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(54) **CAPTURE AND RELEASE OF ACID GASSES USING TUNABLE ORGANIC SOLVENTS WITH AMINOPYRIDINE**

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B01D 53/48 (2006.01)
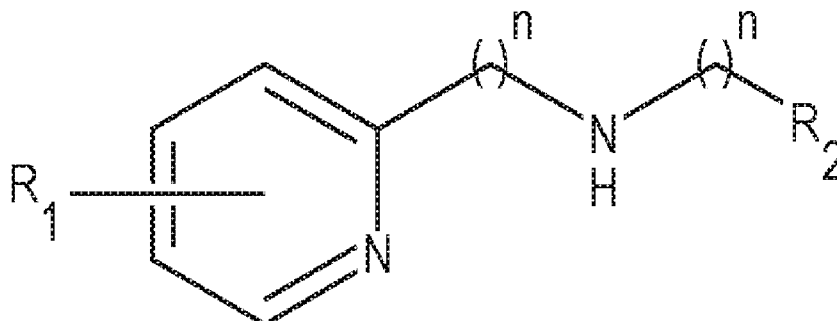(Continued)

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None
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(57) **ABSTRACT**

A class of water lean, organic solvents that can bind with various acid gasses to form acid gas bound molecules having a high degree of intramolecular hydrogen bonding which enables their use as regenerable solvents for acid gas capture. Unlike the other devices described in the prior art, the present invention takes advantage of shortened distances between the portions of the molecule that form hydrogen bonds within the structures when loaded with an acid gas so as to create a molecule with a higher internal bonding affinity and a reduced proclivity for agglomeration with other molecules.

2 Claims, 4 Drawing Sheets

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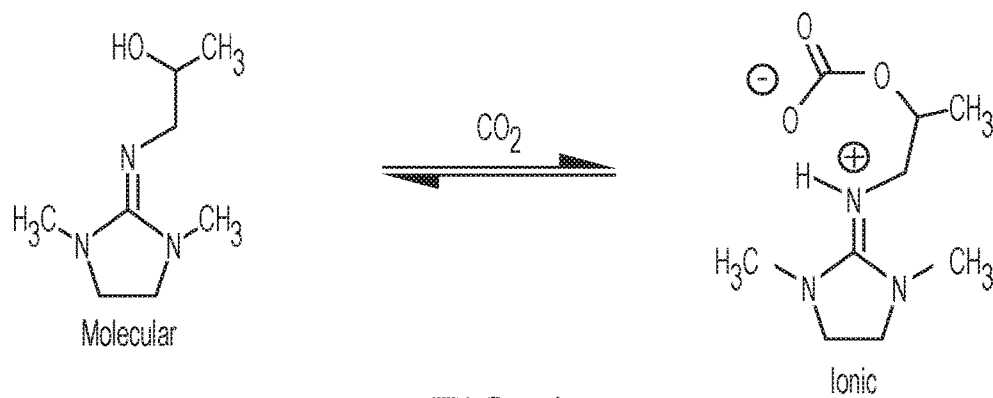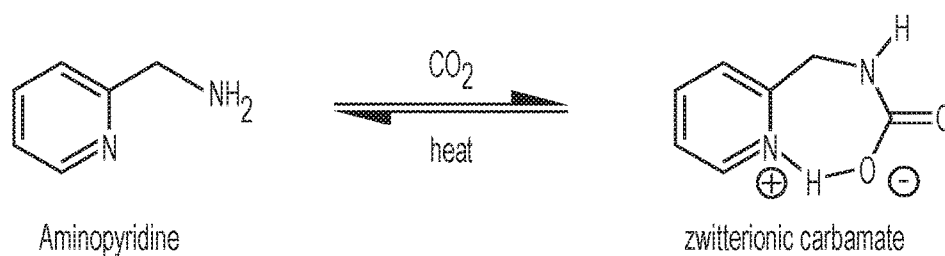Final Office Action for U.S. Appl. No. 15/410,523, filed Jan. 19, 2017, Notification dated Aug. 8, 2018.
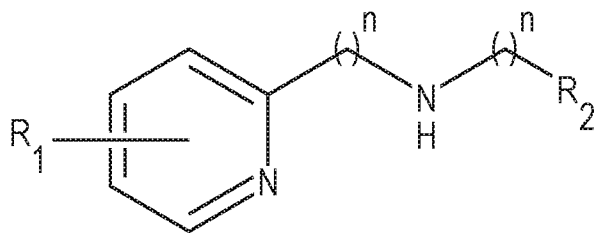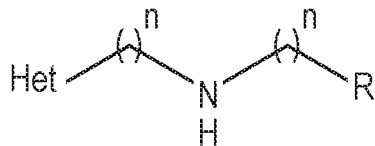

