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ABSTRACT

The main objective of this project is to measure heat of dissolution of CO₂ in carefully selected mixed alkanolamine solvent systems, and provide such directly measured data that might be used for efficient design of CO₂ capture processes, or for better understanding of thermodynamics of CO₂- alkanolamine systems. Carbon dioxide is one of the major greenhouse gases, and the need for stabilization of its composition in earth's atmosphere is vital for the future of mankind. Although technologies are available for capture and storage of CO₂, these technologies are far too expensive for economical commercialization. Reduction of cost would require research for refinement of the technology. For more economical CO₂ capture and regeneration, there is a need for development of more efficient solvent systems. In this project we will extend the thermodynamic database by measuring heat of solution data of CO₂ in mixed solvents made of MEA (monoethanolamine), MDEA (methyldiethanolamine), piperazine, and water. Mixed solvents of different compositions will be selected and in each case data will be measured at temperatures 40 and 80C and various partial pressures of CO₂. At the end of the project, observations, conclusions, and recommendations will be derived for the choice of mixed solvents for efficient CO₂ capture with potential for commercialization.

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Introduction

Carbon dioxide is one of the major greenhouse gases, and the need for stabilization of its composition in earth's atmosphere is vital for the future of mankind. Although technologies are available for capture and storage of CO₂, these technologies are far too expensive for economical commercialization. Reduction of cost would require research for refinement of the technology. The idea of capturing CO₂ from the flue gas of power plants did not start with concern about the greenhouse effect. Rather, it gained attention as a possible economic source of CO₂, especially for use in enhanced oil recovery operations where CO₂ is injected into oil reservoirs to increase the mobility of the oil and, therefore, the productivity of the reservoir. Several commercial CO₂ capture plants were constructed in the late 1970s and early 1980s in the US. The North American Chemical Plant in Trona, CA, which uses the carbonation of brine to produce CO₂, started operation in 1978 and is still operating today. However, when the price of oil dropped in mid-1980s, the recovered CO₂ was too expensive for enhanced oil recovery operations and all of the other CO₂ capture plants were closed.

Historically, CO₂ capture processes have required significant amounts of energy, which reduces the power plant's net power output. For example, the output of a 500 MW (net) coal-fired power plant may be reduced to 400 MW (net) after CO₂ capture. This imposes an "energy penalty" of 20%. The energy penalties of current capture technologies range from about 30% for conventional coal to about 15% for advanced coal. It is desired that in the next decade these numbers be brought to 50% of their current values.

To date, all commercial CO₂ capture plants use processes based on chemical absorption with the monoethanolamine (MEA) solvent. MEA was developed over 60 years ago as a general, non-selective solvent to remove acid gases, such as CO₂ and H₂S, from natural gas streams. The process was modified to incorporate inhibitors to resist solvent degradation and equipment corrosion when applied to CO₂ capture from flue gas. Also, the solvent strength was kept relatively low, resulting in large equipment sizes and high regeneration energy requirements. The process allowed flue gas to contact an MEA solution in the absorber. The MEA selectively absorbed the CO₂ and was then sent to a stripper. In the stripper, the CO₂-rich MEA solution was heated to release almost pure CO₂. The lean MEA solution was then recycled to the absorber.

Other processes have been considered to capture CO₂ from the flue gas of a power plant, e.g., membrane separation, cryogenic fractionation, and adsorption using molecular sieves. These processes are even less efficient and more expensive than the chemical absorption. The reason can be attributed to the very low CO₂ partial pressure in the flue gas. Therefore, a high priority research need is to formulate new solvents that can significantly reduce the energy penalty associated with chemical absorption. The new solvents must increase the loading (amount of CO₂ dissolved per unit amount of solvent), and the rate of CO₂ dissolution while maintaining a low heat of solution, so as to minimize the energy requirements during the solvent regeneration.

For the processes based on the absorption of CO₂ by aqueous alkanolamines, the energy penalty or the cost of the process depends mostly on three factors: (1) the loading of CO₂ (moles of CO₂ absorbed per mole of amine), (2) the rate of CO₂ absorption, and (3) the energy requirement for the release of CO₂ in the stripper. For a number of solvents, detailed studies are available in the literature for the first two factors. Aqueous MEA solvents suffer from the limitation that CO₂ loading cannot exceed much higher than 0.5. An amine that is considered as a potential replacement for MEA is methyldiethanolamine (MDEA) because of the high loading of CO₂ (approaching 1) which is attributed to the stoichiometry of the reaction forming carbamate. However, the rate of CO₂ absorption by MDEA is too low for commercial applications. Mixed solvents containing MEA and MDEA, and diethanolamine (DEA) and MDEA in water seem to provide good solutions to give high absorption rates as well as CO₂ loading. Recently researchers have also started looking at other additives to aqueous MEA and MDEA mixtures to enhance solubility and rate of absorption of CO₂. These include sulfolane, N-methylpyrrolidone (NMP), and piperazine (PZ). Of these, piperazine seems to be the most effective in increasing the solubility of CO₂. The data available in the literature indicate that aqueous mixtures of MEA, MDEA and piperazine have potential to provide a solvent system superior to aqueous MEA solvent of the current commercial capture plants. However, a true determination of this is difficult without a detailed study of the relative energy requirements for each of the solvents. Such a study is not available in the literature, mostly because of lack of experimental data on the heats of dissolution of CO₂ in the aqueous alkanolamine solvents. Data are available only for a few systems and at limited conditions.

For more economical CO₂ capture and regeneration, there is a need for development of more efficient solvent systems. In this project we will extend the thermodynamic database by measuring heat of solution data of CO₂ in mixed solvents made of MEA (monoethanolamine), MDEA (methyldiethanolamine), piperazine, and water. Mixed solvents of different compositions will be selected and in each case data will be measured at temperatures 40 and 80C and various partial pressures of CO₂. At the end of the project, observations, conclusions, and recommendations will be derived for the choice of mixed solvents for efficient CO₂ capture with potential for commercialization.

