

COMPOSITION AND PROCESS FOR REMOVAL OF ACID GASES

This invention relates to a composition and method
5 for removing acid gases such as, for example, H_2S , CO_2 and
COS from a fluid stream containing same.

Purification of fluids involves removal of impurities
from fluid streams. Various fluid purification methods are
10 known and practiced. These fluid purification methods
generally fall in one of the following categories:
absorption into a liquid, adsorption on a solid,
permeation through a membrane, chemical conversion to
another compound, and condensation. The absorption
15 purification method involves the transfer of a component
of a fluid to a liquid absorbent in which said component
is soluble. If desired, the liquid containing the
transferred component is subsequently stripped to
regenerate the liquid. See, for example, A. Kohl and R.
20 Nielsen, "Gas Purification", 5th edition, Gulf Publishing,
1997; A. Kohl and F.C. Riesenfeld "Gas Purification", 4th
edition, Gulf Publishing, 1985; A. Kohl and F.C.
Riesenfeld "Gas Purification", 3rd edition, Gulf
Publishing, 1979; and "The Gas Conditioning Fact Book"
25 published by The Dow Chemical of Canada, Limited, 1962;
all incorporated herein by reference.

Aqueous solutions of various primary, secondary and
tertiary alkanolamines, such as, for example,
30 monoethanolamine (MEA), diethanolamine (DEA),
diglycolamine (DGA), diisopropanolamine (DIPA),
methyldiethanolamine (MDEA) and triethanolamine (TEA),
have been used as absorbent liquids to remove acid gases
from liquid and gas streams. In a regeneration method,
35 the aqueous alkanolamine solution containing acid gas is
then subjected to heat to regenerate the aqueous
alkanolamine solution.

Primary alkanolamines such as MEA and DGA, or secondary alkanolamines such as DEA or DIPA are generally suitable for highly exhaustive removal of CO₂, however they have disadvantage of requiring large expenditure of energy for regeneration.

Tertiary alkanolamines, especially MDEA and TEA, require less energy consumption for regeneration, but since they do not react directly with CO₂, they do not remove CO₂ completely from the fluid stream. Tertiary alkanolamines are, however, suitable for selective removal of H₂S from a fluid containing both H₂S and CO₂, since the absorption rate for H₂S is about the same for all alkanolamines.

The chemistry of acid gas reactions with aqueous alkanolamine treating solutions is well known and is described in many publications such as, for example, the aforementioned publications and references cited therein, and publications described below and references cited therein.

Canadian Patent No. 1,091,429 (G. Sartori et al) describes the use of aqueous solutions containing water-soluble primary monoamines having a secondary carbon atom attached to the amino group in gas purification applications. Primary monoamines having a secondary carbon atom attached to the amino group specifically mentioned in this reference as being suitable are 2-amino-1-propanol, 2-amino-1-butanol, 2-amino-3-methyl-1-butanol, 2-amino-1-pentanol, 2-amino-1-hexanol and 2-aminocyclohexanol. It is notable that this reference is completely silent as to degradability and corrosivity of these primary monoamines which have a secondary carbon atom attached to the amino group.

Chem. Eng. Comm., 1996, Vol. 144, pp. 103-112,
"Effects of Composition on the Performance of Alkanolamine

Blends for Gas Sweetening", describes the influence of blend composition and components on some of the parameters which can be used to monitor the performance of amine blends for aqueous blends of MDEA and MEA, MDEA and DEA, and MDEA and DIPA.

48th Annual Laurance Reid Gas Conditioning Conference, March 1-4, 1998, pp. 146-160, "Amine Degradation Chemistry in CO₂ Service", describes the degradation chemistry of various ethanolamines in CO₂ service. The paper promotes gas-treating solvents which are not formulated with primary or secondary ethanolamines as a solution for the loss rates associated with the use of various ethanolamines such as MDEA, MMEA and DEA.

Primary and secondary alkanolamines can also be used as activators in combination with tertiary alkanolamines to remove CO₂ down to as low as 100 parts per million (ppm) or less requiring less regeneration energy than is required using the primary or secondary alkanolamines alone.

