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Abstract:

Density and viscosity for monoethanolamine (MEA) solution are important for estimation of mass transfer in CO$_2$ removal by absorption.

A literature search on density, viscosity, surface tension and contact angle was performed. Density and viscosity data for unloaded MEA solution are presented in several articles. Density and viscosity for loaded MEA solution was found in Weiland et al. (1998). This article presents data for 10, 20, 30 and 40 weight percent loaded MEA solution at 25 ˚C. No data for loaded solution above 25 ˚C was found.

The object of the experimental work was to perform density and viscosity measurements above 25 ˚C.

CO$_2$ loaded MEA solution was prepared by bubbling CO$_2$ through the MEA solution. To analyse the amount of CO$_2$ absorbed in the loaded MEA solution, a procedure from StatoilHydro and one from SINTEF were tested. After several tests, the method from StatoilHydro was replaced with the method from SINTEF. This method gave the most reliable results and was easier to execute. Samples with varying loading and fixed concentration were prepared by mixing loaded and unloaded solution with the same concentration together.

20, 30, 40, 50, 70, 90 and 100 wt % unloaded MEA solution were prepared and measured for density and viscosity at 25, 40, 50, 70 and 80 ˚C. For loaded MEA solution, 20, 30 and 40 wt % MEA with 0.1, 0.2, 0.3, 0.4 and 0.5 moles of CO$_2$/moles of MEA were prepared and measured for density and viscosity at the same temperature range as for unloaded MEA solution. The experimental work was executed in co-operation with StatoilHydro.

Density and viscosity measurements were then compared with literature data and values calculated form Aspen HYSYS. The viscosity measurements were in excellent accordance with literature values at 25 ˚C, with less then 4 % deviation. The measurements at higher temperatures were compared to correlations on viscosity and density from Weiland et al. (1998). The maximum deviation for the viscosity was 12 %, and 1.5 % for the density.

Density and viscosity for MEA solutions show a significant dependence on the MEA concentration and CO$_2$ loading, and decreases with increasing temperature.

Mass transfer correlations from Shetty & Cerro, Billet & Schultes, and Onda et al. with Bravo & Fair were studied in order to observe change of mass transfer due to change in viscosity and density. A change in viscosity of 12 % (maximum deviation) gave a difference of about 2 % in mass transfer coefficient for Shetty & Cerro and Billet & Schultes, and less then 9 % for Onda et al. with Bravo & Fair. This shows that accurate viscosity data is not that important in calculation of mass transfer coefficients due to other uncertain parameters.

The correlations form Weiland et al. (1998) can therefore be used for calculations of density and viscosity.

PREFACE

This project is executed in the 4th semester of the master education in process technology at Telemark University College.

Density and viscosity for monoethanolamine (MEA) solutions are important for estimation of mass transfer in CO_2 removal by absorption. These properties are measured and compared to literature data.

StatoilHydro has been an important co-operation partner during the project. A special thanks to the supervisors, Berit F. Fostås, Dag A. Eimer and Lars Erik Øi, and Bjarne Nenseter and Morten Tande for help with the experimental work.

Porsgrunn, 5 June 2008

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Trine Gusfre Amundsen

TABLE OF CONTENT

1 INTRODUCTION

This main thesis is the final part of the education for master in process technology at Telemark University Collage. The work is performed in co-operation with StatoilHydro at their research center in Porsgrunn.

To design an industrial absorption column and application to the absorption models, it requires knowledge of parameters such as mass transfer coefficients of corresponding physical and chemical processes and the gas/liquid interfacial area. In addition, to calculate these parameters, certain physical properties of the liquid phase must be known: density, viscosity, or surface tension.

Measurements of density and viscosity for MEA at different concentrations in unloaded and CO_2 loaded solutions are performed. These physical properties can then be used to calculate mass transfer coefficients for absorption, the interfacial area of gas/liquid and the absorption rate.

An excel spreadsheet with mass transfer correlations for packed absorption column, was carried out during a summer job at the research center in 2007. Mass transfer coefficients and gas/liquid interfacial area can therefore be calculated.

The report consists of a theoretical and an experimental part. The theoretical part describes the CO_2-absorption process with monoethanolamine, design methods, physical properties and a literature study on the physical properties. The experimental part describes the measurement instruments and methods, the measurement results and the results from some mass transfer correlations. The results will be compared to literature, and the different mass transfer correlations will be discussed. A correlation from Weiland et al. for calculation of viscosity and density will be used to compare the results when no data from the literature is given.

2 CO$_2$ ABSORPTION

The purpose of the Kyoto agreement is to reduce emissions of greenhouse gases into the atmosphere. Carbon dioxide is a greenhouse gas, and contributes to increase the global warming and produce long term climate changes. Several techniques to remove CO$_2$ from gas mixtures have been studied since 1970 (Desideri and Paolucci, 1999). [3]

This chapter presents an overview of the process, the design methods and physical properties that are of interest.

2.1 Process Description

Alkanolamine systems are the current technology of choice for CO$_2$ capture from flue gas. In this paper, monoethanolamine (MEA) is the only amine considered. The following chapters describe the reaction mechanism for MEA and the CO$_2$ absorption and desorption process.

2.1.1 Reaction for MEA with CO$_2$

MEA ($HO-CH_2-CH_2-NH_2$) is a primary amine that produces a carbamate ion when it reacts with CO$_2$. The main advantages with using MEA water solution are high CO$_2$ reactivity, high removal efficiency and low molecular weight. The main drawback is the stability of the carbamate ion that results in a more heat demanding regeneration.

The zwitterion mechanism introduced by Caplow (1968) and Danckwerts (1979), is generally accepted as the reaction mechanism for carbamate formation between CO$_2$ with primary and secondary alkanolamines. The reaction steps involve the formation of a zwitterion (reaction 1), before removal of a proton by a base, B (reaction 2). The base can be an amine, an OH^- or H_2O. Reaction 1 and 2 presents the reaction steps for a primary amine as MEA. [13]

$$CO_2 \;+\; RNH_2 \;\overset{k_2}{\leftrightarrow}\; RNH_2^+COO^- \qquad\qquad (1)$$

$$RNH_2^+COO^- \;+\; B \;\leftrightarrow\; RNHCOO^- \;+\; BH^+ \qquad\qquad (2)$$

The reaction rate, $-r_{CO2}$ [mole/m$^3\cdot$s], can be calculated by the product of the second order reaction rate constant, k_2, and the concentrations of MEA and CO_2. [13]

$$-r_{CO2} = k_2 \cdot C_{MEA} \cdot C_{CO2} \tag{3}$$

Versteeg et al. (1995) concluded that there are extremely good agreement between the results obtained by the various researchers with an Arrhenius-plot for the reaction. The second order reaction rate constant, k_2 [m^3/mole$\cdot$s], (shown in equation 1) can therefore be estimated. [13]

$$k_2 = 4.4 \times 10^8 \exp\left(-\frac{5400}{T}\right) \tag{4}$$

Equation 4 is valid for MEA up to 40 ˚C. The temperature, T, is given in Kelvin. [13]

2.1.2 CO$_2$ Absorption and Desorption Process Description

Figure 2 - 1 presents the CO$_2$ removal process.

Flue gas containing CO$_2$ enters the absorber column, and is counter-current contacted with aqueous lean amine solution. Rich amine solution with absorbed CO$_2$ is transported through a counter-current heat exchanger, where it is pre-heated by lean amine solution before entering the desorber column. Heat is provided by steam in a reboiler to the desorber column, and the chemical equilibrium between MEA and MEA carbamat is reversed. The gas leaving the desorber contains CO$_2$ and water. Water is removed and transported back into the process. This results in a pure CO$_2$ gas stream.

Lean amine solution from the desorber is then transported through the counter-current heat exchanger and an additional cooler, before being recycled to the absorber column. The temperature is reduced to improve the removal efficiency.

A reclaimer takes a slip stream from the desorber to remove heat stable salts and high molecular weight degradation products. [1]
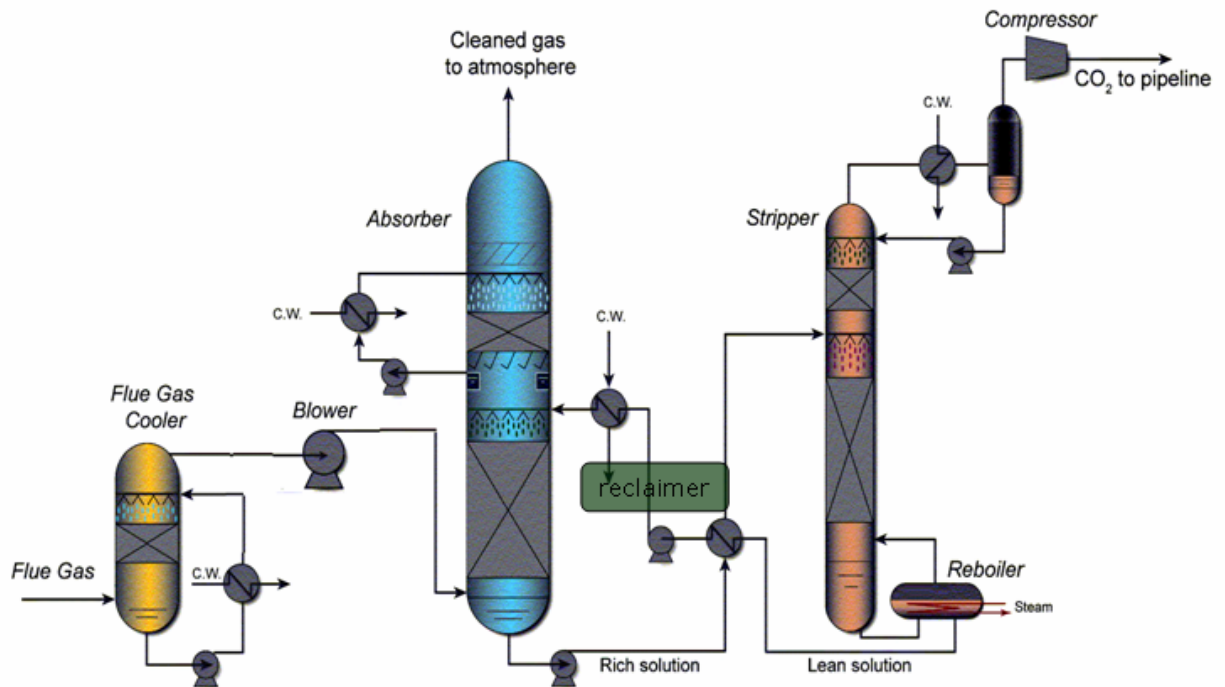
Figure 2 - 1: CO$_2$ absorption and desorption flow diagram from StatoilHydro.

2.2 Design Methods

Absorption is defined as transfer of a component from a gas to a liquid phase. A theoretical calculation of important design factors are given below.

2.2.1 Transfer Rate

The transfer rate for component A, N_A [mole/m^2·s], is calculated by the product of the mass transfer coefficient and the difference of component A at the bulk and at the interface. [17]

$$N_A = k_c \cdot (c_{A,b} - c_{A,i}) = k_p \cdot (p_{A,b} - p_{A,i}) = y_c \cdot (y_{A,b} - y_{A,i}) \tag{5}$$

As shown above, there are different ways of calculating the transfer rate. It can be calculated by the use of concentration, c, partial pressure, p, or fraction, y. b and i in the equation denotes for bulk and interface.

2.2.2 Amount Absorbed

The amount absorbed of component A, F_A *[mole/s]*, is calculated by the product of the transfer rate and the interfacial area. The partial pressure equation for transfer rate is used, and gives the following equation for calculating the amount absorbed. [17]

$$F_A = N_A \cdot a \cdot V = k_p \cdot (p_b - b_i) \cdot a \cdot V \tag{6}$$

The interfacial area is a product of the specific interfacial area, a [m^2/m^3], and the absorption volume, V [m^3].

2.2.3 Packing Height

A large specific interfacial area is important in absorption. Structured packing compared to random packing has a larger specific interfacial area, and gives a lower pressure drop. Structured packing is the most efficient packing material, but is also the most expensive material. The packing height, z [m], can be calculated. [17]

$$z = HTU \cdot NTU = \frac{G}{k_y \cdot a} \cdot \int_{Btm.}^{Top} \frac{1}{y - y_i} dy = \frac{L}{k_x \cdot a} \cdot \int_{Btm.}^{Top} \frac{1}{x - x_i} dx \qquad (7)$$

where

G = gas flow per column cross area, [mole/m^2·s]

k_y = mass transfer coefficient, [mole/m^2·s]

a = specific interfacial area, [m^2/m^3]

y = mole fraction of absorbed component

y_i = mole fraction at the interface.

If there is no resistance against mass transfer in the liquid phase, y_i will be the mole fraction in equilibrium with the liquid.

2.2.4 Absorber Area

The absorber area, $A_{Absorber}$ [m^2], can be calculated by the ration of the gas volume flow, Q_g [m^3/s], to the gas velocity, v [m/s].

$$A_{Absorber} = \frac{Q_g}{v_g} \qquad (8)$$

Normal gas velocity for air through a packing section at atmospheric pressure is 1 - 3 m/s. If the gas velocity is to low, the absorber column is unnecessary wide. If the gas velocity is too high, the pressure drop is unnecessary high, and can cause flooding.

2.2.5 Absorber Diameter

The calculated absorber area can then be used to calculate the absorber diameter, $D_{Absorber}$ [m^2].

$$D_{Absorber} = \sqrt{\frac{4 \cdot A_{Absorber}}{\pi}} \tag{9}$$

2.2.6 Mass Transfer Coefficients

There are plenty of correlations for calculating the mass transfer coefficient. Shetty & Cerro, Billet & Schultes, and Onda et al. with Bravo & Fair are studied to observe the change of mass transfer due to change in viscosity and density. The results are presented in chapter 6. [2]

See appendix 11 for nomenclature and input to the correlations.

The equation from Shetty and Cerro calculate the mass transfer coefficient for liquid, k_L, for structured packing. The mass transfer coefficient for gas, k_G is calculated from Rocha et al.

$$k_L = \frac{0.4185 D_L}{b} \sqrt{\frac{\sin\alpha}{l_{ratio}}} \left(\frac{4\rho_L q}{\mu_L} \right)^{1/3} \left(\frac{\rho_L^{\,2} g b^3}{\mu_L^{\,2}} \right)^{1/6} Sc_L^{\,1/2} \tag{10}$$

$$k_G = 0.054 \frac{D_G}{s} \left[\frac{\rho_G s (u_{Le} + u_{Ge})}{\mu_G} \right]^{0.8} Sc_G^{\,0.33} \tag{11}$$

The equations from Billet and Schultes calculate the mass transfer coefficient for liquid and gas for random packing.

$$k_L = C_L \left(\frac{\rho_L g}{\mu_L} \right)^{1/6} \left(\frac{D_L}{d_h} \right)^{0.5} \left(\frac{u_L}{a_p} \right)^{1/3} \tag{12}$$

$$k_G = C_G \frac{a_p^{\,0.5} D_G}{\sqrt{d_h (\varepsilon - h_L)}} \left(\frac{\rho_G u_G}{a_p \mu_G} \right)^{3/4} Sc_G^{\,1/3} \tag{13}$$

The equation from Onda et al. and Bravo and Fair calculate the mass transfer coefficient for liquid and gas for random packing.

$$k_L = \frac{0.0051}{\left(a_p d_p\right)^{-0.4}} \left(\frac{\mu_L g}{\rho_L}\right)^{1/3} \left(\frac{\rho_L u_L}{a_e \mu_L}\right)^{2/3} Sc_L^{-0.5} \tag{14}$$

$$k_G = c\left(\frac{D_G}{a_p d_p^{\ 2}}\right)\left(\frac{\rho_G u_G}{a_p \mu_G}\right)^{0.7} Sc_G^{\ 1/3} \tag{15}$$

2.3 Physical Properties

Viscosity, density, surface tension and contact angel are important physical properties for the CO_2 removal process. An overview of the properties is presented in this chapter.

2.3.1 Viscosity

Viscosity, μ (or η which is used later) is defined as a shearing stress, τ per unit area divided by a velocity gradient, $\Delta x / \Delta y$. [10], [11]

$$\mu = \frac{\tau}{\Delta v / \Delta y} = \tau \cdot \left(\frac{\Delta y}{\Delta v}\right) \tag{16}$$

A shear rate can be defined as the force required to slide one area layer of a substance over another.

The definition of viscosity can be derived from equation 16.

$$\mu = \frac{N}{m^2} \cdot \frac{m}{m/s} = \frac{N \cdot s}{m^2} = Pa \cdot s$$

In most scientific work, the viscosity is expressed in poise, P. 1 P equals 0.1 Pa·s, 1 Pa·s equals 1000 mPa·s and 1 cP = 1 mPa·s.

In Newtonian fluids the shear rate is directly proportional to the velocity gradient, where the constant of the proportionally is dynamic viscosity.

Kinetic viscosity is the ratio of the viscosity to the density, and is expressed in m^2/s.

$$\gamma = \frac{\mu}{\rho}$$ (17)

2.3.2 Density

Density, ρ is a measure of a given property per volume. Mass density is defined as mass, m per unit volume, V expressed in kg/m^3.

$$\rho = \frac{m}{V}$$ (18)

2.3.3 Surface Tension

Surface tension, σ is a property of the surface of a liquid, and is caused by the attraction between the molecules of the liquid by the various intermolecular forces. Surface tension is defined as the force exerted in the plane of the surface per unit length, and is usually expressed in units of dynes per centimeter. In the SI system 1 dyne/cm is equal to 1 mJ/m^2 which is equal to 1 mN/m. [11]

2.3.4 Contact Angle

A contact angle, θ is the angle where the liquid/vapor interface meets a solid surface. The contact angle is specific for any given system, and plays an important role in the boundary condition. The contact angle can be measured using a contact angle goniometer. [16]

The figure below shows the geometry of all the forces acting. The contact angle between the liquid and the solid is the angle the tangent to the surface makes with the solid surface.

Figure 2 - 2: The forces show a contact angle less than 90˚ where the meniscus is concave (left) and greater than 90˚ where the meniscus is convex (right). f_A denotes adhesive (klebrende) force, f_{la} denotes liquid-air (horizontal) force component and f_{ls} denotes liquid-solid (vertical) force component.

The contact angle can be calculated from the geometry of the forces. Some examples are shown below.

$$f_A = f_{la} \sin \theta \qquad\qquad (19)$$

$$f_{ls} = - f_{la} \cos \theta \qquad\qquad (20)$$

The contact angle is 180˚ when the liquid/solid surface tension is exactly equal to the liquid/air surface tension. The forces are also in direct proportion to their respective surface tension, as shown below.

$$\sigma_{ls} = - \sigma_{la} \cos \theta \qquad\qquad (21)$$

3 LITERATURE STUDY ON PHYSICAL PROPERTIES

A literature study on the physical properties, density, viscosity, surface tension and contact angle, was preformed. The results are presented in this chapter.

3.1 Density, Viscosity and Surface Tension for Unloaded MEA Solution

Data for density and viscosity for unloaded MEA are well presented in the literature. No data for contact angel were found, but some data for surface tension was presented from Vàzquez et al. (1997).

3.1.1 Density for Unloaded MEA Solution

Table 3 - 1 and 3 - 2 present data from Lee and Lin (1995) with density for pure MEA and for MEA + water at 30, 40 and 50 ˚C. [5]

Table 3 - 1: Density for pure MEA at 30, 40 and 50 ˚C from Lee and Lin (1995).

Density for Pure MEA	
Temp. [˚C]	Density [g/cm^3]
30	1.0090
40	0.9999
50	0.9918

Table 3 - 2: Density for MEA (1) and water (2) at 30, 40 and 50 ˚C at different mole fractions.

	Density for MEA (1) + Water (2)		
x_1	Density [g/cm^3]		
	30 ˚C	40 ˚C	50 ˚C
0.1	1.007	1.002	0.997
0.2	1.017	1.010	1.004
0.3	1.021	1.015	1.008
0.4	1.024	1.016	1.009
0.5	1.023	1.015	1.008
0.6	1.020	1.013	1.005
0.7	1.018	1.010	1.002
0.8	1.015	1.007	0.999
0.9	1.012	1.004	0.996

Table 3 - 3 presents data from Mandal et al. (2003) with density for 30 wt % MEA solution from 20 to 50 ˚C. [9]

Table 3 - 3: Density for 30 wt % MEA solution from 20 to 50 ˚C from Mandal et al. (2003).

Density for 30 wt % MEA Solution	
Temp. [˚C]	Density [g/cm^3]
20	1.015
25	1.012
30	1.009
35	1.005
40	1.003
45	1.001
50	0.998

Table 3 - 4 presents data from Ludvigshafen with density for 30 wt % MEA solution for 25 to 80 ˚C. [7]

Table 3 - 4: Density for 30 wt % MEA solution from 25 to 80 ˚C for Ludvigshafen.

Density for 30 wt % MEA Solution	
Temp. [˚C]	Density [g/cm^3]
25	1.015
40	1.002
50	0.994
70	0.976
80	0.968

Gas Conditioning and Processing present density for different MEA concentrations at different temperatures. Table 3 - 5 presents data for 20 to 90 wt % MEA solutions at 20 to 80 ˚C. [8]

Table 3 - 5: Density for unloaded 20, 30, 40, 50, 70 and 90 wt % MEA solutions from 20 to 80 ˚C, from Gas Conditioning and Processing.

Density for Unloaded MEA Solutions						
Temp. [˚C]	Density [g/cm^3]					
	20 wt %	30 wt %	40 wt %	50 wt %	70 wt %	90 wt %
20	1.007	1.013	1.018	1.024	1.030	1.023
40	0.999	1.003	1.007	1.011	1.016	1.008
60	0.990	0.993	0.996	1.000	1.001	0.993
80	0.978	0.980	0.982	0.985	0.986	0.976

Table 3 - 6 presents data form Leibush and Shorina with density for 20, 40 and 100 wt % unloaded MEA solution from 25 to 80 ˚C. [6]

Table 3 - 6: Density for unloaded 20, 40 and 100 wt % MEA solutions form 25 to 80 ˚C, from Leibush and Shorina.

Density for Unloaded MEA Solutions			
Temp. [˚C]	Density [g/cm^3]		
	20 wt %	40 wt %	100 wt %
25	1.004	1.018	1.015
40	0.998	1.009	1.003
50	0.993	1.003	0.994
70	0.982	0.990	0.978
80	0.976	0.983	0.970

3.1.2 Viscosity for Unloaded MEA Solution

Table 3 - 7 presents data form Lee and Lin (1995) with viscosity for pure MEA at 30, 40 and 50 ˚C. [5]

Table 3 - 7: Viscosity for pure MEA at 30, 40 and 50 ˚C form Lee and Lin (1995).

Viscosity for Pure MEA	
Temp. [˚C]	Viscosity [mPa·s]
30	15.00
40	9.94
50	6.87

Table 3 - 8 and 3 - 9 present data from Mandal et al. (2003) with viscosity for 30 wt % MEA solution, for 20 to 50 ˚C and for pure MEA for 20 to 80 ˚C. [9]

Table 3 - 8: Viscosity for 30 wt % MEA at 20 to 50 ˚C from Mandal et al. (2003).

Viscosity for 30 wt % MEA Solution	
Temp. [˚C]	Viscosity [mPa·s]
20	2.63
25	2.20
30	2.10
35	1.85
40	1.60
45	1.50
50	1.29

Table 3 - 9: Viscosity for pure MEA from 20 to 80 ˚C from Mandal et al. (2003).

Viscosity for Pure MEA	
Temp. [˚C]	Viscosity [mPa·s]
20	24.10
25	18.98
30	15.11
35	12.28
40	10.02
45	8,.55
50	6.972
60	5.047
70	3.779
80	2.912

Table 3 - 10 presents data from Lee and Lin (1995) with viscosity for different concentration of MEA solutions at 30, 40 and 50 ˚C. [5]

Table 3 - 10: Viscosity for MEA (1) and water (2) at 30, 40 and 50 ˚C from Lee and Lin (1995) at different mole fractions.

