TITLE: Heat of Dissolution Measurements for CO₂ in Mixed Alkanolamine Solvents

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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.

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, April 2004 to September 2004, the apparatus for the heat of dissolution measurements was tested and used for measurement of data for aqueous MDEA – CO₂ system. Heat of solution of CO₂ and solubility of CO₂ were measured at two temperatures and for two aqueous solutions of MDEA of different compositions. Data were compared with the corresponding values available in the literature, and satisfactory agreements were observed.

During these preliminary measurements, it was observed that for complete dissolution of CO₂ in the aqueous MDEA solution, the CO₂ flow rate must be below 15 sccm (standard cubic centimeters per minute). The mass flow meter made by Matheson Company with a scale of 0 – 250 sccm was used to set and control the CO₂ flow rate, and did not allow the measurement of low gas flow rates with sufficient accuracy. A mass flow meter with a scale of 0 – 20 sccm made by Omega Company has been purchased and is currently being installed. This will increase the accuracy of future measurements significantly. Another modification that was found necessary involves installation of a check valve to prevent back flow of the liquid into the gas line.

In the next quarter, measurements will be continued for the CO₂ –MDEA system at a temperature of 15°C and a 20 weight% MDEA solution. This will be followed by measurements for CO₂ –MEA system at two sets of conditions. The results will be carefully compared with data available in the literature. Measurements with mixed solvents will be initiated upon completion of this stage of the project.

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1. 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 80°C 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.

2. Experimental Apparatus and Procedure

Experimental Apparatus

The experimental apparatus for measuring the heats of adsorption of CO₂ in alkanolamine solutions is shown in Fig 2.1. The apparatus is a modified version of the experimental setup used for measuring the heats of mixing of two liquids in earlier studies.¹

The isothermal micro-calorimeter made by Calorimetry Sciences Corporation was used for the measurements. The calorimeter operates with a temperature range of -40 – 80 °C. The main body of the calorimeter contains a bath with a temperature stability of ± 0.0005 °C at 25 °C. To increase the temperature stability of the bath it is provided with an auxiliary bath which helps maintain the bath temperature to the set point. The bath is filled with water for measurements at temperatures higher than 10 °C and with a mixture of ethylene glycol and water for temperatures below 10 °C. The calorimeter is equipped with four wells each of which houses one cell. Three cells serve as sample cells, and the fourth cell is used as the reference cell. The instrument can detect heat effects as small as 40 μ J and changes in heat flow as small as 0.1 μ W. It has a low noise level of ± 0.1 μ W and base line stability of 1 μ W.

The diagram of the flow mixing cell used is given in Fig 2.2. The cell consists of two inlets and an outlet each of 1/16" size. The inlet tubes run parallel to each other all the way down to the mixing point. The inlet tubes first enter a thermal equilibration chamber where they coil around so as to increase the residence time of the inlet fluids and to achieve the desired temperature. Then they enter the mixing zone where they meet at the bottom of the zone in a tee. The other end of the tee is connected to the outlet tube. The outlet tube coils around inside the mixing zone thereby allowing more residence time for the mixing fluids and also allowing more time for the temperature in the outlet tube to come to the desired temperature either by removing or adding heat. The outlet tube then exits the calorimeter.

The isothermal micro-calorimeter was set at the required temperature and allowed to reach equilibrium overnight. The calorimeter can measure heats as small as 40 μ J and changes in heat effects as small as 10 μ W. The alkanolamine solution was prepared based on the required weight percent at room temperature. The isocratic pump with a precision of 0.2% was then calibrated for the prepared solution at room temperature and the solution was pumped at a constant flow rate through the flow cell in the calorimeter. The data acquisition program was started to monitor the heats during the experiment. The CO₂ was then allowed to flow into the calorimeter at a known flow rate as controlled by the mass flow meter with a precision of 1%. The controller on the mass flow meter was set at pre-determined set point to control the flow rate of the gas. The outlet was connected to a pressure gauge to monitor the pressure of the system and a back-pressure regulator to

maintain the system at required pressure. The waste was released in the fume hood to let the fumes coming from the collection tank to dissipate.

Figure 2.1: Experimental Setup For CO₂ + Alkanolamine system Enthalpy measurements

Figure 1. Diagram of a flow mixing cell.

