5-1-2018

Method of Increasing Mass Transfer Rate of Acid Gas Scrubbing Solvents

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**Recommended Citation**
Lippert, Cameron Anthony; Liu, Kunlei; Brandewie, Christine Marie; Remias, Joseph Eugene; and Sarma, Moushumi, "Method of Increasing Mass Transfer Rate of Acid Gas Scrubbing Solvents" (2018). *Center for Applied Energy Research Faculty Patents*. 50.  
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A method and catalysts for increasing the overall mass transfer rate of acid gas scrubbing solids is disclosed. Various catalyst compounds for that purpose are also disclosed.

8 Claims, 2 Drawing Sheets
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METHOD OF INCREASING MASS TRANSFER RATE OF ACID GAS SCRUBBING SOLVENTS

This document claims priority of U.S. Provisional Patent Application Ser. No. 61/925,693, filed on Jan. 10, 2014, the full disclosure of which is incorporated herein by reference.

TECHNICAL FIELD

The present invention relates generally to various methods and catalysts for increasing the overall mass transfer rate of acid gas scrubbing solvents utilizing various catalyst compounds.

BACKGROUND

The cleanup of acid gases or sour gas, such as CO₂ in particular, from natural gas and in oil refining has been an extensively practiced technology. The industrial removal of CO₂ from natural gas dates back to the 1930s. In the 21st century, due to the potential impact of anthropogenic CO₂ emissions on the climate, post-combustion CO₂ capture has gained tremendous attention. While several technologies exist for the removal of acid gases one of the most commonly employed practices is the use of aqueous amines. Of these amines, tertiary amines are often used for natural gas applications due to their low energy of regeneration. For post-combustion CO₂ capture applications primary and secondary amines tend to be in part favored by their faster rate at the low gaseous CO₂ concentration condition. Regardless of the application, the mass transfer rate in the absorber column dictates the size of the column (capital cost) used and, consequently, has a substantial impact on the overall process cost. A simplified process depicting a thermal swing process is presented in FIG. 1. An aqueous amine solution is circulated between the absorber and stripper. The gas, containing CO₂, enters the bottom of the absorber where it contacts the aqueous amine absorbent removing it from the gas stream. The liquid solution, CO₂ rich amine solution, is then passed through a heat exchanger to improve efficiency before being heated to a higher temperature in the stripper. The stripper removes the CO₂ as a gas from the amine solution to produce a lean, or CO₂ deficient solution. The lean solution is returned to the absorber by way of the heat exchanger to repeat the process. In order to minimize system capital (absorber cost) it is important to maximize the overall mass transfer rate for the scrubber system as there is a direct correlation between the two. This invention relates to methods for this purpose as well as to catalyst compounds useful in those methods.

SUMMARY

A method is provided for increasing the overall mass transfer rate of acid gas scrubbing solvents. The method comprises adding a catalyst compound to a fluid stream including an acid gas and an acid gas scrubbing solvent wherein that catalyst compound has a chemical formula:

where:
(a) M is any group VII B through XII B element;
(b) x is neutral σ₉⁻ or a donor or monovalent anion;
(c)
In an alternative embodiment, the method comprises adding a catalyst compound to a fluid stream including an acid gas and an acid gas scrubbing solvent wherein that catalyst compound has a chemical formula:

where $A$ is monovalent anion: Cl, Br, I, F, PF$_6$, BF$_4$, acetate, trifluoroacetate, ClO$_4$, N$_2$O$_5$, and

Q is monovalent cation: PR$_3$, R$^-$alkyl, cyclic alkyl, Aryl, 0-alkyl, 0-Aryl

NR$_3$, R$^-$alkyl, cyclic alkyl, N-heterocyclic ring, imidazole; and

(b) $x$ is neutral Si$_n$O$_m$ or a donor or monovalent anion;
(c) $E_{1}=N$, P, S, B

$E_{2}=N$, P, S, 0, B

In an alternative embodiment, the method comprises adding a catalyst compound to a fluid stream including an acid gas and an acid gas scrubbing solvent wherein that catalyst compound has a chemical formula:

where $R_f$ = H, any alkyl, RCOOH ($R^-$alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH ($R^-$alkyl ranging from 0-5 carbons), -[OCH$_2$CH$_2$]$_m$ (m=number of repeat units); OH; S$_2$O$_5$; N$_2$O$_5$; amine, amide, carbonyl, Cl, Br, I, F, BF$_4$, CH$_2$Qt [Ar]

$R_f$ = H, any alkyl, RCOOH ($R^-$alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH ($R^-$alkyl ranging from 0-5 carbons), -[OCH$_2$CH$_2$]$_m$ (m=number of repeat units); OH; S$_2$O$_5$; N$_2$O$_5$; amine, amide, carbonyl Cl, Br, I, F, BF$_4$, CH$_2$Qt [Ar]