Viscosity for MEA (1) + Water (2)			
x_1	Viscosity [mPa·s]		
	30 ˚C	40 ˚C	50 ˚C
0.1	1.91	1.48	1.21
0.2	3.87	2.84	2.16
0.3	6.67	4.62	3.36
0.4	9.68	6.48	4.62
0.5	12.3	8.13	5.65
0.6	14.0	9.26	6.38
0.7	15.2	9.92	6.84
0.8	15.4	10.1	6.94
0.9	15.3	10.0	6.93

Gas Conditioning and Processing (1982) presents viscosity for different MEA concentrations at different temperatures. Table 3 - 11 present data for 20 to 100 wt % (pure) MEA solution at 25 to 80 ˚C. [8]

Table 3 - 11: Viscosity for 20, 30, 40, 50, 70, 90 and 100 wt % MEA solutions from 25 to 80 ˚C form Gas Conditioning and Processing.

Viscosity for MEA Solutions							
Temp. [˚C]	**Viscosity [mPa·s]**						
	20 wt %	**30 wt %**	**40 wt %**	**50 wt %**	**70 wt %**	**90 wt %**	**100 wt %**
25	1.80	2.6	3.8	5.5	12.0	18.0	20.0
40	1.30	1.7	2.3	3.0	6.0	9.0	10.0
50	0.95	1.4	1.8	2.5	4.0	6.0	7.0
70	0.67	0.88	1.2	1.5	2.5	3.0	3.4
80	0.56	0.72	0.9	1.2	1.8	2.2	2.5

3.1.3 Surface Tension for Unloaded MEA Solution

Table 3 - 12 presents data from Vàzquez et al. (1997) with surface tension for MEA solutions from 25 to 50 ˚C. For all binary mixtures, the value of the mole fraction, x_A, correspond to 0 to 100 mass%, at 10 mass% intervals, of MEA. [12]

Table 3 - 12: Surface tension for unloaded MEA at 25, 30, 35, 40, 45 and 50 ˚C, form Vàzquez et al. (1997).

	Surface Tension, σ [mN/m] for MEA (A) + Water (B)					
x_A	**Temp. [˚C]**					
	25	**30**	**35**	**40**	**45**	**50**
0.000	72.01	71.21	70.42	69.52	68.84	67.92
0.015	68.45	67.66	66.68	65.99	65.32	64.40
0.032	65.97	65.17	64.41	63.50	62.83	61.92
0.049	64.09	63.29	62.51	61.63	60.96	60.05
0.069	62.63	61.84	51.06	60.17	59.49	58.59
0.112	60.41	59.61	58.84	57.94	57.27	56.36
0.164	58.74	57.94	57.15	56.27	55.58	54.67
0.228	57.31	56.52	55.74	54.84	54.16	53.25
0.307	55.99	55.20	54.43	53.52	52.84	51.93
0.407	54.66	53.86	53.07	52.18	51.49	50.58
0.541	53.18	52.37	51.58	50.69	50.00	49.09
0.726	51.38	50.57	49.77	48.88	48.18	47.27
1.000	48.95	48.14	47.34	46.43	45.73	44.81

3.2 Density and Viscosity for Loaded MEA Solution

Literature data for density and viscosity for CO_2 loaded MEA solution was difficult to find. Weiland et al. (1998) presents density and viscosity for loaded MEA solution at 25 ˚C. Kohl and Riesenfeld presents density for 30 wt % MEA with 0.1 mole CO_2 per mole MEA.

3.2.1 Density for Loaded MEA Solution

Weiland et al. (1998) presents density data for loaded MEA solution at 25 ˚C from 0 to 0.5 mole CO_2 per mole MEA for 10, 20, 30 and 40 wt %. Table 3 - 13 present density data for 20, 30 and 40 wt % MEA solution. [14]

Table 3 - 13: Density for loaded 20, 30 and 40 wt % MEA at 25 ˚C from Weiland et al. (1998).

Density for Loaded MEA Solution at 25 ˚C			
CO_2 loading	Density [g/cm^3]		
[mol CO_2/mol MEA]	20 wt %	30 wt %	40 wt %
0.00	1.007	1.013	1.017
0.05	1.015	1.023	1.032
0.10	1.022	1.033	1.043
0.15	1.030	1.044	1.056
0.20	1.038	1.054	1.070
0.25	1.046	1.065	1.082
0.30	1.053	1.073	1.096
0.35	1.059	1.085	1.114
0.40	1.066	1.095	1.126
0.45	1.072	1.106	1.139
0.50	1.079 *	1.117	1.147

* In the article, this value is presented as 1.179 instead of 1.079 which is most likely the correct value.

Table 3 - 14 presents data from Kohl and Riesenfeld (1979) with density for 30 wt % loaded MEA with 0.1 mole CO_2 per mole MEA. [4]

Table 3 - 14: Density for 30 wt % MEA solution with 0.1 mole CO_2/mole MEA at 25, 40 and 50 ˚C, from Kohl and Riesenfeld.

Density for 30 wt % MEA Solution with 0.1 mole CO_2/mole MEA	
Temp. [˚C]	Density [g/cm^3]
25	1.032
40	1.024
50	1.018

3.2.2 Viscosity for loaded MEA Solution

Weiland et al. (1998) presents viscosity data for loaded MEA solution at 25 ˚C from 0 – 0.5 mole CO_2 per mole MEA, for 10, 20, 30 and 40 wt %. Table 3 - 15 presents viscosity data for 20, 30 and 40 wt % MEA solutions. [14]

Table 3 - 15: Viscosity for loaded 20, 30 and 40 wt % MEA solutions at 25 ˚C from Weiland et al. (1998).

Viscosity for Loaded MEA Solutions at 25 ˚C			
CO_2 loading	Viscosity [mPa·s]		
[mol CO_2/mol MEA]	20 wt %	30 wt %	40 wt %
0.0	1.72	2.52	3.41
0.1	1.83	2.72	3.76
0.2	1.90	2.92	4.30
0.3	1.98	3.21	4.97
0.4	2.12	3.51	5.90
0.5	2.22	3.82	6.73

3.3 Density and Viscosity for Water

Table 3 - 16 presents data from Mandal et al. (2003) with viscosity for water from 20 to ˚80 C. [9]

Table 3 - 16: Viscosity for water from 20 to 80 ˚C from Mandal et al. (2003).

Viscosity for Water	
Temp. [˚C]	Viscosity [mPa·s]
20	1.050
25	0.900
30	0.845
35	0.800
40	0.668
45	0.650
50	0.559
60	0.476
70	0.412
80	0.363

Table 3 - 17 presents data from Weast (1984-1985) with density for water from 25 to 80 ˚C. [15]

Table 3 - 17: Density for water from 25 to 80 ˚C from Weast (1984-1985).

Density for Water	
Temp. [˚C]	Density [g/cm^3]
25	0.9971
40	0.9922
50	0.9881
70	0.9778
80	0.9718

3.4 Density, Viscosity and Surface Tension Results for Unloaded MEA Solution from Aspen HYSYS

Aspen HYSYS is a process and simulation tool. To calculate the physical properties for MEA in Aspen HYSYS, an amine package must be used. Some disadvantages with this package are that it is only valid for concentrations of MEA up to 30 wt % and from 25 to 125 ˚C. Aspen HYSYS will above these ranges extrapolate the data. Some data for density, viscosity and surface tension for unloaded MEA from Aspen HYSYS is presented in table 3 - 18, 3 - 19 and   3 - 20.

Table 3 - 18: Density for unloaded 20, 30, 40, 50, 70, 90 and 100 wt % MEA solutions from 25 to 80 ˚C, from Aspen HYSYS.

Density for unloaded MEA Solutions							
Temp. [˚C]	Density [g/cm^3]						
	20 wt %	30 wt %	40 wt %	50 wt %	70 wt %	90 wt %	100 wt %
25	1.003	1.006	1.009	1.012	1.018	1.024	1.027
40	0.999	1.002	1.006	1.009	1.016	1.023	1.026
50	0.995	0.998	1.002	1.006	1.013	1.021	1.024
70	0.986	0.990	0.994	0.998	1.006	1.015	1.019
80	0.980	0.984	0.989	0.993	1.002	1.010	1.015

Table 3 - 19: Viscosity for unloaded 30, 50, 70, 90 and 100 wt % MEA solutions from 25 to 80 ˚C, from Aspen HYSYS.

Viscosity for Unloaded MEA Solutions					
Temp. [˚C]	Density [g/cm^3]				
	30 wt %	50 wt %	70 wt %	90 wt %	100 wt %
25	2.15	4.59	9.82	13.56	20.54
40	1.39	2.72	5.33	11.81	18.00
50	1.08	2.02	3.79	10.72	16.41
70	0.70	1.23	2.18	8.73	13.46
80	0.58	1.00	1.75	7.83	12.12

Table 3 - 20: Surface tension for unloaded 30, 50, 70, 90 and 100 wt % MEA solutions from 25 to 80 ˚C, from Aspen HYSYS.

Surface Tension for Unloaded MEA Solutions					
Temp. [˚C]	Density [g/cm^3]				
	30 wt %	50 wt %	70 wt %	90 wt %	100 wt %
25	64.84	60.04	55.24	27.90	45.31
40	62.69	57.89	53.09	26.89	43.81
50	61.26	56.46	51.66	26.29	42.78
70	58.40	56.60	48.80	24.75	40.64
80	56.97	52.17	47.37	24.00	39.53

3.5 Correlations form Weiland et al.

Weiland et al. (1998) presents densities and viscosities of partially carbonated monoethanolamine (MEA), diethanolamine (DEA) and N-methyldiethanolamine (MDEA) at 25 ˚C. [14]

There is very little information available concerning the effect of acid gas loading on the physical properties of amine treating solutions used in gas processing. Density and viscosity are important in mass transfer rate modelling of absorbers and regenerators because these properties affect the liquid-film coefficient for mass transfer.

The density was measured using hydrometers calibrated against distilled water, pure amines, and sodium chloride solutions at 25 ˚C. Kinetic viscosity was measured using Cannon-Fenske viscometers. The viscosity, η, was calculated from the product of the measured kinetic viscosity and density.

A large batch of amine of known concentration was made. The solution was loaded to saturation by bubbling carbon dioxide at 1 atm pressure through a sintered glass Dreschel head. Varying proportions of the unloaded and the loaded solutions were then mixed together to produce a set of samples having a fixed amine-to-water ratio but with varying loading. The amine concentrations and carbon dioxide loadings were also checked titrimetrically.

Viscosity and density data for partially loaded MEA at 298 K (25 ˚C) were combined with available literature to develop correlation for MEA solution viscosity and MEA solution density. These correlations can be used up to 40 wt % MEA, 0.6 mol CO_2/mol MEA, and up to a maximum temperature of 398 K (125 ˚C).

Weiland et al. (1998) concluded that increasing carbon dioxide loadings significantly increased both the density and the viscosity.

3.5.1 Viscosity Correlation

Equation 22 presents the correlation for the MEA solution viscosity, η. [14]

$$\frac{\eta}{\eta_{H2O}} = \exp\left(\frac{[(a \cdot \Omega + b) \cdot T + (c \cdot \Omega + d)][\alpha(e \cdot \Omega + f \cdot T + g) + 1]\Omega}{T^2}\right)$$

(22)

Where

η = viscosity of the amine solution [mPa·s]

η_{H2O} = viscosity of the water [mPa·s]

α = CO_2 loading [mole of CO_2/mole of amine]

Ω = mass percent of amine [wt %]

T = temperature [K]

Coefficients for the solvent viscosity are given in table 3 - 22.

Table 3 - 21: Parameters for the MEA solution viscosity correlation presented in equation 22.

Parameters for Viscosity Correlation for MEA	
a	0
b	0
c	21.186
d	2373.
e	0.01015
f	0.0093
g	-2.2589
std. div.	0.0732

3.5.2 Density Correlation

Equation 23 presents the correlation for the amine solution density, ρ which is given by the average molecular weight divided by its total molar volume. [14]

$$\rho = \frac{x_{Am} \cdot M_{Am} + x_{H2O} \cdot M_{H2O} + x_{CO2} \cdot M_{CO2}}{V} \tag{23}$$

Where

ρ = amine solution density [g/ml]

V = molar volume of the solution [ml/mol]

x_i = mole fraction

M_i = molecular weight

The amine solution density can be calculated on the basis of pure component molar volume together with excess molar volumes (due to interactions of various species).

The molar volume of an ideal solution is the sum of the components multiplied by their respective mole fractions. With ideal solution, no reactions or ionization are assumed.

Loaded amine solutions are not ideal, and they certainly require additional terms to account for amine + water and amine + carbon dioxide interactions, in addition to the use of molar volume for dissolved CO_2, which is unrelated to its pure component value. Equation 24 presents the molar volume expression, V.

$$V = x_{Am} \cdot V_{Am} + x_{H2O} \cdot V_{H2O} + x_{CO2} \cdot V_{CO2} + x_{Am} \cdot x_{H2O} \cdot V^{*} + x_{Am} \cdot x_{CO2} \cdot V^{**} \tag{24}$$

The molar volume expression of pure amine was developed using pure component density data from the literature. Equation 25 presents the molar volume expression for pure amine, V_{Am}.

$$V_{Am} = \frac{M_{Am}}{a \cdot T^2 + b \cdot T + c} \tag{25}$$

The molar volume associated with the interaction between carbon dioxide and amine, V^{**} are presented in equation 26.

$$V^{**} = d + e \cdot x_{Am} \tag{26}$$

Coefficients for the solvent density are given in table 3 - 22.

Table 3 - 22: Parameters for the MEA solution density correlation presented in equation 22.

Parameters for Density Correlation for MEA	
a	-5.351 62(-7)
b	-4.514 17(-4)
c	1.194 51
d	0
e	0
M	61.08
V_{CO2}	0.047 47
V^{*}	-1.821 8
std. div.	0.002 21

4   EXPERIMENTAL METHODS

This chapter describes how unloaded and loaded amine solutions are prepared, the measurement instruments and the measurements methods. Due to few data in the literature on surface tension and contact angle, only density and viscosity were measured.

4.1   Preparation of MEA Solutions

The preparation of different amine concentrations and loadings are described in this chapter.

4.1.1 Unloaded MEA Solution

Unloaded MEA solution with different concentrations was prepared by mixing pure MEA together with distillated water. The density and molecular weight for water and MEA were used to calculate the weight of each component. Concentration and temperature ranges for the measurement are presented below.

Concentration range: 20, 30, 40, 50, 70, 90 and 100 wt %.

Temperature range: 25, 40, 50, 70 and 80 ˚C.

The results of the 35 measurements of viscosity and 35 measurements of density are presented in chapter 5.

4.1.2 Loaded MEA Solution

Loaded MEA solution was prepared by bubbling CO_2 through the solution. The concentration and loading range was based on literature data from Weiland et al. (1998), which presents density and viscosity for 0 to 0.5 mole CO_2/mole MEA at 10 wt %, 20 wt %, 30 wt % and 40 wt % MEA, but only at 25 ˚C. Concentration, temperature and loading ranges for the measurement are presented below.

Concentration range: 20, 30 and 40 wt %.

Temperature range: 25, 40, 50, 70 and 80 ˚C.

Loading range: 0.1, 0.2, 0.3, 0.4 and 0.5 mole CO_2/mole MEA

This results in 75 measurements of viscosity and 75 measurements of density. The results are presented in chapter 5.

4.1.3 Procedure for Loading the MEA Solutions

Figure 4 - 1 illustrates the equipments that are used to load the MEA solution with CO_2.
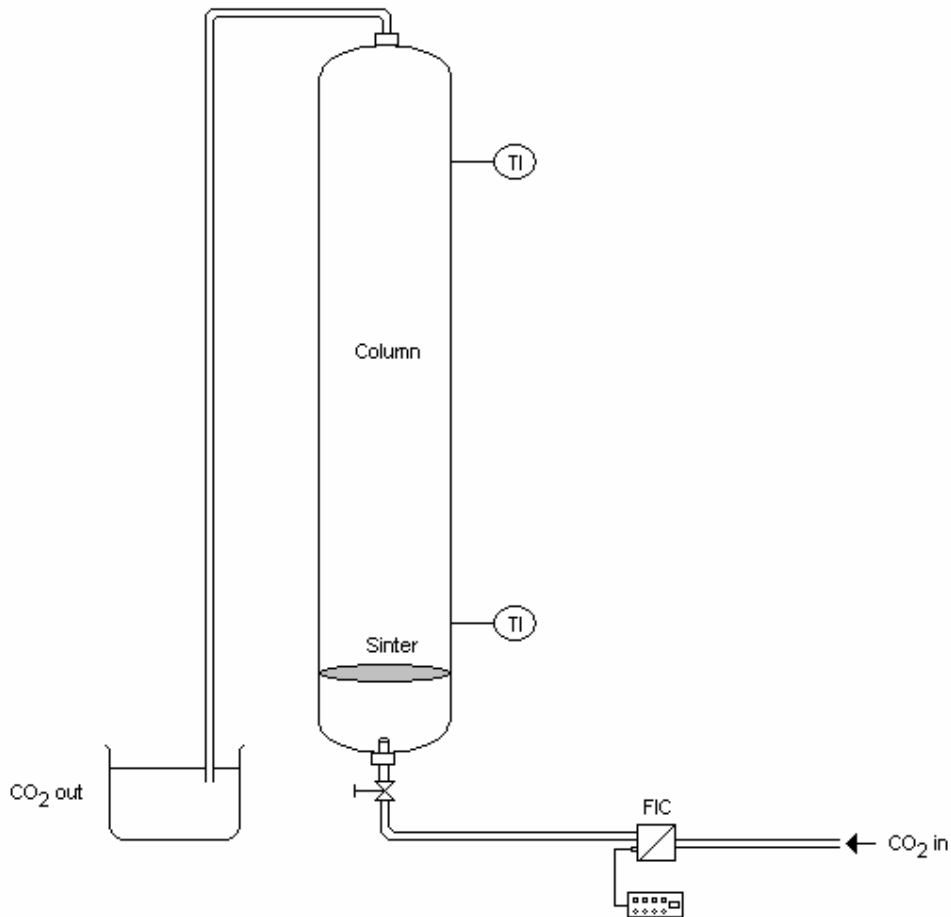

Figure 4 - 1: Equipment used to load MEA solutions with CO_2.

The gas enters a glass column with a 2 μm pore size sinter inside. A mass flow indicator controller ensures the amount of CO_2 into the column. Temperature elements are used to observe the temperature in the solution. The gas stream out is led to a flaks with water. When the solution is saturated with CO_2, bubbling is observed in the flask.

The reaction between CO_2 and MEA solution is exothermic, and will therefore increase the temperature of the solution in the column. The temperature is also a good parameter to use to observe when the solution is saturated. The temperature will then decrease.

It is important to ensure small bubbles of CO_2 to increase the contact area between CO_2 and MEA solution in the column. After several experiments, a mass flow controller of maximum 530 ml CO_2 per min was used. 20 and 30 wt % MEA was loaded in 1 hour, and 40 wt % MEA was loaded in 2 hours.

Another parameter that can ensure that right amount of CO_2 is added, is a phase difference in the liquid. After only a few minutes of bubbling, a phase difference in the bottom of the column will be observed. The temperature at this phase difference is approximately 20 – 40 ˚C higher then in the rest of the liquid, dependent on wt % MEA. Maximum temperature measured at the phase difference, meanwhile loading the different solutions, are 40 ˚C for 20 wt % MEA, 52 ˚C for 30 wt % MEA and 69 ˚C for 40 wt % MEA.

Change in viscosity is observed at the phase difference. This phase difference will be moving higher and higher up the column, small bubbles are observed above and large bubbles below. When the phase difference is moved up through the solution, the temperature will gradually decrease. The solution is then saturated with CO_2. See figure 4 - 2.

The loaded solution is then analyzed to evaluate the moles of CO_2 per moles of MEA. The method is described in the next chapter.

Figure 4 - 2: The phase difference in the MEA solution in the glass column used to load the different MEA solutions. CO_2 is bubbled through the sinter, where large bubbles are observed between the sinter and the phase difference and small bubbles above.

4.1.4 Method for Analyzing the Number of Moles of CO_2 in the MEA Solution

To analyze the loading in the MEA solution, two different methods were tested. They were both based on precipitation of $BaCO_3$, which is filtered out before titration with HCl and then NaOH. See appendix 2, 3, 4 and 5 for more specified procedure and calculations.

The first method was given by StatoilHydro in Trondheim. This method is used for loading analysis in MDEA solutions. This method gave low results on CO_2 loading for MEA and did not fit literature data. Several changes were done, but no improved results were obtained. In contact with SINTEF in Trondheim, a new method was presented. This method gave good results on the same samples as analyzed with the first method. Both methods are described below.

The method from StatoilHydro in Trondheim starts with 5 ml sample mixed together with 50 ml degassed, distillated water and 10 ml 3 M NaOH. 10 ml of this mixture was further mixed together with 50 ml 0.3 M $BaCl_2$. This mixture was heated up to its boiling point, and stored a day or two before further analyze. $BaCl_2$ reacted with the CO_2 in the sample, to $BaCO_3$ that were filtered out. The filter cake were added some water, and then titrated with 0.1 M HCl. HCl reacts with $BaCO_3$ and produce CO_2, Ba^{2+} and H_2O. HCl was added to the solution until the pH reached 2. At this pH, no CO_2 is combined with Ba^{2+} as $BaCO_3$. The solution was then boiled for 5 minutes before titration with 0.1 M NaOH back to pH value equal 7. The volume of the HCl and NaOH added to the solution were used in the calculations, together with the weights of water, 0.3 M $BaCl_2$ and 3 M NaOH. The calculation of mole CO_2 is similar for both methods, and is described in the last part of this chapter.

The method from SINTEF starts with 0.5 – 1.0 gram sample mixed together with 41,7 ml 0.3 M $BaCl_2$ and 50 ml 0.1 M NaOH. This mixture was the boiled in 4 to 5 minutes, cooled down in a bath and then filtrated. The filter cake is then added 50 ml degassed, distillated water and then titrated with 0.1 M HCl to the sample is clear. A clear sample will be obtained when the pH value is around 2. It is important with good stirring when both HCl and NaOH are added to the sample. After titration with HCl, NaOH is titrated into the sample to increase the pH value to 5.27. This value is the cover point for the acid base titration. Excess of HCl will not exist at this level. The volume of HCl and NaOH added by titration, and the weight of the sample analysed, are used in the calculation.

Reaction 27 and 28 presents the chemistry of the analysis.

$$Ba^{2+} \;+\; CO_2 \;+\; 2OH \;\rightarrow\; BaCO_3 \;+\; H_2O \tag{27}$$

$$BaCO_3 \;+\; 2HCl \;\rightarrow\; BaCl_2 \;+\; CO_2 \;+\; H_2O \tag{28}$$

Excess of HCl is titrated with NaOH. Reaction 29 presents the chemistry.

$$HCl \;+\; NaOH \;\rightarrow\; NaCl \;+\; H_2O \tag{29}$$
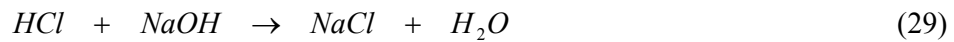
The calculation of mole CO_2 per gram sample used for both methods is presented below.

$$n_{CO2\,pr.\,gram\,sample} = \frac{n_{CO2} - n_{CO2,\,BS}}{m_{sample}} \tag{30}$$

$$n_{CO2} = \frac{C_{HCl} \cdot V_{HCl} - C_{NaOH} \cdot V_{NaOH}}{2} \tag{31}$$

$$n_{CO2,BS} = \frac{C_{HCl} \cdot V_{HCl} - C_{NaOH} \cdot V_{NaOH}}{2} \tag{32}$$

The factor of 2 is due to 2 mole HCl gives 1 mole CO_2

4.1.5 Preparation of Different MEA Solutions with Different Loading

Large batches of amine solutions with 20, 30 and 40 wt % MEA concentration were made up. Unloaded and high loaded solutions were mixed together to produce a set of samples with 0.1, 0.2, 0.3, 0.4 and 0.5 mole CO_2/mole MEA. When high loading is ensured, samples with lower loading are made by diluting the high loaded solutions. This is done with a spreadsheet where the mass of loaded and unloaded solution are calculated. The results are presented in chapter 5.

4.2 Measurement Instruments

The measurements instruments used to measure density and viscosity are described in this chapter.

4.2.1 Density Meter

Density, ρ is measured with an Anton Paar DMA 4500 with an intern measurement cell. The sample is injected with a squirt. The results are given with $1 \cdot 10^{-5}$ g/cm^3 accuracy.

