Heat of Dissolution Measurements for CO_2 in Mixed Alkanolamine Solvents

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Outline

- Introduction
- Review of Literature
- Experimental Apparatus
- Heat of Solution Data
- Data Analysis
- Discussion of Thermodynamic Models
- Continuing and Future Work

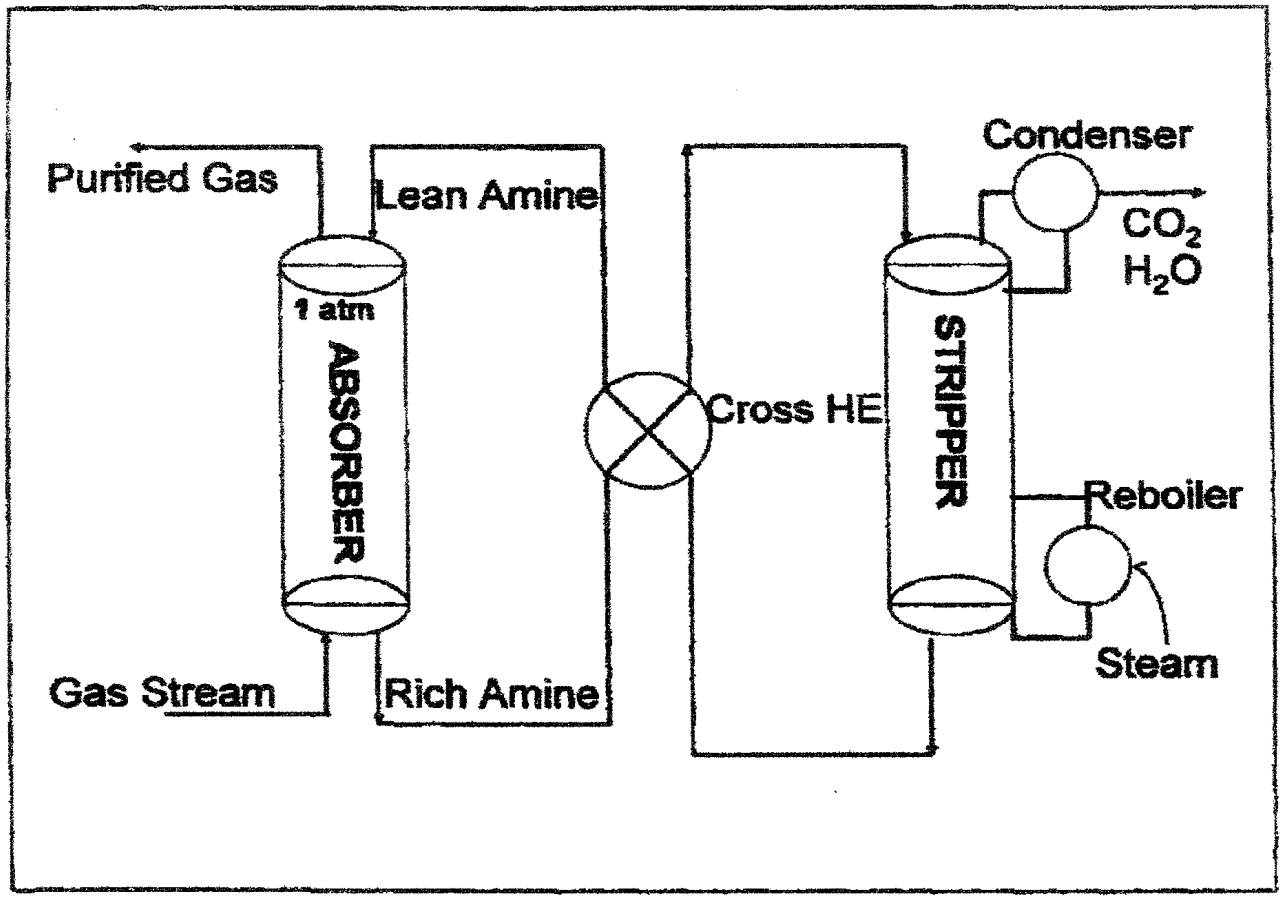


Figure 1. Absorption / stripping process for CO_2 removal with alkanolamines.

Reaction Mechanisms

Ionization of water

- $2H_2O \leftrightarrow H_3O^+ + OH^-$

Dissociation of carbon dioxide

- $2H_2O + CO_2 \leftrightarrow H_3O^+ + HCO_3^-$

Dissociation of bicarbonate

- $H_2O + HCO_3^- \leftrightarrow H_3O^+ + CO_3^{2-}$

Dissociation of protonated alkanolamine

- $H_2O + RR'R''NH^+ \leftrightarrow H_3O^+ + RR'R''N$

Carbamate reversion to bicarbonate

- $H_2O + RNHCOO^- \leftrightarrow RNH_2 + HCO_3^-$

Desired Properties of Alkanolamine Solvent

- High solubility of CO_2 at ambient temperature
- Rapid solubility drop with increase in temperature
- High absorption and desorption rates
- Low heat duty in the stripping process
- Low corrosion and circulation rates

Available Solubility Data

Aqueous solvents of pure alkanolamines

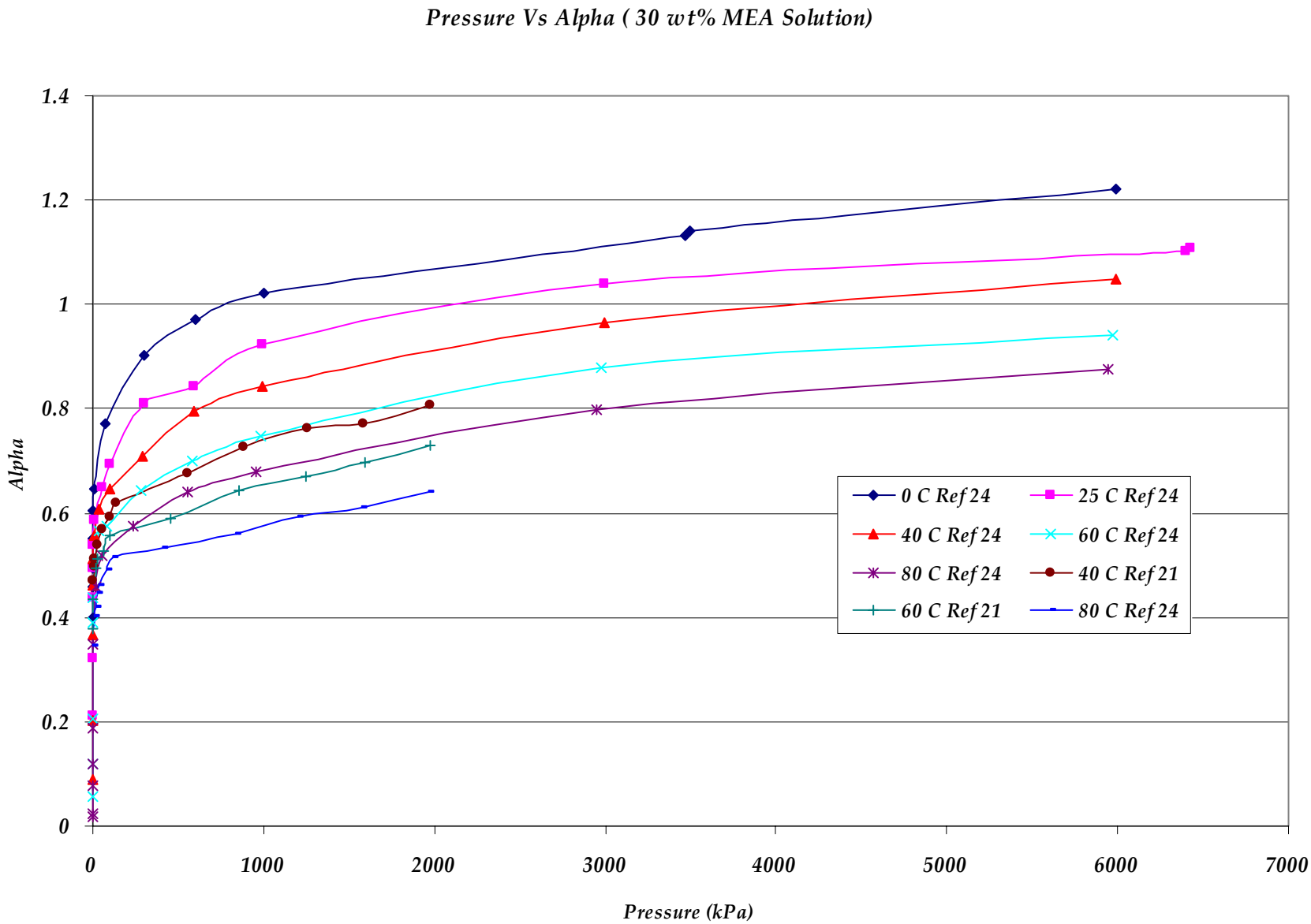
1. MEA (10 to 30 wt%, 0 to 120^{0}C)
2. DEA (10 to 50 wt%, 0 to 120^{0}C)
3. MDEA (10 to 55 wt%, 0 to 120^{0}C)
4. PZ (Piperazine) (5 to 30 wt%, 40 to 120^{0}C)

