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(54) **Title**: REMOVAL OF CARBON DIOXIDE FROM A GAS STREAM BY USING AQUEOUS IONIC LIQUID

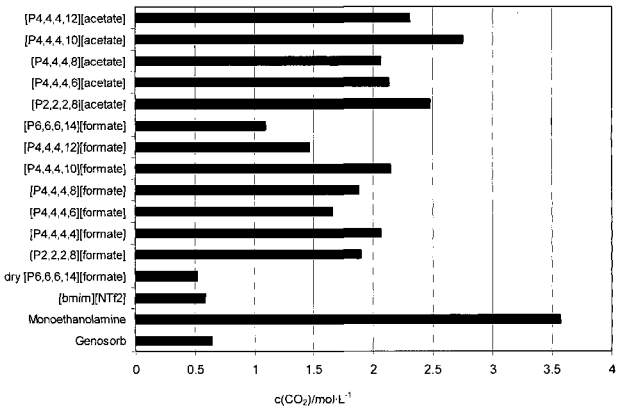


Figure 1

(57) **Abstract**: The present invention relates to the separation of gases, and more specifically to an inventive process for the removal of carbon dioxide gas using carefully selected ionic liquid absorbents together with water in a carefully selected ratio.

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REMOVAL OF CARBON DIOXIDE FROM A GAS STREAM BY USING AQUEOUS IONIC LIQUID

The present invention relates to the separation of gases, and more specifically to an inventive process for the removal of carbon dioxide gas using carefully selected liquid absorbents.

The separation of carbon dioxide from gas streams is an extremely active field of research, due to the increasing concern about global warming from the greenhouse effect, and the common belief that the build up of carbon dioxide in the atmosphere is a contributing factor.

In the field of natural gas processing, separation of carbon dioxide and other acidic (sour) gases from the natural gas stream is also of importance to improve the fuel quality and to avoid corrosion problems in metal pipelines.

Separation of carbon dioxide is also important in the field of biogas. Biogas is the result of microbial degradation of organic waste. Biogas streams contain large amounts of carbon dioxide (and other acid gases) and water vapour in addition to the methane and light hydrocarbons of interest. Hence, removal of carbon dioxide to improve the quality of biogas is necessary as for natural gas.

Carbon dioxide removal processes are of importance in the field of life support systems. For human occupied sealed systems containing a breathing gas mixture, such as submarines and SCBA gear as well as underground mining shelters and spacecraft, the build-up of metabolites such as carbon dioxide and water vapour must be removed to maintain life. Current technologies rely on carbon dioxide scrubbers (typically a solid material such as lithium hydroxide or zeolites) as well as a separate dehumidifier (see for example BioPak 240). As is the case for natural gas and biogas treatment, the process may be simplified by combing the two procedures in one step.

For both of these reasons, the implementation of carbon dioxide separation processes in industry has gained importance over the last few decades.

The technologies used for the purpose of carbon dioxide separation can be divided into three groups: liquid absorbents, solid absorbents or adsorbents, and membranes. Liquid

absorbents are by far the most commonly used of these, and can in turn be divided into physical and chemical absorbents.

In the field of natural gas processing, chemical absorbents are often preferred, since they generally have higher absorption capacities for carbon dioxide. The energy efficiency of chemical absorption processes is determined largely by the energy demands of regenerating the absorbent by desorption of the carbon dioxide.

The most commonly used chemical absorbents for carbon dioxide removal include aqueous amine solutions, chilled ammonia and hot aqueous potassium carbonate. However, these require high temperatures to be recycled, in general far above 100 °C. In addition, the high basicity and solvent strength of these systems often leads to other problems such as corrosion of pipelines and other steel parts in the plant. Another drawback of these liquid chemical absorption systems, in particular the aqueous amine systems, is that the amines are volatile and toxic and thus can contaminate the gas stream with loss of absorbent, and also represent a hazard in the workplace. With hot aqueous potassium carbonate absorbents, the major drawbacks include high operating temperatures and the tendency of the salts to crystallize/precipitate during processing. Dilution of the solutions so as to minimize corrosion or crystallization/precipitation issues entails a consequent reduction in carbon dioxide absorption capacity.

Ionic liquids are a class of compounds which have been the subject of intense research over the past few decades. The term “ionic liquid” as used herein refers to a liquid that is capable of being produced by melting a solid, and when so produced consists solely of ions. The term “ionic liquid” includes both compounds having high melting temperature and compounds having low melting points, e.g. at or below room temperature (i.e. 15 to 30°C). The latter are often referred to as “room temperature ionic liquids” and are often derived from organic salts having pyridinium- and imidazolium-based cations. A feature of ionic liquids is that they have particularly low (essentially zero) vapour pressures. Many organic ionic liquids have low melting points, for example, less than 100°C, particularly less than 80°C, and around room temperature, e.g. 15 to 30°C, and some have melting points well below 0°C.

An ionic liquid may be formed from a homogeneous substance comprising one species of cation and one species of anion, or it can be composed of more than one species of cation and/or anion. Thus, an ionic liquid may be composed of more than one species of cation and one species of anion. An ionic liquid may further be composed of one species of cation, and more than one species of anion.

Ionic liquids generally exhibit a set of appealing physicochemical characteristics that typically include extremely low vapour pressure, wide liquid range, non-degradability, non-flammability, good thermal stability and excellent ability to solubilise a large range of compounds. Due to the potential for controlling the properties of ionic liquids by judicious choice of the constituent ions, and the multiple combinations of ions that can result in low-melting salts, ionic liquids have been proposed for a broad range of applications.

Ionic liquids have been proposed as an alternative to chemical and physical acid gas absorbents for a number of reasons including: (i) the possibility of controlling their properties by the selection of the cation and anion components; (ii) the limited tendency of ionic liquids to crystallize under operating conditions; and (iii) the potential to prevent contamination of the gaseous streams by the absorbent due to the negligible vapour pressure of ionic liquids.

Anderson *et al*. (Accounts of Chemical Research, 2007, volume 40, pages 1208 to 1216) have reviewed the absorption of a number of different gases in pyridinium, imidazolium and ammonium ionic liquids. The molar enthalpies (ΔH) of gas dissolution were determined for the group of gases tested, and the low values observed indicate that only physical absorption takes place. In particular, carbon dioxide is said to interact with the ionic liquids by means of dispersion, dipole/induced dipole interactions and electrostatic effects.

The use of ionic liquids as chemical CO_2 absorbers has also been reported. Bates *et al*. (Journal of the American Chemical Society, 2002, volume 124, pages 926 to 927) have reported the use of a basic imidazolium ionic liquid having an amine functionality tethered to the imidazolium cation to sequester carbon dioxide as a carbamate. However, the high viscosity of these ionic liquids both before, and especially after, carbon dioxide sequestration appears to be a serious limitation for their potential use in industrial processes.

Carvalho *et al.* (Journal of Physical Chemistry B, 2009, volume 113, pages 6803 to 6812) have reported the use of 1-butyl-3-methylimidazolium ionic liquids having acetate and trifluoroacetate anions as absorbents for carbon dioxide. This document teaches that purifying the ionic liquid by removal of water prior to use is essential to avoid a reduction in carbon dioxide absorbing capacity which is reported to take place when water is present in the ionic liquid. A number of prior art documents are cited by Carvalho *et al.*, each of which support the deleterious effect of using wet ionic liquids for carbon dioxide absorption.

The absorption of carbon dioxide by ionic liquids containing imidazolium cations is also disclosed by Shiflett *et al.* (Journal of Physical Chemistry B, 2008, volume 112, pages 16654 to 16663). Again, the ionic liquids are purified by removing water under vacuum with heating for a period of 5 days, emphasizing the need for the ionic liquids to be dry. A single phosphonium ionic liquid (tetra-n-butylphosphonium formate) was also analysed, again in the absence of water, and shown to absorb modest amounts of carbon dioxide by a physical absorption mechanism.

The present inventors have found, however, that the use of imidazolium ionic liquids in industrial processes is seriously limited by the instability of these ionic liquids to many of the components found in natural gas streams. Reaction of the imidazolium ions with components of the gaseous stream can lead to loss of absorbent, and contamination of the remaining absorbent with degradation products of the ionic liquid. The instability of imidazolium ionic liquids has been discussed in detail by Aggarwal, V. K. *et. al.* (Chemical Communications 2002, 1612-1613) and Earle, M. J. at the ACS symposium Washington DC 2001 (Abstracts of Papers of the American Chemical Society, 2001, volume 221, 161). There is therefore a need in the art for alternative ionic liquid absorbents that are both capable of absorbing useful quantities of carbon dioxide from gaseous streams, while also being resistant to degradation during processing.

The present invention is based on the surprising discovery that, contrary to the teaching in the art to rigorously dry ionic liquids that are used to absorb carbon dioxide, selected classes of ionic liquids demonstrate a marked improvement in carbon dioxide absorption capacity in the presence of water. More specifically, it has been found that mixtures of water and ionic liquids comprising tetrasubstituted phosphonium or tetrasubstituted ammonium cations with anions

that are conjugate bases of carboxylic acids, in fact demonstrate a marked improvement in carbon dioxide absorption capacity when compared to the ionic liquid alone in the absence of water.

In addition, it has been found that the selected ionic liquids are extremely stable to the processing conditions used for separation of carbon dioxide from gaseous streams, and are highly resistant to degradation by other contaminants that may be present in the gaseous streams.

