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(54) ABSORPTION HEAT PUMP WITH SORBENT COMPRISING LITHIUM CHLORIDE AND AN ORGANIC CHLORIDE SALT

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(57) ABSTRACT

An absorption heat pump with a sorbent which comprises lithium chloride and at least one salt Q^+Cl^- with an organic cation Q^+ and the shared anion chloride, the organic cation Q^+ having a molar mass of not more than 200 g/mol, exhibits an improved degassing range of the working medium composed of refrigerant and sorbent.

ABSORPTION HEAT PUMP WITH SORBENT COMPRISING LITHIUM CHLORIDE AND AN ORGANIC CHLORIDE SALT

[0001] The invention is directed to an absorption heat pump having an improved degassing range of the working medium.

[0002] Classical heat pumps are based on a circuit of a refrigerant via an evaporator and a condenser. In the evaporator, a refrigerant is vaporised and heat is withdrawn from a first medium due to the heat of vaporisation taken up by the refrigerant. The vaporised refrigerant is then brought to a higher pressure with a compressor and condensed in the condenser at a higher temperature than in the evaporation, resulting in the heat of vaporisation being liberated again and heat being passed to a second medium at a higher temperature level. The liquefied refrigerant is subsequently depressurised again to the pressure of the evaporator.

[0003] The classical heat pumps have the disadvantage that they consume a large amount of mechanical energy for compression of the gaseous refrigerant. Absorption heat pumps, on the other hand, have a reduced mechanical energy requirement. Absorption heat pumps have, in addition to the refrigerant, the evaporator and the condenser of a classical heat pump, a sorption medium, an absorber and a desorber. In the absorber, the vaporised refrigerant is absorbed in the sorption medium at the pressure of the evaporation and the refrigerant is subsequently desorbed again from the sorption medium in the desorber by introduction of heat at the higher pressure of the condensation. The compression of the liquid working medium composed of refrigerant and sorption medium requires less mechanical energy than the compression of the refrigerant vapour in a classical heat pump; the consumption of mechanical energy is replaced by the heat energy used for desorption of the refrigerant.

[0004] The size of the circuit of sorption medium via absorber and desorber required for operation of an absorption heat pump is determined essentially by the degassing range of the working medium of the absorption heat pump; for the present purposes, the working medium is the mixture of sorption medium and refrigerant in the circuit via absorber and desorber of the absorption heat pump and the term degassing range refers to the difference in the refrigerant content between refrigerant-depleted working medium and refrigerant-rich working medium. To be able to construct compact and inexpensive absorption heat pumps, there is therefore a need for absorption heat pumps having a large degassing range.

[0005] A large part of the absorption heat pumps used in industry uses a working medium which contains water as refrigerant and lithium bromide as sorption medium. However, this working medium has an unsatisfactory degassing range in many applications, since in the case of a working medium composed of water and lithium bromide the water concentration in the working medium must not go below from 35 to 40% by weight because otherwise crystallization of lithium bromide and thus solidification of the working medium can occur.

[0006] Working media which contain water as refrigerant and lithium chloride as sorption medium are not used industrially in absorption heat pumps since in the case of such working media in most applications the degassing range has to be kept even smaller than in the case of working media composed of water and lithium bromide in order to avoid crystallization of lithium chloride.

[0007] WO 2005/113702 describes absorption heat pumps which use a working medium having an ionic liquid as sorption medium, with the ionic liquid preferably having unlimited miscibility with the refrigerant. Although the problem of crystallization of the sorption medium can be avoided when using ionic liquid as sorption medium, the degassing range achieved is generally no better than in the case of working media composed of water and lithium bromide, especially not for working media containing water as refrigerant.

[0008] WO 2006/134015 describes, in Example VII a), the use of the ionic liquids 1-ethyl-3-methylimidazolium methylsulphonate, 1-ethyl-3-methylimidazolium acetate and 1-ethyl-3-methylimidazolium hydroxide as additives for a working medium composed of lithium bromide and water in order to reduce the crystallisation temperature of the sorption medium. However, the proportions of water, lithium bromide and ionic liquid which should be present in the working medium are not disclosed and nothing is disclosed about the influence of the additive on the degassing range of the working medium.

