Mathematical Models for Physicochemical Properties of Different Amine-based Solvents in Post combustion CO_2 Capture

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Abstract

In order to reduce global CO_2 emissions, CO_2 capture based on absorption in an amine/water mixture is an established method. To develop such processes, correct physicochemical properties like densities and viscosities are important.

The first objective of this work is to explore mathematical correlations for fitting viscosity data for aqueous Monoethanolamine (MEA) and Methyldiethanolamine (MDEA). A second objective is to evaluate the prediction of viscosity based on parameters independent of viscosity measurements.

13 developed correlations have been evaluated by comparing the maximum deviation of fitted models to the measured property, and by determining the average absolute relative deviation (AARD%). Python 3.6, MATLAB R2020b and Excel were used as the tools for regression.

The results indicated that viscosity for aqueous amines was better correlated by Eyring's viscosity model based on NRTL (Non-Random-Two Liquid model) rather than a Redlich-Kister correlation. The achieved AARD% of aqueous MEA were 2.39 for Redlich-Kister, 1.87 for Eyring-NRTL and 1.88 for the segment-based Eyring-NRTL model. The same trend was achieved for aqueous MDEA with AARD% of 3.04, 2.23 and 1.88 for different approaches.

The possibility of using data from vapor/liquid equilibrium parameters to predict viscosity in MEA/water and MDEA/water was evaluated. Using parameters in the equilibrium model NRTL from the simulation program Aspen HYSYS in a model from Karunarathne indicated that it is possible to predict viscosity reasonably well without experimental viscosity data.

Keywords: density, viscosity, Eyring's viscosity model

1. Introduction

Physicochemical properties of liquid amine mixtures have been studied as they are highly important in designing process equipment like absorption and desorption columns, heat exchangers and reboilers in the post-combustion CO_2 capture process. Viscosity is a highly influential physical property on both hydrodynamics and the mass transfer phenomenon in the absorption column. Viscosity appears in most of the mass transfer correlations for random and structures packings and heat transfer correlations for the heat exchangers. The measured viscosity data are fitted to semi-empirical and empirical mathematical expressions to calculate values for unmeasured conditions.

Eyring's viscosity model provides a theoretical background for viscosity by considering the motions of molecules from one place to another vacant position. The energy that needs to be overcome for such a motion is known as the free energy of activation for viscous flow ΔG^* (potential-energy barrier). Eyring developed the following equation for liquid viscosity (Bird *et al.*, 2002; Eyring, 1936):

$$\eta = \frac{hN_A}{V} exp\left(\frac{\Delta G^*}{RT}\right) \tag{1}$$

Where, $\eta, V, h, \Delta G^*, N_A, R, T$ are dynamic viscosity, molar volume, Planck's constant, free energy of activation for viscous flow, Avogadro's number, universal gas constant and temperature respectively.

Wu (1986) discussed an overview of the evolution of models for predicting the viscosity of liquid mixtures and the connection between the excess free energy of activation for viscous flows $\Delta G^{E*}$and Gibbs free energy of mixing ΔG. Martins *et al.* (2000) discussed the applicability of the UNIQUAC model along with Eyring's viscosity model for multicomponent liquid mixtures. In addition to the size and shape parameters for each pure component, the model requires only two adjustable parameters per binary system that can be determined by measured viscosities (Martins *et al.*, 2001). Cao *et al.* (1992) developed a model for viscosity of pure liquids and liquid mixtures based on statistical thermodynamics, local compositions, and Eyring's absolute rate theory. A further developed model was discussed by Cao *et al.* (1993) in which the molecular size was introduced to the model. The new model can predict both viscosity and activity coefficients of liquid mixtures and it was named as viscosity-thermodynamic model (UNIMOD). Weirong and Lempe (2006) combined cubic equations of states with Eyring's viscosity model to calculate viscosities in liquid mixtures. The different mixing rules of van Laar-type (VL) and Redlich-Kister-type (RK) were adopted for the comparison. Novak (2003) presented a model based on Eyring viscosity model and the NRTL model for describing deviations from ideal mixtures. The viscosity model was presented and evaluated using data from polymer-solvent systems. An extended work from Novak *et al.* (2004) transformed the original component-based Eyring-NRTL viscosity model into a segment-based Eyring-NRTL viscosity model for polymer-solvent and polymer-polymer systems that provided a more physically realistic model for large molecules. Matin *et al.* (2013) examined the use of an Electrolyte-NRTL model for the prediction of the viscosity of CO_2-loaded aqueous amine solutions. The study revealed that the Gibbs free energy of mixing as the appropriate thermodynamic quantity to replace the activation energy term for viscous in Eyring's viscosity model for liquid mixtures.

