactants and zwitterionic surfactants and an ionic liquid, the mixture of volatile substance and absorbent obtained during the absorption is brought into contact with a gas phase in a subsequent desorption at an elevated temperature relative to the absorption and an increased pressure relative to the absorption, such that at least some of the volatile substance is desorbed from the mixture and the absorbent remaining after the desorption of the volatile substance is returned to the absorption, the desorbed volatile substance is condensed at the pressure used for the desorption, the resulting condensate is then evaporated at a pressure which is lower than the pressure of the desorption and at least as high as the pressure in the absorption, and the gas phase obtained during the evaporation of the condensate is brought into contact with the film of the absorbent.

In another aspect, there is provided an absorption refrigerating machine for carrying out a process as defined above, comprising an absorber, a desorber, an

evaporator, a condenser and a working medium of an absorbent and a volatile substance, where the absorber comprises a device for bringing a gas phase containing the volatile substance into contact with a film made of absorbent characterized in that

the absorbent comprises a wetting-promoting additive from the group of nonionic surfactants and zwitterionic surfactants and an ionic liquid.

In yet another aspect, there is provided the use of a mixture of

a) an absorbent comprising a wetting-promoting additive from the group of nonionic surfactants and zwitterionic surfactants and an ionic liquid, and

b) a volatile substance selected from water, ammonia and carbon dioxide as working medium in an absorption refrigerating machine.

Detailed description

The invention provides a process for the absorption of a volatile substance from a gas phase in a liquid absorbent in which the gas phase is brought into contact with a film of the absorbent and in which the absorbent comprises an ionic liquid and a wetting-promoting additive.

Using the process according to the invention, compared with the processes known from the prior art, a more rapid and, in terms of time, more stable mass transfer is achieved in the absorption, and the absorption can be carried out without problems in smaller apparatuses.

In the process according to the invention, the absorbent comprises at least one ionic liquid and at least one wetting-promoting additive. Preferably, the absorbent comprises one or more ionic liquids in a total amount of from 20 to 99.9% by weight and one or more wetting-promoting additives in a total amount of from 0.01 to 10% by weight.

Within the context of the invention, an ionic liquid is a salt or a mixture of salts of anions and cations, where the salt or the mixture of salts has a melting point of less than 100°C.

Preferably, the ionic liquid consists of one or more salts of organic cations with organic or inorganic anions. Mixtures of two or more salts with different

organic cations and the same anion are particularly preferred.

Suitable organic cations are, in particular, cations of
5 the general formulae (I) to (V):



in which

15 R^1, R^2, R^3, R^4 are identical or different and are hydrogen, a linear or branched aliphatic or olefinic hydrocarbon radical having 1 to 30 carbon atoms, a cycloaliphatic or cycloolefinic hydrocarbon radical having 5 to 40 carbon atoms, an aromatic hydrocarbon
20 radical having 6 to 40 carbon atoms, an alkylaryl radical having 7 to 40 carbon atoms, a linear or branched aliphatic or olefinic hydrocarbon radical having 2 to 30 carbon atoms and interrupted by one or more groups -O-, -NH-, -NR'-, -O-C(O)-, -(O)C-O-,
25 -NH-C(O)-, -(O)C-NH-, -(CH₃)N-C(O)-, -(O)C-N(CH₃)-, -S(O₂)-O-, -O-S(O₂)-, -S(O₂)-NH-, -NH-S(O₂)-, -S(O₂)-N(CH₃)- or -N(CH₃)-S(O₂)-, a linear or branched aliphatic or olefinic hydrocarbon radical having 1 to 30 carbon atoms terminally functionalized by OH, OR',
30 NH₂, N(H)R' or N(R')₂, or a blockwise or randomly composed polyether radical of the formula -(R⁵-O)_n-R⁶,

