**Collection of VLE Data for
Acid Gas - Alkanolamine Systems
Using Fourier Transform Infrared Spectroscopy**

Technical Report

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Abstract

The industrial standard process for the purification of natural gas is to remove acid gases, mainly hydrogen sulfide and carbon dioxide, by the absorption and reaction of these gases with alkanolamines. The natural gas industry requires vapor - liquid equilibrium (VLE) data to develop more energy efficient amine mixtures. Some energy reductions have been realized in the past decade by applying such amine systems as "hindered" amines, methyldiethanolamine (MDEA), and MDEA based amine mixtures. However, the lack of reliable and accurate VLE data impedes the commercial application of these more efficient alkanolamine systems.

The first objective of this project is to improve the accuracy of vapor - liquid equilibrium measurements at low hydrogen sulfide concentrations. The second objective is to make VLE measurements for amine mixtures. By improving the accuracy of the VLE data on MDEA and other amines, energy savings can be implemented in the many existing absorption units already in use. If about 25% of the existing 95.3 billion SCFD gas purification capacity is converted to these new amine systems, the energy saved is estimated to be 3×10^{14} BTU/yr.

Introduction

The industrial standard process for the purification of natural gas is to remove acid gases, mainly hydrogen sulfide (H_2S) and carbon dioxide (CO_2), by the absorption and reaction of these gases with alkanolamines. Monoethanolamine (MEA) and diethanolamine (DEA) are the predominate alkanolamines used by natural gas processors, refiners, ammonia producers, and synthetic gas producers. The gas stream contaminated with acid gases, called a sour gas stream, is fed to an absorber column where it is contacted counter currently with a solution of alkanolamine and water.

After the acid gases are absorbed, the reacted alkanolamine, or rich amine, is transported to a regeneration or stripper column. By the application of heat, the chemical reaction is reversed and the acid gases are stripped from the solution. Because the regenerator is operated at elevated temperature, the lean amine stream is cross-exchanged with the rich amine stream for heat recovery. Excessive pumping energy and reboiler duty are consumed when these gas purification units are operated within equilibrium pinch zones, where there is a lack of accurate VLE data for acid gas - alkanolamine mixtures.

Inadequate models for VLE, kinetics, and mass transport hinder the industry from converting operations to more energy efficient amine mixtures. In addition to energy waste, the inefficient gas purification operations result in the combustion of additional fossil fuel, primarily natural gas, to produce the energy required for the purification process. The wasted energy also results in the release into the atmosphere of additional CO₂, CO, and NO_x combustion products.

Some energy reductions have been realized in the past decade by adopting such amine systems as "hindered" amines, methyldiethanolamine (MDEA), or MDEA based amine mixtures.^[1,2,3] MDEA based amines have demonstrated greater solvent capacity and selective absorption for H₂S in many applications now serviced by MEA and DEA. Additional advantages for MDEA amine systems are an improved corrosion performance, a lower heat of reaction, a higher solution concentration, and an improved solution stability. Designs that incorporate these advantages of MDEA based amines can reduce the pumping energy and reboiler duty of amine operations from 25 to 60%.

However, the lack of reliable and accurate VLE data impedes the commercial use of these more efficient alkanolamine systems. The most critically deficient area for VLE data occurs in the lean amine equilibrium pinch zones in the bottom of the stripper and top of the absorber. The lean pinch zones typically have H₂S partial pressures less than 0.1 psia and loadings less than 0.01 mol/mol of amine. Other important areas include the high temperature pinch zones within the absorber and the rich amine equilibrium pinch zone in the bottom of the absorber. The rich pinch zones can have extremely high acid gas partial pressures but usually they are less than 200 psia.

Natural gas processors and petroleum refiners are the two major industries using alkanolamine purification. The amount of gas processed by these industries is about 95.3 billion standard cubic feet per day (BSCFD). MDEA based amines have the potential of saving energy in more than 28 BSCFD of this total processed volume. Without new accurate amine VLE data for MDEA based amine mixtures, 25 BSCFD of this processed gas will not realize energy savings. The energy savings potential for the conversion of 25 BSCFD capacity to these more efficient amines is estimated to be 3×10^{14} BTU/yr. At current gas prices, this amount of energy is equivalent to about \$500 million a year.

Scope of Investigation

This project has two major objectives. The first is to improve the accuracy of vapor - liquid equilibrium measurements at low hydrogen sulfide concentrations. The second is to measure VLE data for amine mixtures. These objectives are pursued in three stages.

Stage I will develop and demonstrate the application of quantitative infrared spectroscopy to VLE measurements of acid gas - DEA systems. The infrared technique will improve the accuracy of conventional methods in the low hydrogen sulfide concentration range. The technique also provides for a more detailed analysis of the liquid phase reaction products than conventional methods.

