University of Kentucky

UKnowledge

Center for Applied Energy Research Faculty Patents

Center for Applied Energy Research

5-1-2018

Method of Increasing Mass Transfer Rate of Acid Gas Scrubbing Solvents

Cameron Anthony Lippert University of Kentucky, cameron.lippert@uky.edu

Kunlei Liu University of Kentucky, kunlei.liu@uky.edu

Christine Marie Brandewie

Joseph Eugene Remias University of Kentucky, joe.remias@uky.edu

Moushumi Sarma University of Kentucky, moushumi.sarma@uky.edu

Follow this and additional works at: https://uknowledge.uky.edu/caer_patents

Part of the Catalysis and Reaction Engineering Commons Right click to open a feedback form in a new tab to let us know how this document benefits you.

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. https://uknowledge.uky.edu/caer_patents/50

This Patent is brought to you for free and open access by the Center for Applied Energy Research at UKnowledge. It has been accepted for inclusion in Center for Applied Energy Research Faculty Patents by an authorized administrator of UKnowledge. For more information, please contact UKnowledge@lsv.uky.edu.



US009957284B2

(12) United States Patent

Lippert et al.

(54) METHOD OF INCREASING MASS TRANSFER RATE OF ACID GAS SCRUBBING SOLVENTS

- (71) Applicant: University of Kentucky Research Foundation, Lexington, KY (US)
- (72) Inventors: Cameron A. Lippert, Lexington, KY (US); Kunlei Liu, Lexington, KY (US); Christine Marie Brandewie, Lexington, KY (US); Joseph Eugene Remias, Woodbridge, VA (US); Moushumi Sarma, Lexington, KY (US)
- (73) Assignee: UNIVERSITY OF KENTUCKY RESEARCH FOUNDATION, Lexington, KY (US)
- (*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 61 days.
- (21) Appl. No.: 14/593,399
- (22) Filed: Jan. 9, 2015
- (65) Prior Publication Data

US 2015/0196875 A1 Jul. 16, 2015

Related U.S. Application Data

- (60) Provisional application No. 61/925,693, filed on Jan. 10, 2014.
- (51) Int. Cl.

BOID 53/14	(2006.01)
C07F 1/08	(2006.01)
C07F 1/10	(2006.01)
C07F 1/12	(2006.01)
C07F 3/06	(2006.01)
C07F 3/08	(2006.01)
C07F 3/10	(2006.01)
C07E 9/00	(2006.01)

(10) Patent No.: US 9,957,284 B2

(45) Date of Patent: May 1, 2018

C07F 11/00	(2006.01)
C07F 13/00	(2006.01)
	(Continued)

- (58) Field of Classification Search NoneSee application file for complete search history.
- (56) References Cited

U.S. PATENT DOCUMENTS

4,231,995	Α	11/1980	Campbell et al.	
5,674,459	А	10/1997	Gohara et al.	
6,890,497	B2	5/2005	Rau et al.	
		(Continued)		

FOREIGN PATENT DOCUMENTS

WO 1999026714 A1 6/1999

OTHER PUBLICATIONS

Zeng et al., "Synthesis, Oxygenation and Catalytic Oxidation Performance of Crown Ether-Containing Schiff Base-Transition Metal Complexes." Adv. Synth. Catal. (2004), 346, 1385-1391.*

Primary Examiner - Daniel Berns (74) Attorney, Agent, or Firm - King & Schickli, PLLC

(57) ABSTRACT

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



(51) Int. Cl. *C07F 15/00 C07F 19/00* (2006.01) (2006.01)

(56) **References Cited**

U.S. PATENT DOCUMENTS

6,923,852	B2	8/2005	Vrotsos
7,255,842	B1	8/2007	Yeh et al.
7,282,189	B2	10/2007	Zauderer
7,514,053	B2	4/2009	Johnson et al.
7,618,478	B2	11/2009	Kumar
7,678,351	B2	3/2010	Iyer et al.
7,699,909	B2	4/2010	Lackner et al.
7,722,842	B2	5/2010	Park et al.
7,739,864	B2	6/2010	Finkenrath et al.
7,766,999	B2	8/2010	На
7,794,690	B2	9/2010	Abatzoglou et al.
7,811,359	B2	10/2010	Tandon et al.
7,819,951	B2	10/2010	White et al.
7,827,778	B2	11/2010	Finkenrath et al.
7,829,053	B2	11/2010	Constantz
7,833,328	B2	11/2010	Lackner et al.