[0009] In Korean J. Chem. Eng., 23 (2006) 113-116, K.-S. Kim et al. propose working media composed of water, lithium bromide and the ionic liquid 1-butyl-3-methylimidazolium bromide, which working media contain lithium bromide and the ionic liquid in a weight ratio of 4:1 and 7:1. In these working media, the ionic liquid acts as anticrystallisation additive which increases the solubility of lithium bromide and reduces the crystallisation temperature. However, nothing about the degassing range of the working media disclosed can be deduced from the solubilities, viscosities and surface tensions disclosed.

[0010] It has now surprisingly been found that the use of a working medium comprising, as sorption medium, lithium chloride and at least one salt Q^+Cl^- having an organic cation Q^+ having a molar mass of not more than 200 g/mol and the shared anion chloride makes it possible to achieve a higher degassing range of the working medium than when using lithium chloride or the salt Q^+Cl^- alone.

[0011] The invention accordingly provides an absorption heat pump comprising an absorber, a desorber, a condenser, an evaporator, a volatile refrigerant and a sorption medium comprising lithium chloride and at least one salt Q^+Cl^- having an organic cation Q^+ and the shared anion chloride, where the organic cation Q^+ has a molar mass of not more than 200 g/mol.

[0012] The absorption heat pump of the invention comprises an absorber, a desorber, a condenser, an evaporator, a volatile refrigerant and a sorption medium. The working medium of the absorption heat pump is a mixture of sorption medium and refrigerant. During operation of the absorption heat pump of the invention, gaseous refrigerant is absorbed in refrigerant-depleted working medium in the absorber to give a refrigerant-rich working medium with liberation of heat of absorption. In the desorber, gaseous refrigerant is desorbed from the obtained refrigerant-rich working medium by supply of heat to give refrigerant-depleted working medium which is recirculated to the absorber. The gaseous refrigerant obtained in the desorber is condensed in the condenser to liberate heat of condensation, the liquid refrigerant obtained is vaporised in the evaporator, taking up heat of vaporisation, and the gaseous refrigerant obtained in the process is recirculated to the absorber.

[0013] The term absorption heat pump, as used in the invention, encompasses all apparatuses by means of which heat is taken up at a low temperature level and given off again at a higher temperature level and which are driven by supply of heat to the desorber. The absorption heat pumps of the invention thus encompass both absorption refrigeration machines and absorption heat pumps in the narrower sense, in which absorber and evaporator are operated at a lower working pressure than desorber and condenser, and absorption heat transformers, in which absorber and evaporator are operated at a higher working pressure than desorber and condenser. In absorption refrigeration machines, the uptake of heat of vaporisation in the evaporator is used for cooling a medium. In absorption heat pumps in the narrower sense, the heat liberated in the condenser and/or absorber is used for heating a medium. In absorption heat transformers, the heat of absorption liberated in the absorber is used for heating a medium, with the heat of absorption being obtained at a higher temperature level than the heat supplied to the desorber. In a preferred embodiment, the absorption heat pump is operated as absorption refrigeration machine and heat is taken up in the evaporator from a medium to be cooled.

[0014] The absorption heat pump of the invention comprises a sorption medium comprising lithium chloride and at least one salt Q^+Cl^- having an organic cation Q^+. Lithium chloride and the salt Q^+Cl^- have the anion chloride in common. The proportion of lithium chloride and salt Q^+Cl^- in the sorption medium is preferably more than 50% by weight and particularly preferably more than 80% by weight. The sorption medium can contain other lithium salts such as lithium bromide, lithium nitrate, lithium formate, lithium acetate and lithium carbonate in addition to lithium chloride. The proportion of lithium chloride in the total amount of lithium salts is preferably more than 80% by weight, particularly preferably more than 90% by weight.

[0015] The sorption medium preferably contains lithium chloride and the salt Q^+Cl^- in a molar ratio at which the melting point of the mixture of lithium chloride and the salt Q^+Cl^- is lower than the melting points of the components lithium chloride and Q^+Cl^-. The sorption medium particularly preferably contains lithium chloride and the salt Q^+Cl^- in a molar ratio which deviates by not more than 25% from the molar ratio of a eutectic mixture of lithium chloride and the salt Q^+Cl^-. At the preferred molar ratios of lithium chloride and the salt Q^+Cl^-, a particularly wide degassing range of the working medium is achieved and the working medium can be used in the absorption heat pump in a particularly wide temperature range.