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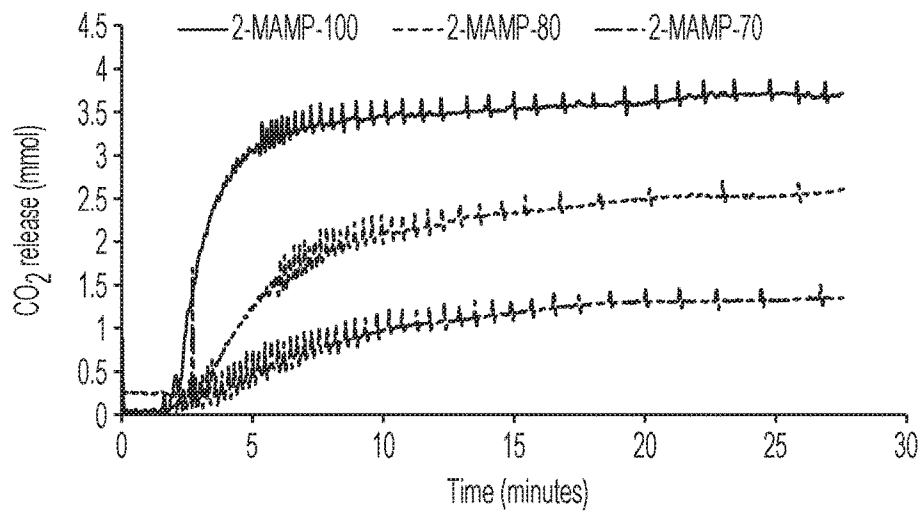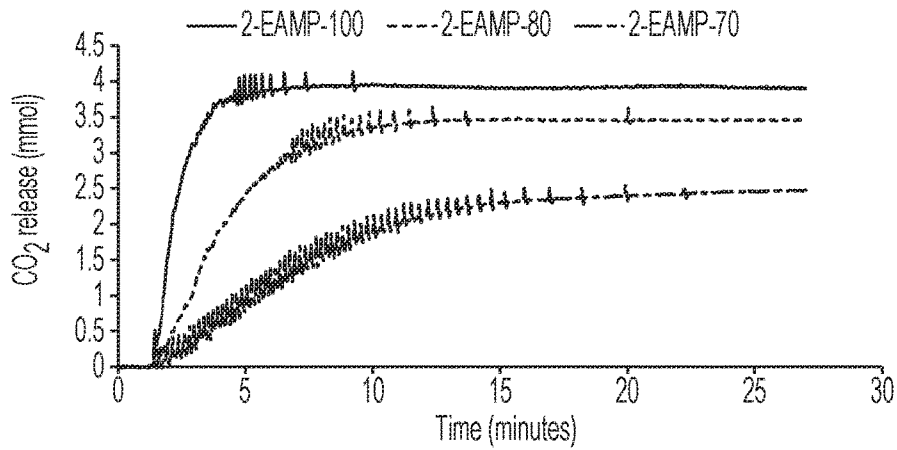
FIG. 1

FIG. 2

FIG. 3A
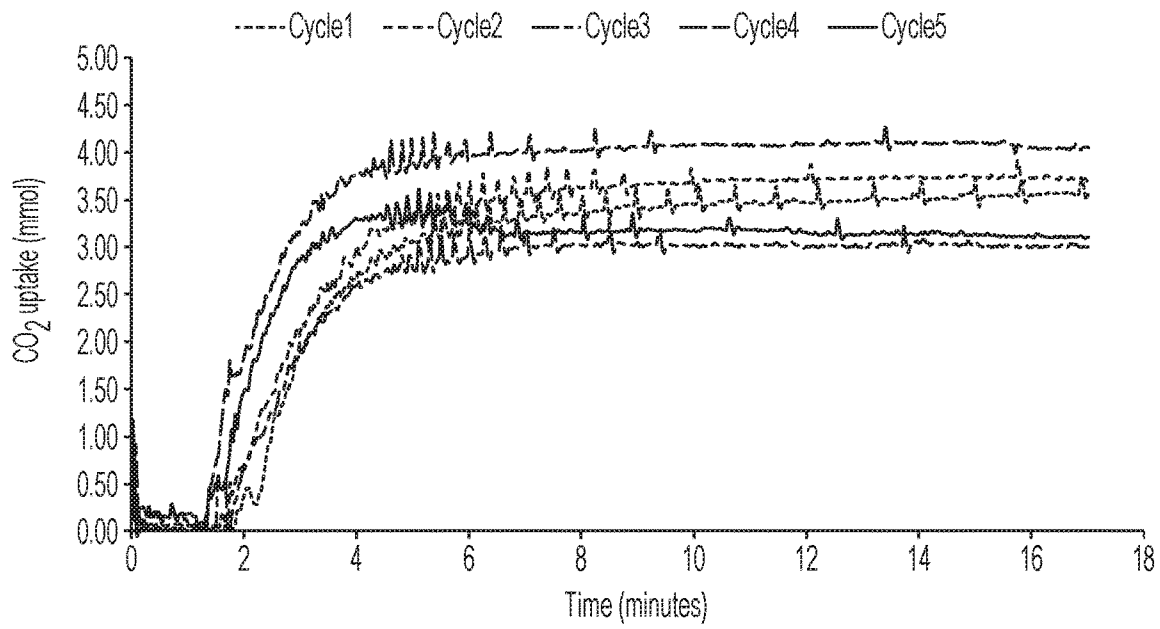

FIG. 3B

FIG. 4

FIG. 5

FIG. 6

CAPTURE AND RELEASE OF ACID GASSES USING TUNABLE ORGANIC SOLVENTS WITH AMINOPYRIDINE

PRIORITY

This invention claims priority from and is a Divisional of U.S. patent application Ser. No. 15/410,523 entitled Capture And Release Of Acid Gasses Using Tunable Organic Solvents With Aminopyridine filed Jan. 19, 2017, which claims priority from provisional patent application No. 62/281,053 entitled System and Process for Tunable Organic Solvents for Selective Capture of CO₂ filed Jan. 20, 2016, and from provisional patent application No. 62/421,416 entitled Capture and Release of Acid Gasses Using Tunable Organic Solvents with Aminopyridine filed Nov. 14, 2016, the contents of all which are incorporated herein by reference.