4.2.1.1 Measurement Principle

The DMA 4500 consist of a U-formed oscillating measurement cell. When the sample is injected into the measurement cell, the oscillation frequency will change as a function of the mass in the sample. Calibrations based on known densities make it possible for the instrument to measure densities in unknown samples, based on the oscillation frequency in the injected sample. The results are shown on a computer screen, one minute after sample injection if the temperature of the sample equals the temperature in the measurement cell.

4.2.2 Viscometer

Viscosity, η is measured with a viscometer, Z1DIN with a double gap. A double gap means that there are two gaps that are measuring the torque [μNm]. The results are given with a 0.1 mPa·s accuracy.

4.2.2.1 Measurement Principle

The measurement cell used is a TEZ180 cell. The instrument measures the sample twice. The results are reported in a table and in a plot with viscosity as a function of shearing stress. The sample is measured with a shear rate, γ, from 10 – 1000 1/s. There are 12 measurement points. A logarithmic scale for the viscosity makes it easier to evaluate the result.

4.3 Measurement Methods

The measurement methods for measuring the density and viscosity are described in this chapter.

4.3.1 Measurement Method for the Density Meter

The procedure for measuring density is described below.

1. The measurement cell is cleaned by injecting distillate water through the cell.
2. The measurement cell is then dried with air.
3. A sample of approximately 5 ml amine solution is injected with a squirt. A new squirt is used at the sample outlet so that the sample injected can be observed and accumulate.
4. The density meter is then measuring the sample.
5. To change the temperature in the cell, go to "Menu", "Temperature setting" and "Set temperature". The measurement will start when the temperature has reached its goal.
6. If then last sample was measured at a high temperature, cool down to 20 ˚C.
7. Finish with point one in the procedure, to ensure that the measurement cell is cleaned after the measurement.

4.3.2 Measurement Method for the Viscometer

The procedure for measuring viscosity is described below.

1. The computer, heating and cooling bath to the instrument is turned on. The password, Physica200, is entered and the measurement program, US200, is selected.
2. The instrument is initialized by entering "Initialization".
3. The position of the instrument is lifted up by entering "Lift Pos". The measurements system can then be installed.
4. 19.5 ml amine solution is added to the measurement system.
5. The position of the instrument decreases by entering "Measurements Pos".
6. 1 ml of ethylene glycol is added on the top of the measurements system, for solvent trap.
7. The normal force on the system is reset by entering "NF Reset".
8. The measurement will start when the temperature in the sample has reached its goal. The temperature of the sample is changed by varying the temperature in the bath.
9. If the last sample was measured at high temperature, cooled down to 20 ˚C.
10. The measurement system is lifted up, by entering "Lift Pos", and then cleaned.

5   EXPERIMENTAL RESULTS AND CORRELATIONS

Density and viscosity for loaded and unloaded MEA solutions at different amine concentrations are measured at 25, 40, 50, 70 and 80 ˚C. The results of the measurements and loading analysis are presented in this chapter.

5.1 Analysis Results

20 wt % MEA were loaded for 1 hour with 530 ml CO_2 per minute. This resulted in a loading at 0.5650 mole CO_2 per mole MEA.

30 wt % MEA were loaded for 1 hour with 530 ml CO_2 per minute. This resulted in a loading at 0.5067 mole CO_2 per mole MEA.

40 wt % MEA were loaded for 1 hour with 530 ml CO_2 per minute. This resulted in a loading at 0.4646 mole CO_2 per mole MEA. This sample was loaded for 1 hour more. This resulted in 0.5105 mole CO_2 per mole MEA.

A sample volume of 40-50 ml solution is necessary for measuring density and viscosity. Samples with lower loading are made by diluting the high loaded solutions, one by one.

See appendix 6, 7, 8 and 9 for detailed information of the dilution.
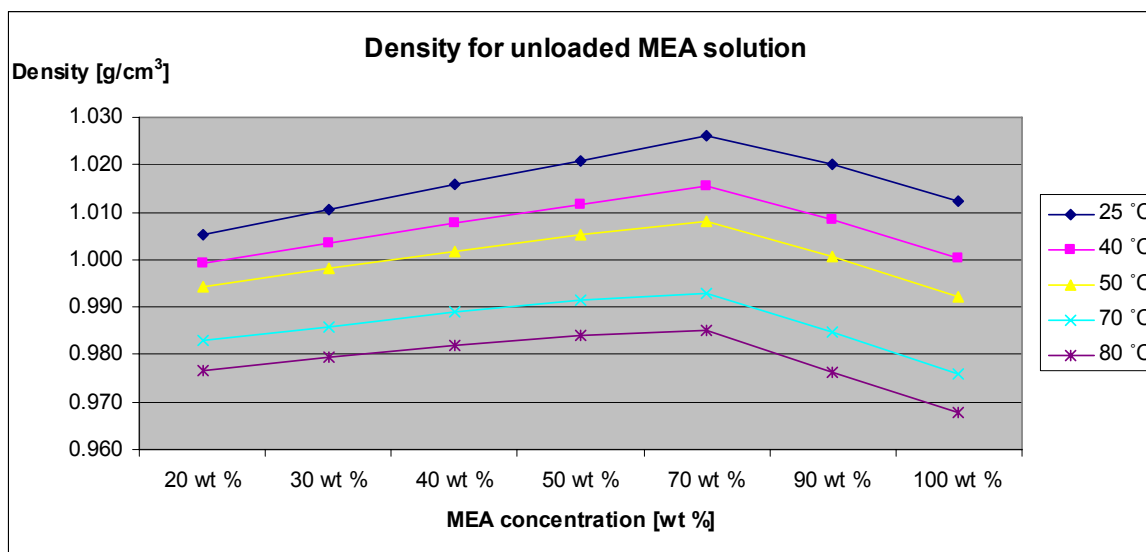
5.2 Density Results

Density results for unloaded and loaded MEA solution are presented in this chapter.

5.2.1 Density Results for Unloaded MEA Solution

Density for unloaded MEA solution at 20, 30, 40, 50, 70, 90 and 100 wt % MEA are measured at 25, 40, 50, 70 and 80 ˚C. Parallel measurements are carried out and the results are given with tree decimals. The results are presented in table 5 - 1 and figure 5 - 1, 5 - 2, 5 - 3 and 5 - 4.

Table 5 - 1: Density results for unloaded 20, 30, 40, 50, 70, 90 and 100 wt % MEA solutions from 25 to 80 ˚C.

Density Results for Unloaded MEA Solutions							
Temp. [˚C]	Density [g/cm^3]						
	20 wt %	30 wt %	40 wt %	50 wt %	70 wt %	90 wt %	100 wt %
25	1.005	1.011	1.016	1.021	1.026	1.020	1.012
40	0.999	1.003	1.008	1.012	1.016	1.008	1.000
50	0.994	0.998	1.002	1.005	1.008	1.001	0.992
70	0.983	0.986	0.989	0.992	0.993	0.985	0.976
80	0.977	0.979	0.982	0.984	0.985	0.976	0.968

Figure 5 - 1: Density results for unloaded MEA solutions as a function of MEA concentration [wt %].
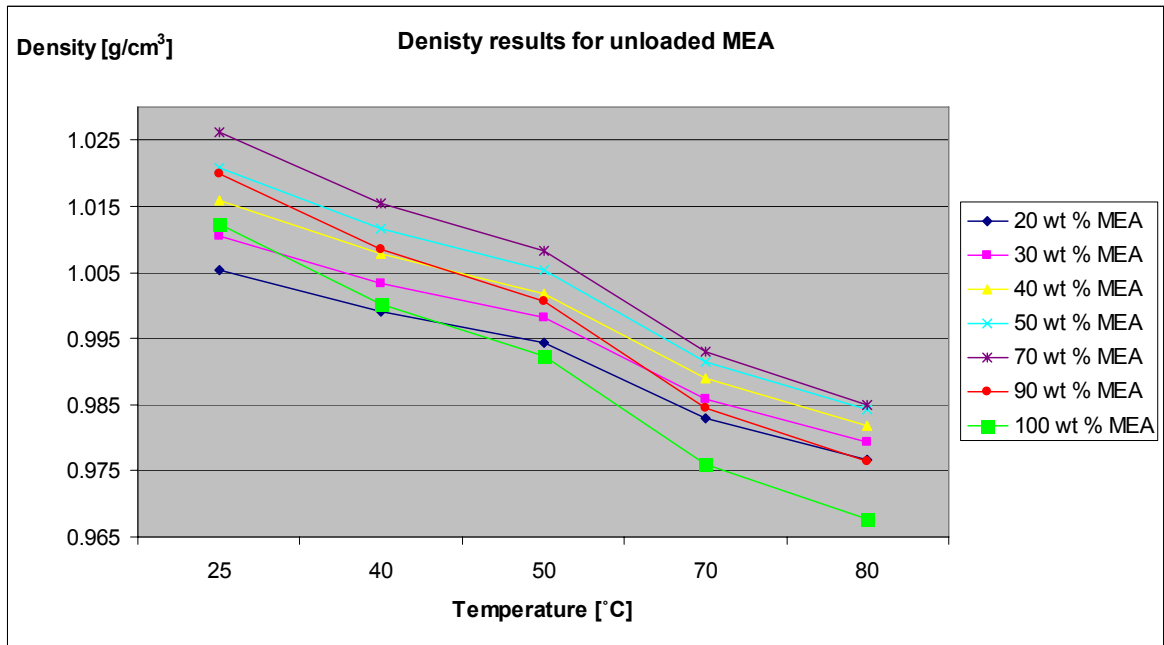
Figure 5 - 2: Density results for unloaded 20, 30, 40, 50, 70, 90 and 100 wt % MEA solutions as a function of temperature [˚C].
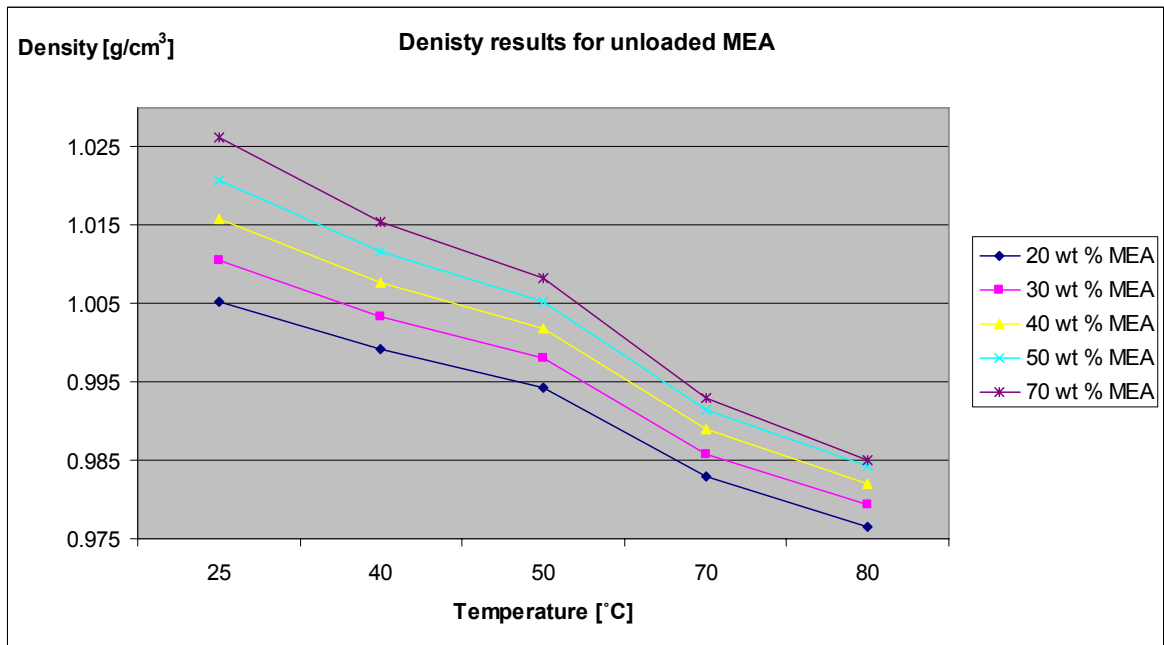

Figure 5 - 3: Density results for unloaded 20, 30, 40, 50 and 70 wt % MEA solutions as a function of temperature [˚C].
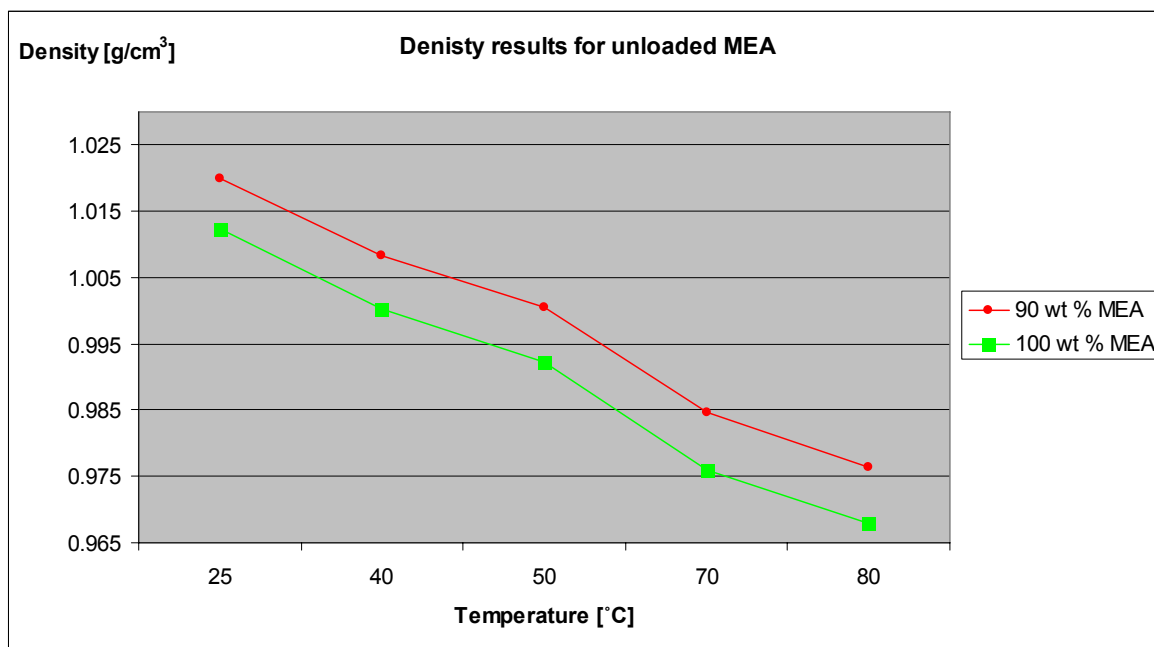
Figure 5 - 4: Density results for unloaded 90 and 100 wt % MEA solutions as a function of temperature [˚C].

5.2.2 Density Results for Loaded MEA Solution

Density for loaded MEA solution at 20, 30 and 40 wt % MEA with 0.1, 0.2, 0.3, 0.4 and 0.5 mole CO_2/mole MEA, are measured at the same temperatures as for the unloaded MEA measurements.

Samples with high loading at high temperature are sometimes difficult to measure, due to vaporization in the measurement cell. The problem is virtualized with – in the tables.

Density results for 20 wt % loaded MEA solution are presented in table 5 - 2 and figure 5 - 5 and 5 - 6.

Table 5 - 2: Density results for 20 wt % loaded MEA solution from 25 to 80 ˚C.

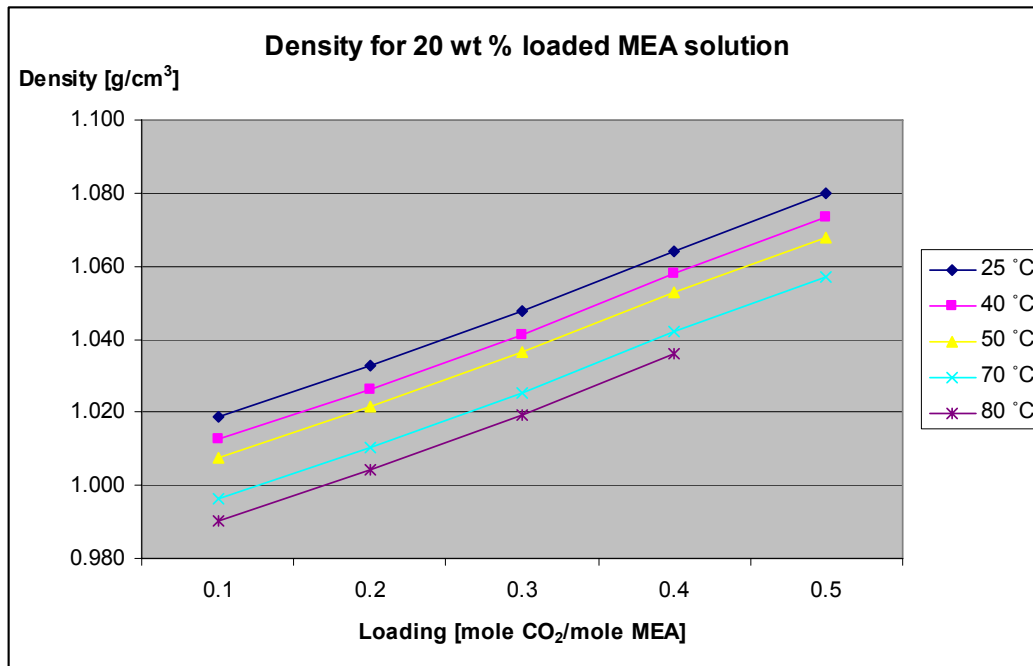| Density Results for 20 wt % Loaded MEA Solution					
Temp. [C]	Density [g/cm³]				
	Loading [mole CO₂/mole MEA]				
	0.1	0.2	0.3	0.4	0.5
25	1.019	1.033	1.048	1.064	1.080
40	1.013	1.026	1.041	1.058	1.074
50	1.008	1.022	1.036	1.053	1.068
70	0.997	1.011	1.025	1.042	1.057
80	0.990	1.004	1.019	1.036	-

Figure 5 - 5: Density results for 20 wt % loaded MEA solution as a function of loading [mole CO₂/mole MEA].

Figure 5 - 6: Density results for 20 wt % loaded MEA solution as a function of temperature [˚C].

Density results for 30 wt % loaded MEA solution are presented in table 5 - 3 and figure 5 - 7 and 5 -8.

Table 5 - 3: Density results for 30 wt % loaded MEA solution from 25 to 80 ˚C.

Density Results for 30 wt % Loaded MEA Solution					
	Density [g/cm^3]				
Temp. [C]	Loading [mole CO_2/mole MEA]				
	0.1	0.2	0.3	0.4	0.5
25	1.028	1.048	1.070	1.096	1.121
40	1.021	1.041	1.063	1.088	1.114
50	1.016	1.036	1.058	1.083	1.108
70	1.004	1.024	1.046	1.072	-
80	0.997	1.018	1.040	1.066	-

Figure 5 - 7: Density results for 30 wt % loaded MEA solution as a function of loading [mole CO_2/mole MEA].
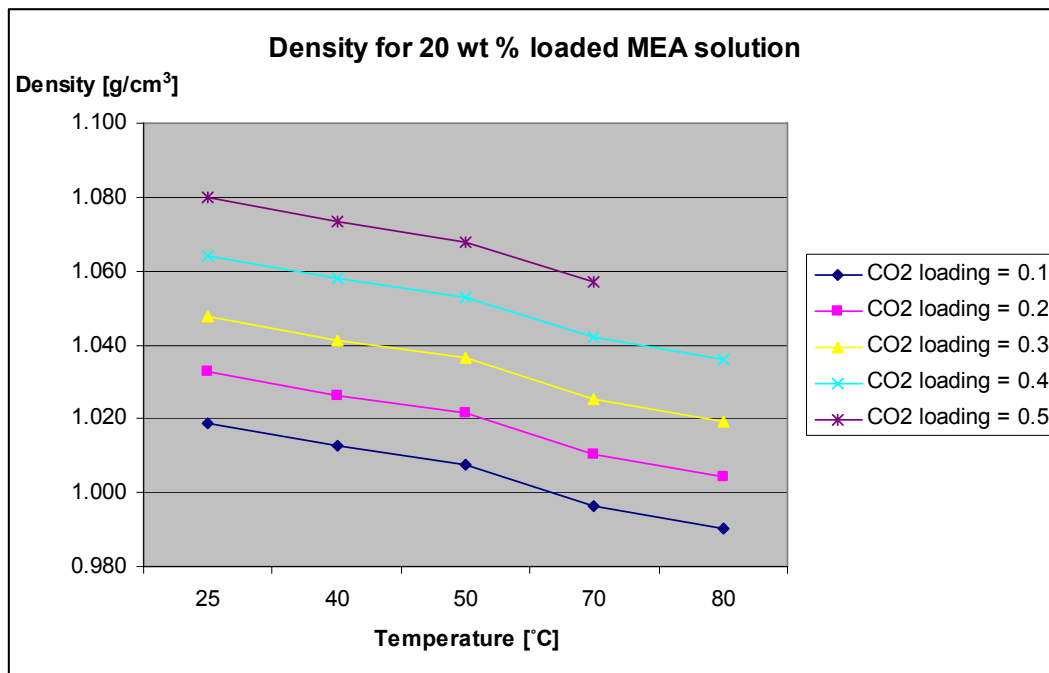
Figure 5 - 8: Density results for 30 wt % loaded MEA solution as a function of temperature [˚C].

Density results for 40 wt % loaded MEA solution are presented in table 5 - 4 and figure 5 - 9 and 5 - 10.

Table 5 - 4: Density results for 40 wt % loaded MEA solution from 25 to 80 ˚C.

