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Investigation of Some New Amines as Regenerative Carbon Dioxide Absorbents

PAUL R. GUSTAFSON AND R. R. MILLER

Inorganic Chemistry Branch
Chemistry Division

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NAVAL RESEARCH LABORATORY
Washington, D.C.

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ABSTRACT

Three amines–monoethanolamine (MEA), 2-(2-aminoethoxy)ethanol (DGA), and 3-amino-1-propanol (MPA)–each mixed with one of a series of organic liquids with high CO_2 solubility and varying proportions of H_2O, were compared with their corresponding aqueous solutions with regard to CO_2 absorption, CO_2 stripping, and solution viscosity. The organic liquids were N,N-dimethylformamide, N-dimethylacetamide, tetramethylene sulfone, N-methyl-2-pyrrolidinone, hexamethylphosphoric triamide, and tetramethylurea.

While some of the organic liquids improved the CO_2 absorption and stripping properties of 4N aqueous MEA to a greater extent than did tetramethylene sulfone, the latter solvent, which has better physical properties for use in submarines, increased the efficiency of 4N MEA about 20%, and when admixed with 5N MPA, the improvement was approximately 36%.

An ω-aminoalkyl alkyl sulfone, 3-(methylsulfonyl)propylamine, CH_3SO_2-$CH_2CH_2CH_2NH_2$, was synthesized and compared with MEA with respect to absorption and stripping efficiency, viscosity, oxidation resistance, foaming, and capacity. A significant improvement over MEA was noted in oxidation resistance, volatility, and stripping efficiency. The absorption efficiency nearly equaled or exceeded the efficiency of MEA, depending on the foaming conditions; however, the CO_2 capacity was lower by 10%. Although the foaming was excessive, it could be controlled by the use of antifoam agents.

Further study is recommended on an engineering-scale CO_2 scrubber, or on an operational unit, of 3-amino-1-propanol (MEA)-tetramethylene sulfone aqueous solutions and also ω-aminoalkyl sulfone or other aminoalkyl tetramethylene sulfone compounds when they become commercially available.

PROBLEM STATUS

This is the final report on this phase of the problem; work is continuing on other phases.

AUTHORIZATION

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INVESTIGATION OF SOME NEW AMINES AS REGENERATIVE CARBON DIOXIDE ABSORBENTS

INTRODUCTION

Monoethanolamine (MEA), the regenerative CO_2 absorbent currently employed in the CO_2 scrubbers on nuclear submarines, has limitations in this use. The more important limitations are its relatively high vapor pressure, toxicity, NH_3 evolution, foaming, poor resistance toward oxidation, and low regeneration efficiency. Regenerative amines investigated previously at NRL, and the experimental procedures used, are discussed in earlier reports (1,2).

Girdler Corporation in the early 1950's evaluated over 250 amines, amine-like compounds, and mixtures for potential Navy use (3). Of these, 40 compounds and several amine mixtures were selected for further study in their laboratory. The three amine mixtures finally recommended by the report for Navy use, while superior to MEA in oxidation resistance and volatility, were inferior to MEA in both the CO_2 absorption rate and the steam requirement for stripping (4).

The work reported herein was undertaken to replace MEA in the shipboard CO_2 scrubber, if possible, or to improve the operational characteristics of MEA. A prime requirement was that any recommendation would not necessitate significant modification of the existing submarine equipment.

This report compares aqueous solutions of MEA, 3-amino-1-propanol (MPA), and 2-(2-aminoethoxy)ethanol (DGA) with corresponding solutions of the amine in organic CO_2 solvents containing varying proportions of H_2O. The organic solvents employed were N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAC), tetramethylene sulfone (TMS),* N-methyl-2-pyrrolidinone (NMP), hexamethylphosphoric triamide (HMPA), and tetramethylurea (TMU). In addition to the above, aqueous soltuions of 3-(methylsulfonyl)-propylamine (MSP) without organic solvents were studied. MSP was not available commercially, and sufficient quantities for the study were synthesized by two different methods (5,6). The equipment and techniques used for the various runs are described in Refs. 1 and 2.

This study disclosed the following general information. The CO_2 absorption rate of an alkanolamine is usually increased when H_2O is replaced by an organic liquid of the DMF type, which may be due to the greater CO_2 solubility in the organic liquid then in H_2O (7). The higher solubility enhances the rate of exchange across the gas/liquid interface, thereby increasing the rate of CO_2 removal from the gas phase. Another beneficial effect of amine-organic CO_2 solvent compositions over corresponding amine-H_2O solutions is that more free amine is produced for a given energy input on regeneration. Generally, amine-organic solvent mixtures containing 0 to 25%† H_2O exhibit less foaming than their aqueous analogs. In this respect, TMS is superior to the other solvents.

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*Marketed under the trade name Sulfolane.

†All solution percentages quoted in this report are in terms of volume-percent, unless otherwise specified.

Three organic CO_2 solvents–TMU (8), NMP (9), and TMS (10)–with some of their physical properties and reported toxicities, are listed in Table 1 in the order of potential suitability for submarine use. These materials possess good thermal stability, noncorrosiveness, and resistance to hydrolytic cleavage. The organic solvents DMF and DMAC were not included in Table 1, because they are less resistant to hydrolysis and possess greater volatilities. HMPA was also excluded on the basis of its highly unpleasant odor. The latter three solvents are judged to be unsuitable for submarine use because of these properties.

Table 1
Organic CO_2 Solvents of Potential Suitability for Submarine Use

Substance	Boiling Point (°C)	Freezing Point (°C)	Flash Point (open cup) (°C)	Oral LD_{50} (albino rats) (g/kg)
TMS ($CH_2CH_2CH_2CH_2SO_2$)	285	27.6	176.6	0.5-5
NMP ($CH_3N(CH_2)_3CO$)	202	-24.4	95	7
TMU ($[(CH_3)_2N]_2CO$)	176.5	-1	148	0.8

A technical bulletin (11) states that TMS possesses excellent thermal stability at temperatures as high as 220°C. According to Deal, et al. (12), the decomposition rate of TMS in air is 0.009% per hr at 200°C, and the corrosion of carbon steel at this temperature, in the presence of small amounts of water, is negligible ($\approx$ 1 mil/yr). The compound is generally inert to acids, alkalies, and mercaptans and resists reaction with reducing chemicals such as zinc. The melting point of the pure compound (27.6°C) is fairly high but is significantly depressed by small quantities of H_2O. For example, 3% H_2O lowers the melting point to approximately 9°C and 7% H_2O to around 1.5°C. Therefore, TMS, as normally supplied, will be in liquid form over the usual range of ambient temperatures.