$R_f$ = H, any alkyl, RCOOH ($R^-$alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH ($R^-$alkyl ranging from 0-5 carbons), -[OCH$_2$CH$_2$]$_m$ (m=number of repeat units); OH; S$_2$O$_5$; N$_2$O$_5$; amine, amide, carbonyl Cl, Br, I, F, BF$_4$, CH$_2$Qt [Ar]

$R_f$ = H, any alkyl, RCOOH ($R^-$alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH ($R^-$alkyl ranging from 0-5 carbons), -[OCH$_2$CH$_2$]$_m$ (m=number of repeat units); OH; S$_2$O$_5$; N$_2$O$_5$; amine, amide, carbonyl Cl, Br, I, F, BF$_4$, CH$_2$Qt [Ar]

where $A$ is monovalent anion: Cl, Br, I, F, PF$_6$, BF$_4$, acetate, trifluoroacetate, ClO$_4$, N$_2$O$_5$, and

Q is monovalent cation: PR$_3$, R$^-$alkyl, cyclic alkyl, Aryl, 0-alkyl, 0-Aryl

0-alkyl, 0-Aryl
NR₃, R⁻alkyl, cyclic alkyl, N-heterocyclic ring, imidazole

(d)

where E₁=N, P, S, B
E₂=N, P, S, 0, B
n=1-10.

In yet another embodiment, the method comprises adding a catalyst compound to a fluid stream including an acid gas and an acid gas scrubbing solvent wherein that catalyst compound has a chemical formula:

where:
(a) Mis any group VII B through XII B element;
(b) x=neutral σ donor or monovalent anion; and
(c)

R₁= H, any alkyl, RCOOH (R⁻alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R⁻alkyl ranging from 0-5 carbons), -[OCH₂CH₂] and repeats thereof; OH; S0₃; N0₂; amine, amide, carbonyl, Cl, Br, I, F, BH₃, [CH₂Q]⁺[A]-; and
[CH₂Q]⁺[A]-

where A=monovalent anion: Cl, Br, I, F, PF₆, BF₄, acetate, trifluoroacetate, ClO₄, N0₃, and
Q=monovalent cation: P(R)₃, R⁻alkyl, cyclic alkyl, Aryl, 0-alkyl, 0-Aryl;
NR₃, R⁻alkyl, cyclic alkyl, N-heterocyclic ring, imidazole; and
R₂=CE; where C=any alkyl, cyclic alkyl, aryl, and E⁻OH, NH₂, N(R)₂, R⁻alkyl, cyclic alkyl, N-heterocyclic ring, imidazole, morpholine.

In one possible embodiment, the catalysts compound has a chemical formula:
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In one possible embodiment, the catalysts compound has a chemical formula:

In any of the embodiments, the neutral sigma donor or monovalent anion may be selected from a group consisting of H₂O, Cl, Br, I, acetate, triflate, perchlorate, nitro, pyridine, ethanol, methanol, tetrahydrofuran, dimethylsulfoxide, carbonate, bicarbonate, sulfate, nitrate and nitrite.

In any of the embodiments, the acid gas scrubbing solvent includes an amine or a mixture of amines, and/or no-amine based solvent such as alkali carbonate/bicarbonate solution.

In any of the embodiments, the acid gas scrubbing solvent includes a mixture of (a) a promoter amine and (b) a tertiary amine.
In one possible embodiment, the acid gas scrubbing solvent includes chemical compounds selected from a group including but not limited to, monoethanolamine (MEA), 1-amino-2-propanol (1AP), 3-amino-1-propanol, 2-amino-1-propanol, 2-amino-1-butanol, 1-amino-2-butanol, 3-amino-2-butanol, 2-(methylamino)ethanol (MAE), 2- (ethylamino)ethanol, morpholine, piperazine (PZ), 1-methylpiperazine (NMP), 2-methylpiperazine, hydroxypropyleridine, 2-piperidineethanol, N-N,N',N'-aminoethylpiperazine (AEP), aminopropylmorpholine, 4-aminopiperidine, 2-amino-2-methyl-1-propanol (AMP), diethanolamine (DEA), disopropanolamine (DIPA), glycine, alanine, -aminomethane, sarcosine, ethylene diamine (EDA), 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, methylhexanediol (MDEA), triethanolamine (TEA), dimethylethanolamine (DMEA), N,N,N,N'-tetramethylethylene diamine, diethylenoethanolamine, 1,4-dimethylpiperazine, N,N,N,N'-tetramethyl-1,6-hexanediamine, N,N,N','N'-tetramethyl-1,8-naphthalenediamine, diethylmonoethanolamine, dipropylmonoethanolamine, 1,4-dimethylpiperazine, N,N,N,N'-tetramethyl-1,6-hexanediame, N,N,N,'N'-tetramethyl-1,8-naphthalenediamine, diethylmonoethanolamine, diethylenetriamine, N,N,N,N',N'-pentamethylenediamine, N,N,N,N',N'-tetramethylenediamine, N,N,N,N',N'-tetrethylammonium chloride (TEA), dimethylethanolamine (DMEA), N,N,N,N',N'-tetramethylethylene diamine, N,N,N',N'-tetramethylene diamine, N,N,N',N'-tetramethylbutane-1,4-diamine, N,N,N',N'-tetramethyl-1,5-pentanediame, alkali carbonate, and mixtures thereof.