This work discussed several approaches to represent viscosities of binary aqueous amine mixtures of Monoethanolamine (MEA) and Methyldiethanolamine (MDEA) that were measured at different amine mole fractions and temperatures. The measured viscosities are available in the literature from our previous works (Karunarathne *et al.*, 2020(a); Karunarathne *et al.*, 2020(b)). There, the applicability of Eyring's viscosity model along with Redlich and Kister type polynomial for the excess free energy for viscous flow have been examined to represent viscosities.

In this study, Redlich-Kister, Eyring-NRTL, segment-based Eyring-NRTL and Eyring's viscosity model were adopted to represent measured viscosities. Different tools in Python 3.6, MATLAB R2020b and Excel were used as the tools for regression and the results were compared. This work confirmed the accuracies reported in the literature by performing the curve fitting through different tools in the Python program. Further, it discusses the applicability of NRTL (non-random two liquid) model based on vapor-liquid equilibrium (VLE) data. The proposed parameters for the NRTL model in Aspen Plus were used along with the correlation discussed in (Karunarathne and Øi, 2019). Finally, the segment-based Eyring-NRTL model was adopted to represent mixture viscosities and relevant fitting parameters were estimated by minimizing the error between correlated and measured viscosities.

2. Methodology

Eyring's viscosity model shown in (1) is applied for the binary mixtures to represent the viscosities. Then a new term called excess free energy of activation for viscous flows ΔG^{E*} is defined as in (2).

$$ln(\eta V) = \sum_{i=1}^{i=2} x_i ln(\eta_i V_i^0) + \frac{\Delta G^{E*}}{RT} \tag{2}$$

A Redlich and Kister type polynomial can be fitted to represent ΔG^{E*} as shown in (3).

$$\begin{gathered}\frac{\Delta G^{E*}}{RT} = x_1 x_2 \sum_{i=1}^{i=2} C_i (1-2x_2)^i \\ C_i = a_i + b_i(T)\end{gathered} \tag{3}$$

The NRTL model provides an expression for the excess Gibbs free energy of mixing ΔG^E as shown in (4). The model parameters are found by fitting the calculated partial pressures through the model into the measured partial pressures in experiments.

$$\frac{\Delta G^E}{RT} = x_1 x_2 \left(\frac{G_{21}\tau_{21}}{x_1 + x_2 G_{21}} + \frac{G_{12}\tau_{12}}{x_1 G_{12} + x_2} \right) \tag{4}$$

$$G_{ij} = \exp\left(-\alpha_{ij} \cdot \tau_{ij}\right) \tag{5}$$

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} + e_{ij} \ln T + f_{ij} T \tag{6}$$

$$\alpha_{ij} = c_{ij} + d_{ij}(T - 273.15K) \tag{7}$$

In this study, model parameters for the MEA + H_2O and MDEA + H_2O were taken from Aspen Plus. The correlation proposed in (8) was adopted to calculate ΔG^{E*} and use in (2) to recalculate mixture viscosities at different amine mole fractions and temperatures. A detailed discussion of developing (8) can be found in (Karunarathne and Øi, 2019) in which the parameters for ΔG^E were taken from (Schmidt *et al.*, 2007) for MEA + H_2O mixtures.

$$\frac{-\Delta G^E}{\Delta G^{E*}} = a + b \cdot x_1 \cdot T + c \cdot T^2 \tag{8}$$

The segment-based Eyring-NRTL model proposed by Novak *et al.* (2004) was adopted to fit the calculated ΔG^{E*} from Eyring's viscosity model for

MEA + H_2O and MDEA + H_2O mixtures. The modified segment-based Eyring-NRTL model to fit $\Delta G^{E*}$is shown from (9) to (10).