Figure 2.2: Diagram of the Flow Cell

A mass flow meter controller system (model 8270 made by Matheson Tri-gas.) was used to accurately control the flow rate of CO₂ into the calorimeter. The flow meter was calibrated for air with a flow range from 0 – 250 sccm, maximum inlet pressure of 500 psi, and an average pressure drop of about 50 psi. The correction factor for CO₂ gas measurements was 0.769 (as provided by Matheson Tri-gas). The controller can control the flow rate with an accuracy of ± 1 % of full scale.

A digital isocratic pump (Lab Alliance Series II) was used to maintain a uniform flow rate of the liquid solvent. The pump can operate at up to a back pressure of 6000 psi and has a flow rate range of 0.01 – 10 ml/min. There is an inbuilt low volume pulse damper before the outlet of the pump. The inlet of the pump is 1/8" Teflon tubing while the outlet is 1/16" stainless steel tubing which goes to the inlet tube of the calorimeter. The pump has an accuracy of ± 2 % and a precision of ± 0.2 % RSD. The pump is equipped with a self cleaning mechanism to clean the head.

T-type thermocouples (made by Omega, Inc.) were used to record the temperature at various points in the system. A 10 – channel Thermocouple reader (made by Omega, Inc.) was used along with the thermocouples. The pressure in the system was measured using a digital pressure gauge (made by Omega, Inc.). It can read up to 10,000 psi and has an accuracy of ± 1 %. For maintaining the pressure in the system fixed back pressure regulators (made by Upchurch Scientific) were used. These back pressure regulators let the fluid pass through them when the upstream pressure in the system is higher than the downstream pressure by an amount equal to the rating of the back pressure regulator. All the tubing except for the inlet of the pump was 1/16" stainless steel tubing. The pump was connected to the reservoir using 1/8" Teflon tubing.

Materials and Experimental Procedure

CO₂ with a purity of $> 99.99\%$ was obtained from National Welders Company. MDEA with a purity of 99.5% was purchased from Sigma-Aldrich Company. The apparatus was leak tested at 750 psi pressure. A plug valve was attached after the back pressure regulator and nitrogen was filled into the system instead of CO₂ till the pressure in the system was 750 psi as shown by the pressure gauge. Once the pressure was reached nitrogen supply was cut off and the system left for 12 hours. After twelve hours the pressure in the system was checked to ensure that there were no leaks in the system. An electronic leak detector was used to find the leaks in the system. After a period of 12 hours when the pressure in the system did not go below 740 psi, it was assumed that there were no leaks in the system.

The calorimeter was adjusted to the experimental temperature and allowed to equilibrate overnight. The solution was made by weighing required amounts of MDEA and water at room temperature. This solution was stirred overnight to ensure complete mixing. The pump was calibrated using this solution for different flow rates. The pump was allowed to pump at known setting and liquid was collected near the waste container for known amount of time. Dividing the amount collected by the time gives the flow rate corresponding to the pump setting. This was repeated twice for five settings (1.0, 0.75,

0.5, 0.25 and 0.1ml/min) and a graph was drawn for flow rate vs pump display setting. A linear curve was obtained and therefore the required flow rates were set from interpolated values.

Once the calorimeter has equilibrated overnight and the temperature is equal to the required temperature the experiment is started. The MDEA solution is pumped in at known flow rate for an initial time of 10 minutes before CO₂ is introduced into the system. The CO₂ is then allowed to flow into the system at a known flow rate. Once CO₂ has started flowing into the system the data acquisition software is started and monitored. The data is displayed as a graph as shown in figure 2.3 every ten seconds. The graph is plotted as Heat per second (Y axis) vs time (X axis).

Figure 2.3: Display from the Data acquisition software

The temperature at which the solution is being pumped in is noted. Once the graph displays a constant value for nearly 15 minutes the flow rate of CO₂ or the flow rate of the pump is changed to a different value. The flow rates of CO₂ were varied between 2 and 15 sccm and MDEA solution flow rates of 0.1 to 1.0 ml/min were used. Once the measurements for a run were completed, the file was converted into a Microsoft Excel worksheet for further analysis.