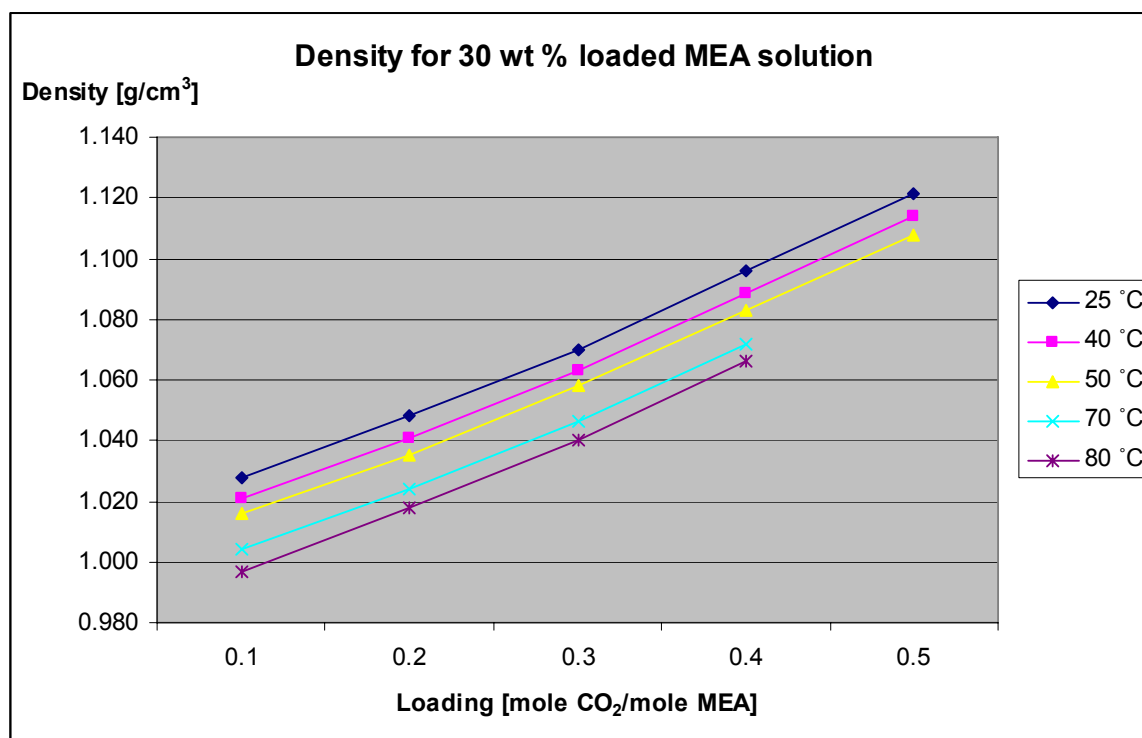| Density Results for 40 wt % Loaded MEA Solution					
Temp. [C]	Density [g/cm^3]				
	Loading [mole CO_2/mole MEA]				
	0.1	0.2	0.3	0.4	0.5
25	1.038	1.063	1.093	1.129	1.160
40	1.030	1.055	1.085	1.121	-
50	1.024	1.049	1.080	1.115	-
70	1.012	1.037	1.068	1.104	-
80	1.005	1.031	1.062	1.098	-

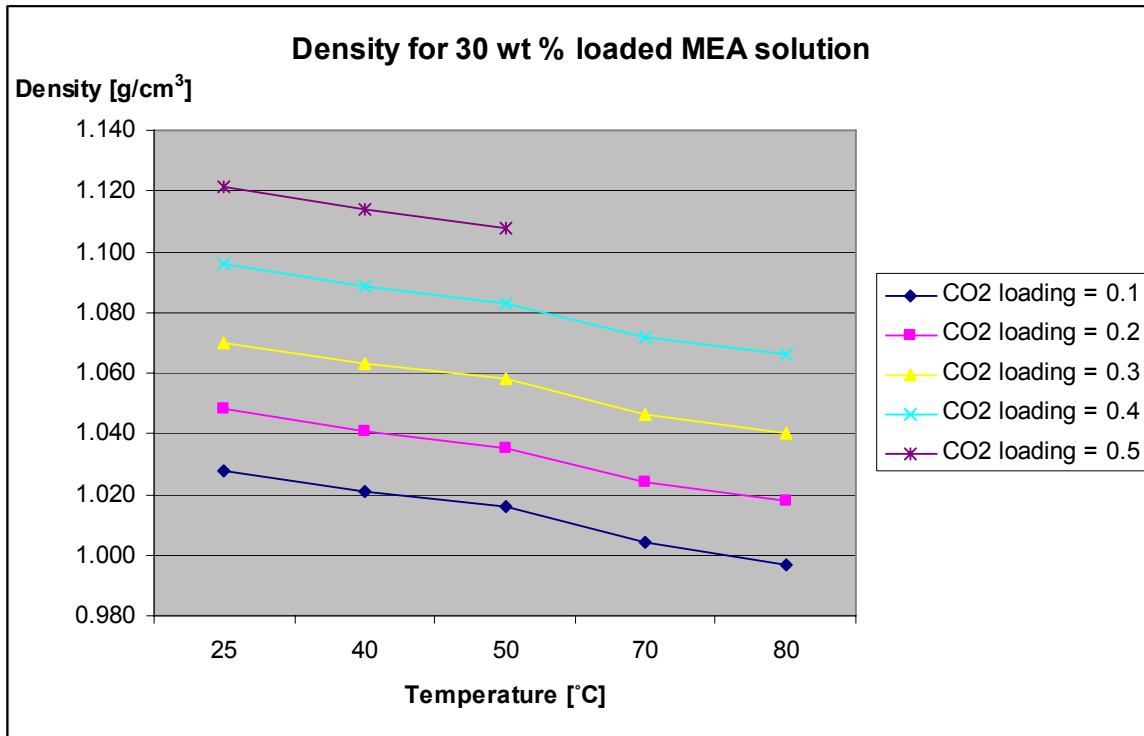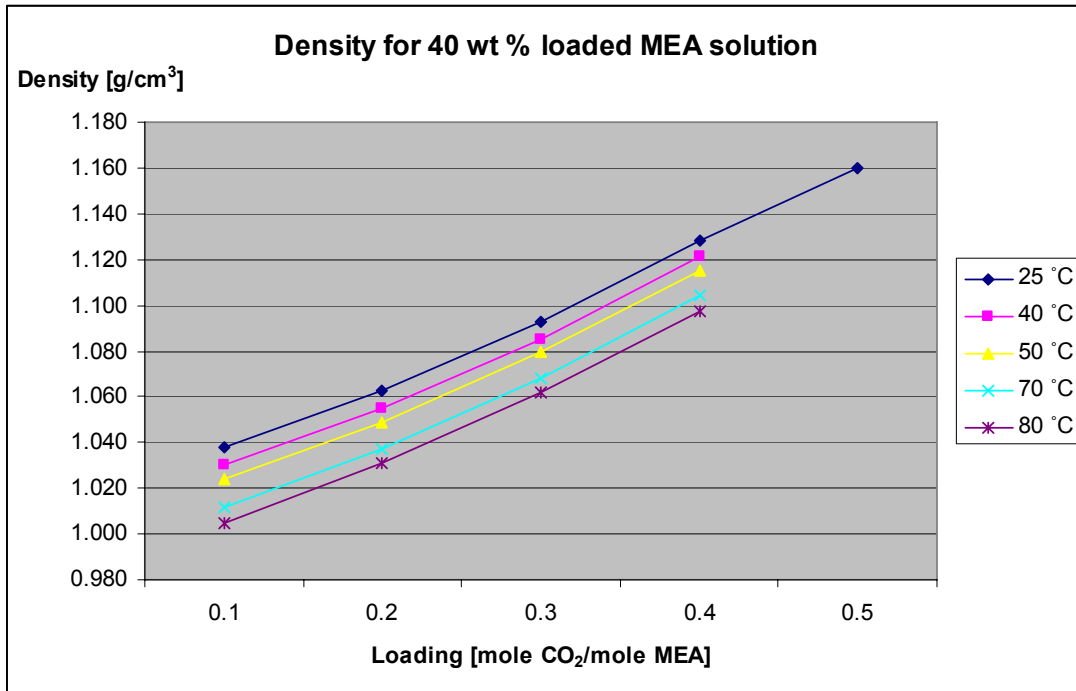*Figure 5 - 9: Density results for 40 wt % loaded MEA solution as a function of loading [mole CO₂/mole MEA].*
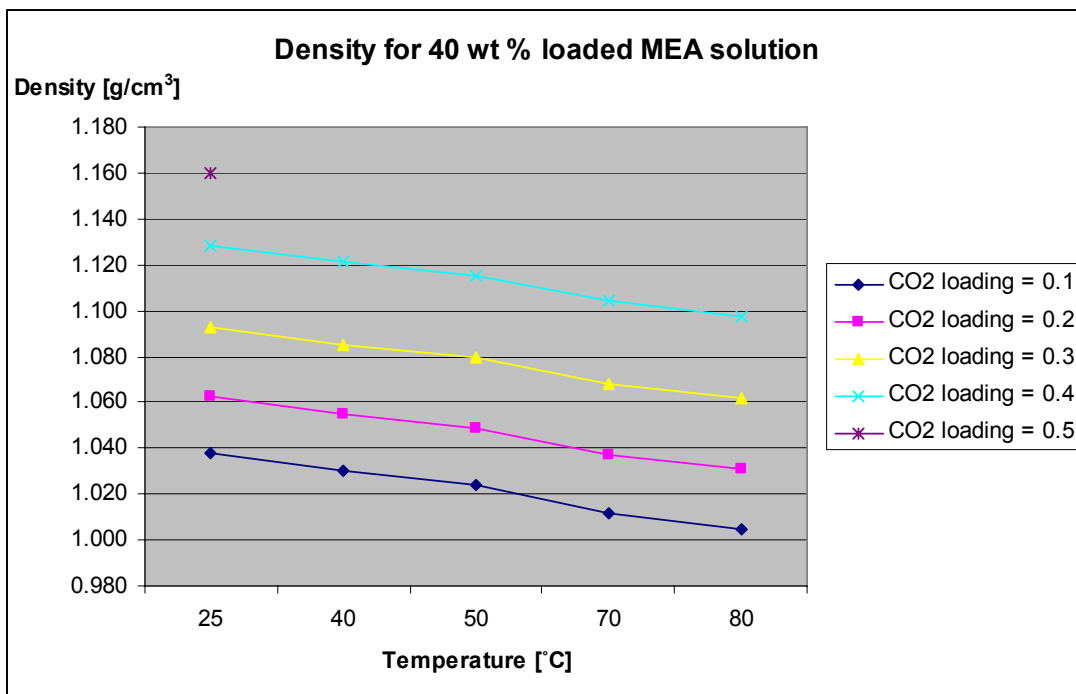
Figure 5 - 10: Density results for 40 wt % loaded MEA solution as a function of temperature [˚C].

5.3 Viscosity Results

Viscosity results for unloaded and loaded MEA solution are presented in this chapter.

5.3.1 Viscosity Results for Unloaded MEA Solution

Viscosity for unloaded MEA solution at 20, 30, 40, 50, 70, 90 and 100 wt % MEA are measured at 25, 40, 50, 70 and 80 ˚C. Parallel measurements are carried out and the results are given with two decimals for unloaded MEA and with one decimal for loaded MEA. This is due to problems with CO_2 vaporization in loaded MEA samples during measurements. The results are presented in table 5 - 5 and figure 5 - 11 and 5 - 12.

Table 5 - 5: Viscosity results for unloaded 20, 30, 40, 50, 70, 90 and 100 wt % MEA solutions from 25 to 80 ˚C.

Viscosity Results for Unloaded MEA Solutions							
Temp. [˚C]	Viscosity [mPa·s]						
	20 wt %	30 wt %	40 wt %	50 wt %	70 wt %	90 wt %	100 wt %
25	1.70	2.48	3.58	5.51	12.46	19.40	17.90
40	1.18	1.67	2.28	3.39	6.96	10.20	9.61
50	0.95	1.33	1.75	2.54	4.94	7.06	6.72
70	0.67	0.92	1.14	1.57	2.79	3.81	3.69
80	0.58	0.77	0.95	1.28	2.18	2.93	2.85
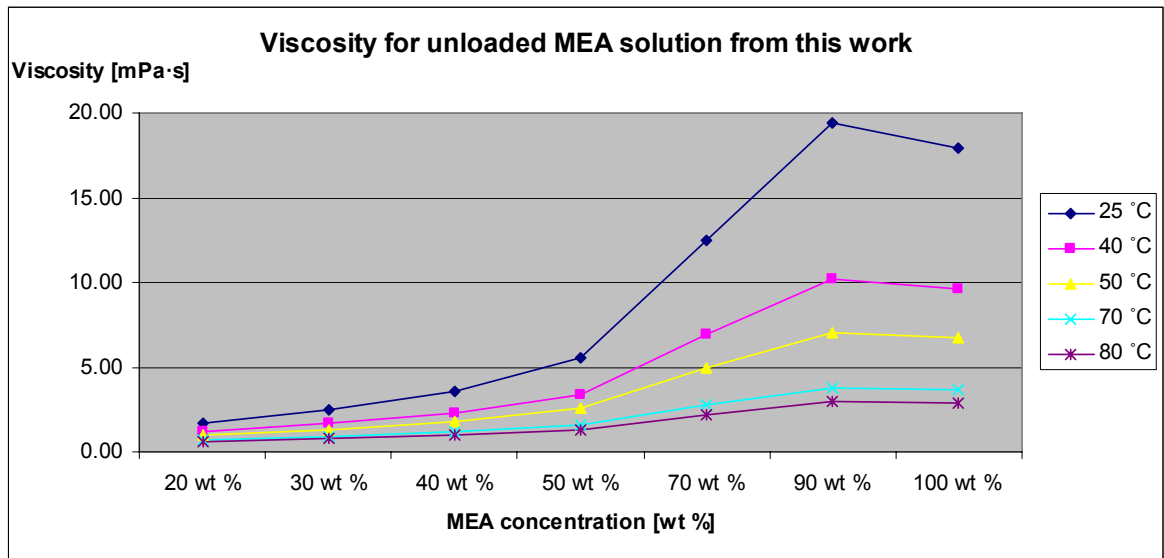
Figure 5 - 11: Viscosity results for unloaded MEA solutions as a function of MEA concentration [wt %].
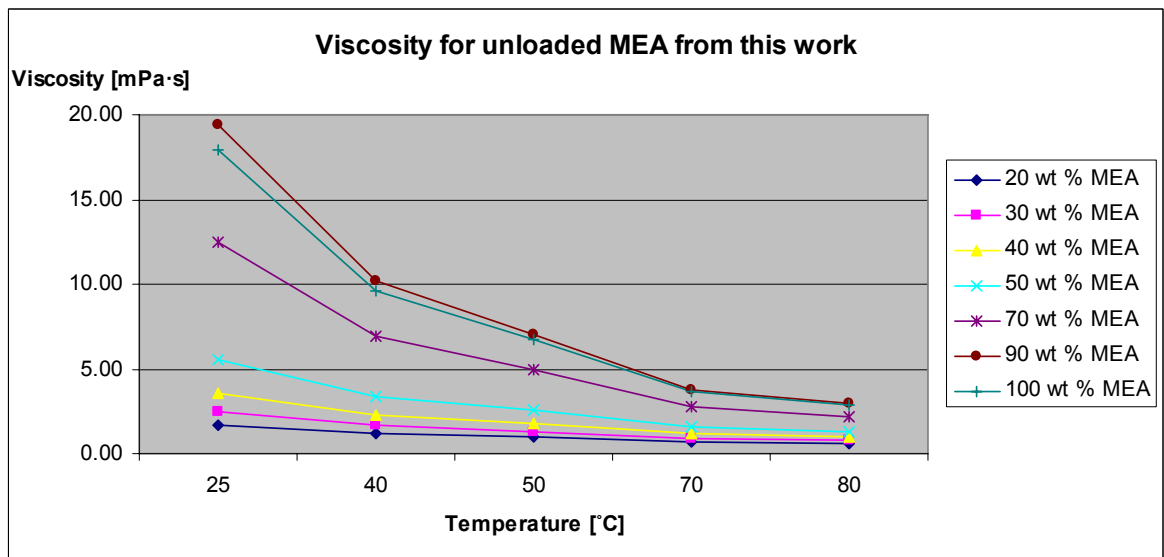
Figure 5 - 12: Viscosity results for unloaded MEA solutions as a function of temperature [˚C].

5.3.2 Viscosity Results for Loaded MEA Solution

Viscosity for loaded MEA solution at 20, 30 and 40 wt % MEA with 0.1, 0.2, 0.3, 0.4 and 0.5 mole CO_2/mole MEA, are measured at the same temperatures as for the unloaded MEA measurements. The results are presented in this chapter.

Results from 20 wt % loaded MEA solution are presented in table 5 - 6 and figure 5 - 13 and 5 - 14.

Table 5 - 6: Viscosity results for 20 wt % loaded MEA solution from 25 to 80 ℃.

Viscosity Results for 20 wt % Loaded MEA Solution					
	Viscosity [mPa·s]				
Temp. [C]	Loading [mole CO_2/mole MEA]				
	0.1	0.2	0.3	0.4	0.5
25	1.8	1.9	1.9	2.1	2.2
40	1.3	1.3	1.3	1.4	1.6
50	1.0	1.0	1.1	1.2	1.3
70	0.7	0.7	0.8	0.8	0.9
80	0.6	0.6	0.7	0.7	0.8

Figure 5 - 13: Viscosity results for 20 wt % loaded MEA solution as a function of loading [mole CO₂/mole MEA].
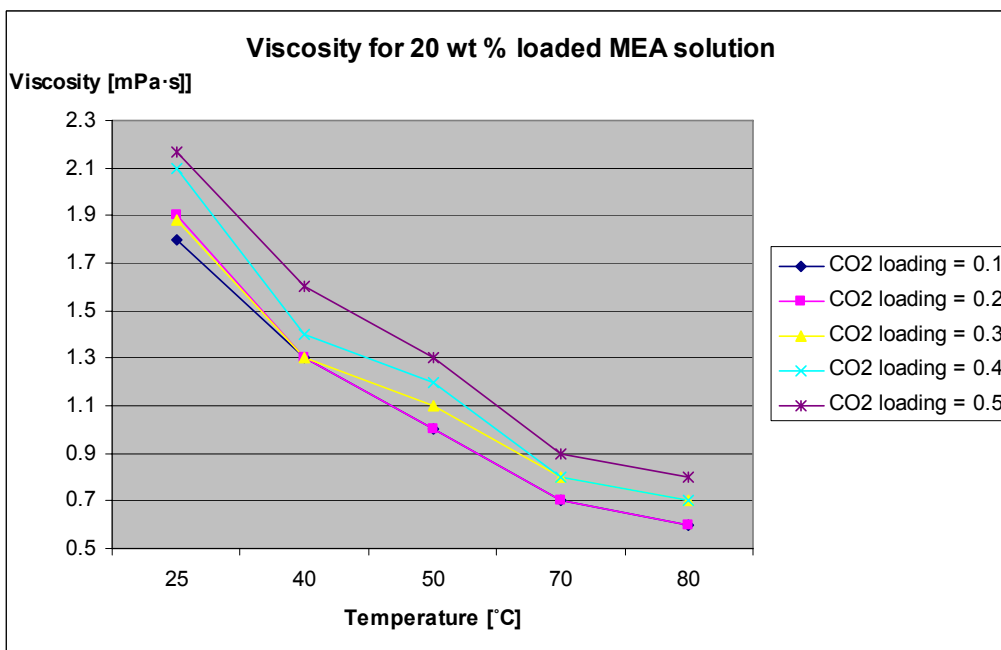
Figure 5 - 14: Viscosity results for 20 wt % loaded MEA solution as a function of temperature [°C].

Results from 30 wt % loaded MEA solution are presented in table 5 - 7 and figure 5 - 15 and 5 - 16.

Table 5 - 7: Viscosity results for 30 wt % loaded MEA solution from 25 to 80 ˚C.

Viscosity Results for 30 wt % Loaded MEA Solution					
	Viscosity [mPa·s]				
Temp. [C]	Loading [mole CO_2/mole MEA]				
	0.1	0.2	0.3	0.4	0.5
25	2.6	2.9	3.1	3.5	3.9
40	1.7	2.0	2.0	2.4	2.7
50	1.4	1.6	1.6	1.9	2.1
70	0.9	1.1	1.1	1.3	1.5
80	0.8	0.9	0.9	1.1	1.3
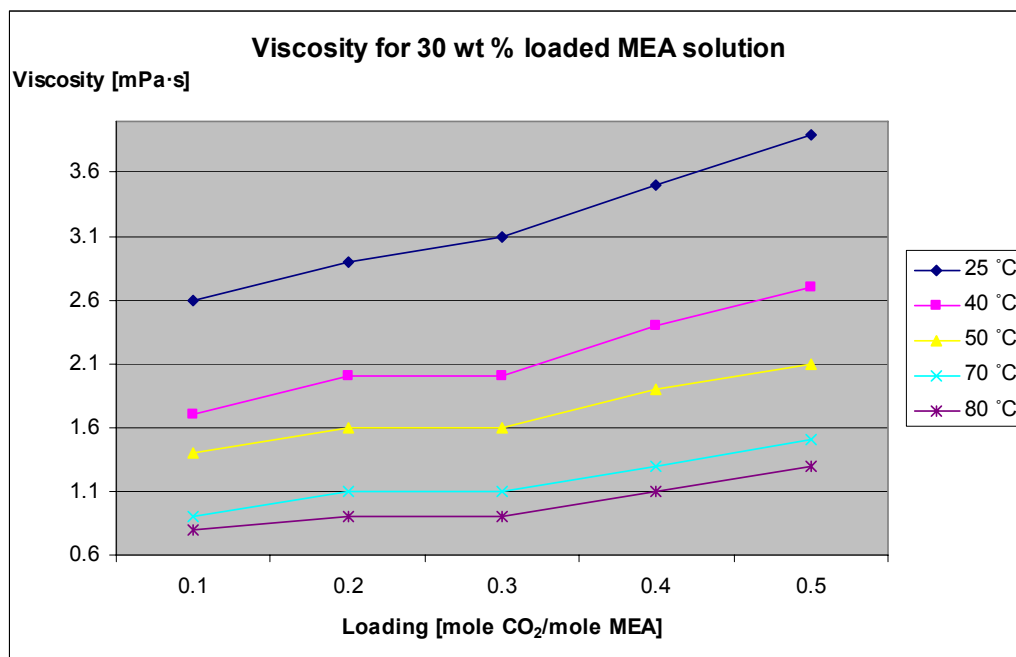
Figure 5 - 15: Viscosity results for 30 wt % loaded MEA solution as a function of loading [mole CO_2/mole MEA].
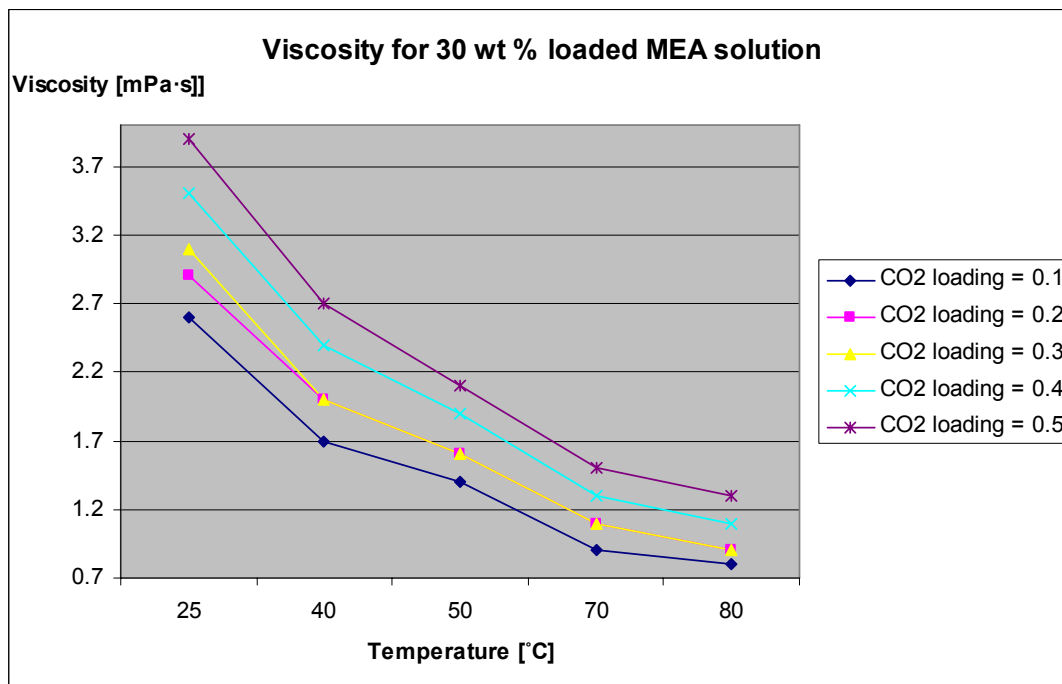
Figure 5 - 16: *Viscosity results for 30 wt % loaded MEA solution as a function of temperature [˚C].*

Results from 40 wt % loaded MEA solution are presented in table 5 - 8 and figure 5 - 17 and 5 - 18.

Table 5 - 8: Viscosity results for 40 wt % loaded MEA solution from 25 to 80 ˚C.