$$\frac{\Delta G^{E*}}{RT} = \tilde{x}_1\tilde{x}_2\left(\frac{G_{21}\,\tau_{21}}{\tilde{x}_1 + \tilde{x}_2 G_{21}} + \frac{G_{12}\tau_{12}}{\tilde{x}_1 G_{12} + \tilde{x}_2}\right) * a \quad (9)$$

$$\tilde{x}_1 = \frac{r_1 x_1}{r_1 x_1 + r_2 x_2},\ \tilde{x}_2 = 1 - \tilde{x}_1 \quad (10)$$

$$G_{12} = \exp\left(-\alpha_{12}\tau_{12}\right),\ G_{21} = \exp\left(-\alpha_{12}\tau_{21}\right) \quad (11)$$

$$\tau_{12} = a_{12} + \frac{b_{12}}{T}\ ,\ \tau_{21} = a_{21} + \frac{b_{21}}{T} \quad (12)$$

The proposed models for the viscosities have been evaluated through average absolute relative deviation and absolute maximum deviation as given in (13) and (14).

$$AARD = \frac{100\%}{N}\sum_{i=1}^{N}\left|\frac{A_i^m - A_i^c}{A_i^m}\right| \quad (13)$$

$$AMD = MAX\left|A_i^m - A_i^c\right| \quad (14)$$

3. Results and Discussion

3.1. Redlich-Kister polynomials

The previous work performed by (Karunarathne *et al.*, 2020(a)) to adopt Redlich and Kister type polynomial to represent calculated ΔG^{E*} from Eyring's viscosity model for MEA + H_2O mixtures as given in (3) was validated. Here, the density correlation proposed in (Karunarathne *et al.*, 2020(a)) for MEA + H_2O mixtures was used to calculate the mixture molar volumes rather than using measured densities. The study reveals AARD of 2.39% and an AMD of 0.84 mPa·s. A similar approach was taken to represent measured viscosities of MDEA + H_2O mixtures.

Table 1: Parameters for Redlich and Kister polynomial for excess free energy of activation for viscous flow of MDEA + H_2O mixtures.

Coefficients	
a_0	30.45
a_1	-20.4
a_2	5.081
b_0	-0.0684
b_1	0.0444
b_2	-0.00394
R^2	0.998

Tab. 1 illustrates the estimated parameters for the Redlich and Kister type polynomial. The calculated AARD and AMD are 3% and 7.2 mPa·s respectively and that is acceptable. Fig. 1 illustrates the goodness of the data fit between calculated and measured viscosities at different amine concentrations and temperatures for MDEA + H_2O mixtures.

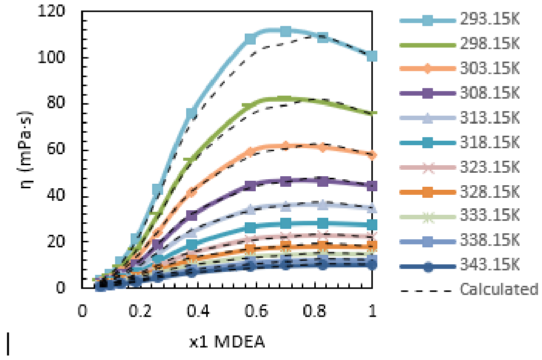

Figure 1: Comparison of calculated viscosity by Redlich-Kister polynomial for ΔG^{E*} with measured viscosity for MDEA + H_2O mixtures.

3.2. Eyring-NRTL model

The applicability of NRTL model for ΔG^{E} to represent ΔG^{E*} was discussed for MEA + H_2O and MDEA + H_2O mixtures. Tab. 2 lists the model parameters of NRTL model from (4) to (7) provided by Aspen Plus and the estimated parameters for correlation (8) are given in Tab. 3. The viscosities were calculated by (2) using pure liquid densities, viscosities and calculated ΔG^{E*} from (8). The calculated AARD and AMD of 1.9% and 1.5 mPa·s for MEA + H_2O mixtures and 3% and 7.2 mPa·s for MDEA + H_2O indicated that this approach could represent viscosity data with acceptable accuracy.

Table 2: Parameters for the NRTL model from Aspen Plus.

