Correlation of Viscosity of Aqueous Solutions of Alkanolamine Mixtures Based on the Eyring's Theory and Wong-Sandler Mixing Rule

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ABSTRACT: A viscosity model, based on Eyring’s absolute rate theory combined with a cubic PR equation of state and Wong-Sandler mixing rule, has been proposed in order to correlate viscosities of aqueous solutions of alkanolamine mixtures at atmospheric pressure and different temperatures. In the proposed method, the energy and size parameters in studied Equation of State (EoS) have been obtained using the Wong – Sandler (WS) mixing rule combined with the NRTL and Wilson Gibbs equations. The NRTL and Wilson parameters for aqueous solutions of alkanolamine mixtures have been correlated using measured viscosity data at atmospheric pressure and different temperatures. The overall average deviation between the experimental and calculated viscosities of studied aqueous solutions of alkanolamine mixtures using Wilson model is 0.92%.

KEY WORDS: WS mixing rule, Viscosity models, Equation of state, NRTL, Wilson.

INTRODUCTION
The viscosity, mostly that of liquid mixtures, is very important in engineering calculations involved in the process design for petroleum and other chemical industries. A reasonable design or analysis of a chemical process seriously depends on the true illustration of the thermophysical properties of the process streams. Among these properties, liquid viscosity emerges as one of the key transport variables needed in process design and development. Several attempts have appeared in the literature dealing with the development of dependable methods for estimating liquid viscosity of binary and multicomponent mixtures. Despite all these efforts, a theoretical description of the viscosity of liquid mixtures nowadays remains deficient due maybe to the poor understanding of the liquid state itself. Therefore, most of the estimation methods for liquid viscosity appearing in the literature are essentially empirical or semi-empirical in nature [1]. Excellent reviews and evaluations of the most important viscosity models so far reported for non-electrolyte pure liquids and liquid mixtures are given by Reid et al. [2], Mehrotra [3], Monnery et al. [4]. Other models for liquid mixture viscosity originally developed under the one-fluid basis are extensions to multicomponent systems through
the use of proper mixing rules. As noted by Poling et al. [5], essentially all viscosity models for liquid mixtures refer to solutions of liquids under or slightly higher than their normal boiling points, for example, they are limited to reduced temperatures of the pure fluids below about 0.7. At these temperature conditions, liquid viscosities are notably sensitive to the structure of the constituent molecules. For an ideal liquid mixture, there is a nearly linear manner between viscosity and composition. For a mixture containing alcohols and/or water, however, its corresponding viscosity-composition function often exhibits a maximum or a minimum and sometimes both of them [6].

A commonly used and suggested liquid mixture viscosity correlation is the Grunberg–Nissan approach [5,6]. The calculation of the low-temperature liquid viscosity for a multicomponent system using this approach is as follows:

$$\ln \eta_m = \sum_{i=1}^{n} x_i \ln \eta_i + \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j G_{ij}$$

(1)

since $G_{ii} = 0$, $x$ is the liquid mole fraction and $G_{ij}$ is an interaction parameter which is a function of the components i and j as well as the temperature (and, in some cases, the composition).

Unfortunately, the Grunberg–Nissan method does not cover aqueous mixtures. Among other approaches, the corresponding-states principle and the Eyring’s absolute rate theory have been also extensively used to represent the viscosity of liquid mixtures.

On the basis of the corresponding-states fundamental rule, Teja & Rice [7] proposed the following liquid mixture viscosity model:

$$\ln (\eta_m) = \ln (\eta) + \frac{1}{2} \left[ \ln (\eta) - \ln (\eta) \right] \frac{\omega_m - \omega^{R1}}{\omega^{R2} - \omega^{RT}}$$

(2)

where the superscripts (R1) and (R2) refer to two reference fluids, $\eta$ is the viscosity, $\omega$ the acentric factor, and $\varepsilon$ is defined here as

$$\varepsilon = \frac{\sqrt[3]{V^2}}{(T M)^{1/2}}$$

(3)

By using two reference fluids and in combination with a van Laar-type of mixing rule, viscosities of non aqueous polar binary liquid mixtures can be correlated over a specific temperature range.

Unfortunately, for forcefully related systems such as aqueous solutions, where a maximum exists in the viscosity-composition curve [8], the performance of the above mentioned models and its extension to ternary systems is not very successful [9].

Lee & Wei [10] proposed a three-reference-fluid corresponding-states viscosity model for both non-aqueous and aqueous solutions. The Lee-Wei approach incorporates oxygen, octane and water as the reference fluids.