R' is an aliphatic or olefinic hydrocarbon radical having 1 to 30 carbon atoms,

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R⁵ is a linear or branched hydrocarbon radical containing 2 to 4 carbon atoms,

n is from 1 to 200, preferably 2 to 60,

5 R^6 is hydrogen, a linear or branched aliphatic or olefinic hydrocarbon radical having 1 to 30 carbon atoms, a cycloaliphatic or cycloolefinic hydrocarbon radical having 5 to 40 carbon atoms, an aromatic hydrocarbon radical having 6 to 40 carbon atoms, an alkylaryl radical having 7 to 40 carbon atoms or a
10 $-C(O)-R^7$ radical,

R^7 is a linear or branched aliphatic or olefinic hydrocarbon radical having 1 to 30 carbon atoms, a cycloaliphatic or cycloolefinic hydrocarbon radical
15 having 5 to 40 carbon atoms, an aromatic hydrocarbon radical having 6 to 40 carbon atoms or an alkylaryl radical having 7 to 40 carbon atoms,

where at least one and preferably each of the radicals
20 R^1 , R^2 , R^3 and R^4 is different from hydrogen.

Cations of the formulae (I) to (V) in which the radicals R^1 and R^3 together form a 4- to 10-membered, preferably 5- to 6-membered, ring are likewise
25 suitable.

Heteroaromatic cations with at least one quaternary nitrogen atom in the ring which carries a radical R^1 as defined above, preferably derivatives of pyrrole,
30 pyrazole, imidazole, oxazole, isoxazole, thiazole, isothiazole, pyridine, pyrimidine, pyrazine, indole, quinoline, isoquinoline, cinnoline, quinoxaline or phthalazine substituted on the nitrogen atom are likewise suitable.

35 Suitable inorganic anions are, in particular, tetrafluoroborate, hexafluorophosphate, nitrate, sulphate, hydrogensulphate, phosphate,

hydrogenphosphate, dihydrogenphosphate, hydroxide, carbonate, hydrogencarbonate and the halides, preferably chloride.

- 5 Suitable organic anions are, in particular, $R^aOSO_3^-$, $R^aSO_3^-$, $R^aOPO_3^{2-}$, $(R^aO)_2PO_2^-$, $R^aPO_3^{2-}$, R^aCOO^- , R^aO^- , $(R^aCO)_2N^-$, $(R^aSO_2)_2N^-$ and NCN^- where R^a is a linear or branched aliphatic hydrocarbon radical having 1 to 30 carbon atoms, a cycloaliphatic hydrocarbon radical having 5 to
- 10 40 carbon atoms, an aromatic hydrocarbon radical having 6 to 40 carbon atoms, an alkylaryl radical having 7 to 40 carbon atoms or a linear or branched perfluoroalkyl radical having 1 to 30 carbon atoms.
- 15 In a preferred embodiment, the ionic liquid comprises one or more 1,3-dialkylimidazolium salts, where the alkyl groups are particularly preferably independently of one another selected from methyl, ethyl, n-propyl, n-butyl and n-hexyl. Particularly preferred ionic
- 20 liquids are salts of one or more of the cations 1,3-dimethylimidazolium, 1-ethyl-3-methylimidazolium, 1-(n-butyl)-3-methylimidazolium, 1-(n-butyl)-3-ethylimidazolium, 1-(n-hexyl)-3-methylimidazolium, 1-(n-hexyl)-3-ethylimidazolium and 1-(n-hexyl)-3-
- 25 butylimidazolium with one of the anions chloride, acetate, methylsulphate, ethylsulphate, dimethylphosphate or methylsulphonate.

In a further preferred embodiment, the ionic liquid

30 comprises one or more quaternary ammonium salts with a monovalent anion and cations of the general formula (I) in which

- R^1 is an alkyl radical having 1 to 20 carbon atoms,
 R^2 is an alkyl radical having 1 to 4 carbon atoms,
 35 R^3 is a radical $(CH_2CHRO)_n-H$ where n is from 1 to 200 and R = H or CH_3 and

R^4 is an alkyl radical having 1 to 4 carbon atoms or a radical $(CH_2CHRO)_n-H$ where n is from 1 to 200 and $R = H$ or CH_3 .