7 842 126 B1	11/2010	Dilmore et al
7 842 264 B2	11/2010	Cooper et al
7 846 240 B2	12/2010	Gal et al
7.846.407 B2	12/2010	Hu
7.850.763 B2	12/2010	White et al.
7,862,788 B2	1/2011	Gal et al.
7,879,305 B2	2/2011	Reddy et al.
7,887,694 B2	2/2011	Constantz et al.
7,895,822 B2	3/2011	Hoffmann et al.
7,896,694 B2	3/2011	Schumann et al.
7,896,953 B1	3/2011	Goswami et al.
7,901,485 B2	3/2011	Mccutchen
7,901,487 B2	3/2011	Rochelle
7,901,488 B2	3/2011	Rochelle et al.
7,906,086 B2	3/2011	Comrie
7,914,758 B2	3/2011	Murray et al.
7,922,792 B1	4/2011	Soong et al.
7,947,239 B2	5/2011	Lackner et al.
7,947,240 B2	5/2011	Vandor
7,966,829 B2	6/2011	Finkenrath et al.
7,993,432 B2	8/2011	Wright et al.
8,012,453 B2	9/2011	Saxena

*cited by examiner





50

METHOD OF INCREASING MASS TRANSFER RATE OF ACID GAS SCRUBBING SOLVENTS

This document claims priority of U.S. Provisional Patent 5 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 gasses or sour gas, such as $C0_2$ in particular, from natural gas and in oil refining has been an extensively practiced technology. The industrial removal of CO_2 from natural gas dates back to the 1930's. In the 21 st 20 century, due to the potential impact of anthropogenic $C0_2$ emissions on the climate, post-combustion C02 capture has gained tremendous attention. While several technologies exist for the removal of acid gasses one of the most commonly employed practices is the use of aqueous amines. 25 Of these amines, tertia_{rv} amines are often used for natural gas applications due to their low energy of regeneration. For post-combustion C02 capture applications primary and secondary amines tend to be in part favored by their faster rate at the low gaseous CO_2 concentration condition. Regardless 30 of the application, the mass transfer rate in the absorber column dictates the size of the columni (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 35 circulated between the absorber 10 and stripper 12. The gas, containing $C0_2$, enters the bottom of the absorber where it contacts the aqueous amine absorbent removing it from the gas stream. The liquid solution, $C0_2$ rich amine solution, is then passed through a heat exchanger 14 to improve effi- $_{40}$ ciency before being heated to a higher temperature in the stripper 12. The stripper 12 removes the CO_2 as a gas from the amine solution to produce a lean, or CO2 deficient solution. The lean solution is returned to the absorber 10 by way of the heat exchanger 14 to repeat the process. 45

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 55 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:



(a) M is any group VII B through XII B element;
(b) x=neutral si_{g m}a donor or monovalent anion;

(c)

where:



where R_1 = H, any alkyl, RCOOH (R⁼alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R⁼alkyl ranging from 0-5 carbons), -[OCH₂CH₂]-m (m=number of repeat units); OH; S0₃; N0₂; amine, amide, carbonyl, Cl, Br, I, F, BH₃, [CH₂Qt [Ar

 R_2 = H, any alkyl, RCOOH (R=alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R=alkyl ranging from 0-5 carbons), -[OCH₂CH₂]-m (m=number of repeat units); OH; S0₃; N0₂; amine, amide, carbonyl Cl, Br, I, F, BH₃, [CH₂Qt [Ar

 R_3 = H, any alkyl, RCOOH (R=alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R=alkyl ranging from 0-5 carbons), -[OCH₂CH₂]-m (m=number of repeat units); OH; SO₃; NO₂; amine, amide, carbonyl Cl, Br, I, F, BH₃, [CH₂Qt [Ar

 R_4 = H, any alkyl, RCOOH (R=alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R=alkyl ranging from 0-5 carbons), -[OCH₂CH₂]-m (m=number of repeat units); OH; S0₃; N0₂; amine, amide, carbonyl Cl, Br, I, F, BH₃, [CH₂Qt [A]-

 R_5 = H, any alkyl, RCOOH (R⁼alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R⁼alkyl ranging from 0-5 carbons), -[OCH₂CH₂]-m (m=number of repeat units); OH; S0₃; N0₂; amine, amide, carbonyl Cl, Br, I, F, BH₃, [CH₂Qt [A]-

 R_6 = H, any alkyl, RCOOH (R=alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R=alkyl ranging from 0-5 carbons), -[OCH₂CH₂]-m (m=number of repeat units); OH; S0₃; N0₂; amine, amide, carbonyl Cl, Br, I, F, BH₃, [CH₂Qt [Ar