3. Design of Preliminary Experiments

Evaluation of Literature Data

The density (kg/liter) and molarity (kmol/m³) of MDEA solution of interest were interpolated and extrapolated (linear) from the available experimental data² for 30 wt %

MDEA solution. The results for 15 wt%, 30 wt%, and 50 wt% MDEA solutions at different temperatures are tabulated in Table 3.1.

Table 3.1: Calculated density and Molarity of MDEA solution at different temperatures

<i>Temp</i>	<i>Calculated(ρ)</i>				<i>Molarity (kmol/m³)</i>		
	<i>H₂O</i>	<i>15wt% MDEA</i>	<i>30wt % MDEA</i>	<i>50 wt% MDEA</i>	<i>15 wt% MDEA</i>	<i>30wt % MDEA</i>	<i>50 wt% MDEA</i>
15	1.0004	1.0151	1.0299	1.0495	1.278	2.593	4.404
16	1.0002	1.0149	1.0295	1.0490	1.278	2.592	4.402
17	1.0000	1.0146	1.0291	1.0485	1.277	2.591	4.400
18	0.9998	1.0143	1.0288	1.0480	1.277	2.590	4.398
19	0.9996	1.0140	1.0284	1.0476	1.276	2.589	4.396
20	0.9994	1.0137	1.0280	1.0471	1.276	2.588	4.394
21	0.9992	1.0134	1.0276	1.0466	1.276	2.587	4.391
22	0.9989	1.0131	1.0272	1.0461	1.275	2.586	4.389
23	0.9987	1.0128	1.0268	1.0456	1.275	2.585	4.387
24	0.9985	1.0125	1.0264	1.0451	1.274	2.584	4.385
25	0.9982	1.0121	1.0261	1.0446	1.274	2.583	4.383
30	0.9969	1.0105	1.0240	1.0421	1.272	2.578	4.373
40	0.9938	1.0067	1.0196	1.0368	1.267	2.567	4.350
50	0.9901	1.0025	1.0148	1.0313	1.262	2.555	4.327
60	0.9858	0.9977	1.0096	1.0255	1.256	2.542	4.303
70	0.9809	0.9925	1.0040	1.0194	1.249	2.528	4.277
75	0.9782	0.9896	1.0011	1.0163	1.246	2.520	4.264
80	0.9754	0.9867	0.9980	1.0131	1.242	2.513	4.251

The solubility and enthalpy data for CO₂ – MDEA, and CO₂ – MEA solutions available in the literature are tabulated in tables 3.2 and 3.3. The intent is to set the conditions for our preliminary measurements, such that literature data are available for comparisons. It is very important to validate the experimental procedures in this way before undertaking new experimental measurements.

Table 3.2: Solubility and enthalpy data (0 – 120 °C) for CO₂ in MDEA solutions

<i>Conc. MDEA</i>	<i>Temp °C</i>	<i>Pressure (kPa)</i>	<i>(a)</i>	<i>Δ H (kJ/molCO₂)</i>	<i>Reference</i>
2.0 – 4.28 M	40	0.0056 – 93.6	0.00314 – 0.842	X	3
10 wt %	25	101.32	0.005 – 0.0154	-49.70 – -50.60	4
20 wt %	25	101.32	0.005 – 0.0142	-48.66 – -48.97	
30 wt %	25	101.32	0.00495 – 0.01562	-47.42 – -50.40	4
4.28 M	100	138 – 4930	0.139 – 0.950	X	5
1.69 M	100	138 – 4930	0.274 – 1.304		