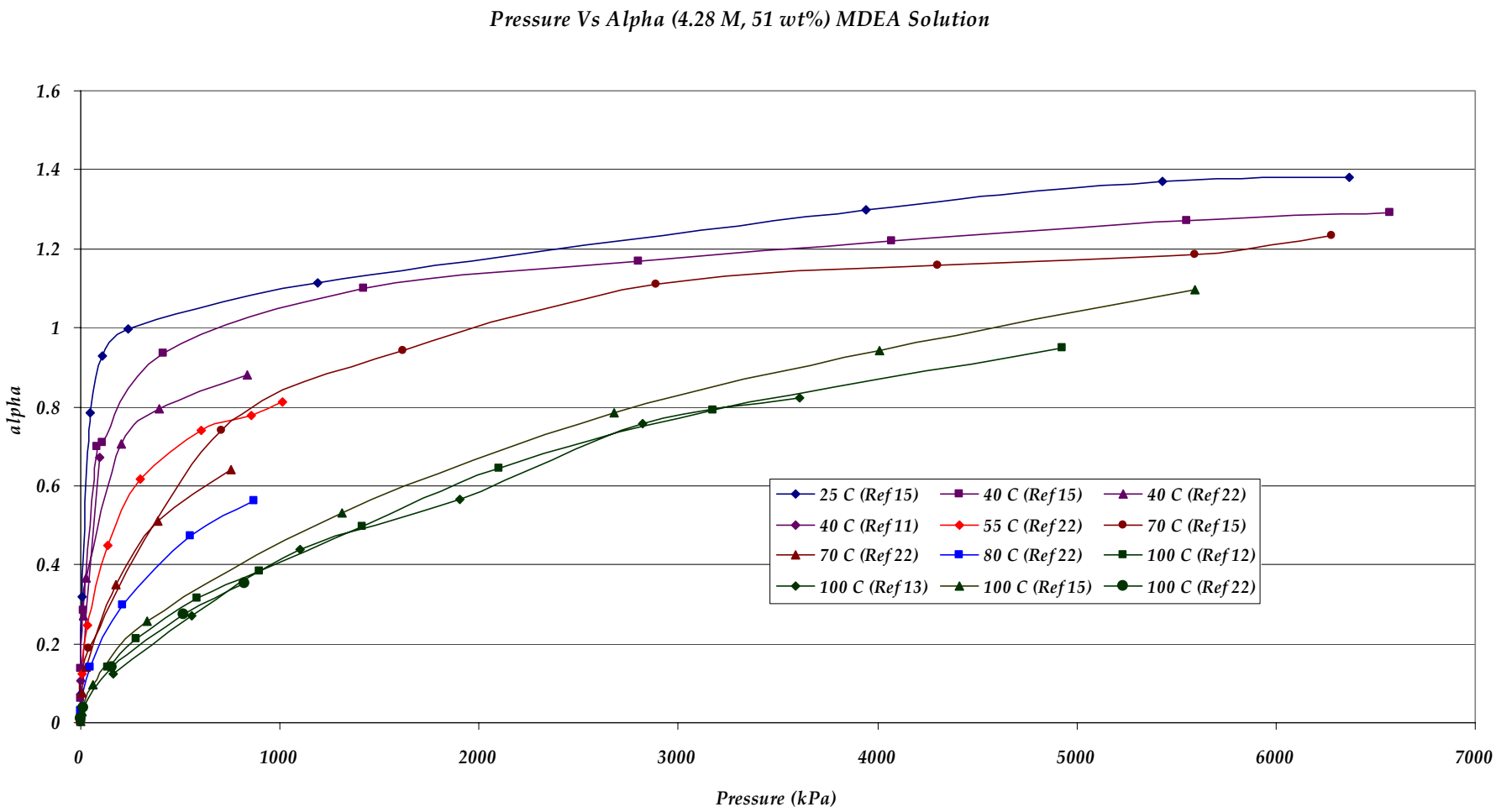
Aqueous solvents of mixed alkanolamines

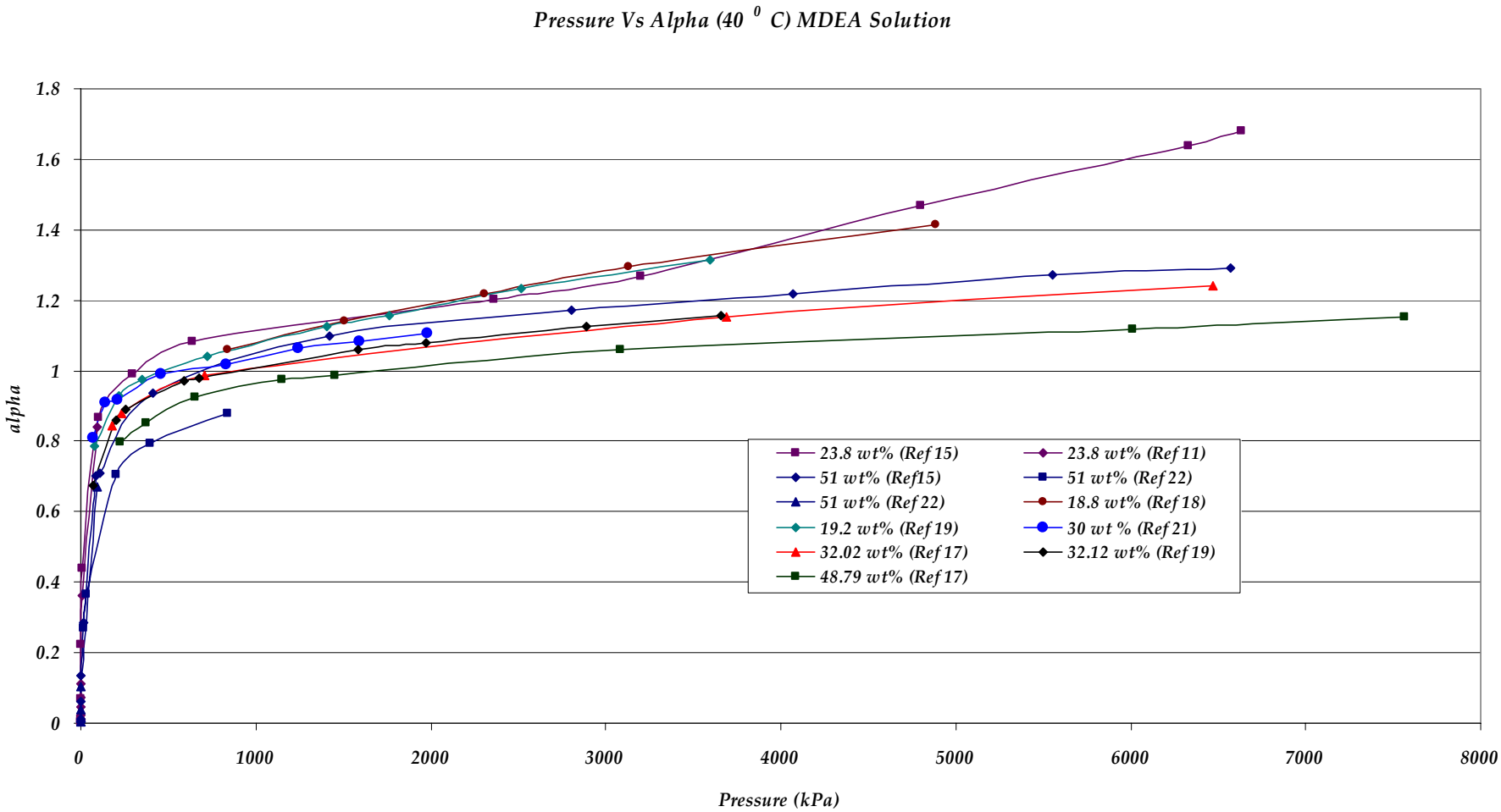
1. MEA + MDEA (Range of compositions, 25 to 120^{0}C)
2. DEA + MDEA (Few compositions, 40 to 120^{0}C)
3. MEA+PZ (Few compositions, 40 to 60^{0}C
4. MDEA + PZ (Few compositions, 30 to 70^{0}C)