Further the catalyst compound is provided at a concentration of between about 0.05 mM and about 100 mM.

Various catalyst compounds are also claimed.

BRIEF DESCRIPTION OF THE DRAWING FIGURES

The accompanying drawings incorporated herein and forming a part of this specification, illustrate several aspects of the present method and together with the description serve to explain certain principles thereof. In the drawings:

FIG. 1 is a schematic illustration of a process for removing acid gas from a fluid stream utilizing solvent and thermal swing regeneration.

FIG. 2 is a plot of mass transfer coefficients versus carbon loading from WWC testing of 30 wt % MEA and 30 wt % MEA with 2 mM CAER-C3P at 40 °C.

DETAILED DESCRIPTION

This document relates generally to methods and catalysts for increasing overall mass transfer rate of acid gas scrubbing solvents as well as to novel transition metal monomer complexes incorporating a single transition metal atom.

The method may be broadly described as comprising adding a catalyst compound to a fluid stream including an acid gas and an acid gas scrubbing solvent. The catalyst compound has a chemical formula:

\[
\text{M} = H, \text{any alkyl, ROOH (R alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R alkyl ranging from 0-5 carbons), } [OCH}_m \text{ (m=number of repeat units); OH; S}_0 \text{; N}_0 \text{; amine, amide, carbonyl, Cl, Br, I, F, BH}_3 \text{, [CH}_2\text{Qt [Ar]
\]

\[
R_2 = \text{H, any alkyl, RCOOH (R alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R alkyl ranging from 0-5 carbons), } [OCH}_m \text{ (m=number of repeat units); OH; S}_0 \text{; N}_0 \text{; amine, amide, carbonyl Cl, Br, I, F, BH}_3 \text{, [CH}_2\text{Qt [Ar]
\]

\[
R_2 = \text{H, any alkyl, RCOOH (R alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R alkyl ranging from 0-5 carbons), } [OCH}_m \text{ (m=number of repeat units); OH; S}_0 \text{; N}_0 \text{; amine, amide, carbonyl Cl, Br, I, F, BH}_3 \text{, [CH}_2\text{Qt [Ar]
\]

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R_2 = \text{H, any alkyl, RCOOH (R alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R alkyl ranging from 0-5 carbons), } [OCH}_m \text{ (m=number of repeat units); OH; S}_0 \text{; N}_0 \text{; amine, amide, carbonyl Cl, Br, I, F, BH}_3 \text{, [CH}_2\text{Qt [Ar]
\]

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R_2 = \text{H, any alkyl, RCOOH (R alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R alkyl ranging from 0-5 carbons), } [OCH}_m \text{ (m=number of repeat units); OH; S}_0 \text{; N}_0 \text{; amine, amide, carbonyl Cl, Br, I, F, BH}_3 \text{, [CH}_2\text{Qt [Ar]
\]

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R_2 = \text{H, any alkyl, RCOOH (R alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R alkyl ranging from 0-5 carbons), } [OCH}_m \text{ (m=number of repeat units); OH; S}_0 \text{; N}_0 \text{; amine, amide, carbonyl Cl, Br, I, F, BH}_3 \text{, [CH}_2\text{Qt [Ar]
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R_2 = \text{H, any alkyl, RCOOH (R alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R alkyl ranging from 0-5 carbons), } [OCH}_m \text{ (m=number of repeat units); OH; S}_0 \text{; N}_0 \text{; amine, amide, carbonyl Cl, Br, I, F, BH}_3 \text{, [CH}_2\text{Qt [Ar]
\]

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R_2 = \text{H, any alkyl, RCOOH (R alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R alkyl ranging from 0-5 carbons), } [OCH}_m \text{ (m=number of repeat units); OH; S}_0 \text{; N}_0 \text{; amine, amide, carbonyl Cl, Br, I, F, BH}_3 \text{, [CH}_2\text{Qt [Ar]
\]

\[
R_2 = \text{H, any alkyl, RCOOH (R alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R alkyl ranging from 0-5 carbons), } [OCH}_m \text{ (m=number of repeat units); OH; S}_0 \text{; N}_0 \text{; amine, amide, carbonyl Cl, Br, I, F, BH}_3 \text{, [CH}_2\text{Qt [Ar]
\]

\[
R_2 = \text{H, any alkyl, RCOOH (R alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R alkyl ranging from 0-5 carbons), } [OCH}_m \text{ (m=number of repeat units); OH; S}_0 \text{; N}_0 \text{; amine, amide, carbonyl Cl, Br, I, F, BH}_3 \text{, [CH}_2\text{Qt [Ar]
\]

\[
R_2 = \text{H, any alkyl, RCOOH (R alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R alkyl ranging from 0-5 carbons), } [OCH}_m \text{ (m=number of repeat units); OH; S}_0 \text{; N}_0 \text{; amine, amide, carbonyl Cl, Br, I, F, BH}_3 \text{, [CH}_2\text{Qt [Ar]
\]

\[
R_2 = \text{H, any alkyl, RCOOH (R alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R alkyl ranging from 0-5 carbons), } [OCH}_m \text{ (m=number of repeat units); OH; S}_0 \text{; N}_0 \text{; amine, amide, carbonyl Cl, Br, I, F, BH}_3 \text{, [CH}_2\text{Qt [Ar]
\]
Specific catalyst compounds useful in this method include, but are not limited to the following:

-\( E_1 = N, P, S, B \)
-\( E_2 = N, P, S, O, B \)
-\( n = 1 - 10 \).