- 60 R₇= H, any alkyl, RCOOH (R=alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R=alkyl ranging from 0-5 carbons), -[OCH₂CH₂]-m (m=number of repeat units); OH; S0₃; N0₂; amine, amide, carbonyl Cl, Br, I, F, BH₃, [CH₂Qt [Ar
- 65 R₈= H, any alkyl, RCOOH (R⁼alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R⁼alkyl ranging from 0-5 carbons), -[OCH₂CH₂]-m (m=number of repeat

10

15

25

40

45

50

55

60

units); OH; S0_3; N0_2; amine, amide, carbonyl Cl, Br, I, F, BH_3, $[\rm CH_2Q]^+[A]^-;$ and

 $[CH_2Q]^+[A]^- =$



where A=monovalent anion: Cl, Br, I, F, PF_6 , BF_4 , acetate, trifluoroacetate, $Cl0_4$, $N0_3$, and

Q=monovalent cation: PR_3 , $R^=$ alkyl, cyclic alkyl, Ary!, 0-alkyl, 0-Aryl

 $\mathrm{NR}_3,\,\mathrm{R}{=}\,\mathrm{alkyl},\,\mathrm{cyclic}$ alkyl, N-heterocyclic ring, imidazole; and

(d)



where $E_1 = N, P, S, B$ $E_2 = N, P, S, 0, B$

n=1-10.

In an alternative embodiment, the method comprises adding a catalyst compound to a fluid stream including an 35 acid gas and an acid gas scrubbing solvent wherein that catalyst compound has a chemical formula:



where:

M is any group VII B through XII B element;

(b) x=neutral si_{g m}a donor or monovalent anion;
(c)





where R₁= H, any alkyl, RCOOH (R⁼alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R⁼alkyl ranging from 0-5 carbons), -[OCH₂CH₂]-m (m=number of repeat units); OH; S0₃; N0₂; amine, amide, carbonyl, Cl, 20 Br, I, F, BH₃, [CH₂Qt [Ar

 R_2 = H, any alkyl, RCOOH (R=alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R=alkyl ranging from 0-5 carbons), -[OCH₂CH₂]-m (m=number of repeat units); OH; S0₃; N0₂; amine, amide, carbonyl Cl, Br, I, F, BH₃, [CH₂Qt [Ar

 R_3 = H, any alkyl, RCOOH (R=alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R=alkyl ranging from 0-5 carbons), -[OCH₂CH₂]-m (m=number of repeat units); OH; S0₃; N0₂; amine, amide, carbonyl Cl, Br, I, F, BH₃, [CH₂Qt [A]-

 R_4 = H, any alkyl, RCOOH (R=alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R=alkyl ranging from 0-5 carbons), -[OCH₂CH₂]-m (m=number of repeat units); OH; S0₃; N0₂; amine, amide, carbonyl Cl, Br, I, F, BH₃, [CH₂Qt [A]-

 R_5 = H, any alkyl, RCOOH (R=alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R=alkyl ranging from 0-5 carbons), -[OCH₂CH₂]-m (m=number of repeat units); OH; S0₃; N0₂; amine, amide, carbonyl Cl, Br, I, F, BH₃, [CH₂Qt [A]-

 R_6 = H, any alkyl, RCOOH (R=alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R=alkyl ranging from 0-5 carbons), -[OCH₂CH₂]-m (m=number of repeat units); OH; S0₃; N0₂; amine, amide, carbonyl Cl, Br, I, F, BH₃, [CH₂Qt [A]-

 R_{7} = H, any alkyl, RCOOH (R⁼alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R⁼alkyl ranging from 0-5 carbons), -[OCH₂CH₂]-m (m=number of repeat units); OH; S0₃; N0₂; amine, amide, carbonyl Cl, Br, I, F, BH₃, [CH₂Qt [Ar

 R_8 = H, any alkyl, RCOOH (R=alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R=alkyl ranging from 0-5 carbons), -[OCH₂CH₂]-m (m=number of repeat units); OH; S0₃; N0₂; amine, amide, carbonyl Cl, Br, I, F, BH₃, [CH₂Qt [Ar; and

[CH₂Qt [Ar



where A=monovalent anion: Cl, Br, I, F, PF_6 , BF_4 , 65 acetate, trifluoroacetate, $Cl0_4$, $N0_3$, and

Q=monovalent cation: PR₃, R⁼alkyl, cyclic alkyl, Ary!, 0-alkyl, 0-Aryl

10

ъ

25

30

35

40

 $NR_3,\,R^{=}alkyl,\,cyclic alkyl,\,N\mbox{-heterocyclic ring, imidazole}$

$$E = E_{E_{1}}^{R_{9}} = \frac{R_{9} R_{10} R_{11}}{R_{10} R_{12}} R_{12} + \frac{R_{9} R_{10} R_{10}}{R_{11} R_{11}}$$

where $E_1=N, P, S, B$ $E_2=N, P, S, 0, B$ 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 sigma donor or monovalent anion; and

(c)





 R_1 = 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]-=

50

55



- where A=monovalent anion: Cl, Br, I, F, PF_{6} , BF_{4} , acetate, trifluoroacetate, $C10_{4}$, $N0_{3}$, and
- Q=monovalent cation: P(R)₃, R⁼alkyl, cyclic alkyl, Ary!, 0-alkyl, 0-Aryl;
- ⁹ 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)₃, R⁼alkyl, cyclic alkyl, N-heterocyclic ring, ⁶ imidazole, morpholine.