It has also been found that mixtures of the selected classes of ionic liquids and water are also highly effective in removing other substances, such as water vapour, from gaseous streams. The mixtures of ionic liquids and water may therefore be used in processes for the combined removal of carbon dioxide and one or more additional substances, such as water, from gaseous streams.

Furthermore, it has been found that carbon dioxide and other substances can be easily desorbed from the mixtures of ionic liquids and water. For instance, carbon dioxide can be desorbed by heating in the presence of a sparging gas (e.g. nitrogen gas), or by pressure reduction, allowing the mixtures to be recycled to the separation process without loss or degradation of the absorbent mixture.

According to the present invention, there is provided a process for removing carbon dioxide from a gaseous stream comprising contacting the gaseous stream with a carbon dioxide absorbent comprising a mixture of an ionic liquid and water in a molar ratio of from 20:80 to 80:20, wherein the ionic liquid has the formula:

$$[Cat^+][X^-]$$

wherein: $[Cat^+]$ represents a cationic species selected from tetrasubstituted phosphonium cations, tetrasubstituted ammonium cations, trisubstituted sulfonium cations, guanidinium cations and quinolinium cations; and

$[X^-]$ represents an anionic species which is a conjugate base of a carboxylic acid.

Preferably, [Cat^+] is selected from tetrasubstituted phosphonium cations, tetrasubstituted ammonium cations, and trisubstituted sulfonium cations having the formulae:

$$[P(R^a)(R^b)(R^c)(R^d)]^+, [N(R^a)(R^b)(R^c)(R^d)]^+ \text{ and } [S(R^b)(R^c)(R^d)]^+$$

wherein R^a, R^b, R^c, and R^d are each independently selected from a C_1 to C_{20} straight chain or branched alkyl group, a C_3 to C_8 cycloalkyl group, or a C_6 to C_{10} aryl group, or wherein any two of R^a, R^b, R^c, and R^d may together form a saturated methylene chain of the formula $-(CH_2)_q-$, where q is an integer of from 4 to 7, or an oxyalkylene chain of the formula $-(CH_2)_2-O-(CH_2)_2-$, wherein said alkyl, cycloalkyl or aryl groups, said methylene chain, or said oxyalkylene chain are unsubstituted or may be substituted by one to three groups selected from: C_1 to C_6 alkoxy, C_2 to C_{12} alkoxyalkoxy, C_6 to C_{10} aryl, -CN, -OH, $-NO_2$, $-CO_2(C_1$ to $C_6)$alkyl, $-OC(O)(C_1$ to $C_6)$alkyl, C_7 to C_{30} aralkyl C_7 to C_{30} alkaryl, and $-N(R^z)_2$, where each R^z is independently selected from hydrogen, methyl, ethyl, n-propyl and iso-propyl, and wherein R^b may also be hydrogen.

More preferably, [Cat^+] is selected from tetrasubstituted phosphonium cations and tetrasubstituted ammonium cations having the formulae:

$$[P(R^a)(R^b)(R^c)(R^d)]^+ \text{ and } [N(R^a)(R^b)(R^c)(R^d)]^+$$

wherein: R^a, R^b, R^c, and R^d as defined above.

Still more preferably, [Cat^+] is selected from tetrasubstituted phosphonium cations having the formula:

$$[P(R^a)(R^b)(R^c)(R^d)]^+$$

wherein: R^a, R^b, R^c, and R^d as defined above.

In the tetrasubstituted phosphonium cations, tetrasubstituted ammonium cations, trisubstituted sulfonium cations defined above, R^a, R^b, R^c, and R^d (where present) are preferably each

independently selected from a C_1 to C_{16} straight chain or branched alkyl group, or any two of R^a, R^b, R^c, and R^d may together form a methylene chain of the formula $-(CH_2)_q-$, where q is an integer of from 4 or 5.

More preferably, R^a, R^b, R^c, and R^d (where present) are preferably each independently selected from a C_1 to C_{16} straight chain or branched alkyl group. Examples of preferred alkyl groups include: n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, and n-tetradecyl.

Still more preferably, R^a, R^b and R^c, (where present) are preferably each independently selected from a C_1 to C_8 straight chain or branched alkyl group, and R^d is preferably a C_4 to C_{16} straight chain or branched alkyl group. Most preferably, R^a, R^b and R^c, (where present) are each the same C_1 to C_8 straight chain or branched alkyl group, and R^d is preferably a C_4 to C_{16} straight chain or branched alkyl group.

In a further preferred embodiment, two of R^a, R^b, R^c, and R^d (where present) taken together form a saturated methylene chain of the formula $-(CH_2)_q-$, where q is an integer of from 4 to 7, or an oxyalkylene chain of the formula $-(CH_2)_2-O-(CH_2)_2-$. Preferably, q is an integer of 4 or 5.

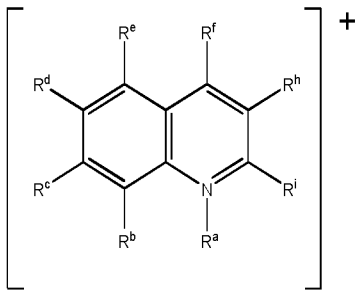
Examples of preferred tetrasubstituted phosphonium cations and tetrasubstituted ammonium cations and trisubstituted sulfonium cations in accordance with the present invention, include those where R^a, R^b and R^c (where present) are each the same alkyl group selected from ethyl, n-butyl and n-hexyl, and where R^d is selected from n-butyl, n-hexyl, n-octyl, n-decyl, n-dodecyl, and n-tetradecyl.

Specific examples of phosphonium cations that may be used in accordance with the present invention include n-butyl-triethylphosphonium, n-hexyl-triethylphosphonium, n-octyl-triethylphosphonium, tetra-n-butylphosphonium, n-hexyl-tri-n-butylphosphonium, n-octyl-tri-n-butylphosphonium, n-decyl-tri-n-butylphosphonium, n-dodecyl-tri-n-butylphosphonium, n-octyl-tri-n-hexylphosphonium, n-decyl-tri-n-hexylphosphonium, n-dodecyl-tri-n-hexylphosphonium, and n-tetradecyl-tri-n-hexylphosphonium.

Specific examples of ammonium cations that may be used in accordance with the present invention include n-butyl-triethylammonium, n-hexyl-triethylammonium, n-octyl-triethylammonium, tetra-n-butylammonium, n-hexyl-tri-n-butylammonium, n-octyl-tri-n-butylammonium, n-decyl-tri-n-butylammonium, n-dodecyl-tri-n-butylammonium, n-octyl-tri-n-hexylammonium, n-decyl-tri-n-hexylammonium, n-dodecyl-tri-n-hexylammonium, n-tetradecyl-tri-n-hexylammonium, choline.

Further examples of ammonium cations include pyrrolidinium, morpholinium, piperidinium which may optionally be substituted as described above.

Where, $[Cat^+]$ is a quinolinium cation, it preferably has the formula:



wherein: R^a, R^b, R^c, R^d, R^e, R^f, R^g, R^h and R^i are each independently selected from hydrogen, a C_1 to C_{20} straight chain or branched alkyl group, a C_3 to C_8 cycloalkyl group, or a C_6 to C_{10} aryl group, or any two of R^b, R^c, R^d, R^e, R^f, R^h and R^i attached to adjacent carbon atoms may form a saturated methylene chain $-(CH_2)_q-$ wherein q is from 3 to 6, and wherein said alkyl, cycloalkyl or aryl groups, or said methylene chain are unsubstituted or may be substituted by one to three groups selected from: C_1 to C_6 alkoxy, C_2 to C_{12} alkoxyalkoxy, C_6 to C_{10} aryl, -CN, -OH, $-NO_2$, $-CO_2(C_1$ to $C_6)$alkyl, $-OC(O)(C_1$ to $C_6)$alkyl, C_7 to C_{30} aralkyl C_7 to C_{30} alkaryl, and $-N(R^z)_2$, where each R^z is independently selected from hydrogen, methyl, ethyl, n-propyl and iso-propyl.

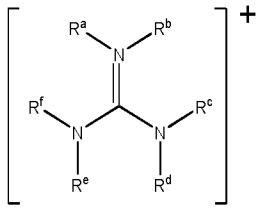
In the above quinolinium cations, R^a is preferably selected from C_1 to C_{20} linear or branched alkyl, more preferably C_2 to C_{20} linear or branched alkyl, still more preferably C_2 to C_{16} linear or

branched alkyl, and most preferably C_4 to C_{10} linear or branched alkyl. Examples of suitable R^a groups include ethyl, butyl, hexyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl and octadecyl.

In the above quinolinium cations, R^b, R^c, R^d, R^e, R^f, R^h and R^i are preferably independently selected from hydrogen and C_1 to C_5 linear or branched alkyl, and more preferably R^b, R^c, R^d, R^e, and R^f are hydrogen.

Examples of preferred quinolinium and cations which may be used in accordance with the present invention include: *N*-(C_8-C_{18})alkyl-quinolinium, and *N*-(C_8-C_{18})alkyl-6-methylquinolinium.