In another possible embodiment, the method may be broadly described as comprising adding a catalyst compound to a fluid stream including an acid gas and an acid gas scrubbing solvent. The catalyst compound has a chemical formula:

-\( R_1, R_2 = H, \text{any alkyl, RCOOH (R=alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R=alkyl ranging from 0-5 carbons), -[OCH_2CH_2]-m (m=number of repeat units); OH; S_0_2; amine, amide, carbonyl, Cl, Br, I, F, BH}_3, [CH_2Q^+]A^- \)
The method includes, but is not limited to the following:

Specific catalyst compounds useful in this embodiment of the method include, but are not limited to the following:

![Diagram]

where A=monovalent anion: Cl, Br, I, F, PF₆, BF₄, acetate, trifluoroacetate, CIO₄, NO₃, and
Q=monovalent cation: PR₃, R⁺-alkyl, cyclic alkyl, Aryl, 0-alkyl, 0-Aryl
NR₃, R⁺-alkyl, cyclic alkyl, N-heterocyclic ring, imidazole

where E₁⁻N, P, S, B
E₂⁻N, P, S, 0, B
n=1-10.
This catalyst contains a 2-coordinate, bidentate moiety from the ligand while monovalent anions occupy the other coordination sites.

Without limiting the scope of the method, a possible example of the system would consist of 0.001-0.1 wt% of catalyst containing a bidentate ligand and more than 20 wt % of amine(s), ethanolamine (MEA), methyldiethanolamine (MDEA), triethanolamine (TEA), dimethylethanolamine (DMEA), 1-amino-2-propanol (1A2P), 2-amino-1-propanol (1A2P), 3-aminopropanol, sodium ion, potassium ion, or combinations thereof, for examples.

Addition of catalyst CAER-C3P (2 mM) to a 30% ethanolamine solution resulted in a 25% increase in mass transfer rate over the working range of the solvent (see FIG. 2). As shown in FIG. 2, a greater enhancement in mass transfer is observed at higher carbon loadings (C/N>0.4, where C/N is the ratio of moles of carbon in solution compared to the moles of amine). This suggests that the rate of the catalyst is on the order of $10^5$ M-1s-1, two orders of magnitude higher than previous state-of-the-art catalyst, [Zn(cyclen)(H2O)]2+. Primary amines react very rapidly with CO2 and in order for a catalyst to contribute to the overall mass transfer second order rate constants must be of the magnitude of $10^5$ M-1s-1. This is the first example of catalysts containing a 2-coordinate, bidentate ligand showing activity in concentrated primary amine solutions.

The success of catalyst CAER-C3P in increasing overall mass transfer rates in 30 wt% MEA opened a new and novel area for catalyst development towards carbon capture purposes. Based on these results we developed a new family of CO2 hydration catalysts that are less synthetically demanding than previous catalysts and thus more cost effective. That new catalyst family is schematically illustrated below.

For any of the embodiments, the neutral sigma donor or monovalent anion may be selected from a group consisting of H2O, Cl, Br, I, acetate, triflate, perchlorate, nitro, pyridine, ethanol, methanol, tetrahydrofuran, dimethylsulfoxide, carbonate, bicarbonate, sulfate, nitrate and nitrite.

For any of the method embodiments the acid gas scrubbing solvent may include an amine. In one possible embodiment the acid gas scrubbing solvent includes a mixture of a...
a promoter amine, selected from a group of primary and secondary amines, and (b) a tertiary amine, and/or (c) non-amine chemical compounds.

Such a mixture is described in detail in copending U.S. patent application Ser. No. 13/853,186, filed on Mar. 29, 2013 and entitled "Solvent and Method for Removal of an Acid Gas from a Fluid Stream", the full disclosure of which is incorporated herein by reference. Promoter amines useful in the present method include, but are not limited to, the primary and secondary amines such as 3-N-sulfonylamino (SA), 3-aminoisopropanitrile (APN), diethyl 2-aminothene phosphonate (EtP2), N-methyltetrahydrothiophen-3-amine, 1,1-dioxide, 2,2'-sulfonyldihexanamine, 3,3'-sulfonyldi-methane, 4,4'-sulfonyldibutanenamine, 2-aminoethyl methyl sulfone, 4-aminobutanenitrile, 6-aminoheptanenitrile, 3-(methylamino)propanenitrile, diethyl [2-(methylamino)ethyl]phosphonate, diethyl (5-aminoethyl)phosphonate, diethyl (6-aminomethyl)phosphonate, 2-(tert-butoxy)ethan-1-amine, N-methyl-2-(2-methyl-2-propoxy)oxyethanamine and mixtures thereof.