Particularly preferred anions are chloride, acetate,
5 methylsulphate, ethylsulphate, dimethylphosphate or
methylsulphonate.

Processes for the preparation of the ionic liquids are
known to the person skilled in the art from the prior
10 art.

The wetting-promoting additive preferably comprises one
or more surfactants from the group of nonionic
surfactants, zwitterionic surfactants and cationic
15 surfactants.

Suitable nonionic surfactants are alkylamine
alkoxylates, amidoamines, alkanolamides, alkylphosphine
oxides, alkyl-N-glucamides, alkyl glucosides, bile
20 acids, alkyl alkoxylates, sorbitan esters, sorbitan
ester ethoxylates, fatty alcohols, fatty acid
ethoxylates, ester ethoxylates and polyether siloxanes.

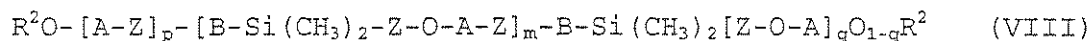
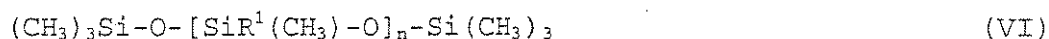
Suitable zwitterionic surfactants are betaines,
25 alkylglycines, sultaines, amphopropionates,
amphoacetates, tertiary amine oxides and
silicobetaines.

Suitable cationic surfactants are quaternary ammonium
30 salts with one or more substituents having 8 to 20
carbon atoms and a melting point of more than $100^\circ C$, in
particular corresponding tetraalkylammonium salts,
alkylpyridinium salts, ester quats, diamidoamine quats,
imidazolinium quats, alkoxyalkyl quats, benzyl quats
35 and silicone quats.

In a preferred embodiment, the wetting-promoting
additive comprises one or more nonionic surfactants of

the general formula $R(OCH_2CHR')_mOH$ where m is from 4 to 40, in which R is an alkyl radical having 8 to 20 carbon atoms, an alkylaryl radical having 8 to 20 carbon atoms or a polypropylene oxide radical having 3 to 40 propylene oxide units and R' is methyl or preferably hydrogen.

In a further preferred embodiment, the wetting-promoting additive comprises a polyether-polysiloxane copolymer which comprises more than 10% by weight of $[Si(CH_3)_2O]$ units and more than 10% by weight of $[CH_2CHR-O]$ units, in which R is hydrogen or methyl. Particular preference is given to polyether-polysiloxane copolymers of the general formulae (VI) to (VIII):



in which

A is a divalent radical of the formula $-[CH_2CHR^3-O]_r-$,

B is a divalent radical of the formula $-[Si(CH_3)_2-O]_s-$,

Z is a divalent linear or branched alkylene radical having 2 to 20 carbon atoms and is preferably $-(CH_2)_3-$,

$n = 1$ to 30 ,

$m = 2$ to 100 ,

$p, q = 0$ or 1 ,

$r = 2$ to 100 ,

$s = 2$ to 100 ;

from 1 to 5 of the radicals R^1 are radicals of the general formula $-Z-O-A-R^2$ and the remaining radicals R^1 are methyl,

- 5 R^2 is hydrogen or an aliphatic or olefinic alkyl radical or acyl radical having 1 to 20 carbon atoms and

R^3 is hydrogen or methyl.

- 10 The wetting-promoting additives are already known to the person skilled in the art from the prior art as additives for aqueous solutions and can be prepared according to processes known from the prior art.

- 15 Preferably, ionic liquid and wetting-promoting additive are selected in such a way and in such amounts that the absorbent has a contact angle of less than 140° on a surface of a steel S235JRG2 towards air. The absorbent particularly preferably has a contact angle of less
20 than 130° and in particular of less than 120° . Commercially available measuring instruments can be used for determining the contact angle. Thus, for example, the contact angle can be determined using the drop contour analysis system DSA 100/DSA 100L or the
25 Universal-Surface-Tester GH100, in each case obtainable from KRÜSS GmbH.