[0016] In the salt Q^+Cl^- the organic cation Q^+ has a molar mass of not more than 200 g/mol and preferably not more than 165 g/mol. The use of one or more salts Q^+Cl^- whose organic cation Q^+ has a low molar mass according to the invention is essential for achieving a wide degassing range of the working medium.

[0017] Suitable organic cations are, in particular, cations of the general formulae (I) to (V):

$$R^1R^2R^3R^4N^+ \tag{I}$$

$$R^1R^2R^3R^4P^+ \tag{II}$$

$$R^1R^2R^3S^+ \tag{III}$$

$$R^1R^2N^+{=}C(NR^3R^4)(NR^5R^6) \tag{IV}$$

$$R^1R^2N^+{=}C(NR^3R^4)(XR^5) \tag{V}$$

[0018] where

[0019] R^1, R^2, R^3, R^4, R^5, R^6 are identical or different and are each hydrogen, a linear or branched aliphatic or olefinic hydrocarbon radical, a cycloaliphatic or cycloolefinic hydrocarbon radical, an aromatic hydrocarbon radical, an alkylaryl radical, a linear or branched aliphatic or olefinic hydrocarbon radical terminally functionalised by OH, OR', NH_2, N(H)R' or $N(R')_2$ or a polyether radical of the formula $—(R^7—O)_n—R^8$, where in the case of cations of formula (V) R^5 is not hydrogen,

[0020] R' is an aliphatic or olefinic hydrocarbon radical,

[0021] R^7 is a linear or branched alkylene radical containing 2 or 3 carbon atoms,

[0022] n is from 1 to 3,

[0023] R^8 is hydrogen or a linear or branched aliphatic or olefinic hydrocarbon radical,

[0024] X is an oxygen atom or a sulphur atom, and

[0025] where at least one and preferably each of the radicals R^1, R^2, R^3, R^4, R^5 and R^6 is different from hydrogen.

[0026] 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 suitable.

[0027] Further suitable cations are heteroaromatic cations having at least one quaternary nitrogen atom in the ring, said atom bearing a radical R^1 as defined above, preferably derivatives of pyrrole, pyrazole, imidazole, oxazole, isoxazole, thiazole, isothiazole, pyridine, pyrimidine, pyrazine, indole, quinoline, isoquinoline, cinnoline, quinoxaline or phthalazine which are substituted on the nitrogen atom.

[0028] The organic cation Q^+ preferably contains a quaternary nitrogen atom. The organic cation Q^+ is preferably a 1,3-dialkylimidazolium ion, 1,3-dialkylimidazolinium ion, N-alkylpyridinium ion, N,N-dialkylpyrrolidinium ion or an ammonium ion having the structure $R^1R^2R^3R^4N^+$, where R^1, R^2 and R^3 are each, independently of one another, hydrogen, alkyl or hydroxyethyl and R^4 is an alkyl radical.

[0029] The organic cation Q^+ is particularly preferably a 1,3-dialkylimidazolium ion in which the alkyl groups are selected independently from among methyl, ethyl, n-propyl and n-butyl. The organic cation Q^+ is particularly preferably 1,3-dimethylimidazolium, 1-ethyl-3-methylimidazolium, 1-(n-butyl)-3-methylimidazolium or 1-(n-butyl)-3-ethylimidazolium.

[0030] In a further particularly preferred embodiment, the salt Q^+Cl^- is choline chloride.

[0031] The salt Q^+Cl^- is preferably thermally stable up to a temperature of 150° C. Preference is given to using salts Q^+Cl^- which have a solubility in water of at least 500 g/l. Preference is given to using salts Q^+Cl^- which are stable to hydrolysis. Hydrolysis-stable salts Q^+Cl^- display less than 5% decomposition by hydrolysis in a mixture with 50% by weight of water when stored at 80° C. for 8000 hours.

[0032] The sorption medium can contain further salts having an organic cation and other anions such as bromide, nitrate, formate, acetate or carbonate in addition to the salt Q^+Cl^-. The proportion of chloride salts Q^+Cl^- in the total amount of organic salts is preferably more than 80% by weight, particularly preferably more than 90% by weight.