COMPARISON OF THE CO_2 ABSORPTION RATES OF AMINE-H_2O AND AMINE-ORGANIC CO_2 SOLVENT-H_2O COMPOSITIONS

Figure 1 compares the aqueous solutions of 4N MEA, 4N MPA, and 6.5N DGA with respect to the rate of CO_2 absorption. MPA is slightly more efficient and DGA significantly less efficient than MEA. The work of Allen (13) supports the MPA data. In 1 hr DGA absorbed 26 volumes (STP) of CO_2 per volume of solution (V_g/V_s), while MEA absorbed 30 and MPA over 31 V_g/V_s units. The amount of CO_2 absorbed in 100 min was approximately the same for all three amines. As would be expected on the basis of normality, the 6.5N DGA solution absorbed nearly 50% more CO_2 than did the 4N amines.

When an organic solvent, such as TMU or NMP, was added, the CO_2 absorption rate for all three amines was increased. These data are shown in Figs. 2 and 3. With MEA (Fig. 2), both TMU and NMP increased the absorption rate about 10%. The rate remained high with the MEA-TMU-20% H_2O mixture, but with the MEA-NMP-25% H_2O mixture, the rate fell below that of the MEA-H_2O mixture after 50 min. This is not considered a serious defect, since 75% of the capacity of the amine was attained by this time. As shown in Fig. 3, the rate increase amounted to 10% with MPA and nearly 20% for DGA. However,

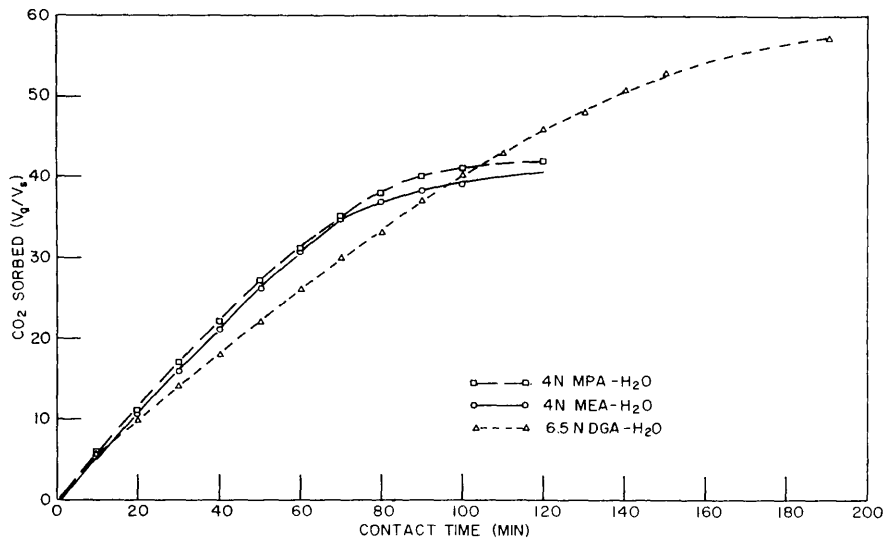


Fig. 1 - CO_2 absorption rate of various amines in H_2O, using a flow rate of 3.3 l/min of 1% CO_2 in air at 1 atm, 88°F, and 100% RH

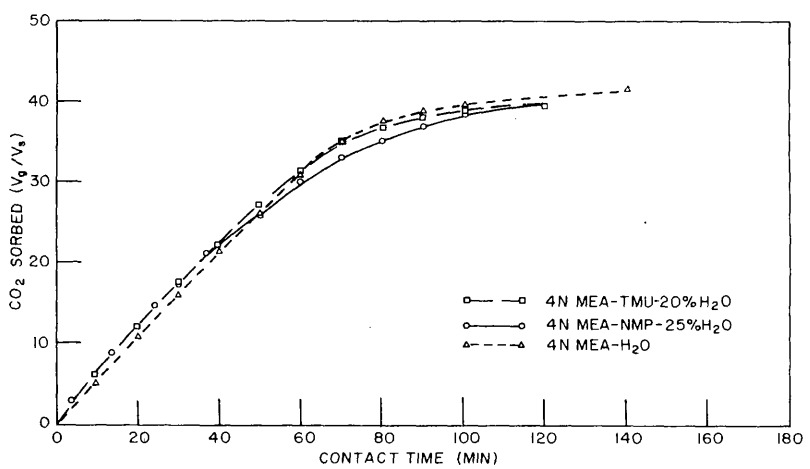


Fig. 2 - CO_2 absorption rates of MEA in organic solvent-H_2O mixtures, using a flow rate of 3.3 l/min of 1% CO_2 in air at 1 atm, 88°F, and 100% RH

the equilibrium CO_2 capacity for the three-component solution (MPA-TMU-H_2O or MPA-NMP-H_2O) dropped to 47 V_g/V_s units from 52 units for the 5N MPA-H_2O mixture. TMU did not lower the absorption capacity of 6.5N DGA.

The CO_2 absorption rates of amine (MEA, DGA, and MPA)-TMS-H_2O compositions are compared with their corresponding amine-H_2O solutions in Table 2. TMS increased the rate for DGA by 10%. When the equilibrium CO_2 loading of 90% was reached (at 110 min), the absorption rate of the TMS composition fell below that of aqueous DGA.

The equivalents of CO_2 absorbed per equivalent of amine were 0.78 for 5.4N DGA-TMS-H_2O and 0.80 for the 6.5N DGA-H_2O solution; a contact time longer than 150 min

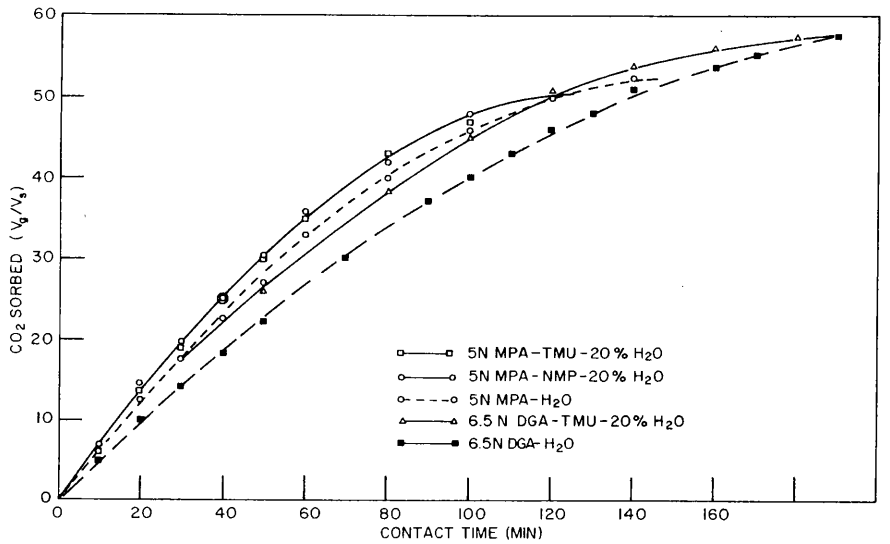


Fig. 3 - CO_2 absorption rate and capacity of MPA and DGA in organic CO_2 solvents, using a flow rate of 3.3 l/min of 1% CO_2 in air at 1 atm, 88°F, and 100% RH