4.28 M	100	162 – 3611	0.123 – 0.823	X	6
	120	276 – 3832	0.091 – 0.497		
35 wt %	40	0.0004 – 100	0.002 – 0.795	X	7
	100	0.963 – 236	0.0077 – 0.271		
2.0 M	25	0.001 – 6380	0.005 – 1.833	X	8
	40	0.00217 – 6630	0.003 – 1.682		
	70	0.00208 – 6020	0.0009 – 1.397		
	100	0.0468 – 5530	0.00218 – 1.218		
4.28 M	25	0.00385 -6370	0.00621 – 1.381		
	40	0.00231 – 6570	0.00202 – 1.290		
	70	0.00161 – 6280	0.00037 – 1.232		
	100	0.277 – 5590	0.00376 – 1.096		
3M	25	2270 – 7910	0.941 -1.302	X	9
3.954 mol/kg	40	176.5 – 6469	0.8442 – 1.2427	X	10
7.994 mol/kg	40	228 -7565	0.796 – 1.1542		
	80	293.1 – 5403	0.315 – 0.945	X	11
1.949 mol/kg	40	837.4 – 4883	1.0595 – 1.4146		
1.994 mol/kg	40	74 – 3598.2	0.7854 – 1.3161	X	12
1.949 mol/kg	60	139.5 – 4024.8	0.7017 – 1.2534		
	100	226.9 – 4080.8	0.2972 -1.0625		
3.971 mol/kg	40	73.5 – 3660.8	0.6732 – 1.1554		
	60	205.4 -3363	0.6681 – 1.0808		
	100	439.7 – 3870.5	0.3453 – 0.8907		
2 M	40	xxxxxx	0.124 – 1.203	X	13
30 wt%	40	2000, 5000, 10000	1.17, 1.22, 1.26	-49	14
	80	2000, 5000, 10000	0.87, 1.20, 1.35	-55	
20 wt %	15	156, 1121	X	-47	15
	60	156, 1121		-54	
40 wt %	15	156, 1121		-49	
	60	156, 1121		-57	
60 wt %	15	156, 1121		-47	
	60	156, 1121		-57	
30 wt %	40	1.2 – 1979	0.244 – 1.108	X	16
	60	1.1 – 1946	0.189 – 1.007		
	80	1.7 – 1197	0.155 – 0.803		
	100	3.0 – 1890	0.186 – 0.644		
3.04 M	55	10.74 – 806.5	0.2088 – 0.911	X	17
	70	6.152 – 806.8	0.0692 – 0.791		
3.46 M	55	115 – 992	0.5019 – 0.8488		
	70	173.5 – 808.5	0.358 – 0.753		
	80	169.8 – 794.8	0.251 – 0.658		
4.28	40	15.4 – 838	0.269 – 0.8806		
	55	8.917 – 1013	0.125 – 0.8128		
	70	9.22 – 754	0.074 – 0.6405		
	80	3.268 – 867.8	0.0303 – 0.561		

Table 3.3: Solubility and enthalpy data (0 – 100 °C) for MEA solutions in literature

<i>Conc. MEA</i>	<i>Temp °C</i>	<i>Pressure (kPa)</i>	<i>(α)</i>	<i>ΔH (kJ/molCO₂)</i>	<i>Reference</i>
2.5 M	40	0.0934 - 92.6	0.354 – 0.676	X	3
	80	1.01 – 228.7	0.267 – 0.620	X	
10 wt %	25	101.32	0.00493 – 0.01482	-79.37 – -81.77	4
20 wt %	25	101.32	0.00423 – 0.01409	-81.71 – -82.91	
30 wt %	25	101.32	0.00488 – 0.01551	-80.33 – -83.15	
4.2 M	100	455 – 3863	0.541 – 0.723	X	6
15.3 wt %	40	15.7 – 2550	0.561 – 1.049	X	16
30 wt %	40	2.2 – 1973	0.471 – 0.806		
	60	1.1 – 1975	0.379 – 0.731		
15.3 wt %	80	4.0 – 1964	0.347 – 0.639	X	18
	40	0.0746 – 120.65	0.305 – 0.713		
	60	2.373 – 161.986	0.437 – 0.665		
30 wt %	80	6.453 – 827.398	0.398 – 0.728	X	19
	0	200 – 20000	0.400 – 1.324		
	25	200 – 20000	0.211 – 1.247		
	40	200 – 20000	0.0888 – 1.180		
	60	220 – 20000	0.0564 – 1.109		
	80	250 – 20000	0.0174 – 1.033		

Experimental Conditions

Experimental enthalpy data are available for MDEA solution (30 wt% and 40 °C, 20, 40, 60 wt% at 15, 60 °C and 10, 20, 30 wt % and 25 °C) in the literature. The pressure at which these experiments were conducted was 14.7 - 10000 kPa. The pressure did not affect the enthalpy. The solubility limit (α) of CO₂ however is a function of pressure. The solubility data for CO₂ in 30 wt% MDEA solution and 40 °C are available for pressures between 1.1 – 1979 kPa. Based on this it was decided to test the enthalpy data and also the solubility data for CO₂ in MDEA 30 wt% solution and 40°C at a pressure of 689.6 kPa (100 psi). The conditions for the other two experiments planned to be conducted with the MDEA solution are tabulated in Table 3.4.