[0033] The absorption heat pump of the invention preferably contains water, methanol, ethanol, 2-propanol, trifluoroethanol, sulphur dioxide, carbon dioxide or ammonia, particularly preferably water, ethanol, 2-propanol or trifluoroethanol and most preferably water, as refrigerant.

[0034] In a preferred embodiment, the salt Q^+Cl^- and the refrigerant are selected so that a solution of lithium chloride in the refrigerant which is saturated at 35° C. has a higher vapour pressure than a mixture of the salt Q^+Cl^- and the refrigerant having the same proportion by weight of refrigerant. Preference is given to using water, methanol, ethanol, 2-propanol or trifluoroethanol and particularly preferably water as refrigerant. Examples of such an embodiment are 1-ethyl-3-methylimidazolium chloride, choline chloride or tetramethylammonium chloride as salt Q^+Cl^- and water as refrigerant. A further-improved degassing range of the working medium can be achieved by a corresponding selection of salt Q^+Cl^- and refrigerant.

[0035] The absorption heat pump of the invention can contain further additives, preferably corrosion inhibitors and/or additives which promote wetting, in the working medium in addition to sorption medium and refrigerant. The proportion of corrosion inhibitors is preferably from 10 to 50 000 ppm, particularly preferably from 100 to 10 000 ppm, based on the mass of the sorption medium. The proportion of additives which promote wetting is preferably from 10 to 50 000 ppm, particularly preferably from 100 to 10 000 ppm, based on the mass of the sorption medium.

[0036] All non-volatile corrosion inhibitors, which are known from the prior art to be suitable for the materials used in the absorption heat pump, can be used as corrosion inhibitors.

[0037] Preferably one or more surfactants from the group consisting of nonionic surfactants, zwitterionic surfactants and cationic surfactants are used as additive which promotes wetting.

[0038] Suitable nonionic surfactants are alkylamine alkoxylates, amidoamines, alkanolamides, alkylphosphine oxides, alkyl-N-glucamides, alkyl glucosides, bile acids, alkyl alkoxylates, sorbitan esters, sorbitan ester ethoxylates, fatty alcohols, fatty acid ethoxylates, ester ethoxylates and polyethersiloxanes.

[0039] Suitable zwitterionic surfactants are betaines, alkylglycines, sultains, amphopropionates, amphoacetates, tertiary amine oxides and silicobetaines.

[0040] Suitable cationic surfactants are quaternary ammonium salts having one or two substituents having from 8 to 20 carbon atoms, in particular corresponding tetraalkylammonium salts, alkylpyridinium salts, ester quats, diamidoamine quats, imidazolinium quats, alkoxyalkyl quats, benzyl quats and silicone quats.

[0041] In a preferred embodiment, the additive which promotes wetting comprises one or more nonionic surfactants of the general formula $R(OCH_2CHR')_nOH$ where m is from 4 to 40 and R is an alkyl radical having from 8 to 20 carbon atoms, an alkylaryl radical having from 8 to 20 carbon atoms or a polypropylene oxide radical having from 3 to 40 propylene oxide units and R' is methyl or preferably hydrogen.

[0042] In a further preferred embodiment, the additive which promotes wetting comprises a polyether-polysiloxane copolymer containing more than 10% by weight of $[Si(CH_3)_2O]$ units and more than 10% by weight of $[CH_2CHR—O]$ units, where R is hydrogen or methyl. Particular preference is given to polyether-polysiloxane copolymers of the general formulae (VI) to (VIII):

$$(CH_3)_3Si—O—[SiR—(CH_3)—O]_n—Si(CH_3)_3 \qquad \text{(VI)}$$

$$R^2O\text{-}A_p\text{-}[B\text{-}A]_n\text{-}A_q\text{-}R^2 \qquad \text{(VII)}$$

$$R^2O\text{-}[A\text{-}Z\,]_p—[B—Si(CH_3)_2—Z—O\text{-}A\text{-}Z]_n—B—Si(CH_3)_2[Z—O\text{-}A]_qO_{1\text{-}q}R^2 \qquad \text{(VIII)}$$