Parameters	MEA+H_2O	MDEA+H_2O
A_{12}	-0.0352	4.75322
A_{21}	1.1605	-1.79134
B_{12}	-438.061	159.444
B_{21}	-110.329	-716.787
$C_{12} = C_{21}$	0.3	0.1
D_{ij} ,E_{ij} , F_{ij}	0	0

Table 3: Estimated parameters for correlation (8).

Coefficients	MEA+H_2O	MDEA+H_2O
a	0.2157	0.1089
b	0.0001957	0.0004605
c	-4.674×10^{-07}	-7.107×10^{-07}
R^2	0.8441	0.9989

The deviations are relatively high at lower temperatures as shown in Fig. 2 to 5. With the increase in temperature, the real mixtures gradually come to a state of ideal mixtures due to the weakening of intermolecular interactions among unlike molecules.

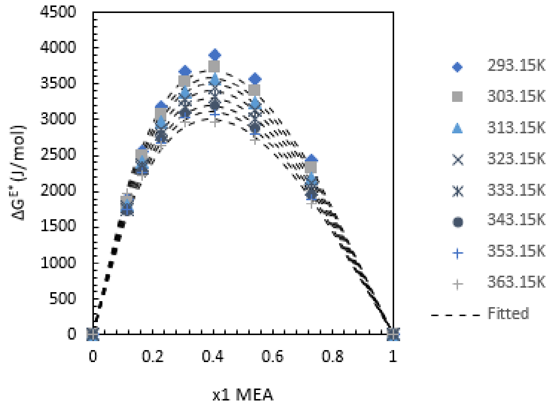

Figure 2: Comparison of calculated ΔG^{E*} using NRTL model and correlation (8) with calculated ΔG^{E*} from measured viscosities and densities for MEA + H2O mixtures.

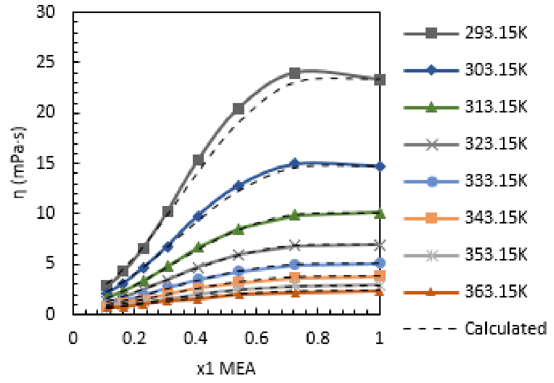

Figure 3: Comparison of calculated viscosities using NRTL model and correlation (8) with measured viscosities for MEA + H2O mixtures.

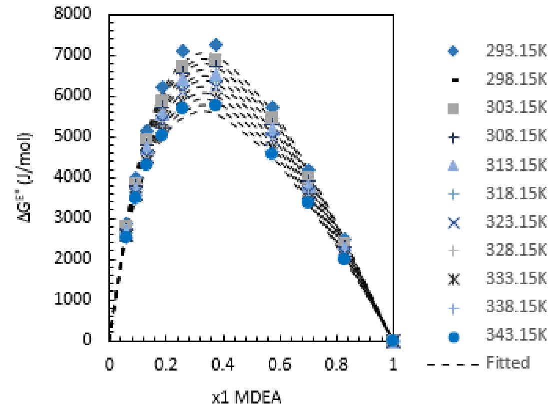

Figure 4: Comparison of calculated ΔG^{E*} using NRTL model and correlation (8) with calculated ΔG^{E*} from measured viscosities and densities for MDEA + H2O mixtures.

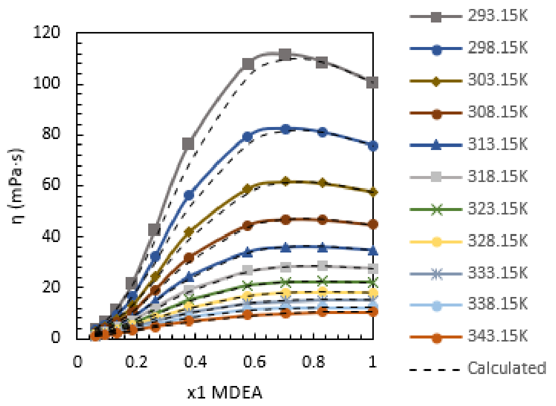

Figure 5: Comparison of calculated viscosities using NRTL model and correlation (8) with measured viscosities for MDEA + H2O mixtures.