Stage II will then expand the technique to include MDEA. Stage III will develop the technique for mixtures of two amines, and measurements will be made of MDEA - DEA amine mixtures.

Significant Results

Apparatus Modifications

The vapor temperature indication system, consisting of an analog to digital converter and a mechanical switching box was replaced by a more stable and precise converter with solid state switches. The vapor temperatures in the vapor circulation system are related to the vapor densities and are used in the vapor calibrations.

Modifications were made to permit measurements at VLE temperatures up to 250 °F instead of the present limit of about 185 °F. Because of high H₂O vapor pressures at higher temperatures, experiments will be performed at a pressure of 30 psia instead of the present 15 psia. New high temperature equipment that was acquired includes a vapor pump, which was modified for the higher temperature and pressure ranges. In addition, tube heaters for the long path cell windows will be installed.

Hydrogen sulfide and carbon dioxide vapor calibrations

Known amounts of hydrogen sulfide were measured at various total pressures near 15 psia with nitrogen as a diluent. From these measurements, frequency regions for hydrogen sulfide were selected, and their spectral areas were calibrated from zero to 1.5 psia hydrogen sulfide. Below 0.1 psia, the H₂S pressures are linear with the absorbance areas. The dependence at higher pressures is progressively non linear but well

behaved and reproducible. Similar calibration measurements were made for CO₂ from near zero to 0.8 psia. The CO₂ pressures are quadratic and well behaved with the spectral areas over this entire pressure range.

Calibration experiments matched in conditions as closely as possible the VLE experiments and included presence of both H₂S and CO₂ over wide ranges of pressures. Carbon dioxide at high pressures in the long pathlength cell shifts the hydrogen sulfide baselines, but the effect of CO₂ can be removed or avoided by using a narrower spectral frequency range for H₂S.

For each calibration pressure of pure H₂S and CO₂, spectral measurements were made at several total pressures of nitrogen near 15 psia to determine the total pressure effect on the absorbance at each sample partial pressure. With this information, experimental spectral measurements are adjusted to a total pressure of 15 psia.

Calibration measurements of CO₂ background levels

Calibration measurements were made of CO₂ background levels within the contained part of the apparatus for a range of nitrogen purge rates at normal experimental conditions. These values are used to calculate residual CO₂ levels in all VLE systems.

Calibration of Druck pressure transducer

Upon discovery of a pressure shift in the Druck pressure transducer readings, the Druck transducer was recalibrated against the Paroscientific transducer under the conditions used in the experiments. Also, the Druck transducer tubing was modified to allow periodic checks of the Druck transducer with the Paroscientific transducer. The cause of the Druck transducer shift is unknown, but periodic measurements with the Paroscientific will test its stability. The Paroscientific transducer is more stable and more accurate than the Druck transducer, but it is not designed for use with corrosive acid gas samples.

H₂S with fixed CO₂ in 20.3 wt% DEA H₂S/DEA at 49.6 °C

VLE measurements were made of progressively increasing pressures of hydrogen sulfide with a fixed amount of carbon dioxide in 20.3 wt% DEA/H₂O at 49.6 °C. Frequency regions were identified for separate measurements in the liquid cell of the CO₂-DEA or carbamate species and the H₂S-DEA species involved in the DEA liquid loading. Also, frequency regions were identified for measuring H₂S at low pressure in the long vapor cell.

Starting with an initial carbon dioxide loading near 0.014 CO₂/DEA mole ratio, H₂S was added and mixed to prepare VLE systems. Five VLE compositions with increasing amounts of H₂S were measured with a fixed total amount of CO₂. The pressures and loading of H₂S and CO₂ are listed in Table 1. The solubility of H₂S in the DEA solution was determined from the FTIR measurements and is shown in Figure 1 (p. 17). Taking into account the significant liquid reactions, the H₂S pressure at low H₂S/DEA loading should be proportional to

$$Fn(H_2S) = \alpha_H \cdot (\alpha_H + \alpha_C) / (1 - \alpha_H - 2 \cdot \alpha_C),$$

where α_H is the H₂S loading and α_C is the CO₂ loading. This function reduces to $\alpha_H \cdot \alpha_H$ at loading approaching zero. This dependence is exhibited for the measured H₂S pressures, shown in Figure 2 (p. 18).