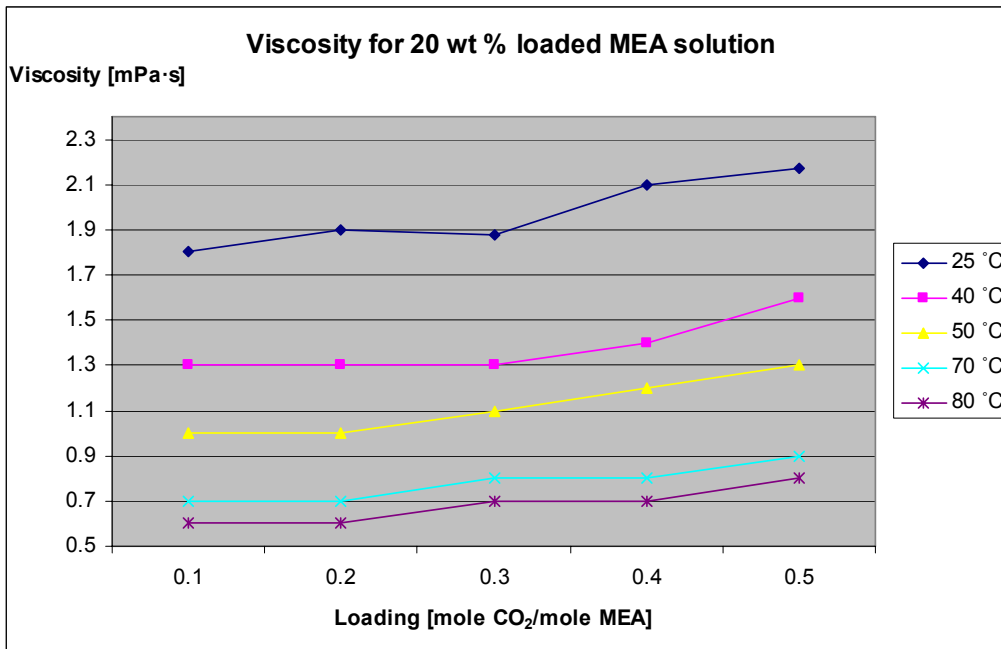| Viscosity Results for 40 wt % Loaded MEA Solution					
	Viscosity [mPa·s]				
Temp. [C]	Loading [mole CO_2/mole MEA]				
	0.1	0.2	0.3	0.4	0.5
25	4.0	4.6	5.1	6.0	7.0
40	2.5	3.0	3.3	4.0	4.6
50	2.0	2.3	2.6	3.1	3.8
70	1.3	1.5	1.7	2.0	2.3
80	1.1	1.3	1.4	1.7	1.9
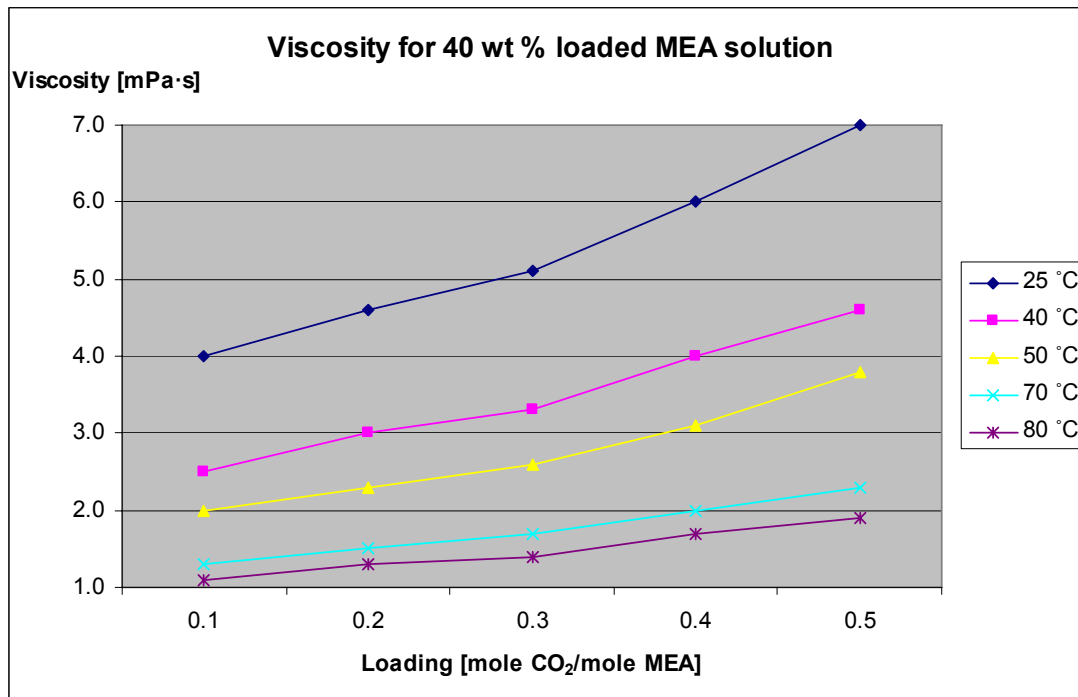
Figure 5 - 17: Viscosity results for 40 wt % loaded MEA solution as a function of loading [mole CO₂/mole MEA].
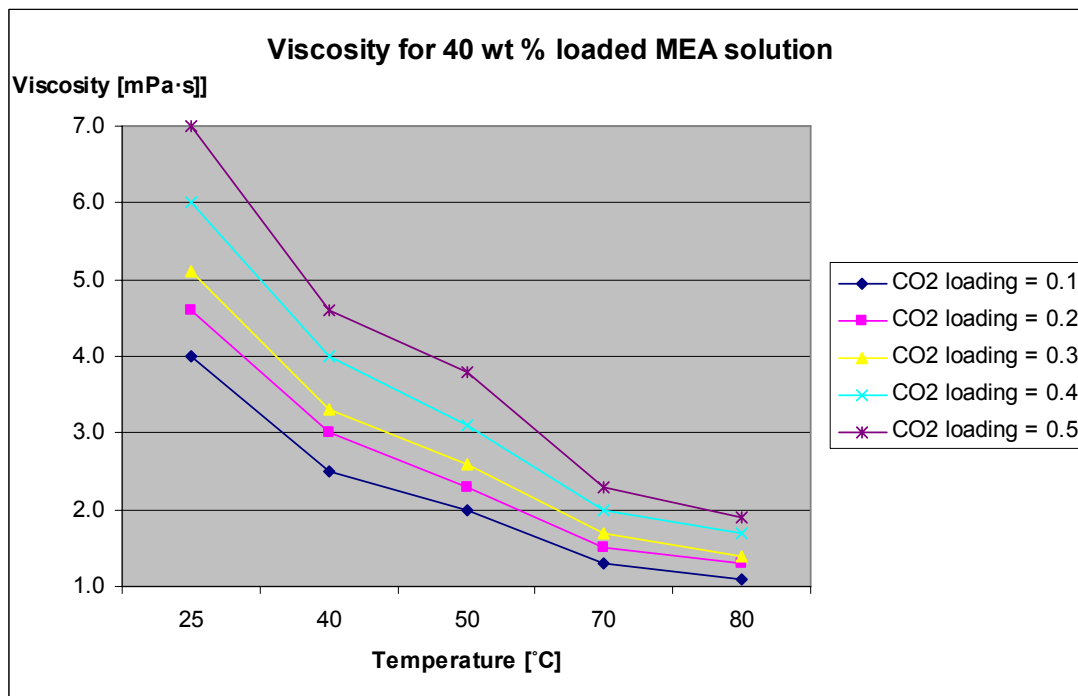
Figure 5 - 18: Viscosity results for 40 wt % loaded MEA solution as a function of temperature [˚C].

5.4 Experimental Results Compared to Literature Results

Experimental results for density and viscosity are compared to literature data for unloaded and loaded MEA solutions with different concentrations and at different temperatures.

5.4.1 Density for Unloaded MEA Solution

Experimental results of density for unloaded MEA solutions are compared to literature results. Figure 5 - 19 presents density for 50 and 70 wt % unloaded MEA solution from 25 to 80 ˚C, from this work and Aspen HYSYS.
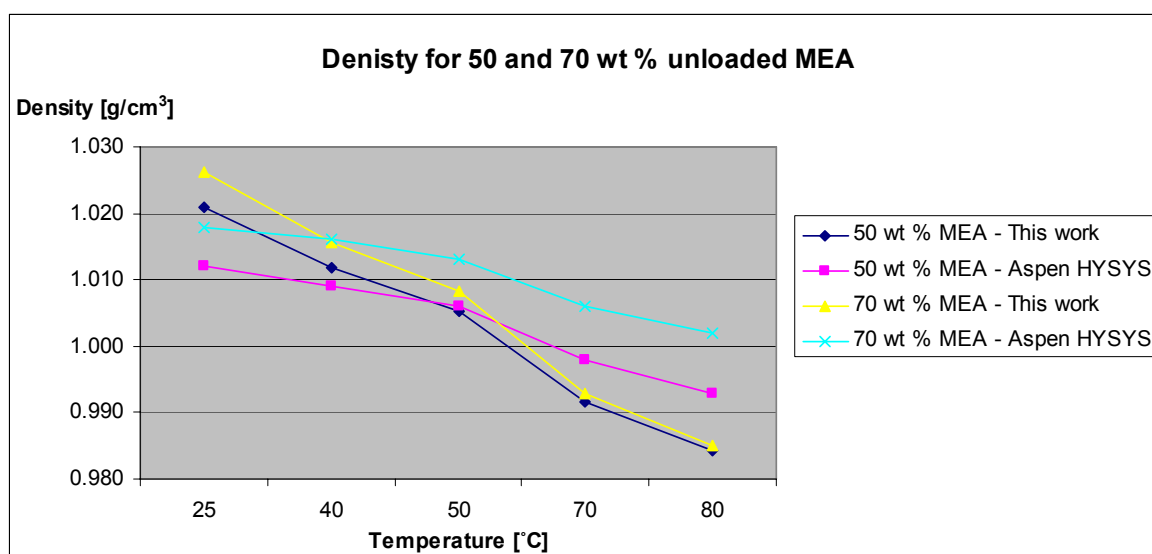
Figure 5 - 19: Density results for 50 and 70 wt % MEA as a function of temperature, from this work and Aspen HYSYS.

Figure 5 - 20 presents density for pure MEA from 25 to 80 ˚C, form this work, Leibush and Shorina and Aspen HYSYS.
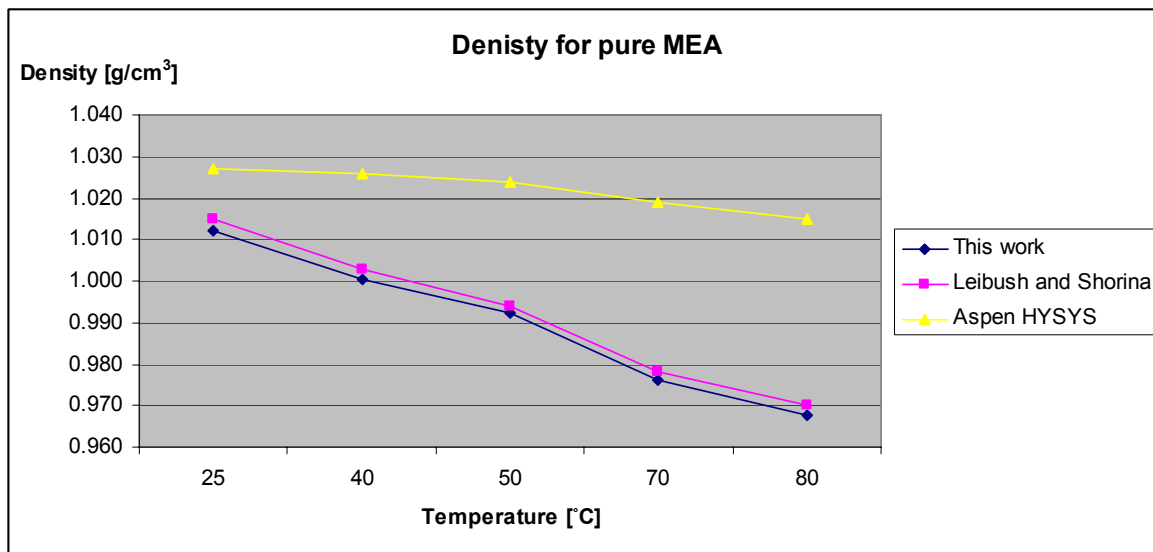
Figure 5 - 20: Density results for pure MEA (100 wt %) as a function of temperature, from this work, Leibush and Shorina and Aspen HYSYS.

Figure 5 - 21 presents density for 30 wt % unloaded MEA solution from 25 to 80 ˚C, form this work, BASF and Aspen HYSYS.
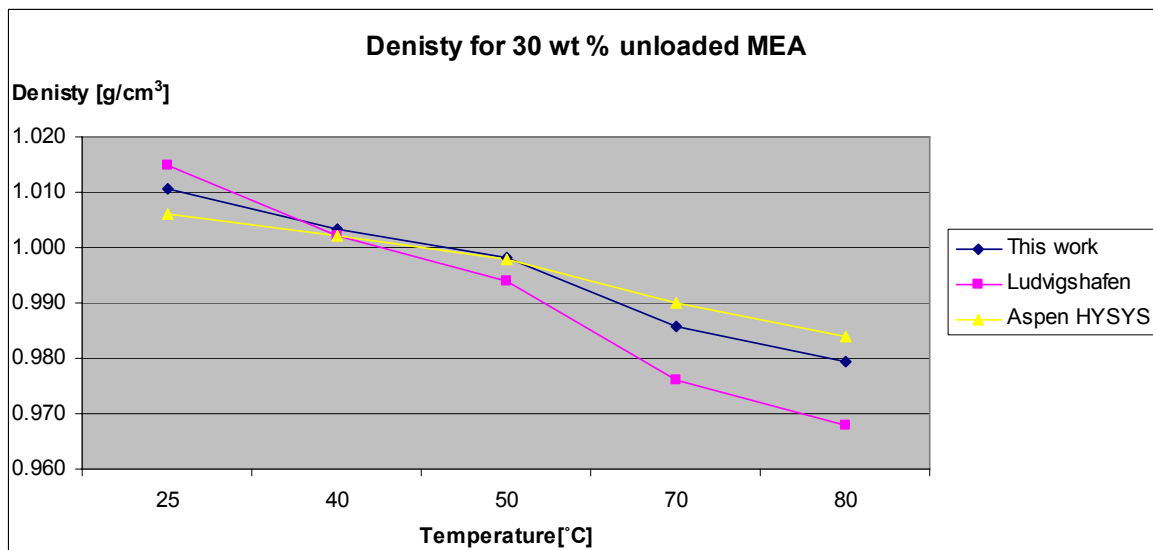
Figure 5 - 21: Density results for 30 wt % MEA as a function of temperature, from this work, BASF and Aspen HYSYS.

Figure 5 - 22 presents density for 20 and 40 wt % unloaded MEA solution from 25 to 80 ˚C, from this work, Leibush and Shorina and Aspen HYSYS.
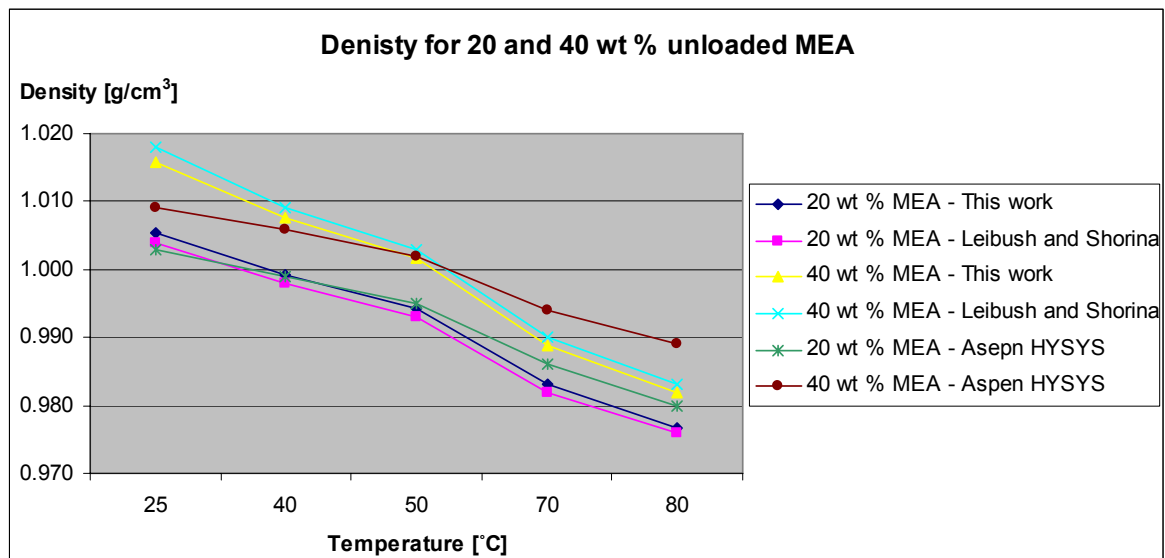
Figure 5 - 22: Density results for 20 and 40 wt % MEA as a function of temperature form this work, Leibush and Shorina and Aspen HYSYS.

5.4.2 Density for Loaded MEA Solution

Experimental results of density for loaded MEA solutions are compared to literature results.

Figure 5 - 23 presents density for 20 wt % loaded MEA solution at 25 ˚C from 0 to 0.5 mole CO_2/mole MEA, from this work and Weiland et al.

Figure 5 - 23: Density for loaded 20 wt % MEA solution at 25 ˚C, from this work and Weiland et al. (1998).

Figure 5 - 24 presents density for 30 wt % loaded MEA solution at 25 ˚C from 0 to 0.5 mole CO_2/mole MEA, from this work and Weiland et al.

Density results for 30 wt % MEA solution at 25 ˚C

Density [g/cm^3]

Figure 5 - 24: Density for loaded 30 wt % MEA solution at 25 ˚C, from this work and Weiland et al. (1998).

Figure 5 - 25 presents density for 40 wt % loaded MEA solution at 25 ˚C from 0 to 0.5 mole CO_2/mole MEA, from this work and Weiland et al.

Figure 5 - 25: Density for loaded 40 wt % MEA solution at 25 ˚C, from this work and Weiland et al. (1998).

Figure 5 - 26 presents density for 30 wt % loaded MEA solution at 0.1 mole CO_2/mole MEA from 25 to 50 ˚C, from this work and Kohl and Riesenfeld.
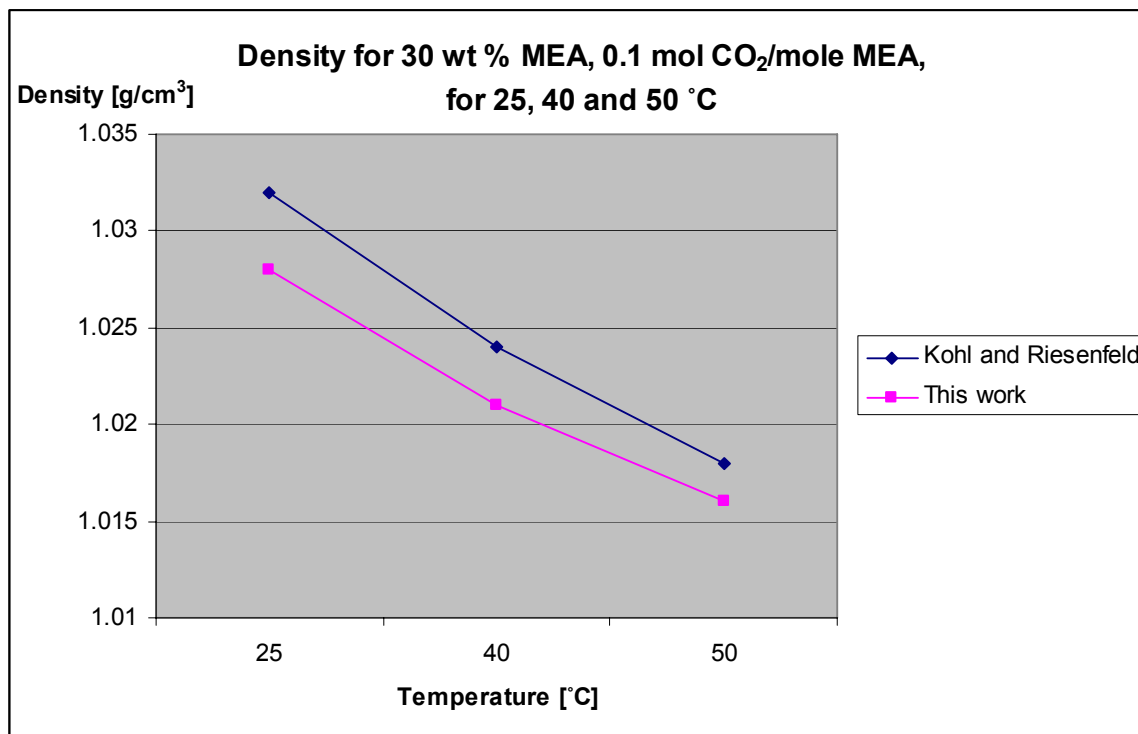
Figure 5 - 26: Density for 30 wt % loaded MEA for 25, 40 and 50 ˚C, from this work and Kohl and Riesenfeld (1979).

5.4.3 Viscosity for Unloaded MEA Solution

Experimental results of viscosity for unloaded MEA solutions are compared to literature results.

Figure 5 - 27 presents viscosity for 30 wt % unloaded MEA solution from 25 to 80 ˚C, from this work, Mandal et al., Gas Conditioning and Processing and Aspen HYSYS.
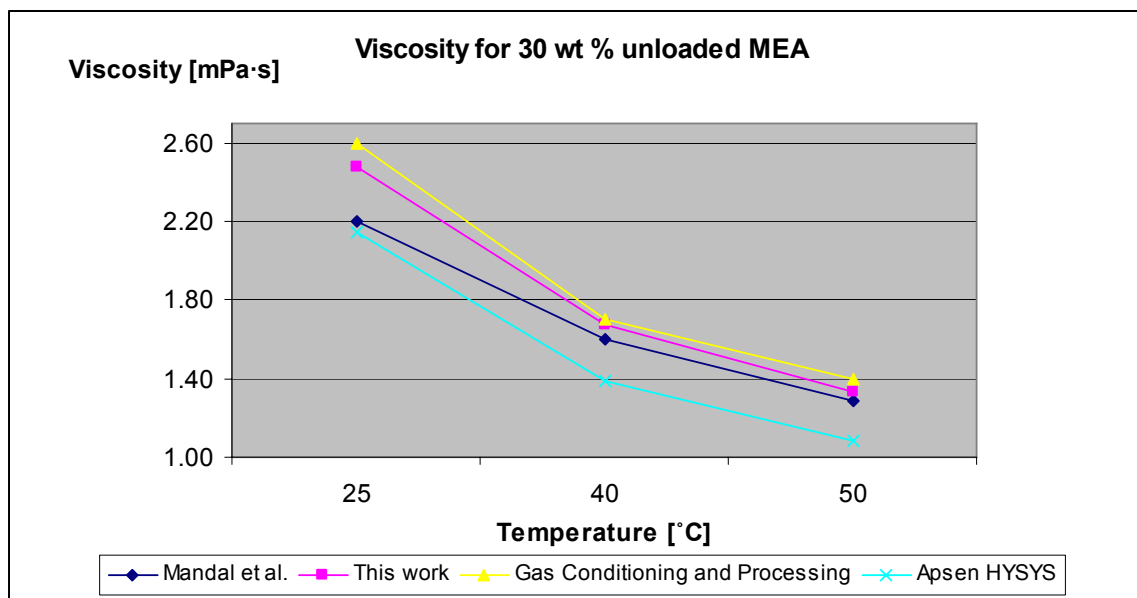
Figure 5 - 27: Viscosity results for 30 wt % MEA as a function of temperature, from this work, Mandal et al., Gas Conditioning and Processing and Aspen HYSYS.

Figure 5 - 28 presents viscosity for pure MEA from 25 to 80 ˚C, from this work, Mandal et al., Gas Condition and Processing, Lee and Lin and Aspen HYSYS.
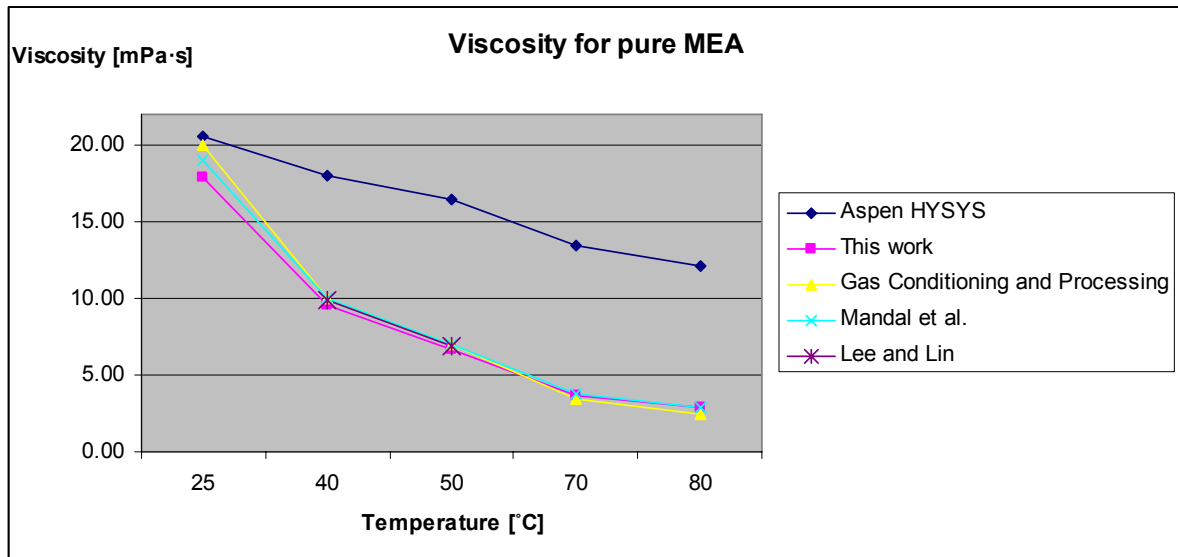
Figure 5 - 28: Viscosity results for pure MEA as a function of temperature, form this work, Mandal et al., Gas Conditioning and Processing, Aspen HYSYS and Lee and Lin.