was required for the latter solution. The saturation value averaged 58 V_g/V_s units. In contrast, the equivalent of CO_2 absorbed per equivalent of MPA at equilibrium saturation for either 4 or 5N MPA-TMS-H_2O mixtures is 0.9. The value approaches 1, e.g. 0.98 to 1.02, for aqueous 4N and 5N MPA solutions and is 0.94 for aqueous 4N MEA. In general, the CO_2 capacity per equivalent of amine is slightly larger with MPA-H_2O and MPA-organic CO_2 solvent compositions than with the corresponding MEA mixtures under identical conditions.

TMS improved the CO_2 absorption rate of DGA but did not affect that of the 5N MPA except near the saturation level. However, TMS hindered the CO_2 absorption rate of the less concentrated 4N MPA and 4N MEA solutions after 50% CO_2 loading.

With TMS in MEA and MPA, a two-phase liquid emulsion developed when approximately 25% of the capacity of the amine was reached. The lighter phase (approximately 30 to 40% solution volume) contained nearly all of the carbonated amine. Phase separations did not occur with DGA-TMS-H_2O compositions during carbonation.

The foaming tendency of these various solutions is shown in Table 3. The average CO_2 values (rounded to the nearest 0.05%) in the effluent gas stream at various CO_2 loadings and their foam column height range are listed for both aqueous and tricomponent amine solutions. The foam column height of the three-component amine solutions did not vary significantly, but as the contact time increased, the average bubble size changed for some solutions. Amine-TMS-H_2O solutions exhibited little tendency toward foaming. In contrast, aqueous MEA and MPA solutions, at times, foamed extensively. Foaming of aqueous DGA solutions was low to moderate.

Of the solvents potentially suitable for use in submarines, TMU is the most effective and TMS the least with respect to improving the CO_2 absorption rate of MEA, DGA, or MPA. The DGA-TMS-H_2O compositions effectively absorb CO_2 to a V_g/V_s of 40. The 4N MPA-TMS-H_2O composition also remains effective to V_g/V_s loadings of 35. TMS retards the effectiveness of 5N MPA after 90% of the equilibrium capacity is reached ($V_g/V_s \approx 47$).

Table 2
Absorption Rate of Various Amines and Tetramethylene Sulfone-Amine Mixtures*

Sample	Absorption Rate of CO_2 (V_g/V_s) After Various Lengths of Time														
	10 min	20 min	30 min	40 min	50 min	60 min	70 min	80 min	90 min	100 min	110 min	120 min	130 min	140 min	150 min
5.4N DGA-TMS-20% H_2O	6	11	16	20	25	29	32	35	38	41	43	45	46	47	–
6.5N DGA-H_2O	5	10	14	18	22	26	30	33	37	40	43	46	48	51	53
4N MPA-TMS-20% H_2O	6	12	17	22	26	30	33	36	37	39	–	40	–	–	–
4N MPA-H_2O	6	11	17	22	27	31	35	38	40	41	–	42	–	–	–
5N MPA-TMS-25% H_2O	6	12	17	22	27	32	36	40	43	46	48	49	50	–	–
5N MPA-H_2O	6	12	18	23	28	32	36	40	43	47	50	52	53	–	–
4N MEA-H_2O	5	11	16	21	26	31	35	37	38	39	–	–	–	42	–
4N MEA-TMS-20% H_2O	5	12	17	22	26	30	33	35	37	39	–	40	–	–	–

*The flow rate was 3.3 l/min of 1% CO_2 in air at 1 atm and 88°F through a 50-ml sample.

Table 3
Percent CO_2 in the Effluent vs CO_2 Loadings*

Sample	Foam Column Height Range (in.)	Effluent CO_2 (%) at CO_2 Loading Indicated								CO_2 loading at Saturation (V_g/V_s)
		0 V_g/V_s	10 V_g/V_s	20 V_g/V_s	30 V_g/V_s	35 V_g/V_s	37 V_g/V_s	40 V_g/V_s	50 V_g/V_s	
4N MEA-H_2O	3-10	0.20	0.10	0.20	0.30	0.40	0.50	0.80	–	42.40
4N MEA-H_2O	3-10	0.15	0.10	0.10	0.30	0.40	0.45	0.70	–	41.90
4N MEA-H_2O	1-10	0.25	0.25	0.25	0.30	0.45	0.55	0.80	–	–
4N MEA-H_2O	1-5	0.20	0.20	0.20	–	–	–	–	–	–
4N MEA-DMAC-25% H_2O	1/2-1	0.10	0.10	0.20	0.35	0.45	0.60	0.75	–	41.2
4N MEA-TMU-20% H_2O	1/2-1	0.05	0.10	0.20	0.40	0.50	0.70	1.00	–	39.8
4N MEA-NMP-25% H_2O	1/2-1	0.10	0.15	0.25	0.45	0.65	0.75	1.00	–	39.2
4N MEA-TMS-20% H_2O	1/2-1	0.10	0.15	0.25	0.50	0.65	0.75	1.00	–	39.5
4N MEA-HMPA-20% H_2O	1/2-1	0.15	0.20	0.30	–	–	–	–	–	–
4N MPA-H_2O	3-10	0.15	0.15	0.20	0.30	0.45	0.50	0.60	–	44.8
4N MPA-TMS-20% H_2O	1/2-1	0.10	0.10	0.25	0.45	0.65	0.75	1.00	–	39.7
5N MPA-H_2O	3-10	0.10	0.10	0.15	0.30	0.40	0.40	0.45	0.65	54.8
5N MPA-TMU-20% H_2O	1/2-1	0.05	0.05	0.15	0.30	0.35	0.40	0.45	1.00	48.7
5N MPA-NMP-20% H_2O	1/2-1	0.05	0.05	0.15	0.30	0.40	0.40	0.50	1.00	48.8
5N MPA-TMS-25% H_2O	1/2-1	0.10	0.15	0.20	0.30	0.35	0.40	0.45	1.00	50.1
6.5N DGA-H_2O	1/2-1	0.20	0.30	0.35	0.45	0.50	0.50	0.50	0.65	57.8
6.5N DGA-H_2O	1/2-1	0.20	0.30	0.40	0.45	0.50	0.50	0.50	0.65	58.9
5.8N DGA-DMF-20% H_2O	1/2-1	0.10	0.10	0.20	0.30	0.30	0.35	0.40	0.60	56.4
6.5N DGA-TMU-20% H_2O	1/2-1	0.10	0.15	0.25	0.35	0.40	0.40	0.45	0.60	57.0
5.4N DGA-NMP-25% H_2O	1/2-1	0.20	0.20	0.30	0.40	0.50	0.50	0.55	1.00	48.1
5.4N DGA-TMS-20% H_2O	1/2-1	0.15	0.20	0.30	0.40	0.50	0.55	0.60	1.00	46.7

*The flow rate was 3.3 l/min of 1.0% CO_2 in air at 88°C and 100% RH through a 50-ml sample.