Where, [Cat^+] is a guanidinium cation, it preferably has the formula:



wherein: R^a, R^b, R^c, R^d, R^e, and R^f are each independently selected from a C_1 to C_{20} straight chain or branched alkyl group, a C_3 to C_8 cycloalkyl group, or a C_6 to C_{10} aryl group, or any two of R^b, R^c, R^d, R^e, R^f, R^h and R^i attached to adjacent carbon atoms may form a saturated methylene chain -$(CH_2)_q$- wherein q is from 3 to 6, and wherein said alkyl, cycloalkyl or aryl groups, or said methylene chain are unsubstituted or may be substituted by one to three groups selected from: C_1 to C_6 alkoxy, C_2 to C_{12} alkoxyalkoxy, C_6 to C_{10} aryl, -CN, -OH, -NO_2, -CO_2(C_1 to C_6)alkyl, -OC(O)(C_1 to C_6)alkyl, C_7 to C_{30} aralkyl C_7 to C_{30} alkaryl, and -$N(R^z)_2$, where each R^z is independently selected from hydrogen, methyl, ethyl, n-propyl and iso-propyl.

In the above guanidium cations, R^a is preferably selected from C_1 to C_{20} linear or branched alkyl, more preferably C_2 to C_{20} linear or branched alkyl, still more preferably C_2 to C_{16} linear or branched alkyl, and most preferably C_4 to C_{10} linear or branched alkyl. Examples of suitable R^a groups include ethyl, butyl, hexyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl and octadecyl.

In the above guanidinium cations, R^b, R^c, R^d, R^e and R^f are preferably selected from C_1 to C_{10} linear or branched alkyl, more preferably, C_1 to C_5 linear or branched alkyl, and most preferably R^b, R^c, R^d, R^e and R^f are each a methyl group.

In accordance with the present invention, $[X^-]$ is preferably selected from anions having the formula $[R^xCO_2]^-$, wherein R^x is selected from hydrogen, a C_1 to C_{10} straight chain or branched alkyl group, a C_3 to C_8 cycloalkyl group, or a C_6 to C_{10} aryl group, wherein said alkyl, cycloalkyl or aryl groups are unsubstituted or may be substituted by one or more groups selected from –F, -Cl, -OH, -CN, $-NO_2$, -SH, =O and $–CO_2H$.

It will be appreciated that where R^x is substituted by a group having the formula $–CO_2^-$, $[X^-]$ will be a dianionic species. It will therefore be appreciated that the present invention is not limited to ionic liquids comprising anions and cations having only a single charge. Thus, the formula $[Cat^+][X^-]$ is intended to encompass ionic liquids comprising, for example, doubly, triply and quadruply charged anions and/or cations. The relative stoichiometric amounts of $[Cat^+]$ and $[X^-]$ in the ionic liquid are therefore not fixed, but can be varied to take account of cations and anions with multiple charges. For example, the formula $[Cat^+][X^-]$ should be understood to include ionic liquid species having the formulae $[Cat^+]_2[X^{2-}]$; $[Cat^{2+}]\ [X^-]_2$; $[Cat^{2+}][X^{2-}]$; $[Cat^+]_3[X^{3-}]$; $[Cat^{3+}][X^-]_3$ and so on.

More preferably, R^x is selected from hydrogen, or a C_1 to C_{10} straight chain or branched alkyl group, wherein said alkyl group is optionally substituted by one or more groups selected from -F and -OH.

Examples of anions which may be used in accordance with the present invention include: formate, acetate, trifluoroacetate, hydroxyacetate, propanoate, pentafluoro-propanoate,

lactate, butanoate, isobutanoate, pivalate, pyruvate, thiolactate, oxalate, tartrate, malonate, succinate, adipate and benzoate.

More preferably, the anion is selected from: formate, acetate, trifluoroacetate, hydroxyacetate, propanoate, pentafluoropropanoate, lactate, butanoate, isobutanoate and pivalate.

In one preferred embodiment, [X^-] is acetate.

In another preferred embodiment, [X^-] is formate.

The ionic liquids used in accordance with the present invention preferably have a melting point of 100 °C or less, more preferably 50 °C or less, and most preferably 25 °C or less. Ionic liquids having lower melting points are less likely to crystallise in the process of the invention, making them easier to handle.

The molar ratio of ionic liquid to water is preferably in the range of from 70:30 to 30:70, still more preferably in the range of from 60:40 to 40:60, still more preferably in the range of from 55:45 to 45:55, and most preferably the molar ratio of ionic liquid to water is 50:50.

The gaseous stream is preferably contacted with the carbon dioxide absorbent at a temperature of from 10 to 80 °C, more preferably from 10 to 50 °C and most preferably from 20 to 30 °C. For example, the gaseous stream may be contacted with the carbon dioxide absorbent at a temperature at or around 25 °C.

The gaseous stream is preferably contacted with the carbon dioxide absorbent at a pressure of from 100 to 2000 kPa, and more preferably from 200 to 1000 kPa. For example. the gaseous stream may be contacted with the carbon dioxide absorbent at a pressure at or around 500 kPa.

The process of the present invention may be used to remove carbon dioxide, and optionally one or more additional substances, from a number of different types of gaseous streams. For example, the process of the present invention may be used to remove carbon dioxide from the exhaust gas from a combustion process, such as the flue gases from furnaces and power

plants. The process of the present invention may also used to remove carbon dioxide, and optionally one or more additional substances, from hydrocarbon-containing gaseous streams, in particular methane-containing gaseous streams. Thus, the process of the invention may advantageously be used from the removal of carbon dioxide, and optionally one or more additional substances, from natural gas and/or biogas. The processes of the present invention may advantageously be used for the removal of carbon dioxide from breathing gas mixtures in life support systems.

Without being bound by any particular theory, it is believed that absorption of carbon dioxide by the mixture of ionic liquid and water occurs at least in part by an acid/base chemical reaction between the ionic liquid anion and carbon dioxide or, more probably, between the ionic liquid anion and H_2CO_3 formed by the dissolution of carbon dioxide in water. However, once the chemical absorption capacity of the ionic liquid is spent, absorption of carbon dioxide continues via physical processes. This is observed experimentally by a distinct change in slope of a graph of CO_2 absorption against CO_2 partial pressure (see Figure 5).

As noted above, carbon dioxide can be easily desorbed from the mixtures of ionic liquids and water by heating in the presence of a sparging gas (e.g. nitrogen gas), or by pressure reduction, allowing the mixtures to be recycled to the separation process without loss or degradation of the absorbent mixture. It has been found that the mixture of ionic liquid and water can be repeatedly recycled to the separation process with little or no decrease in the carbon dioxide absorption capacity of the absorbent.

It will be appreciated that where the ionic liquid/water absorbent is also used to remove water from the gas stream, then it will be necessary to periodically or continuously remove water from the absorbent so as to maintain the water content of the absorbent within the limits indicated above.

Water may be removed from the absorbent for example by drying at 60 to 80 ^{o}C under vacuum or by sparging a dry gas at elevated temperature.

Where the process of the invention is operated continuously, a portion of the absorbent is continuously or periodically removed from the process to remove carbon dioxide and optionally

water so as to restore the composition of the absorbent. The absorbent is subsequently recycled to the to the carbon dioxide removal process.

In accordance with the process of the present invention, a gaseous stream is recovered having reduced content of carbon dioxide, and optionally one or more other substances such as water, when compared to the composition of the gaseous stream fed to the process.

It will be appreciated that the process of the present invention may be integrated into processing plants as one stage of a multi-stage processing of gaseous streams. For instance, the process of the present invention could be used in a natural gas refinery as one stage in the production of a commercial natural gas product, wherein other stages could include removal of nitrogen and removal of heavy hydrocarbons. Alternatively, the process of the present invention could be used in a flue gas treatment plant as one stage of a multi-stage processing of flue gases, where other stages could for instance include removal of particulates and catalytic conversion of NO_x.

In another aspect, the present invention provides the use of a process as defined in above to absorb carbon dioxide and at least one other substance from a gaseous stream. Preferably, the at least one other substance is water.

In a further aspect, the present invention provides the use of an ionic liquid as defined above for absorbing carbon dioxide and water from a gaseous stream.

The present invention will now be described by way of Examples, and with reference to the attached figures, wherein:

Figure 1 is a histogram showing the carbon dioxide solubility in the ionic liquid/water mixtures described in Example 1 at 500 kPa and at 25 ^{o}C. Figure 1 also shows the carbon dioxide solubilities of the comparative absorbent systems discussed in Examples 3, 4 and 5;

Figure 2 shows the variation of carbon dioxide solubility with water content for a variety of ionic liquids;

Figure 3 is the FTIR spectrum of nitrogen gas saturated with water;

Figure 4 is the FTIR spectrum of the nitrogen gas of Figure 3 after being bubbled through an absorbent ionic liquid composition;

Figure 5 shows the CO_2 uptake of a mixture of tributylmethylphosphonium propanoate and water in an ionic liquid:water ratio of 40:60 (see Example 9); and

Figure 6A shows the IR spectrum of air spiked with CO_2. Figure 6B shows the corresponding IR spectrum when the air spiked with CO_2 has been bubbled through tributylmethylphosphonium propanoate and water in an ionic liquid;water ratio of 40:60 (see Example 10).

Examples

Example 1

This example describes the general experimental method used to determine the solubility of carbon dioxide in the ionic liquid water mixtures.

In a typical experiment, the volume of a pressure vessel [Parr pressure system] was first determined by evacuating it under reduced pressure and subsequently pumping a known amount of gas at a certain temperature and pressure into the vessel. Measurement of the amount of gas was read as the volume of gas at standard conditions from the mass flow controller [BROOKS Smart Massflow]. The ideal gas law was used to calculate the actual volume of the pressure vessel.