Chevalier et al. [11] and Gaston-Bonhomme et al. [12] adapted and incorporated the UNIFAC activity coefficient method into the structure of the Eyring’s absolute rate theory to predict liquid mixture viscosities as follows:

$$\ln \eta_m = \sum_{i=1}^{n} x_i \ln (\eta_i) - \ln V_m + \frac{\Delta_g^{EC} + \Delta^{ER}_{g'}}{RT}$$

(4)

where $\Delta_g^{EC}$ which is a combinatorial term, is the same as that in the UNIQUAC model whereas the residual term $\Delta^{ER}_{g'}$ is computed using the UNIFAC method as modified by the above mentioned authors. The method, termed UNIFAC-VISCO, was successfully applied in the prediction of viscosities of mixtures containing molecules that differ considerably in size.

Based on the Eyring’s absolute rate theory, Cao et al. [13] also developed a UNIFAC-based method for liquid mixture viscosities.

For the methods based on the Eyring’s theory, the estimation of the activation Gibbs energy of flow plays an important role. McAllister [14] calculated this quantity by using an empirical cubic composition-dependent function. The resulting model is very successful in correlating viscosities of liquid mixtures. However, its parameters are strongly temperature- dependent and for ternary systems, additional ternary parameters are necessary.

Lee et al. [15] combined the Eyring’s theory with Patel-Teja Equation of State (PTEoS) to form an Eyring-Patel-Teja viscosity model. This model correlates the viscosities of binary systems very well even at elevated pressures and is successfully extended to ternary systems. However, the results for aqueous solutions are not very satisfactory possibly because the Redlich-Kister(RK)-type mixing rule was employed [16] which is not very suitable for multicomponent systems[17].
Aqueous solutions of alkanolamines are usually used in industrial processes for sour gas purification (e.g., natural, refinery, and synthesis gas streams) primarily to eliminate acid gases, such as CO$_2$ and H$_2$S. The alkanolamines that have been widely utilized in such sweetening processes are monoethanolamine (MEA), diethanolamine (DEA), and N-methyldiethanolamine (MDEA) in aqueous solution of a single amine.

In the past few years, aqueous solutions of mixed alkanolamines (a primary or secondary alkanolamine with a tertiary alkanolamine) have received rising attention for the simultaneous removal of CO$_2$ in the presence of H$_2$S from different gas streams since those solutions combine the advantages of each sole amine with the aim to generate a considerable improvement in absorption capacity as well as selective reactions and easier regeneration of the acid gas-loaded mixed amines solutions [18].

Amine molecules are often used as organic base compounds in several industrial processes. Particularly, for the optimized design of these processes, reliable experimental data are needed. For these compounds, volumetric properties such as density and its derived properties are important thermodynamic properties which characterize the chemical nature. These quantities provide important information on their molecular interactions. This is even more obvious in the case of associating substances like amines [19].

Based on the capabilities and limitations of the liquid viscosity models described above, in this paper, we propose an Eyring-theory-based model coupled with a Peng–Robinson cubic equation of state to properly correlate liquid viscosity of aqueous solutions of triethanolamine (TEA) + sulfolane (TMS) and diisopropanolamine (DIPA) + sulfolane (TMS) over a wide range of temperature in low concentrations and at atmospheric pressure. In this work the Wong-Sandler (WS) mixing rules coupled with PR EOS are used to calculate the excess Gibbs free energy and molar volumes of aqueous solutions of alkanolamine mixtures needed within the Eyring’s framework to correlate the viscosities of studied solutions at different temperatures.

**VISCOSITY MODEL**

Along with the absolute rate theory of Eyring, the dynamic viscosity $\eta$ can be estimated by [20]:

$$\eta_m V_m = \eta_m V_m = N_A h_0 \exp \left( \frac{\Delta G^*}{RT} \right)$$

(5)

Where, $\Delta G^*$ is the activation Gibbs energy of flow that is needed to get rid of molecules within the fluid from their energetically most favorable state to the activated state and the quantities $V_m$, $N_A$ and $h_0$ represent the molar volume, the Avogadro and the Planck constant, respectively. Eq.(5) can be used either for pure fluids or for mixtures. For a liquid solution the activation Gibbs energy of flow can be separated into a hypothetical ideal solution part and an excess part.

$$\Delta G^* = \Delta G^{*\text{id}} + G^{*E}$$

(6)

From the ideal activation Gibbs energy of flow the viscosity of an ideal solution is given by

$$\left( \eta_m V_m \right)_{\text{id}} = N_A h_0 \exp \left( \frac{\Delta G^{*\text{id}}}{RT} \right)$$

(7)

By combining Eqs. (6), (7), and (5) the following viscosity equation of liquid mixtures is obtained.