The increase in CO_2 absorption efficiency shown by such compounds as TMU, DMAC, and DMF may result from the presence of the functional groups

$$CH_3\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}N\!<,\ H\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}N\!<,\ \text{and}\ >\!N\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}N\!<.$$

Compounds containing these groups, in general, possess a greater CO_2 solubility than does H_2O (7).

A COMPARISON OF REGENERATION, OR CO_2 STRIPPING, EFFICIENCIES

A regenerative amine not only must absorb CO_2 efficiently but should release the CO_2 rapidly when heated to temperatures in the 100 to 150°C range. MEA meets this requirement, but an improvement in the stripping efficiency of MEA or its replacement by an amine with a lower heat requirement would be desirable.

The CO_2 stripping efficiency of MEA was improved when H_2O was replaced by DMAC under the conditions in Fig. 4. Comparing anhydrous 4N MEA-DMAC with 4N aqueous MEA on a time basis, the anhydrous system evolved nearly twice as much CO_2. After 2 hr of heating, regeneration of the free amine (MEA) in the anhydrous composition was essentially complete but was only 50% complete with the MEA-H_2O mixture. However, if the solution itself must supply steam as a purge gas, as is often the case, some H_2O must be present. The support given by steam at reduced air flows is shown in Fig. 5. The evolution of CO_2 from the anhydrous MEA-DMAC solution dropped below that of aqueous MEA when the air purge gas flow was lowered to 0.6 l/min. Reduction of the purge gas flow did not retard the stripping rate of the MEA-DMAC-25% H_2O composition to the same extent as that of the anhydrous solution. The CO_2 stripping rate of aqueous MEA was essentially unaffected by the lowered flow rate.

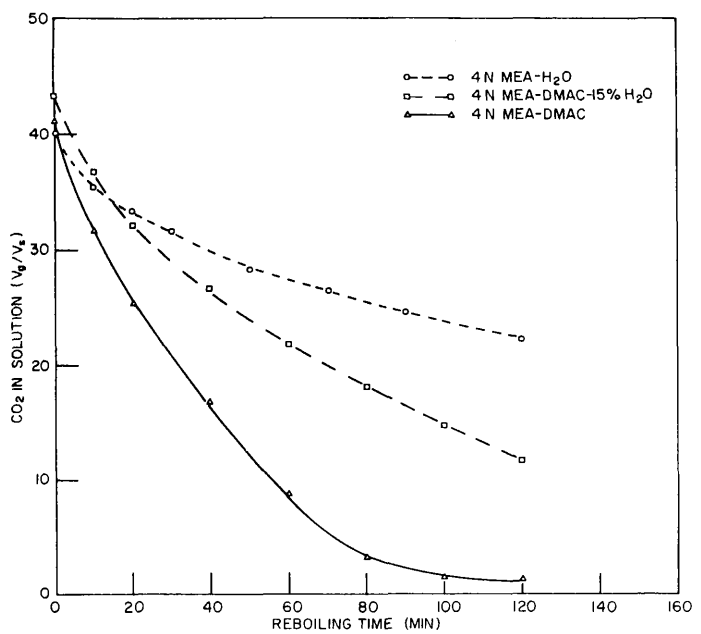


Fig. 4 - Stripping properties of MEA-DMAC-H_2O mixtures, using an air purge at 3 l/min. The samples were in a 100° C H_2O bath at 1 atm.

Figure 6 shows that the organic solvents DMF and NMP did not improve the rate of CO_2 evolution from DGA, but their use did result in lower residual CO_2. Lower levels of retained CO_2 are important because of a beneficial effect on the CO_2 absorption rate in the succeeding absorption cycle.

Table 4 lists the stripping results for the three amines MEA, MPA, and DGA with the various solvents under nonstirred conditions. The retained CO_2 after any given time interval was determined by two methods: (a) continuous monitoring of the purge gas after it passed the sample and water condenser with an infrared CO_2 analyzer and (b) periodic sampling of the amine solution and determination of the CO_2 content by a gasometric method (4).

The most efficient solvents were DMF and DMAC, followed by TMU, TMS, and NMP. One of the 4N MEA-H_2O samples was carbonated with 100% CO_2, rather than the 1% CO_2-air mixture normally used, forcing the CO_2 saturation to a higher level. Regardless of

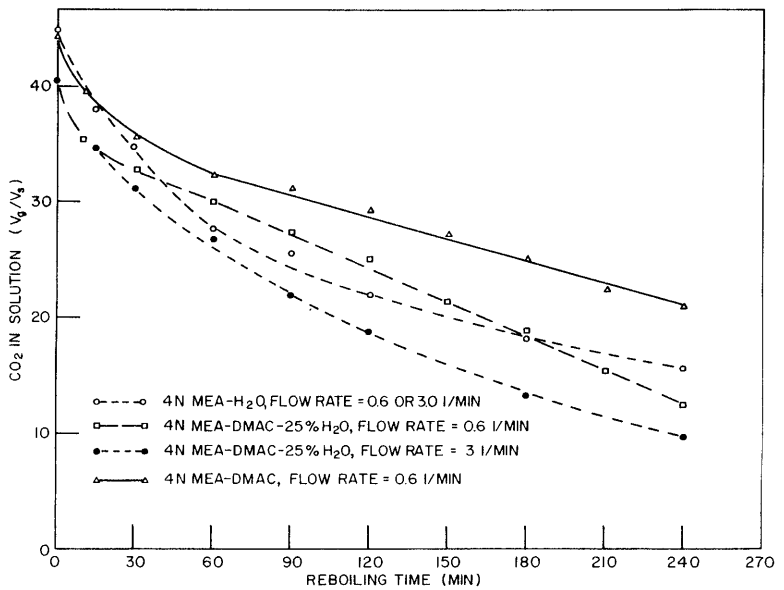


Fig. 5 - Stripping properties vs purge gas flow rate the sample temperature was 92°C, and the pressure was 1 atm.