Tertiary amines and carboxylate salts useful in the present method include but are not limited to methyl diethanolamine (MDEA), triethanolamine (TEA), N,N,N',N'-tetraalkyl-1,8-naphthalenediamine, N,N,N',N'-tetraalkylbenzylamine, 1,4-diallylpiperaizine, N,N,N',N'-tetraalkyl-1,6-hexanediamine, N,N,N',N'-tetraalkyl-1,5-pentanedianime, N,N,N',N'-tetraalkyl-1,4-butanediamine, N,N,N',N'-tetraalkyl-1,2-ethanediamine, N,N,N',N'-tetraakis(2-hydroxyethyl) ethylenediamine, N,N,N',N'-pentakallyldiethylenetriamine, N,N,N',N'-pentakallyldipropylaminetetramine, N,N,N',N'-pentakallylcyclohexylamine, N,N,N',N'-pentakallylcyclohexylamine, N,N,N',N'-triaalkylbis (aminoethyl)ether, N,N-dimethyl-2-(2-aminooxyethoxy) ethanol, alkali carbonates where alkyl represents any methyl, ethyl, propyl, butyl isomer, and mixtures thereof.

In one possible embodiment, the catalyst compound is provided in the fluid stream with a concentration of between 75.1 mM and 100 mM. In another possible embodiment the catalyst compound is provided in the fluid stream with a concentration of between 50.1 mM and 75.1 mM. In yet another possible embodiment, the catalyst compound is provided in the fluid stream with a concentration of between 50.1 mM and 75.1 mM. In yet another possible embodiment, the catalyst compound is provided in the fluid stream with a concentration of between 50.1 mM and 75.1 mM.

In any of the embodiments, the catalyst compound must be stable under the relatively high temperature conditions (e.g. between perhaps 70 and 170 °C) found within the stripper 12. The present catalyst compounds meet this requirement.

The following examples further illustrate how to synthesize or manufacture certain representative catalysts used in the method of increasing the overall mass transfer rate of acid gas scrubbing solvents.

Example 1

Preparation of [H₄L₇][Cl]: A 100 mL round bottom flask was charged with 30 mL EtOH and 1-(3-Formyl-4-hydroxybenzyl)-3-triethylphosphonium chloride (4.334 g 10.03 mmol). An ethanolic solution of 2-Amino-2-methyl propanol (0.912 g 10.24 mmol) was added drop wise to the solution. The mixture was heated at reflux for two hours. The solvent was removed under vacuum to give yellow solids. The yellow solids were washed with ethanol (3x15 mL) and diethyl ether (3x15 mL) and collected via filtration (4.425 g, 78%).

Preparation of CAER-C7z: A 100-mL round-bottom flask was charged with [H₄L₇][Cl] (5.043 g, 10.01 mmol) and EtOH (30 mL) and was added to make a colorless slurry. Triethyl amine 3.2 mL (23.023 mmol) was added slowly under vigorous stirring. An ethanolic solution of ZnCl₂ (1.632 g, 12.0 mmol) was added drop wise to the mixture. The mixture was heated at reflux for two hours. The solution was cooled to 25 °C and a pale yellow solid precipitated out of solution. The pale yellow solid was collected by filtration and washed with ethanol (3x15 mL) and diethyl ether (3x15 mL) to give the desired product (4.852 g, 85%).

Example 2

Preparation of [H₄L₈][Cl]: A 100 mL round bottom flask was charged with EtOH (30 mL) and 1-(3-Formyl-4-hydroxybenzyl)-3-triethylphosphonium chloride (4.327 g, 10.01 mmol). An ethanolic solution of monoethanolamine (0.9 mL, 15.01 mmol, 5 mL) was added drop wise to the solution and the mixture was heated at reflux for two hours. The solvent was removed under reduced pressure to give a yellow residue. Diethyl ether was added to the reaction vessel and stirred overnight to give a yellow powder which was collected via filtration and washed with diethyl ether (3x30 mL) (4.452 g, 93%).

Preparation of CAER-C8z: A 100-mL round-bottom flask was charged with [H₄L₈][Cl] (4.812 g, 10.12 mmol) and EtOH (30 mL) and was added to make a clear solution. Triethyl...
ylamine (3.2 mL, 23.023 mmol) was added slowly while stirring. An ethanolic solution of ZnCl₂ (1.687 g, 12.35 mmol, 5 mL) was added dropwise to the mixture. The mixture was heated at reflux for two hours. The mixture was cooled to 25 °C. and a pale yellow solid was collected via filtration and washed with ethanol (3x15 mL) then diethyl ether (3x15 mL) to give the desired product (4.688 g, 86%).