Table 3.4: Experimental conditions for enthalpy measurement of CO₂ + MDEA System

$\downarrow$ Temp / wt % $\rightarrow$	20 wt %	30 wt %	Pressure, kPa $\downarrow$
15 °C	X		689.6
40 °C		X	689.6
75 °C	X		689.6

Table 3.5 gives the interpolated solubility data for CO₂ in 30 wt% MDEA solution at 40 °C as inferred from the literature values.

Table 3.5: Solubility of CO₂ in 30 wt% MDEA at 40 °C from references

MDEA [kmol/m ³] /Temp	P, [kPa]	α (molCO ₂ / mol MDEA)(Ref)	Average
2.567/ 40 ⁰ (30 wt%)	101.32	0.7297(10)* 0.8340(6) 0.8533(14)	0.7915 $\pm$ 0.0618
	689.6	0.9916(10)* 1.0651(6) 1.0061(14)	1.0284 $\pm$ 0.0368
	3448.2	1.2329(10)* 1.2778(6)	1.2554 $\pm$ 0.0225
	5172.4	1.460(6)	

* The pressure is total pressure of the system not the partial pressure of CO₂.

The expected flow rates of CO₂ (SCCM) in 1ml/min of 30 wt% MDEA solution at 40 °C were calculated from the solubility data available in the literature and were interpolated. Table 3.6 gives the interpolated values.

The expected flow rates of CO₂ (sccm) with 1 ml/min of solvent flow rate were calculated from the solubility data available in the literature to give an estimate of the CO₂ flow rates that would be required in the experiment. As an example, for 1 ml/min flow rate of 30 wt% MDEA solution at 40°C and at the saturation point CO₂ flow rate of approximately 60 sccm would be required. These calculations were used to provide guidance in designing the experiments.

4. Experimental Results

Results at 40 °C, 100 psi and 30 wt% MDEA solution

The flow rate of the pump was calibrated for 30 wt% MDEA solution under the conditions of the experiment. A back pressure of 1000 psi was used just on the pump when the experiment was being done i.e. a total pressure of 1100 psi was applied on the pump. The system pressure was maintained at 100 psi using a fixed back pressure cartridge. The flow rate of CO₂ was maintained using a Matheson mass flow controller with a scale of 0 – 250 sccm of air. The correction factor for CO₂ was 0.769.

When the flow rate of CO₂ was above 18 sccm as shown by the Matheson display the CO₂ was bubbling out which implied that the CO₂ was not dissolving completely i.e. the residence time for CO₂ in the calorimeter was not sufficient for complete dissolution. This limitation led the introduction of MDEA solution at lower flow rates and the pump was calibrated at lower flow rates as well. A flow rate of 0.2 ml/min was chosen for the experimental run. The data which came from the run indicated low enthalpy values. This led us to check the flow rates of CO₂ using a Omega flow meter. The values which were shown by the Omega flow meter did not correspond to the flow meter settings of the Matheson. This limitation led to the addition of Omega flow meter after the Matheson Flow controller and the flow rates of CO₂ were recorded to attain an average CO₂ flow rate for each run. The experimental results are tabulated in the tables 4.1 and 4.2. Table 4.1 includes all the data measured, whereas Table 4.2 only lists data points where Omega flow meter was used to record the gas flow rates. The corresponding enthalpy curves are shown in Figures 4.1 and 4.2.