EXECUTIVE SUMMARY

The main objective of this project is to measure heat of dissolution of CO₂ in carefully selected mixed alkanolamine solvent systems, and provide such directly measured data that might be used for efficient design of CO₂ capture processes, or for better understanding of thermodynamics of CO₂- alkanolamine systems. Carbon dioxide is one of the major greenhouse gases, and the need for stabilization of its composition in earth's atmosphere is vital for the future of mankind. Although technologies are available for capture and storage of CO₂, these technologies are far too expensive for economical commercialization. Reduction of cost would require research for refinement of the technology. For more economical CO₂ capture and regeneration, there is a need for development of more efficient solvent systems. In this project we will extend the thermodynamic database by measuring heat of solution data of CO₂ in mixed solvents made of MEA (monoethanolamine), MDEA (methyldiethanolamine), piperazine, and water. Mixed solvents of different compositions will be selected and in each case data will be measured at temperatures 40 and 80C and various partial pressures of CO₂. At the end of the project, observations, conclusions, and recommendations will be derived for the choice of mixed solvents for efficient CO₂ capture with potential for commercialization.

During the current period of performance, September 2003 to March 2004, the apparatus for the heat of dissolution measurements has been designed and built. The apparatus consists of a CO₂ gas cylinder, a mass flowmeter, a liquid solvent metering pump, the isothermal micro-calorimeter with the flow cells made by Calorimetry Sciences Corporation (CSC), a back pressure regulator, switch valve for online chromatographic analysis, the GC, and many thermocouples and pressure sensors. The apparatus has been pressure tested for leaks. MEA-CO₂ system has been chosen as the test system. Data for this system will be measured over a range of CO₂ compositions, at a single temperature of 25°C, and a fixed composition of aqueous solution. The measured data will be compared with the limited data available in the literature for this system. The data measurements have just begun.

Simultaneously, a more thorough literature search was carried out for enthalpy data on CO₂-alkanolamine systems. The available literature data for aqueous CO₂-MEA, CO₂-MDEA, CO₂-DEA, CO₂-MDEA-Sulfolane, and CO₂-MDEA-PZ systems have been extracted and compiled. The variables for data measurements are temperature, CO₂ composition or partial pressure, and the composition of the aqueous mixture. Design of our data measurements should be such that the result will be a complete data set for the CO₂-MEA-MDEA-PZ system. This design will be completed in the next phase of the project.

EXPERIMENTAL APPARATUS

During the current period of performance, September 2003 to March 2004, the apparatus for the heat of dissolution measurements has been designed and built. The apparatus consists of a CO₂ gas cylinder, a mass flowmeter, a liquid solvent metering pump, the isothermal micro-calorimeter with the flow cells made by Calorimetry Sciences Corporation (CSC), a back pressure regulator, switch valve for online chromatographic analysis, the GC, and many thermocouples and pressure sensors. Specifications of some major equipment are given below.

Isothermal micro-calorimeter (IMC): The calorimeter is made by Calorimetry Sciences Corporation (CSC), and has the following specifications,

- **High Sensitivity:** Detectable Heat Effect 10 μcal (40 μJoules)
- **Response Time:** Raw Signal $t=150$ sec, Deconvoluted Signal, $t=15$ sec
- **Baseline Stability:** 0.25 $\mu\text{cal/sec/hr}$ (1 μWatt)
- **Low Noise Level:** ± 0.025 $\mu\text{cal/sec}$ (± 0.1 μWatt)
- **Sample Well Size and Configuration:** Standard cylindrical dimensions: 3.81 cm dia. x 7.32 cm deep, four test wells of which one serves as the reference well.
- **Measurement Well Volume:** 15 ml to 150ml (custom sizes also available)
- **Temperature Stability:** $\pm 0.0005^\circ\text{C}$ at 25°C

The IMC is a heat flow design for the absolute maximum in sensitivity. The ultra-stable liquid bath yields superior operation over the entire temperature range. It is designed specifically to measure very slow or very small heat changes. Since virtually all chemical and physical processes are accompanied by changes in heat, the IMC is a universal detector that can be used to follow the progress of slow reactions at modest temperatures. The IMC can detect changes in heat flow as small as 25 nanocalories/sec (0.1 μWatt) and heat effects as small as 10 μcal (40 μJoules) in the temperature range from -40 to $+80^\circ\text{C}$. The IMC can provide both kinetic and thermodynamic information for almost any process occurring in any sample. The measurements are non-destructive and can be made on solid or liquid samples.

The measurements are done in four sample wells, of which one serves as a reference well. The instrument outputs represent the heat duties for the sample cells relative to the reference well for an isothermal operation. For our application two flow mixing cells (purchased from CSC) are used, one serves as the sample cell and the other one as the reference cell. A cross-section of the flow mixing cell is shown in Figure 1. The flow cell has two inlet tubes and one outlet tube each 1/16" OD. It is provided with a top access cover which acts as an insulator. The two inlet tubes run into the inlet flow thermal equilibration chamber where they coil around thereby increasing the residence time of the inlet fluids, and allowing for thermal equilibration at the desired temperature. At the exit of the thermal equilibration chamber, the tubes run into a thermal shunt. The shunt consists of a tee, the exit end of the tee goes into the flow heat exchanger which is the heat signal measurement zone. This line consists of concentric 1/32" and 1/16" OD

tubing, with the gas (CO₂) flowing through the inner tubing and the liquid solvent flows through the annulus. At the bottom of the flow heat exchanger, the two fluids are mixed, the mixture flows through coiled tubing and exits the calorimetric well.