U.S. Patent Nos. 5,209,914 and 5,366,709 show how activators such as ethylmonoethanolamine (EMEA) or butylmonoethanolamine (BMEA) can be used with MDEA to achieve better CO₂ removal than MDEA alone.

U.S. Patent No. 4,336,233 discloses that the use of a combination of piperazine and MDEA results in an improved acid gas removal. However, one particular disadvantage of piperazine is that piperazine carbamate formed from the reaction of piperazine and CO₂ is not soluble in the aqueous MDEA/piperazine solution. Thus, the additive level is limited up to about only 0.8 moles/liter, which severely limits the capacity of the solvent, or requires higher circulation rates to treat the same amount of fluid than other MDEA/alkanolamine activator blends require.

The primary disadvantage of using primary and secondary alkanolamines such as MEA, DEA and DIPA is that CO₂ reacts with these alkanolamines to form degradation compounds such as oxazolidinones and ethylenediamines.

5 C. J. Kim, Ind. Eng. Chem. Res. 1988, 27, and references cited therein show how DEA reacts with CO₂ to form 3-(2-hydroxyethyl)-2-oxazolidinone (HEO) and N,N,N'-tris(2-hydroxyethyl)ethylenediamine (THEED). This reference also shows how DIPA reacts to form 3-(2-
10 hydroxypropyl)-5-methyl-2-oxazolidinone (HPMO). These degradation compounds reduce the amount of alkanolamine available for acid gas removal, increase the viscosity of the solution and potentially increase the corrosivity of the solvent.

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It is evident that there is still a great need and interest in the gas purification industry for alkanolamine compounds which will be effective in the removal of acidic gases from fluid streams and will have improved
20 degradation properties compared to alkanolamines commonly used for this purpose.

It has now been discovered that 1-amino-2-butanol and its derivatives are effective in removing acidic gases
25 from fluid stream and that they have superior degradation properties as compared to alkanolamines conventionally used in the gas purification industry.

In the context of the present invention the term
30 "fluid stream" encompasses both a gaseous stream and liquid stream.

In one aspect the present invention is an aqueous solution adapted for use in the removal of acidic gases
35 from a fluid stream containing same, said aqueous solution comprising an effective amount of an alkanolamine of the formula



or mixtures thereof wherein R is H, $-CH_2CH(OH)CH_2CH_3$, an alkyl group having from 1 to 6 carbon atoms, an aryl group
5 having from 6 to 12 carbon atoms, an aralkyl group having from 6 to 12 carbon atoms, or a cycloalkyl group having from 3 to 6 carbon atoms.

In another aspect the present invention is a process
10 for removing acidic gases from a fluid stream containing same, said process comprising contacting said fluid stream containing acidic gases with an aqueous solution comprising an effective amount of an alkanolamine of the formula

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or mixtures thereof wherein R is H, $-CH_2CH(OH)CH_2CH_3$, an alkyl group having from 1 to 6 carbon atoms, an aryl group
20 having from 6 to 12 carbon atoms, an aralkyl group having from 6 to 12 carbon atoms, or a cycloalkyl group having from 3 to 6 carbon atoms.

The alkanolamines of the formula I above are
25 surprisingly found to be effective for removing acidic gases, particularly CO_2 , H_2S , COS or mixtures thereof, from a fluid stream containing same and yet exhibit much improved degradation properties compared to alkanolamines conventionally used in the gas purification industry.
30 These compounds are known and their synthesis is described in various publications such as, for example, J. Zienko, M. Stoyanova-Antoszczyszyn and J. Myszkowski, Chemik 1/1991, pp. 8-9, and references cited therein.

35 The alkanolamines of formula I in which R is H, $-CH_2CH(OH)CH_2CH_3$, or an alkyl group having from 1 to 6 carbon atoms are preferred in the practice of the present invention with those in which R is H, $-CH_2CH(OH)CH_2CH_3$, or

an alkyl group having from 1 to 4 carbon atoms being further preferred. 1-Amino-2-butanol (MBA) and bis(1-hydroxybutyl)-amine (DBA), N-methyl-2-hydroxybutylamine and N-ethyl-2-hydroxybutylamine are particularly preferred, with 1-amino-2-butanol and bis(1-hydroxybutyl)amine (DBA) being the most preferred alkanolamines for use in the present invention.

