Applicability of NRTL Model for Prediction of the Viscosity of Alkanolamine + Water Mixtures

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Abstract

This study discusses the applicability of the non-random two-liquid (NRTL) model to represent viscosity for MEA (monoethanol amine) + H_2O and AMP (2-amino-2-methyl-1-propanol) + MEA (monoethanol amine) + H_2O mixtures under different amine concentrations at temperature ranges of 293.15 K– 363.15 K and 293.15 K – 343.15 K respectively. The NRTL model is adopted to determine excess Gibbs free energy of mixing ΔG^{E*} and the Eyring's viscosity model based on absolute rate theory is used to obtain excess free energy of activation for viscous flow ΔF^{E*}. The correlations are proposed for ΔF^{E*} as a function of concentration of the components, temperature and ΔG^{E*}. Correlations are capable of representing measured viscosities at 1.3 % and 0.3 % of absolute average relative deviation (AARD %) for MEA + H_2O and AMP + MEA + H_2O mixtures respectively. These deviations are acceptable for engineering calculations and correlations can be used in process design and simulations like Aspen HYSYS and ASPEN Plus.

Keywords: NRTL model, Eyring's viscosity model, MEA, AMP

1   Introduction

In the design of units involving liquid flow like gas/liquid separators and heat exchangers, it is important to predict reasonably accurate physical properties like viscosity. Correlations depending on parameters from experiments are available for some systems. Estimation methods without the need for fitted parameters is a possibility. A possibility to use parameters from e.g. vapor/liquid equilibrium models to predict viscosity.

In post combustion CO_2 capture, the physical properties of aqueous alkanolamine solutions is a key factor in various aspects such as equipment design, modeling and simulations of absorber and desorber columns. Physical properties are present in various mass and heat transfer correlations and interfacial area correlations that are necessary to evaluate in engineering applications. Accordingly, the viscosity data of aqueous alkanolamine mixtures are highly relevant to build correlations to predict viscosities for unmeasured conditions. Further correlations developed for the viscosity of aqueous alkanolamines can be used to develop correlations for the viscosity of CO_2 loaded alkanolamine mixtures.

Correlations based on statistical regression for the viscosity data have high uncertainties beyond the experimental range. The approach of Redlich-Kister (Redlich and Kister, 1948) type polynomial to fit physical properties is widely used and Islam *et al.*, (2004) and Hartono *et al.*, (2014) have taken this approach for viscosity data of aqueous MEA solutions. The Grunberg and Nissan model was used by Mandal *et al.*, (2003) to correlate different aqueous tertiary mixtures. The McAllister model (McAllister, 1960) based on Eyring's absolute rate theory for dynamic viscosity (Eyring, 1936) is used by Amundsen *et al.*, (2009) and Lee and Lin, (1995) for aqueous MEA solutions and found the parameters to fit measured viscosities. These models are capable of predicting viscosities at acceptable accuracies within the experimental range and can be used in engineering designs.

The thermodynamic information like vapor-liquid equilibrium (VLE) of liquid mixtures can be combined with a viscosity model and such models may be stated as thermodynamics-viscosity models (Cao *et al.*, 1993). The VLE data delivers information about molecular interaction, which can be used in local composition models like nonrandom two-liquid (NRTL) and UNIQUAC. This approach has been applied several times for various multicomponent liquid mixtures. Martins *et al.*, (2000) discussed the applicability of the UNIQUAC model for the viscosity predictions of binary and ternary systems. Novak *et al.*, (2004) discussed segment based Eyring-NRTL viscosity model, which was concerned about the similarities between intermolecular friction and viscosity with a local composition model like NRTL to model excess properties as both are affected by nearest neighbor molecules. The viscosity of electrolyte solutions using Eyrings's absolute rate theory has been discussed to replace excess free energy of activation for viscous flow with Gibbs free energy of mixing (Hu, 2004). For electrolyte solutions of MEA (monoethanol amine) + H_2O + CO_2, the excess free energy of activation for viscous flow was replaced by the Gibbs free energy of mixing that was calculated using the electrolyte-NRTL model (Matin *et al.*, 2013).