Gas mass flowmeter: The mass flowmeter (model FMA-8503 made by Omega, Inc.) is used to accurately monitor and measure the flow rate of carbon dioxide gas. It has a flow range of 0 to 100 SCCM (standard cubic centimeters per minute), operating pressures upto 4500 psi, and operating temperatures from 4°C to 66°C. It has an accuracy of ±1% full scale, and the flow sensor produces an output signal linear to the mass flow rate for use in recording and for control purposes.

Solvent metering pump: Lab Alliance Series II digital isochratic pump is used to pump the liquid solvent. It has a flow range of 0.01 to 9.99 ml/min, and a pressure rating 6000 psi.

Gas chromatograph: The liquid mixture at the exit of the calorimeter is periodically analyzed by an on-line gas chromatograph (GC) made by Agilent Technologies Inc. (model HP6890). The analysis is done using a packed column and thermal conductivity detector.

Procedure: A schematic of the experimental apparatus is shown in Figure 2. The liquid solvent is pumped at the desired rate by setting the metering pump, and carbon dioxide is introduced through the other inlet tubing with the desired flow rate set by the mass flowmeter. The calorimeter is set at the desired measurement temperature, and the pressure is set by the back pressure regulator and displayed by the digital pressure gage. The measurements are done in the sample cell with the reference cell kept empty. The calorimeter gives a signal in μW which is recorded. Once a stable signal is obtained, heat of mixing is easily calculated by dividing the signal by the molar flow rate of the mixture. Composition of the mixture is calculated from the inlet flow rates of the pure solvent and the CO₂ gas. For further check on the mixture composition, periodically mixture samples are analyzed by an on-line GC. At a fixed temperature and pressure, the liquid solvent flow rate is kept constant at about 1 ml/min and measurements are done at increasing flow rates of the gas starting at 5 SCCM, and in increments of 5 SCCM. As CO₂ composition in the mixture is increased, initially the heat signal is expected to increase. However beyond the solubility limit of CO₂ the heat signal should not change with further increase in the gas flow rate. At this point the measurements are stopped. Indirectly this also allows for an estimate of the solubility of CO₂ in the liquid solvent.

The apparatus has been pressure tested for leaks. MEA-CO₂ system has been chosen as the test system. Data for this system will be measured over a range of CO₂ compositions, at a single temperature of 25°C, and a fixed composition of aqueous solution. The measured data will be compared with the limited data available in the literature for this system. The data measurements have just begun, and will be completed in the next quarter of the project.

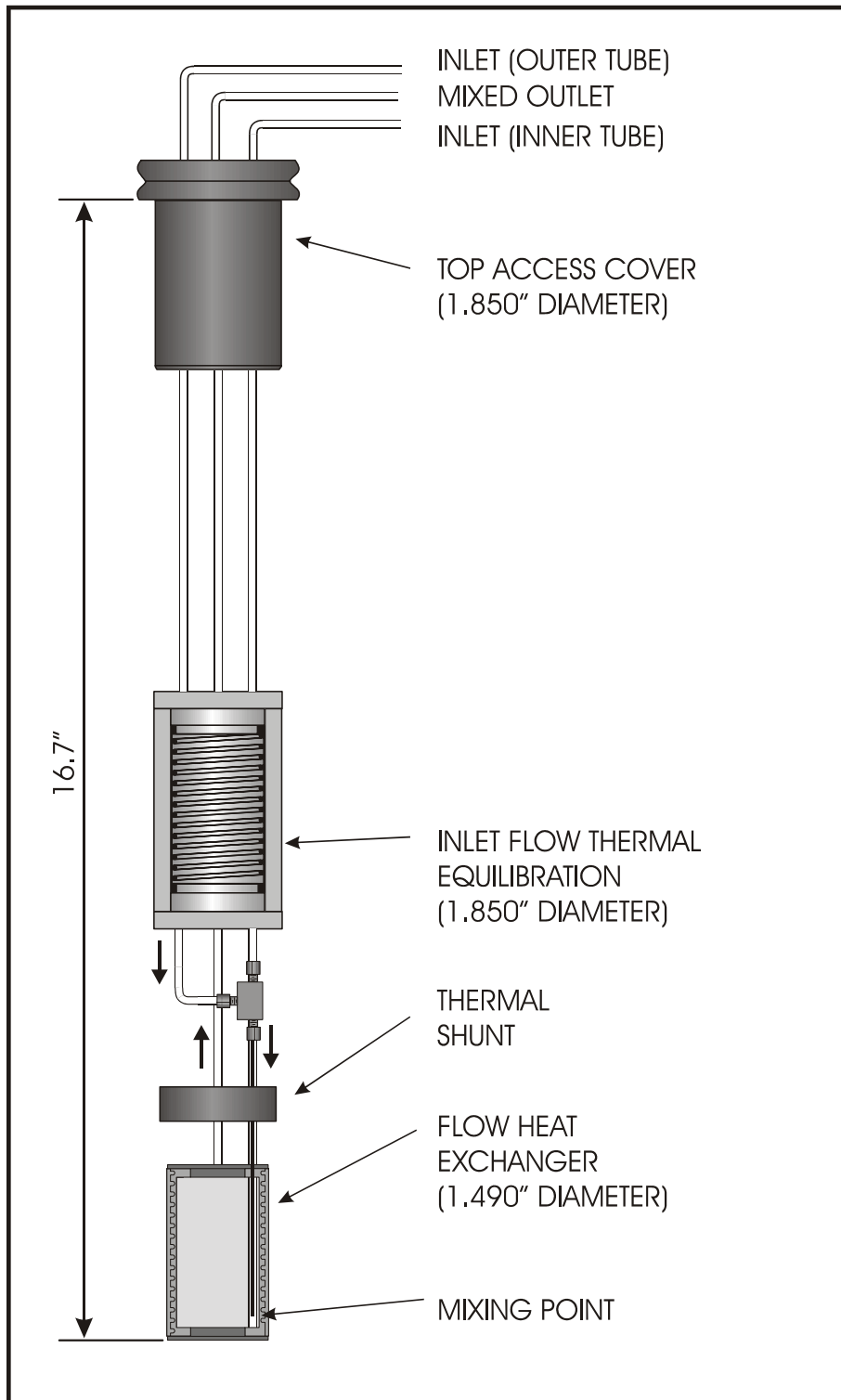


Figure 1. Diagram of a flow mixing cell.