The alkyl group having from 1 to 6 carbon atoms contemplated by R in formula I can be straight or branched chain alkyl group. Non-limiting examples of such alkyl groups are methyl, ethyl, propyl, isopropyl, butyl, isobutyl, pentyl, and hexyl.

The aryl group having from 6 to 12 carbon atoms contemplated by R in formula I can be substituted or non-substituted. Non-limiting examples of suitable aryl groups are phenyl and tolyl.

The aralkyl group having from 6 to 12 carbon atoms contemplated by R in formula I can be substituted or unsubstituted. Non-limiting examples of suitable aralkyl groups are benzyl and phenethyl.

The cycloalkyl group having from 3 to 12 carbon atoms contemplated by R in formula I can be substituted or unsubstituted. Non-limiting examples of suitable cycloalkyl groups are cyclohexyl and methylcyclohexyl.

In the present invention, the aqueous solution of an alkanolamine of formula I can be used alone, or in combination with tertiary alkanolamines such as, for example, methyldiethanolamine (MDEA), dimethylethanolamine (DMEA) and triethanolamine (TEA) to remove acidic gases from fluids.

The alkanolamine of formula I is present in the aqueous solution of the present invention in an amount effective to remove acidic gases from a fluid stream.

5 When the alkanolamine of formula I is used alone, it is typically present in an amount of from 7 to 50, preferably from 15 to 40, more preferably from 20 to 30, percent by weight based on the total weight of the aqueous solution.

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The optimal amount of the alkanolamine of formula I will depend on the fluid stream composition, outlet fluid requirement, circulation rate, and energy available for stripping the solvent. A person of ordinary skill in the art would readily determine the optimal amount of the alkanolamine of formula I.

When the alkanolamine of formula I is used as an activator in combination with a tertiary alkanolamine, the amount used can vary quite widely, but it is generally present in an amount of from 1 to 30, preferably from 5 to 20, more preferably from 7 to 15, percent by weight based on the total weight of the aqueous solution. The tertiary alkanolamine is generally used in an amount of from 25 to 60, preferably from 25 to 40, more preferably from 30 to 40, percent by weight based on the total weight of the aqueous solution.

30 The process of the present invention can be carried out in any conventional equipment for the removal of acidic gases from fluids and detailed procedures are well known to a person of ordinary skill in the art. See, for example, U.S. Patent No. 1,783,901 (Bottoms) and subsequent improvements which are known in the art.

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The process according to the present invention can be conveniently carried out in any suitable absorber. The great number of absorbers used for gas purification

operations include packed, plate, or spray towers. These absorbers are interchangeable to a considerable extent although certain specific conditions may favor one over the other. In addition to conventional packed, plate, or spray towers, specialized absorber towers have been developed to meet specific process requirements. Examples of these specific towers include impingement-plate scrubbers and turbulent contact scrubbers. The process of the present invention can be carried out in either packed, plate, or spray towers, and can contain other peripheral equipment as necessary for optimal process operation. Such peripheral equipment may include an inlet gas separator, a treated gas coalescor, a solvent flash tank, a particulate filter and a carbon bed purifier. The inlet gas flow rate vary depending on the size of the equipment but is typically between 5 and 100 million standard cubic feet per day (SCFD). The solvent circulation rate will depend on the amine concentration, the gas flow rate, gas composition, total pressure and treated fluid specification. The solvent circulation rate is typically between 5 and 5000 gallons per minute (gpm). Pressure inside the absorber can vary between 0 and 1200 psig depending on the type of fluid being processed.

The absorbers, strippers and peripheral equipment useful for carrying out the process of the present invention are well known in the art and are described in many publications including the aforementioned references.