H₂S with added CO₂ in 20.3 wt% DEA H₂S/DEA at 49.6 °C

Starting with an initial hydrogen sulfide loading $\alpha_H \sim 0.056$, carbon dioxide was added to 20.3 wt% DEA/H₂O at 49.6 °C. Six VLE compositions were measured and the data are listed in Table 2. The added CO₂ decreased the H₂S solubility and increased the initial H₂S pressure as shown in Figure 3 (p. 19). From the same measurements, the solubility of CO₂ in the DEA solution was determined and is shown in Figure 4 (p. 20). Taking into account the significant liquid reactions, the CO₂ pressure at CO₂ loading approaching zero should be proportional to

$$Fn(CO_2) = \alpha_C \cdot (\alpha_C + \alpha_H) / (1 - \alpha_H - 2 \cdot \alpha_C)^2,$$

where α_C is the CO₂ loading and α_H is the H₂S loading. This function reduces to $\alpha_C \cdot \alpha_C$ at loading approaching zero. This dependence is exhibited for pressures below 0.001 psia, as shown in Figure 5 (p. 21).

H₂S with residual CO₂ in 20.2 wt% DEA H₂S/DEA at 49.8 °C

Eleven VLE measurements were made of a system composed of hydrogen sulfide and carbon dioxide in 20.2 wt% DEA/H₂O at 49.8 °C. Only H₂S was added to the DEA solution, but a small amount of initial CO₂ accounted for a CO₂/DEA mole ratio of ~ 0.008 . The residual CO₂ is from desorbing cell and tubing surfaces and a small amount in the DEA, which for all of the VLE studies was distilled to remove most of the original CO₂ and other ethanolamines.

The solubilities of H₂S and CO₂ in the DEA solution were determined from the FTIR measurements, and are listed in Table 3. The solubilities of H₂S are shown together with literature data by Leibush⁴ in Figure 6 (p. 22). The CO₂ pressures and values of $Fn(CO_2)$ are shown to be linear for these pressures below 0.0012 psia in Figure 7 (p. 23).

The values of H_2S/DEA for this system shown in Figure 6 (p. 22) with an initial CO_2/DEA loading of 0.009, are shown in Figure 8 (p. 24) together with values shown in Figure 1 (p. 17) for hydrogen sulfide in 20.3 wt % DEA with an initial CO_2/DEA loading of 0.014. In this study, the effect of CO_2 on the solubility at low concentrations of H_2S is demonstrated with higher H_2S pressures at a given H_2S/DEA loading measured for the larger CO_2 loading condition.

In the low pressure region, the curvature in the H_2S pressures (log-log plot) is caused by CO_2/DEA loading. This curvature is accounted for at low loading in the $F_n(H_2S)$ function as discussed above. The H_2S pressures and $F_n(H_2S)$ values are shown in Figure 9 (p. 25) for H_2S pressures < 0.003 psia, where the dependence is linear as expected.

H_2S with residual CO_2 in 20.2 wt% DEA H_2S/DEA at 40.0 °C

VLE measurements were made of hydrogen sulfide and carbon dioxide in 20.2 wt% DEA/ H_2O at 40.0 °C. The DEA sample from the previous experiment was lowered from 49.8 °C to 40.0 °C. A total of four VLE compositions with increasing amounts of H_2S with fixed CO_2 were measured. The solubilities of H_2S and CO_2 in the DEA solution are listed in Table 4. The H_2S solubility is shown together with literature data by Lal⁵ and Lawson⁶ in Figure 10 (p. 26). The CO_2 pressures and values of $F_n(CO_2)$ are shown to be linear for these pressures below 0.0015 psia in Figure 11 (p. 27).

H_2S with added CO_2 in 20.2 wt% DEA H_2S/DEA at 40.0 °C

Measurements were made of carbon dioxide and hydrogen sulfide in the 20.2 wt% DEA/ H_2O system, discussed above, as amounts of CO_2 were added to the system. The solubilities of four VLE compositions of H_2S and CO_2 in the DEA solution are listed in Table 5. The solubilities of H_2S for these four compositions and the compositions for the previous experiment when no CO_2 was added are shown in Figure 12 (p. 28). Also, the solubilities of CO_2 for these compositions and for those of the previous experiment are shown in Figure 13 (p. 29), where the initial rise in CO_2 pressure and decrease in CO_2 loading is caused by the additions of H_2S .

In these studies, the effects of CO_2 and H_2S on the solubility of H_2S and CO_2 in the DEA system are measured and demonstrated.

H₂S with residual CO₂ in 50.0 wt% MDEA at 39.9 °C

Methyldiethanolamine (MDEA) samples from Aldrich were vacuum distilled to remove other amines and most carbon dioxide. A 50 wt% MDEA/H₂O sample was prepared and transferred to the VLE cell for the first MDEA study. Calibration measurements in the vapor and liquid were then made on the MDEA/H₂O without any H₂S or added CO₂.