Available Heat of Mixing Data

- Limited data in aqueous MEA, DEA and MDEA solvents
- Limited data in mixed solvents MEA+MDEA and MDEA+PZ


Pressure Vs Alpha (30 wt% MEA Solution)
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Alpha
0
1000
2000
3000
4000
5000
6000
7000
Pressure (kPa)
0 C Ref 24
25 C Ref 24
40 C Ref 24
60 C Ref 24
80 C Ref 24
40 C Ref 21
60 C Ref 21
80 C Ref 24

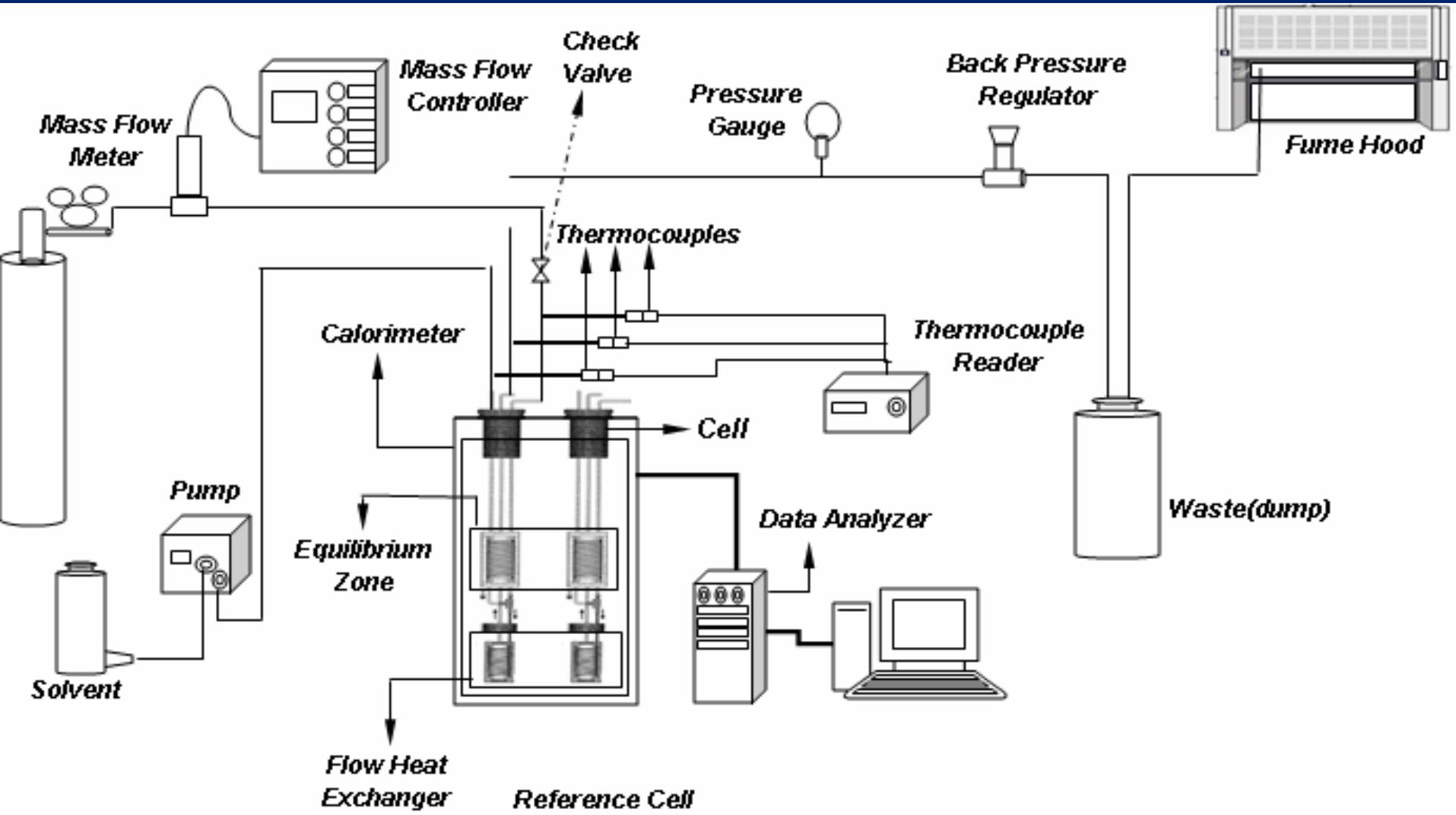

Pressure Vs Alpha (4.28 M, 51 wt%) MDEA Solution
alpha
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
1000
2000
3000
4000
5000
6000
7000
Pressure (kPa)
25 C (Ref 15)
40 C (Ref 15)
40 C (Ref 22)
40 C (Ref 11)
55 C (Ref 22)
70 C (Ref 15)
70 C (Ref 22)
80 C (Ref 22)
100 C (Ref 12)
100 C (Ref 13)
100 C (Ref 15)
100 C (Ref 22)


Pressure Vs Alpha (40 0 C) MDEA Solution
alpha
Pressure (kPa)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
0
1000
2000
3000
4000
5000
6000
7000
8000
23.8 wt% (Ref 15)
23.8 wt% (Ref 11)
51 wt% (Ref15)
51 wt% (Ref 22)
51 wt% (Ref 22)
18.8 wt% (Ref 18)
19.2 wt% (Ref 19)
30 wt % (Ref 21)
32.02 wt% (Ref 17)
32.12 wt% (Ref 19)
48.79 wt% (Ref 17)

Objectives of this project

- Measure solubility and heat of solution data for CO_2 in aqueous MEA and MDEA
- Measure solubility and heat of solution data for CO_2 in aqueous mixtures of MEA, MDEA and PZ
- Make recommendations for the solvent with optimum composition
- Explore other additives with desirable properties

Experimental Setup



Apparatus

- Isothermal Calorimeter
  - - 40 ^{0} C – 80 ^{0} C
  - Detectable heat effect 40 μJ
  - Temperature Stability ± 0.0005 ^{0} C at 25 ^{0} C
  - Detectable heat changes 0.1 μW
  - Low noise levels