A known volume of a tetraalkylphosphonium ionic liquid having the formula ($[P_{n\cdot n\cdot n\cdot m}][R^xCO_2]$, where n and m are integers which indicate the number of carbon atoms in the alkyl chain, and R^x is hydrogen or a C_1 to C_{10} alkyl) and water (*ca*. 5.0 mL) was placed in the pressure vessel, degassed for 5 min under reduced pressure. The carbon dioxide was then pumped into the stirred pressure vessel (1000 rpm) through the mass flow controller up to 500 kPa and at 25.0 °C. The system was allowed to equilibrate for 15 min or until no more gas was added according to the mass flow controller.

Calculation of the total amount of gas introduced in the pressure vessel was conducted from the reading in the mass flow controller. The actual amount of gas in the gas phase was calculated by the ideal gas law, where the volume of the gas phase was equal to the volume of the pressure vessel minus the volume of the liquid phase. The amount of gas dissolved in the liquid phase was calculated by subtracting the actual amount of gas in the gas phase from the total amount of gas introduced in the pressure vessel.

Results expressed as a molar concentration ($mol\cdot L^{-1}$) and as SCF/100gal are shown in Table 1, where mole fraction water indicates the mole fraction of water in the mixture of ionic liquid and water The amount of water in the liquid mixtures was quantified by Karl-Fischer titration, and/or ^1H NMR.

Table 1

Ionic Liquid	Mole fraction water	Solubility ($mol \cdot L^{-1}$)	Solubility (SCF/100gal)
$P_{2,2,2,8}$ formate	0.50	1.900	600.34
$P_{4,4,4,4}$ formate	0.51	2.070	654.05
$P_{4,4,4,6}$ formate	0.50	1.66	538.47
$P_{4,4,4,8}$ formate	0.53	1.877	605.47
$P_{4,4,4,10}$ formate	0.53	2.149	692.46
$P_{4,4,4,12}$ formate	0.52	1.464	473.19
$P_{6,6,6,14}$ formate	0.48	1.100	347.56
$P_{2,2,2,8}$ acetate	0.53	2.480	783.6
$P_{4,4,4,6}$ acetate	0.49	2.137	689.26
$P_{4,4,4,8}$ acetate	0.51	2.067	666.34
$P_{4,4,4,10}$ acetate	0.49	2.753	886.26
$P_{4,4,4,12}$ acetate	0.48	2.307	743.29

Example 2

Solubility of carbon dioxide in recycled tetraalkylphosphonium carboxylate/water mixtures

The mixtures of ionic liquids and water containing absorbed carbon dioxide from Example 1 were recycled by stirring in a glass round bottom flask attached to a reflux condenser while N_2 gas was bubbled through the solution for 15 min at 60 to 70 °C. The water content of the resulting solutions was determined by Karl-Fischer titration and, if needed, additional water was added up to the desired composition. Solubility of carbon dioxide in the resulting liquid mixtures of $[P_{4\cdot4\cdot4\cdot4}][HCO_2]$, and water was measured as described in Example 1. After a first recycle, the solubility of carbon dioxide was found to be 2.01 $mol \cdot L^{-1}$. After a second recycle, the solubility of carbon dioxide was found to be 2.07 $mol \cdot L^{-1}$. Thus, it can be observed that the ability of the absorbent to absorb carbon dioxide is not reduced after recycling.

Comparative Example 3

Solubility of carbon dioxide in 1-butyl-3-methylimidazolium bis[(trifluoromethyl)-sulfonyl]imide

The solubility of carbon dioxide in dry 1-butyl-3-methylimidazolium bis[(trifluoromethyl)-sulfonyl]imide ([bmim][NTf_2]) was measured at 500 kPa and at 25.0 °C as described in Example 1. This ionic liquid was chosen as a comparative example of a strictly physical CO_2 absorber. The solubility of carbon dioxide in the ionic liquid was found to be 0.594 mol·L^{-1}. By way of a further comparison, the solubility of carbon dioxide in Genosorb®, a commercially available absorbent solvent based on polyethylene glycol dimethyl ethers. The solubility of carbon dioxide in Genosorb® was found to be 0.64 mol·L^{-1}.

Comparative Example 4

Solubility of carbon dioxide in dry [$P_{6\cdot6\cdot6\cdot14}$][CH_3CO_2]

The solubility of carbon dioxide in dry [$P_{6\cdot6\cdot6\cdot14}$][CH_3CO_2] (<0.25 wt% water content) was measured at 500 kPa and at 25.0 °C as described in Example 1. The solubility of carbon dioxide in the ionic liquid was found to be 0.52 mol·L^{-1}.

Comparative Example 5

Solubility of carbon dioxide in monoethanolamine/water mixtures

The solubility of carbon dioxide in a mixture of monoethanolamine (MEA) and water (30:70 MEA/H_2O weight ratio) was measured at 500 kPa and at 25.0 °C as described in Example 1. This liquid solution was chosen as a comparative example of a carbon dioxide chemical absorber used commercially in industry, especially in natural gas processing operations. The solubility of carbon dioxide in the monoethanolamine/water mixture was found to be 3.57 mol·L^{-1}.

Example 6

Solubility of methane in tetraalkylphosphonium carboxylate/water mixtures

The solubility of methane in the $[P_{4\cdot4\cdot4\cdot4}][HCO_2]$/water mixture of Example 1 was measured at 500 kPa and 25.0 °C as described in Example 1. The amount of water in the liquid mixture was quantified by Karl-Fischer titration, and/or ^1H NMR. The solubility of methane in the ionic liquid/water mixture was found to be 0.07 $mol\cdot L^{-1}$, clearly demonstrating the selectivity of the process of the invention.

Example 7

Separation of methane from a CO_2/CH_4 gas mixture using tetraalkylphosphonium carboxylate/water mixtures

A known amount of $[P_{4\cdot4\cdot4\cdot4}][HCO_2]$/water mixture (*ca*. 10 mL) was placed in a pressure vessel and degassed by stirring for 5 min under reduced pressure. A gas mixture containing 7.22 mol% CO_2 in CH_4 (model natural gas) was then pumped into the reactor up to a pressure of *ca*. 3000 kPa. The mixture was vigorously stirred at 25.0 °C until pressure equilibration, which took about 10 min. The gas was then sampled out and analysed on the chromatographic gas analyser. The ratio of CO_2 was found to have been reduced to 2.32 mol%.

Example 8

Variation of carbon dioxide absorption with water content

The solubility of carbon dioxides in absorbents comprising the ionic liquids $[P_{4\cdot4\cdot4\cdot4}][HCO_2]$, $[P_{4\cdot4\cdot4\cdot4}][CH_3CO_2]$, and $[P_{6\cdot6\cdot6\cdot14}][HCO_2]$ with varying amounts of water was measured. The results are shown in Figure 2.

Example 9

Chemical and physical absorption

To observe the chemical and physical absorption behaviour of ionic liquid/water mixtures, the solubility of CO_2 in a mixture of tributylmethylphosphonium propanoate and water at a ratio of 40:60 (ionic liquid:water) was plotted against CO_2 partial pressure. As shown in Figure 5,

typical chemical absorption behaviour is observed at low CO_2 pressure, with the CO_2 uptake increasing asymptotically as the 1:1 molar ratio is approached. Once the saturation pressure is reached (i.e. a 1:1 molar ratio of ionic liquid and CO_2), the system switches to the linear response expected of a physical CO_2 absorber. The linear increase in absorption is observed continuously to the highest CO_2 partial pressure observed.

Example 10

Separation of carbon dioxide from air

The removal of carbon dioxide from air was examined by analysis of IR absorption spectra. Figure 6A shows the IR absorption spectrum of air containing an elevated level of CO_2 (ca. 40 mol%). The same air/CO_2 mixture was bubbled through a mixture of tributylmethyl-phosphonium propanoate and water in an ionic liquid: water ratio of 40:60) over a period of 20 minutes. As shown in Figure 6B, the IR absorption peaks due to the carbon dioxide stretching frequencies are not observed, indicating that substantially all CO_2 has been removed from the CO_2/air mixture.

Example 11

Removal of water

The removal of water by the ionic liquid compositions of the invention was examined by bubbling nitrogen gas saturated with water through $[P_{6\cdot6\cdot6\cdot8}][HCO_2]$ at 15 ^oC. The Fourier transform infrared spectra (FTIR) of the gas were measured both before and after contact with the ionic liquid (see Figures 3 and 4 respectively). It will be observed that the peaks in the region 3400 to 4000 cm^{-1} attributable to water are significantly reduced.

CLAIMS

1. A process for removing carbon dioxide from a gaseous stream comprising contacting the gaseous stream with a carbon dioxide absorbent comprising a mixture of an ionic liquid and water in a molar ratio of from 20:80 to 80:20 and recovering a gaseous stream having reduced carbon dioxide content, wherein the ionic liquid has the formula:

$$[Cat^+][X^-]$$

wherein: $[Cat^+]$ represents a cationic species selected from tetrasubstituted phosphonium cations, tetrasubstituted ammonium cations, trisubstituted sulfonium cations, guanidinium cations and quinolinium cations; and
$[X^-]$ represents an anionic species which is a conjugate base of a carboxylic acid.