STATEMENT AS TO RIGHTS TO INVENTIONS MADE UNDER FEDERALLY-SPONSORED RESEARCH AND DEVELOPMENT

This invention was made with Government support under Contract DE-AC0576RL01830 awarded by the U.S. Department of Energy. The Government has certain rights in the invention.

BACKGROUND OF THE INVENTION

Field of the Invention

The invention generally relates to acid gas capture and more particularly to reversible acid gas capture systems and processes.

Background Information

The release of greenhouse and acid gases into the air produces local and global effects on the environment. The combustion of fossil fuels generates acid gases such as carbon dioxide (CO_2), sulfur oxides (SO_2 and COS), sulfides (H_2S) and nitrogen oxides (NOx). Fixed combustion sources, such as coal burning power plants, generate significant acid gas emissions released in their flue gas. The capture and removal of the acid gases including carbon dioxide (CO_2), sulfur oxides (SO_2, SO_3, COS, CS_2), hydrogen sulfide (H_2S), and nitrogen oxides (NOx) from flue gas will become an even greater issue as coal becomes more prominent in the world's future energy consumption. The capture of significant amounts of greenhouse and acid gases from emission sources is desired to reduce the environmental effects of these sources.

Current aqueous flue gas scrubbing technologies are typically too energy intensive to be used industrially or often require the use of toxic materials which further complicates implementation. Various current aqueous scrubbing technologies remove sulfur oxides and nitrogen oxides from flue gas, and trap these acid gases as basic salts of their acid gases (thiocarbonates, dithiocarbonates, sulfites and nitrate) using a highly basic solution of caustic soda or lime. In these examples the binding is stoichiometric and irreversible and results in a base that cannot be reused.

Various binding organic liquid (BOLs) acid gas capture strategies such as those developed by Phillip Jessop, David Heldebrant, Philip Koech and others are described in various applications and patents such as U.S. Pat. No. 7,700,299. These technologies are a significant improvement over the prior art and have shown great promise in providing a solution to these problems. However, in some circumstances, these binding organic liquids can be limited by problems related to an increase in viscosity with CO_2 loading which impacts the ability of these materials to be pumped and transferred from one location to another, and has created various problems related to their scaling up and broader utilization. What is needed is a form of binding organic liquid that remains in a less viscous state when bound with the acid gas so as to allow pumping and transportation of the liquid sorbents from one location to another. What is also needed is a process for tuning binding organic liquids so as to retain a desired low viscosity or other features. What is also needed is a form of a binding organic liquid that retains a desired level of viscosity and also allows for facile release of acid gasses and regeneration of the sorbent material. The present invention meets these needs.

Additional advantages and novel features of the present invention will be set forth as follows and will be readily apparent from the descriptions and demonstrations set forth herein. Accordingly, the following descriptions of the present invention should be seen as illustrative of the invention and not as limiting in any way.

SUMMARY

The present application includes a description of a class of water lean, organic solvents that can bind with various acid gasses to form structures having a high degree of intramolecular (internal) hydrogen bonding when bound to their acid gas which enables their use as regenerable solvents for acid gas capture. Unlike the other devices described in the prior art, the present invention takes advantage of shortened distances between the portions of the molecule that form hydrogen bonds within the structures when loaded with an acid gas so as to create a molecule with a higher internal bonding affinity and a reduced proclivity for agglomeration with other molecules.

In one set of embodiments, results of various modified CO_2 binding organic liquids (CO₂BOLs) are described with various designs for tuning such materials to effectuate acid gas capture, with charge neutrality in the resulting bound materials so as to impart desired characteristics such as lowered levels of viscosity to the resulting bound materials.

In another set of embodiments, water-lean non-aqueous amine-based solvents that form zwitterionic carbamates for acid gas capture are described. In another set of embodiments, example structures of various of these materials including various types of amino pyridines are shown as are acid gas capture methods and processes that utilize these materials.