- The absorbent preferably has a viscosity at 20°C of from 1 to 15 000 mPa*s, particularly preferably 2 to
30 3000 mPa*s and in particular 5 to 1000 mPa*s, in each case determined in accordance with DIN 53019.

- In the process according to the invention, a gas phase which comprises a volatile substance is brought into
35 contact with a film of the absorbent. Besides the volatile substance, the gas phase can also comprise further substances which are not absorbed. The gas phase can likewise also be a vapour phase which

consists essentially only of vapour of the volatile substance.

5 In the process according to the invention, the film of the absorbent can be generated on any suitable surface, for example on surfaces made of metal, glass, enamel or polymers such as, for example, polyethylene. Preferably, the absorption is carried out with a film of the absorbent on a metal surface since then the heat
10 of absorption which is released during the absorption can be better dissipated and the apparatus used for the absorption can be smaller in design.

15 In a preferred embodiment of the process, the film of the absorbent is generated in a falling-film apparatus. Apparatuses suitable for this embodiment are known to the person skilled in the art from the area of evaporation technology as falling-film evaporators.

20 In a further preferred embodiment of the process, the film of the absorbent is generated on a structured packing. Structured packings are known to the person skilled in the art from the field of absorption and distillation technology. The structured packing here
25 can consist of any suitable material, such as metal, ceramic or plastic. Generating the film of the absorbent on a structured packing has the advantage that the absorption can be carried out in apparatuses with a smaller volume. Preference is given to using
30 structured packings of sheet metal or metal fabric with which the apparatus used for the absorption can be designed to be particularly small and light. As an alternative to structured packings, however, it is also possible to use randomly packed beds.

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Preferably, in the process according to the invention, the mixture of volatile substance and absorbent obtained during the absorption is brought into contact

with a gas phase in a subsequent desorption at an elevated temperature relative to the absorption and/or a reduced pressure relative to the absorption, such that at least some of the volatile substance is desorbed from the mixture and the absorbent remaining after the desorption of the volatile substance is returned to the absorption. This makes it possible for the absorbent to be used several times for the absorption.

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In the embodiment with the desorption of the volatile substance, the process is preferably carried out such that the desorption takes place through a membrane which separates the mixture of volatile substance and absorbent from the gas phase into which the volatile substance is desorbed. In this embodiment, it is also possible to use wetting-promoting additives which effect increased foaming of the absorbent without resulting in foam development during the desorption.

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In a preferred embodiment of the process according to the invention, the gas phase is an azeotropic mixture of two or more volatile substances with similar boiling points or an azeotropic mixture of two or more volatile substances, where at least one of the substances is preferably absorbed. This embodiment makes it possible to remove an impurity, which is present in the product but difficult to separate off by distillation, in a distillation process through a gas scrubbing of the distillation product obtained in vapour form.

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In an alternative embodiment, the absorption is carried out in a rectification column, where the absorbent is preferably introduced close to the top of the column so that it acts like an extractive solvent in the rectification column.

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In a further embodiment, the gas phase is a combustion waste gas and the volatile substance is carbon dioxide, so that the process separates carbon dioxide from a combustion waste gas.

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In a preferred embodiment of the process according to the invention with additional desorption, the desorption takes place at an increased pressure relative to the absorption, the desorbed volatile substance is condensed at the pressure used for the desorption, the resulting condensate is then evaporated at a pressure which is lower than the pressure of the desorption and is at least as high as the pressure in the absorption, and the gas phase obtained during the evaporation of the condensate is brought into contact with the film of the absorbent. In this embodiment, the volatile substance is preferably water, ammonia or carbon dioxide. Preferably, the gas phase comprises essentially only the volatile substance and no further substances which are not absorbed in the absorbent.