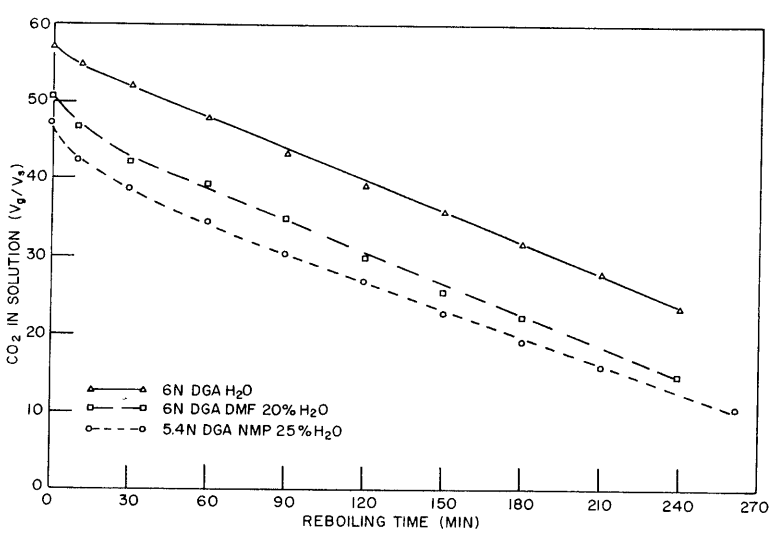


Fig. 6 - Stripping properties of aqueous DGA vs DGA in organic solvents. The sample temperature was 92°C, and the pressure was 1 atm.

Table 4
Stripping of Various Amine-Solvent Compositions*

Sample	CO_2 Loading of Samples (V_g/V_s)												
	Reboiling Time (min)								CO_2 Removal			Fraction Available to 0.50% CO_2 Effluent	
	0	20	40	60	90	120	180	240	First 20 Min	Av/Min (over 3 hr)	Total CO_2 Stripped	After Stripping	Initial Zero Loading
4N MEA-NMP-25% H_2O	39.2	33.1	30.7	28.7	25.6	22.4	12.4	8.7	6.1	0.17	30.5	23	32
4N MEA-DMAC-25% H_2O	40.2	32.9	30.1	26.9	22.2	18.8	13.2	9.8	7.3	0.17	30.4	26	36
4N MEA-H_2O†	45.7	38.2	33.6	27.6	25.6	22.2	18.4	15.8	–	–	–	21	37
4N MEA-H_2O‡	39.3	34.2	30.5	28.5	25.0	21.8	18.8	16.4	5.1	0.13	22.9	21	37
5N MPA-NMP-20% H_2O	48.8	44.0	41.2	38.4	35.0	31.9	24.2	18.7	4.8	0.17	30.1	21	40
5N MPA-TMU-20% H_2O	48.7	43.5	40.8	37.7	33.0	28.8	21.1	18.5	5.2	0.17	30.2	22	41
5N MPA-DMF-20% H_2O	48.0	42.2	37.4	33.2	27.5	23.6	18.6	13.0	5.8	0.19	35.0	28	41
5N MPA-H_2O	52.8	48.9	47.3	45.4	41.2	39.8	32.2	28.7	3.9	0.13	24.1	12	41
5N MPA-H_2O	53.8	49.2	46.2	43.2	39.8	37.0	33.0	28.5	4.6	0.14	25.3	12	41
6.5N DGA-TMU-20% H_2O	56.4	52.4	48.4	45.7	41.6	38.0	28.4	23.0	4.0	0.19	33.4	15	38
6.5N DGA-H_2O	57.8	51.0	47.3	44.3	40.3	36.9	32.4	27.0	6.8	0.17	30.8	13	40
6.5N DGA-H_2O‡	51.1	46.0	43.2	40.9	38.0	36.3	33.0	26.0	5.1	0.14	25.1	14	40

*The experimental conditions were as follows: boiling water bath, 1 atm pressure, and an air purge at 3 l/min over the liquid surface.
†Carbonated with 100% CO_2.
‡Not carbonated to equilibrium loading.

this initial loading, however, the residual CO_2 content in both solutions was approximately the same. The MEA-organic CO_2 solvent-H_2O compositions, compared with their corresponding aqueous MEA solutions, stripped more efficiently and retained only 2/3 as much CO_2. TMU did not increase the stripping efficiency of DGA to any significant extent, probably because the amount of TMU added ($\approx$ 15%) was too low. Table 4 also lists the available CO_2 capacity to the 0.5% CO_2 effluent level after stripping. For example, a 4N MEA-DMAC-H_2O solution could absorb 26 V_g/V_s units of CO_2 before the effluent CO_2 concentration would reach 0.5%, but a 4N MEA-H_2O solution would absorb only 21 V_g/V_s units under the same conditions of gas flow, temperature, influent CO_2, etc. DMF increased the effective loading of 5N MPA-H_2O more than two-fold (28 V_g/V_s units).

Table 5 compares the stripping rates of amine-TMS-H_2O mixtures with the corresponding aqueous amine. The incorporation of TMS significantly improved the stripping efficiencies of all of the amines studied. The DGA data must be normalized to equivalent concentrations to make the improvement apparent.

PREDICTED PERFORMANCE IMPROVEMENT

The data in the previous sections can be used to calculate the overall performance of the various amine and amine-solvent solutions when used in dynamic cyclic absorption-desorption operations. Such calculations were made for TMS solutions and compared with 4N MEA-H_2O, the solution currently used in submarine operation. Based on the rate and capacity data in Tables 2, 3, and 5, a 4N MEA-TMS-H_2O mixture would process about 20% more CO_2 in the same time frame and maintain a lower average CO_2 concentration in the effluent than would 4N MEA-H_2O alone. Similarly, 5N MPA-TMS-H_2O compared with 4N MEA-H_2O shows even greater improvement; for the same cyclic operation, the TMS-containing solutions would process 36% more CO_2. In the same manner, it can be shown that a 5.4N DGA-TMS-H_2O solution would process 25% more CO_2 than 4N MEA-H_2O. The DGA-TMS mixture has the additional attractive feature of not becoming a two-phase system when carbonated.