2. A process according to Claim 1, wherein $[Cat^+]$ is selected from:

$$[P(R^a)(R^b)(R^c)(R^d)]^+,\ [N(R^a)(R^b)(R^c)(R^d)]^+ \text{ and } [S(R^b)(R^c)(R^d)]^+$$

wherein: R^a, R^b, R^c, and R^d are each independently selected from a C_1 to C_{20} straight chain or branched alkyl group, a C_3 to C_8 cycloalkyl group, or a C_6 to C_{10} aryl group, or wherein any two of R^a, R^b, R^c, and R^d together form a methylene chain of the formula $-(CH_2)_q-$, where q is an integer of from 4 to 7, wherein said alkyl, cycloalkyl or aryl groups, or said methylene chain are unsubstituted or may be substituted by one to three groups selected from: C_1 to C_6 alkoxy, C_2 to C_{12} alkoxyalkoxy, C_6 to C_{10} aryl, -CN, -OH, $-NO_2$, $-CO_2(C_1$ to $C_6)$alkyl, $-OC(O)(C_1$ to $C_6)$alkyl, C_7 to C_{30} aralkyl C_7 to C_{30} alkaryl, and $-N(R^z)_2$, where each R^z is independently selected from hydrogen, methyl, ethyl, n-propyl and iso-propyl, and wherein R^b may also be hydrogen.

3. A process according to Claim 2, wherein $[Cat^+]$ is selected from:

$$[P(R^a)(R^b)(R^c)(R^d)]^+ \text{ and } [N(R^a)(R^b)(R^c)(R^d)]^+$$

wherein: R^a, R^b, R^c, and R^d are as defined in Claim 2.

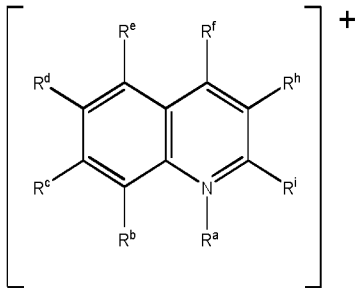
4. A process according to Claim 3, wherein $[Cat^+]$ is selected from:

$$[P(R^a)(R^b)(R^c)(R^d)]^+$$

wherein: R^a, R^b, R^c, and R^d are as defined in Claim 2.

5. A process according any one of Claims 2 to 4, wherein R^a, R^b, R^c, and R^d are each independently selected, where present, from a C_1 to C_{16} straight chain or branched alkyl group, or wherein any two of R^a, R^b, R^c, and R^d together form a methylene chain of the formula $-(CH_2)_q-$, where q is an integer of from 4 or 5.

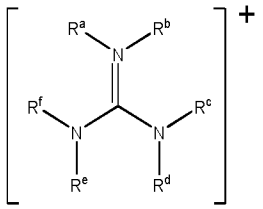
6. A process according to Claim 1, wherein $[Cat^+]$ is selected from quinolinium cations of the formula:



wherein: R^a, R^b, R^c, R^d, R^e, R^f, R^g, R^h and R^i are each independently selected from hydrogen, a C_1 to C_{20} straight chain or branched alkyl group, a C_3 to C_8 cycloalkyl group, or a C_6 to C_{10} aryl group, or any two of R^b, R^c, R^d, R^e, R^f, R^h and R^i attached to adjacent carbon atoms may form a saturated methylene chain $-(CH_2)_q-$ wherein q is from 3 to 6, and wherein said alkyl, cycloalkyl or aryl groups, or said methylene chain are unsubstituted or may be substituted by one to three groups selected from: C_1 to C_6 alkoxy,

C_2 to C_{12} alkoxyalkoxy, C_6 to C_{10} aryl, -CN, -OH, $-NO_2$, $-CO_2(C_1$ to $C_6)$alkyl, $-OC(O)(C_1$ to $C_6)$alkyl, C_7 to C_{30} aralkyl C_7 to C_{30} alkaryl, and $-N(R^z)_2$, where each R^z is independently selected from hydrogen, methyl, ethyl, n-propyl and iso-propyl.

7. A process according to Claim 1, wherein $[Cat^+]$ is selected from guanidinium cations of the formula:



wherein: R^a, R^b, R^c, R^d, R^e, and R^f are each independently selected from a C_1 to C_{20} straight chain or branched alkyl group, a C_3 to C_8 cycloalkyl group, or a C_6 to C_{10} aryl group, or any two of R^b, R^c, R^d, R^e, R^f, R^h and R^i attached to adjacent carbon atoms may form a saturated methylene chain $-(CH_2)_q-$ wherein q is from 3 to 6, and wherein said alkyl, cycloalkyl or aryl groups, or said methylene chain are unsubstituted or may be substituted by one to three groups selected from: C_1 to C_6 alkoxy, C_2 to C_{12} alkoxyalkoxy, C_6 to C_{10} aryl, -CN, -OH, $-NO_2$, $-CO_2(C_1$ to $C_6)$alkyl, $-OC(O)(C_1$ to $C_6)$alkyl, C_7 to C_{30} aralkyl C_7 to C_{30} alkaryl, and $-N(R^z)_2$, where each R^z is independently selected from hydrogen, methyl, ethyl, n-propyl and iso-propyl.

8. A process according to any one of the preceding claims, wherein $[X^-]$ is selected from anions having the formula $[R^xCO_2]^-$, wherein R^x is selected from hydrogen, a C_1 to C_{10} straight chain or branched alkyl group, a C_3 to C_8 cycloalkyl group, or a C_6 to C_{10} aryl group, wherein said alkyl, cycloalkyl or aryl groups are unsubstituted or may be substituted by one or more groups selected from –F, -Cl, -OH, -CN, $-NO_2$, -SH, =O, and $–CO_2H$.

9. A process according to Claim 8, wherein [X^-] is selected from: formate, acetate, trifluoroacetate, hydroxyacetate, propanoate, pentafluoro-propanoate, lactate, butanoate, isobutanoate, pivalate, pyruvate, thiolactate, oxalate, tartrate, malonate, succinate, adipate and benzoate.

10. A process according to Claim 9, wherein [X^-] is selected from: formate, acetate, trifluoroacetate, hydroxyacetate, propanoate, pentafluoropropanoate, lactate, butanoate, isobutanoate and pivalate.

11. A process according to Claim 10, wherein [X^-] is selected from formate and acetate.

12. A process according to any one of the preceding claims, wherein the ionic liquid has a melting point of 100 ^oC or less.

13. A process according to Claim 12, wherein the ionic liquid has a melting point of 50 ^oC or less.

14. A process according to Claim 13, wherein the ionic liquid has a melting point of 25 ^oC or less.

15. A process according any one of the preceding claims, wherein the molar ratio of ionic liquid to water is from 70:30 to 30:70.

16. A process according to Claim 15, wherein the molar ratio of ionic liquid to water is from 60:40 to 40:60.

17. A process according to Claim 16, wherein the molar ratio of ionic liquid to water is from 55:45 to 45:55.

18. A process according to Claim 17, wherein the molar ratio of ionic liquid to water is about 50:50.

19 A process according to any one of the preceding claims, wherein the gaseous stream is contacted with the carbon dioxide absorbent at a temperature of from 10 to 80 °C

20 A process according to Claim 19, wherein the gaseous stream is contacted with the carbon dioxide absorbent at a temperature of from 10 to 50 °C

21 A process according to Claim 20, wherein the gaseous stream is contacted with the carbon dioxide absorbent at a temperature of from 20 to 30 °C.

22 A process according to any one of the preceding claims, wherein the gaseous stream is contacted with the carbon dioxide absorbent at a pressure of from 100 to 2000 kPa.

23. A process according to Claim 22, wherein the gaseous stream is contacted with the carbon dioxide absorbent at a pressure of from 200 to 1000 kPa.

24 A process according to any one of the preceding claims wherein carbon dioxide is subsequently released from the carbon dioxide absorbent.

25. A process according to Claim 24, wherein the carbon dioxide is subsequently released by subjecting the carbon dioxide absorbent to reduced pressure, or by sparging the carbon dioxide absorbent with a gas at elevated temperature.

26. A process according to any one of the preceding claims, wherein the gaseous stream is a hydrocarbon-containing gaseous stream.

27. A process according to Claim 26, wherein the gaseous stream is a methane-containing gaseous stream.

28. A process according to Claim 27, wherein the gaseous stream is a natural gas stream.

29. A process according to Claim 27, wherein the gaseous stream is a biogas-derived stream.

30. A process according to any one of claims 1 to 25, wherein the gaseous stream is a flue gas stream.

31. A process according to any one of claims 1 to 25, wherein the gaseous stream is a breathing gas stream for a life support system.

32. Use of a process as defined in any one of Claims 1 to 25 to absorb carbon dioxide and at least one other substance from a gaseous stream.

33. Use according to Claim 32, wherein the at least one other substance is water.

34. Use of an ionic liquid as defined in any one of Claims 1 to 14 for absorbing carbon dioxide and water from a gaseous stream.

35. Use of a process according to any one of claims 1 to 25, to remove carbon dioxide from a hydrocarbon-containing gaseous stream.

36. Use according to Claim 35, wherein the gaseous stream is a methane-containing gaseous stream.

37. Use according to Claim 35 or Claim 36, wherein the gaseous stream is a natural gas stream.

38. Use according to Claim 35, wherein the gaseous stream is a biogas-derived stream.

39. Use of a process according to any one of claims 1 to 25, to remove carbon dioxide from a flue gas stream.

40. Use of a process according to any one of claims 1 to 25, to remove carbon dioxide from a breathing gas stream for a life support system.