In this embodiment, the process according to the invention is suitable for operation in an absorption refrigerating machine. An absorption refrigerating machine for carrying out this embodiment comprises an absorber, a desorber, an evaporator, a condenser and a working medium of an absorbent and a volatile substance, where the absorber comprises a device for bringing a gas phase containing the volatile substance into contact with a film made of absorbent, and the absorbent comprises an ionic liquid and a wetting-promoting additive. The absorption refrigerating machines according to the invention can be constructed more compactly and allow a higher degree of effectiveness than the absorption refrigerating machines known from the prior art. Furthermore, they are more robust in operation and insensitive towards

shocks and vibrations and are therefore better suited for mobile use, e.g. in vehicles and on ships.

5 Preferably, in an absorption refrigerating machine, a working medium is used which is a mixture of an absorbent and a volatile substance, where the absorbent comprises an ionic liquid and a wetting-promoting additive, and the volatile substance is water, ammonia or carbon dioxide.

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Examples

Several working media according to the present invention suitable for use in an absorption
15 refrigerating machine were prepared and investigated. The composition and also the properties of the working media are shown in Tables 1 and 2. The ionic liquids EMIM chloride (1-ethyl-3-methylimidazolium chloride), EMIM acetate (1-ethyl-3-methylimidazolium acetate),
20 MMIM DMP (1-methyl-3-methylimidazolium dimethylphosphate) and TEGO® IL 2MS (bis(hydroxyethyl)dimethylammonium methanesulphonate) are commercially available under these names from Evonik Goldschmidt GmbH. The corrosion inhibitor REWOCOROS® AC 101 and the wetting-
25 promoting additive TEGOPREN® 5840 (a polyether-modified polysiloxane) are commercially available from Evonik Goldschmidt GmbH. The working media from Tables 1 and 2 were prepared by mixing the respective ionic liquid, the refrigerant water, the corrosion inhibitor
30 REWOCOROS® AC 101 and the wetting-promoting additive TEGOPREN® 5840 in the proportions given in Tables 1 and 2 at 25°C. The contact angle on an S235JRG2 steel surface was determined at 25°C using a DSA 100/DSA 100L drop contour analysis system.

Table 1

Example	1*	2	3*	4
Ionic liquid	EMIM acetate	EMIM acetate	EMIM chloride	EMIM chloride
Ionic liquid in % by wt.	90	90	90	90
Water in % by wt.	10.0	9.4	10.0	9.4
REWOCOROS® AC 101 in % by wt.	0	0.5	0	0.5
TEGOPREN® 5840 in % by wt.	0	0.1	0	0.1
Contact angle	111	105	117	74
Water partial pressure at 35°C in mbar	4.4	4.5	3.9	4.0

*not according to the invention

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Table 2

Example	5*	6	7*	8
Ionic liquid	MMIM DMP	MMIM DMP	TEGO® IL 2MS	TEGO® IL 2MS
Ionic liquid in % by wt.	90	90	90	90
Water in % by wt.	10.0	9.4	10.0	9.4
REWOCOROS® AC 101 in % by wt.	0	0.5	0	0.5
TEGOPREN® 5840 in % by wt.	0	0.1	0	0.1
Contact angle	96	60	108	104
Water partial pressure at 35°C in mbar	5.1	5.3	15.2	15.4

*not according to the invention

Patent claims

1. Process for the absorption of a volatile substance from a gas phase in a liquid absorbent,
5 where the gas phase is brought into contact with a film of the absorbent, characterized in that
the absorbent comprises a wetting-promoting additive from the group of nonionic surfactants and zwitterionic surfactants and an ionic liquid,
10 the mixture of volatile substance and absorbent obtained during the absorption is brought into contact with a gas phase in a subsequent desorption at an elevated temperature relative to
15 the absorption and an increased pressure relative to the absorption, such that at least some of the volatile substance is desorbed from the mixture and the absorbent remaining after the desorption of the volatile substance is returned to the
20 absorption, the desorbed volatile substance is condensed at the pressure used for the desorption, the resulting condensate is then evaporated at a pressure which is lower than the pressure of the desorption and at least as high as the pressure in
25 the absorption, and the gas phase obtained during the evaporation of the condensate is brought into contact with the film of the absorbent.
2. Process according to claim 1,
30 characterized in that
the desorption takes place through a membrane which separates the mixture of volatile substance and absorbent from the gas phase into which the volatile substance is desorbed.
- 35 3. Process according to claim 1 or 2, characterized in that