$$\left( \eta_m V_m \right) = \left( \eta V \right)_{\text{id}} \exp \left( \frac{G^{*E}}{RT} \right)$$

(8)

Where $\left( \eta_m V_m \right)_{\text{id}}$ can be estimated by a simple combination of the viscosities of the pure fluids $\left( \eta_i^0 V_i^0 \right)$:

$$\left( \eta V \right)_{\text{id}} = \exp \left[ \sum_{i=1}^{e} x_i \ln \left( \eta_i^0 V_i^0 \right) \right]$$

(9)

There are several ways to calculate the excess activation Gibbs energy of flow ($G^{*E}$) in the literature. One such calculation is to relate it to the excess Gibbs free energy ($G^E$). Wei & Rowley [21] proposed a simple relation

$$G^{*E} = kG^E$$

(10)

where $k$ is a proportional factor. Rather than using the above expression, the value of $G^{*E}$ can be directly calculated from an equation of state, with $k = 1$ as follows:

$$G^{*E} = G^E = RT \sum_{i=1}^{e} x_i \left( \ln \varphi_i - \ln \varphi_i^0 \right)$$

(11)

Within this framework, the use of an equation of state is useful since it allows the simultaneous determination
of the fugacity coefficient of \( i \) in the mixture \( \phi_i(x, T, P) \),
the molar volume of the liquid mixture \( V_m(x, T, P) \),
the fugacity coefficient of the pure fluid \( \phi_0^i(T, P) \) and
the molar volume of the pure liquid \( V^i_0(T, P) \). In the present
work, the calculation of these properties was performed
via the use of the one-fluid Peng–Robinson [22] Cubic
Equation of State (C EoS) [1].

\[
p = \frac{RT}{V-b} - a(T)(\frac{RT}{P_c})^2 - bV + b(V-b)
\]

With

\[
a(T) = 0.457235 - 0.077996RT
\]

\[
b = \frac{0.3796 + 1.4850 - 0.16440 + 0.016670}{P_c}
\]

where \( \alpha(T) = (1 + k(1 - \sqrt{T_i}))^2 \)

\[
\alpha(T) = \left(1 + k \left(1 - \sqrt{T_i}\right)\right)^2
\]

The application of Eq. (12) to highly non-ideal
mixtures should be done by incorporating a suitable
compositional dependence of \( a \) and \( b \) parameters into the C EoS.
The mixing rules proposed by Wong & Sandler [23]
that combine excess free-energy models with a C EoS
were used for this purpose

\[
a_m = RTD - \frac{D}{1-D}
\]

\[
b_m = \frac{Q}{1-D}
\]

With

\[
D = \sum x_i \frac{a_i}{b_iRT} + \frac{G_{\text{EX}}^i}{CRT}
\]

\[
Q = \sum x_i x_j \left(\frac{1}{2} \left( b_i - \frac{a_i}{RT} \right) + \left( b_j - \frac{a_j}{RT} \right) \right)(1-k_{ij})
\]

Where \( C \) is a constant that depends on the EoS
\((-0.6232252 \text{ for PR})\). The above mixing rules satisfy the
low-density boundary condition: quadratic composition
dependence of the second virial coefficient (Eq. (20)) and
the high-density condition: \( A_{\text{EoS}}^{\text{EX}} = G_i^{\text{EX}} \text{ at infinite}
pressure (Eq. (19)). The WS approach thus produces the
desired equation of state behavior at both low and high
densities without being density dependent and allows
extrapolation over wide ranges of temperature and
pressure. We have set the binary interaction parameters \( k_{ij} \)
in Eq. (20) to zero in our work. Using the PR EoS and
WS mixing rule, fugacity equation becomes [24]:

\[
\ln \left(\frac{\overline{Z}_{ij}(T, P, x)}{x_i} \right)_{T, N} = \frac{1}{b_i} \left( \frac{\partial N_b}{\partial N_i} \right)_{T, N,m} (Z-1) - \ln \left( Z - \frac{bP}{RT} \right) + \frac{a}{2\sqrt{2bRT}} \left( \frac{1}{Na} \left( \frac{\partial^2 Q}{\partial N_i^2} \right)_{T, N,m} - \frac{1}{b} \left( \frac{\partial N_b}{\partial N_i} \right)_{T, N,m} \right) \times \ln \left( \frac{ZRT + (1 + \sqrt{2})bP}{ZRT + (1 - \sqrt{2})bP} \right)
\]

Where

\[
\frac{1}{N} \left( \frac{\partial^2 Q}{\partial N_i^2} \right)_{T, N,m} = R T D \left( \frac{\partial N_b}{\partial N_i} \right)_{T, N,m} + R T h \left( \frac{\partial N_b}{\partial N_i} \right)_{T, N,m}
\]

\[
\frac{1}{N} \left( \frac{\partial^2 Q}{\partial N_i^2} \right)_{T, N,m} = 2 \sum_j x_j \left( b - \frac{a}{RT} \right)_{ij}
\]

\[
\left( \frac{\partial \gamma_i}{\partial N_i} \right)_{T, N,m} = \frac{a_i}{RT h} + \ln \frac{\gamma_i}{C}
\]
Table 1: Dynamic Viscosity for Pure DIPA, TEA, and TMS[25].