[0043] where

[0044] A is a divalent radical of the formula $—[CH_2CHR^3—O]_r—$,

[0045] B is a divalent radical of the formula $—[Si(CH_3)_2—O]_s—$,

[0046] Z is a divalent linear or branched alkylene radical having from 2 to 20 carbon atoms, preferably $—(CH_2)_3—$,

[0047] n is from 1 to 30,

[0048] m is from 2 to 100,

[0049] p, q are each 0 or 1,

[0050] r is from 2 to 100,

[0051] s is from 2 to 100,

[0052] from 1 to 5 of the radicals R^1 are radicals of the general formula $—Z—O\text{-}A\text{-}R^2$ and the remaining radicals R^1 are each methyl,

[0053] R^2 is hydrogen or an aliphatic or olefinic alkyl radical or acyl radical having from 1 to 20 carbon atoms and

[0054] R^3 is hydrogen or methyl.

[0055] The additives which promote wetting are known to those skilled in the art from the prior art as additives for aqueous solutions and can be prepared by methods known from the prior art.

[0056] In a preferred embodiment of the absorption heat pump of the invention, the refrigerant-containing vapour phase and the sorption medium-containing liquid phase are separated from one another by a semipermeable membrane in the absorber and/or desorber, with the semipermeable membrane being permeable to the refrigerant and impermeable to the sorption medium.

[0057] The semipermeable membrane is preferably a solution diffusion membrane. A solution diffusion membrane has virtually no pores. For a solution diffusion membrane the selective permeability of the membrane for the refrigerant is due to the refrigerant dissolving in the material of the membrane and diffusing through the membrane, while the sorption medium is insoluble in the material of the membrane. The suitability of a solution diffusion membrane for the absorption heat pump of the invention can therefore be determined by a person skilled in the art by simple tests on the solubility of refrigerant and sorption medium in the material of the membrane.

[0058] For the embodiment using water as refrigerant, it is possible to use any pore-free membrane, known to those skilled in the art from the technical fields of dialysis, reverse osmosis and pervaporation as being suitable for the removal of salts from aqueous salt solutions, as solution diffusion membrane.

[0059] The material used for the solution diffusion membrane is preferably a hydrophilic or hydrophilically functionalised polymer containing polyvinyl alcohol, polyimide, polybenzimidazole, polybenzimidazolone, polyamide hydrazide, cellulose ester, cellulose acetate, cellulose diacetate, cellulose triacetate, cellulose butyrate, cellulose nitrate, polyurea, polyfuran, polyethylene glycol, poly(octylmethylsiloxane), polysiloxane, polyalkylsiloxane, polydialkylsiloxane, polyester-polyether block copolymer, polysulphone, sulphonated polysulphone, polyamide, in particular aromatic polyamide, polyether, polyether ether ketone, polyester, polyether-urea composite, polyamide-urea composite, polyether sulphone, polycarbonate, polymethyl methacrylate, polyacrylic acid or polyacrylonitrile. It is likewise possible to use mixtures or copolymers of two or more of these polymers.

Particular preference is given to solution diffusion membranes composed of cellulose acetate, crosslinked polyethylene glycol, crosslinked polydimethylsiloxane or a polyester-polyether block copolymer.

[0060] In a further preferred embodiment, the semipermeable membrane is a microporous membrane. For the purposes of the invention, microporous membranes are membranes which have pores extending through the membrane, the pores having a minimum diameter in the range from 0.3 nm to 100 μm. The membrane preferably has pores in the range from 0.3 nm to 0.1 μm.

[0061] Preference is given to using a microporous membrane which is not wetted by the working medium composed of sorption medium and refrigerant. Here, the term wetting refers to a contact angle between working medium and microporous membrane of less than 90 degrees, which leads to penetration of working medium into pores of the membrane as a result of capillary forces. The contact angle between working medium and microporous membrane is preferably greater than 120 degrees, particularly preferably greater than 140 degrees. The use of a nonwetting microporous membrane can also prevent flow of the liquid working medium through the pores of the membrane to the vapour side of the membrane in the case of a pressure on the side of the liquid working medium which is higher than that on the vapour side. The suitability of a microporous membrane for the absorption heat pump of the invention can therefore be determined by a person skilled in the art by determining the contact angle between the working medium and the membrane.