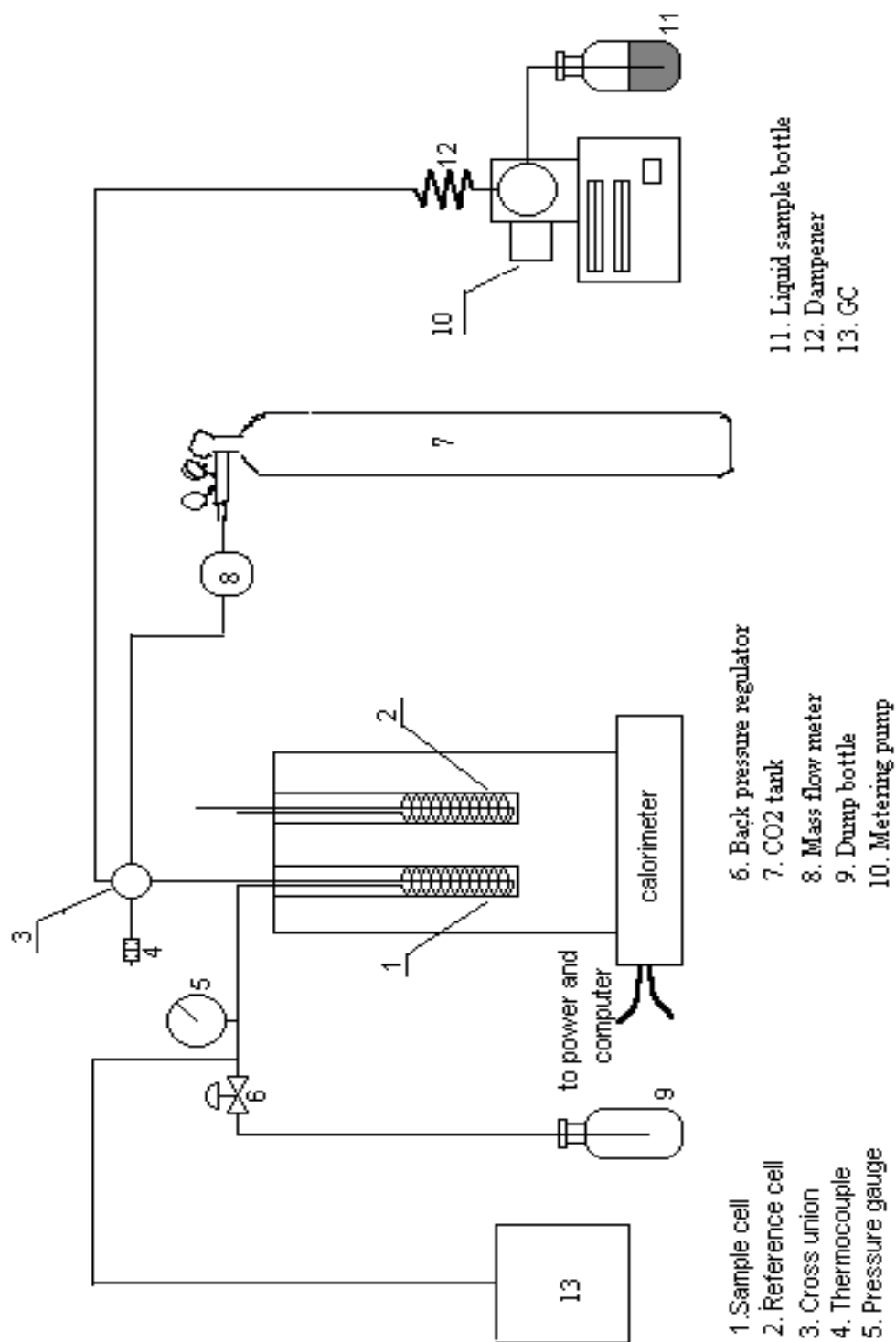


Figure 2: Experimental apparatus for heat of dissolution measurements.

LITERATURE DATA AND DESIGN OF EXPERIMENTS

A thorough literature search was carried out for solubility and enthalpy data for mixtures of carbon dioxide and alkanolamines. The available data are listed in Tables 1 and 2. It is clear that extensive data are available for solubility of CO₂ in aqueous solutions of MEA, DEA, MDEA and their mixtures over a range of temperatures and compositions. Literature data also indicate that enhancement in solubility is obtained by use of additives especially piperazine and sulfolane. It is however clear from Table 2 that enthalpy data are relatively scarce. Data are available for heat of mixing of CO₂ at 25°C in aqueous solutions of MEA of three different compositions and a fixed partial pressure of the gas. Corresponding data in aqueous solutions of MDEA and DEA are available over a wider range of temperatures. Data at two temperatures 25°C and 40°C and fixed partial pressure of CO₂ are available for heat of mixing of the gas in aqueous mixtures of MDEA and piperazine. For a comprehensive analysis of the relative economics of solvents for application in CO₂ capture, more extensive data over a wider range of temperatures, solvent compositions, and gas partial pressures would be required. A detailed design of experiments involving solvents MEA, MDEA, piperazine and water is currently under way and will be completed in the next quarter of the project.