Table 5
Effect of TMS on Stripping Rate*

Sample	CO_2 Loading of Samples (V_g/V_s)													
	Reboiling Time (min)									CO_2 Removal			Fraction Available to 0.50% CO_2 in the Effluent	
	0	10	20	40	60	90	120	150	180	First 20 Min	Av/Min (over 3 hr)	Total CO_2 Stripped	After Stripping	Initial Zero Loading
3.5N MEA-TMS-25% H_2O	37.2	28.5	23.2	16.5	12.0	8.0	6.0	4.7	4.3	14.0	0.18	32.9	22	27
4N MEA-TMS-20% H_2O	41.8	35.1	28.4	18.4	13.1	8.1	5.1	3.5	3.1	13.4	0.22	38.7	27	30
4N MEA-H_2O	42.3	37.3	33.5	28.0	26.7	22.6	18.5	16.4	14.3	8.8	0.16	28.0	23	37
4N MEA-H_2O	43.4	35.6	32.0	26.3	23.0	19.0	16.9	15.4	14.0	11.4	0.16	29.4	23	37
4N MPA-TMS-20% H_2O	41.4	30.6	34.3	17.0	11.7	8.3	6.9	5.0	4.6	17.1	0.20	36.8	26	31
4N MPA-TMS-20% H_2O	34.1†	28.8	24.8	19.5	15.2	10.2	7.4	5.0	–	–	–	–	26	31
4N MPA-H_2O	44.5	39.2	35.5	30.2	26.9	24.5	22.1	20.7	19.3	9.0	0.14	25.2	18	37
5N MPA-TMS-25% H_2O	47.1	38.7	33.2	25.7	20.9	16.2	12.7	9.8	8.0	13.9	0.22	39.1	33	41
5N MPA-H_2O	54.8	48.7	45.3	40.7	38.0	35.0	32.5	30.0	28.2	9.5	0.15	26.6	13	41
5N DGA-TMS-25% H_2O	42.9	34.5	29.2	20.5	15.2	9.2	5.8	3.4	1.8	13.7	0.23	41.1	31	34
5N DGA-TMS-25% H_2O	36.1†	30.4	25.4	18.7	14.7	10.0	7.0	5.0	3.0	–	–	–	–	–
6.5N DGA-H_2O	58.7	52.7	48.7	42.0	36.8	29.8	22.0	18.0	15.0	10.0	0.24	43.7	27	40
6.5N DGA-H_2O	58.3	51.0	46.0	38.0	32.0	25.0	20.0	16.0	12.0	12.3	0.26	46.3	27	40

*The experimental conditions were as follows: boiling water bath, 1 atm of pressure, and an air purge at 3 l/min over the liquid surface with the sample being stirred.
†These runs were started at higher initial CO_2 loadings without stirring. Data for the indicated V_g/V_s were anomalous and are not included. It was these runs which demonstrated the need for stirring.

PREPARATION AND STUDY OF A NEW AMINE

A compound with attractive properties and not previously evaluated is 3-(methylsulfonyl) propylamine, $CH_3SO_2CH_2CH_2CH_2NH_2$. The literature states that this compound is strongly alkaline, is not volatile in steam, possesses a melting point of 44°C, and can be distilled at 165 to 168°C at 6 mm without decomposition (14). The material was not readily available commercially so research quantities were synthesized by the oxidation of 3-(methylthio) propylamine to the sulfone with either hydrogen peroxide or potassium permanganate (6).

Figure 7 compares the CO_2 absorption rate of a MSP-H_2O mixture with a MEA-H_2O mixture. For samples without antifoam agents, the rate for MSP was superior to MEA until 70% of the CO_2 capacity of the amine was filled. MSP foamed extensively, and a larger quantity of foam suppressant was required for it than for MEA. With both amines, the absorption efficiencies decreased on the addition of antifoam agent, but the absorption rates were equal for the same foam column height and the same quantity of antifoam agent. When additional foam suppressant was required, the rate for MSP fell to 90% of that for MEA. The equilibrium CO_2 capacity of MSP is approximately 90% of MEA for the same conditions and normalities.

On stripping, MSP evolves CO_2 faster than does MEA (Fig. 8). MSP lost 27 V_g/V_s units, while MEA evolved only 22 V_g/V_s units for the same 30-min period. The residual CO_2 after stripping (under the same conditions) was lower for MSP, regeneration being 92% complete for the sulfone amine and only 75% complete for MEA.

A comparison of Figs. 7 and 9 illustrates the advantage of the nearly complete regeneration of MSP. Although the normalities of both solutions in Fig. 9 are lower due to necessary dilutions after previous sampling than those in Fig. 7, the CO_2 absorption efficiency of MSP remained essentially unchanged for 35 min, while for MEA the CO_2 in the effluent was 1.5 times that of the original 3.5N MEA after only 15 min.

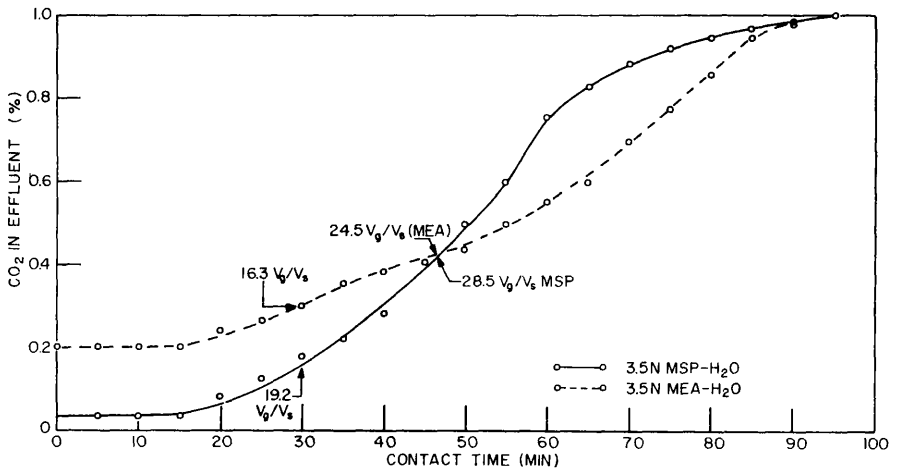


Fig. 7 - CO_2 absorption rate of MEA and MSP, using a flow rate of 3.3 l/min of 1% CO_2 in air at 88°F, 100% RH, and 1 atm. There were no additives.