Example 3

Preparation H₂L₉: A 100-mL round-bottom flask was charged salicylaldehyde (1.95 mL, 16.5 mmol) and EtOH (10 mL) to make a clear solution. Ethanolamine (1 mL, 16.6 mmol) was added dropwise to the above solution with continuous stirring. The solution was stirred at room temperature (25 °C.) for one hour and the solvent was removed under vacuum to give the product as a viscous, yellow-orange oil (2.219 g, 81%).

Preparation of CAER-C₉z: A 100-mL round-bottom flask was charged with H₂L₉ (1.656 g, 10.01 mmol) and EtOH (30 mL) to make a clear solution. Triethylamine (3.2 mL, 23.0 mmol) was added while stirring. An ethanolic solution of ZnCl₂ (1.687 g, 12.35 mmol, 5 mL) was added dropwise to the mixture. The mixture was heated at reflux for two hours. The mixture was cooled to 25 °C. and a pale yellow solid was collected via filtration and washed with ethanol (3x15 mL) then diethyl ether (3x15 mL) to give the desired product (2.199 g, 80%).

Example 4

Preparation of H₂L₁₀: A 100-mL round-bottom flask was charged salicylaldehyde (3 mL, 28.3 mmol) and EtOH (10 mL) to make a clear solution. 2-Amino-2-methyl-1-propanol (2.677 g, 16.6 mmol) was added to the above solution with continuous stirring. The solution was stirred at room temperature for one hour and the solvent was removed under vacuum to give a yellow residue. The yellow residue was dissolved in dichloromethane (5 mL) and n-pentane was added (20 mL) to produce a yellow powder. The yellow powder was collected via filtration and washed with ether (3x15 mL) to give the desired product (4.767 g, 87%).

Preparation of CAER-C₁₀z: A 100-mL round-bottom flask was charged with H₂L₁₀ (1.933, 10.0 mmol) and EtOH (30 mL) to make a clear solution. Triethylamine (3.2 mL, 23 mmol) was added while stirring. An ethanolic solution of ZnCl₂ (1.687 g, 12.35 mmol) was added dropwise to the mixture. The mixture was stirred for 48 hr at room temperature (25 °C.). The solvent was reduced under vacuum to 5 mL and acetonitrile was added to the solution to give a pale yellow powder. The pale yellow solid was collected via filtration and washed with acetonitrile (3x15 mL) then diethyl ether (3x15 mL) to give the desired product (2.456 g, 81%).

Example 5

Preparation of H₂L₁₁: A 100-mL round-bottom flask was charged salicylaldehyde (2.7 mL, 25 mmol) and EtOH (10 mL) to make a clear solution. 2-methoxymethylamine (2 mL, 23 mmol) was added to the solution with continuous stirring. The solution was stirred at room temperature for two hour and the solvent was removed under reduced vacuum to give the desired product as a dark yellow-orange, viscous liquid (3.769 g, 83%).

Preparation of CAER-C₁₁z: A 100-mL round-bottom flask was charged with H₂L₁₁ (1.793, 10.01 mmol) and acetonitrile (30 mL) to make a clear solution. Triethylamine (3.2 mL, 23.0 mmol) was added while stirring. An acetonitrile solution of ZnCl₂ (1.687 g, 12.35 mmol) was added dropwise to the mixture. The mixture was heated at reflux for 3 hours. The solvent was removed under reduced pressure to give a yellow oil. Diethyl ether was added to the oil to give a yellow powder which was collected via filtration. The yellow powder was washed with diethyl ether (3x15 mL) to give the desired product (2.444 g, 85%).

Example 6

Preparation of H₂L₁₂: A 100-mL round-bottom flask was charged salicylaldehyde (2.06 mL, 19.5 mmol) and EtOH (10 mL) to make a clear solution. 4-(Aminomethyl)piperidine (2.0256 g, 17.8 mmol) was added to the solution with continuous stirring. The solution was stirred at room temperature for two hours at which point the solvent was removed under reduced pressure to give the desired product as a yellow powder (3.521 g, 87%).

Preparation of CAER-C₁₂z: A 100-mL round-bottom flask was charged with H₂L₁₂ (2.19, 10.0 mmol) and acetonitrile (30 mL) to make a clear solution. Triethylamine (3.2 mL, 23.023 mmol) was added while stirring. An acetonitrile solution of ZnCl₂ (1.776 g, 12.50 mmol) was added dropwise to the mixture. The mixture was stirred for 48 hr at room temperature (25 °C.). The solvent was reduced under vacuum to 5 mL and acetonitrile was added to the solution to give a pale yellow powder. The pale yellow solid was collected via filtration and washed with acetonitrile (3x15 mL) then diethyl ether (3x15 mL) to give the desired product (2.456 g, 81%).
added dropwise to the mixture. The mixture was stirred at room temperature (25°C) for 3 hours at which point a yellow powder was generated. The yellow powder was collected via filtration and washed with acetonitrile (3x15 mL) and diethyl ether (3x15 mL) to give the desired product (2.668 g, 83%).