Table 4.1: Experimental values at 40 °C, 100 psi, 30 wt% MDEA solution

<i>Display Reading SCCM</i>	<i>CO2 Flow Rate SCCM</i>	<i>CO2 Moles/sec</i>	<i>MDEA Flow Rate</i>	<i>MDEA Moles/sec</i>	<i>Loading of CO2</i>	<i>Enthalpy mJ/sec</i>	<i>Enthalpy ΔH kJ/mol CO2</i>	<i>Enthalpy ΔH kJ/mol MDEA</i>
6	3.89	2.894E-06	1	4.310E-05	0.067	-144.366	-49.878	-3.350
6	4.12	3.065E-06	0.5	2.154E-05	0.142	-159.170	-51.923	-7.389
3*	1.8326	1.364E-06	0.2	8.620E-06	0.158	-89.777	-65.841	-10.415
11	7.58	5.640E-06	0.5	2.155E-05	0.262	-282.701	-50.125	-13.121
6*	4.3919	3.268E-06	0.2	8.620E-06	0.379	-184.145	-56.352	-21.363
16	11.41	8.490E-06	0.5	2.154E-05	0.394	-408.804	-48.154	-18.977
9*	6.3572	4.730E-06	0.2	8.620E-06	0.549	-260.153	-55.000	-30.180
5	3.42	2.545E-06	0.1	4.313E-06	0.590	-130.485	-51.278	-30.257
10*	6.9951	5.205E-06	0.2	8.620E-06	0.604	-276.093	-53.047	-32.029
11*	7.6495	5.692E-06	0.2	8.625E-06	0.660	-275.417	-48.390	-31.932
12*	8.3279	6.196E-06	0.2	8.623E-06	0.719	-299.738	-48.373	-34.759
13*	9.0336	6.721E-06	0.2	8.622E-06	0.780	-326.403	-48.562	-37.855

7	4.81	3.579E-06	0.1	4.313E-06	0.830	-180.539	-50.446	-41.864
14*	9.7647	7.265E-06	0.2	8.623E-06	0.843	-347.942	-47.890	-40.349
15*	10.5146	7.823E-06	0.2	8.622E-06	0.907	-367.054	-46.918	-42.573
8	5.60	4.169E-06	0.1	4.309E-06	0.967	-210.598	-50.521	-48.872
9	6.28	4.673E-06	0.1	4.313E-06	1.084	-214.768	-45.963	-49.801
11	8.04	5.982E-06	0.1	4.313E-06	1.387	-215.069	-35.952	-49.871
13	9.42	7.009E-06	0.1	4.313E-06	1.625	-215.212	-30.705	-49.904

*The omega flow meter was not used to record the flow rate of CO₂ for these data points

Figure 4.1: Heats of dissolution vs the Loading of CO₂

Table 4.2: Experimental values at 40 °C, 100 psi, 30 wt% MDEA solution
when Omega flow meter was used to measure the flow rate of CO₂

<i>Display Reading SCCM</i>	<i>CO2 Flow Rate SCCM</i>	<i>CO2 Moles/sec</i>	<i>MDEA Flow Rate</i>	<i>MDEA Moles/sec</i>	<i>Loading of CO2</i>	<i>Enthalpy mJ/sec</i>	<i>Enthalpy ΔH kJ/mol CO2</i>	<i>Enthalpy ΔH kJ/mol MDEA</i>
6	3.89	2.894E-06	1	4.310E-05	0.067	-144.366	-49.878	-3.350
6	4.12	3.065E-06	0.5	2.154E-05	0.142	-159.170	-51.923	-7.389
11	7.58	5.640E-06	0.5	2.155E-05	0.262	-282.701	-50.125	-13.121
16	11.41	8.490E-06	0.5	2.154E-05	0.394	-408.804	-48.154	-18.977
5	3.42	2.545E-06	0.1	4.313E-06	0.590	-130.485	-51.278	-30.257
7	4.81	3.579E-06	0.1	4.313E-06	0.830	-180.539	-50.446	-41.864
8	5.60	4.167E-06	0.1	4.309E-06	0.967	-210.598	-50.543	-48.872
9	6.28	4.673E-06	0.1	4.313E-06	1.084	-214.768	-45.963	-49.801
11	8.05	5.990E-06	0.1	4.313E-06	1.389	-215.069	-35.907	-49.871
13	9.42	7.009E-06	0.1	4.313E-06	1.625	-215.212	-30.705	-49.904

Figure 4.2: Heats of dissolution vs the Loading of CO₂

The saturation (α) value of CO₂ was determined graphically as shown in the figure 4.3.