VLE measurements were made of hydrogen sulfide in a 50.0 wt% MDEA at 39.9 °C. Following the measurements of three H₂S concentrations, the aqueous MDEA sample was discovered to have been transported out of the VLE cell. The long vapor cell, short vapor cell, and vapor pump were subsequently opened and cleaned of liquid sample.

Bubbling tests with aqueous MDEA samples exhibited foaming that could result in two-phase flow. As a result of these tests modifications were made in the vapor lines, and vapor flow rates are now controlled below the threshold for significant foaming. Also, additional modifications were made to prevent VLE cell liquid from being transported into the long vapor cell or other parts of the vapor circulation network. The most significant modification was the installation of a heated 500 cm³ cell to perform as a liquid trap just outside the liquid port of the VLE cell.

In addition, a pressure relief device with a teflon coated rupture disk had developed a leak, and sample liquid was transported to a vapor scrubbing chamber. This pressure relief device was redundant to other high pressure safety heads, so it was removed and the line capped.

Following the apparatus modifications and reassembly, a new sample of 50 wt% MDEA was prepared and VLE measurements at 40 °C were continued. The VLE H₂S data from the second experiment are presented in Table 6 and are displayed in Figure 14 (p. 30) together with preliminary data by Robinson⁷ and data reported by Jou⁸.

CO₂ in 50.0 wt% MDEA/H₂O at 40.0 °C

VLE measurements were made of six concentrations of carbon dioxide in a 50 wt% MDEA at 40.0 °C. The CO₂ spectral areas and pressures from this experiment were tested by running a calibration check of the carbon dioxide vapor. The CO₂ spectral areas were consistent, but the pressures measured with the Druck pressure transducer were found to be high compared with values measured with a Paroscientific quartz pressure transducer. The Druck transducer was subsequently calibrated against the Paroscientific transducer under the conditions used in the experiments. The calibration pressure values for H₂S and CO₂ were then recalculated.

Following recalibration of the Druck pressure transducer, eight VLE measurements at 40.0 °C were made of carbon dioxide with a freshly made sample of 50.0 wt% MDEA. The VLE CO₂ data from this experiment are presented in Table 7 and are displayed in Figure 15 (p. 31) together with preliminary data by Robinson⁹ and literature data by Jou¹⁰. The behavior of the data at pressures below 0.008 psia is shown in Figure 16 (p. 32), where five CO₂ pressures below 0.008 psia are plotted as a function of

$$Fn(CO_2) = \alpha_c \cdot \alpha_c / (1 - \alpha_c),$$

α_c is the CO₂ loading, and $Fn(CO_2)$ is the expected behavior as the CO₂/MDEA loading approaches zero. This function reduces to $\alpha_c \cdot \alpha_c$ at loading approaching zero.

CO₂ in 23.0 wt% MDEA at 40.0 °C

Seven VLE measurements at 40.0 °C were made of carbon dioxide with a new sample of 23.0 wt% MDEA. The VLE CO₂ solubility data are listed in Table 8 and are displayed in Figure 17 (p. 33) together with preliminary data by Robinson (1994)⁹ and literature data by Jou (1982)¹⁰. These 23.0 wt% MDEA data for CO₂ are shown together with the previous measured 50.0 wt% MDEA data for CO₂ (Figure 15, p. 31) in Figure 18 (p. 34).

The behavior of the data at pressures below 0.004 psia is shown in Figure 19 (p. 35), where four CO₂ pressures are plotted as a function of

$$Fn(CO_2) = \alpha_c \cdot \alpha_c / (1 - \alpha_c),$$

where α_c is the CO₂ loading, and $Fn(CO_2)$ is the expected behavior as the CO₂/MDEA loading approaches zero. This function reduces to $\alpha_c \cdot \alpha_c$ at loading approaching zero.

H₂S with $\alpha_{CO_2} \sim 0.076$ in 23.0 wt% MDEA at 40.0 °C

Six VLE measurements were made of H₂S and CO₂ in 23.0 wt% MDEA at 40.0 °C as hydrogen sulfide was added to the last VLE sample of the CO₂/MDEA system (with initial CO₂/MDEA loading, $\alpha_{CO_2} \sim 0.076$) discussed above. The VLE data for both H₂S and CO₂ are presented in Table 9, and the H₂S solubility in the presence of CO₂ is shown in Figure 20 (p. 36).

The behavior of H₂S pressure at low concentration is shown in Figure 21 (p. 37), where four H₂S pressures are plotted against

$$Fn(H_2S) = \alpha_H \cdot (\alpha_H + \alpha_c) / (1 - \alpha_H - \alpha_c).$$

The H₂S and CO₂ loading is α_H and α_c , respectively, and $Fn(H_2S)$ is the expected behavior as the H₂S /MDEA loading approaches zero. $Fn(H_2S)$ approaches $\alpha_H \cdot \alpha_H$ as the loading approaches zero.