Example 7

Preparation of (H2L7)[BF4]: A 100 mL round bottom flask was charged with EtOH (30 mL) and 5-(1-methylimidazolymethyl)-2-hydroxybenzaldehyde chloride (2.528 g, 10.0 mmol). An ethanolic solution of 2-Amino-2-methyl propanol (0.912 g 10.24 mmol) was added drop wise to the solution. The mixture was heated at reflux for two hours. The solvent was removed under reduced pressure to give a yellow powder which was collected via filtration and washed with ethanol (3x15 mL) and diethyl ether (3x15 mL) to give the desired product (2.872 g, 89%).

Preparation of CAER-C13z: A 100 mL round-bottom flask was charged with (H2L13)[Cl] (3.238 g, 10.01 mmol) and EtOH (30 mL) to make a clear solution. Triethylamine (3.2 mL, 23.023 mmol) was added while stirring. An ethanolic solution of ZnCl2 (1.687 g, 13.2 mmol, 5 mL) was added dropwise to the mixture. The mixture was heated at reflux for two hours to give a bright yellow powder which was collected via filtration and washed with ethanol (3x15 mL) then diethyl ether (3x15 mL) to give the desired product (1.8449 g, 62%).

Example 8

Preparation of (H2L7)[BF4]: A 100 mL round bottom flask was charged with EtOH (30 mL) and 5-(triphenylphosphine-methyl)-2-hydroxybenzaldehyde tetrafluoroborate (4.842 g, 10.0 mmol) of. An ethanolic solution of 2-Amino-2-methyl propanol (0.912 g 10.2 mmol) was added drop wise to the solution. The mixture was heated at reflux for two hours. The solvent was removed under reduced pressure to give a yellow residue. Diethyl ether was added to the reaction vessel and stirred overnight to give a yellow powder which was collected via filtration and washed with diethyl ether (3x15 mL) to give the desired product (4.956 g, 89%).

Preparation of CAER-C14z: A 100-mL round-bottom flask was charged with (H2L7)[BF4] (1.1108 g, 2.002 mmol) and MeOH (50 mL) to make a colorless slurry. Triethylamine (0.332 mL, 2.30 mmol) was added to the stirred mixture. An ethanolic solution of ZnBF4 (0.2868 g, 1.12 mmol, 5 mL) was added dropwise to the mixture. The mixture was heated at reflux for one hour. The solution mixture was cooled to room temperature (25°C) to give a yellow powder which was collected via filtration and washed with ethanol (3x15 mL) and diethyl ether (3x15 mL) to give the desired product (1.011 g, 86%).

Example 9

Preparation of CAER-C15z: A 100-mL round-bottom flask was charged with (H2L9) (1.986 g, 12.02 mmol) and EtOH (15 mL) to make a clear solution. Triethylamine (1.95 mL, 13.8 mmol) was added while stirring. An ethanolic solution of ZnCl2 (1.804 g, 13.2 mmol, 5 mL) was added dropwise to the mixture. The mixture was heated at reflux for two hours to give a bright yellow powder which was collected via filtration and washed with ethanol (3x15 mL) then diethyl ether (3x15 mL) to give the desired product (1.8449 g, 62%).

Example 10

Preparation of CAER-C16z: A 100-mL round-bottom flask was charged with (H2L10) (5.500 g, 28.5 mmol) and EtOH (20 mL) to make a clear solution. Triethylamine (7.93 mL, 57.0 mmol) was added while stirring. An ethanolic solution of ZnCl2 (4.264 g, 30.8 mmol, 5 mL) was added dropwise to the mixture. The mixture was stirred at room
temperature (25°C) for 48 hr. The solvent was removed under reduced pressure to give a yellow residue and acetonitrile was added to give a yellow powder which was collected via filtration and washed with acetonitrile (3x15 mL) then diethyl ether (3x15 mL) to give the desired product (4.1758 g, 51%).

Example 11

Preparation of CAER-C3p: To a 100-mL round-bottom flask was added [H2LP]Cl2 (5.002 g, 5.63 mmol), EtOH (40 mL), and triethylamine (1.75 mL, 12.0 mmol) was added to give a clear yellow solution. Zinc chloride (1.363 g, 10.00 mmol) dissolved in EtOH (10 mL) was added, producing a pale yellow slurry. The reaction flask was immersed in a silicon fluid bath at 85°C and was stirred for 3 h, producing a pale yellow precipitate which was collected via filtration through a medium porosity glass fritted funnel. The pale yellow powder was washed with EtOH then ether (3x20 mL) and air dried to give the desired product (5.679 g, 93%).

The foregoing has been presented for purposes of illustration and description. It is not intended to be exhaustive or to limit the embodiments to the precise form disclosed. Obvious modifications and variations are possible in light of the above teachings. All such modifications and variations are within the scope of the appended claims when interpreted in accordance with the breadth to which they are fairly, legally and equitably entitled.