Flow Cell

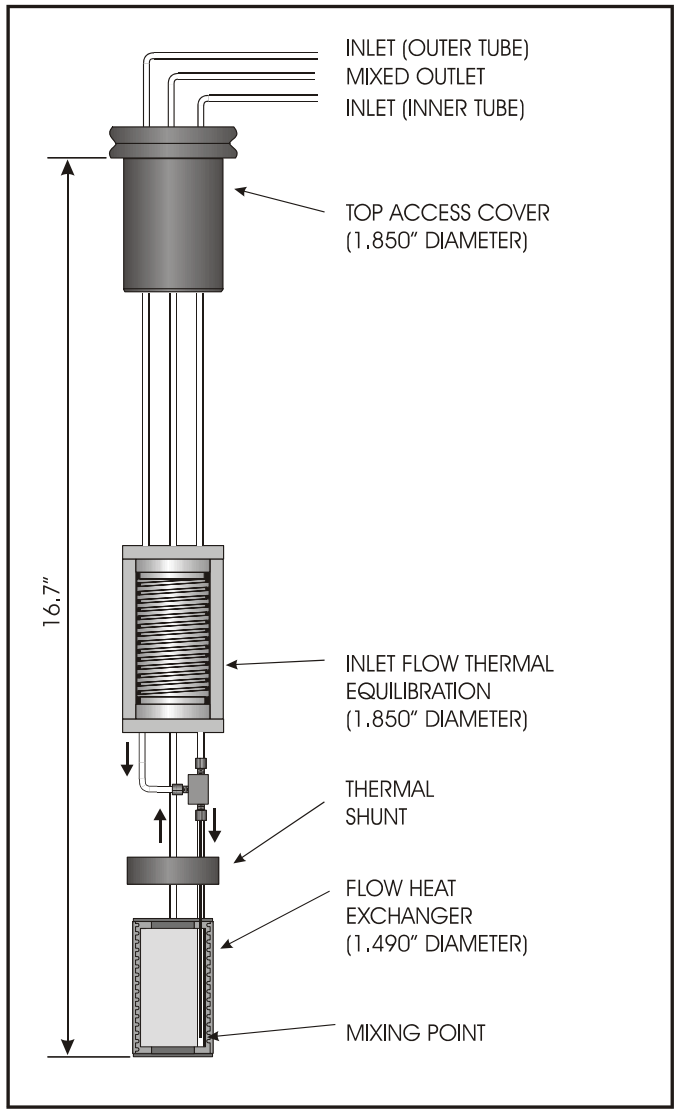
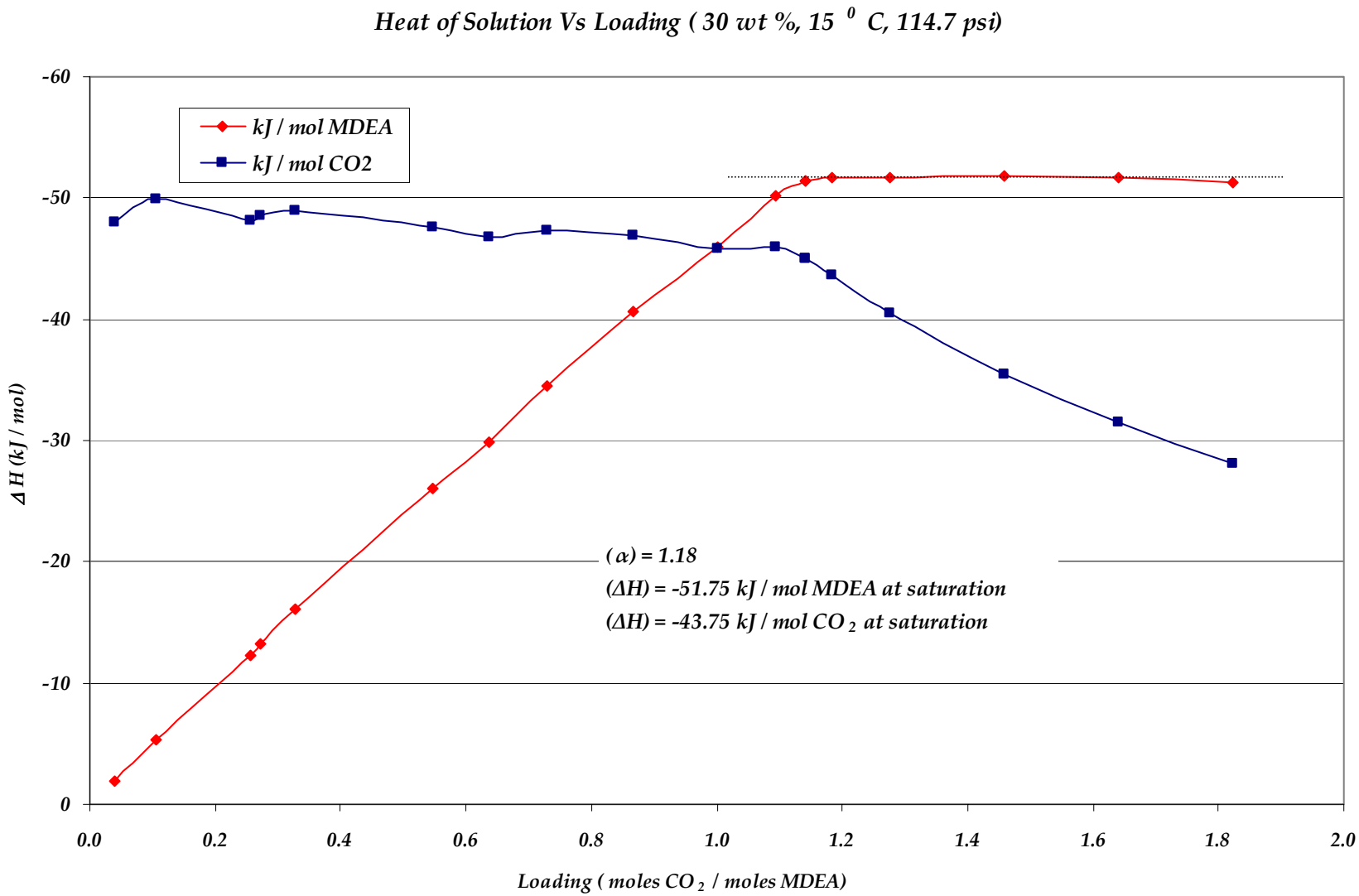
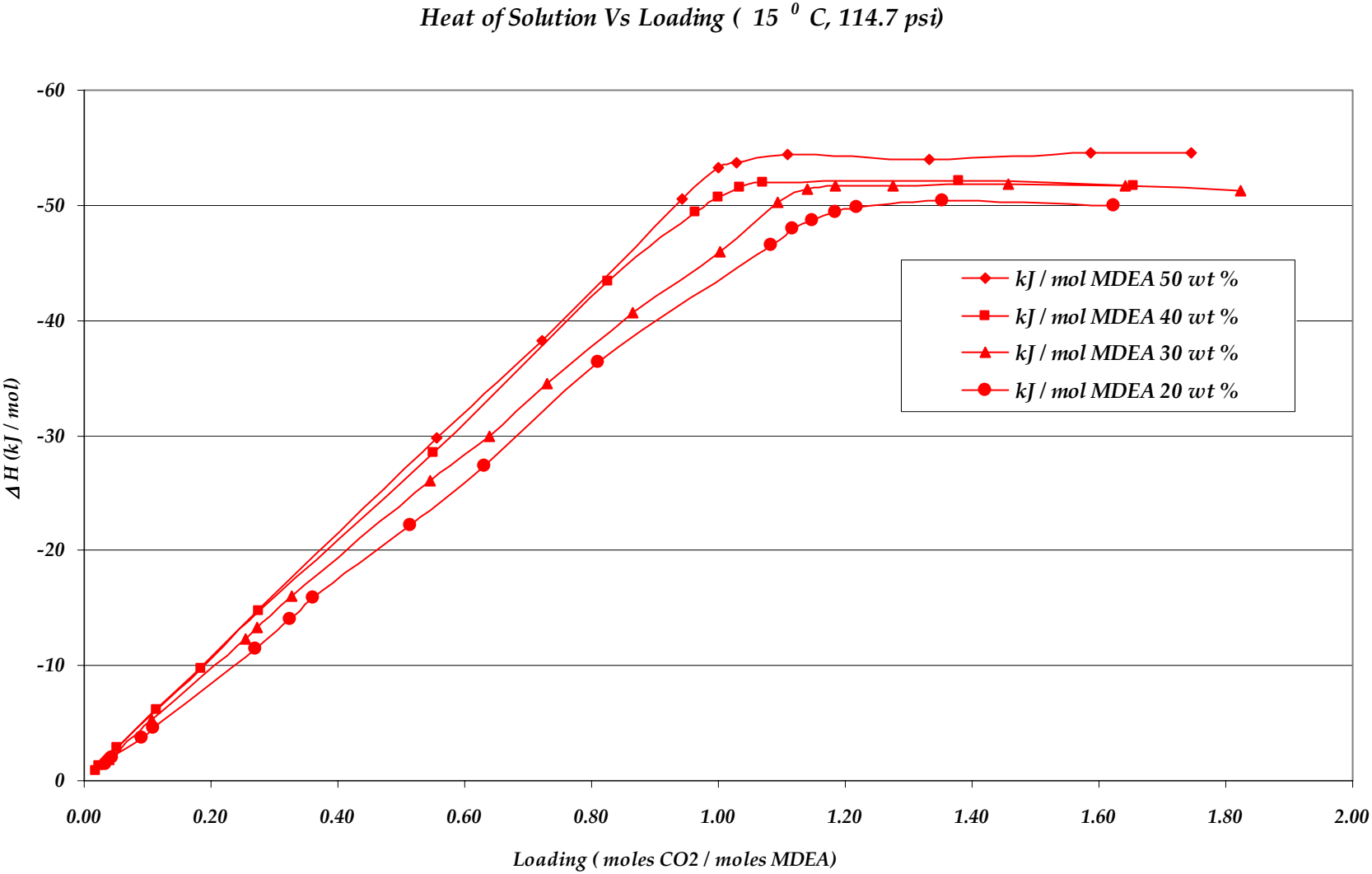