Figure 1

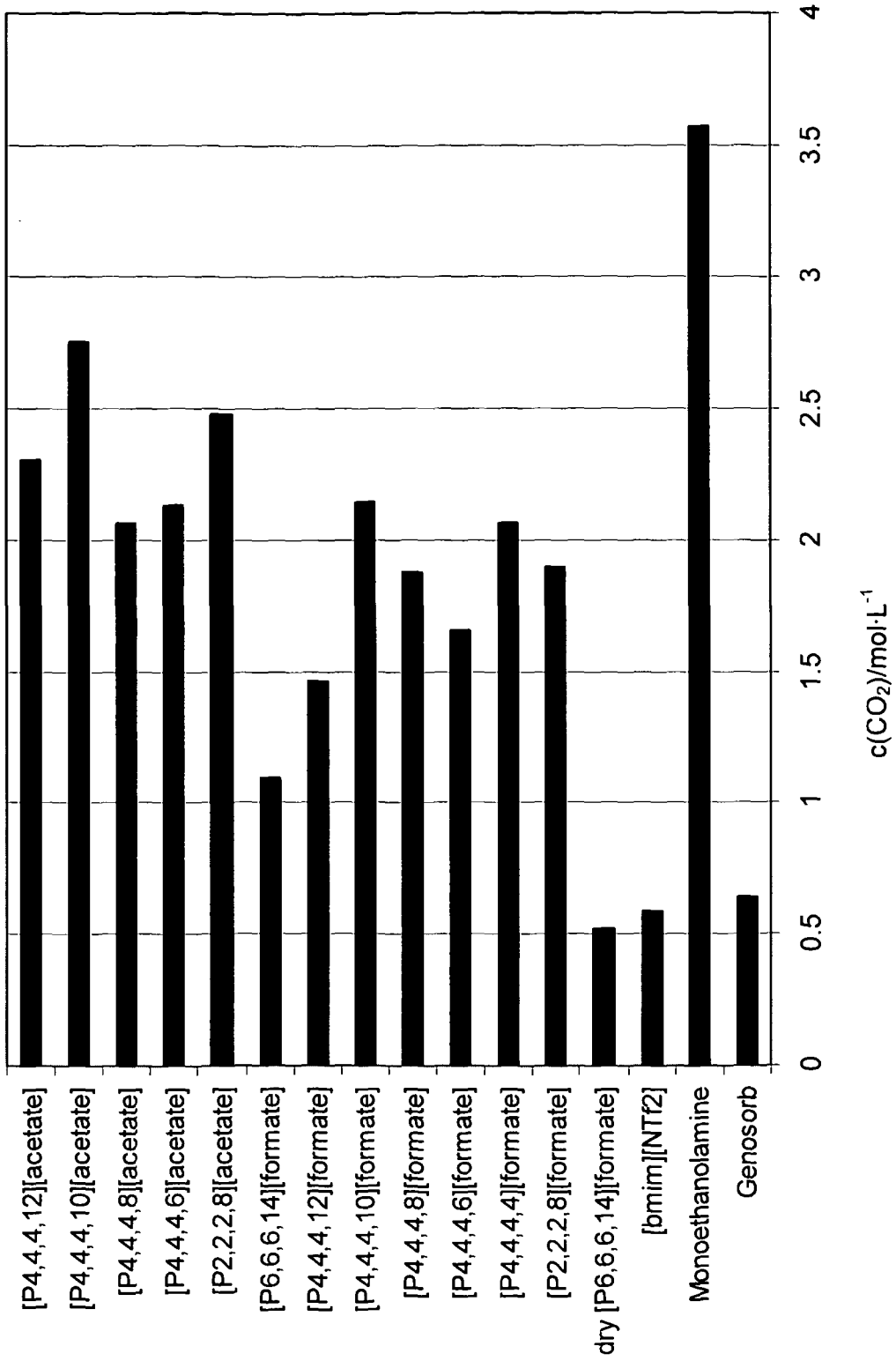
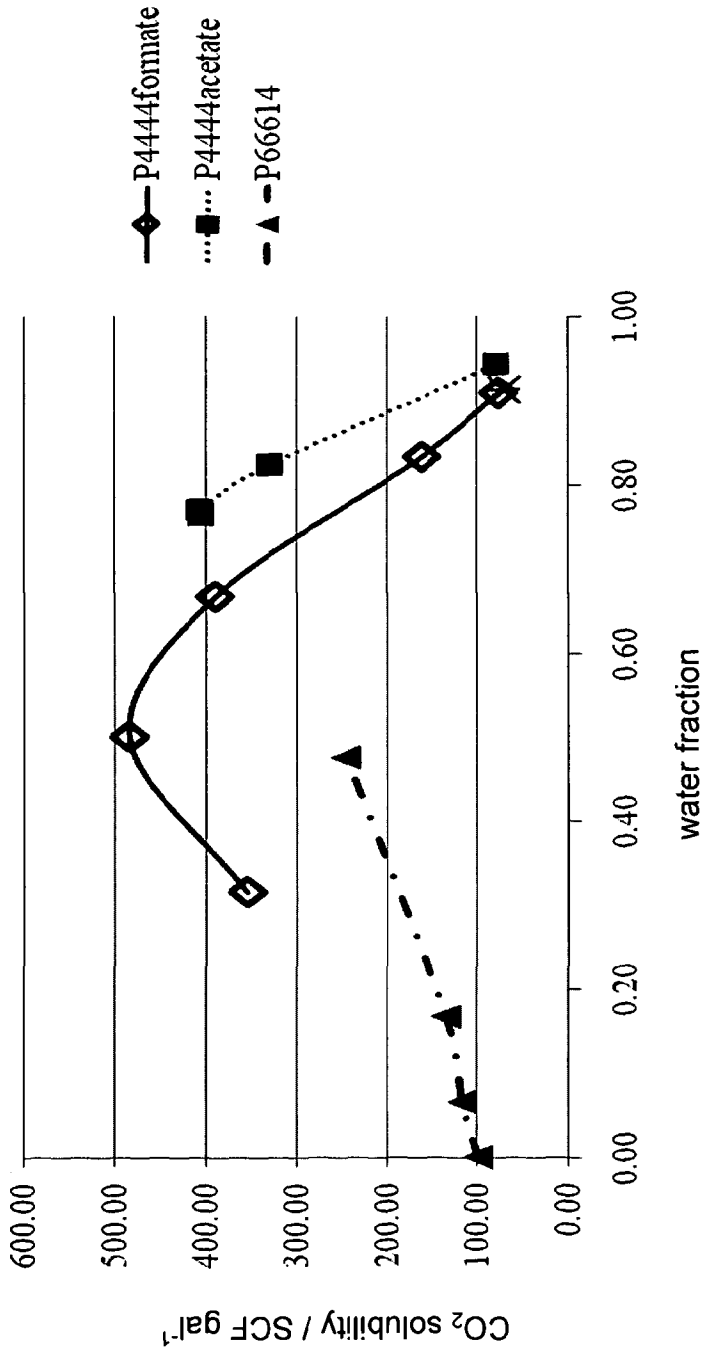

0
0.5
1
1.5
2
2.5
3
3.5
4
c(CO2)/mol·L-1
[P4,4,4,12][acetate]
[P4,4,4,10][acetate]
[P4,4,4,8][acetate]
[P4,4,4,6][acetate]
[P2,2,2,8][acetate]
[P6,6,6,14][formate]
[P4,4,4,12][formate]
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[P4,4,4,6][formate]
[P4,4,4,4][formate]
[P2,2,2,8][formate]
dry [P6,6,6,14][formate]
[bmim][NTf2]
Monoethanolamine
Genosorb

Figure 2


P4444formate
P4444acetate
P66614
600.00
500.00
400.00
300.00
200.00
100.00
0.00
0.00
0.20
0.40
0.60
0.80
1.00
water fraction
CO2 solubility / SCF gal-1