What is claimed:

1. A compound having a chemical formula:

where:

(a) M is any group VII B through XII B element;
(b) x = neutral sigma donor or monovalent anion; and
(c)
where $A =$ monovalent anion: Cl, Br, I, F, PF$_6, BF_4,$
acetate, trifluoroacetate, ClO$_4, NO_3,$ and
Q=monovalent cation: P(R)$_3, R^+=$alkyl, cyclic alkyl, Aryl,
0-alkyl, 0-Aryl;
N(R)$_3, R^+=$alkyl, cyclic alkyl, N-heterocyclic ring, imida-
zole; and
R$_2^+=$CE; where C$^+=$any alkyl, cyclic alkyl, aryl, and E$^+=$OH
or NH$_2.$

2. A compound consisting of a chemical formula:

$$R_1 = H, \text{any alkyl, } RCOOH (R^+=$alkyl ranging from 0-10
carbons); OligoPEG, phosphate, ROH (R$^+=$alkyl rang-
ing from 0-5 carbons); OH; S$O_3; NO_2; \text{amine, amide,}
carbonyl, Cl, Br, I, F, BH$_3, [CH_2Q]^+[A]^{-}; \text{and}
[CH_2Q]^+[A]^{-}$

3. A method of increasing overall mass transfer rate of
acid gas scrubbing solvents, comprising:
adding a catalyst compound to a fluid stream including an
acid gas and an acid gas scrubbing solvent, said catalyst
compound having a chemical formula:
where:

(a) Mis any group VII B through XII B element;
(b) $x$=neutral si$_{m,a}$ donor or monovalent anion; and
(c) $R_1$, $R_2$, $R_3$=any alkyl, RCOOH (R=alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R=alkyl ranging from 0-5 carbons); OH; SO$_3$; NO$_2$; amine, amide, carbonyl Cl, Br, I, F, BH$_3$; and [CH$_2$Q]+[A]~

where A=monovalent anion: Cl, Br, I, F, PF$_6$, BF$_4$, acetate, trifluoroacetate, C$_{10}$H$_{14}$, N$_2$O, and
Q=monovalent cation: P(R)$_3$, R=alkyl, cyclic alkyl, Aryl, 0-alkyl, 0-aryl
N(R)$_3$, R=alkyl, cyclic alkyl, N-heterocyclic ring, imidazole R$_2$=CE; where C=any alkyl, cyclic alkyl, aryl, and E=OH or NH$_2$.

4. The method of claim 3, wherein said neutral si$_{m,a}$ donor or monovalent anion is selected from a group consisting of $\text{H}_2$O, Cl, Br, F, I, acetate, triflate, perchlorate, nitro, pyridine, ethanol, methanol, tetrahydrofuran, dimethylsulfoxide, carbonate, bicarbonate, sulfate, nitrate, nitrite.

5. The method of claim 3, wherein said acid gas scrubbing solvent includes an amine.

6. The method of claim 3, wherein said acid gas scrubbing solvent includes a mixture of a primary amine, secondary amine, or a tertiary amine.

7. The method of claim 3, wherein said acid gas scrubbing solvent includes a material selected from a group consisting of monoethanolamine (MEA), 1-amino-2-propanol (1A2P), 3-amino-1-propanol, 2-amino-1-propanol, 2-amino-1-butanol, 1-amino-2-butanol, 3-amino-2-butanol, 2-(alkylamino) ethanolamine (MAE), diglycolamine, morpholine, piperazine (PZ), 1-methylpiperazine (NMP), 2-methylpiperazine, hydroxypiperidine, hydroxyalkylpiperazine, 2-piperidineethanol, N-aminoethylpiperazine (AEP), aminopropylmorpholine, 4-aminopiperidine, 3-aminopiperidine, 2-amino-piperidine, diethanolamine, 2-amino-2-methyl-1-propanol (AMP), diethanolamine (DEA), disopropanamine (DIPA), glycine, alanine, R-alanine, sarcosine, isopropanolamine, benzylamine, methyl-diethanolamine (MDEA), triethanolamine (TEA), alkali carbonate, N,N,N-dialkylethanolamine, N,N,N,N-tetraalkyl-1,8-naphthalenediamine, N,N-dialkylbenzylamine, 1,4-dialkylpiperazine,
N,N,N',N'-tetraalkyl-1,6-hexanediameine, N,N,N',N'-tetraalkyl-1,5-pentanediameine, N,N,N',N'-tetraalkyl-1,4-butanediameine, N,N,N',N'-tetraalkyl-1,3-propanediameine, N,N,N',N'-tetraalkyl-1,2-ethanediameine, N,N,N',N'-tetraakis (2-hydroxyethyl)ethylenediameine, N,N,N',N',N''-pentaalkyl-

diethylenetriameine, N,N,N',N',N''-pentaalkylpropylam-

inetamine, N,N'-dialkylcyclohexyamine, N,N,N',N'-
tetraalkylbis(aminooethyl)ether, N,N'-dimethyl-2(2-
aminoethoxy)ethanol, where alkyl represents any methyl, ethyl, propyl, butyl isomer, and mixtures thereof.

8. The method of claim 3, wherein said catalyst compound is provided at a concentration of between about 0.05 mM and about 100 mM.

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