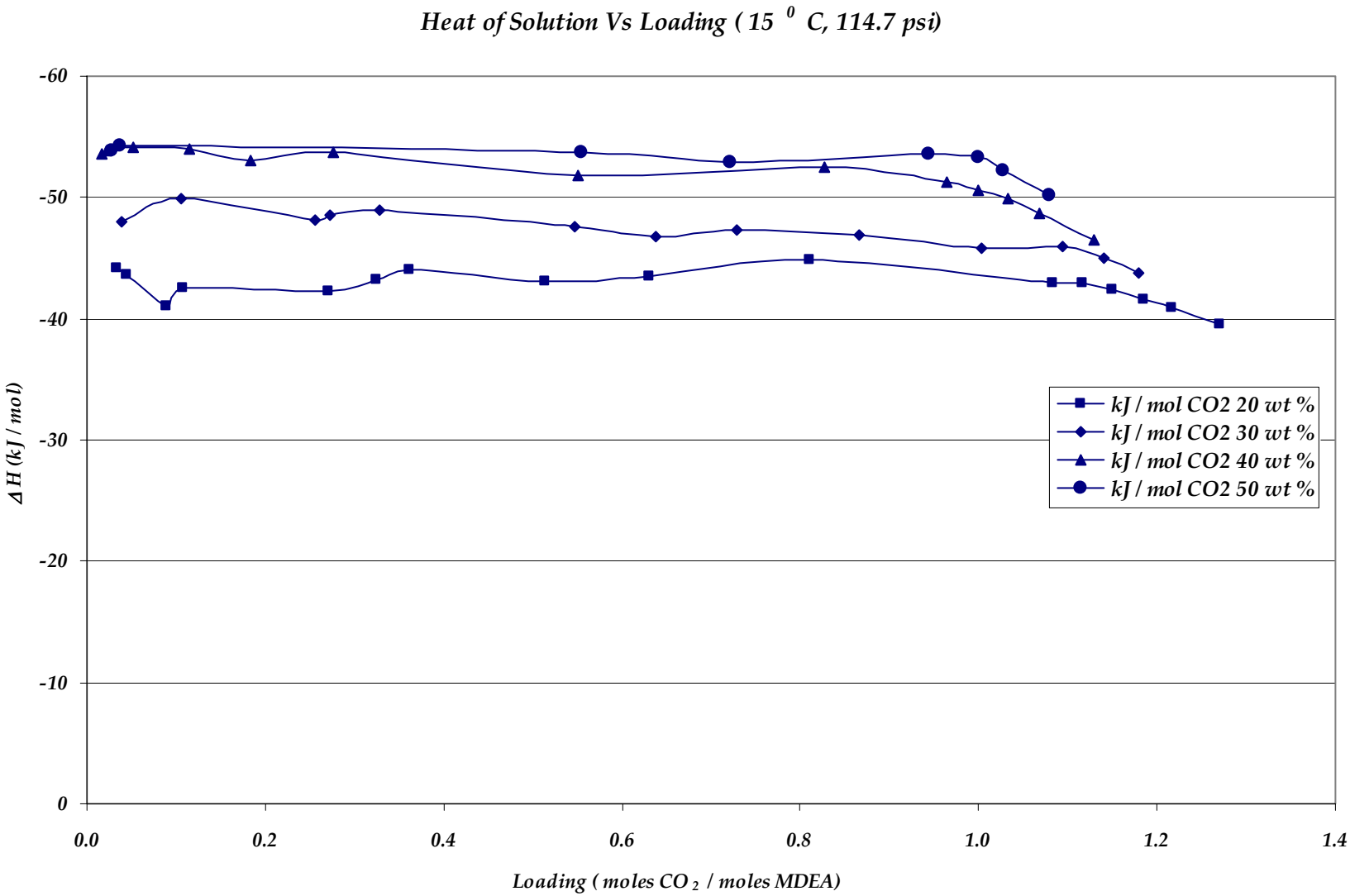
Figure 1. Diagram of a flow mixing cell.