This study investigates the possibility to relate excess Gibbs free energy of mixing with the excess free energy of activation for viscous flow from Eyring's absolute rate theory to predict viscosities at different compositions and temperatures of MEA + H_2O and AMP (2-amino-2-methyl-1-propanol) + MEA + H_2O mixtures. Measured density and viscosity data were used to calculate the excess free energy of activation for viscous flow. The NRTL model was adopted for calculating excess Gibbs free energy of mixing and compared with the excess free energy of activation for viscous flow for the considered mixtures. Finally, viscosity predictions were compared with measured data and the accuracy was determined by calculating average absolute relative deviation (AARD %).

2 Methodology

2.1 Dynamic Viscosity Based on Eyring's Absolute Rate Theory

A universal model to predict the viscosity of any solution is challenging as solutions exhibit different characteristics that are difficult to discuss in one model. Most of the amine solutions and their blends that are discussed in amine-based CO_2 capture shows Newtonian behavior as the molecular weights are less than 5000 g·mol^{-1} (Bird *et al.*, 2002). Introducing a qualitative picture of the mechanism of momentum transport of liquids, Eyring and coworkers developed a model to predict the viscosity of liquids from other physical properties (Eyring, 1936; Bird *et al.*, 2002). Eyring's viscosity model for Newtonian fluids is given in (1) and is valid for both pure liquids and liquid mixtures (Martins *et al.*, 2000).

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

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

In order to compare with ideal solutions and to calculate the excess free energy of activation properties ΔF^{E*}, following (2) and (3) are obtained by using (1).

$$ln(\eta V) = ln(\eta V)_{ideal} + \frac{\Delta F^{E*}}{RT} \tag{2}$$

$$ln(\eta V) = \sum_i x_i ln(\eta_i V_i^o) + \frac{\Delta F^{E*}}{RT} \tag{3}$$

Where, x_i, η_i, V_i^o and ΔF^{E*} are mole fraction, viscosity of pure liquids, molar volume of pure liquids and excess free energy of activation for viscous flow respectively.

In this approach, the combination of terms of an ideal mixture and excess energy leads to an expression of viscosity in a real mixture. The ideal term of the (2) is calculated using the properties of pure liquids as given in the (3). The term $\Delta F^{E*}/RT$ describes the non-ideality of the solution viscosity (Matin *et al.*, 2013) and an appropriate model can enhance the prediction of the viscosity. Here, the possibility of using Gibbs free energy of mixing is discussed as it has been related in various ways to ΔF^{E*} in the literature. Generally, it is related as Gibbs free energy, excess Gibbs energy through proportionality factor, Gibbs free energy of mixing and Gibbs free energy of mixing multiplied by a general constant (Matin *et al.*, 2013). This study investigates the excess Gibbs free energy of mixing for MEA + H_2O and AMP + MEA + H_2O mixtures and compares it with ΔF^{E*} calculated from the measured density and viscosity data. The NRTL model was adopted to calculate Gibbs free energy of mixing for different compositions and temperatures of the mixtures.

2.2 NRTL Model

The local composition theory explains the deviation of local compositions from the bulk composition due to different strength of attractions among the molecules in the mixture. The non-random two liquid model (NRTL) is based on the local composition theory as Wilson's model (Wilson, 1964), which explains the composition variations. For a solution of m components, the excess Gibbs free energy of mixing is given as (Prausnitz *et al.*, 1999)

$$\frac{\Delta G^{E*}}{RT} = \sum_{i=1}^{m} x_i \frac{\sum_{j=1}^{m} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{m} G_{li} x_l} \tag{4}$$

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} \tag{5}$$

$$G_{ji} = exp(-\alpha_{ji}\tau_{ji}) \quad (\alpha_{ji} = \alpha_{ij}) \tag{6}$$

Where, g_{ji} and g_{ii} are energy parameters to characterize *i-j* and *i-i* interactions respectively. α_{ji} is a non-randomness parameter.

Then the ΔG^*_{mix} is calculated as a sum of both ideal mixing and an excess term due to the non-ideal behavior of the solutions.

A study performed by Schmidt *et al.*, (2007) on VLE and NRTL model for various aqueous amine solutions provide binary interaction parameters for MEA + H_2O mixtures. A similar work done by Hartono *et al.*, (2013) found relevant parameters for AMP + H_2O mixtures. There is a lack of information about interaction parameters between AMP and MEA. Hence, for the tertiary AMP + MEA + H_2O system, parameters from two binary solutions were used for the calculations. It is also possible to use the commercial process simulation program Aspen Plus to perform all the

Table 1. Summary of the Compositions and Temperatures Considered for the Density and Viscosity Measurements of Aqueous Amine Mixtures.