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



7

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



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



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



In one possible embodiment, the catalysts compound has ${}_{45}$ a chemical formula:



In one possible embodiment, the catalysts compound has 5 a chemical formula:



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



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



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



40 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 H_20 , Cl, Br, F, I, acetate, triflate, perchlorate, nitro, 0 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 one possible embodiment the acid gas scrubbing solvent includes a mixture of (a) a promoter amine and (b) a tertiary amine.

where:

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 (1A2P), 3-amino-1-propanol, 2-amino-5 1-propanol, 2-amino-1-butanol, l-amino-2-butanol, 3-amino-2-butanol, 2-(methylamino)ethanonol (MAE). 2-(ethylamino)ethanol, morpholine, piperazine (PZ), 1-methylpiperazine (NMP), 2-methylpiperazine, hydroxyp- 10 iperadine, 2-piperidineethanol, N-aminoethylpierazine (AEP), aminopropylmorpholine, 4-aminopiperidine, 2-amino-2-methyl-1-propanol (AMP), diethanolamine (DEA), diisopropanolamine (DIPA), glycine, alanine, -al-15 annine, sarcosine, ethylene diamine (EDA), 1,3-propanediamine, 1,4-butanediamine, 1,5-pentanediamine, 1,6-hexanediamine, methyldiethanolamine (MDEA), triethanolamine (TEA), dimethylethanolamine (DMEA), N,N,N',N'-tetram- 20 ethy1-1,8-naphthalenediamine, diethylmonoethanolamine, 1,4-dimethylpiperazine, N dipropylmonoethanolamine, N,N',N'-tetramethyl-1,6-hexanediamine, N,N,N',N'-tetrakis (2-hydroxyethyl)ethylenediamine, N,N,N',N',N"-pentam-25 ethyldiethylenetriamine, N,N,N',N'-tetramethylethylenediamine, N,N,N',N'-tetramethylpropane-1,3-diamine, N,N,N', N'-tetramethylbutane-1,4-diamine, N,N,N',N'-tetramethyl-1,5-pentanediamine, alkali carbonate, and mixtures thereof. 30

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 the specification, illustrate several aspects of the present method and together with the description 40 serve to explain certain principles thereof. In the drawings:

FIG. 1 is a schematical 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 45 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 55 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:



10

(b) M is any group VII B through XII B element;(b) x=neutral sigma donor or monovalent anion;(c)



where R=H, 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; S0₃; N0₂; amine, amide, carbonyl, Cl, Br, I, F, BH₃, [CH₂Qt [Ar

R₂= H, any alkyl, RCOOH (R⁼alkyl ranging from 0-10 35 carbons); OligoPEG, phosphate, ROH (R⁼alkyl ranging from 0-5 carbons), -[OCH₂CH₂]-m (m=number of repeat units); OH; S0₃; N0₂; amine, amide, carbonyl Cl, Br, I, F, BH₃, [CH₂Qt [Ar

 R_3 = H, any alkyl, RCOOH (R⁼alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R⁼alkyl ranging from 0-5 carbons), -[OCH₂CH₂]-m (m=number of repeat units); OH; S0₃; N 0₂; amine, amide, carbonyl Cl, Br, I, F, BH₃, [CH₂Qt [Ar

 R_4 = H, any alkyl, RCOOH (R=alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R=alkyl ranging from 0-5 carbons), -[OCH₂CH₂]-m (m=number of repeat units); OH; S0₃; N 0₂; amine, amide, carbonyl Cl, Br, I, F, BH₃, [CH₂Qt [A]-

 R_5 = H, any alkyl, RCOOH (R⁼alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R⁼alkyl ranging from 0-5 carbons), -[OCH₂CH₂]-m (m=number of repeat units); OH; S 0₃; N 0₂; amine, amide, carbonyl Cl, Br, I, F, BH₃, [CH₂Qt [A]-

 R_6 = H, any alkyl, RCOOH (R=alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R=alkyl ranging from 0-5 carbons), -[OCH₂CH₂]-m (m=number of repeat units); OH; S0₃; N 0₂; amine, amide, carbonyl Cl, Br, I, F, BH₃, [CH₂Qt [Ar