H₂S with $\alpha_{\text{CO}_2} \sim 0.0053$ in 23.0 wt% MDEA at 40.0 °C, Expt. 1

Eight VLE measurements were made of hydrogen sulfide and residual carbon dioxide (initial $\alpha_{\text{CO}_2} = 0.0053$) in a sample of 23.0 wt% MDEA at 40.0 °C. The data are discussed below.

H₂S with $\alpha_{\text{CO}_2} \sim 0.00076$ in 23.0 wt% MDEA at 40.0 °C, Expt. 2

Nine VLE measurements at 40.0 °C were made of hydrogen sulfide and residual carbon dioxide (initial $\alpha_{\text{CO}_2} = 0.00076$) with a sample of 23.0 wt% MDEA. The H₂S values from this experiment, Expt. 2, are displayed in Figure 22 (p. 38) together with the H₂S values from the previous experiment, Expt. 1, at the same temperature.

VLE data, shown in Figure 22 (p. 38), from these two experiments of hydrogen sulfide and residual carbon dioxide in 23.0 wt% MDEA at 40.0 °C appeared to be shifted systematically by an amount more than the experimental error. Conditions for the two experiments were identical except for the vapor flow rate. When the flow rate was restored to the former value, the previously measured values were reproduced.

Spectra measurements were then made over a range of vapor flow rates, and pressure measurements were made from within the VLE cell and the vapor cells to determine the size of the effect. The vapor flow controller and gauge upstream of the VLE cell caused a significant reduction of pressure within the VLE cell. Measurements of pressure shifts and spectra measurements as functions of flow rate were made to allow adjustment of previous measurements to a common VLE cell pressure.

Following these test measurements, the flow controller was moved downstream of the VLE cell. Additional pressure measurements over a wide range of vapor flow rates were then made to confirm that significant pressure effects were not caused by the flow controller in its new position. The revised data from Expt. 1 and Expt. 2, adjusted for a total pressure of 15 psia, are presented in Tables 10 and 11 and displayed in Figure 23 (p. 39). The slight tailing of the lowest H₂S pressures in Expt. 1 is caused by the higher amount of residual CO₂ in this system.

The behavior of the H₂S pressure values at low pressure for Expt. 1 and Expt. 2 is shown in Figures 24 (p. 40) and 25 (p. 41), where H₂S pressures are plotted as a function of

$$Fn(\text{H}_2\text{S}) = \alpha_{\text{H}} \cdot (\alpha_{\text{H}} + \alpha_{\text{C}}) / (1 - \alpha_{\text{H}} - \alpha_{\text{C}}).$$

The behavior of the CO₂ pressure values at low pressure is shown in Figures 26 (p. 42) and 27 (p. 43), where CO₂ pressures are plotted as a function of

$$Fn(\text{CO}_2) = \alpha_{\text{C}} \cdot (\alpha_{\text{C}} + \alpha_{\text{H}}) / (1 - \alpha_{\text{H}} - \alpha_{\text{C}}).$$

H₂S with $\alpha_{\text{CO}_2} \sim 0.00074$ in 23.0 wt% MDEA at 40.0 °C, Expt. 3

Following the modifications to the vapor flow system, an additional set of VLE measurements was made of H₂S with residual CO₂ in 23.0 wt% MDEA at 40.0 °C (Expt. 3) and compared with the measurements of the previous two experiments, Expt. 1 and Expt. 2, of the same system. Data from the eight VLE measurements of this experiment are presented in Table 12, and the H₂S values are displayed in Figure 28 (p. 44) together with the adjusted values from Expt. 1 and Expt. 2.

The residual carbon dioxide is low and nearly the same in the samples measured in Expt. 2 and Expt. 3. These data are shown also in Figure 29 (p. 45) together with preliminary data by Robinson⁷. The low pressure tailing of the Robinson data is an indication of significant residual carbon dioxide.

The carbon dioxide measured in these experiments consisted of residual CO₂ amounts from the sample and from apparatus surfaces. In addition, small amounts of CO₂ are added during additions of hydrogen sulfide because of a small CO₂ impurity in the original H₂S sample. The added CO₂ produces CO₂ pressures of ~ 0.00002 to 0.0001 psia, which is very small but measurable with the FTIR technique. This CO₂ measurement precision permits determination of residual CO₂, which affects the solubility of hydrogen sulfide in the alkanolamines.