Solution	Composition / wt % (by weight)		Temperature / K
MEA + H₂O	0 – 100 (MEA)		293.15 – 363.15
AMP + MEA + H₂O	21/9/70	(AMP/MEA/H₂O)	293.15 – 343.15
	24/6/70		
	27/3/70		

excess free energy of mixing calculations as it has binary interaction parameters for many components in the data banks. For the missing binary interactions parameters of NRTL model, the UNIFAC model can be used to make estimations.

The density and viscosity of mixtures were measured using a DMA 4500 vibrational density meter and Physica MCR 101 rheometer with a double-gap pressure cell XL from Anton Paar. The properties were measured at different compositions and temperatures as given in Table 1.

3   Results and Discussion

The spontaneous mixing of MEA and H₂O gives negative values for Gibbs free energy of mixing. The excess Gibbs free energy ΔG^{E*} of mixing was analyzed for the compositions of x_{MEA} from 0 to 1 of MEA + H₂O mixtures. Figure 1 illustrates the calculated ΔG^{E*} from the NRTL model under different MEA concentrations and temperatures. The calculated ΔF^{E*} from measured density and viscosity is positive while the excess viscosity η^{E} calculated from (7) gives negative values for the low MEA concentration region indicating weak intermolecular attractions and gives positive values for high MEA concentration region signifying strong interactions.

$$\eta^E = \eta - \sum_{i=1}^{n} x_i \eta_i \qquad (7)$$

(n=2 for MEA + H₂O mixtures and n=3 for AMP + MEA + H₂O mixtures)

The ratio of $\Delta G^{E*}/\Delta F^{E*}$ was determined and following correlations is proposed with $R^2 = 0.99$.

$$-\Delta G^{E*}/\Delta F^{E*} = f(x_{MEA}, T) \qquad (8)$$

$$f(x_{MEA}, T) = a + b x_{MEA} T + c T^2 \qquad (9)$$

The suggested correlation was used to replace ΔF^{E*} in (3) and the viscosities were obtained accordingly. Figure 2 illustrates the comparison between measured viscosity and the correlation fit for aqueous MEA. The fit was in good agreement with measured data with AARD of 1.3% and AMD (maximum deviation) of 1.0 mPa·s as given in Table 4. This deviation is acceptable for engineering calculations and can be used to develop

correlations for the CO₂ loaded solutions. The estimated parameters for the correlation shown in (9) are given in Table 2.
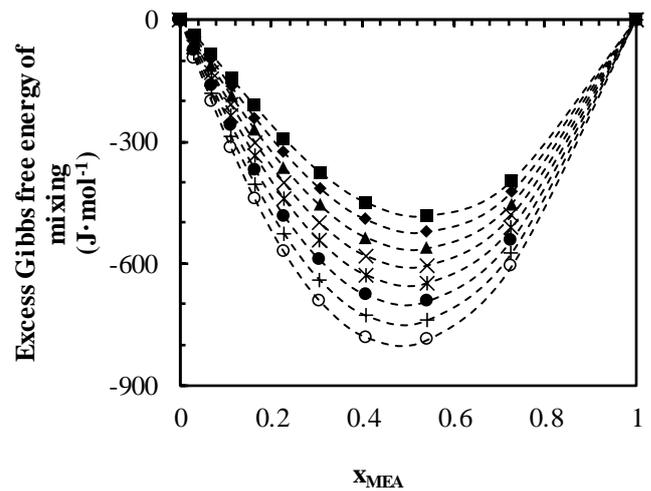