In one set of embodiments, the invention may include a method for tuning the viscosity of a binding organic liquid comprising the step of adjusting the structure of the acid gas capture molecule by modifying the internal hydrogen bonding distances within the structure to produce a neutral acid gas capture material with a reduced proclivity for agglomeration with other molecules and a resulting lowered viscosity. In some instances this distance between such hydrogen bonded portions may be less than about 2 angstroms. In another embodiment of the invention an acid gas capture material may have a binding organic liquid with a structure that binds to an acid gas and results in a charge neutral molecule. In another set of embodiments a gas-selective capture sorbent for capture and chemical binding of an acid gas is described having an amino pyridine that reversibly binds an acid gas under a first set of conditions and releases

that acid gas under a second set of conditions. The amino pyridine, or other heteroaromatic compounds such as triazines, pyrimidines, or imidazoles in such a sorbent may have any of a variety of features including being a primary or secondary amino pyridine; having at least one R group with a carbon number selected from C1 to C18; having an R group selected from the group consisting of methyl, ethyl, propyl, iso-propyl, butyl, iso-butyl, aryl, and combinations thereof; or having a least one R group that is an alkyl amine or a dialkyl amine. In some embodiments the amino pyridine may be selected from the group of 2-[(methylamino)methyl] pyridine (2-MAMP), 3-[(methylamino)methyl]pyridine (3-MAMP), 4-[(methylamino)methyl]pyridine (4-MAMP), 2-[(ethylamino)methyl]pyridine (2-EAMP), 4-[(ethyl-amino)methyl]pyridine (4-EAMP) and 2-[(methylamino) ethyl]pyridine (2-MAEP); and derivatives and combinations thereof. In some embodiments the capture solvent may retain a viscosity at or below about 300 cP at a maximum loading of acid gas at temperature at or below 40° C. therein.

In other embodiments, these amino pyridine solvents transform from liquids to solid upon CO_2 capture. The resultant solid can be separated from the liquids in order to intensify the CO_2-rich materials thus saving energy of regeneration by thermal heating of less material. In one set of experiments these solid CO_2-rich materials were regenerated at 120° C. to form the liquid sorbent.

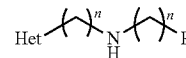In another set of embodiments the amino pyridine has the structure:
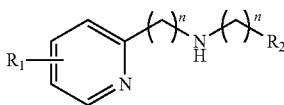
wherein at least one of the R groups includes an alkyl amine or a dialkyl amine. In addition, in this embodiment, at least one of the R groups may be selected from the group consisting of Me, Et, Pr, iPr, Bu, iBu, t-Bu, cyclobutyl, cyclopentyl, and cyclohexyl. In some embodiments, R1 and R2 may each include a hetero-alkyl group selected from OMe, OEt, OPr, OBu, Ot-Bu, $N(Me)_2$, and $N(Et)_2$. In some applications the capture solvent may comprise up to about 10% water by weight. In other applications the methylene repeat units (n) can be any number up to 100 (n≤100).

In another application of the invention an embodiment is described which is a method for capturing an acid gas from a stream. The method includes the step of contacting the stream with a gas selective capture sorbent having an amino pyridine that reversibly binds the acid gas under a first set of conditions to form a bound solvent, and releases the acid gas under a second set of conditions to release the bound solvent and regenerate the sorbent. In some applications, this process includes moving the bound solvent to another location and exposing the bound sorbent to a second set of conditions. In some applications, the amino pyridine sorbent is a liquid. The acid gas may be CO_2, SO_2, COS, CS_2, H_2S, and combinations thereof. The second set of conditions may include heating the bound solvent to a temperature between from 70° C. to 100° C., shifting polarity of the sorbent from neutral form to the non-polar amino pyridine form, or separating solid phase zwitterionic carbamate salts or ana-logues thereof formed in the sorbent from a liquid phase comprising gas-lean amino pyridines therein to at least partially regenerate the sorbent.

In some of these embodiments, the capture solvent may include using a gas-selective capture solvent having an amino pyridine that reversibly binds an acid gas under a first set of conditions and releases that acid gas under a second set of conditions. The amino pyridine in such a sorbent may have any of a variety of features including being a secondary amino pyridine; having at least one R group with a carbon number selected from C1 to C18; having an R group selected from the group consisting of methyl, ethyl, propyl, iso-propyl, butyl, iso-butyl, aryl, and combinations thereof; or having a least one R group that is an alkyl amine or a dialkyl amine. In some embodiments the amino pyridine may be selected from the group of 2-MAMP; 3-MAMP; 4-MAMP; 2-EAMP; 4-EAMP; 2-MAEP; and derivatives and combinations thereof. In some embodiments the capture solvent may retain a viscosity at or below about 300 cP at a maximum loading of acid gas therein. In another set of embodiments, the sorbents contain other heteroaromatic bases that can be used to bind with acid gasses and create similar sorbents as aminopyridines. Examples of such structures include aminopyrazines, aminopyrimidines, aminopy-razines, aminoindoles, aminoimidazoles, aminotriazoles, aminotriazines, and other similar structures. An example of such a structure designed for CO_2 capture has the structure:

$Het^=$ Pyridine, Pyridazine, Pyrimidine, pyrazine, indole, Imidazole, triazole and triazine

wherein at least one of the R groups includes an alkyl amine or a dialkyl amine. In addition, in this embodiment, at least one of the R-groups may be selected from the group consisting of Me, Et, Pr, iPr, Bu, iBu, t-Bu, cyclobutyl, cyclopentyl, and cyclohexyl. In some embodiments, R1 and R2 may each include a hetero-alkyl group selected from OMe, OEt, OPr, OBu, Ot-Bu, $N(Me)_2$, and $N(Et)_2$. In some embodiments, the heteroaromatic rings consist of at least one nitrogen atom such as pyrazine, pyridazine, pyrimidine, indole, imidazole, benzimidazole, triazole and triazine. In some applications the capture solvent may comprise up to about 10% water by weight.