The behavior of the H₂S pressure values at low pressure for Expt. 3 is shown in Figure 30 (p. 46), where four H₂S pressures below 0.004 psia are plotted as a function of $F_n(\text{H}_2\text{S}) = \alpha_H \cdot (\alpha_H + \alpha_C) / (1 - \alpha_H - \alpha_C)$. The behavior of the CO₂ pressure values at low pressure is shown in Figure 31 (p. 47), where eight CO₂ pressures below 0.0004 psia are plotted as a function of $F_n(\text{CO}_2) = \alpha_C \cdot (\alpha_C + \alpha_H) / (1 - \alpha_H - \alpha_C)$.

Accomplishments

The FTIR technique that has been developed should be applicable to any alkanolamine or alkanolamine mixture. Measurements of hydrogen sulfide and carbon dioxide can be measured alone or together. Hydrogen sulfide can presently be measured to pressures down to ~ 0.0005 psia and carbon dioxide to ~ 0.00002 psia.

The FTIR apparatus is capable of measuring monthly two acid gas/ethanolamine systems, which includes measurements of carbon dioxide/ethanolamine loading caused by residual amounts of carbon

dioxide that are present in any experimental sample and cannot be completely removed from any apparatus.

Project Economic Update

The original estimate of this project's economic impact of 3×10^{14} BTU saved in the year 2010 was based on energy estimates by Don Ballard¹¹ and on our estimate of the gas purification capacity in the U.S. Several estimates of energy savings have been made subsequently.

Two major industries, natural gas processing and petroleum refining, were considered in the latest estimates. The Oil and Gas Journal¹² reports the 1989 capacity for U.S. gas processing was 66×10^9 SCFD. We have estimated refinery capacity from published refinery capacity values and operating values from the Amoco Refining Co. in Texas City, TX.^{13,14} Our estimate for the total amount of gas processed in refineries for 1990 was 29.3×10^9 SCFD. The relevant calculations are outlined in a letter to Mr. Norm Swift dated July 15, 1991.

The amount of gas processed by these industries was about 95.3 billion standard cubic feet per day (BSCFD). MDEA based amines have the potential of saving energy in greater than 28 BSCFD of this total processed volume. Our original estimate was based on the conversion of only 25 BSCFD of this volume. Our present estimate of this project's energy impact on the U.S. energy consumption is between 1 and 3.5×10^{14} BTU saved in the year 2010.

References

- 1 Miessner, R. E. III, *Energy Progress*, 4, no. 1, 17, (1984).
- 2 Schendel, R. L., *Oil & Gas J*, 80, no. 43, 158, (1982).
- 3 United Gas Pipe Line Co., *Oil & Gas J*, 82, no. 2, 87 (1984).
- 4 Leibush, A. G. and Shneerson, A. L., *Zh Prikl Khim*, 23, 145 (1950).
- 5 Lal, D., Otto, F. D., and Mather, A. E., *Can. J. of Chem. Eng.*, 63, 681 (1985).
- 6 Lawson, J. D. and Garst, A. W., *J. Chem. Eng. Data*, 21, no.1, 20, (1976).
- 7 DB Robinson, Research Ltd., *Vapor-Liquid Equilibrium Studies*, GRI Progress Report, p. 21, July 1 - September 30, 1993.
- 8 Jou, F. -Y., Otto, F. D., and Mather, A. E., *Solubility of Mixtures of H₂S and CO₂ in a MDEA Solution*, AIChE Meeting, Paper 140b, p. 15, November 2-7, 1986.

- 9 DB Robinson, Research Ltd., *Fundamental Studies of Acid Gas Treating by Aqueous Alkanolamines*, GRI Annual Report, p. 5, January -December 1994.
- 10 Jou, F. -Y., Mather, A. E., and Otto, F. D, *Solubility of H₂S and CO₂ in Aqueous Methyldiethanolamine Solutions*, Ind. Eng. Chem. Process Des. Dev., 21, 539-544 (1982).
- 11 Ballard, Don, *Energy Progress*, 6, no. 2, 112, (1986).
- 12 True, Warren R., "Worldwide Gas-processing Growth Slows", *Oil & Gas Journal*, Jul. 9, (1990).
- 13 Corbett, Richard A., "Capacity Rise Reflects Return to Better Times for U.S. Refiners", *Oil & Gas Journal*, 87, 49+, Mar. (1989).
- 14 Lucas, Kathleen, Amoco Refining, Texas City, TX, personal communication, Jul. (1991).