CONCLUSIONS AND PLANS FOR THE NEXT QUARTER

During the first six months of the project, the experimental apparatus for the heat of dissolution of CO₂ in aqueous alkanolamine solvents has been designed and built. Experimental measurements for the CO₂-MEA systems have been initiated. A thorough literature search for all solubility and enthalpy data for CO₂ in aqueous alkanolamine solvents has been completed and the data have been compiled.

During the next phase of the project, heat of mixing data for CO₂ in three compositions of aqueous MEA solutions at 25°C and over a range of gas compositions will be completed. A comprehensive design of experiments for future data measurements for heat of mixing of CO₂ in aqueous mixtures of MEA, MDEA, and piperazine will be completed and a timetable for all data measurements will be prepared.

Table 1. Literature data for solubility of CO₂ in aqueous alkanolamine solvents

<i>Aqueous Solvent</i>	<i>SCCM of CO₂</i>	<i>Temperatures (°C)</i>	<i>CO₂ Partial Pressure (kPa)</i>	<i>Reference</i>
<i>MEA (2.5 kmol/m³)</i>	14.952 – 37.856	40, 80	0.0934 – 228.7	1
<i>MEA (4.2 M)</i>	50.897 – 68.0198	100	455 – 3863	9
<i>MEA (15.3 wt %)</i>	31.4777 – 58.8594	40	15.7 – 2550	39
<i>MEA (15.3 wt %)</i>	0.9539 – 40.8481	40, 60, 80, 100, 120, 140	0.03 – 930.99	15
<i>MEA (30 wt %)</i>	12.7369 – 45.2247	40, 60, 80, 100	1.1 – 1975	39
<i>MEA (10, 20, 30 wt %)</i>	1.2934 – 4.7264	25	265	6
<i>MEA (15.2, 30 wt %)</i>	10.0851 – 91.4997	104, 140, 176, 200 212, 248, 274, 284	1.3332 – 2786.438	27
<i>MEA (30 wt %)</i>	0.2222 – 146.4361	0, 25, 40, 60, 80, 100, 120, 150	0.0012 – 19954	18
<i>DEA (50 %)*</i>	=====	25, 35, 45, 55	0 – 101.325	5
<i>DEA (4.2 M)</i>	28.1299 – 68.208	100	93 – 3742	9
<i>DEA (10, 20, 30 wt %)</i>	1.2875 – 4.6088	25	265	6
<i>DEA (10, 20, 30 wt %)</i>	12.3709 – 91.3309	100 – 200, 205	165.5 - 4137	25
<i>DEA (25, 50 wt %)</i>	9.9068 – 62.1571	100, 150, 175, 200, 225, 250	2.0 - 4373	27
<i>DEA (0.5, 2, 3.5, 5, 6.5, 8 N)</i>	0.5488 – 76.608	0, 25, 50, 75, 100, 120, 140	0.6895 – 6894.75	28
<i>DEA (30 wt %)</i>	25.8215 – 46.4661	40, 60, 80	4.85 – 357.3	38
<i>MDEA (2.0, 4.28 kmol/m³)</i>	0.2701 – 64.3301	40	0.0056 – 93.6	1

MDEA (4.28 M)	1.2463 – 3.0679	40	0.108 – 0.730	3
MDEA (1.69, 4.28 M)	1.2463 – 125.017	100, 140, 160, 180, 200	138 - 4930	7
MDEA (4.28 M)	8.7243 – 78.9026	100, 120	162 – 3832	9
MDEA (3.954 mol/kg)	74.771 – 110.0736	40	176.5 – 6469	22
MDEA (7.994 mol/kg)	22.559 – 206.6848	40, 80, 120	228 – 7565	22
MDEA (2.0 mol/dm³)	5.552 – 53.8944	40	1 - 370	31
MDEA (30 wt %)*	~ 0 – 78.9262	40, 60, 80, 100	100 - 20000	20*
MDEA (30 wt %)	4.4565 – 31.8569	40, 60, 80, 100	1.1 – 1979	39
MDEA (50 mass %)	0.8175 – 46.2564	25, 50, 75, 100	0.78 – 140.4	36
MDEA (2, 4.28 kmol/m³)	0.0166 – 82.1184	25, 40, 70, 100, 120	0.001 - 6630	17
MDEA (3 M)	63.2352 – 82.5216	25	2270 - 7080	19
MDEA (4.28 kmol/m³)	0.8724 – 84.4248	40,55, 70, 80, 100	0.876 - 1013	40
MDEA (3.46 kmol/m³)	13.4857 – 65.7854	55, 70, 80, 90	115 – 992	40
MDEA (3.04 kmol/m³)	6.6666 – 62.0355	55, 70	6.152 – 806.8	40
MDEA (30 wt %)	28.7517 – 76.1074	40, 80, 120	2000,5000,10000	32
MDEA (10, 20, 30 wt %)	1.5034 – 4.7495	25	265	6
MDEA (1.949 mol/kg)	46.256 – 61.7568	40	837.4 – 4883	23
MDEA (1.99, 1.95, 3.97 mol/kg)	0 – 100.688	40, 60, 100, 120, 140	73.5 – 5036.7	26
MDEA (35, 50 wt %)	1.71 – 16.5745	25, 40, 80, 95, 100	354.6375 – 830.865	35
MDEA (4.28M)	5.3603 – 41.3056	30, 40, 55, 70	0.507 – 42.06	41
MDEA (35 wt %)	0.1315 – 52.2886	40, 100	0.004 – 262	16
PZ (0.6 M)	2.154 – 12.9024	40, 70	0.032 - 40	2
PZ (1.995 mol/kg)	28.8736 – 75.3984	40, 60, 80	13.3 – 8421	24
PZ (2.035 mol/kg)	24.8416 – 74.8608	60, 100, 120	155.6 – 9131	24
PZ (3.964 mol/kg)	75.242 – 120.2656	60, 80	42.8 – 9560	24
PZ (3.950 mol/kg)	44.3744 – 104.899	100, 120	175.6 - 8999	24