5.4.4 Viscosity for Loaded MEA Solution

Experimental results of viscosity for loaded MEA solutions are compared to results from Weiland et al. (1998).

Figure 5 - 29 presents viscosity for 20 wt % loaded MEA solution at 25 ˚C from 0 to 0.5 mole CO_2/mole MEA, from this work and Weiland et al.
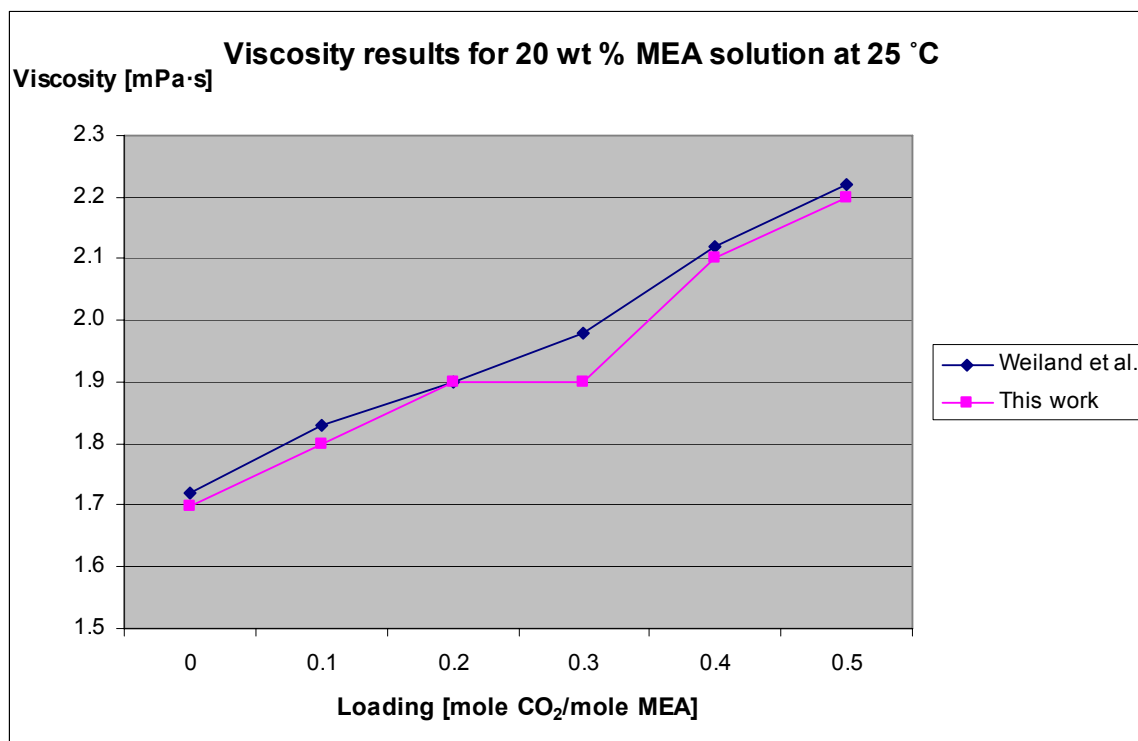
Figure 5 - 29: Viscosity for loaded 20 wt % MEA solution at 25 ˚C, from this work and Weiland et al. (1998).

Figure 5 - 30 presents viscosity for 30 wt % loaded MEA solution at 25 ˚C from 0 to 0.5 mole CO_2/mole MEA, from this work and Weiland et al.
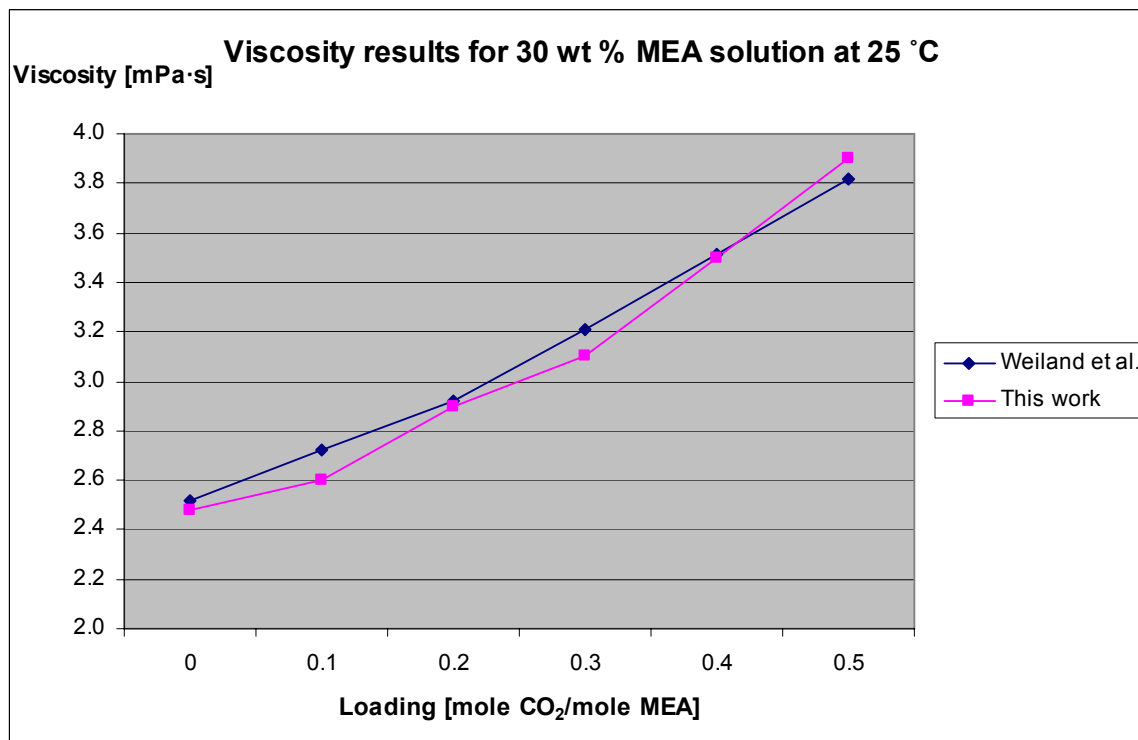
Figure 5 - 30: Viscosity for loaded 20 wt % MEA solution at 25 ˚C, from this work and Weiland et al. (1998).

Figure 5 - 31 presents viscosity for 40 wt % loaded MEA solution at 25 ˚C from 0 to 0.5 mole CO_2/mole MEA, from this work and Weiland et al.
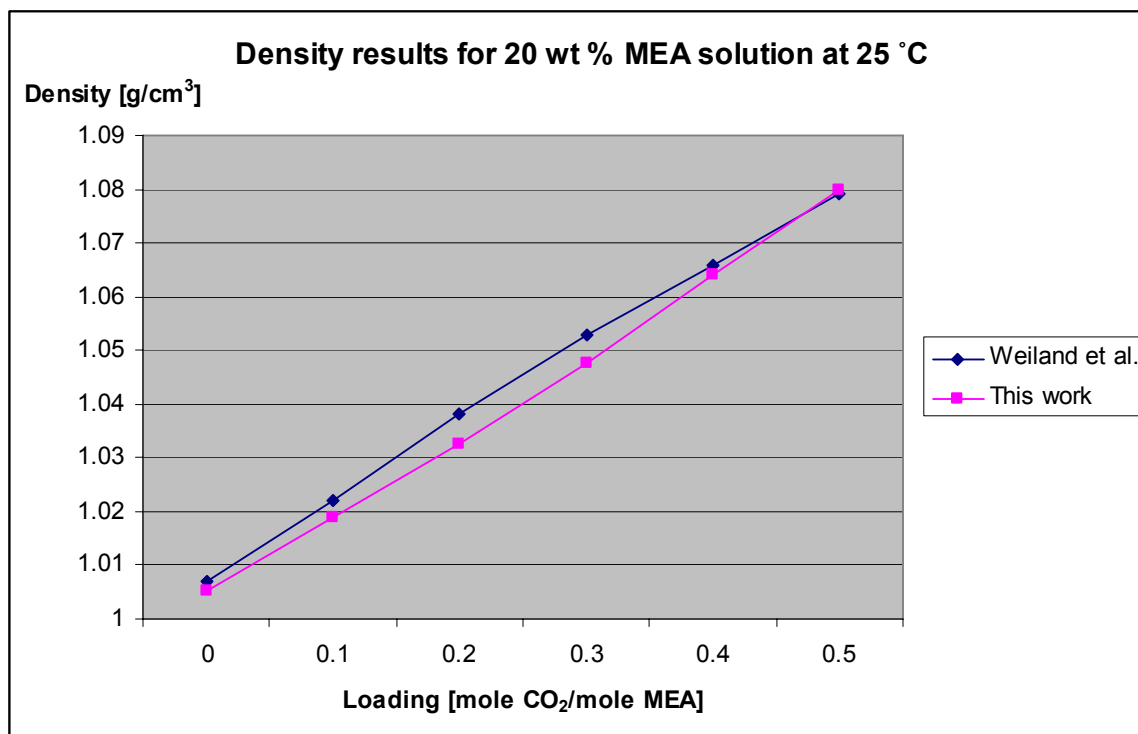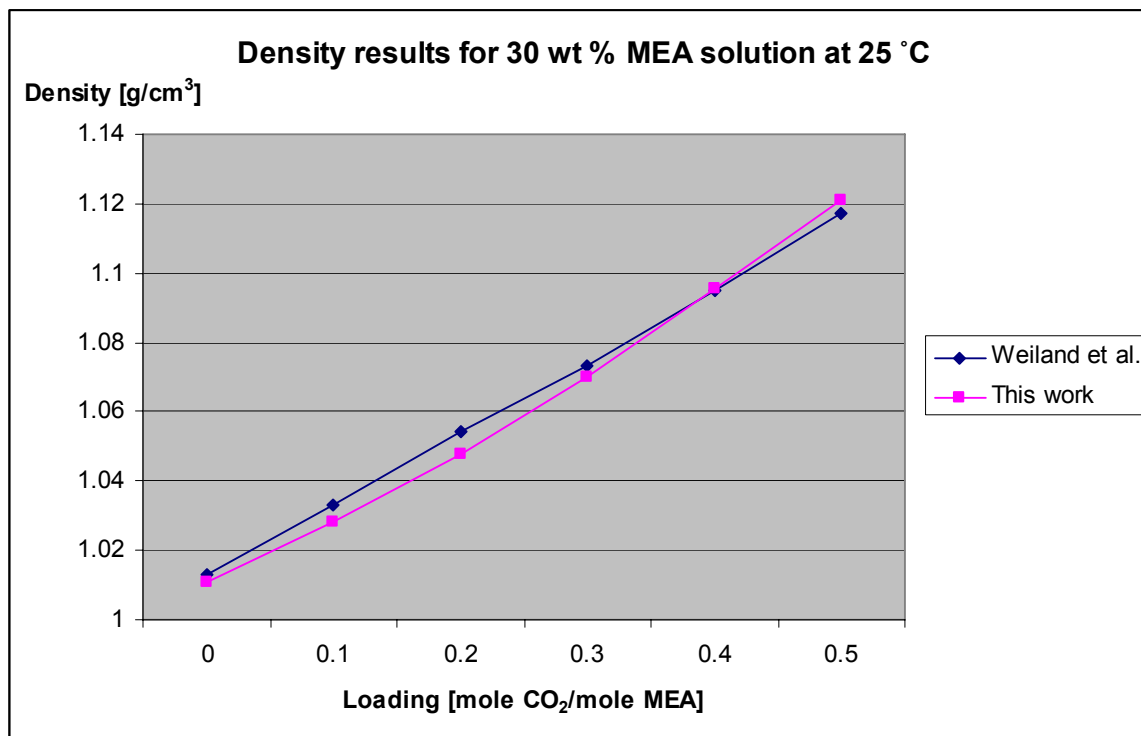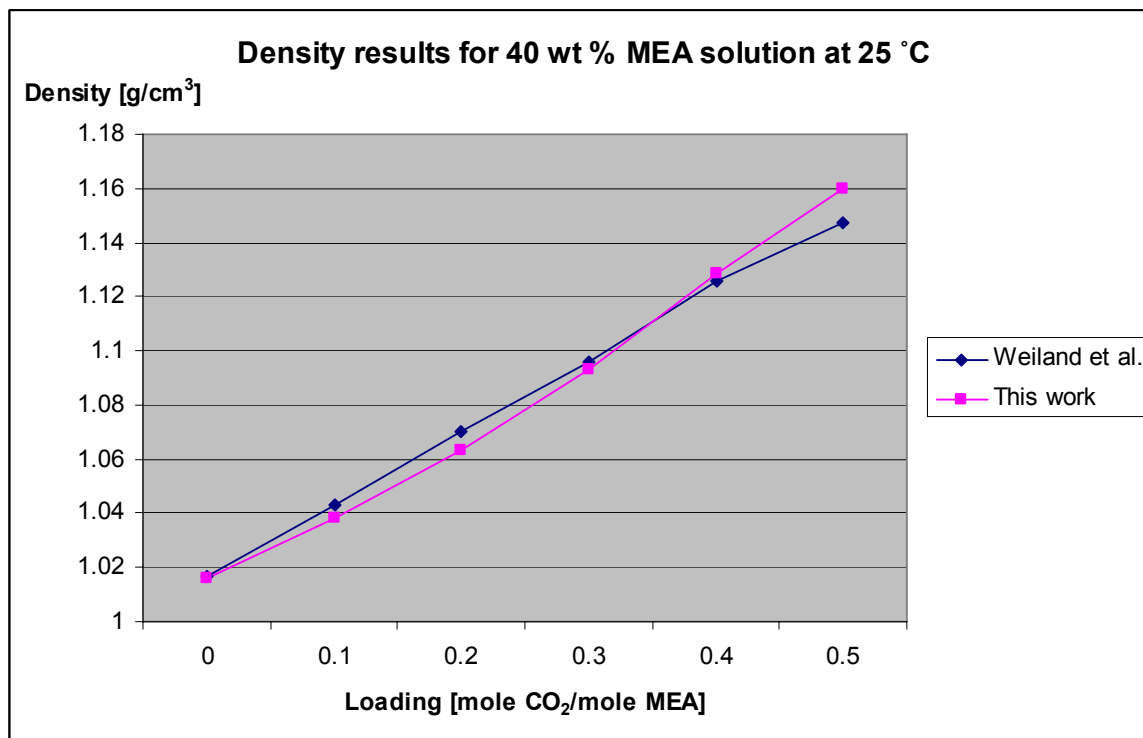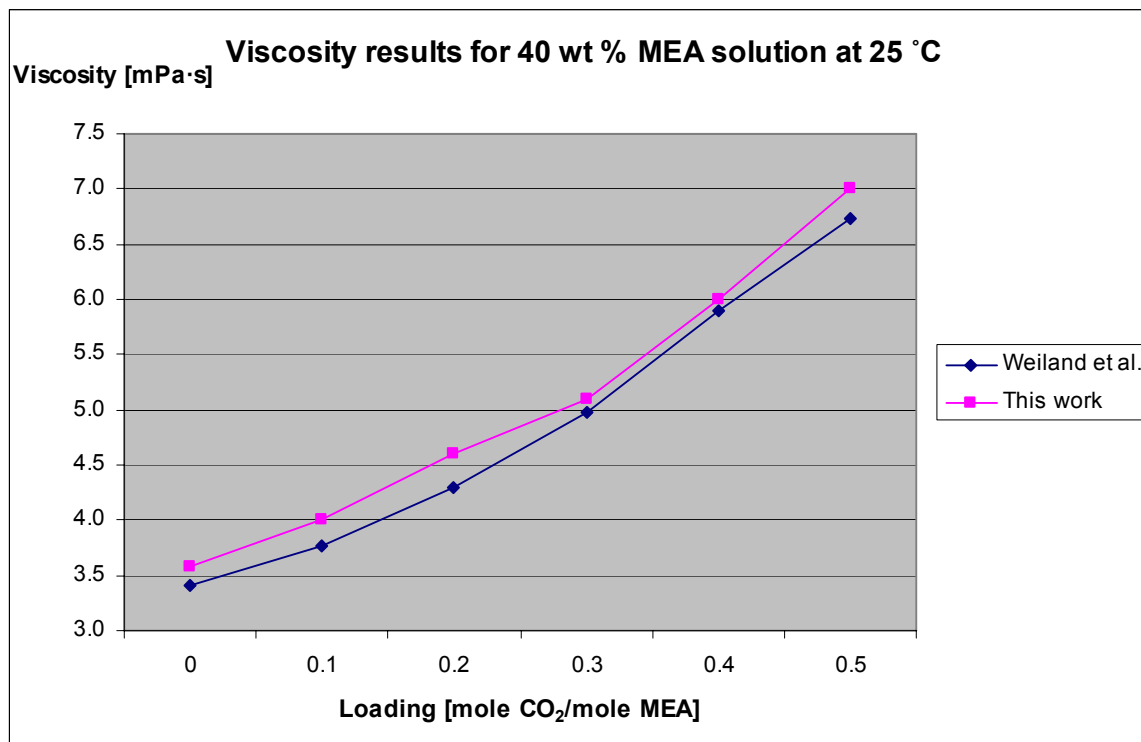

Figure 5 - 31: Viscosity for loaded 20 wt % MEA solution at 25 ˚C, from this work and Weiland et al. (1998).

5.5 Correlation Results from Weiland et al.

Viscosity and density are calculated from correlations presented in Weiland et al. (1998). [14]

5.5.1 Viscosity Correlation Results

The correlation for viscosity includes viscosity of water. To calculate the viscosity at different temperatures, the viscosity of water needs to change with the temperature. A correlation for the viscosity of water from J. F. Swindells, in the Handbook of Chemistry and Physics is used. [15]

$$\log_{10}\frac{\eta_T}{\eta_{20}} = \frac{1.3272\cdot(20-T)-0.001053\cdot(T-20)^2}{T+105} \tag{32}$$

Table 5 - 9 presents calculations for the water viscosity, performed to check the correlation.

Table 5 - 9: Viscosity of water, from Handbook of chemistry and physics, and viscosity for water calculated by the correlation, are presented from 20 to 80 ˚C.

Temperature	Viscosity of water	Viscosity of water calculated by the correlation
[˚C]	[mPa·s]	
20	1.0020	1.0020
25	0.8904	0.8905
40	0.6529	0.6530
50	0.5468	0.5469
70	0.4042	0.4042
80	0.3547	0.3548

The viscosity was calculated for 20, 30 and 40 wt % loaded MEA solutions at 25 ˚C, and compared to results in the Weiland article and to experimental results. See appendix 10 for input to the correlations.

Table 5 - 10 to 5 -12 present viscosity for 20, 30 and 40 wt % loaded MEA solutions at 25 ˚C, from this work, viscosity correlation and Weiland et al.

Table 5 - 10: Viscosity results for 20 wt % loaded MEA solutions at 25 ˚C from viscosity correlation, Weiland et al. and this work.

Viscosity Results for 20 wt % Loaded MEA Solutions at 25 ˚C			
Loading	Viscosity from correlation	Viscosity from Weiland et al.	This work
[mole CO_2/mole MEA]	[mPa·s]		
0	1.67	1.72	1.7
0.1	1.75	1.83	1.8
0.2	1.83	1.9	1.9
0.3	1.91	1.98	1.9
0.4	2.01	2.12	2.1
0.5	2.09	2.22	2.2

Table 5 - 11: Viscosity results for 30 wt % loaded MEA solutions at 25 ˚C from viscosity correlation, Weiland et al. and this work.

Viscosity Results for 30 wt % Loaded MEA Solutions at 25 ˚C			
Loading	Viscosity from correlation	Viscosity from Weiland et al.	This work
[mole CO_2/mole MEA]	[mPa·s]		
0	2.46	2.52	2.48
0.1	2.67	2.72	2.6
0.2	2.90	2.92	2.9
0.3	3.15	3.21	3.1
0.4	3.43	3.51	3.5
0.5	3.73	3.82	3.9

Table 5 - 12: Viscosity results for 40 wt % loaded MEA solutions at 25 ˚C from viscosity correlation, Weiland et al. and this work.

Viscosity Results for 40 wt % Loaded MEA Solutions at 25 ˚C			
Loading	**Viscosity from correlation**	**Viscosity from Weiland et al.**	**This work**
[mole CO$_2$/mole MEA]	**[mPa·s]**		
0	3.79	3.41	3.58
0.1	4.33	3.76	4.0
0.2	4.95	4.3	4.6
0.3	5.66	4.97	5.1
0.4	6.46	5.9	6.0
0.5	7.39	6.73	7.0

The viscosity was then calculated with the correlation for 20, 30 and 40 wt % loaded MEA solution from 25 to 80 ˚C. The results were compared to the experimental results.

Table 5 - 13 to 5 - 17 present viscosity for 20 wt % loaded MEA solutions with 0.1 to 0.5 mole CO$_2$/mole MEA from 25 to 80 ˚C, from this work and viscosity correlation.

Table 5 - 13: Viscosity results from viscosity correlation and experimental work for 20 wt % MEA solutions with 0.1 mole CO$_2$/mole MEA.

Viscosity Results for 20 wt % MEA Solutions with 0.1 mole CO$_2$/mole MEA		
Temperature	**Viscosity from correlation**	**This work**
[˚C]	**[mPa·s]**	
25	1.75	1.8
40	1.21	1.3
50	0.98	1.0
70	0.69	0.7
80	0.59	0.6

Table 5 - 14: Viscosity results from viscosity correlation and experimental work for 20 wt % MEA solutions with 0.2 mole CO_2/mole MEA.

Viscosity Results for 20 wt % MEA Solutions with 0.2 mole CO_2/mole MEA		
Temperature	Viscosity from correlation	This work
[˚C]	[mPa·s]	
25	1.83	1.9
40	1.27	1.3
50	1.03	1.0
70	0.72	0.7
80	0.62	0.6

Table 5 - 15: Viscosity results from viscosity correlation and experimental work for 20 wt % MEA solutions with 0.3 mole CO_2/mole MEA.

Viscosity Results for 20 wt % MEA Solutions with 0.3 mole CO_2/mole MEA		
Temperature	Viscosity from correlation	This work
[˚C]	[mPa·s]	
25	1.91	1.9
40	1.34	1.3
50	1.09	1.1
70	0.76	0.8
80	0.66	0.7

Table 5 - 16: Viscosity results from viscosity correlation and experimental work for 20 wt % MEA solutions with 0.4 mole CO_2/mole MEA.

Viscosity Results for 20 wt % MEA Solutions with 0.4 mole CO_2/mole MEA		
Temperature	Viscosity from correlation	This work
[˚C]	[mPa·s]	
25	2.00	2.1
40	1.40	1.4
50	1.15	1.2
70	0.81	0.8
80	0.69	0.7

Table 5 - 17: Viscosity results from viscosity correlation and experimental work for 20 wt % MEA solutions with 0.5 mole CO_2/mole MEA.

Viscosity Results for 20 wt % MEA Solutions with 0.5 mole CO_2/mole MEA		
Temperature	Viscosity from correlation	This work
[˚C]	[mPa·s]	
25	2.09	2.2
40	1.47	1.6
50	1.20	1.3
70	0.85	0.9
80	0.73	0.8

Table 5 - 18 to 5 - 22 present viscosity for 30 wt % loaded MEA solutions with 0.1 to 0.5 mole CO_2/mole MEA from 25 to 80 ˚C, from this work and viscosity correlation.

Table 5 - 18: Viscosity results from viscosity correlation and experimental work for 30 wt % MEA solutions with 0.1 mole CO_2/mole MEA.