⁶⁰ R₇= H, any alkyl, RCOOH (R⁼alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R⁼alkyl ranging from 0-5 carbons), -[OCH₂CH₂]-m (m=number of repeat units); OH; S0₃; N 0₂; amine, amide, carbonyl Cl, Br, I, F, BH₃, [CH₂Qt [Ar

68 R₈= H, any alkyl, RCOOH (R⁼alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R⁼alkyl ranging from 0-5 carbons), -[OCH₂CH₂]-m (m=number of repeat

units); OH; S03; N02; amine, amide, carbonyl Cl, Br, I, F, BH_3 , $[CH_2Q]^+[A]^-$; and

 $[CH_2Q]^+[A]^{-=}$



where A=monovalent anion: CI, Br, I, F, FF 6, BF4, acetate, trifluoroacetate, Cl04, N03, and

Q=monovalent cation: PR3, R=alkyl, cyclic alkyl, Ary!, 0-alkyl, 0-Aryl

NR3, R=alkyl, cyclic alkyl, N-heterocyclic ring, imidazole; and

(d)



where E1=N, P, S, B $E_2 = N, P, S, 0, B$ n=1-10.

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



(a) Mis any group VII B through XII B element; (b) x=neutral sigma donor or monovalent anion;



where R1= H, any alkyl, RCOOH (R=alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R=alkyl ranging from 0.5 carbons), -[OCH2CH2]-m (m=number of repeat units); OH, S0₃; N0₂; amine, amide, carbonyl, Cl, 65 Br, I, F, BH₃, [CH₂Qt [Ar

R2= H, any alkyl, RCOOH (R=alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R=alkyl ranging



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:



where:

20

25

30

15

60

from 0.5 carbons), -[OCH₂CH₂]-m (m=number of repeat units); OH; S0₃; N0₂; amine, amide, carbonyl Cl, Br, I, F, BH₃, [CH₂Qt [A]-

 R_3 = H, any alkyl, RCOOH (R=alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R=alkyl ranging from 0-5 carbons), -[OCH₂CH₂]-m (m=number of repeat units); OH; S0₃; N0₂; amine, amide, carbonyl Cl, Br, I, F, BH₃, [CH₂Qt [Ar

 R_4 = H, any alkyl, RCOOH (R=alkyl ranging from 0-10 p carbons); OligoPEG, phosphate, ROH (R=alkyl ranging from 0-5 carbons), -[OCH₂CH₂]-m (m=number of repeat units); OH; SO₃; NO₂; amine, amide, carbonyl Cl, Br, I, F, BH₃, [CH₂Qt [Ar

 $\begin{array}{l} R_{5} = \text{ H, any alkyl, RCOOH (R=alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R=alkyl ranging from 0-5 carbons), -[OCH_{2}CH_{2}]-m (m=number of repeat units); OH; SO_{3}; NO_{2}; amine, amide, carbonyl Cl, Br, I, F, BH_{3}, [CH_{2}Qt [A]- 20 \end{array}$

 R_6 = H, any alkyl, RCOOH (R=alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R=alkyl ranging from 0-5 carbons), -[OCH₂CH₂]-m (m=number of repeat units); OH; SO₃; NO₂; amine, amide, carbonyl Cl, Br, I, F, BH₃, [CH₂Qt [Ar ²⁵

 R_7 = H, any alkyl, RCOOH (R⁼alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R⁼alkyl ranging from 0-5 carbons), -[OCH₂CH₂]-m (m=number of repeat units); OH; SO₃; NO₂; amine, amide, carbonyl Cl, Br, I, F, ₃₀ BH₃, [CH₂Qt [Ar

 R_8 = H, any alkyl, RCOOH (R⁼alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R⁼alkyl ranging from 0-5 carbons), -[OCH₂CH₂]-m (m=number of repeat units); OH; SO₃; NO₂; amine, amide, carbonyl Cl, Br, I, F, ³⁵ BH₃, [CH₂Qt [Ar ; and

[CH₂Qt [Ar ⁼



where A=monovalent anion: Cl, Br, I, F, PF $_{6},$ BF4, acetate, trifluoroacetate, Cl04. N 03, and

Q=monovalent cation: PR₃, R⁼alkyl, cyclic alkyl, Ary!, 0-alkyl, 0-Aryl

 $N\!R_3,\,R^=alkyl,$ cyclic alkyl, N-heterocyclic ring, imidazole

(d)



where $E_1=N$, P, S, B $E_2=N$, P, S, 0, B n=1-10. Specific catalyst compounds useful in this embodiment of the method include, but are not limited to the following:



Still further, the method relates to a more efficient removal of carbon dioxide from a gaseous stream containing carbon dioxide and/or other acidic gases. In particular, the method separates carbon dioxide from a gas mixture using a combination of a homogeneous $C0_2$ hydration catalyst in the presence of an amine(s) and/or ionic carbonate/bicarbonate. The combination of catalyst and amine(s) and/or chemicals provides an overall increase in mass transfer rate resulting in either 1) lower capital cost for CCS due to smaller absorber tower, or 2) reduced energy cost in the stripper from obtaining a more carbon rich solution. The catalysts have the ability to react with $C0_2$ in the gas stream to form bicarbonate which reacts with the amine(s) to form an ammonium bicarbonate or carbamate where the $C0_2$ is now considered absorbed.

⁵⁰ It was originally believed that C0₂ hydration catalyst required a 4-coordinate ligand in order to stabilize the metal center and show C0₂ hydration activity under carbon capture conditions. However, recent results obtained at the ⁵⁵ CAER show that catalysts containing 2-coordinate (bidentate) ligands of the general structure



⁶⁵ are capable of increasing the overall mass transfer of carbon capture by aqueous capture solutions. A recent catalyst identified by the CAER



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 20 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), methylydiethanolamine (MDEA), triethanolamine (TEA), dimethylethanolamine (DMEA), l-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 30 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 35 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)(H₂0)]²+. Primary amines react very rapidly 40 with C 0₂ and in order for a catalyst to contribute to the overall mass transfer second order rate constants must of the magnitude of 10^5 M-1s-1. This is the first example of catalysts containing a 2-coordinate, bidentate ligand show- 45 ing 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 C 0₂ hydration catalysts that are less synthetically demanding than previous catalysts and thus more cost effective. That new catalyst family is schematically illustrated below.





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:



where:

(a) M is any group VII B through XII B element;
(b) x=neutral si_{g m}a donor or monovalent anion; and
(c)



For any of the embodiments, the neutral sigma donor or monovalent anion may be selected from a group consisting of H_2O , Cl, Br, F, 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 seconda_{ry} amines, and (b) a terti_{ary} 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, 5 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-sulfonylamine (SA), 3-aminopropionitrile (APN), diethyl 2-aminoethanephosphonate (EtP2), N-methyltetrahydrothiophen-3-amine 1,1-dioxide, 2,2'-sulfonyldiethanamine, 3,3'-sulfonyldipropaneamine, 4,4'-sulfonyldibutanenamine, 2-aminoethyl 15 methyl sulfone, 4-aminobutanenitrile, 6-aminohexanenitrile, 3-(methylamino)propanenitrile, diethyl [2-(methylamino)ethyl]phosphonate, diethyl (3-aminopropyl)phosphodiethyl (4-aminobutyl)phosphonate, nate, diethyl (5-aminopentyl)phosphonate, diethyl (6-aminohexyl)phos- 20 phonate, 2-(tert-butoxy)ethan-l-amine, N-methyl-2-[(2methyl-2-propanyl)oxy]ethanamine and mixtures thereof.

Tertiary amines and carbonate based salts useful in the present method include but are not limited to methyldiethanolamine (MDEA), triethanolamine (TEA), N.N.-dialkyle- 25 thanolamine, N,N,N',N'-tetraalky-1,8-naphthalenediamine, N,N,-dialkylbenzylamine, 1,4-dialkylpiperazine, N,N,N',N'tetraalkyl-1,6-hexanediamine, N,N,N',N'-tetraalkyl-1,5-pentanediamine, N.N.N', N'-tetraalkyl-1,4-butanediamine, N.N. N',N'-tetraalkyl-1,3-propanediamine, N,N,N',N'-tetraalkyl- 30 N,N,N',N'-tetrakis(2-hydroxyethyl) 1,2-ethanediamine, ethylenediamine, N,N,N',N',N"-N,N,N',N',N''pentaalkyldiethylenetriamine, pentaalkyldipropylaminetriamine, N.N.dialkylcyclohexylamine, N,N,N',N'-tetraalkylbis 35

N,N,-dimethyl-2(2-aminoethoxy) (aminoethyl)ether, 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 40 about 0.05 mM and about 50 mM. In another possible embodiment the catalyst compound is provided in the fluid stream with a concentration of between 50.1 mM and 75 mM. In yet another possible embodiment, the catalyst compound is provided in the fluid stream with a concentration of 45 between about 75.1 mM and 100 mM.