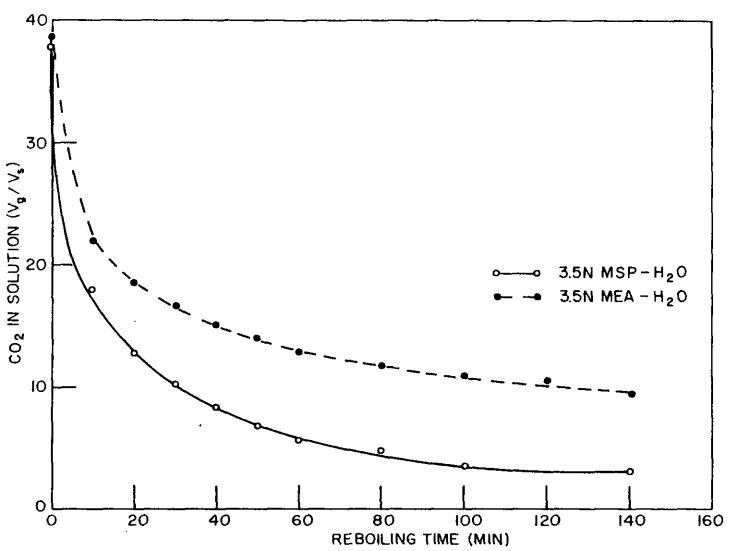


Fig. 8 - Stripping properties of MEA and MSP, using a N_2 purge gas at a flow rate of 500 cc/min at 1 atm. A 50-ml sample was used in an oil bath at 125°C.

The oxidation stability of MSP is high relative to that of MEA. As shown in Fig. 10, the only significant evolution of NH_3 from MSP occurred after 4 days, and the rate at that time was only about 4% as great as for MEA. Normality loss for the 6-day period amounted to 1.4% for MSP and 16% for MEA.

Table 6 summarizes various critical properties of MSP relative to MEA.

The MSP and TMS studies indicate another sulfone amine that should be studied–3-(methylamine)tetramethylene sulfone or derivations containing longer side chains. This compound contains both the alkyl sulfonyl propylamine fragment and the TMS structure

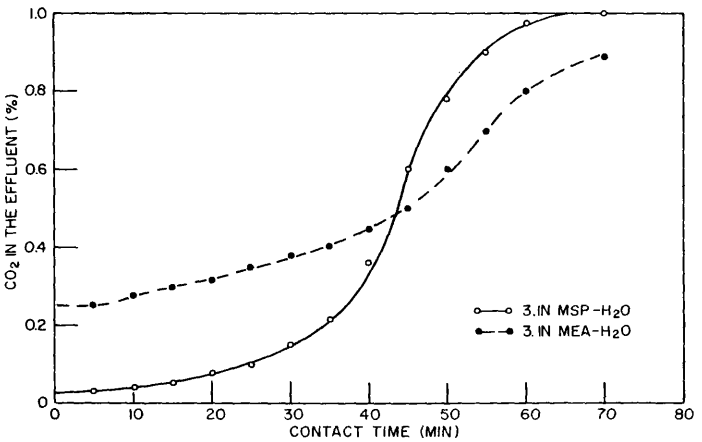


Fig. 9 - Effect of initial stripping cycle on second absorption cycle, using a flow rate of 3.3 l/min of 1% CO_2 in air at 88°F and 100% RH at 1 atm.

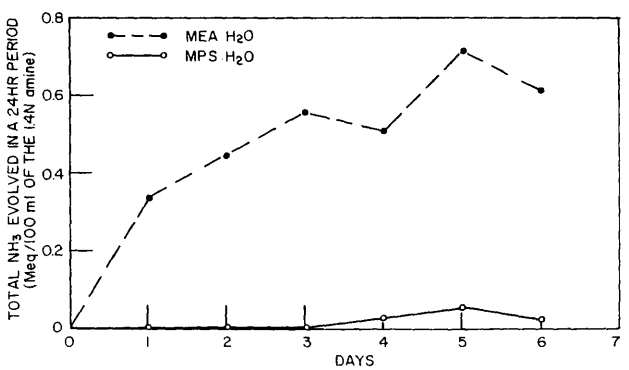
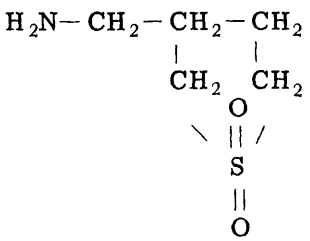


Fig. 10 - Dynamic test of MSP stability with no additive present, using a flow rate of 100 ml/min of 2% CO_2 in air at 55°C

and, therefore, may combine such desirable properties as low foam tendency and high CO_2 absorption rate. The structural formula of this compound is



VISCOSITY

The absolute viscosities of aqueous solutions of MSP, MEA, MPA, and DGA are compared with their TMS analogs in Table 7. The viscosities were determined by standard

Table 6
Comparison of MEA and MSP Properties

Property	MEA	MSP
Volatility	High, 760 mm (170°C)	Low, 6 mm (168°C)
CO_2 absorption rate (relative)	1	0.9-1.2 (depending on foam conditions)
CO_2 capacity (relative)	1	0.9
Stripping rate (relative)	1	1.3 (at 30 min)
Oxidation Stability	Poor	High
Melting point of 4N solution	-12°C	-17°C
Thermal Stability	Poor	Stable to 180°C
Alkalinity (relative)	1	<1
Odor	Ammoniacal	Low
Foaming tendency	Fair	Poor

Table 7
Viscosities of Various Amine-Solvent Compositions

Material	CO_2 Absorbed (V_g/V_s)	Absolute Viscosity at 30°C (cp)
4N MEA-H_2O	0	1.8
4N MEA-H_2O	47	2.0
4.5N MEA-H_2O	0	2.4
4.5N MEA-H_2O	50	3.3
4N MEA-TMS-20% H_2O	0	6.0
4N MEA-TMS-20% H_2O	37	3.7 (20°C)*
5N MPA-H_2O	0	3.3
5N MPA-H_2O	55	4.3
5N MPA-TMS-25% H_2O	0	7.6
5N MPA-TMS-25% H_2O	47	6.8 (20°C)*
6.5N DGA-H_2O	0	9.4
6.5N DGA-H_2O	58	16.4
5.4N DGA-TMS-20% H_2O	0	9.7
5.4N DGA-TMS-20% H_2O	42	14.1
4N MSP-H_2O	0	3.6
4N MSP-H_2O	40	6.7

*Sample separated into two liquid phases during viscosity determination.

methods (average of 5 to 10 determinations (15)) using the appropriate Cannon Fenske viscometers. The obtained kinetic viscosities were then converted to absolute values. Carbonated amine-TMS solutions separated rapidly into two phases; therefore, a series of very-short-time-interval runs on well-mixed samples were made at room temperature (20°C) with a 1-ml pipet instead of the regular Ostwald viscosity pipet. The amine-organic solvent-H_2O combinations are more viscous than the aqueous solutions. The retarding effect exerted by this high viscosity on convectional heat transfer during stripping can be significantly reduced by stirring. The effect on pumping requirements was not calculated.