Viscosity Results for 30 wt % MEA Solutions With 0.1 mole CO_2/mole MEA		
Temperature	Viscosity from correlation	This work
[˚C]	[mPa·s]	
25	2.67	2.6
40	1.79	1.7
50	1.42	1.4
70	0.96	0.9
80	0.81	0.8

Table 5 - 19: Viscosity results from viscosity correlation and experimental work for 30 wt % MEA solutions with 0.2 mole CO_2/mole MEA.

Viscosity Results for 30 wt % MEA Solutions with 0.2 mole CO_2/mole MEA		
Temperature	Viscosity from correlation	This work
[˚C]	[mPa·s]	
25	2.90	2.9
40	1.96	2.0
50	1.56	1.6
70	1.05	1.1
80	0.89	0.9

Table 5 - 20: Viscosity results from viscosity correlation and experimental work for 30 wt % MEA solutions with 0.3 mole CO_2/mole MEA.

Viscosity Results for 30 wt % MEA Solutions with 0.3 mole CO_2/mole MEA		
Temperature	Viscosity from correlation	This work
[˚C]	[mPa·s]	
25	3.15	3.1
40	2.14	2.0
50	1.70	1.6
70	1.16	1.1
80	0.98	0.9

Table 5 - 21: Viscosity results from viscosity correlation and experimental work for 30 wt % MEA solutions with 0.4 mole CO_2/mole MEA.

Viscosity Results for 30 wt % MEA Solutions with 0.4 mole CO_2/mole MEA		
Temperature	Viscosity from correlation	This work
[˚C]	[mPa·s]	
25	3.43	3.5
40	2.33	2.4
50	1.87	1.9
70	1.27	1.3
80	1.08	1.1

Table 5 - 22: Viscosity results from viscosity correlation and experimental work for 30 wt % MEA solutions with 0.5 mole CO_2/mole MEA.

Viscosity Results for 30 wt % MEA Solutions with 0.5 mole CO_2/mole MEA		
Temperature	Viscosity from correlation	This work
[˚C]	[mPa·s]	
25	3.72	3.9
40	2.55	2.7
50	2.04	2.1
70	1.40	1.5
80	1.18	1.3

Table 5 - 23 to 5 - 27 present viscosity for 40 wt % loaded MEA solutions with 0.1 to 0.5 mole CO_2/mole MEA from 25 to 80 ˚C, from this work and viscosity correlation.

Table 5 - 23: Viscosity results from viscosity correlation and experimental work for 40 wt % MEA solutions with 0.1 mole CO_2/mole MEA.

Viscosity Results for 40 wt % MEA Solutions with 0.1 mole CO_2/mole MEA		
Temperature	Viscosity from correlation	This work
[˚C]	[mPa·s]	
25	4.33	4.0
40	2.79	2.5
50	2.16	2.0
70	1.40	1.3
80	1.16	1.1

*Table 5 - 24: Viscosity results from viscosity correlation and experimental work for 40 wt %
MEA solutions with 0.2 mole CO_2/mole MEA.*

Viscosity Results for 40 wt % MEA Solutions with 0.2 mole CO_2/mole MEA		
Temperature	Viscosity from correlation	This work
[˚C]	[mPa·s]	
25	4.95	4.6
40	3.21	3.0
50	2.50	2.3
70	1.62	1.5
80	1.34	1.3

*Table 5 - 25: Viscosity results from viscosity correlation and experimental work for 40 wt %
MEA solutions with 0.3 mole CO_2/mole MEA.*

Viscosity Results for 40 wt % MEA Solutions with 0.3 mole CO_2/mole MEA		
Temperature	Viscosity from correlation	This work
[˚C]	[mPa·s]	
25	5.66	5.1
40	3.69	3.3
50	2.88	2.6
70	1.87	1.7
80	1.55	1.4

*Table 5 - 26: Viscosity results from viscosity correlation and experimental work for 40 wt %
MEA solutions with 0.4 mole CO_2/mole MEA.*

Viscosity Results for 40 wt % MEA Solutions with 0.4 mole CO_2/mole MEA		
Temperature	**Viscosity from correlation**	**This work**
[˚C]	**[mPa·s]**	
25	6.46	6.0
40	4.24	4.0
50	3.32	3.1
70	2.17	2.0
80	1.8	1.7

*Table 5 - 27: Viscosity results from viscosity correlation and experimental work for 40 wt %
MEA solutions with 0.5 mole CO_2/mole MEA.*

Viscosity Results for 40 wt % MEA Solutions with 0.5 mole CO_2/mole MEA		
Temperature	**Viscosity from correlation**	**This work**
[˚C]	**[mPa·s]**	
25	7.39	7.0
40	4.87	4.6
50	3.82	3.8
70	2.51	2.3
80	2.09	1.9

5.5.2 Density Correlation Results

The density was calculated for 20, 30 and 40 wt % loaded MEA solutions at 25 ˚C, and compared to results in the Weiland article and to experimental results.

Table 5 - 28 to 5 - 30 present density for 20, 30 and 40 wt % loaded MEA solutions at 25 ˚C, from this work, density correlation and Weiland et al.

Table 5 - 28: Density results for 20 wt % loaded MEA solution at 25 ˚C from density correlation, Weiland et al. and this work.

Density Results for 20 wt % Loaded MEA Solutions at 25 ˚C			
Loading	Density from correlation	Density from Weiland et al.	This work
[mole CO_2/mole MEA]	[g/cm^3]		
0	1.002	1.007	1.005
0.1	1.017	1.022	1.019
0.2	1.032	1.038	1.033
0.3	1.047	1.053	1.048
0.4	1.062	1.066	1.064
0.5	1.077	1.079	1.080

Table 5 - 29: Density results for 30 wt % loaded MEA solutions at 25 ˚C from density correlation, Weiland et al. and this work.

Density Results for 30 wt % Loaded MEA Solutions at 25 ˚C			
Loading	Density from correlation	Density from Weiland et al.	This work
[mole CO_2/mole MEA]	[g/cm^3]		
0	1.004	1.013	1.011
0.1	1.026	1.033	1.028
0.2	1.048	1.054	1.048
0.3	1.071	1.073	1.070
0.4	1.094	1.095	1.096
0.5	1.117	1.117	1.121

Table 5 - 30: Density results for 40 wt % loaded MEA solutions at 25 ˚C from density correlation, Weiland et al. and this work.

Density Results for 40 wt % Loaded MEA Solutions at 25 ˚C			
Loading	**Density from correlation**	**Density from Weiland et al.**	**This work**
[mole CO_2/mole MEA]	**[g/cm^3]**		
0	1.005	1.017	1.016
0.1	1.034	1.043	1.038
0.2	1.064	1.070	1.063
0.3	1.095	1.096	1.093
0.4	1.127	1.126	1.129
0.5	1.159	1.147	1.160

The density was then calculated with the correlation for 20, 30 and 40 wt % loaded MEA solutions from 25 to 80 ˚C. The results were compared to the experimental results.

Table 5 - 31 to 5 - 35 present density for 20 wt % loaded MEA solutions with 0.1 to 0.5 mole CO_2/mole MEA from 25 to 80 ˚C, from this work and density correlation.

Table 5 - 31: Density results from density correlation and experimental work for 20 wt % MEA solutions with 0.1 mole CO_2/mole MEA.

Density Results for 20 wt % MEA Solutions With 0.1 mole CO_2/mole MEA		
Temperature	**Density from correlation**	**This work**
[˚C]	**[g/cm^3]**	
25	1.017	1.019
40	1.015	1.013
50	1.013	1.008
70	1.010	0.997
80	1.008	0.990

Table 5 - 32: Density results from density correlation and experimental work for 20 wt % MEA solutions with 0.2 mole CO_2/mole MEA.

Density Results for 20 wt % MEA Solutions with 0.2 mole CO_2/mole MEA		
Temperature	Density from correlation	This work
[˚C]	[g/cm^3]	
25	1.032	1.033
40	1.029	1.026
50	1.028	1.022
70	1.024	1.011
80	1.022	1.004

Table 5 - 33: Density results from density correlation and experimental work for 20 wt % MEA solutions with 0.3 mole CO_2/mole MEA.

Density Results for 20 wt % MEA Solutions with 0.3 mole CO_2/mole MEA		
Temperature	Density from correlation	This work
[˚C]	[g/cm^3]	
25	1.047	1.048
40	1.044	1.041
50	1.042	1.036
70	1.039	1.025
80	1.037	1.019

Table 5 - 34: Density results from density correlation and experimental work for 20 wt % MEA solutions with 0.4 mole CO$_2$/mole MEA.

Density Results for 20 wt % MEA Solutions with 0.4 mole CO$_2$/mole MEA		
Temperature	Density from correlation	This work
[˚C]	[g/cm^3]	
25	1.062	1.064
40	1.059	1.058
50	1.057	1.053
70	1.054	1.042
80	1.052	1.036

Table 5 - 35: Density results from density correlation and experimental work for 20 wt % MEA solutions with 0.5 mole CO$_2$/mole MEA.

Density Results for 20 wt % MEA Solutions with 0.5 mole CO$_2$/mole MEA		
Temperature	Density from correlation	This work
[˚C]	[g/cm^3]	
25	1.077	1.080
40	1.074	1.074
50	1.073	1.068
70	1.069	1.057
80	1.067	-

Table 5 - 36 to 5 - 40 present density for 30 wt % loaded MEA solutions with 0.1 to 0.5 mole CO_2/mole MEA from 25 to 80 ˚C, from this work and density correlation.

Table 5 - 36: Density results from density correlation and experimental work for 30 wt % MEA solutions with 0.1 mole CO_2/mole MEA.

Density Results for 30 wt % MEA Solutions with 0.1 mole CO_2/mole MEA		
Temperature	Density from correlation	This work
[˚C]	[g/cm^3]	
25	1.026	1.028
40	1.022	1.021
50	1.020	1.016
70	1.014	1.004
80	1.012	0.997

Table 5 - 37: Density results from density correlation and experimental work for 30 wt % MEA solutions with 0.2 mole CO_2/mole MEA.

Density Results for 30 wt % MEA Solutions with 0.2 mole CO_2/mole MEA		
Temperature	Density from correlation	This work
[˚C]	[g/cm^3]	
25	1.048	1.048
40	1.044	1.041
50	1.042	1.036
70	1.036	1.024
80	1.034	1.018

Table 5 - 38: Density results from density correlation and experimental work for 30 wt % MEA solutions with 0.3 mole CO_2/mole MEA.

Density Results for 30 wt % MEA Solutions with 0.3 mole CO_2/mole MEA		
Temperature	Density from correlation	This work
[˚C]	[g/cm^3]	
25	1.071	1.070
40	1.067	1.063
50	1.064	1.058
70	1.059	1.046
80	1.056	1.040

Table 5 - 39: Density results from density correlation and experimental work for 30 wt % MEA solutions with 0.4 mole CO_2/mole MEA.

Density Results for 30 wt % MEA Solutions with 0.4 mole CO_2/mole MEA		
Temperature	Density from correlation	This work
[˚C]	[g/cm^3]	
25	1.094	1.096
40	1.090	1.088
50	1.087	1.083
70	1.081	1.072
80	1.079	1.066

Table 5 - 40: Density results from density correlation and experimental work for 30 wt % MEA solutions with 0.5 mole CO_2/mole MEA.

Density Results for 30 wt % MEA Solutions with 0.5 mole CO_2/mole MEA		
Temperature	Density from correlation	This work
[˚C]	[g/cm^3]	
25	1.117	1.121
40	1.113	1.114
50	1.110	1.108
70	1.105	-
80	1.102	-

Table 5 - 41 to 5 - 45 present density for 40 wt % loaded MEA solutions with 0.1 to 0.5 mole CO_2/mole MEA from 25 to 80 ˚C, from this work and density correlation.

Table 5 - 41: Density results from density correlation and experimental work for 40 wt % MEA solutions with 0.1 mole CO_2/mole MEA.

Density Results for 40 wt % MEA Solutions with 0.1 mole CO_2/mole MEA		
Temperature	Density from correlation	This work
[˚C]	[g/cm^3]	
25	1.034	1.038
40	1.029	1.030
50	1.026	1.024
70	1.019	1.012
80	1.016	1.005

Table 5 - 42: Density results from density correlation and experimental work for 40 wt % MEA solutions with 0.2 mole CO_2/mole MEA.

Density Results for 40 wt % MEA Solutions with 0.2 mole CO_2/mole MEA		
Temperature	Density from correlation	This work
[˚C]	[g/cm^3]	
25	1.064	1.063
40	1.059	1.055
50	1.056	1.049
70	1.049	1.037
80	1.045	1.031

Table 5 - 43: Density results from density correlation and experimental work for 40 wt % MEA solutions with 0.3 mole CO_2/mole MEA.

Density Results for 40 wt % MEA Solutions with 0.3 mole CO_2/mole MEA		
Temperature	Density from correlation	This work
[˚C]	[g/cm^3]	
25	1.095	1.093
40	1.090	1.085
50	1.086	1.080
70	1.079	1.068
80	1.075	1.062

Table 5 - 44: Density results from density correlation and experimental work for 40 wt % MEA solutions with 0.4 mole CO_2/mole MEA.

Density Results for 40 wt % MEA Solutions with 0.4 mole CO_2/mole MEA		
Temperature	Density from correlation	This work
[˚C]	[g/cm^3]	
25	1.127	1.129
40	1.121	1.121
50	1.117	1.115
70	1.110	1.104
80	1.106	1.098

Table 5 - 45: Density results from density correlation and experimental work for 40 wt % MEA solutions with 0.5 mole CO_2/mole MEA.

Density Results for 40 wt % MEA solution with 0.5 mole CO_2/mole MEA		
Temperature	Density from correlation	This work
[˚C]	[g/cm^3]	
25	1.159	1.160
40	1.153	-
50	1.149	-
70	1.141	-
80	1.137	-

6 MASS TRANSFER CORRELATIONS

Mass transfer correlations from Shetty & Cerro, Billet & Schultes, and Onda et al. and Bravo & Fair are studied to observe change of mass transfer due to change of viscosity and density. [2]

Mass transfer coefficients for gas and liquid are calculated for 30 wt % MEA solutions with different loadings at 25 ˚C.

Appendix 11 presents a nomenclature and input for calculation of mass transfer coefficients.

The mass transfer coefficient for gas, k_G is independent of density and viscosity of liquid, and will therefore not be affected by the change in loading, MEA concentration or temperature. The results are presented in table 6 - 1.

Table 6 - 1: Mass transfer coefficient results from change in loading for 30 wt % MEA solution at 25 ˚C.

Mass Transfer Coefficient Results						
mole CO_2/ mole MEA	$\alpha_{CO2} = 0$	$\alpha_{CO2} = 0.1$	$\alpha_{CO2} = 0.2$	$\alpha_{CO2} = 0.3$	$\alpha_{CO2} = 0.4$	$\alpha_{CO2} = 0.5$
ρ [kg/m^3]	1011	1028	1048	1070	1096	1121
η [kg/(m·s)]	2.48E-03	2.60E-03	2.90E-03	3.10E-03	3.50E-03	3.90E-03
Correlation	k_L [m/s]					
Shetty and Cerro	8.57E-05	8.53E-05	8.40E-05	8.34E-05	8.20E-05	8.09E-05
Billet and Schultes	3.24E-04	3.23E-04	3.18E-04	3.16E-04	3.11E-04	3.06E-04
Onda et al. and Bravo and Fair	6.11E-04	5.96E-04	5.53E-04	5.32E-04	4.91E-04	4.57E-04

Maximum deviation for measurement and correlation results for viscosity is 12 %, which is for 40 wt % MEA at 0.3 mole CO_2/mole MEA and at 40 ˚C. This deviation is used to calculate the deviation of mass transfer coefficients. Table 6 - 2 presents the results.

Table 6 - 2: Mass transfer coefficient results from maximum deviation of viscosity.

Mass Transfer Coefficient Results for Maximum Deviation of Viscosity			
Correlation	Viscosity from correlation result	Viscosity from measurement results	Deviation [%]
	k_L [m/s]		
Shetty and Cerro	8.13E-05	8.27E-05	1.7
Billet and Schultes	3.08E-04	3.13E-04	1.6
Onda et al. and Bravo and Fair	4.67E-04	5.11E-04	8.6

Maximum deviation for measurement and correlation results for density is only 1.8 %. The calculation of mass transfer coefficient deviation is therefore not performed.

7 DISCUSSION

The main objective of this master thesis was to measure physical properties in different concentrations of monoethanolamine (MEA) solutions, at different temperatures and CO_2 loadings.

Density and viscosity are important physical properties for estimation of mass transfer coefficients in CO_2 absorption. The measurements were performed to estimate the effect of CO_2 absorbed in the liquid.

Measurements of density and viscosity were performed for 20, 30, 40, 50, 70, 90 and 100 wt % unloaded MEA solutions. CO_2 loaded MEA solutions were measured at 20, 30 and 40 wt % MEA, at 0.1, 0.2, 0.3, 0.4 and 0.5 moles of CO_2 per moles of MEA. All measurements were performed at 25, 40, 50, 70 and 80 ˚C.

Loaded solutions were performed by bubbling CO_2 through a sinter in a glass column filled with MEA solution. The loaded solutions were analysed with the SINTEF method, based on precipitation of $BaCO_3$. A method from StatoilHydro was also tested without any luck for MEA solutions. This method was also based on precipitation of $BaCO_3$, but the sample was diluted with distillate water, which probably caused the problems. This testing took a lot of time, but resulted in a method that is easier and that takes less time to execute. High loaded solutions were then diluted with unloaded solution to produce a set of samples with different loadings and fixed concentration. The dilutions were performed by weighing a part of unloaded and loaded solutions, with an accuracy of 0.1 mg for the weight.

Viscosities were measured with a viscometer and densities with a density meter. The accuracy of the viscometer is given with 0.1 mPa·s, and the density meter with $1·10^{-5}$ g/cm^3. Measurements at high temperature for high loaded solutions results in some difficulties. 1 ml ethylene glycol is used as a solvent trap in the viscometer. At high temperatures for high loaded solutions, some CO_2 evaporates through the solvent trap. The measurement results are therefore only given with 1 decimal, to eliminate inaccurate results. The same condition effects the density measurements. CO_2 bubbles are formed in the measurements cell, and the density meter is unable to measure the density.

Density and viscosity results for unloaded MEA solutions show a significant dependence on the concentration of MEA in the solutions. The density and viscosity increase up to a certain concentration. The density and viscosity decrease with increasing temperature for a given concentration.

Density and viscosity for CO_2 loaded MEA solutions increase with increased CO_2 loading, and decrease with increased temperature for a given loading.

A literature study was performed to find comparable data for the measurement results. Density and/or viscosity data for unloaded MEA solutions were found in Lee and Lin (1995), Mandal et al. (2003), Ludvigshafen, Gas Condition and Processing and Leibush and Shorina. Some data for surface tension for different MEA solutions was found in Vàzquez et al. (1997). Results from Aspen HYSYS were also used for comparison with density, viscosity and surface tension for unloaded MEA solutions.

Literature data for CO_2 loaded MEA solutions were difficult to find, but Weiland et al. (1998) presents density and viscosity data for 10, 20, 30 and 40 wt % MEA solutions from 0 to 0.5 mole CO_2/mole MEA, at 25 ˚C. This article also presents a density and viscosity correlation. These correlations are for MEA solutions valid up to 40 wt % MEA, 0.6 mole CO_2/mole MEA and 125 ˚C. Density data for 30 wt % MEA solutions at 0.1 mole CO_2/mole MEA at 25, 40 and 50 ˚C was found in Kohl and Riesenfeld (1979). These data along with results from the correlations were used for comparison with measurement results at 25 ˚C.

Density for 50 and 70 wt % unloaded MEA solutions from 25 to 80 ˚C was compared to results from Aspen HYSYS. Figure 5 - 19 presents the results. Aspen HYSYS results for MEA solutions are valid up to 30 wt % MEA. Above this value, Aspen HYSYS is extrapolating the data. As the figure shows, Aspen HYSYS is not a good source to use above the valid conditions. This counts also for the comparison of density for pure (100 wt %) MEA from 25 – 80 ˚C, as figure 5 - 20 presents. Aspen HYSYS miscalculates the data, compared to measurement results and Leibush and Shorina results. For 30 wt % MEA solutions from 25 to 80 ˚C, Aspen HYSYS, Ludvigshafen and measurement results are quite similar for the density. The results are presented in figure 5 - 21. The last comparison of density for unloaded MEA solutions is for 20 and 40 wt % MEA solutions. Measurement results and Leibush and Shorina results are so to speak equal. For 20 wt % MEA, also results from Aspen HYSYS are quite similar. For 40 wt % MEA, Aspen HYSYS miscalculates as shown in figure 5 - 22.

Density results for CO_2 loaded MEA solutions were compared to data from Weiland et al. and Kohl and Riesenfeld. Density for 20, 30 and 40 wt % MEA solutions at 25 ˚C are quite similar to results from Weiland et al. Figure 5 - 23, 5 - 24 and 5 - 25 presents the results. As the figures shows, the results from the measurements are so to speak equal especially for the highest loadings. Results for 0.1, 0.2 and 0.3 mole CO_2/mole MEA are some what lower then the Weiland et al. results. The reason may be because of inaccurate analyse results. If the analysed loadings are some higher then calculated the dilution will decrease the loadings more than calculated for the samples. This will result in loader sample loadings, and may therefore be the reason for the deviation form the results from Weiland and Kohl and Riesenfeld. It is not prevented that the results from Weiland may also be incorrect. Figure 5 - 26 presents measurement results and Kohl and Riesenfeld results for 30 wt % MEA solutions at 25, 40 and 50 ˚C. The measurement results are also here some lower than literature results.

Weiland et al. analyse all the samples with a titrimetrical method. This method also involves uncertainties. In this work only the high loaded solutions were analysed for determination of mole CO_2 in the sample. Due to time consuming work to establish the right analysis method, the diluted samples were not analysed to check if the loading were correct compared to the calculations.

Viscosity results for 30 wt % unloaded MEA solutions were compared to Mandal et al., Gas Conditioning and Processing and Aspen HYSYS. Figure 5 - 27 presents the results. Results from the measurements and results from Gas Conditioning and Processing are quite similar. There is some bigger difference in results compared to Mandal et al., especially for 25 ˚C, and to results from Aspen HYSYS. Mandal et al. presents viscosity for pure MEA at 20 ˚C at 24.10 mPa·s, which are some what higher then what is presented in the safety, health and environmental data sheet from StatoilHydro, on 20 mPa·s. Viscosity results for pure MEA were compared to Aspen HYSYS, Gas Conditioning and Processing, Mandal et al. and Lee and Lin. Figure 5 - 28 presents the results, where all data except from Aspen HYSYS, due to invalid area, are quite similar.

Viscosity results for loaded MEA solution at 25 ˚C were compared to results from Weiland et al. Figure 5 - 29, 5 - 30 and 5 - 31 present the results. Measurement results compared to Weiland et al. results vary some, but are still quite similar.

To compare measurement results to literature data above 25 ˚C, a density and viscosity correlation introduced by Weiland et al. are used. The viscosity correlation is dependent on weight % MEA, loading, temperature, viscosity of water at the given temperature and seven parameters given by Weiland et al.. A correlation from Swindells in the Handbook of Chemistry and Physics was used to calculate the viscosity of water at the given temperature. The density correlation is dependent on the molar volume of solution and MEA, and six parameters given by Weiland et al.. In calculation of the molar volume for MEA the temperature is included. The density correlation is also dependent on the molar volume associated with the interaction between CO_2 and MEA. The parameters in this calculation are zero, and results in a molar volume associated with the interaction between CO_2 and MEA equal to zero. Parameter a and b in the density correlation are negative with a negative number in a brackets, as shown in table 3 - 22. These values are for a = -5.35162(-7) and b = -4.51417(-4). Calculations show that these parameters are exalted in the negative number in the brackets. a is therefore $-5.35162 \cdot 10^{-7}$ and b is $-4.51417 \cdot 10^{-4}$. This gives a molar volume for MEA around 60 ml/mole, which seems reasonable compared to the molar volume of water at 18 ml/mole, due to the components density and molar weight.

The correlation results are compared to results from Weiland et al. and measurement results at 25 ˚C. For temperatures above 25 ˚C, the measurement results are compared to correlation results.

Mass transfer correlations from Shetty & Cerro, Billet & Schultes, and Onda et al. with Bravo & Fair were studied in order to observe change of mass transfer due to change in viscosity and density. Figure 6 - 1 presents mass transfer coefficient results for liquid, k_L for 30 wt % MEA solutions from 0 to 0.5 mole CO_2/mole MEA. Input values to the correlations are given from John Arild Svendsen and Dag A. Eimer.