[0062] For the embodiment using water as refrigerant, preference is given to using a hydrophobic microporous membrane as semipermeable membrane. Suitable hydrophobic microporous membranes are known to a skilled person in the technical field of functional clothing as membranes which are watertight and permeable to water vapour.

[0063] Preference is given to using hydrophobic microporous membranes composed of polyethylene, polypropylene, polytetrafluoroethylene, polyvinylidene fluoride or fluoroalkyl-modified polymers. It is likewise possible to use mixtures or copolymers of two or more of these polymers. Further suitable membranes are inorganic hydrophobic microporous membranes or composite membranes comprising an inorganic hydrophobic microporous material, for example membranes whose pores are formed by silicalite or hydrophobised silica.

[0064] The semipermeable membrane is preferably arranged on a porous support layer. Arrangement on a porous support layer makes it possible to achieve a mechanically stable membrane unit even when using a thin semipermeable membrane. This allows more rapid mass transfer through the membrane and thus a smaller and more compact construction of the absorber. The support layer is preferably arranged on the side of the semipermeable membrane adjoining the vapour phase. Such an arrangement of the support layer leads to a lower resistance to mass transfer than arrangement of the support layer on the side of the membrane facing the liquid working medium.

[0065] The porous support layer can comprise either inorganic or organic materials. The membrane is preferably arranged on a porous support layer composed of a hydrophobic polymer, in particular a polyolefin, a polyester or polyvinylidene fluoride. The support layer can additionally contain reinforcements, e.g. by means of layers of fabric.

[0066] In a preferred embodiment, the semipermeable membrane is arranged in the form of hollow fibres. The embodiment of the membrane in the form of hollow fibres allows a particularly compact construction of absorber and/or desorber and operation with a higher pressure difference between the vapour phase and the liquid phase.

[0067] The absorption heat pump of the invention preferably has a two-stage or multistage, particularly preferably two-stage, construction, as described, for example, for absorption refrigeration machines in F. Ziegler, R. Kahn, F. Summerer, G. Alefeld "Multi-Effect absorption chillers", Rev. Int. Froid 16 (1993) 301-311.

[0068] The absorption heat pump of the invention preferably has an additional heat exchanger by means of which heat is exchanged between the refrigerant-depleted working medium which is fed from the desorber to the absorber and the refrigerant-rich working medium which is fed from the absorber to the desorber. A countercurrent heat exchanger is particularly preferably used for this purpose.

[0069] In a preferred embodiment, at least one of the system components absorber, desorber, condenser and evaporator has a wall surface made of a polymeric material via which heat is exchanged with the surroundings. The polymeric material is in this case preferably a polyamide, a polyimide or polyether ether ketone. As polyamide, preference is given to using polyamide 12. As polyimide, preference is given to using a polyimide of benzophenonetetracarboxylic dianhydride and a mixture of tolylene diisocyanate and methylenedi (phenyl diisocyanate), which can be obtained under the trade name P84 from Evonik Fibres. Corrosion of the heat-exchanging surfaces can be avoided by the use of a polymeric material. At the same time, a high heat transfer coefficient can be achieved by the use of a polyamide, a polyimide or polyether ether ketone, allowing a compact construction of the absorption heat pump.

[0070] The following examples illustrate the invention without limiting the subject matter of the invention.

EXAMPLES

Examples 1 to 6

Degassing Range Using 1-ethyl-3-methylimidazolium chloride (EMIMCl) as Organic Salt

[0071] The maximum achievable degassing range was determined for operation of an absorption refrigeration machine at a pressure in the evaporator and absorber of 10 mbar, a temperature in the absorber of 35° C., a pressure in the desorber and condenser of 50 mbar and a maximum temperature in the desorber of 85° C. For this purpose, the sorption medium was mixed with various amounts of water, the vapour pressure was measured in each case and in this way the content of water was determined at which the mixture with sorption medium had a vapour pressure of 10 mbar at 35° C. or a vapour pressure of 50 mbar at 85° C. respectively. In addition, the minimum content of water was determined at which a homogeneous mixture without undissolved lithium salt is obtained at 35° C. The mixture having a vapour pressure at 35° C. of 10 mbar corresponds to the most refrigerant-rich working medium which can be used in operation of the absorption refrigeration machine. The most refrigerant-depleted working medium which can be used in operation of the absorption refrigeration machine is the mixture having a vapour pressure of 50 mbar at 85° C. or, if such a mixture exceeds the solubility limit of the lithium salt at 35° C., the homogeneous mixture having the minimum content of water. The degassing range is calculated as the difference in the mass fraction of the refrigerant water between the most refrigerant-rich working medium and the most refrigerant-depleted working medium. The results are shown in Table 1.