Tables

Table 1. H₂S with fixed CO₂ in 20.3 wt% DEA at 49.6 °C

H ₂ S Pressure psia	H ₂ S/MDEA mole ratio	CO ₂ Pressure psia	CO ₂ /MDEA mole ratio
0	0	0.00018	0.01422
0.0014	0.00926	0.00028	0.01426
0.0050	0.01826	0.00043	0.01424
0.0156	0.03151	0.00062	0.01422
0.0258	0.04158	0.00075	0.01421
0.0459	0.0566	0.00096	0.01418

Table 2. H₂S with added CO₂ in 20.3 wt% DEA at 49.6 °C

H ₂ S Pressure psia	H ₂ S/MDEA mole ratio	CO ₂ Pressure psia	CO ₂ /MDEA mole ratio
0.0483	0.05604	0.0029	0.02207
0.0508	0.05536	0.0049	0.03014
0.0584	0.05465	0.0082	0.04117
0.0637	0.05368	0.0138	0.05902
0.0746	0.05190	0.0284	0.09083
0.0858	0.04964	0.0492	0.1212

Table 3. H₂S with residual CO₂ in 20.2 wt% DEA at 49.8 °C

H ₂ S Pressure psia	H ₂ S/MDEA mole ratio	CO ₂ Pressure psia	CO ₂ /MDEA mole ratio
0	0	0.00004	0.008827
0.0004	0.00472	0.00005	0.008825
0.0009	0.00842	0.00005	0.008825
0.0027	0.01701	0.00008	0.008821
0.0085	0.03086	0.00011	0.008818
0.0235	0.04948	0.00018	0.008807
0.0519	0.07445	0.00027	0.008795
0.0989	0.1050	0.00044	0.00877
0.167	0.1377	0.00056	0.00875
0.279	0.1791	0.00075	0.00872
0.512	0.2384	0.0011	0.00867

Table 4. H₂S with residual CO₂ in 20.2 wt% DEA at 40.0 °C

H ₂ S Pressure psia	H ₂ S/MDEA mole ratio	CO ₂ Pressure psia	CO ₂ /MDEA mole ratio
0.403	0.2550	0.00055	0.008745
0.525	0.2946	0.00075	0.008717
0.785	0.3488	0.0011	0.008670
1.123	0.3988	0.0014	0.008614

Table 5. H₂S with added CO₂ in 20.2 wt% DEA at 40.0 °C

H ₂ S Pressure psia	H ₂ S/MDEA mole ratio	CO ₂ Pressure psia	CO ₂ /MDEA mole ratio
1.123	0.3988	0.0014	0.008614
1.133	0.3928	0.0050	0.014442
1.196	0.3747	0.0279	0.04589
1.373	0.3342	0.1292	0.1158

Table 6. H₂S with residual CO₂ in 50.0 wt% MDEA at 39.9 °C

H ₂ S Pressure psia	H ₂ S/MDEA mole ratio	CO ₂ Pressure psia	CO ₂ /MDEA mole ratio
0	0	0.00015	0.00091
0.0008	0.00173	0.00019	0.00092
0.0050	0.00491	0.00026	0.00092
0.0159	0.00989	0.00037	0.00094
0.0432	0.01774	0.00051	0.00093
0.108	0.03136	0.00070	0.00092
0.428	0.06712	0.00108	0.00091

Table 7. CO₂ in 50.0 wt% MDEA at 40.0 °C

CO ₂ Pressure psia	CO ₂ /MDEA mole ratio
0.00006	0.00063
0.00035	0.00122
0.0011	0.00209
0.0034	0.00362
0.0074	0.00538
0.0153	0.00802
0.0342	0.01221
0.0972	0.02237

Table 8. CO₂ loading in 23.0 wt% MDEA at 40.0 °C

CO ₂ Pressure psia	CO ₂ /MDEA mole ratio
0.00004	0.00126
0.00024	0.00266
0.00077	0.00480
0.00310	0.00953
0.01337	0.02071
0.0590	0.04662
0.1324	0.07582

Table 9. H₂S with $\alpha_{\text{CO}_2} \sim 0.076$ in 23.0 wt% MDEA at 40.0 °C

H ₂ S Pressure psia	H ₂ S/MDEA mole ratio	CO ₂ Pressure psia	CO ₂ /MDEA mole ratio
0	0	0.1324	0.07582
0.0060	0.00340	0.1377	0.07468
0.0138	0.00836	0.1408	0.07351
0.0283	0.01516	0.1477	0.07198
0.0660	0.02994	0.1619	0.06943
0.171	0.06523	0.1947	0.06516
0.541	0.1413	0.2527	0.05797

Table 10. H₂S with $\alpha_{\text{CO}_2} \sim 0.0053$ in 23.0 wt% MDEA at 40.0 °C