In the process of the present invention, a fluid containing an acid gas is contacted with an aqueous solution comprising an effective amount of an alkanolamine of formula I at a temperature of from ambient temperature (approximately 25°C, 77°F) up to 93°C (200°F).

Temperatures inside the stripper tower, if one is employed, can vary between 82°C (180°F) and 127°C (260°F). The stripper overhead pressure is typically between 0 and

20 psig. Optionally, corrosion inhibitors, scale inhibitors and antifoam agents may be employed.

The following examples are offered to illustrate but not limit the invention. Percentages, ratios and parts are by weight unless stated otherwise.

EXAMPLES 1 TO 3 AND COMPARATIVE EXAMPLES C-1 TO C-3

10 Dissolved CO₂ experiments were performed by sparging the compressed CO₂ (Liquid Carbonic HI-DRY Grade; greater than 99.99 percent purity) through a Cole-Palmer 0-150 ml/min. flowmeter at a rate of 50 ml/min. for 90 min. into an aqueous solution (200 ml) comprising MDEA (2.94 mole; 15 35 percent) and an additive (1.68 mole) contained in a 250 ml jacketed beaker. The aqueous solution was stirred with a magnetic stir bar while continually sparging with CO₂. The temperature of the solution (31°C) was adjusted using a GCA Precision R10 circulating bath and was monitored using 20 a thermometer. A polycarbonate cover with slits for the thermometer, gas entrance and exit was used on top of the beaker to prevent CO₂ in the atmosphere from entering the solution. After 90 minutes of continuous sparging, the solution was analyzed for dissolved CO₂ according to ASTM 25 Method No. D 513 "Total and Dissolved CO₂ in Water". The additives used and results obtained are given in Table 1 below.

30 Table 1
CO₂ Reaction with MDEA/Additive

Example	Aqueous Solution	Wt % CO ₂ Absorbed in 90 minutes
1	MDEA + MBA (Run 1)	4.25
2	MDEA + MBA (Run 2)	4.01
3	MDEA + DBA	3.76
C-1	MDEA + MEA	4.16
C-2	MDEA + DEA	3.76

C-3	MDEA + 1.68M EMEA	3.71
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This data shows that the aqueous solutions containing MBA absorbed more CO₂ than those containing DEA or EMEA. The amount of CO₂ absorbed by the solutions containing MBA (average: 4.13 percent by weight) is statistically similar to the amount of CO₂ absorbed by the solution containing MEA (4.16 percent by weight). Likewise, the amount of CO₂ absorbed by the aqueous solution containing DBA is also statistically similar to amount of CO₂ absorbed by the aqueous solutions containing DEA or EMEA.

EXAMPLES 4 and 5 AND COMPARATIVE EXAMPLES C-4 and C-5

Autoclave degradation tests were performed on equimolar amine solutions using 0.050 mole of CO₂ per mole of amine at 126.7°C (260°F). An aqueous solution (1100 ml.) containing MDEA (35 percent by weight; 2.94 mole) and either EMEA (15 percent by weight; 1.68 mole), DEA (17.7 percent by weight; 1.68 mole) or MBA (15 percent by weight; 1.68 mole) was added to a 2 liter Parr autoclave. Then each solution was loaded with CO₂ such that the CO₂ loading was 0.050 mole of CO₂ per mole of total amine. The solution was then heated for 28 days at 126.7°C (260°F). After 28 days, the solutions were analyzed by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) to determine the amount of the amine additive remaining in the solution and for the presence of degradation/conversion products. The results obtained are given in Table 2 below.

Table 2
Degradation Tests

Example	Aqueous Solution	Amine Additive Remaining after 28 Days	Degradation / Conversion Product
4	MDEA + MBA (Run 1)	15.1 wt%	none

5	MDEA + MBA (Run 2)	14.99 wt%	none
C-4	MDEA + EMEA	10.6 wt%	yes (3 wt%)
C-5	MDEA + DEA	9.39 wt%	yes (2.2 wt%)

This data clearly shows the unexpected advantage of MBA over EMEA and DEA. The data demonstrates that substantially all of MBA remains in the solution after 28 days with no detection of any degradation product while during the same time substantial amount of EMEA and DEA has been lost due to their reactivity with CO₂ and conversion into undesirable reaction products.