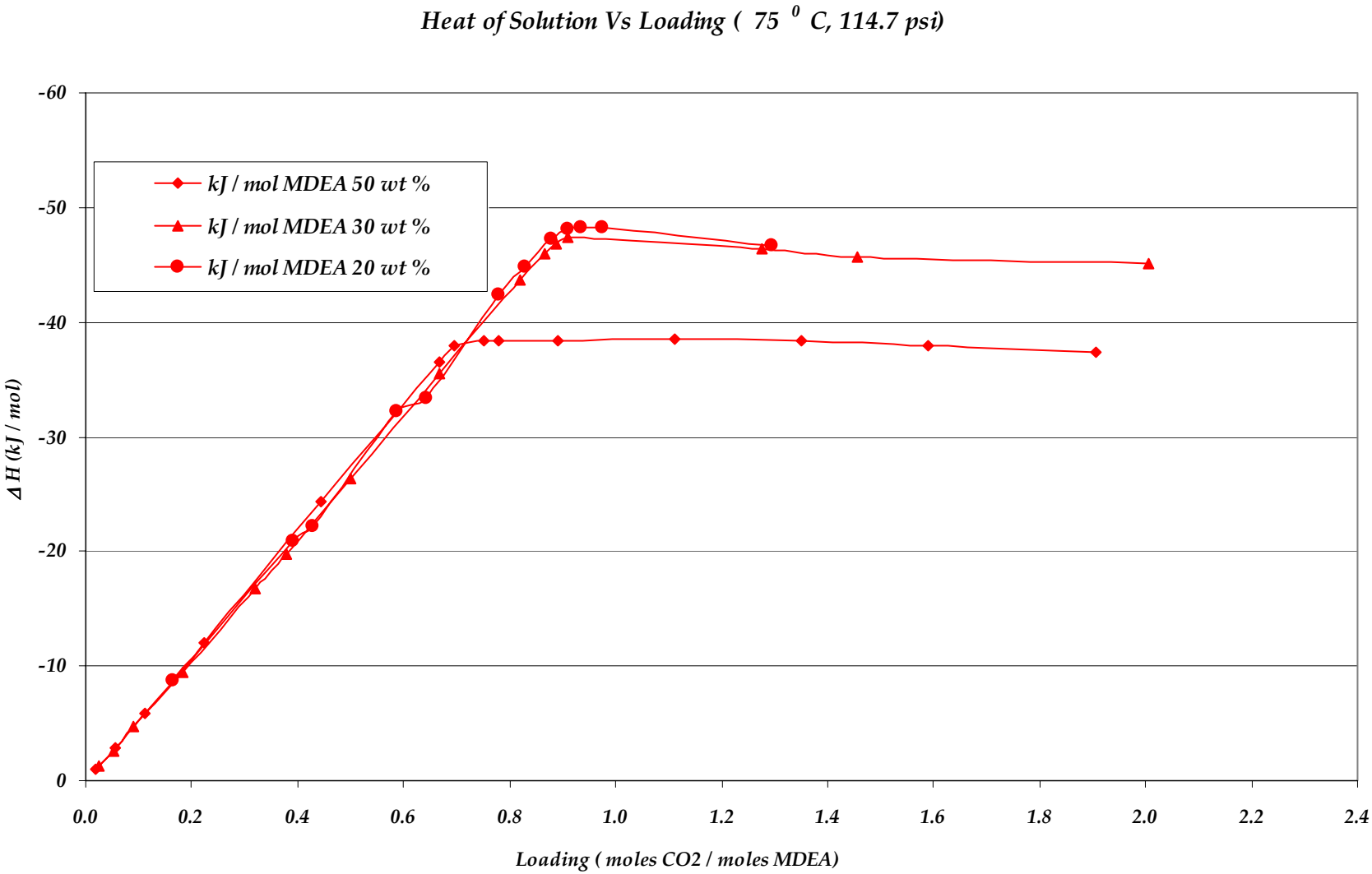
Apparatus Continued

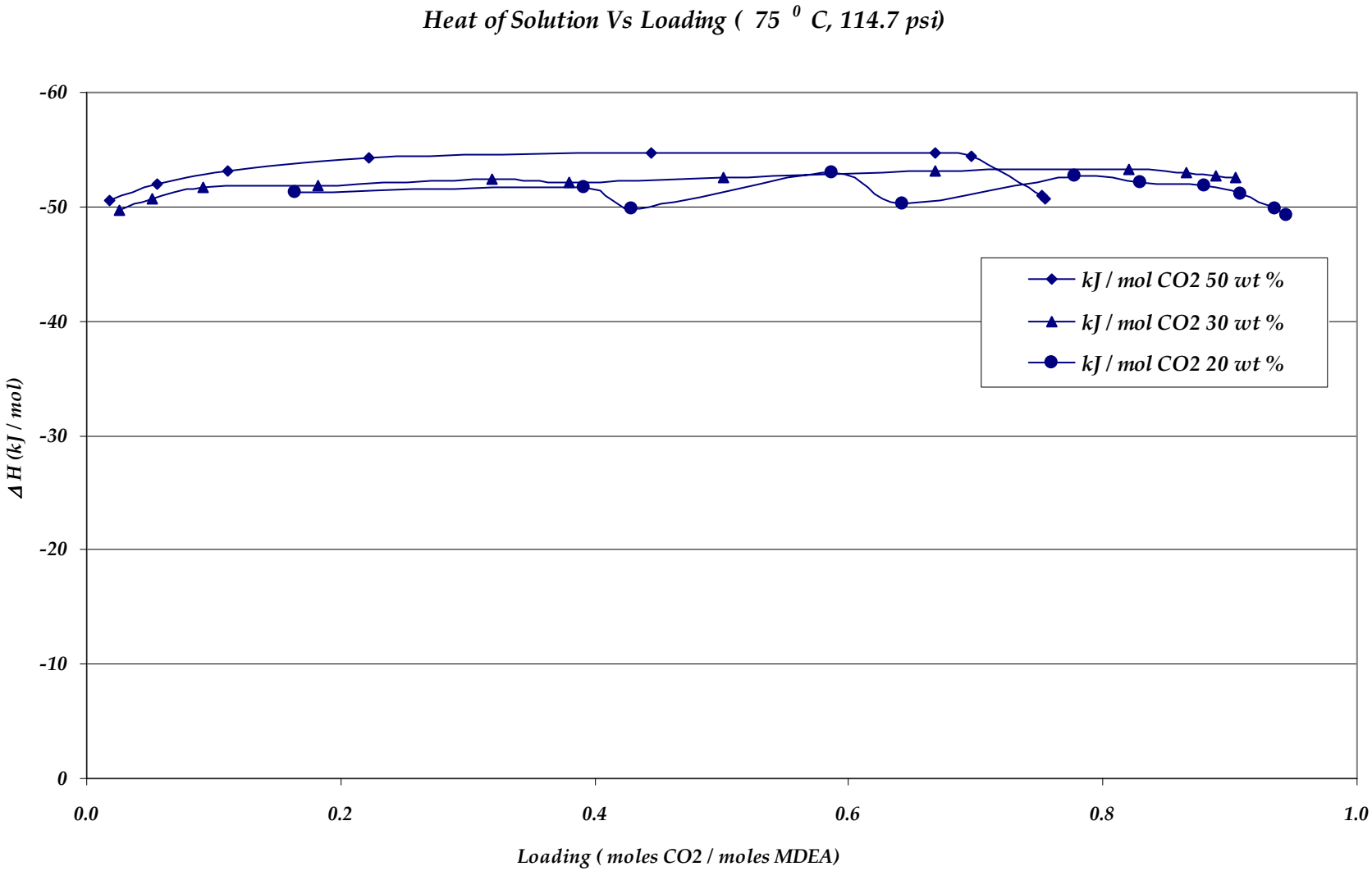
- Mass Flow Controller
  - 0 – 20 SCCM of CO_2
  - Accuracy of 0.2% Full scale
- Pump
  - 0 – 9.9 ml/min
  - Accuracy of 0.1% Full scale
  - 6000 psi pressure rating
- Back Pressure Regulator
  - Fixed Back Pressure

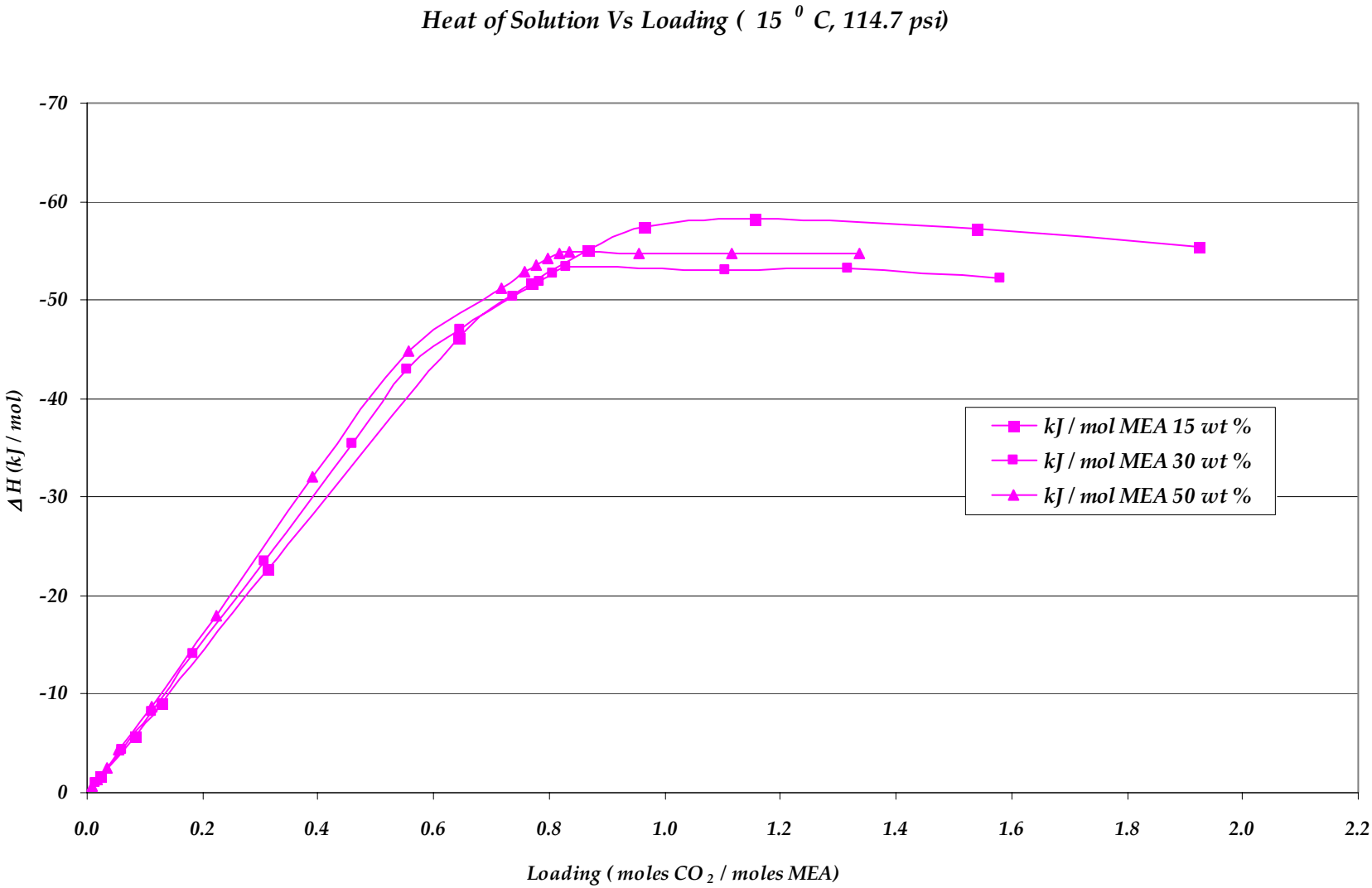

Heat of Solution Vs Loading (30 wt %, 15 0 C, 114.7 psi)
kJ / mol MDEA
kJ / mol CO2
-60
-50
-40
-30
-20
-10
0
Δ H (kJ / mol)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
Loading (moles CO 2 / moles MDEA)
(α) = 1.18
(ΔH) = -51.75 kJ / mol MDEA at saturation
(ΔH) = -43.75 kJ / mol CO 2 at saturation