<table>
<thead>
<tr>
<th>T/K</th>
<th>DIPA</th>
<th>TEA</th>
<th>TMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>303.15</td>
<td>1267.80</td>
<td>449.14</td>
<td>10.23</td>
</tr>
<tr>
<td>313.15</td>
<td>298.87</td>
<td>224.20</td>
<td>7.84</td>
</tr>
<tr>
<td>323.15</td>
<td>86.67</td>
<td>119.28</td>
<td>6.18</td>
</tr>
<tr>
<td>333.15</td>
<td>30.16</td>
<td>67.20</td>
<td>4.89</td>
</tr>
<tr>
<td>343.15</td>
<td>12.32</td>
<td>39.87</td>
<td>4.21</td>
</tr>
</tbody>
</table>

Table 2: Dynamic Viscosity (η/mPa.s) of (TEA+TMS +H₂O) mixture [26].

<table>
<thead>
<tr>
<th>x TEA</th>
<th>x TMS</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>0.0812</td>
<td>0.0000</td>
<td>4.127</td>
</tr>
<tr>
<td>0.0847</td>
<td>0.0102</td>
<td>4.514</td>
</tr>
<tr>
<td>0.0682</td>
<td>0.0235</td>
<td>3.490</td>
</tr>
<tr>
<td>0.0527</td>
<td>0.0316</td>
<td>2.714</td>
</tr>
</tbody>
</table>

Table 3: Dynamic Viscosity (η/mPa.s) of (DIPA+TMS +H₂O) mixture[26].

<table>
<thead>
<tr>
<th>x DIPA</th>
<th>x TMS</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>0.0709</td>
<td>0.0000</td>
<td>5.424</td>
</tr>
<tr>
<td>0.0611</td>
<td>0.0235</td>
<td>4.213</td>
</tr>
<tr>
<td>0.0490</td>
<td>0.0328</td>
<td>3.150</td>
</tr>
</tbody>
</table>

\[
\tau_{ij} = \left( g_{ij} - g_{jj} \right) / RT \tag{28}
\]

\[
\Delta g_k = g_{ij} - g_{jj} = g_{ik} + a_{2k} T \tag{29}
\]

Which \( \alpha = 0.2 \)

and Wilson \( G_T^{\text{EX}} \) model is:

\[
\frac{g_T^E}{RT} = \sum_{i=1}^{m} x_i \ln \left( \sum_{j=1}^{m} x_j A_{ij} \right) \tag{30}
\]

\[
A_{ij} = \frac{v_i}{v_j} \exp \left( \frac{-\left( \lambda_{ij} - \lambda_{jj} \right)}{RT} \right) \tag{31}
\]

\[
\Delta \lambda_k = \lambda_{ij} - \lambda_{jj} = a_{ik} + a_{2k} T \tag{32}
\]

In which the effect of the molar volume term can be neglected. The final form of the viscosity model is thus obtained by combining Eqs. (8) and (11):

\[
\eta^{\text{id}} = \frac{\eta V^{\text{id}}}{V_m} \exp \left[ \sum_{i=1}^{c} x_i \left( \ln \varphi_i - \ln \varphi_i^0 \right) \right] \tag{33}
\]

The calculation of the kinematic viscosity for ideal solution \( (\eta V)^{\text{id}} \), Eq. (7), requires the value of the viscosity of the pure component \( \eta_i^0 \) at the temperature of interest that are given in Table 1 [25].