EXAMPLES 6 AND 7 AND COMPARATIVE EXAMPLES C-6 AND C-7

Autoclave degradation tests were performed on equimolar amine solutions using 0.050 mole of CO₂ per mole of amine at 126.7°C (260°F). An aqueous solution (1100 ml.) containing MDEA (35 percent by weight) and either EMEA (15 percent by weight), BMEA (15 percent by weight), MBA (15 percent by weight), or DBA (15 percent by weight) was added to a 2 liter Parr autoclave. Then each solution was loaded with CO₂ such that the CO₂ loading was 0.050 mole of CO₂ per mole of total amine. The solution was then heated for 28 days at 126.7°C (260°F). After 28 days, the solutions were analyzed by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) to determine the amount of the amine additive remaining in the solution and for the presence of degradation/conversion products. The amount of EMEA, BMEA, MBA (two runs) and DBA remaining in the solution after 28 days was 10.6, 10.4, 15.1, 14.99 and 12.3 weight percent, respectively. EMEA converted to 3 weight percent of N,N'-(2-hydroxyethyl)ethylene-diamine. BMEA converted to 3.2 weight percent of N,N'-dibutyl-N-(2-hydroxyethyl)ethylenediamine plus a small amount (less than 0.5 weight percent) of N-butyl-2-oxazolidinone. MBA showed very little degradation. Less than 0.2 weight percent what is possibly an oxazolidinone or substituted ethylenediamine was detected by GC and GC/MS. DBA converted to 2.9 weight percent of a product that is preliminary identified as N-(2-hydroxy-butyl)-2-oxazolidinone by GC/MS analysis. The results are given in Table 3 below.

Table 3
Degradation Tests

Example	Aqueous Solution	Amine Additive Remaining after 28 Days	Degradation / Conversion Product
6	MDEA + MBA (Run 1)	15.1 wt%	Yes (<0.2 wt%)
7	MDEA + MBA (Run 2)	14.99 wt%	Yes (<0.2 wt%)
8	MDEA + DBA	12.3 wt%	Yes (2.9 wt%)
C-6	MDEA + EMEA	10.6 wt%	Yes (3 wt%)
C-7	MDEA + DEA	9.39 wt%	Yes (3.7 wt%)

5 This data also shows the unexpected advantage of MBA
and DBA over EMEA and BMEA. The data demonstrates that
substantially all of MBA remains in the solution after 28
days with essentially no detection of any degradation
product while during the same time substantial amount of
10 EMEA and DEA has been lost due to their reactivity with CO₂
and conversion into undesirable reaction products.

EXAMPLE 9 AND COMPARATIVE EXAMPLE C-8

15 Autoclave degradation tests were performed on 2.80
mole amine solutions using 0.050 mole of CO₂ per mole of
amine at 126.7°C (260°F). An aqueous solution (1100 ml.)
containing MEA (17.7 percent by weight, 2.80 mole) or MBA
(25 percent by weight, 2.80 mole) was added to a 2 liter
20 Parr autoclave. Then each solution was loaded with CO₂
such that the CO₂ loading was 0.050 mole of CO₂ per mole of
total amine. The solution was then heated for 28 days at
126.7°C (260°F). After 28 days, the solutions were
analyzed by gas chromatography (GC) and gas
25 chromatography/mass spectrometry (GC/MS) to determine the
amount of the amine additive remaining in the solution and
for the presence of degradation/conversion products. The
amount of MEA and MBA remaining in the solution after 28
days was 16.47 and 24.71 weight percent, respectively. GC
30 and GC/MS did not positively identify any of small

degradation peaks for either MEA or MBA runs. The results are given in Table 4 below.