Figure 4.3: The saturation point for CO₂ at 40 °C, 100 psi, and 30 wt% MDEA solution

The saturation loading (α) for CO₂ was found to be 0.9752 at 40 °C, 100 psi, 30 wt% MDEA solution. The α from literature is 1.0284 ± 0.0368 . The value obtained from the experiment is a little lower. The value from literature has been interpolated between pressure and concentrations. The enthalpy obtained was -49.259 kJ/mol of CO₂. the enthalpy value reported under similar conditions of temperature and weight percent of MDEA solution is -49 kJ/mol of CO₂ [22] .

Results at 75 °C, 100 psi and 20 wt% MDEA solution

Similar to the previous run, the data measured at 75°C and 20 wt% MDEA solution are given in Table 4.3, and Figures 4.4 and 4.5.

Table 4.3: Experimental values at 75 °C, 100 psi, 20 wt% MDEA solution

CO ₂ Flow Rate SCCM	CO ₂ Moles/sec	MDEA Flow Rate	MDEA Moles/sec	Loading of CO ₂	Enthalpy mJ/sec	Enthalpy DH kJ/mol CO ₂	Enthalpy DH kJ/mol Mdea
4.96	3.690E-06	0.10	2.847E-06	1.2962	-128.414	-34.796	-45.102
4.85	3.609E-06	0.13	3.701E-06	0.9751	-172.501	-47.802	-46.613
5.01	3.728E-06	0.14	3.986E-06	0.9353	-185.591	-49.787	-46.566
4.52	3.363E-06	0.13	3.701E-06	0.9088	-172.092	-51.171	-46.503
5.05	3.757E-06	0.15	4.270E-06	0.8800	-194.830	-51.852	-45.628
5.08	3.780E-06	0.16	4.555E-06	0.8299	-196.966	-52.111	-43.245
5.06	3.765E-06	0.17	4.839E-06	0.7780	-198.335	-52.680	-40.984
4.91	3.653E-06	0.20	5.694E-06	0.6416	-183.710	-50.286	-32.262
4.49	3.341E-06	0.20	5.693E-06	0.5868	-176.849	-52.937	-31.062
4.93	3.668E-06	0.30	8.543E-06	0.4294	-182.696	-49.806	-21.387
4.49	3.341E-06	0.30	8.540E-06	0.3912	-172.677	-51.688	-20.220
1.89	1.406E-06	0.30	8.540E-06	0.1647	-72.164	-51.317	-8.450

Figure 4.4: Heats of dissolution vs the Loading of CO₂

Figure 4.5: The saturation point for CO₂ at 40 °C, 100 psi, and 30 wt% MDEA solution

The saturation loading (α) was found to be 0.8861 at 75 °C, 100 psi pressure and 20 wt % MDEA solution. The interpolated values from literature indicate a value between 0.8 – 0.9. The values could not be interpolated exactly since the literature data were at different temperatures and weight percentages. The enthalpy value reported in literature is -57 kJ/mol CO₂ [23] (interpolated). The value obtained in the experiment is -51.8432 kJ/mol CO₂.

5. Conclusions and Plans for Next Quarter

During the current period of performance, April 2004 to September 2004, the apparatus for the heat of dissolution measurements was tested and used for measurement of data for aqueous MDEA – CO₂ system. Heat of solution of CO₂ and solubility of CO₂ were measured at two temperatures and for two aqueous solutions of MDEA of different compositions. Data were compared with the corresponding values available in the literature, and satisfactory agreements were observed.

During these preliminary measurements, it was observed that for complete dissolution of CO₂ in the aqueous MDEA solution, the CO₂ flow rate must be below 15 sccm (standard cubic centimeters per minute). The mass flow meter made by Matheson Company with a scale of 0 – 250 sccm was used to set and control the CO₂ flow rate, and did not allow the measurement of low gas flow rates with sufficient accuracy. A mass flow meter with a scale of 0 – 20 sccm made by Omega Company has been purchased and is currently being installed. This will increase the accuracy of future measurements significantly. Another modification that was found necessary involves installation of a check valve to prevent back flow of the liquid into the gas line.

In the next quarter, measurements will be continued for the CO₂ –MDEA system at a temperature of 15°C and a 20 weight% MDEA solution. This will be followed by measurements for CO₂ –MEA system at two sets of conditions. The results will be carefully compared with data available in the literature. Measurements with mixed solvents will be initiated upon completion of this stage of the project.

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