the absorbent comprises one or more ionic liquids in a total amount of from 20 to 99.9% by weight and one or more wetting-promoting additives in a total amount of from 0.01 to 10% by weight.

- 5
4. Process according to any one of the preceding claims,
characterized in that
the absorbent has a contact angle towards air of
10 less than 140° on a surface of a steel S235JRG2.
5. Process according to any one of the preceding claims,
characterized in that
15 the ionic liquid consists of salts of organic cations with organic or inorganic anions.
6. Process according to any one of the preceding claims,
20 characterized in that
the ionic liquid comprises one or more 1,3-dialkylimidazolium salts.
7. Process according to any one of claims 1 to 5,
25 characterized in that
the ionic liquid comprises one or more quaternary ammonium salts of the general formula $R^1R^2R^3R^4N^+A^-$,
in which
30 R^1 is an alkyl radical having 1 to 20 carbon atoms,
 R^2 is an alkyl radical having 1 to 4 carbon atoms,
 R^3 is a radical $(CH_2CHRO)_n-H$ where n is from 1 to 200 and R = H or CH_3 ,
 R^4 is an alkyl radical having 1 to 4 carbon atoms
or a radical $(CH_2CHRO)_n-H$ where n is from 1 to 200
35 and R = H or CH_3 and
 A^- is a monovalent anion.

8. Process according to any one of the preceding claims,
characterized in that
the wetting-promoting additive comprises one or
more nonionic surfactants of the general formula
 $R(\text{OCH}_2\text{CH}_2)_m\text{OH}$ where m is from 4 to 40, in which R
is an alkyl radical having 8 to 20 carbon atoms,
an alkylaryl radical having 8 to 20 carbon atoms
or a polypropylene oxide radical having 3 to 40
propylene oxide units.
9. Process according to any one of the preceding claims,
characterized in that
the wetting-promoting additive comprises a
polyether-polysiloxane copolymer which comprises
more than 10% by weight of $[\text{Si}(\text{CH}_3)_2\text{O}]$ units and
more than 10% by weight of $[\text{CH}_2\text{CHR-O}]$ units, in
which R is hydrogen or methyl.
10. Process according to any one of the preceding claims,
characterized in that
the absorption is carried out with a film of the
absorbent on a metal surface.
11. Process according to any one of the preceding claims,
characterized in that
the film of the absorbent is generated in a
falling-film apparatus.
12. Process according to any one of Claims 1 to 10,
characterized in that
the film of the absorbent is generated on a
structured packing, preferably a structured
packing of sheet metal or metal fabric.

13. Process according to any one of the preceding claims,
characterized in that
the volatile substance is water, ammonia or carbon
dioxide.
14. Absorption refrigerating machine for carrying out
a process according to one of the preceding
claims, comprising an absorber, a desorber, an
evaporator, a condenser and a working medium of an
absorbent and a volatile substance, where the
absorber comprises a device for bringing a gas
phase containing the volatile substance into
contact with a film made of absorbent
characterized in that
the absorbent comprises a wetting-promoting
additive from the group of nonionic surfactants
and zwitterionic surfactants and an ionic liquid.
15. Use of a mixture of
a) an absorbent comprising a wetting-promoting
additive from the group of nonionic surfactants
and zwitterionic surfactants and an ionic liquid,
and
b) a volatile substance selected from water,
ammonia and carbon dioxide
as working medium in an absorption refrigerating
machine.