[0072] The data in Table 1 show that, according to the invention, a higher degassing range is achieved using a sorption medium composed of 1-ethyl-3-methylimidazolium chloride and lithium chloride than when using 1-ethyl-3-methylimidazolium chloride or lithium chloride as sorption medium. An improved degassing range is also achieved compared to the industrially used sorption medium lithium bromide.

TABLE 1

Degassing range of sorption media using water as refrigerant

Example	Sorption medium	Mass fraction of water for 10 mbar at 35° C.	Mass fraction of water for 50 mbar at 85° C.	Mass fraction of water for solubility limit at 35° C.	Degassing range
1 *	LiCl	0.61	***	0.53	0.08
2 *	EMIMCl	0.17	0.1		0.07
3	EMIMCl/ LiCl 1:1 **	0.45	***	0.34	0.11
4	EMIMCl/ LiCl 2:1 **	0.37	***	0.24	0.13
5	EMIMCl/ LiCl 3:1 **	0.35	0.2	0.03	0.15
6 *	LiBr	0.45	0.34	0.34	0.11

* not according to the invention

** weight ratio of EMIMCl to LiCl

*** for homogeneous mixtures of sorption medium and water, the vapour pressure at 85° C. is always higher than 50 mbar

Examples 7 to 11

Vapour Pressure of Working Media Containing Water as Refrigerant

[0073] The vapour pressure of working media which contained as sorption medium an organic salt and lithium chloride in a mass ratio of 3:1 and as refrigerant water in a proportion by mass of 10 and 40% by weight was determined at 35, 50 and 60° C. In the case of mixtures which contained undissolved lithium salt, no vapour pressure was determined. The results are shown in Table 2.

[0074] The experimental data show that in the case of a combination of lithium chloride and an organic salt having an anion other than chloride, undissolved lithium salt is present at low contents of water of 10% by weight in the working medium, while in the case of a combination of lithium chloride with an organic salt having the shared anion chloride, a single-phase liquid working medium is surprisingly obtained even at such low contents of water. In addition, a lower vapour pressure is achieved using the sorption media according to the invention even at higher water contents of 40% by weight, which is advantageous for a two-stage absorption heat pump and allows three-stage operation of an absorption heat pump.

TABLE 2

Vapour pressure of working media containing a sorption medium composed of an organic salt and lithium chloride in a mass ratio of 3:1 and water as refrigerant

Example	Organic salt	Proportion of water in % by weight	Vapour pressure in mbar at 35° C.	50° C.	60° C.
5	EMIM Cl	10	2.7	3.3	3.6
		40	18	46	65
7	BMIM Cl	10	2	4	9
8	Choline	10	<3	4	8
	chloride	40	18	48	79
9 *	EMIM CF_3COO	10	**	**	28
		40	29	65	109
10 *	EMIM SCN	10	**	**	**
		40	**	**	**
11 *	EMIM CH_3COO	10	**	**	**
		40	26	54	90

* not according to the invention

** undissolved lithium salt

BMIM = 1-butyl-3-methylimidazolium

1-12. (canceled)

13. An absorption heat pump comprising an absorber, a desorber, a condenser, an evaporator, a volatile refrigerant and a sorption medium, wherein said sorption medium comprises lithium chloride and at least one salt Q^+Cl^- comprising an organic cation Q^+ and the shared anion chloride, and wherein the organic cation Q^+ has a molar mass of not more than 200 g/mol.

14. The absorption heat pump of claim **13**, wherein the sorption medium contains lithium chloride and the salt Q^+Cl^- in a molar ratio at which the melting point of the mixture of lithium chloride and salt Q^+Cl^- is lower than the melting points of the components lithium chloride and Q^-Cl^-.

15. The absorption heat pump of claim **14** wherein the sorption medium contains lithium chloride and the salt Q^+Cl^- in a molar ratio which deviates by not more than 25% from the molar ratio of a eutectic mixture of lithium chloride and the salt Q^+Cl^-.