Primary and secondary amines useful in the present method include but are not limited to monoethanolamine (MEA), 1-amino-2-propanol (1A2P), 3-amino-1-propanol, 2-amino-1-propanol, 2-amino-1-butanol, 3-amino-2-buta- 50 no!, l-amino-2-butanol, 2-(alkylamino)ethanonol (MAE), diglycolamine, morpholine, piperazine (PZ), 1-methylpiperazine (NMP), 2-methylpiperazine, hydroxypiperadine, hydroxymethylpiperazine, 2-piperidineethanol, N-aminoethylpierazine (AEP), aminopropylmorpholine, 4-aminopi- 55 was charged with EtOH (30 mL) and 1-(3-Formyl-4-hyperidine, 3-aminopiperidine, 2-amino-piperidine, dietha-2-amino-2-methyl-1-propanol nolamine. (AMP)diethanolamine (DEA), diisopropanolamine (DIPA), glycine, alanine, -alannine, sarcosine, isopropanolamine, benzylamine, ethylene diamine (EDA), 1,3-propanediamine, 60 1,4-butanediamine, 1,5-pentanediamine, 1,6-hexanediamine.

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 65 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 (H₂L7)[Cl]: A 100 mL round bottom flask was charged with 30 mL EtOH and 1-(3-Formyl-4-hydroxybenzyl)-3-triphenylphosphonium 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 (H₂L7)[Cl] (5.043 g, 10.01 mmol) and EtOH (30 mL) was added to make a colorless slur_{rv}. 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, 5 mL) was added drop wise to the mixture. The mixture was heated at reflux for two hours. The solution was cooled to $25\degree$ 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 (H₂L8)[Cl]: A 100 mL round bottom flask droxybenzyl)-3-triphenylphosphonium 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 (H₂L8)[Cl] (4.812 g, 10.12 mmol) and EtOH (30 mL) was added to make a clear solution. Trieth-

15

45

50

65

ylamine (3.2 mL, 23.023 mmol) was added slowly while stirring. An ethanolic solution of $ZnCl_2$ (1.687 g 12.35 mmol, 5 mL)) was added drop wise 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 ⁵ 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 tern-25 perature (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 H_2L9 (1.656 g, 10.01 mmol) and EtOH 30 (30 mL) to make a clear solution. Triethylamine (3.2 mL, 23.0 mmol) was added while stirring. An ethanolic solution of ZnC1₂ (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 35 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 55 (2.6775 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 60 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-ClOz: A 100-mL round-bottom flask was charged with $H_2L1O(1.933, 10.0 \text{ mmol})$ and EtOH (30 mL) to make a clear solution. Triethylamine (3.2 mL, 23 mmol) of 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 H_2L11 : A 100-mL round-bottom flask was charged salicylaldehyde (2.7 mL, 25 mmol) and EtOH (10 mL) to make a clear solution. 2-methoxyethylamine (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-Cl1 z A 100-mL round-bottom flask was charged with H₂L11 (1.793, 10.01 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, 5 mL) 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.
40 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 power (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 ZnC1₂ (1.776 g, 12.50 mmol) was

20

added dropwise to the mixture. The mixture was stirred at room temperature $(25^{\circ} \text{ C}.)$ 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 5 (2.668 g, 83%).

Example 7



Preparation of (H_2L13)[CI]: A 100 mL round bottom flask was charged with EtOH (30 mL) and 5-(1-methylimidazolemethyl)-2-hydroxybenzaldehyde chloride (2.528 g 10.0 mmol). An ethanolic solution of 2-Amino-2-methyl propano! (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) 30 to give the desired product (2.872 g, 89%).

Preparation of CAER-C13z: A 100-mL round-bottom flask was charged with (H_2L13) [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 etha-101 solution of ZnCl₂ (1.687 g, 12.35 mmol) was added dropwise to the mixture. The mixture was heated at reflux for two hours at which point a yellow powder was produced which was collected via filtration and washed with ethanol (3x15 mL) then diethyl ether (3x15 mL) to give the desired 40 product (3.123 g, 81%).

Example 8



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%).

22

Preparation of CAER-C14z: A 100-mL round-bottom flask was charged with (H_2L7) [BF4] (1.1108 g 2.002 mmol) and MeOH (30 mL) to make a colorless slurry. Triethylamine (0.332 m, L 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 two hours. 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 (H_2L7)[BF₄]: A 100 mL round bottom flask was charged EtOH (30 mL) and 5-(triphenylphosphinemethyl)-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 65 solution. The mixture was heated at reflux for two hours. The solvent was removed under reduced pressure to give a

Preparation of CAER-C16z: A 100-mL round-bottom flask was charged with H_2L10 (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

35

40

45

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 ⁵ g_{p} 51%).