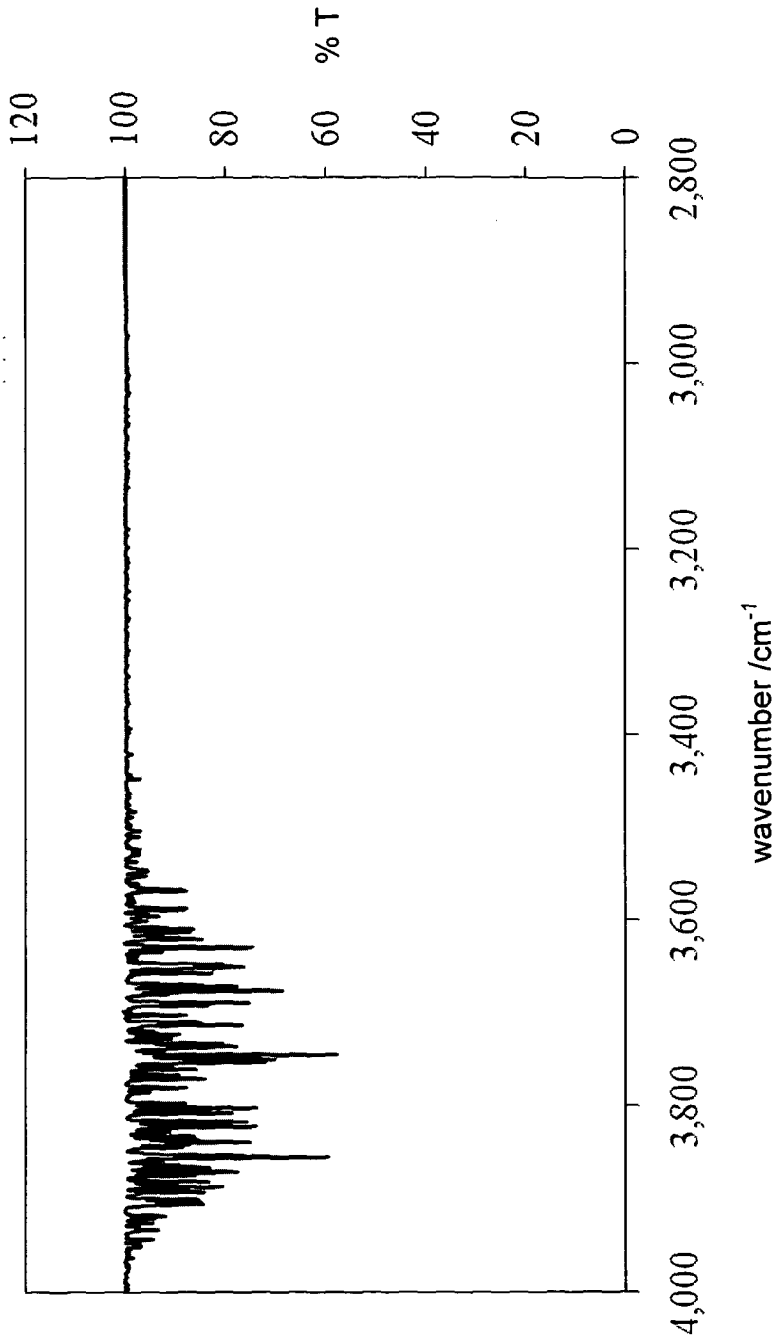

% T
120
100
80
60
40
20
0
4,000
3,800
3,600
3,400
3,200
3,000
2,800
wavenumber /cm-1

Figure 3

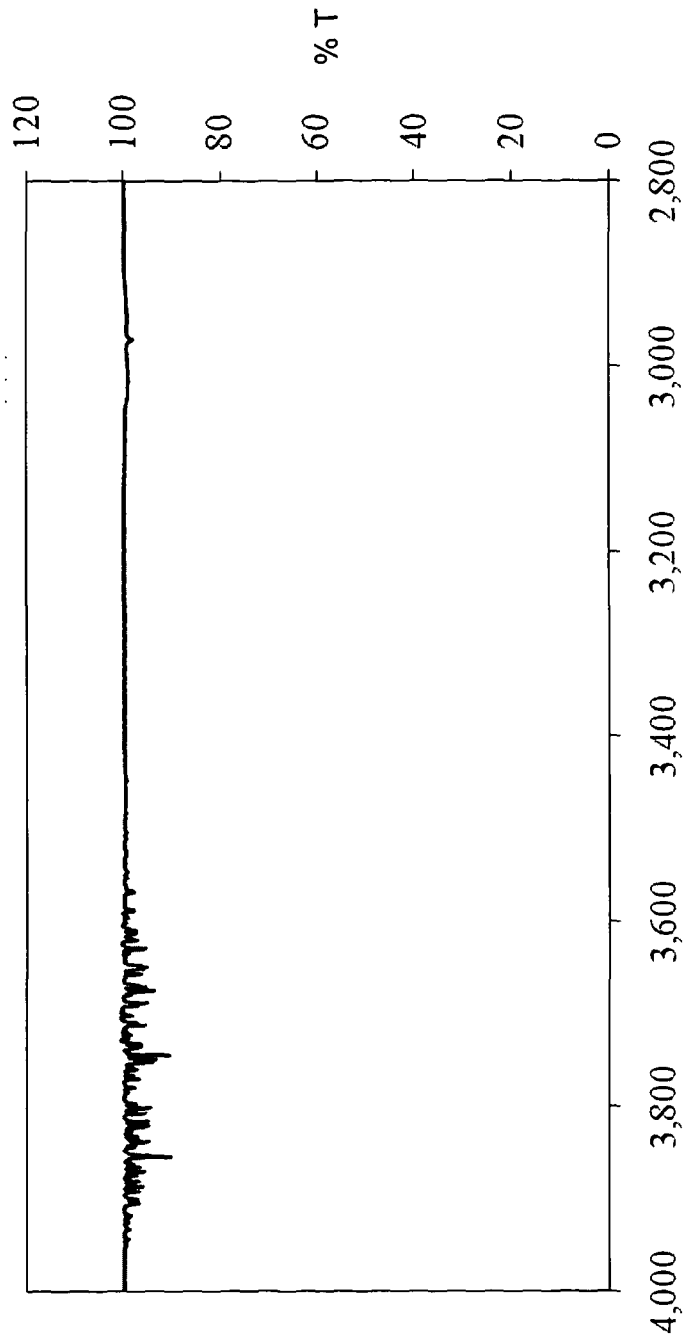

% T
120
100
80
60
40
20
0
4,000
3,800
3,600
3,400
3,200
3,000
2,800
wavenumber /cm-1

Figure 4

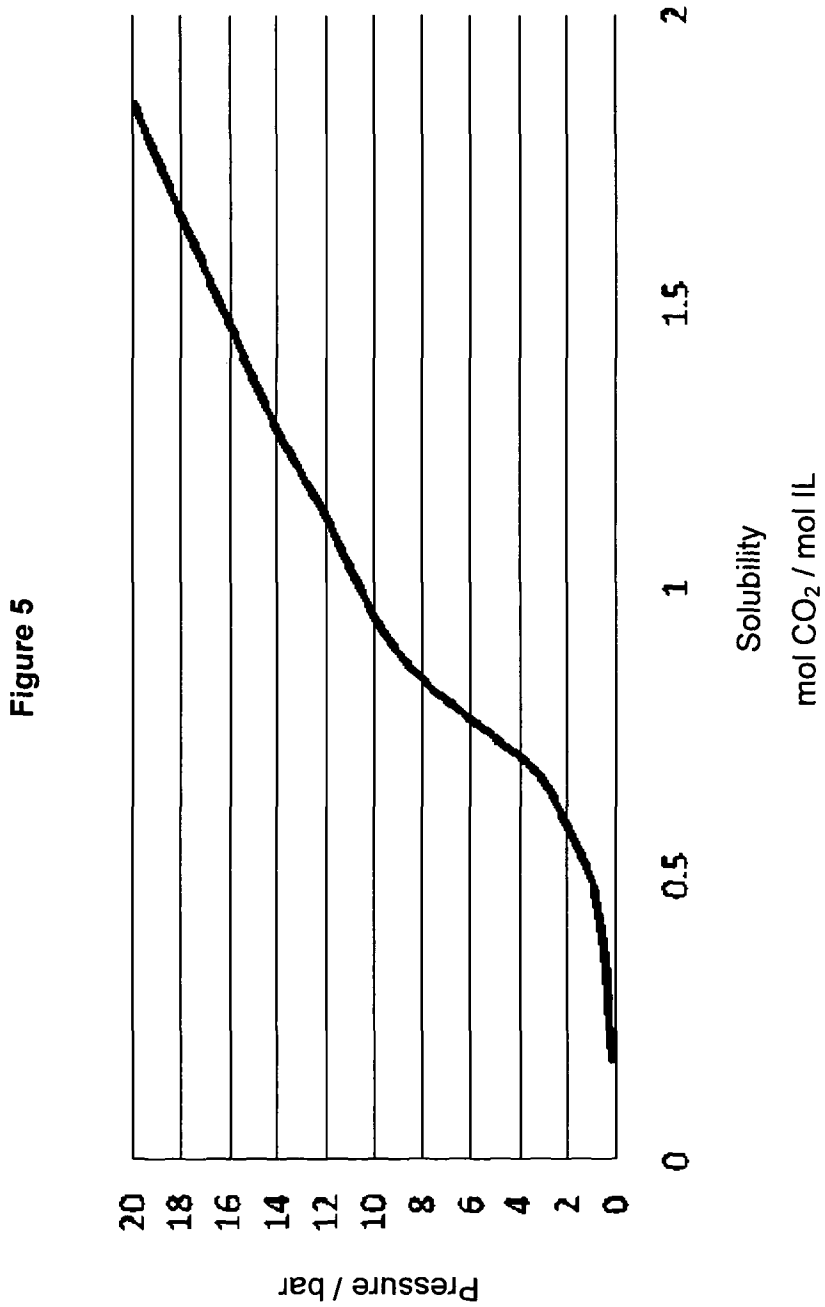

Pressure / bar
20
18
16
14
12
10
8
6
4
2
0
0
0.5
1
1.5
2
Solubility
mol CO_2 / mol IL