RESULTS AND DISCUSSION

Eq. (33) was applied to the correlation of experimental liquid viscosities of ternary mixtures including aqueous solutions of alkanolamine mixtures [26]. Experimental results of viscosities of two different ternary aqueous solutions of alkanolamines at atmospheric pressure and at different temperatures are given in Tables 2 and 3. Table 2 shows experimental viscosity values for triethanolamine + sulfolane + water mixture and Table 3 shows experimental viscosity values for diisopropanolamine + sulfolane + water mixture.
The correlation results obtained at atmospheric pressure are summarized in Tables 4-7 for two studied ternary aqueous alkanolamine systems. The resulting percent of A.A.D.s between calculated and observed viscosity data is defined by:

$$\text{AAD} = 100 \left| \frac{1}{N} \sum_{i=1}^{N} \frac{\eta_{\text{exp}} - \eta_{\text{calc}}}{\eta_{\text{exp}}} \right|$$

Tables 4 and 5 show the binary NRTL parameters at atmospheric pressure obtained using the PR–WS-NRTL model for Triethanolamine + Sulfolane + water and
Table 7: Viscosity Parameters for DIPA(1)+TMS(2)+H₂O(3) mixture in PR-Eyring-WS-Wilson model.

<table>
<thead>
<tr>
<th>$\Delta \lambda_i$</th>
<th>$a_k$(kJ/mol)</th>
<th>$a_{k'}$(kJ/mol.K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta \lambda_1 = \lambda_{12} - \lambda_{22}$</td>
<td>1263</td>
<td>-2.353</td>
</tr>
<tr>
<td>$\Delta \lambda_2 = \lambda_{13} - \lambda_{33}$</td>
<td>-6.162</td>
<td>-0.003</td>
</tr>
<tr>
<td>$\Delta \lambda_3 = \lambda_{11} - \lambda_{31}$</td>
<td>-8.344</td>
<td>0.034</td>
</tr>
<tr>
<td>$\Delta \lambda_4 = \lambda_{23} - \lambda_{33}$</td>
<td>-4.824</td>
<td>-0.002</td>
</tr>
<tr>
<td>$\Delta \lambda_5 = \lambda_{21} - \lambda_{11}$</td>
<td>0.424</td>
<td>-0.007</td>
</tr>
<tr>
<td>$\Delta \lambda_6 = \lambda_{32} - \lambda_{22}$</td>
<td>1.614</td>
<td>-0.008</td>
</tr>
</tbody>
</table>

Fig. 1: Comparison of calculated viscosities of the system TEA(1)+TMS(2)+H₂O by PR-Eyring-WS-NRTL model with experimental values Experimental values: $\odot$: $x_2=0$; $\Box$: $x_2=0.0102$; $\triangle$: $x_2=0.0235$; $\Phi$: $x_2=0.0315$.

Diisopropanolamine + Sulfolane + water ternary systems. Figs.1 and 2 compare the correlated values of viscosities systems obtained using PR-WS-NRTL model with the experimental values at different temperature for the Triethanolamine + Sulfolane + water and Diisopropanolamine + Sulfolane + water systems.

Tables 6 and 7 show the binary Wilson parameters at atmospheric pressure obtained using the PR-WS-Wilson model. Figs. 3 and 4 compare the correlated values of viscosities for two studied ternary aqueous alkanolamine solutions with the experimental values at different temperatures using PR-WS-Wilson model.

As seen in Table 8, the PR-WS-Wilson model correlates better the experimental results for the viscosities of two studied ternary aqueous alkanolamine solutions at different temperatures.

CONCLUSIONS

The PR CEoS has been incorporated into the absolute rate theory of Eyring to calculate the viscosity of aqueous alkanolamine solutions. A Wong–Sandler $G^G$-mixing rule based on the zero pressure reference state, using the NRTL and Wilson excess Gibbs free energy models, was also employed.

The experimental viscosities of ternary (DIPA+TMS+H₂O) and (TEA+TMS+H₂O) systems at different temperatures were correlated using the above mentioned models. Both the PR–WS–NRTL and PR–WS–Wilson models correlate accurately the experimental data, but the accuracy of the PR–WS–Wilson model in correlating the viscosity of the studied solutions is better than that of the PR–WS–NRTL model.
Table 8: The AAD% between the calculated and measured viscosity using WS-NRTL and WS-Wilson models

<table>
<thead>
<tr>
<th></th>
<th>AAD%</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TEA+TMS+water</td>
<td>DIPA+TMS+water</td>
<td>overall</td>
</tr>
<tr>
<td>NRTL</td>
<td>1.64</td>
<td>0.77</td>
<td>1.21</td>
</tr>
<tr>
<td>Wilson</td>
<td>1.24</td>
<td>0.60</td>
<td>0.92</td>
</tr>
</tbody>
</table>

Fig. 3: Comparison of calculated viscosities of the system TEA(1)+TMS(2)+H$_2$O by PR-Eyring-WS-Wilson model with experimental values: ○: $x_2=0$; □: $x_2=0.0102$; △: $x_2=0.0235$; ◻: $x_2=0.0315$.

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