Example 11

Preparation of CAER-C3p: To a 100-mL round-bottom flask was added [H2LP]C12 (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 %° C and was stirred for 3 h, producing a pale yellow precipitate which was collected via filtration through a medium porosity glass fritted f=e1. 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. ²⁵ 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. ³⁰

What is claimed:

1. A compound having a chemical formula:



where:



(b) x=neutral signa 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); OH; S0₃; N0₂; amine, amide, carbonyl, Cl, Br, I, F, BH₃, [CH₂Q]+[A]-; and [CH₂Q]+[A]-=



ъ

20

- where A=monovalent anion: Cl, Br, I, F, PF₆, BF₄, acetate, trifluoroacetate, $C10_4$, $N0_3$, and
- Q=monovalent cation: P(R)₃, R⁼alkyl, cyclic alkyl, Ary!, 0-alkyl, 0-Aryl;
- N(R)₃, R⁼alkyl, cyclic alkyl, N-heterocyclic ring, imidazole; and
- $R_2^{=}CE;$ where $C^{=}\text{any}$ alkyl, cyclic alkyl, aryl, and $E^{=}OH$ or $NH_2.$
- 2. A compound consisting of 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)





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



- 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, Ary!, 0-alkyl, 0-Aryl;
- $N(R)_3$, R=alkyl, cyclic alkyl, N-heterocyclic ring, imidazole; and
- $R_2{=}CE; \mbox{where } C{=}\mbox{any alkyl, cyclic alkyl, aryl, and } E{=}OH \mbox{ or } NH_2.$
- 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:



(a) Mis any group VII B through XII B element;

- (b) x=neutral $\dot{s_{g m}}a$ donor or monovalent anion; and
- (c)

where:





 R_1 = H, any alkyl, RCOOH (R=alkyl ranging from 0-10 carbons); OligoPEG, phosphate, ROH (R=alkyl ranging from 0-5 carbons); OH; S0₃; N0₂; amine, amide, carbonyl Cl, Br, I, F, BH₃, [CH₂Q]+[A]-; and

 $[CH_2Q]+[A]-=$



where A=monovalent anion: Cl, Br, I, F, PF_6 , BF_4 , acetate, trifluoroacetate, $C10_4$, $N0_3$, and

²⁰ Q=monovalent cation: P(R)₃, R=alkyl, cyclic alkyl, Ary!, 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 40 NH2.

4. The method of claim 3, wherein said neutral $s_{i_g m}a$ donor or monovalent anion is selected from a group consisting of H₂0, Cl, Br F, I, acetate, triflate, perchlorate, nitro, pyridine, ethanol, methanol, tetrahydrofuran, dimethylsul-45 foxide, 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, seconda_{ry}
50 amine, or a tertia_{ry} 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-buta-55 no!, l-amino-2-butanol, 3-amino-2-butanol, 2-(alkylamino) ethanonol (MAE), diglycolamine, morpholine, piperazine (PZ), 1-methylpiperazine (NMP), 2-methylpiperazine, hydroxypiperadine, hydroxyalkylpiperazine, 2-piperidineethanol, N-aminoethylpierazine (AEP), aminopropyl-@ morpholine, 4-aminopiperidine, 3-aminopiperidine, 2-amino-piperidine, diethanolamine, 2-amino-2-methyl-1propanol (AMP), diethanolamine (DEA), diisopropanolamine (DIPA), glycine, alanine, R-alannine, sarcosine, isopropanolamine, benzylamine, methyldiethanolamine (MDEA), triethanolamine (TEA), alkali carbonate, N,N,-65

dialkylethanolamine, N,N,N',N'-tetraalky-1,8-naphthalenediamine, N,N,-dialkylbenzylamine, 1,4-dialkylpiperazine, N,N,N',N'-tetraalkyl-1,6-hexanediamine, N,N,N',N'-tetraalkyl-1,5-pentanediamine, N,N,N',N'-tetraalkyl-1,4-butanediamine, N,N,N',N'-tetraalkyl-1,3-propanediamine, N,N,N',N'-tetraalkyl-1,2-ethanediamine, N,N,N',N'-tetrakis (2-hydroxyethyl)ethylenediamine, N,N,N',N'-,N'-tetrakis (2-hydroxyethyl)ethylenediamine, N,N,N',N'',N''-pentaalkyldiethylenetriamine, N,N,N',N',N''-pentaalkyldipropylaminetnamine, N,N,-dialkylcyclohexylamine, N,N,N',N'tetraalkylbis(aminoethyl)ether, N,N,-dimethyl-2(2aminoethoxy)ethanol, where alkyl represents any methyl, ethyl, propyl, butyl isomer, and mixtures thereof. 10

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.

* * * * *