H ₂ S Pressure psia	H ₂ S/MDEA mole ratio	CO ₂ Pressure psia	CO ₂ /MDEA mole ratio
0	0	0.00042	0.00530
0.0004	0.00443	0.00069	0.00533
0.0016	0.01007	0.00105	0.00537
0.0044	0.01666	0.00150	0.00542
0.0098	0.02641	0.00211	0.00546
0.0230	0.04147	0.00309	0.00548
0.0739	0.08167	0.00509	0.00540
0.388	0.2027	0.00975	0.00500

Table 11. H₂S with $\alpha_{\text{CO}_2} \sim 0.00076$ in 23.0 wt% MDEA at 40.0 °C

H ₂ S Pressure psia	H ₂ S/MDEA mole ratio	CO ₂ Pressure psia	CO ₂ /MDEA mole ratio
0	0	0.000007	0.000755
0.00010	0.00271	0.000016	0.000765
0.00055	0.00737	0.000031	0.000782
0.0022	0.01317	0.000047	0.000785
0.0054	0.02046	0.000072	0.000799
0.0113	0.03025	0.00011	0.000814
0.0290	0.05073	0.00018	0.000825
0.0915	0.09769	0.00031	0.000841
0.379	0.2147	0.00061	0.000844

Table 12. H₂S with $\alpha_{\text{CO}_2} \sim 0.00074$ in 23.0 wt% MDEA at 40.0 °C

H ₂ S Pressure psia	H ₂ S/MDEA mole ratio	CO ₂ Pressure psia	CO ₂ /MDEA mole ratio
0	0	0.000021	0.000743
0.0004	0.00595	0.000023	0.000746
0.0016	0.01259	0.000027	0.000748
0.0074	0.02564	0.000053	0.000747
0.0307	0.05332	0.000068	0.000749
0.134	0.1248	0.00011	0.000745
0.465	0.2404	0.00024	0.000734
0.764	0.3130	0.00035	0.000727

Figure 1. H_2S Solubility in 20.3 wt% DEA at 49.6 °C

Figure 2. H_2S at low pressure in 20.3 wt% DEA at 49.6 °C

Figure 3. H_2S Solubility with CO_2 in 20.3 wt% DEA at 49.6 °C

Figure 4. CO₂ Solubility with H₂S in 20.3 wt% DEA at 49.6 °C

Figure 5. CO_2 at low pressure in 20.3 wt% DEA at 49.6 °C

Figure 6. H_2S Solubility in 20.2 wt% DEA at 49.8 °C

Figure 7. CO_2 at low pressure in 20.2 wt% DEA at 49.8 °C

Figure 8. H_2S with added CO_2 in 20 wt% DEA at 50 °C

Figure 9. H_2S at low pressure in 20.2 wt% DEA at 49.8 °C

Figure 10. H_2S Solubility in 20.2 wt% DEA at 40.0 °C

Figure 11. CO₂ at low pressure in 20.2 wt% DEA at 40.0 °C

Figure 12. H_2S Solubility with CO_2 in 20.2 wt% DEA at 40.0 °C

Figure 13. CO_2 Solubility with H_2S in 20.2 wt% DEA at 40.0 °C

Figure 14. H_2S Solubility in 50.0 wt% MDEA at 39.9 °C

Figure 15. CO_2 Solubility in 50.0 wt% MDEA at 40.0 °C

Figure 16. CO₂ at low pressure in 50.0 wt% MDEA at 40.0 °C

Figure 17. CO_2 Solubility in 23.0 wt% MDEA at 40.0 °C

Figure 18. CO₂ Solubility in MDEA at 40.0 °C

Figure 19. CO₂ at low pressure in 23.0 wt% MDEA at 40.0 °C

Figure 20. H_2S Solubility with CO_2 in 23.0 wt% MDEA at 40.0 °C

Figure 21. H_2S at low pressure with CO_2 in 23.0 wt% MDEA at 40°C

Figure 22. H_2S Solubility in 23.0 wt% MDEA at 40.0 °C

Figure 23. H_2S Solubility in 23.0 wt% MDEA at 40.0 °C

Figure 24. H_2S at low pressure in 23.0 wt% MDEA at 40.0 °C

Figure 25. H_2S at low pressure in 23.0 wt% MDEA at 40.0 °C

Figure 26. CO_2 at low pressure in 23.0 wt% MDEA at 40.0 °C

Figure 27. CO_2 at low pressure in 23.0 wt% MDEA at 40.0 °C

Figure 28. H_2S Solubility in 23.0 wt% MDEA at 40.0 °C

Figure 29. H_2S Solubility in 23.0 wt% MDEA at 40.0 °C

Figure 30. H_2S at low pressure in 23.0 wt% MDEA at 40°C

Figure 31. CO₂ at low pressure in 23.0 wt% MDEA at 40.0 °C