MDEA + MEA				
(2.0 + 2.0 kmol/m³)	6.7738 – 69.9776	40, 80	0.0506 – 312.9	1
(2.06 + 1.0 M)	22.6195 – 49.3517	100	134.8 – 1905	9
(3.4 + 0.8 M)	4.7936 – 84.7508	70, 100, 120, 140, 160, 180	190 – 3876	9
(2.1 + 2.1 M)	6.2317 – 87.9146	70, 100, 120, 140, 160, 180	137 – 3859	9
(24 + 6 wt %)	12.4143 – 68.1112	40, 60, 80, 100	1.12 – 2080	29
(12 + 18 wt %)	14.7898 – 78.0232	40, 60, 80, 100	1.37 – 1973	29
(18 + 12 wt %)	15.3332 – 73.7082	40, 60, 80, 100	0.9 – 2016	39
(6 + 24 wt %)	23.3334 – 84.2979	40, 60, 80, 100	1.5 - 1987	39
(27 + 7 wt %)	1.5169 – 4.7852	25	265	6
MDEA + DEA				
(2.0 + 2.0 kmol/m³)	2.1504 – 71.8592	40, 80	0.136 – 309.3	1
(3.4 + 0.8 M)	4.0266 – 87.3393	70, 100, 120, 140, 160, 180	65 - 3807	9
(2.1 + 2.1 M)	4.3142 – 88.9692	70, 100, 120, 140, 160, 180	224 - 3845	9
(15 + 10 wt %)	11.5248 – 66.0128	40	3.5 – 2612	13
(20 + 10 wt %)	15.5232 – 68.992	40, 120	2.8 – 2833.6	13
(10 + 20 wt %)	22.9130 – 90.2272	40	4.5 – 2377.1	13
(35 + 10 wt %)	29.3238 – 88.5651	40	3.8 – 2638.3	13
MDEA + PZ				
(4 + 0.6 M)	0.6182 – 29.3664	40, 70	0.033 – 7.48	3
(1.53 + 0.17 kmol/m³)	14.737 – 37.3184	50, 70	21.18 – 688.8	30
(1.35 + 0.35 kmol/m³)	13.2899 – 36.3664	50, 70	17.6 – 586.9	30
(3.15 + 0.35 kmol/m³)	11.5248 – 66.0128	30, 50, 70	16.73 – 573	30

(2.8 + 0.7 kmol/m³)	15.5232 – 68.992	30, 50, 70	15.6 – 935.3	30
(4.77 + 0.53 kmol/m³)	22.9130 – 90.2272	50, 70	35.83 – 753.7	30
(3.75 + 1.55 kmol/m³)	29.3238 – 88.5651	50, 70	13.16 – 678.3	30
(4.28 + 0.103, 0.308, 0.696 kmol/m³)	0.3737 – 2.5778	104	8.722 – 9.297	40
(3.46 + 0.103, 0.154, 0.206 kmol/m³)	0.3147 – 0.4704	103	8.196 – 8.591	40
(1.72 + 0.103, 0.154, 0.206 kmol/m³)	0.2861 – 0.4289	101	7.148 – 7.537	40
(1.975 + 1.966 mol/kg)	56.5824 – 100.307	80	180.7 – 6400	24
(4 + 0.6 M)	0.1546 – 32.0454	22, 40, 70	0.015 – 27.3	4
(4.21 + 0.1, 0.041, 0.21 M)	8.4672 – 47.8912	30, 40, 55, 70,	3.307 – 69.43	41
(3.04, 1.75 + 0.1 M)	11.0835 – 36.8256	40	4.51 – 32.14	41
MDEA + SULFOLANE				
(20.9 + 30.5 wt %)	1.8852 – 61.5442	40, 100	0.43 – 5770	31
MDEA + H₂SO₄				
(1.989 + 0.9936 mol/kg)	4.032 – 22.848	40, 60, 100, 120, 140	190.5 – 10607	23
(3.992 + 0.9862 mol/kg)	3.853 – 56.672	40, 80, 120	172 - 2530	23
MDEA + Na₂SO₄				
(1.968 + 1.009 mol/kg)	36.96 – 53.6704	40, 60	128.7 – 4294	23
(1.952 + 0.9933 mol/kg)	3.127 – 46.0544	100, 140	331.5 - 4536	23
MEA + N-methylpyrrolidone				
(15 wt %) non - aqueous	14.3837 – 81.0668	25, 50, 100	33.8 – 2178.9	11
MEA + Sulfolane				

<i>(15, 30 wt %)</i>	13.066 – 94.3216	30, 50, 100	1.5 – 2210.5	12
<i>DEA + N-methylpyrrolidone</i>				
<i>(15, 30 wt %) non - aqueous</i>	1.8071 – 91.5283	25, 50, 100	24.2 - 2211	11
<i>DEA + 2-amino-2-methyl-1-propanol</i>				
<i>(25 + 5 wt %)</i>	20.9321 – 63.9148	40, 100	162 – 2908	13
<i>(20 + 10 wt %)</i>	17.6298 – 53.2623	40, 100	22 - 2597	13
<i>(6 + 24 wt %)</i>	3.3491 – 10.35419	40, 60, 80	1.61 – 269.9	38
<i>(12 + 24 wt %)</i>	8.7691 – 19.1233	40, 60, 80	11.0 – 364.9	38
<i>(18 + 12 wt %)</i>	13.1536 – 28.6849	40, 60, 80	3.8 – 357.3	38

Table 2. Literature data for Heats of mixing of CO₂ in aqueous alkanolamine solvents