Figure 1. The variation of excess Gibbs free energy vs MEA mole fraction and temperatures: 293.15 K, 'o'; 303.15 K, '+'; 313.15 K, '●'; 323.15 K, 'ж'; 333.15 K, 'x'; 343.15 K, '▲'; 353.15 K, '◆'; 363.15 K, '■'.
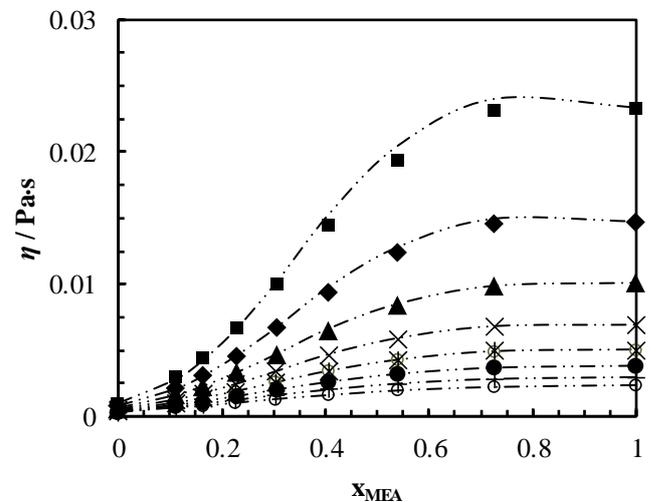

Figure 2. Comparison of measured viscosity of MEA + H₂O mixtures with correlation at temperatures: 293.15 K, '■'; 303.15 K, '◆'; 313.15 K, '▲'; 323.15 K, 'x'; 333.15 K, 'ж'; 343.15 K, '●'; 353.15 K, '+'; 363.15 K, 'o'. The dash — dotted lines represent the correlation.

Table 2. Estimated Parameters for Correlation of Viscosity of Aqueous MEA.

MEA (wt%)	Temperature (K)	No. points	Parameters
0 – 100	293.15 – 363.15	72	$a = 0.2801 \pm 0.008$ $b = (5.557 \pm 0.0164) \times 10^{-04}$ $c = (-1.623 \pm 0.0735) \times 10^{-06}$

Table 3. The Estimated Binary Parameters for the Correlation Shown in (10-13).

Parameter		AMP + MEA	MEA + H$_2$O	AMP + H$_2$O
A_0	a_{00}	-1.724 x10^4	141.854	-117.059
	a_{01}	-9.370	0.562	0.296
	a_{02}	-2.516	0.598	0.623
A_1	a_{10}	-1.870 x10^5	-143.070	141.824
	a_{11}	-97.727	-0.992	-0.040
	a_{12}	101.381	0.540	0.609
A_2	a_{20}	5.812 x10^6	111.435	-119.768
	a_{21}	5.348 x10^3	0.473	0.558
	a_{22}	-2.233 x10^3	-0.168	-0.067

The ΔG^{E*} for AMP + MEA + H$_2$O mixtures were examined using the NRTL model. Figure 3 shows the calculated ΔG^{E*} for the mixtures considered in this work. The ΔG^{E*} is negative for the considered AMP concentrations and temperatures. Further, negative η^E implies weak intermolecular interactions for the range of AMP concentrations and temperatures. As discussed in the MEA + H$_2$O mixtures, the ratio (r) of $-\Delta G^{E*}/\Delta F^{E*}$ was determined and a correlation was proposed as given in (10-13) to find the best fit for AMP + MEA + H$_2$O mixtures.

$$-\Delta G^{E*}/\Delta F^{E*} = f\left(x_{AMP}, x_{MEA}, x_{H_2O}, T\right) \tag{10}$$

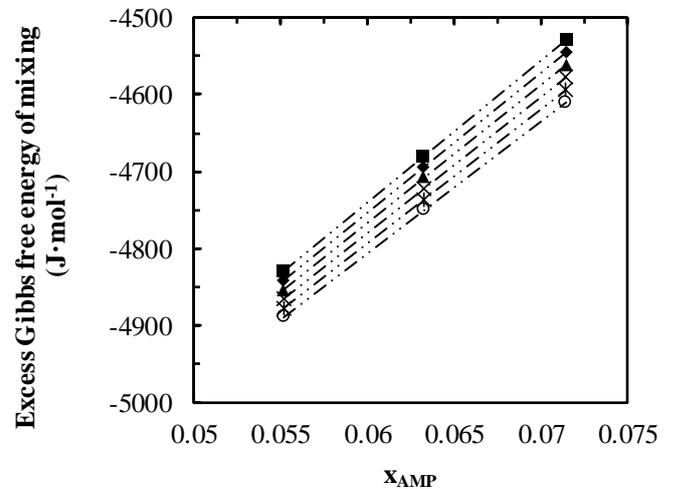The ratio $-\Delta G^{E*}/\Delta F^{E*} = r_{12} + r_{23} + r_{13}$ (11)