Figure 5

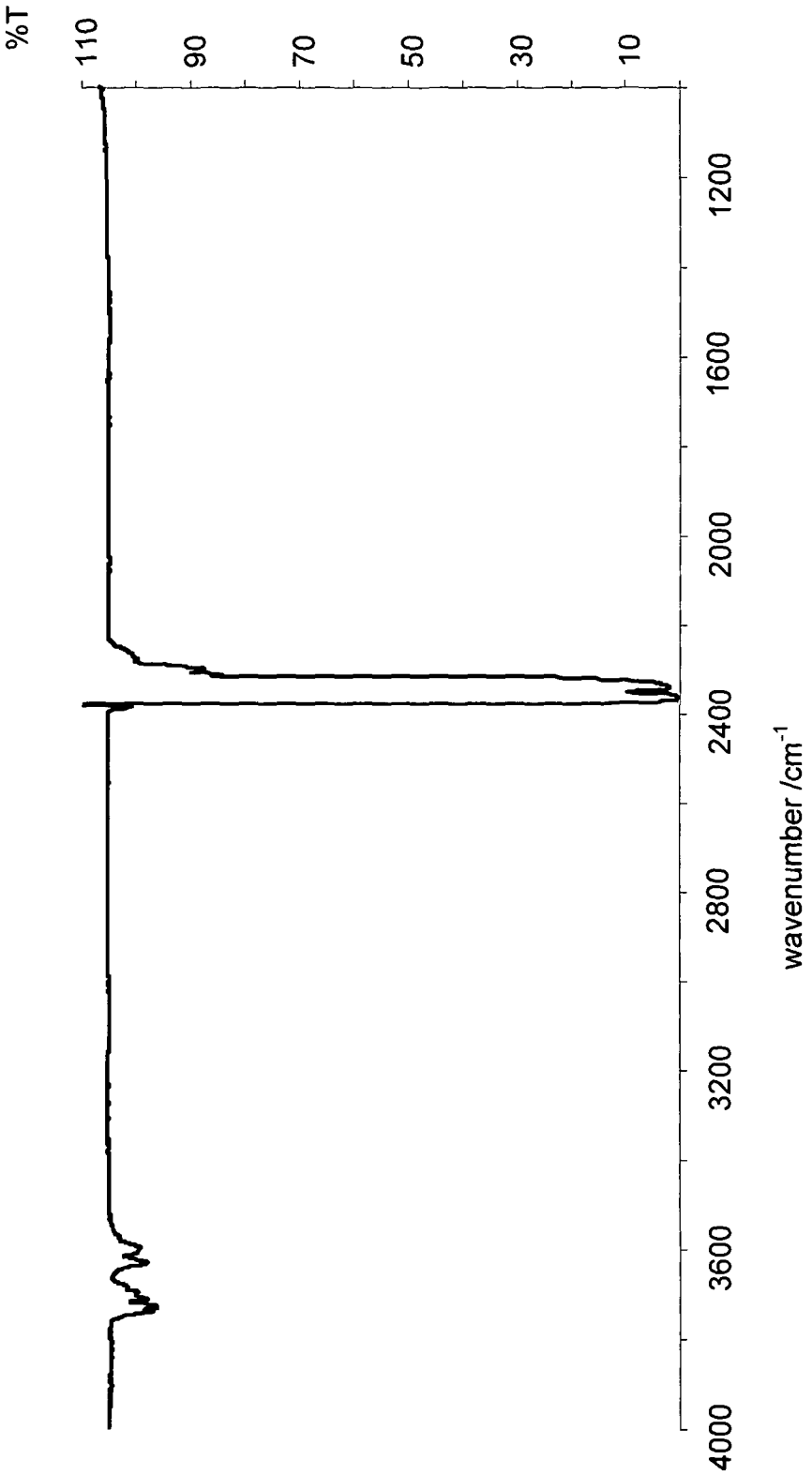

%T
110
90
70
50
30
10
4000
3600
3200
2800
2400
2000
1600
1200
wavenumber /cm-1

Figure 6A

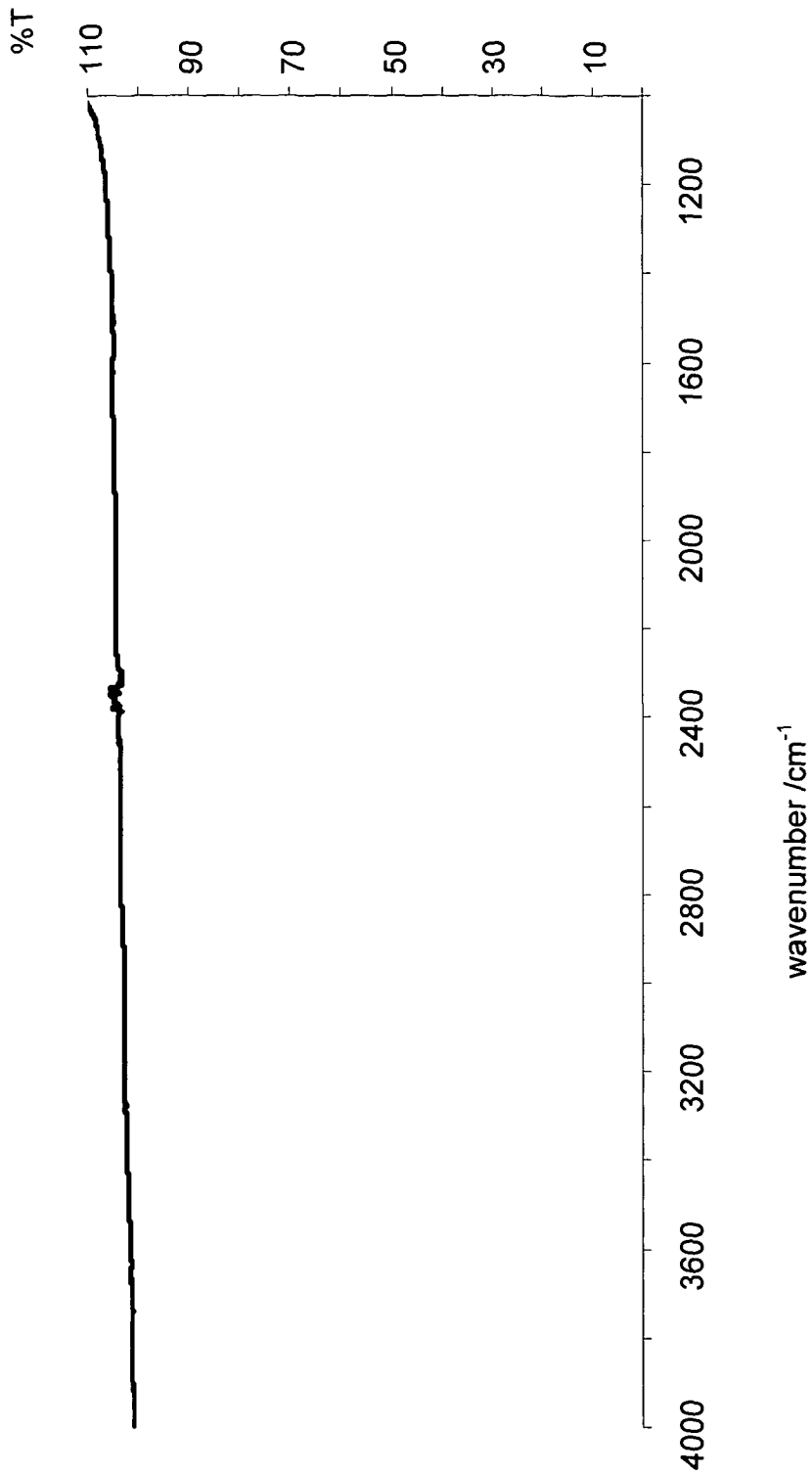

%T
110
90
70
50
30
10
4000
3600
3200
2800
2400
2000
1600
1200
wavenumber /cm-1

Figure 6B

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2011/050546

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/14
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 01/74472 A1 (UNIV CALIFORNIA [US]; SPENCER DWAIN F [US]; CURRIER ROBERT P [US]) 11 October 2001 (2001-10-11) abstract page 3, lines 14-28 page 5, line 31 - page 6, line 5 page 7, line 8 - page 8, line 32 page 13, lines 21-28 page 16, line 7 - page 17, line 2 -----	1-40
X	US 2005/274258 A1 (SPENCER DWAIN F [US]) 15 December 2005 (2005-12-15) abstract paragraphs [0001], [0011], [0021], [0022], [0025] - [0037], [0047], [0053], [0054], [0057] ----- -/--	1-40

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
6 June 2011	14/06/2011

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Howe, Patrick

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2011/050546

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 10 2004 053167 A1 (DEGUSSA [DE]) 4 May 2006 (2006-05-04) abstract paragraphs [0001], [0036] - [0038], [0041] - [0046] -----	1-40
A	WO 2007/021463 A2 (EXXONMOBIL RES & ENG CO [US]; WANG FRANK CHENG-YU [US]; SISKIN MICHAEL) 22 February 2007 (2007-02-22) abstract paragraphs [0001], [0014] - [0020] -----	1-40
A	WO 2007/030888 A1 (COOL ENERGY LTD [AU]; HART ALLAN [AU]; AMIN ROBERT [AU]) 22 March 2007 (2007-03-22) abstract claims 1,12,15 -----	1-40

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2011/050546

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 0174472 A1	11-10-2001	EP 1283740 A1	19-02-2003
		JP 2003528721 T	30-09-2003
		US 6352576 B1	05-03-2002
US 2005274258 A1	15-12-2005	NONE	
DE 102004053167 A1	04-05-2006	WO 2006048182 A1	11-05-2006
WO 2007021463 A2	22-02-2007	CA 2618338 A1	22-02-2007
		CN 101258218 A	03-09-2008
		EP 1924667 A2	28-05-2008
		JP 2009504373 T	05-02-2009
		KR 20080033534 A	16-04-2008
		US 2009220399 A1	03-09-2009
WO 2007030888 A1	22-03-2007	AU 2006291954 A1	22-03-2007
		AU 2010201570 A1	13-05-2010
		CA 2622570 A1	22-03-2007
		CN 101283078 A	08-10-2008
		EA 200800827 A1	30-06-2008
		EP 1931755 A1	18-06-2008
		NZ 566742 A	30-07-2010
		US 2010147022 A1	17-06-2010