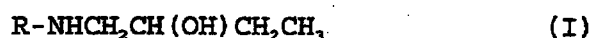
Table 4
Degradation Tests

Example	Aqueous Solution	Amine Additive Remaining after 28 Days	Degradation
9	MBA	24.71 wt%	1.2 wt%
C-8	MEA	16.47 wt%	6.9 wt%



WHAT IS CLAIMED IS:

1. An aqueous solution adapted for use in the removal of acidic gases from a fluid stream containing same, said aqueous solution comprising an effective amount of an alkanolamine of the formula



- 10 or mixtures thereof wherein R is H, $-CH_2CH(OH)CH_2CH_3$, an alkyl group having from 1 to 6 carbon atoms, an aryl group having from 6 to 12 carbon atoms, an aralkyl group having from 6 to 12 carbon atoms, or a cycloalkyl group having from 3 to 6 carbon atoms.

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2. The aqueous solution according to Claim 1 wherein the alkanolamine of formula I is present in an amount of from 7 to 50 percent by weight.

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3. The aqueous solution according to Claim 1 further comprising a tertiary alkanolamine.

4. The aqueous solution of Claim 3 wherein the alkanolamine of formula I is present in an amount of from 1 to 30 percent and the tertiary alkanolamine is present in an amount of from 25 to 60 percent.

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5. The aqueous solution according to Claim 3 wherein the tertiary alkanolamine is selected from the group consisting of methyldiethanolamine, dimethylethanolamine and triethanolamine.

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6. The aqueous solution according to Claim 1 or Claim 3 wherein R in formula I is H, $-CH_2CH(OH)CH_2CH_3$, or an alkyl group having from 1 to 6 carbon atoms.

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7. The aqueous solution according to Claim 1 or Claim 35 wherein the alkanolamine of formula I is



selected from the group consisting of 1-amino-2-butanol, bis(1-hydroxybutyl)amine, N-methyl-2-hydroxybutylamine and N-ethyl-2-hydroxybutylamine.

5 8. The aqueous solution according to Claim 7 wherein the alkanolamine of formula I is present in an amount of from 1 to 30 percent by weight and further containing methyldiethanolamine in an amount of from 25 to 60 percent by weight.

10 9. The aqueous solution according to Claim 7 wherein the alkanolamine of formula I is a mixture of 1-amino-2-butanol and bis(1-hydroxybutyl)amine.

15 10. A process for removing acidic gases from a fluid stream containing same, said process comprising contacting said fluid stream with an aqueous solution comprising an effective amount of an alkanolamine of the formula

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or mixtures thereof wherein R is H, $-CH_2CH(OH)CH_2CH_3$, an alkyl group having from 1 to 6 carbon atoms, an aryl group
25 having from 6 to 12 carbon atoms, an aralkyl group having from 6 to 12 carbon atoms, or a cycloalkyl group having from 3 to 6 carbon atoms.

11. The process according to Claim 10 wherein
30 the alkanolamine of formula I is present in an amount of from 7 to 50 percent by weight.

12. The process according to Claim 10 wherein
the aqueous solution further comprises a tertiary
35 alkanolamine.

13. The process according to Claim 12 wherein
the alkanolamine of formula I is present in an amount of



from 1 to 30 percent and the tertiary alkanolamine is present in an amount of from 25 to 60 percent.

14. The process according to Claim 12 wherein the tertiary alkanolamine is selected from the group consisting of methyldiethanolamine, dimethylethanolamine and triethanolamine.

15. The process according to Claim 10 or Claim 12 wherein R in formula I is H, $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$, or an alkyl group having from 1 to 6 carbon atoms.

16. The process according to Claim 10 or Claim 12 wherein the alkanolamine of formula I is selected from the group consisting of 1-amino-2-butanol, bis(1-hydroxybutyl)amine, N-methyl-2-hydroxybutylamine and N-ethyl-2-hydroxybutylamine.

17. The process according to Claim 16 wherein the alkanolamine of formula I is present in an amount of from 1 to 30 percent by weight and the solution further contains methyldiethanolamine in an amount of from 25 to 60 percent by weight.

18. The process according to Claim 16 wherein the alkanolamine of formula I is a mixture of 1-amino-2-butanol and bis(1-hydroxybutyl)amine.