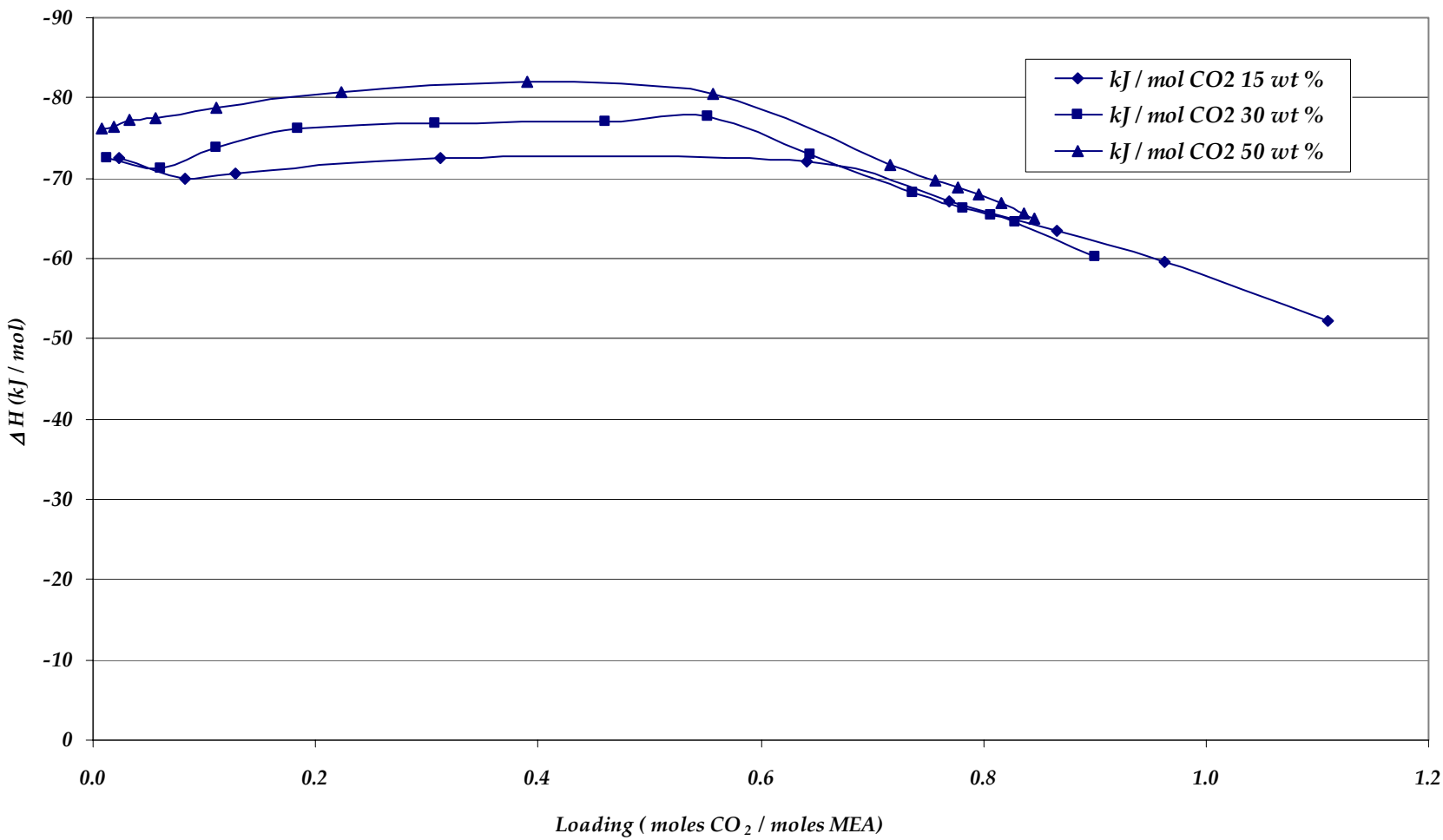

Heat of Solution Vs Loading (15 0 C, 114.7 psi)
-60
-50
-40
-30
-20
-10
0
Δ H (kJ / mol)
0.00
0.20
0.40
0.60
0.80
1.00
1.20
1.40
1.60
1.80
2.00
Loading (moles CO2 / moles MDEA)
kJ / mol MDEA 50 wt %
kJ / mol MDEA 40 wt %
kJ / mol MDEA 30 wt %
kJ / mol MDEA 20 wt %

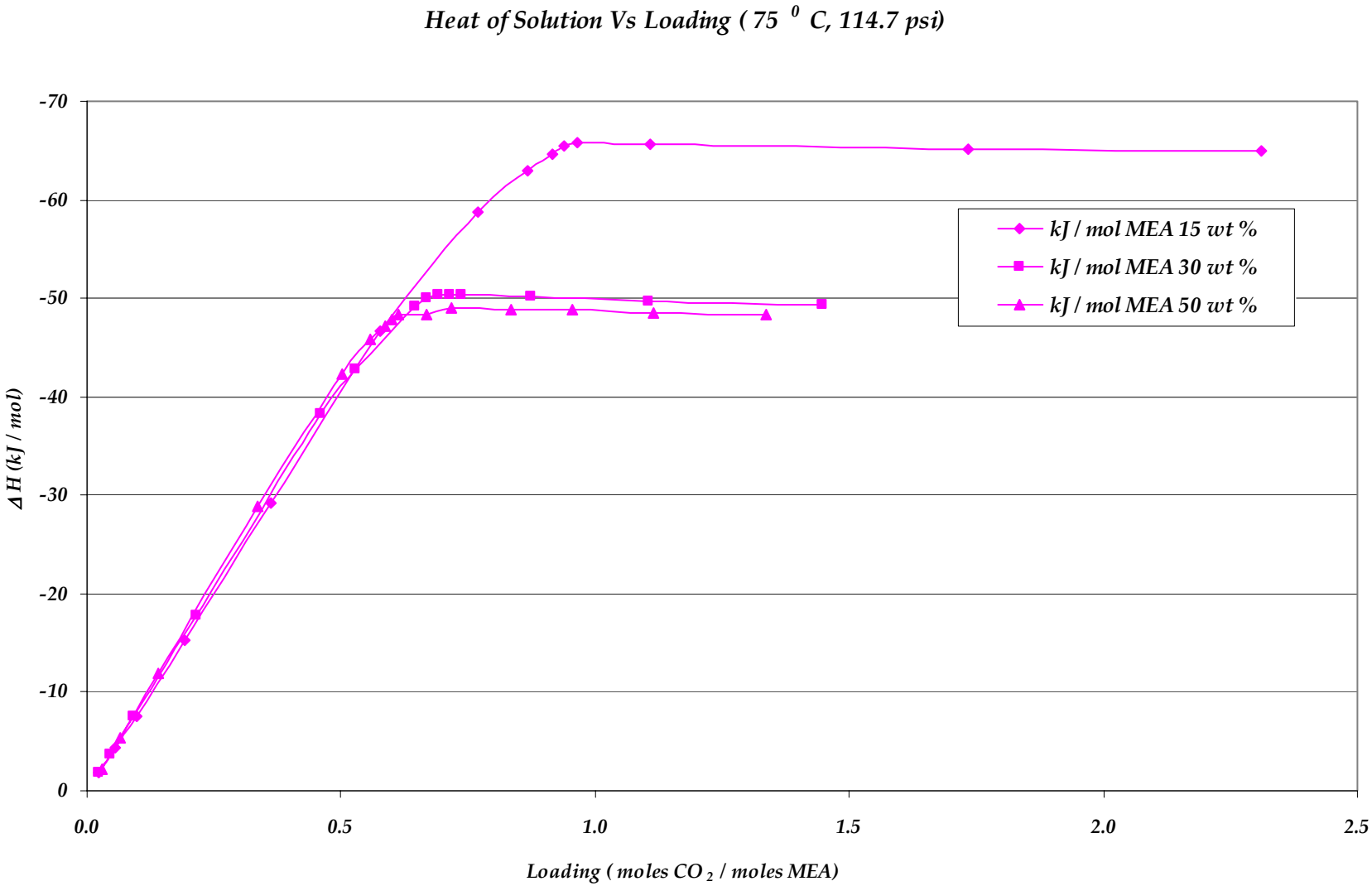

Heat of Solution Vs Loading (15 0 C, 114.7 psi)
-60
-50
-40
-30
-20
-10
0
Δ H (kJ / mol)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Loading (moles CO 2 / moles MDEA)
kJ / mol CO2 20 wt %
kJ / mol CO2 30 wt %
kJ / mol CO2 40 wt %
kJ / mol CO2 50 wt %

