The effect of CO_2 loading on the flow behaviour of amine and water mixtures

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ABSTRACT

The understanding of flow behaviour of liquid is essential in chemical engineering applications in many aspects such as equipment design, process modelling and simulations. This study examines the effect of the presence of CO_2 in amine + H_2O mixtures of monoethanol amine (MEA) + H_2O and 2-amino-2-methyl-1-propanol (AMP) + MEA + H_2O. The relationship between shear stress and shear rate was investigated under different shear rates for both aqueous amine and CO_2 loaded aqueous amine mixtures. The study reveals that considered mixtures behave according to the Newtonian fluids indicating that the presence of CO_2 has a minimum effect on CO_2 loaded aqueous amine mixtures.

INTRODUCTION

The viscosity of liquid mixtures is important in chemical engineering applications as they are used in heat and mass transfer correlations in industrial processes[1]. In post-combustion CO_2 capture, viscosity data are involved in process simulations and design of the absorber-desorber system. The correlations are required to use the measured viscosities to perform engineering calculations for the design and mathematical modelling of the absorber column.

Understanding of the flow behaviour of amine + H_2O + CO_2 mixtures leads to the development of theoretical viscosity models with high accuracy. Semi-theoretical models like Eyring's viscosity model[2] based on absolute rate theory provide a theoretical basis for the viscosity with a parameter to correlate with measured viscosities.

Eyring pointed out that the individual molecules in a liquid at rest undergo rearrangements through molecular movements. These motions lay the foundation of the viscosity model by introducing the term of free energy of activation for viscous flow. This parameter is useful to extract the thermodynamic and structural information of pure and liquid mixtures. The proportionality between shear stress and shear rate was assumed in the model derivation[3].

The increase of CO_2 concentration in aqueous amine mixtures increases the viscosity. The studies performed by Weiland et al.[4] and Hartono et al.[5] show the viscosity variations with amine concentration, CO_2 loading and temperature in different amine + H_2O + CO_2 mixtures.

Amine + H_2O + CO_2 solution is a mixture of various ions with carbamates, bicarbonates and protonated amines. The ionic strength of the mixture increases with the increase of dissolved CO_2 and at the same time solution pH decreases. Matin et al.[6] explained how the increase of CO_2 loading could affect the viscosity in the solution. At higher CO_2 loadings, the ionic strength is high and the solution has a greater polarity. This could lead to cluster formation, higher viscosity and even phase separation.

The motivation for this study is to examine the effect of CO_2 loading on fluid behaviour of CO_2 loaded aqueous amine solutions. Both aqueous amine mixtures and CO_2 loaded aqueous amine mixtures were studied investigating the relationship between shear stress vs shear rate.

METHODOLOGY

This section discusses the experimental method for the sample preparation, CO_2 loading analysis and viscosity measurements.

Sample preparation

Table 1 lists a description of the materials used in this study. The aqueous solutions were prepared by mixing amines with degassed deionized water using a rotary evaporator. The weights of the materials were measured by using an electronic balance from METTLER TOLEDO (XS403S) having a resolution of 1 mg. Series of aqueous amine + H_2O mixtures were prepared and used to make CO_2 loaded solution by bubbling CO_2 through the solution.

Table 1. Materials used in this study.

Material	Purity [a]	source
MEA	≥ 0.995	Sigma-Aldrich
AMP	≥ 0.99	Sigma-Aldrich
CO_2	0.9999	AGA Norge AS

[a] mole fraction as given by the supplier.

CO_2 loading analysis

A titration method was adopted to determine the amount of CO_2 present in the amine + H_2O mixtures. 50 ml of each from 0.1M NaOH and 0.3M $BaCl_2$ solutions were added to a 0.1-0.2g of CO_2 loaded aqueous amine solution and boiled for approximately 10 min to fix dissolved CO_2 as $BaCO_3$. Then precipitated $BaCO_3$ was filtered and transferred into 100 ml of distilled water and titrated with 0.1M HCl until the solution pH reaches a value of 2. Subsequently, the solution was boiled and cooled again and titrated with 0.1M NaOH. Another titration was performed between 1g of CO_2 loaded solution dissolved in 100 ml of distilled water with 1M of HCl to determine the amine concentration.