Various advantages and novel features of the present invention are described herein and will become further readily apparent to those skilled in this art from the follow-ing detailed description. In the preceding and following descriptions I have shown and described only the preferred embodiment of the invention, by way of illustration of the best mode contemplated for carrying out the invention. As will be realized, the invention is capable of modification in various respects without departing from the invention. Accordingly, the drawings and description of the preferred embodiment set forth hereafter are to be regarded as illus-trative in nature, and not as restrictive.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows an example of one exemplary embodiment of the invention.

FIG. 2 shows an example of another embodiment of the invention

FIGS. 3A and 3B show the structures of various other embodiments of the invention.

FIGS. 4 and 5 show the rates of CO_2 release and sorbent regeneration in various examples of the invention

FIG. **6** shows the recyclability of one example of the present invention over several load and unload cycles.

DETAILED DESCRIPTION OF THE INVENTION

The following description includes various embodiments of the present invention. It will be clear from this description of the invention that the invention is not limited to these illustrated embodiments but that the invention also includes a variety of modifications and embodiments thereto. Therefore the present description should be seen as illustrative and not limiting. While the invention is susceptible of various modifications and alternative constructions, it should be understood that there is no intention to limit the invention to the specific form disclosed, but, on the contrary, the invention is to cover all modifications, alternative constructions, and equivalents falling within the spirit and scope of the invention as defined in the claims.

The present detailed description includes various modified CO_2 binding organic liquids (CO_2BOLs) and various designs for tuning such materials to effectuate acid gas capture while imparting desired characteristics such as lowered levels of viscosity to the resulting bound materials. While these embodiments are shown and described in the context of CO_2, it is to be understood that the invention is not limited thereto but includes other acid gasses as well. In one set of embodiments, water-lean non-aqueous amine-based solvents that form zwitterionic carbamates for acid gas capture are described. In another set of embodiments examples structures of various materials including various types of amino pyridines are shown as are acid gas capture methods and processes that utilize these materials.

In one typical application and usage, the present invention includes a series of water lean or non-aqueous sorbents that are able to bind acid gasses such as CO_2, SO_2, COS, CS_2, etc. at standard temperature and pressures (STP) to form liquid carbamate salts with a generally high gravimetric capacity (~20 wt %) but retain a desired level of viscosity. As such the bound sorbents may be pumped or transferred from one location to another which enables the acid gas in one location to be captured under a first set of process conditions and then moved to another location where the acid gas can be removed by subjecting the bound material to a second set of conditions and ideally the sorbent regenerated for later use. Stripping of these acid gasses and regeneration of the underlying sorbent can take place when conditions, such as temperature, pressure or other stimuli are altered. This enables a cyclical process to take place wherein acid gasses are captured, bound, and then subsequently released with these binding materials recycled for reuse.

The solvents described in the present application have low thermal regeneration temperatures (70-100° C.) and low CO_2-rich solvent viscosity compared to other water-lean materials. The regeneration temperature can be lowered further to 60° C. by applying polarity swing assisted regeneration (PSAR) making it feasible to utilize lower grade heat from the power plant for acid gas stripping resulting in energy savings. While others have utilized aqueous acid gas capture technologies made up of primary and secondary alkanol amines such as monoethanolamine (MEA) or diethanolamine (DEA) in water for chemical absorption of acid gas capture materials like CO_2, high regeneration temperatures (>120° C.), high steel corrosion due to the water load, and thermal degradation render these types of materials undesirable. In addition, most of these other solvents when amine-based require a co-solvent such as water or an added organic to dissolve the carbamate salt. The present embodiments which are amine-based operate in much less harsh (milder) conditions and do not require a co-solvent to dissolve the CO_2 carrier to enable processing.

In one set of embodiments principles and methods for the tunability of acid gas capture binding organic liquids for acid gas capture such as CO_2 binding in CO_2BOLs are described. A series of discoveries made at Pacific Northwest National Laboratory in Richland, Wash. USA by Vanda Glezakou, Roger Rousseau, and others have shown that single component CO_2-rich CO_2BOLs do not exist entirely as zwitterionic species but rather in a dynamic equilibrium between alkyl carbonic acid (the acid form [A]) and the zwitterion form [Z]. Tests performed on that zwitterion form revealed that various aspects of acid gas capture (and CO_2 capture specifically) by water-lean solvent systems can be controlled by deliberate molecular modifications. Specifically, it was found that close proximity of amine and alcohol moieties and tunable acid/base equilibria play important roles in determining CO_2 adsorption kinetics and bulk liquid viscosity.