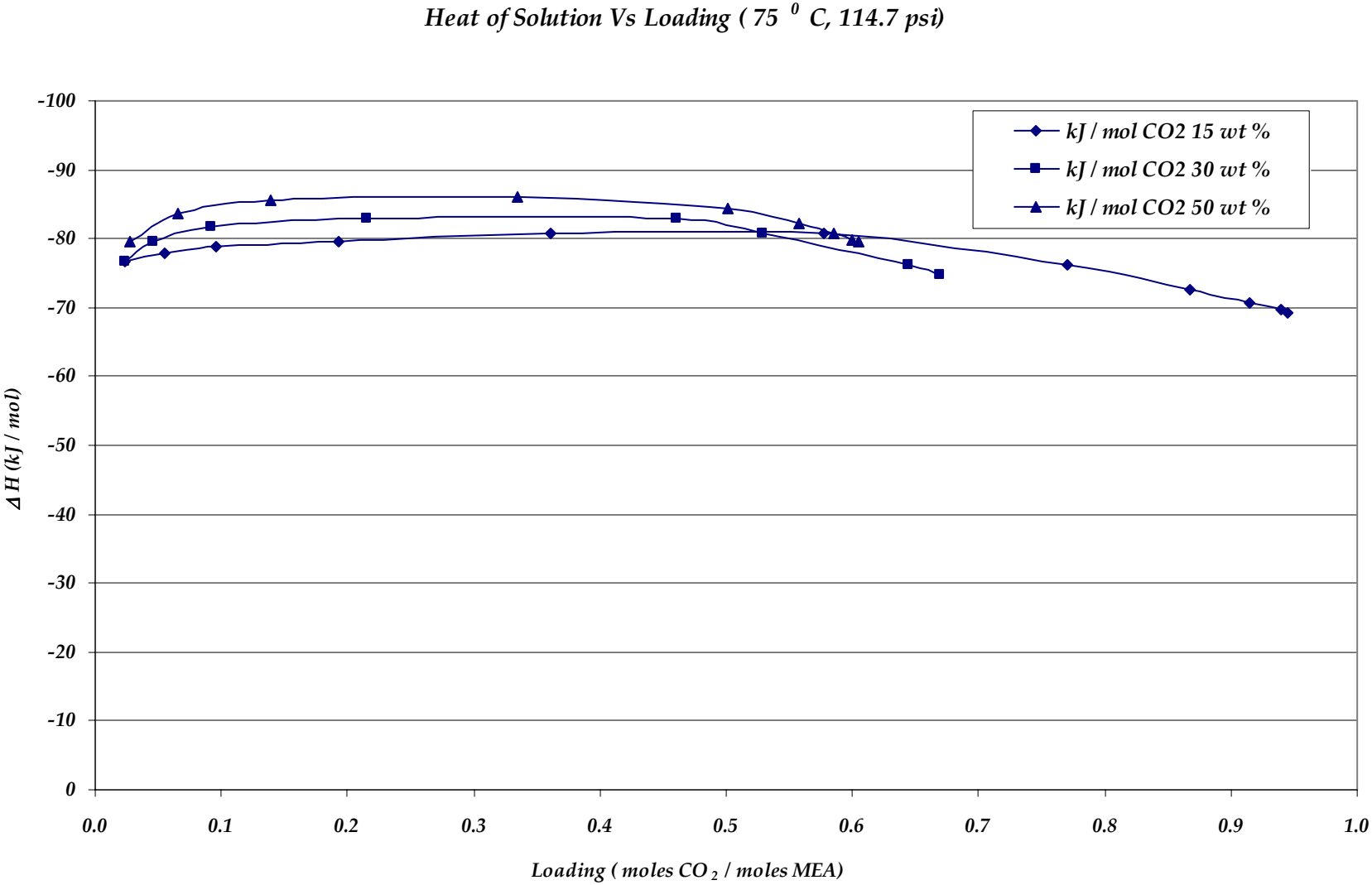

Heat of Solution Vs Loading (75 0 C, 114.7 psi)
kJ / mol MDEA 50 wt %
kJ / mol MDEA 30 wt %
kJ / mol MDEA 20 wt %
Δ H (kJ / mol)
-60
-50
-40
-30
-20
-10
0
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
Loading (moles CO2 / moles MDEA)


Heat of Solution Vs Loading (75 0 C, 114.7 psi)
-60
-50
-40
-30
-20
-10
0
Δ H (kJ / mol)
0.0
0.2
0.4
0.6
0.8
1.0
Loading (moles CO2 / moles MDEA)
kJ / mol CO2 50 wt %
kJ / mol CO2 30 wt %
kJ / mol CO2 20 wt %


Heat of Solution Vs Loading (15 0 C, 114.7 psi)
-70
-60
-50
-40
-30
-20
-10
0
Δ H (kJ / mol)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
Loading (moles CO 2 / moles MEA)
kJ / mol MEA 15 wt %
kJ / mol MEA 30 wt %
kJ / mol MEA 50 wt %


Heat of Solution Vs Loading (15 0 C, 114.7 psi)
-90
-80
-70
-60
-50
-40
-30
-20
-10
0
Δ H (kJ / mol)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
Loading (moles CO 2 / moles MEA)
kJ / mol CO2 15 wt %
kJ / mol CO2 30 wt %
kJ / mol CO2 50 wt %


Heat of Solution Vs Loading (75 0 C, 114.7 psi)
-70
-60
-50
-40
-30
-20
-10
0
Δ H (kJ / mol)
0.0
0.5
1.0
1.5
2.0
2.5
Loading (moles CO 2 / moles MEA)
kJ / mol MEA 15 wt %
kJ / mol MEA 30 wt %
kJ / mol MEA 50 wt %


Heat of Solution Vs Loading (75 0 C, 114.7 psi)
kJ / mol CO2 15 wt %
kJ / mol CO2 30 wt %
kJ / mol CO2 50 wt %
-100
-90
-80
-70
-60
-50
-40
-30
-20
-10
0
Δ H (kJ / mol)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Loading (moles CO 2 / moles MEA)

Two parameter Margules Equation fits the data well

$$H_{mixing} = (a + b\,X_{CO2})\,X_{CO2}\,(1 - X_{CO2})$$

Temp and wt %	*Experimental molCO_2 / mol MDEA*	*Literature mol CO_2/ mol MDEA*	*Experimental Enthalpy kJ/mol CO_2*	*Literature Enthalpy kJ/mol CO_2*
40^{0}C, 30 wt %	*0.98*	*1.03*	*-50.5*	*-49*
15^{0}C, 20 wt%	*1.27*		*-42.5*	-45
15^{0}C, 30 wt %	*1.18*		*-47.0*	
15^{0}C, 40 wt %	*1.13*		*-52.5*	-50
15^{0}C, 50 wt %	*1.08*		*-53.5*	
75^{0}C, 20 wt%	0.945		-51.5	
75^{0}C, 30 wt%	0.905		-52.5	
75^{0}C, 50 wt %	*0.755*	0.74 (70^{0}C)	*-55.5*	

Temp and wt %	*Experimental mol CO_2 / mol MEA*	*Literature mol CO_2/ mol MEA*	*Experimental Enthalpy kJ/mol CO_2*	*Literature Enthalpy kJ/mol CO_2*
15^{0}C, 15 wt %	*1.11*		*-71.5*	
15^{0}C, 30 wt%	*0.90*	0.92	*-76.0*	-82 (25^{0}C)
15^{0}C, 50 wt %	*0.85*		*-80.5*	
75^{0}C, 15 wt %	*0.94*		*-80.0*	
75^{0}C, 30 wt %	*0.675*	0.65	*-82.0*	
75^{0}C, 50 wt %	*0.605*		*-86.0*	

Thermodynamic Model
(Chen & Evans; Austgen & Rochelle)

- Reactions are expressed by temperature dependent equilibrium constants or kinetic rate expressions
- Activities in liquid solutions expressed by electrolyte NRTL model
- Equations are solved for composition of each species by Gibbs free energy minimization technique

Summary of Accomplishments

- An apparatus for measurement of solubility and heat of solution data for CO_2 in aqueous alkanolamines has been built
- The apparatus was used to measure data for different strengths of aqueous MEA and MDEA solvents at two temperatures, 15^0C, 75^0C
- The data were analyzed and the heats of solution were expressed as a function of CO_2 composition

Continuing and Future Work

- Data measurements at more temperatures
- Data measurements for mixtures of aqueous MEA, MDEA and PZ of selected relative compositions
- Analysis of data and recommendations for optimum solvent for CO_2 removal

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  Dawn Chapman, Technical Monitor