<i>Aqueous Solvent</i>	<i>Type of Data</i>	<i>Temperatures (°C)</i>	<i>CO₂ Partial Pressure (kPa)</i>	<i>Reference</i>
<i>MEA (10, 20, 30 wt %)</i>	Enthalpy	25	265	6
<i>MDEA (10, 20, 30 wt %)</i>	Enthalpy	25	265	6
<i>MDEA (20, 40, 60 wt %)</i>	Enthalpy	15, 60, 115, 149	156 -1121	33
<i>MDEA (30 wt %)</i>	Enthalpy	40, 80, 120	2000, 5000, 10000	32
<i>DEA (10, 20, 30 wt %)</i>	Enthalpy	25	265	6

<i>DEA (2.0, 3.5, 5.0 M)</i>	Enthalpy	25, 70	1121	34
<i>DEA (2.0, 3.5, 5.0 M)</i>	Enthalpy	25, 50, 75	=====	21
<i>DGA (10, 20, 40, 60 wt %)</i>	Enthalpy	15, 60, 115, 149	156, 225, 570, 1121	8
<i>MDEA + MEA</i>				
<i>(27 + 7 wt %)</i>	Enthalpy	25	=====	6
<i>MDEA + Sulfolane</i>				
<i>(20 + 10 wt %)</i>	Enthalpy	25, 40	295	37
<i>(20 + 20 wt %)</i>	Enthalpy	25, 40	295	37
<i>(20 + 30 wt %)</i>	Enthalpy	25, 40	295	37
<i>(10 + 10 wt %)</i>	Enthalpy	25, 40	295	37
<i>(30 + 30 wt %)</i>	Enthalpy	25, 40	295	37
<i>MDEA + PZ</i>				
<i>(18.7 + 10 wt %)</i>	Enthalpy	25, 40	295	37
<i>(30 + 10 wt %)</i>	Enthalpy	25, 40	295	37

References

1. Austgen D. M., Rochelle G. T. and Chen C. C., “*Model of vapor – liquid equilibria for aqueous acid gas – alkanolamine systems. 2. Representation of H₂S and CO₂ solubility in aqueous MEA and CO₂ solubility in aqueous mixtures of MDEA with MEA or DEA*”, *Ind. Eng. Chem. Res.*, 1991, 30, 543 – 555
2. Bishnoi S. and Rochelle G. T., “*Absorption of CO₂ into aqueous PZ: Reaction Kinetics, Solubility and Mass Transfer*”, *Chem. Eng. Sci.*, 2000, 55, 5531 – 5543
3. Bishnoi S. and Rochelle G. T., “*Thermodynamics of PZ / MDEA / H₂O / CO₂*”, *Ind. Eng. Chem. Res.*, 2002, 41, 604 – 612
4. Bishnoi S. and Rochelle G. T., “*Absorption of CO₂ in Aqueous PZ / MDEA*”, *AIChE J.*, 2002, 48, 2788 – 2799
5. Bottoms R.R., “*Organic bases for gases purification*”, *Ind. Eng. Chem.*, 1931, 23, 501 – 504
6. Carson J. K., Marsh K. N. and Mather A. E., “*Enthalpy of solution of CO₂ in (H₂O + MEA, or DEA, or N–MDEA) and (H₂O + MEA + N–MDEA) at T = 298.15 K*”, *J. Chem. Thermo.*, 2000, 32, 1285 – 1296
7. Chakma A. and Meisen A., “*Solubility of CO₂ in aqueous MDEA and N,N–Bis(hydroxyethyl)PZ solutions*”, *Ind. Eng. Chem. Res.*, 1987, 26, 2461 - 2466
8. Christensen S. P., Christensen J. J. and Izatt R. M., “*Enthalpies of solution of CO₂ in aqueous DGA solutions*”, *Thermo. Acta*, 1986, 106, 241 – 251
9. Dawodu O. F. and Meisen A., “*Solubility of CO₂ in aqueous mixtures of alkanolamines*”, *J. Chem Eng. Data*, 1994, 39, 548 – 552
10. Glasscock D. A., Critchfield J. E. and Rochelle G. T., “*CO₂ Absorption / Desorption in mixtures of MDEA with MEA or DEA*”, *Chem. Eng. Sci.*, 1991, 46, 2829 – 2841
11. Guevara F. M., Libreros E. R. and Trejo A., “*Solubility of CO₂ in binary mixtures of N–Methylpyrrolidone with alkanolamines*”, *J. Chem. Eng. Data*, 1992, 37, 4 – 7
12. Guevara F. M., Libreros E. R. and Trejo A., “*Gas solubility of CO₂ and H₂S in mixtures of sulfolane with MEA*”, *Fluid Phase Equilibria*, 1993, 86, 225 – 231