Viscosity measurements

Viscosity measurements were performed using a Physica MCR 101 double-gap rheometer from Anton Paar. A liquid sample with 7ml was poured into the pressure cell. 4 bar of pressure was applied using N_2 gas to avoid amine escape due to evaporation. Variable shear rates of 200, 400, 600, 800 and 1000 1/s were maintained at the temperature of 303.15 K during the study and viscosity was measured via measured torque and shear stress by the instrument. Viscosities of both CO_2 unloaded and CO_2 loaded aqueous amine mixtures were analysed to examine the possible deviations from Newtonian behaviour.

RESULTS AND DISCUSSION

The study was performed for two types of amine + H_2O + CO_2 mixtures. Table 2 gives the details of the mixtures used in this study with relevant amine concentrations and CO_2 loadings.

Table 2. Mixtures considered in this study.

Mixtures	
MEA+H_2O+CO_2	CO_2 loading
MEA wt%	(mol CO_2 / mol amine)
30	0
	0.543
40	0
	0.548
50	0
	0.495
AMP+MEA+H_2O+CO_2	CO_2 loading
(AMP / MEA) wt%	(mol CO_2 / mol amine)
21/9	0
	0.518
24/6	0
	0.508
27/3	0
	0.511

MEA + H_2O + CO_2 mixtures contain monoethanol amine with the concentrations of 30, 40 and 50 wt% in aqueous solutions. The corresponding CO_2 loaded MEA solutions have 0.543, 0.548 and 0.495 mol CO_2/mol MEA respectively.

Fig. 1 illustrates the relation between shear stress and shear rate for CO_2 unloaded aqueous mixtures. The increase of MEA percentage in the mixtures increases the viscosity. Considered unloaded solutions exhibit the proportionality between shear stress and shear rate indicating that aqueous MEA solutions behave as a Newtonian fluid.

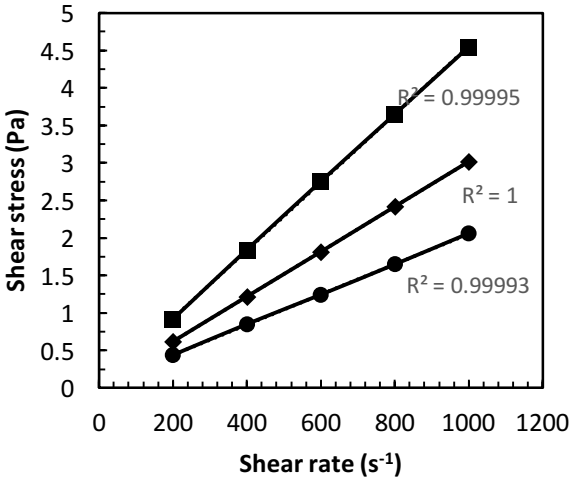

Figure 1. Shear stress vs shear rate of MEA + H_2O mixtures at 303.15 K: 30 wt% '●', 40 wt% '◆', 50 wt% '■'.

A similar study that was performed for the CO_2 loaded aqueous MEA solutions is shown in Fig. 2. The presence of CO_2 in aqueous MEA solution increases the viscosity. Fig. 2 illustrates that MEA + H_2O + CO_2 mixtures behave as Newtonian fluids as the shear stress is directly proportional to the shear rate. The formation of different ions has not affected much to change the nature of the fluid.