The maximum deviation for viscosity from correlation results compared to measurement results was 12 %. This gave a difference of about 2 % in mass transfer coefficient for Shetty & Cerro and Billet & Schultes and less 9 % for Onda et al. with Bravo & Fair. Figure 6 - 2 presents the results.

8 CONCLUSION

The main objective of this master thesis was to measure physical properties in different concentrations of monoethanolamine (MEA) solutions, at different temperatures and CO_2 loadings.

Density and viscosity for MEA solution are important for estimation of mass transfer in CO_2 removal by absorption. These properties are measured for 20, 30, 40, 50, 70, 90 and 100 wt % unloaded MEA solutions at 25 to 80 ˚C, and for 20, 30 and 40 wt % loaded MEA solutions at 25 to 80 ˚C, for 0.1, 0.2, 0.3, 0.4 and 0.5 mole CO_2/mole MEA.

Measurement results for MEA solutions were in good consistent to literature results. Increasing CO_2 loading significantly increase both the density and the viscosity, meanwhile increased temperature reduce both the density and viscosity.

Weiland et al. (1998) presents correlations for calculating the density and the viscosity. These correlations were used to compare measurement results with correlation results above 25 ˚C for loaded MEA solution. Maximum deviation for density from density correlation compared to measurement results was 1.5 %. Maximum deviation for viscosity from viscosity correlation compared to measurement results was 12 %.

Mass transfer correlations from Shetty & Cerro, Billet & Schultes, and Onda et al. with Bravo & Fair were studied in order to observe change of mass transfer due to change in viscosity and density. The maximum deviation for viscosity on 12 % gave a difference of about 2 % in mass transfer coefficient for Shetty & Cerro and Billet & Schultes, and less then 9 % for Onda et al. with Bravo & Fair. This shows that accurate viscosity data is not that important in calculation of mass transfer coefficients due to other uncertain parameters.

The correlations from Weiland et al. (1998) can therefore be used for calculations of density and viscosity.

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APPENDIX

Appendix 1:   Assignment text
            (*F4203 Master Thesis - CO$_2$ absorption in alkaline solution*)

Appendix 2:   Chemicals and equipments for analysis of CO$_2$ in amine solution form SINTEF
            (*Kjemikalier og utstyr for analyse av CO$_2$ i aminløsning (SINTEF)*)

Appendix 3:   Spreadsheet to the SINTEF method

Appendix 4:   Chemicals and equipments for analysis of CO$_2$ in amine solution by means of
            precipitation titration form StatoilHydro
            (*Kjemikalier og utstyr for analyse av CO$_2$ i aminløsning ved hjelp av
            fellingstitreing (StatoilHydro)*)

Appendix 5:   Spreadsheet to the StatoilHydro method

Appendix 6:   Analyse results and dilution for 20 wt % MEA

Appendix 7:   Analyse results and dilution for 30 wt % MEA

Appendix 8:   Analyse results and dilution for 40 wt % MEA (1)

Appendix 9:   Analyse results and dilution for 40 wt % MEA (2)

Appendix 10: Input to viscosity correlation from Weiland et al.

Appendix 11: Nomenclature and input for calculation of mass transfer coefficients

Høgskolen i Telemark

Avdeling for teknologiske fag

F4203 Master Thesis

CO_2 absorption in alkaline solution

<u>Student:</u> **Trine Gusfre Amundsen**

<u>Responsible professor (at HiT):</u> Lars Erik Øi

<u>Assistant advisor:</u> Dag Eimer, Berit Fostås, StatoilHydro Porsgrunn

<u>Aim:</u>

Contribute to improvements in the accuracy of design of CO_2 absorption in alkaline solutions.

<u>Detailed text:</u>

Running experiments where CO_2 is absorbed in a well-defined alkaline solution.
The experimental work must be done at the StatoilHydro facilities at Herøya where supervision and appropriate safety measures will be taken care of. For the interpretation work it is considered that Aspen HYSYS may be a reasonable tool, but Aspen Plus could be made available. Access to use in-house StatoilHydro software for the column may also be a possibility, possibly combined with making special fits of equilibrium data.

The idea is to obtain a proper definition of what the column is capable of with respect to mass transfer as characterised by mass transfer coefficients and interfacial area. (It is not foreseen a separation of these two sizes).

Background for the thesis:

This task must be seen in the context of the need for removing CO_2 from exhaust gases. In its turn, this problem arises from the need to curb the emission of climate gases needed done to reduce global warming. The preferred method for removal of CO_2 from natural gas or combustion gas is by absorption in alkaline solutions. There are serious uncertainties in the physical properties for designing such a process.

StatoilHydro is completing a new test rig to be used for research in the area described. In this test rig there is an absorption column that needs to be verified.

Practical conditions:

The working place will be StatoilHydro in Porsgrunn.

Formal acceptance (with thesis description as defined above):

Student's date and signature: 14/3-08 *Trine G. Amundsen*

Responsible professor' date and signature: 14/3 – 2008 *Klaus Ruth Øi*

The thesis work has delivery date 6.6.2008.

Appendix 2 - Kjemikalier og utstyr for analyse av CO_2 i aminløsning (SINTEF)

Kjemikalier:

Destillert vann
0,3 M $BaCl_2$
0,1 M HCl
0,1 M NaOH

Utstyr:

Titrator (785 DMP Titrino fra Metrohm)
250 ml Erlenmeyer (EM) kolbe med plastpropp (med kapillarrør)
0,6 μm membranfilter
Vakuum filtertrakt
250 ml begerglass
Automatpipette eller fullpipetter
Vekt
Magnetrører
Varmeplate

Fremgangsmåte for titrering av CO_2 i aminprøve, v.h.a. 785 DMP Titrator

1   Vei inn nøyaktig 0,5 – 1 g prøve. Noter vekten.

2   Tilsett 41,7 ml 0,3 M $BaCl_2$ og 50 ml 0,1 M NaOH i EM kolben med prøven.

3   Sett proppen med kapillarrøret i for å unngå opptak av CO_2 fra lufta.

4   Kok opp bandingen forsiktig og hold den kokende i 5 min.

5   Kolben avkjøles til romtemperatur i et vannbad.

6   Løsningen filtreres i filtertrakten gjennom membranfilteret.

7   Filterkaken og filtratet vaskes med 200 ml destillert vann. Del opp vaskingen i 4 x 50 ml slik at utfelling på glassveggen i kolbene også kommer med.

8   Legg filteret med filterkaken i et 250 ml begerglass. Vask filtertrakten med 50 ml destillert vann over i begerglasset, for å sikre at hele utfellingen med.

9   Titrer løsningen med 0,1 M HCl i overskudd slik at utfelt $BaCO_3$ løses igjen. Løsningen blir da blank. Det er viktig med god røring under oppløsningen. Noter forbruket av HCl.

10   Tilbaketitrer med 0,1 M NaOH til pH = 5.27 (omslagspunktet for syrebase titreing). Noter forbruket av NaOH.

11   Utfør en blindtest etter samme prosedyre som nevnt ovenfor.

Reaksjonsligninger:

$$Ba^{2+} \ + \ CO_2 \ + \ 2OH \ \rightarrow \ BaCO_3 \ + \ H_2O$$

$$BaCO_3 \ + \ 2HCl \ \rightarrow \ BaCl_2 \ + \ CO_2 \ + \ H_2O$$

Overskudd av HCL som ikke forbrukes i reaksjonen, titreres med NaOH.

$$HCl \ + \ NaOH \ \rightarrow \ NaCl \ + \ H_2O$$
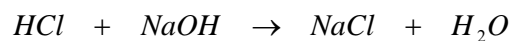
Beregning:

Antall mol CO_2 løst i prøven kan beregnes på følgene måte.

$$n_{CO2 \ per \ g \ prøve} = \frac{n_{CO2} - n_{CO2,PB}}{m_{Prøve}}$$

$$n_{CO2} = \frac{C_{HCl} \cdot V_{HCl} - C_{HCl} \cdot V_{HCl}}{2}$$

$$n_{CO2,PB} = \frac{C_{HCl} \cdot V_{HCl} - C_{HCl} \cdot V_{HCl}}{2}$$

Faktoren på 2 kommer fra at 2 mol HCl gir 1 mol CO_2.

Innveiing av kjemikaliene:

Prøve nummer	Mengde prøve [g]
A	
B	

Appendix 3 – Spreadsheet to the SINTEF method

	$m_{Prøve}$ [g]	V_{HCl} [ml]	V_{HCl} [l]	V_{NaOH} [ml]	V_{NaOH} [l]	n_{CO2} [mol]	$n_{CO2\ korr\ for\ bp}$ [mol/kg]	$n_{CO2\ gj.s.}$ [mol/kg]
A	0.8294	39.6340	0.0396	8.5748	0.0086	0.001553	1.848276	
								1.8501
B	0.9074	44.8120	0.0448	10.8045	0.0108	0.001700	1.851857	
BP		1.8400	0.0018	1.4400	0.0014	0.000020		

Konsentrasjon [M]
HCl   **0.1**
NaOH   **0.1**

Vekt % MEA	mol MEA pr. kg prøve
20	3.2744

α_{CO2} **0.5650**   mol CO_2/mol MEA

aaa   Input

bbb   Resultater

Appendix 4 - Kjemikalier og utstyr for analyse av CO_2 i aminløsning ved hjelp av fellingstitrering (StatoilHydro)

Kjemikalier:

Destillert vann (Vannet bør også være degasset)
3,0 M NaOH
0,3 M $BaCl_2$
0,1 M HCl
0,1 M NaOH

Utstyr:

Titrator (785 DMP Titrino fra Metrohm)
100 ml målekolbe
0,45 µm Cellulosefilter samt filteroppsats
250 ml begerglass
Pipetter (5-2 x 10-3 x15-2 x 50 ml)
Vekt
Vannstrålepumpe
Magnetrører
Varmeplate

Fremgangsmåte for titrering av CO_2 i aminprøve, v.h.a. 785 DMP Titrator

1   Vei inn nøyaktig i en 100 ml målekolbe. Noter vektene.

        10 ml 3,0 M NaOH
        5 ml prøve
        50 ml destillert, degasset vann

2   Vei inn nøyaktig i en ny 100 ml målekolbe. Noter vektene.

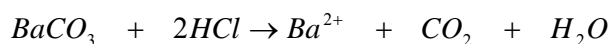   10 ml prøveløsning (Tillaget i punkt 1 i prosedyren)
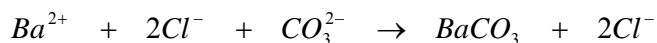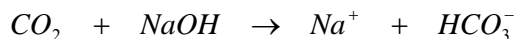   50 ml 0,3 M $BaCl_2$

3   Rist kolben forsiktig. Det dannes $BaCO_3$ som felles ut til hvitt bunnfall.
        Ikke la væsken komme opp på halsen av kolben.

4   Lag en blindprøve på samme måte, som beskrevet i punkt 1 og 2 over.

Det benyttes ikke prøve i blindprøven.

5   Varm opp kolbene så vidt til kokepunkt. Pass på så det ikke støtkoker. For å oppnå fullstendig utfelling kan kolbene stå på varmeplaten et par timer eller to døgn uten varmetilførsel.

6   Kolbene avkjøles til romtemperatur.

7   Filtrer gjennom et 0,45 μm Millipore filter. Filteret med filterkaken vaskes med 300 ml destillert, degasset vann. Dette for å få en nøytral filterkake.

8   Legg filteret med filterkaken i et 250 ml begerglass. Spyl filtertoppen med destillert, degasset vann over i begerglasset. Tørk filtertoppen med filterpapir hvis mye bunnfall henger fast.

9   Titrer løsningen med 0,1 M HCl for å løse $BaCO_3$ mens løsningen varmes opp. Noter forbruket av HCl. Total syretilsats benyttes i beregningene.

10   La løsningene koke i 5 minutter, før de avkjøles til romtemperatur. Et vannbad kan benyttes for å reduseres avkjølingstiden.

11   Titrer deretter med 0,1 M NaOH. Noter forbruket av NaOH. Forbruket av NaOH frem til pH 7 benyttes i beregningene.

12   Utfør samme prosedyre for bindprøven.

Reaksjonsligninger:

$$CO_2 \;+\; NaOH \;\rightarrow\; Na^+ \;+\; HCO_3^-$$

$$HCO_3^- \;+\; NaOH \;\rightarrow\; Na^+ \;+\; CO_3^{2-} \;+\; H_2O$$

$$Ba^{2+} \;+\; 2Cl^- \;+\; CO_3^{2-} \;\rightarrow\; BaCO_3 \;+\; 2Cl^-$$

$$BaCO_3 \;+\; 2HCl \rightarrow Ba^{2+} \;+\; CO_2 \;+\; H_2O$$

Overskudd av HCL som ikke forbrukes i reaksjonen, titreres med NaOH.

$$HCl \ + \ NaOH \ \rightarrow \ NaCl \ + \ H_2O$$
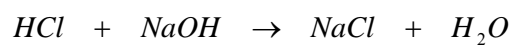
Beregning:

Et regneark benyttes for å beregne antall mol CO_2 løst i prøven.

Innveiing av kjemikaliene:

1

Prøve nummer	10 ml 3.0 M NaOH [g]	5 ml prøve [g]	50 ml degasset, destillert vann [g]
A			
B			
BP			

2

Prøve nummer	10 ml prøveløsning [g]	50 ml 0,3 M BaCl$_2$ [g]
A1		
A2		
B1		
B2		
BP		

Appendix 5 – Spreadsheet to the StatoilHydro method

Prøve	Vekt H_2O [g]	Vekt NaOH [g]	Vekt prøve [g]	Sum [g]
A	49.3630	11.3526	5.8941	66.6097
B	49.4990	11.1274	5.8180	66.4444
BP	49.6220	11.2189		60.8409

aaa Input

bbb Resultater

Prøve	Vekt $BaCl_2$ [g]	Vekt prøve[g]	Sum [g]	#g i $BaCl_2$ [g]
A 1	52.4271	10.2390	62.6661	0.9060
A 2	52.48	10.2229	62.7029	0.9046
BP	52.7376	10.247	62.9846	

Prøve	Vekt $BaCl_2$ [g]	Vekt prøve[g]	Sum [g]	#g i $BaCl_2$ [g]
B 1	52.65	10.2393	62.8893	0.8966
B 2	52.6007	10.2454	62.8461	0.8971
BP	52.7376	10.247	62.9846	

Prøve	V_{HCl} [l]	C_{HCl} [mol/l]	V_{NaOH} [l]	C_{NaOH} [l]
A 1	0.055384	0.1	0.0015	0.1
A 2	0.053572	0.1	0.0054	0.1
BP	0.00125	0.1	0.0011	0.1

Prøve	V_{HCl} [l]	C_{HCl} [mol/l]	V_{NaOH} [l]	C_{NaOH} [l]
B 1	0.056234	0.1	0.0057	0.1
B 2	0.05521	0.1	0.0010	0.1
BP	0.00125	0.1	0.0011	0.1

Prøve	mol CO_2	mol CO_2 (Korrigert for BP)	mol CO_2 i væsken	mengde CO_2 [g]
A 1	0.0027	0.0027	0.00297	0.1306
A 2	0.0024	0.0024	0.00266	0.1169
BP	0.00000537			

Prøve	mol CO_2	mol CO_2 (Korrigert for BP)	mol CO_2 i væsken	mengde CO_2 [g]
B 1	0.0025	0.0025	0.00281	0.1236
B 2	0.0027	0.0027	0.00302	0.1328
BP	0.00000537			

Gj.snittlig antall mol CO_2 i væsken		0.00281	0.1237
Avvik		0.0002	0.0097
		RSD%	7.83

Gj.snittlig antall mol CO_2 i væsken		0.00291	0.1282
Avvik		0.0001	0.0064
		RSD%	5.03

Total avarage	0.002862	mol CO_2 i væsken

Appendix 6 - Analysis and dilution results for 20 wt % MEA solutions

mol CO_2 per g prøve	0.001850	mol/g
mol MEA per g prøve	0.003274	mol/g
α_{CO2}	**0.5650**	mol/mol
m $_{prøve}$ til fortynning	**7**	g
Prøven inneholder av mol CO_2	0.012950	mol
Prøven inneholder av mol MEA	0.022921	mol
$\alpha_{CO2, ny}$	**0.1**	mol/mol
n $_{MEA}$ totalt	0.129505	mol
n $_{MEA}$ ny tilsats	0.106584	mol
m $_{MEA}$ ny tilsats	6.5101	g
vekt % MEA	**20**	vekt %
m $_{H2O}$ ny tilsats	32.5507	g
m $_{MEA}$ løsning i ny tilsats	**39.0609**	g

Ny loading	Mengde loaded MEA løsning [g]	Mengde unloaded MEA løsning [g]
0.5	50	7.801
0.4	35	17.326
0,3	25	26.501
0.2	15	32.851
0.1	7	39.061

Mengde loaded MEA løsning innveid [g]	Mengde unloaded MEA løsning innveid [g]
49.995	7.805
35.001	17.297
25.008	26.500
15.004	32.849
7.008	39.074

aaa	Input
bbb	Resultater

Appendix 7 - Analysis and dilution results for 30 wt % MEA solutions

mol CO_2 per g prøve	0.002489	mol/g
mol MEA per g prøve	0.004912	mol/g
α_{CO2}	**0.5067**	mol/mol
m $_{prøve}$ til fortynning	**8**	g
Prøven inneholder av mol CO_2	0.019909	mol
Prøven inneholder av mol MEA	0.039293	mol
$\alpha_{CO2 , ny}$	**0.1**	mol/mol
n $_{MEA}$ totalt	0.199086	mol
n $_{MEA}$ ny tilsats	0.159794	mol
m $_{MEA}$ ny tilsats	9.7602	g
vekt % MEA	**30**	vekt %
m $_{H2O}$ ny tilsats	32.5340	g
m $_{MEA}$ løsning i ny tilsats	**42.2942**	g

Ny loading	Mengde loaded MEA løsning [g]	Mengde unloaded MEA løsning [g]
0.5	50	0.868
0.4	40	13.868
0,3	30	26.868
0.2	17	33.888
0.1	8	42.294

Mengde loaded MEA løsning innveid [g]	Mengde unloaded MEA løsning innveid [g]
50.007	0.854
40.011	13.871
30.009	26.853
16.997	33.887
7.994	42.296

aaa	Input
bbb	Resultater

Appendix 8 - Analysis and dilution results for 40 wt % MEA solutions (1)

mol CO_2 per g prøve	0.003043	mol/g
mol MEA per g prøve	0.006549	mol/g
α_{CO2}	**0.4646**	mol/mol
m $_{prøve}$ til fortynning	**8**	g
Prøven inneholder av mol CO_2	0.024342	mol
Prøven inneholder av mol MEA	0.052390	mol
$\alpha_{CO2 , ny}$	**0.1**	mol/mol
n $_{MEA}$ totalt	0.243422	mol
n $_{MEA}$ ny tilsats	0.191031	mol
m $_{MEA}$ ny tilsats	11.6682	g
vekt % MEA	**40**	vekt %
m $_{H2O}$ ny tilsats	29.1705	g
m $_{MEA}$ løsning i ny tilsats	**40.8387**	g

Ny loading	Mengde loaded MEA løsning [g]	Mengde unloaded MEA løsning [g]
0.5		
0.4	40	9.048
0,3	30	23.084
0.2	18	33.344
0.1	8	40.839

Mengde loaded MEA løsning innveid [g]	Mengde unloaded MEA løsning innveid [g]
40.005	9.041
30.003	23.096
18.003	33.346
8.009	40.849

aaa	Input
bbb	Resultater

Appendix 9 - Analysis and dilution results for 40 wt % MEA solutions (2)

mol CO_2 per g prøve	0.003343	mol/g
mol MEA per g prøve	0.006549	mol/g
α_{CO2}	**0.5105**	mol/mol
m $_{prøve}$ til fortynning	**40**	g
Prøven inneholder av mol CO_2	0.133718	mol
Prøven inneholder av mol MEA	0.261952	mol
$\alpha_{CO2, ny}$	**0.5**	mol/mol
n $_{MEA}$ totalt	0.267435	mol
n $_{MEA}$ ny tilsats	0.005484	mol
m $_{MEA}$ ny tilsats	0.3350	g
vekt % MEA	**40**	vekt %
m $_{H2O}$ ny tilsats	0.8374	g
m $_{MEA}$ løsning i ny tilsats	**1.1724**	g

Ny loading	Mengde loaded MEA løsning [g]	Mengde unloaded MEA løsning [g]
0.5	40	1.172
0.4		
0.3		
0.2		
0.1		

Mengde loaded MEA løsning innveid [g]	Mengde unloaded MEA løsning innveid [g]
40.399	1.184

aaa	Input
bbb	Resultater

Appendix 10 - Input to viscosity and density correlation from Weiland et al.

Input		
T	25	˚C
T	298.15	K
η_{H20}	0.8905	mPa·s
Ω	40	wt %
α	0.10	mole CO_2/mole MEA
x_{Am}	0.1643	mole
x_{H2O}	0.81927	mole
x_{CO2}	0.01643	mole
M_{Am}	61.08	g/mole
M_{H2O}	18	g/mole
M_{CO2}	44	g/mole
V_{H2O}	18	ml/mole

x_{AM} [mole]

20 wt % MEA = 0.0687 mole MEA

30 wt % MEA = 0.1122 mole MEA

40 wt % MEA = 0.1643 mole MEA

x_{CO2} [mole]

Loading	mole CO_2		
[mole/mole]	20 wt % MEA	30 wt % MEA	40 wt % MEA
0.2	0.00687	0.01122	0.01643
0.2	0.01374	0.02244	0.03286
0.3	0.02061	0.03366	0.04929
0.4	0.02748	0.04488	0.06572
0.5	0.03435	0.05610	0.08215

Appendix 11 - Nomenclature and input for calculation of mass transfer coefficients

ρ_L	Density for liquid [kg/m³]	1045	kg/m³	
μ_L	Viscosity for liquid [kg/(m·s)]	1.30E-03	kg/(m·s)	
D_L	Diffusion coefficient for liquid [m²/s]	2.08E-09	m²/s	
l_{ratio}	Ratio of actual path length to path for α = 90 ° in rad.	1.57	rad	
b	Corrugation base length [m]	0.05	m	
α	Corrugation inclination angle [°]	45	°	Mellapak 250 Y
q	Liquid flow rate per unit packing width [m³/(m·s)]	3.18E-04	m³/(m·s)	
g	Gravitational constant [m/s²]	9.81	m/s²	
Sc_L	Schmidt number for gas, defined by μ/(ρ·D) [-]	598.0861	-	
D_G	Diffusion coefficient for gas [m²/s]	1.69E-05	m²/s	
s	Corrugation side length [m]	0.05	m	
ρ_G	Density for gas [kg/m³]	1.14	kg/m³	
u_{Le}	U_{rel} is relative velocity between gas an	39.95753	m/s	
u_{Ge}	liquid phases (U_{rel} = u_{Ge} + u_{Le})	67.192	m/s	
μ_G	Viscosity for gas [kg/(m·s)]	1.95E-05	kg/(m·s)	
Sc_G	Schmidt number for liquid, defined by μ/(ρ·D) [-]	1.01E+00	-	
C_L	Packing specific constants for liquid [-]	1.192	-	50 mm metal pall rings
d_h	Hydraulic diameter of packing defined by 4·ε/a_p [m]	0.047179	m	
$a_{p,s}$	Packing specific surface area for structured packings [m²/m³]	250	m²/m³	
$a_{p,r}$	Packing specific surface area for random packings [m²/m³]	78	m²/m³	
C_G	Packing specific constants for gas [-]	0.41	-	50 mm metal pall rings
ε	Void fraction of packing [m³/m³]	0.92	m³/m³	
h_L	Liquid hold-up [m³/m³]	0.05	m³/m³	
u_G	Superficial velocity for gas [m/s]	2.63	m/s	
d_p	Particle diameter defined by 6·(1-ε)/a_p [m]	7.50E-02	m	
a_e	Effective specific interface area [m²/m³]	58.74	m²/m³	
u_L	Superficial velocity for liquid [m/s]	8.50E-02	m/s	
c	Packing-specific constant [-]	5.23	-	