The close proximity of the guanidine and alcohol moieties facilitates the concerted mechanism of CO_2 binding by the nucleophilic alcohol and concurrent proton transfer to the guanidine. The overall effect is fast CO_2 binding kinetics associated with low entropic contribution to the free energy barrier. This proximity also enables stronger internal H-bonding that favorably reduces viscosity. A high acidity at the alcohol site allows for a more efficient CO_2 activation at the transition state and an efficient proton transfer to the amine. In some embodiments non-charged CO_2 capture solvent systems obtained by adjusting the acid/base properties of the solvent molecules, so that a significant fraction of the CO_2-loaded molecules can exist in a partial or non-charged (acid) form may be preferable. This adjustment can be achieved by either increasing the acidity of the alcohol or by decreasing the basicity of the amine. Experiments have shown that non-charged CO_2 capture systems exhibit appreciably lower viscosities than the analogous zwitterionic form due to decreased ionic interactions. The guidelines outlined here for controlling CO_2 uptake kinetics and viscosity reduction can be ubiquitously applied to both carbonate and carbamate solvent systems.

This proximity also enables stronger internal H-bonding that favorably affects viscosity and assists in enabling acid gas bound moieties to be pumped from one location to another. In one set of experiments the presence of a high acidity at the alcohol site allows for a more efficient CO_2 activation at the transition state and an efficient proton transfer to the amine. This then leads to the concept that by adjusting the acid/base properties of the solvent molecules so as to obtain a charge neutral molecule rather than an ionic molecule as the art currently describes, that CO_2 capture systems that exhibit appreciably lower viscosities than the analogous zwitterionic forms could be designed.

Referring first to FIG. **1**, an example of one exemplary embodiment of the invention is shown. FIG. **1** shows the methodology for the capture of an acid gas, in this case CO_2 by a binding organic liquid containing liquid. From experiments it has been shown that the acid gas binding free energy is one of the deciding criteria in the design of gas separation solvents. In this particular instance, the binding organic liquid has been designed with angles that allow for a closer hydrogen bonding proximity between the positive portion of the capture molecule and the negative portion of the bound CO_2 which results in reducing the charge on the zwitterion moving the molecule toward a charge neutral arrangement

and a resulting desired lower viscosity because the individual molecules are structured in such a way so as to reduce agglomeration of CO_2-bound molecules. These lower viscosities in turn enable higher loadings of the bound CO_2, and flow and pumpability of the gas capture liquid to be maintained.

A series of simulations on various capture molecules (in this case CO_2BOLs) including IPADM-2-BOL, IPADM-3-BOL, IPATBM-2-BOL, and PADM-2-BOL showed that solvated CO_2 in the vicinity of the alcohol where the radial rC-O distances were less than 2.00 Å binds CO_2 in the form of an alkylcarbonate, while the H atom that originally belonged to the OH group remains on the guanidine N. For radial distances greater than 2.20 Å, 1-IPADM-2-BOL remains in its alcohol form, and CO_2 is mostly linear with the $\angle OCO$ angle averaging ~175°. The angle decreases to ~165° for rC-O distances between 2.0 and 2.2 Å. CO_2 binding happens in an effectively concerted mechanism: at rC-O—2.00 Å, the $\angle OCO$ angle decreases to ~165° for rC-O distances between 2.0 and 2.2 Å. CO_2 binding happens in an effectively concerted mechanism: at rC-O distances of ~2.00 Å, the $\angle OCO$ angle becomes ~150° with a simultaneous H transfer to the nitrogen of the guanidine base. The CO_2 structure is consistent with a partial charge transfer to form a CO_2 (δ−) moiety and subsequent formation of a CO_3-moiety in the IPADM-2-BOL. This stronger hydrogen bonding, coupled with charge neutrality, contributes to a reduction in agglomeration in the acid gas rich environment. This reduction in agglomeration in turn results in overall reduced viscosity in the system. In other embodiments, viscosity is adjusted based upon monitoring the free energy profile (i.e., ΔG ([A]−[Z]) kJ/mol) and tuning the acid-base equilibria ($Keq=[A]/[Z]$) between the solvated and bound CO_2 states.

The free energy profile for binding CO_2 to IPADM-2-BOL proceeds with a barrier of 16.5±1.2 kJ/mol and a binding free energy of −5.8±1.6 kJ/mol. The binding free energy is consistent with the experimentally obtained values for diazabicyclo[5.4.0]-undec-7-ene (DBU) containing dual-component CO_2BOLs that range between −5.7 to −9.7 kJ/mol. This implies that at 40° C., there is an equilibrium between solvated and bound CO_2. The free energy barrier of 16.5 kJ/mol and the activation energy of 9.8 kJ/mol are compatible with the experimental observation that this process readily occurs at 40° C.

For aqueous monoethanolamine (MEA) capture liquids, the energy barrier is more than twice that of CO_2BOLs: density functional methods give a barrier of 35.5 kJ/mol for dry MEA, and from 16 kJ/mol up to ~63 kJ/mol for wet MEA; activation free energy estimates with the Arrhenius relation from experimental data are ~46.7 kJ/mol. An estimate of activation free energy is only ~7 kJ/mol higher than the activation energy, which is indicative of a small entropic contribution at the transition state, owing to the proximity of the acid/base moieties in the single component systems: unlike dual component systems, solvent re-organization at the transition state is not required. The relatively low barrier then suggests that capture in CO_2BOLs is likely to be diffusion limited. Because the solvent viscosity increases exponentially with CO_2 loading, the capture rate will decrease as more CO_2 is added. These phenomena were observed when the CO_2 absorption rates of single and dual-component CO_2BOL solvents where measured with wetted-wall experiments. These findings and understandings enable the design of liquid carbamates that will have increased CO_2 uptake capability, and enable the design of carbamate salts with decreased viscosities. By tuning the

proximity of the alcohol and the amine so as to create structures that when bound to an acid gas have a preference for their own internal hydrogen bonding rather than agglomeration with other structures and creating molecules that are preferentially more charge neutral than ionic, the problems of high viscosity in an acid gas rich state as exists in other embodiments is reduced.