SUMMARY

The replacement of part of the H_2O in an alkanolamine (monoethanolamine (MEA), 3-amino-1-propanol (MPA), and 2-(2-aminoethoxy)ethanol (DGA)) solution by an organic CO_2 solvent generally results in an improvement in both the absorption and stripping capabilities of the amine but may also result in a decrease of up to 10% in the equilibrium CO_2 capacity. For use in submarines, tetramethylene sulfone (TMS) is a more suitable solvent for this purpose than the others studied. One disadvantage is that TMS forms an emulsion with MEA and MPA during carbonation. The emulsion disappears on stripping.

The system showing the largest improvement through the use of TMS was 5N MPA. The 5N MPA-H_2O mixture alone is considerably inferior to 4N MEA-H_2O because the stripping efficiency is significantly less under the same conditions. However, with TMS added, the available CO_2 loading capacity after stripping is 2-1/2 times that of aqueous 5N MPA and approximately 1-1/2 that of aqueous 4N MEA, and the average effluent CO_2 level should be lower. Additionally, MPA possesses a lower volatility and a higher oxidation resistance than does MEA. However, a factor favoring MEA is that 5N MEA-TMS-H_2O solutions would probably evolve more CO_2 than 5N MPA-TMS-H_2O mixtures under the same stripping conditions.

TMS improves both the absorption and stripping rates of DGA by about 5 to 10%. The relatively high boiling point (221°C) and excellent stripping properties of DGA favor its consideration, especially under pressurized absorption conditions.

With either MPA, DGA, or their corresponding organic CO_2 solvent mixtures, agitation during the stripping is a necessity to overcome the retarding effect of high viscosity. Strict adherence to a 25-vol-% H_2O content is not necessary, but because of the flash points exhibited by some of these materials, there may be a fire hazard during abnormal operation if some H_2O is not present. For this reason, an initial H_2O content of at least 25% is suggested. The H_2O is also necessary for providing steam as a purge gas during stripping.

In addition to amine-organic CO_2 solvent-H_2O composition, the aminoalkyl sulfones, such as 3-(methylsulfonyl)propylamine (MSP), with their low volatilities, high thermal stabilities, and excellent oxidation resistance, offer possibilities of significant improvements over the amine-H_2O solutions now in use. A MSP-TMS-H_2O mixture would be a worthwhile system for further investigation.

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REFERENCES

1. Gustafson, P.R., "Investigation of 1,4-Cyclohexanebis(methylamine) as a Regenerative Carbon Dioxide Absorbent," NRL Report 6417, Aug. 25, 1966

2. Gustafson, P.R., "CO_2 Absorption Properties of Some New Amines," Chapter 5 in "The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines," R.R. Miller and V.R. Piatt, editors, NRL Report 6722, June 18, 1968

3. Reitmeier, R.E., Atwood, K., et al., The Girdler Corporation, "Carbon Dioxide Absorbents," Report on Contract NObs-50023, June 1, 1950

4. Reitmeier, R.E., Atwood, K., et al., The Girdler Corporation, "Carbon Dioxide Absorbents," Final report on Contract NObs-50023, Aug. 1, 1950

5. Schneider, W., "Uber Cheirolin, das Senfol des Goldlacksamens. Sein Abbau und Aufbau," Ann. 375:207 (1910)

6. Brighton, K.W., and Reid, E.E., "Several Alkyl-B-Thioethylamines and the Corresponding Ureas, Sulfoxides and Sulfones," J. Am. Chem. Soc. 65:458 (1943)

7. Quinn, E.L., and Jones, C.L., "Carbon Dioxide," Am. Chem. Soc. Monograph, New York:Reinhold, pp. 105-106, 1936

8. Technical Bulletin on Tetramethylurea, The Ott Chemical Company, Muskegon, Michigan, Jan. 1968

9. "M-Pyrol," General Aniline and Film Corporation, Technical Bulletin 7543-038, copyright 1961-1965

10. "Sulfolane," Shell Chemical Company, Technical Bulletin IC:63-13R, Mar. 1964

11. "Sulfolane," Shell Chemical Company, Technical Bulletin IC:63-13R, p.5, Mar. 1964

12. Deal, C.H., Evans, H.D., Oliver, E.D., and Papadopoulos, M.N., "A Better Way to Extract Aromatics," Shell Development Company, Petrol. Refiner 38 (No. 9):185-92 (1959)

13. Allen, J.P., "Carbon Dioxide Management II. CO_2 Absorption by Amine Solutions," FDFE-TM-64-27, Air Force Systems Command; Air Force Flight Dynamics Lab, Wright Patterson Air Force Base, Ohio, Aug. 5, 1964

14. Schneider, W., "Uber Cheirolin, das Senfol des Goldlacksamens. Sein Abbau und Aufbau," Ann. 375:226 (1910)

15. "ASTM Standards," Philadelphia:American Society for Testing Materials, Part 7, p. 213, 1958

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13. ABSTRACT

Three amines—monoethanolamine (MEA), 2-(2-aminoethoxy)ethanol (DGA), and 3-amino-1-propanol (MPA)—each mixed with one of a series of organic liquids with high CO_2 solubility and varying proportions of H_2O, were compared with their corresponding aqueous solutions with regard to CO_2 absorption, CO_2 stripping, and solution viscosity. The organic liquids were N,N-dimethylformamide, N,N-dimethylacetamide, tetramethylene sulfone, N-methyl-2-pyrrolidinone, hexamethylphosphoric triamide, and tetramethylurea.

While some of the organic liquids improved the CO_2 absorption and stripping properties of 4N aqueous MEA to a greater extent than did tetramethylene sulfone, the latter solvent, which has better physical properties for use in submarines, increased the efficiency of 4N MEA about 20%, and when admixed with 5N MPA, the improvement was approximately 36%.

An ω-aminoalkyl alkyl sulfone, 3-(methylsulfonyl)propylamine, $CH_3SO_2CH_2CH_2CH_2NH_2$, was synthesized and compared with MEA with respect to absorption and stripping efficiency, viscosity, oxidation resistance, foaming, and capacity. A significant improvement over MEA was noted in oxidation resistance, volatility, and stripping efficiency. The absorption efficiency nearly equaled or exceeded the efficiency

(Continues)

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of MEA, depending on the foaming conditions; however, the CO_2 capacity was lower by 10%. Although the foaming was excessive, it could be controlled by the use of antifoam agents.

Further study is recommended on an engineering-scale CO_2 scrubber, or on an operational unit, of 3-amino-1-propanol (MEA)-tetramethylene sulfone aqueous solutions and also ω-aminoalkyl sulfone or other aminoalkyl tetramethylene sulfone compounds when they become commercially available.

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