13. Guevara F. M., Libreros E. R., Martinez A. R. and Trejo A., "Solubility of CO₂ in aqueous mixtures of DEA with MDEA and 2-amino-2-methyl-1-propanol", *Fluid Phase Equilibria*, 1998, 150 - 151, 721 - 729
14. Haimour N. and Sandall O. C., "Absorption of CO₂ into aqueous MDEA", *Chem. Eng. Sci.*, 1984, 39, 1791 - 1796
15. Jones J. H., Froning H. R. and Claytor E. E., "Solubility of acidic gases in aqueous MEA", *J. Chem. Eng. Data*, 1959, 4, 85 - 92
16. Jou F. Y., Carroll J. J., Mather A. E. and Otto F. D., "The Solubility of CO₂ and H₂S in a 35% Aqueous solution of MDEA solutions", *Can. J. Chem. Eng.*, 1993, 71, 264 - 268
17. Jou F. Y., Mather A. E. and Otto F. D., "Solubility of H₂S and CO₂ in aqueous MDEA solutions", *Ind. Eng. Chem. Proc. Des. Dev.*, 1982, 21, 539 - 544
18. Jou F. Y., Mather A. E. and Otto F. D., "The solubility of CO₂ in 30 mass % MEA solution", *Can. J. Chem. Eng.*, 1995, 73, 140 - 147
19. Jou F. Y., Mather A. E., Otto F. D. and Carroll J. J., "Experimental investigation of the phase equilibria in the CO₂ - C₃H₈ - 3 M MDEA system", *Ind. Eng. Chem. Res.*, 1995, 34, 2526 - 2529
20. Jou F. Y., Otto F. D. and Mather A. E., "Vapor - Liquid equilibrium of CO₂ in aqueous mixtures of MEA and MDEA", *Ind. Eng. Chem. Res.*, 1994, 33, 2002 - 2005
21. Kharim A. and Mather A. E., "Enthalpy of solution of CO₂ in DEA solutions", *Can. J. Chem. Eng.*, 1980, 58, 660 - 662
22. Kamps A. P. S., Balaban A., Jodecke M., Kuranov G., Smirnova N. A. and Maurer G., "Solubility of Single Gases CO₂ and H₂S in aqueous solution of N-MDEA at temperatures from 313 to 393 K and pressures up to 7.6 MPa: New experimental data and model extension", *Ind. Eng. Chem. Res.*, 2001, 40, 696 - 706
23. Kamps A. P. S., Rumpf B., Maurer G., Anoufrikov Y., Kuranov G. and Smirnova N. A., "Solubility of CO₂ in H₂O + N-MDEA + (H₂SO₄ or Na₂SO₄)", *AIChE J.*, 2002, 48, 168 - 177
24. Kamps A. P. S., Xia J. and Maurer G., "Solubility of CO₂ in (H₂O + PZ) and in (H₂O + MDEA + PZ)", *AIChE J.*, 2003, 49, 2662 - 2670
25. Kennard M. L. and Meisen A., "Solubility of CO₂ in aqueous DEA solutions at elevated temperatures and pressures", *J. Chem. Eng. Data*, 1984, 29, 309 - 312

26. Kuranov G., Rumpf B., Smirnova N. A. and Maurer G., "Solubility of single gases CO_2 and H_2S in aqueous solutions of N -MDEA in the temperature range 313 – 413 K at pressures up to 5 MPa", *Ind. Eng. Chem. Res.*, 1996, 35, 1959 - 1966
27. Lawson J. D. and Garst A. W., "Gas sweetening data: equilibrium solubility of H_2S and CO_2 in aqueous MEA and aqueous DEA solutions", *J. Chem. Eng. Data*, 1976, 21, 20 – 30
28. Lee J. I., Otto F. D. and Mather A. E., "Solubility of CO_2 in aqueous DEA solutions at high pressures", *J. Chem. Eng. Data*, 1972, 17, 465 - 468
29. Li M. H. and Shen K. P., "Densities and solubilities of solutions of CO_2 in H_2O + MEA + N -MDEA", *J. Chem. Eng. Data*, 1992, 37, 288 – 290
30. Liu H. B., Zhang C. F. and Xu G. W., "A study of equilibrium solubility for CO_2 in MDEA-PZ- H_2O solution", *Ind. Eng. Chem. Res.*, 1999, 38, 4032 – 4036
31. MacGregor R. J. and Mather A. E., "Equilibrium solubility of H_2S and CO_2 and their mixtures in a mixed solvent", *Can. J. Chem. Eng.*, 1991, 69, 1357 – 1366
32. Mathonat C., Majer V., Mather A. E. and Grolier J. P. E., "Enthalpies of absorption and solubility of CO_2 in aqueous solutions of MDEA", *Fluid Phase Equilibria*, 1997, 140, 171 – 182
33. Merkle K. E., Christensen J. J. and Izatt R. M., "Enthalpies of absorption of CO_2 in aqueous MDEA solutions", *Thermo. Acta*, 1987, 121, 437 - 446
34. Oscarson J. L., Van Dam R. H, Christensen J. J. and Izatt R. M., "Enthalpies of absorption of CO_2 in aqueous DEA solutions", *Thermo. Acta*, 1989, 146, 107 – 114
35. Pacheco M. A., Kaganoi S. and Rochelle G. T., " CO_2 absorption into aqueous mixtures of DGA and MDEA", *Chem. Eng. Sci.*, 2000, 55, 5125 – 5140
36. Park M. K. and Sandall O. C., "Solubility of CO_2 and N_2O in 50 mass % MDEA", *J. Chem. Eng. Data*, 2001, 46, 166 – 168
37. Schafer B., Mather A. E. and Marsh K. N., "Enthalpies of solution of CO_2 in mixed solvents", *Fluid Phase Equilibria*, 2002, 194 – 197, 929 – 935
38. Seo D. J. and Hong W. H., "Solubilities of CO_2 in aqueous mixtures of DEA and 2-amino-2-methyl-1-propanol", *J. Chem. Eng. Data*, 1996, 41, 258 – 260

39. Shen K. P. and Li M. H., “Solubility of CO_2 in aqueous mixtures of MEA with MDEA”, *J. Chem. Eng. Data*, 1992, 37, 96 – 100
40. Xu G. W., Zhang C. F., Qin S. J., Gao W. H. and Liu H. B., “Gas – Liquid equilibrium in a CO_2 -MDEA- H_2O system and the effect of PZ on it”, *Ind. Eng. Chem. Res.*, 1998, 37, 1473 – 1477
41. Xu G. W., Zhang C. F., Qin S. J. and Wang Y. W., “Kinetics study on absorption of CO_2 into solutions of activated MDEA”, *Ind. Eng. Chem. Res.*, 1992, 31, 921 – 927