Inspired by these findings, single component amines (e.g., amino pyridines) with various pendant coordinating bases were designed to create structures having a high degree of internal hydrogen bonding and/or acid-base equilibria favoring the non-charged acid state (e.g., [1:1] acid [A]: zwitterion [Z] ratio) upon capture and binding of the acid gas in the bound material.

In one set of embodiments, modified CO_2 binding organic liquids with structures favoring internal hydrogen bonded species in the bound material were utilized that gave resulting viscosities that were reduced compared to those forming primarily zwitterionic species. For example a modified 1-IPADM-2-BOL was created that formed 34% internal (neutral charged) hydrogen bonded species and 66% external hydrogen bonded species that gave a resulting viscosity of ~110 (cP) at a CO_2 loading of 25 wt %.

In another set of embodiments, five modified CO_2BOLs (1-MEIPADM-2-BOL, 1-IPADM-2-BOL, 1-IPADM-3-BOL, 1-IPATBM-2-BOL, PADM-2-BOL) were utilized. Table 1 lists fractions of internal hydrogen bonded species formed in these sorbent liquids at a CO_2 loading of 25 wt %.

TABLE 1

CO_2 Binding Organic Liquid	Internal H-Bonded Species (P_{int})	Viscosity (MD Simulation) (cP)	Viscosity (Experimental) (cP)
1-MEIPADM-2-BOL	52%	114	75
1-IPADM-2-BOL	34%	149	171
1-IPADM-3-BOL	21%	190	270
1-IPATBM-2-BOL	2%	499	Very viscous
1-PADM-2-BOL	<1%	950	Solid

As these data show, selecting or modifying structures of the sorbent liquid and/or tuning acid-base equilibria to obtain an increasing number of internal hydrogen-bonded species in the bound material reduces viscosity of these CO_2 binding organic liquids.

In another set of experiments, various CO_2 binding organic liquids were modified and tuned. The acid-base equilibria between the (solvated) organic acid and the conjugate base (i.e., bound CO_2 state) in the capture liquid were adjusted, decreasing the free energy profile, and increasing the number of charge neutral species that resulted in decreasing the viscosity in the resulting CO_2-bound material.

In one example, modified CO_2 binding organic liquids were created with reduced acidity of the pendant R-group of the coordinating base. A IPADM-2-BOL was modified by attaching an oxime moiety to the alcohol group of the coordinating base, reducing the free energy from 21.6 kJ/mol to −3.1 kJ/mol and tuning the acid-base equilibrium yielding a ratio of neutral-to-charged species (acid [A]: zwitterion [Z]) in the capture liquid from 1/4000 to 3/1 in the bound material. This resulted in lower viscosity and improved capture capacity.

In another set of embodiments, modified CO_2 binding organic liquids were utilized with structures modified to reduce basicity of the pyridine core, for example, by attaching acidic or electronegative moieties to the core structure.

A 1-IPADM-2-BOL was modified by attaching fluorine to the pyridine core reducing the free energy in the capture liquid from 21.6 kJ/mol to −5.4 kJ/mol and tuning the acid-base equilibrium yielding a ratio of neutral-to-charged species in the capture liquid from 1/4000 to 8/1 in the bound material, resulting in lower viscosity and improved capture capacity.

In another set of embodiments, a class of novel amino pyridine solvents was created. These non-aqueous amines demonstrated a high CO_2 capture capacity regeneration temperatures less than 100° C., durability for absorption and regeneration over multiple cycles without degradation, and a high water tolerance. The structures of various examples of these materials are shown in FIGS. **2-3**.

In one set of embodiments, these amino pyridine solvents were created that were liquids at both CO_2 free and rich states, and were structurally predisposed to stabilize the incipient carbamic acid upon reaction with CO_2 through formation of stable 7 and 8 membered rings, respectively, via hydrogen bonding by the acidic proton and the 2-pyridine nitrogen. These solvents utilize the amine chemistry to bind CO_2 as carbamates, with internal hydrogen bonds that enable liquid products, thus allowing for water-free or -lean CO_2 capture liquids that otherwise would be unachievable under standard amine compositions of matter. These aminopyridine materials have unprecedented high CO_2 capture capacity ~20 wt %, with low regeneration energy. These amino pyridines form a new class of materials with potential applications in acid gas capture from flue gas of coal fired power plants, separation of acid gasses from natural gas streams and biogas, co-capture of acid gasses such as CO_2, SO_2, CO_2, CS_2 and H_2S, and other combinations of acid gasses from natural gas and biogas streams.