3.3. *Segment-based Eyring-NRTL model*

In the fitting of the segment-based model for MEA+H2O mixtures, a problem with the relation was noticed. The small value of α_{12} in the parameter overview in Tab. 4 essentially renders G_{21} and G_{12} redundant, as the (11) reduces to the value of 1.

$$G_{12} = \exp(0 \cdot \tau_{12}) = 1$$
$$G_{21} = \exp(0 \cdot \tau_{21}) = 1$$

The results imply that (9) could be reduced to a function without G_{21} and G_{12}, which would exclude the nonrandomness parameter (α) from the correlation.

$$\frac{\Delta G^{E*}}{RT} = \tilde{x}_1 \tilde{x}_2 \left(\frac{\tau_{21}}{\tilde{x}_1 + \tilde{x}_2} + \frac{\tau_{12}}{\tilde{x}_1 + \tilde{x}_2} \right) * a \qquad (15)$$

Table 4: Estimated parameters for Segment-based Eyring-NRTL correlation for excess free energy of activation for viscous flow of MEA + H2O mixtures.

Parameters	**MEA +H$_2$O**
a	-8.173
a_{12}	0.2936
a_{21}	0.3271
α_{12}	4.56×10^{-11}
b_{12}	-403.6
b_{21}	1.712
r	1.52
R^2	0.995

The formula appeared to work better for Aqueous MEA if the entire formula was multiplied by -1, and if parameters α_{12}, b_{12} and r were set to contain positive numbers. Resulting in the parameters in Table 5 for (9) to (12).

Table 5: Estimated parameters for Segment-based Eyring-NRTL model correlation (improved) for MEA + H_2O mixtures.

Parameters	MEA +H_2O
a	-1
a_{12}	-14.89
a_{21}	16.71
α_{12}	0.041
b_{12}	4827
b_{21}	-6891
r	1.675
R^2	0.998

The alternative correlation gave a high coefficient of determination (R^2) with the value of 0.998, meaning that the fit for excess free energy of activation for viscous flow for MEA + H_2O mixtures became slightly better than with the Redlich-Kister correlation. The goodness of the fit for both ΔG^{E*} and measured viscosity can be seen in Fig. 6 and 7 respectively. Further, calculated AARD and AMD were 1.2 % and 1.04 mPa·s respectively.

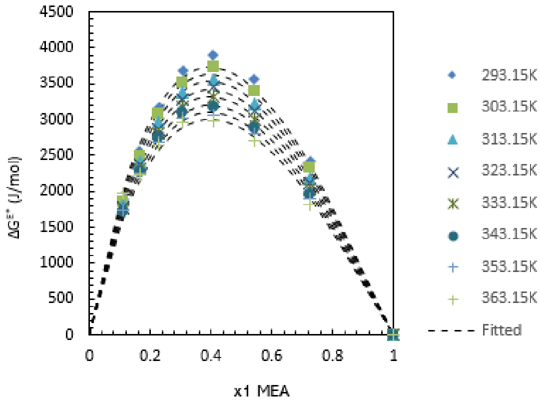

Figure 6: Estimated excess free energy of activation from the Segment-based Eyring NRTL model for aqueous MEA.

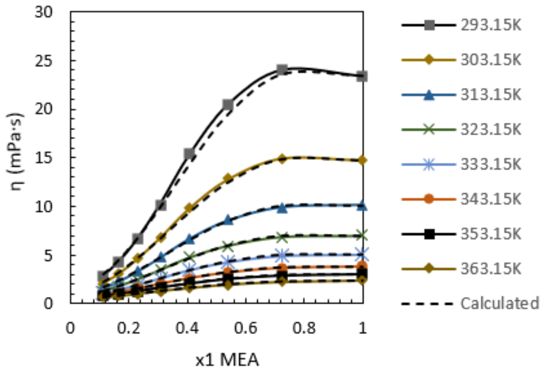

Figure 7: Comparison of measured and calculated viscosity by the segment-based Eyring-NRTL model for aqueous MEA.