16. The absorption heat pump of claim **13**, wherein the proportion of lithium chloride and the salt Q^+Cl^- in the sorption medium is more than 50% by weight.

17. The absorption heat pump of claim **13**, wherein the refrigerant is selected from the group consisting of: methanol, ethanol, 2-propanol, trifluoroethanol, sulphur dioxide, carbon dioxide and ammonia.

18. The absorption heat pump of claim **13**, wherein the refrigerant is water.

19. The absorption heat pump of claim **13**, wherein a solution of lithium chloride in the refrigerant which is saturated at 35° C. has a higher vapour pressure than a mixture of the salt Q^+Cl^- and the refrigerant having the same proportion by weight of refrigerant.

20. The absorption heat pump of claim **13**, wherein the organic cation Q^+ is selected from the group consisting of: 1,3 dialkylimidazolium ions; 1,3-dialkyl-imidazolinium ions; N-alkylpyridinium ions; N,N-dialkylpyrrolidinium ions; and ammonium ions having the structure $R^1R^2R^3R^4N^+$, wherein R^1, R^2 and R^3 are each, independently of one another, hydrogen, alkyl or hydroxyethyl and R^4 is an alkyl radical.

21. The absorption heat pump of claim **13**, wherein said absorption heat pump is operated as absorption refrigeration machine and heat is taken up in the evaporator from a medium to be cooled.

22. The absorption heat pump of claim **13**, wherein said absorption heat pump has a two-stage construction.

23. The absorption heat pump of claim **13**, wherein a vapour phase containing refrigerant and a liquid phase containing sorption medium are separated from one another by a semipermeable membrane in the absorber and/or desorber and the semipermeable membrane is permeable to the refrigerant and impermeable to the sorption medium.

24. The absorption heat pump of claim **13**, wherein at least one of the components absorber, desorber, condenser and evaporator has a wall surface made of a polymeric material selected from among polyamides, polyimides and polyether ether ketone via which heat is exchanged with the surroundings.

25. The absorption heat pump of claim **15**, wherein the proportion of lithium chloride and the salt Q^+Cl^- in the sorption medium is more than 50% by weight.

26. The absorption heat pump of claim **25**, wherein the refrigerant is selected from the group consisting of: methanol, ethanol, 2-propanol, trifluoroethanol, sulphur dioxide, carbon dioxide and ammonia.

27. The absorption heat pump according of claim **25**, wherein the refrigerant is water.

28. The absorption heat pump of claim **17**, wherein the organic cation Q^+ is selected from the group consisting of: 1,3 dialkylimidazolium ions; 1,3-dialkyl-imidazolinium ions; N-alkylpyridinium ions; N,N-dialkylpyrrolidinium ions; and ammonium ions having the structure $R^1R^2R^3R^4N^+$, wherein R^1, R^2 and R^3 are each, independently of one another, hydrogen, alkyl or hydroxyethyl and R^4 is an alkyl radical.

29. The absorption heat pump of claim **18**, wherein the organic cation Q^+ is selected from the group consisting of: 1,3 dialkylimidazolium ions; 1,3-dialkyl-imidazolinium ions; N-alkylpyridinium ions; N,N-dialkylpyrrolidinium ions; and ammonium ions having the structure $R^1R^2R^3R^4N^+$, wherein R^1, R^2 and R^3 are each, independently of one another, hydrogen, alkyl or hydroxyethyl and R^4 is an alkyl radical.

30. The absorption heat pump of claim **29**, wherein a vapour phase containing refrigerant and a liquid phase containing sorption medium are separated from one another by a semipermeable membrane in the absorber and/or desorber and the semipermeable membrane is permeable to the refrigerant and impermeable to the sorption medium.

31. The absorption heat pump of claim **30**, wherein the proportion of lithium chloride and the salt Q^+Cl^- in the sorption medium is more than 50% by weight.

32. The absorption heat pump of claim **31**, wherein the sorption medium contains lithium chloride and the salt Q^+Cl^- in a molar ratio which deviates by not more than 25% from the molar ratio of a eutectic mixture of lithium chloride and the salt Q^+Cl^-.

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