In one set of experiments six of these non-aqueous amine examples (2-MAMP, 3-MAMP, 4-MAMP, 2-EAMP, 4-EAMP, 2-MAEP) were shown to capture CO_2 with high capture capacity. All of these example compounds were liquids in the CO_2-rich state at room temperature, with a viscosity less than 300 cP at 40° C. Table 2 shows the CO_2 capture capacity at 25° C. of a set of six of these compounds. Table 3 shows the CO_2 capture capacity at 40° C. These results demonstrate that the CO_2 capture capabilities of these amine materials are approximately equivalent. The slight increase in capture capacity at 40° C. is due to a reduced viscosity due to the rise in temperature from the exothermic reaction of CO_2 with amines.

TABLE 2

Compound	CO_2 Wt %	CO_2 Mol %
2-MAMP	19.7	54.8
3-MAMP	19.5	54.1
4-MAMP	19.7	54.8
2-EAMP	18.2	56.5
4-EAMP	18.3	56.7
2-MAEP	17.8	55.2

TABLE 3

Compound	CO_2 Wt %	CO_2 Mol %
2-MAMP	21.1	58.5
3-MAMP	20.0	54.9
4-MAMP	18.6	51.5
2-EAMP	14.0	43.3
4-EAMP	16.7	51.8
2-MAEP	19.3	59.8

After the CO_2 is captured and held by the compounds as zwitterionic carbamate salts under a first set of conditions, the carbamate salts can be subjected to a second set of conditions such as higher temperatures, a reduction in pressure, mixing with other materials, or other activities which will cause the bound CO_2 or other acid gas to be released and the underlying sorbent to be regenerated. Table 4 shows the results of a set of experiments performed on these same six compounds, wherein temperatures were raised and the percentage of CO_2 released was measured. These examples show that most of these amine based sorbent materials can be sufficiently regenerated at temperatures of 100° C., while 2-EAMP has a regeneration temperature of 80° C. The rates of regeneration of these various materials at various temperatures are shown in FIGS. **4** and **5**. As these figures show, the rates of regeneration are relatively fast with most of these materials releasing the bulk of their captured CO_2 within 5 minutes. Some materials such as 2-EAMP can be completely stripped at a lower temperature (80° C.) in less than 10 minutes. In other embodiments other materials may release at different temperatures including lower temperatures.

TABLE 4

Compound	70° C.	80° C.	100°	120° C.
2-MAMP	33.8	60.5	90.3	—
3-MAMP	31.1	51.0	77.5	—
4-MAMP	35.1	51.3	93.8	—
2-EAMP	85	95.8	—	—
4-EAMP	71.4	85.1	98.8	—
2-MAEP	—	34.6	76.4	90.3

In addition to acid gas release and regeneration of the solvent using changes in temperature, regeneration can be effectuated or supported using swings in pressure or polarity. In another set of experiments embodiments of water-lean solvents were constructed that would switch polarity upon binding with an acid gas such as CO_2. When subjected to an external induced polarity reduction these materials released the CO_2 and were regenerated to their prior form and were capable of reuse for acid gas capture. This process, named polarity swing assisted regeneration (PSAR), can be coupled with other methodologies for regeneration and enables for example the regeneration of materials at a lower temperature than would ordinarily be required or expected. In one set of experiments CO_2 rich 2-EAMP was able to be 81 percent stripped and regenerated at 60° C. using PSAR with decane as anti-solvent.

Experiments run on these amino pyridine compounds also demonstrated that over repeated cycles of CO_2 absorption at 25° C. and stripping and regeneration of the sorbent at 100° C. that the integrity of the underlying amino pyridine solvent remained intact with no signs of degradation. Furthermore, while viscosity increased with CO_2 loading, the viscosity of these amino pyridine compounds at lower temperatures generally remained at less than or equal to the viscosity of other compounds at higher temperatures (viscosity of 2-MAEP at 40° C. is nearly the same as viscosity of IPADM-2 BOL at 75° C.). Furthermore, the addition of up to 10 percent water to these liquids did not demonstrate any negative effect upon the CO_2 uptake and release. A mixture of CO_2 rich 2-MAMP with ten percent water remained a

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liquid with no precipitate, and maintained a bicarbonate-to-carbamate ratio of 5:4 per ^{13}C NMR analysis.

While various preferred embodiments of the invention are shown and described, it is to be distinctly understood that this invention is not limited thereto but may be variously embodied to practice within the scope of the following claims. From the foregoing description, it will be apparent that various changes may be made without departing from the spirit and scope of the invention as defined by the following claims.

What is claimed is:

1. A method for capturing a target acid gas from a stream containing the target acid gas, the method comprising the step of;

contacting the stream with a gas selective capture sorbent comprising an amino pyridine having the structure
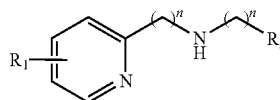
wherein each of the n is greater than zero but less than or equal to 100, and R1 and R2 each include a hetero-alkyl group whereby the target acid gas reversibly binds to the gas selective capture sorbent to form a bound solvent sorbent that while bound under a first set of conditions, releases the target acid gas under a second set of conditions.

2. The method of claim 1 wherein R1 and R2 each include a hetero-alkyl group selected from OMe, OEt, OPr, OBu, Ot-Bu, N(Me)2, and N(Et)2.

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