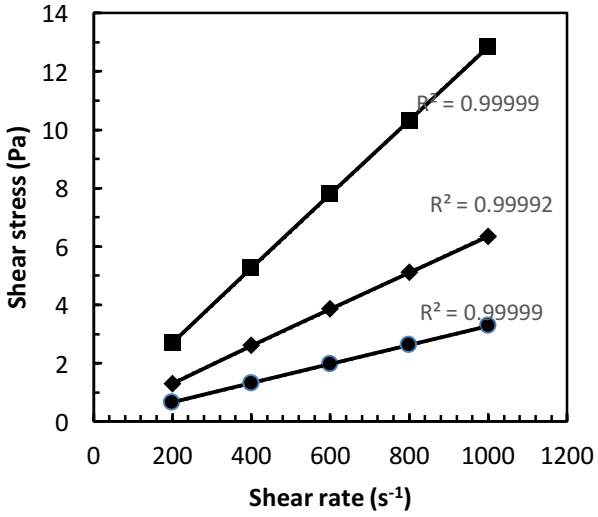

Figure 2. Shear stress vs shear rate of MEA + H_2O + CO_2 mixtures at 303.15 K: 30 wt% '●', 40 wt% '◆', 50 wt% '■'.

AMP is a sterically hindered amine and it does not form stable carbamate by reacting with CO_2. The CO_2 is converted into the form of carbonate and bicarbonate and increase the ion concentration in the mixture. The mixtures of AMP + MEA + H_2O and AMP + MEA + H_2O + CO_2 were examined for deviations from the Newtonian behaviour. AMP + MEA + H_2O + CO_2 mixtures contain 2-amino-2-methyl-1-propanol and monoethanol amine with different amine concentrations. The total amine weight percentage of all mixtures is 30 wt% and the remaining 70 wt% is H_2O. Corresponding CO_2 loadings of the solutions are given in Table 2.

Fig. 3 to 5. illustrate the comparison of relation between shear stress and shear rate of AMP + MEA + H_2O and AMP + MEA + H_2O + CO_2 mixtures. The variation in the amine concentrations caused the changes in viscosities in the mixtures. The excess properties such as excess volume, excess viscosity and excess free energy of activation for viscous flow indicates what type of intermolecular interactions are present indicating whether they are dispersion forces,

weak interaction or strong interactions like H-bonds in AMP + MEA + H_2O mixtures. Both CO_2 loaded and unloaded solutions show a linear relationship (R^2>0.99) between shear stress and shear rate. Accordingly, this reveals that solutions exhibit a Newtonian behaviour and formation of ionic species due to that the reaction between CO_2 and amines has not changed its flow characteristics compared to AMP + MEA + H_2O mixtures under considered different amine concentrations.

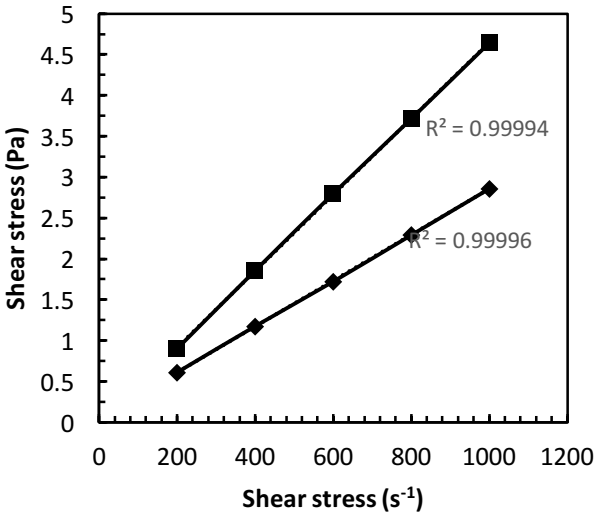

Figure 3. Shear stress vs shear rate of 21 wt % AMP + 9 wt% MEA + 70 wt% H_2O mixtures at 303.15 K: aqueous solution '◆', CO_2 loaded aqueous solution '■'.

The CO_2 loadings considered in this study for all CO_2 loaded mixtures are relatively high compared to the CO_2 loading in rich amine stream in an absorber column. Here it is assumed that the flow behaviour at less loading values exhibit the same as the results obtained.