The viscosities of MDEA + H_2O mixtures were found through fitted segment-based Eyring-NRTL model for calculated ΔG^{E*}. Relevant density data to calculate molar volumes were found from the fitted density data into a Redlich and Kister type polynomial discussed in Chapter 5.4.1 (Larsen, 2021). The calculated ΔG^{E*} from segment-based Eyring-NRTL model shown in Figure 8 considered estimated parameters from Tab. 6. The result was used to portray the viscosity in Figure 9, where the calculated values gave an AARD of 1.9% and an AMD of 8.1 mPa·s.

Table 6: Estimated parameters for segment-based Eyring-NRTL model for excess free energy of activation for viscous flow of MDEA + H_2O mixtures.

Parameters	MDEA + H_2O
a	1
a_{12}	-2.504
a_{21}	-3.817
α_{12}	-0.101
b_{12}	1596
b_{21}	2937
r	2.349
R^2	0.999

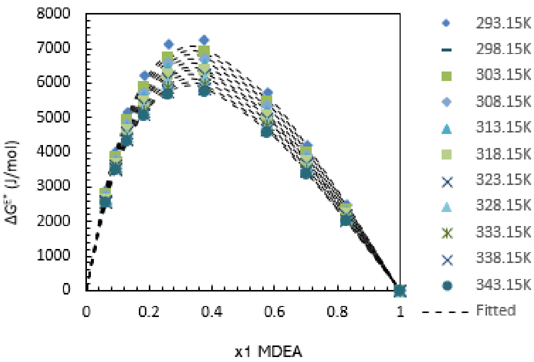

Figure 8: Fitted excess free energy of activation from the Segment-based Eyring-NRTL model for aqueous MDEA.

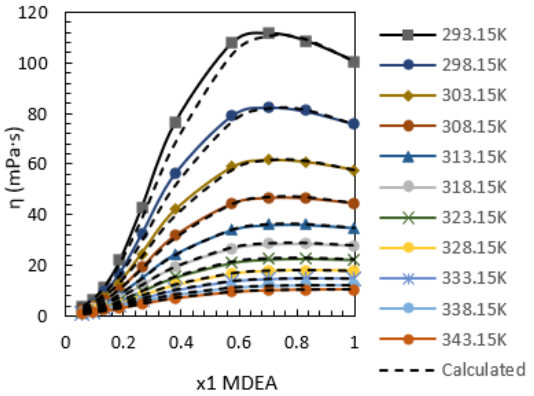

Figure 9: Comparison of calculated and measured viscosity of aqueous MDEA through the Segment-based Eyring-NRTL model.

4. Conclusion

Physicochemical properties are important in designing amine-based post combustion CO_2 capture processes as it can affect the mass transfer of CO_2 and the packing height of absorption/desorption columns. In this work, it was also found that viscosity seems to have a greater impact than density in the CO_2 capture process.

For the models for viscosity for aqueous amines, the applied methods of Redlich-Kister, Eyring-NRTL and segment-based Eyring-NRTL for ΔG^{E*} gave an AARD% of 2.39, 1.87 and 1.88 for MEA + H_2O mixtures respectively. Further, For MDEA + H_2O mixtures, these approaches were able to represent viscosities with an AARD% of 3.04, 2.23 and 1.88 respectively. The results revealed that the performed calculations connected to the NRTL model worked better for both mixtures. Eyring's model was connected to a correlation proposed in the literature and it showed the feasibility to apply the NRTL model and estimated parameters from VLE data in Aspen Plus to represent measured viscosities. In the segment-based Eyring-NRTL model, the estimation of all parameters was made possible by a correction factor. As future work, this study could extend to examining the applicability of VLE models like UNIQUAC and UNIFAC along with Eyring's viscosity model to make predictions for viscosities of binary aqueous amine mixtures.

Nomenclature

Letters	Description
A_i^m	Measured property
A_i^c	Calculated property
ΔG	Gibbs free energy of mixing
ΔG^E	Excess Gibbs free energy of mixing
ΔG^*	Free energy of activation for viscous flow
ΔG^{E*}	Excess free energy of activation for viscous flow
h	Planck‘s constant
N_A	Avogadro's number
r	Average number of segments
R	Universal gas constant
T	Temperature
V	Molar volume
x_i	Mole fraction
$\widetilde{x_i}$	Segment of moles
η	Dynamic viscosity
α	Non-randomness factor
τ	Interaction energy between different species

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