$$r_{jk} = x_j x_k \sum_{i=0}^{n} A_i \left(x_j - x_k\right)^i \tag{12}$$

$$A_i = a_{io} + a_{i1}(T) + a_{i2}(T)^2 \tag{13}$$

The proposed correlation was able to represent measured viscosities with acceptable accuracy as illustrated by AARD and AMD in Table 4. Figure 4 shows the comparison of the correlation with measured data in which maximum deviations were observed at low temperatures. These deviations are smaller compared to the MEA + H$_2$O mixtures since only three different compositions were considered for the study.

Table 4. Calculated AARD% and AMD (mPa·s) for Comparison of Correlation with Measured Data.

Mixture	AARD (%)	AMD (mPa·s)
MEA + H$_2$O	1.3	1.0
AMP + MEA + H$_2$O	0.3	0.02

Figure 3. The variation of excess Gibbs free energy vs AMP mole fractions and temperatures: 293.15 K, '○'; 303.15 K, 'ж'; 313.15 K, 'x'; 323.15 K, '▲'; 333.15 K, '◆'; 343.15 K, '■'.

The viscosity of CO$_2$ loaded AMP + MEA + H$_2$O mixtures are highly important in the design and mathematical modelling and simulations of CO$_2$ capture process based on absorption. The correlation discussed in this study for AMP + MEA + H$_2$O mixtures can be adopted to developed viscosity correlations for CO$_2$ loaded solutions using measured data. For use in e.g. a process simulation program like Aspen HYSYS or Aspen Plus, It is shown that the viscosities can be estimated by Hartono's correlation (Hartono *et al.*, 2014) with fitted parameters for MEA + H$_2$O mixtures with AARD 4.2 % and the semiempirical model discussed in this work can estimate viscosity with 1.3% AARD. Mandal *et al.*, (2003) used the Grunberg and

Nissan correlation (Li and Lie, 1994) to fit the viscosity data with 3.08% AARD and it is higher than that from this study for AMP + MEA + H₂O mixtures.
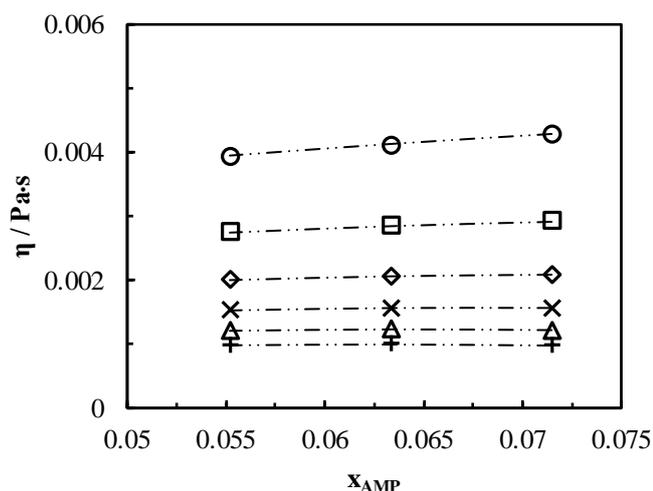

Figure 4. Comparison of measured viscosity of AMP + MEA + H₂O mixtures with correlation at temperatures: 293.15 K, '○'; 303.15 K, '□'; 313.15 K, '◇'; 323.15 K, 'x'; 333.15 K, '△'; 343.15 K, '+'. The dash — dotted lines represent the correlation.

4   Conclusion

This work presents the applicability of the NRTL model to represent viscosities of MEA + H₂O and AMP + MEA + H₂O mixtures. The Eyring's viscosity model was adopted to determine excess free energy of activation for viscous flow. Correlations based on the regression for the ratio between excess Gibbs free energy of mixing from NRTL model and excess free energy of activation for viscous flow was proposed to represent measured viscosities. The accuracy of the correlation predictions are acceptable as the AARD (%) is 1.3 and 0.3 for MEA + H₂O and AMP + MEA + H₂O mixtures respectively. The NRTL model is available in the Aspen Plus commercial software to determine vapor – liquid equilibrium. In this paper, it is shown that these types of correlations can be integrated to determine viscosity in aqueous alkanolamines.

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