The study shows that increase of ionic strength due to the presence of CO_2 in all considered amine + H_2O + CO_2 mixtures have minimum effect on variations in the flow behaviour even though CO_2 increases the viscosity considerably. This enables to omit the count for time-dependent change in viscosity and a non-linear stress-strain behaviour in the correlation development.

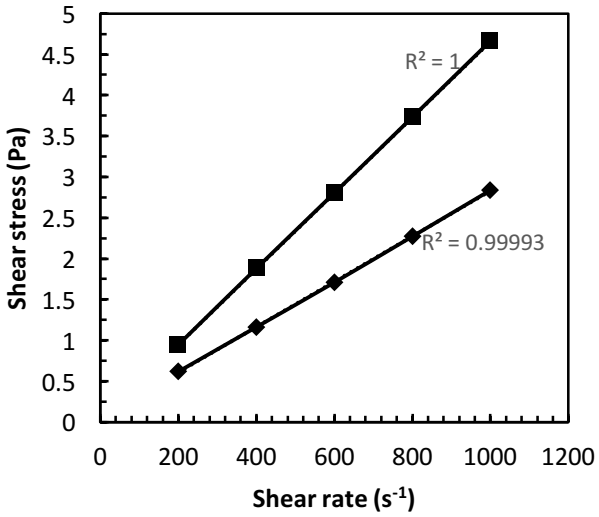

Figure 4. Shear stress vs shear rate of 24 wt % AMP + 6 wt% MEA + 70 wt% H_2O mixtures at 303.15 K: aqueous solution '◆', CO_2 loaded aqueous solution '■'.

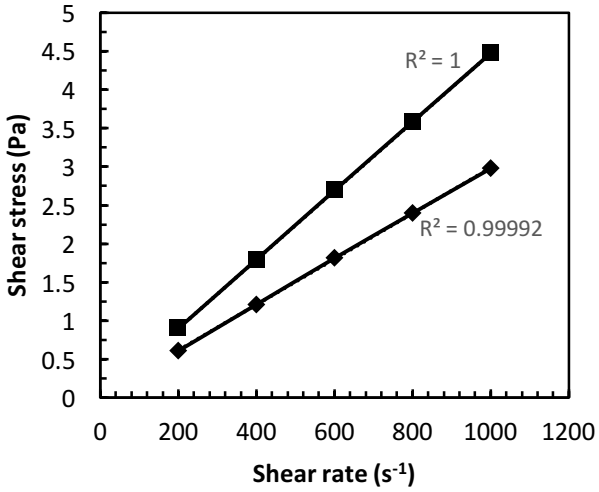

Figure 5. Shear stress vs shear rate of 27 wt % AMP + 3 wt% MEA + 70 wt% H_2O mixtures at 303.15 K: aqueous solution '◆', CO_2 loaded aqueous solution '■'.

The Eyring's viscosity representation for Newtonian fluids can be adopted to fit viscosity data to obtain a correlation with

composition and temperature as independent variables.

CONCLUSION

This study examined the fluid behaviour of different amine + H_2O and amine + H_2O + CO_2 mixtures to investigate any deviations due to the presence of CO_2 in the amine + H_2O mixtures.

First, MEA + H_2O and AMP + MEA + H_2O mixtures were studied in which the shear stress was measured under different shear rates. The observations reveal a linear relationship between shear stress and shear rate ($R^2 > 0.99$) indicating that both MEA + H_2O and AMP + MEA + H_2O mixtures behave as Newtonian fluids under different amines concentrations.

Subsequently, the same mixtures under the presence of dissolved CO_2 were examined to observe their variation of shear stress with different shear rates. Generally, the addition of CO_2 increases the viscosity. The shear stress vs shear rate relationship was linear ($R^2 > 0.99$) indicating that considered amine + H_2O + CO_2 mixtures well behave as Newtonian fluids. The formation of ionic species due to the reaction between amine with CO_2 has a negligible effect on flow behaviour. Accordingly, the viscosity models developed based on the fundamentals of Newtonian fluids can be adopted to correlate measured viscosity data.

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