Thermodynamic Parameters Modeling of Viscous Flow Activation in Ethylene Glycol-Water Fluid Systems

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ABSTRACT: Calculation of excess quantities of ethylene glycol + water binary fluid systems at seven absolute temperatures (293.15 to 353.15) K from experimentally determined values of density and shear viscosity were presented in previous work. The examination of related functions beside the quality of correlation from several equations on these experimental values has also been reported. Considering the quasi-equality between Arrhenius activation energy of viscosity $E_a$ and the enthalpy of activation for viscous flow $\Delta H^*$, over with their individual's contribution separately we can define partial molar activation energy $E_{a1}$ and $E_{a2}$ for ethylene glycol with water respectively. Correlation between Arrhenius parameters also shows desirable Arrhenius temperature. Comparison to the vaporization temperature in the fluid vapor equilibrium, and the limiting corresponding partial quantities permit us to predict value of the boiling points of the pure constituents. New empirical equations to estimate the boiling point are developed.

KEYWORDS: Binary fluid systems; Shear viscosity; Arrhenius activation energy; Ethylene glycol; boiling temperature.

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Research Article
INTRODUCTION

Recently we have initiated research work on application of thermodynamic/transport properties of some fluid systems in lately suggested correlation equations [1–13]. After thorough survey of literature and experimental values reported already [14], we have extended our idea of investigating the viscosity Arrhenius behavior along with a new parameter named as Arrhenius temperature \( T_\Delta \), in ethylene glycol (EG) + water (W) systems from 293.15 K to 353.15 K. Ethylene glycol is an important raw material for the polyester fibers industry [14]. In addition, EG (1,2-ethanediol) is the simplest diol where glycols find prevalent application in the explosives, pharmaceutical, aviation and in some industries, domains, and applications [14]. Generally, data of ethylene glycol (EG) + water (W) binary systems are required for the conception of the heat-exchanger materials used with antifreeze and its production such as in solar energy units, motor vehicles, heat pumps, solar energy, and water heating/cooling systems [14–25].

Furthermore, we considered that the activation energy is practically a thermodynamic state function and partial activation energies have been calculated to discuss the individual contributions of pure fluids in all the component systems under study. The new introduced parameter designated as current Arrhenius temperature \( T_\Delta \) related to each pure fluid constituent \( i \) will lead us to reliably simulate the boiling point value of the pure fluid components in the present system. We can add that the present work indicates various future directions that researchers can undertake to investigate the effect of variable shear viscosity on heat and mass transfer enhancements of nano fluids suspended in a binary base fluid. In addition, the absolute temperature dependence study of nano fluids and their thermo-physical quantities are very important because it influences the flow characteristics and, through that, influences the heat transfer performance in the cooling system [22–36]. In this way in future works, we will introduce the effects of nano fluids and their characteristics through some nano liquid features, that is, taking into consideration the reports lighting the synthesis, morphological, textural characterization and, thermal stability of nano particles [22–36]. In addition, a comprehensive understanding of the dominant factors and the trends affecting the transport process and heat transfer in nanofluids is essential for development and design. In this context, new correlation will be developed for the nanofluids attributes in terms of particles volumetric concentration and absolute temperature measurements.

VISCOSITY ARRHENIUS BEHAVIOR

Viscosity Results

In the present study, the shear viscosity \( \eta \) and density \( \rho \) values for EG (1) + W (2) fluid systems with mole composition of EG are used which have been reported in earlier work [14] where these measured quantities values of EG + W binary fluid system were used to calculate the excess molar volumes \( V^E \) and shear viscosity deviations \( \Delta \eta \) of this binary fluid system, and then fitted to the popular Redlich-Kister (RK) expression. In addition and in the same context, the deviations of shear viscosity \( \Delta \eta \) with the mole composition \( x_1 \) of EG and the variation of excess molar volume \( V^E \) were likewise fitted to the Herráez, Belda, reduced RK, relative reduced (RK) and Grunberg-Nissan equations, and these quantities were interpreted in terms of specific or nonspecific interactions and the subsequent discussions were evenly reported in previous papers [14,37–40].

The negative values of \( V^E \) may possibly be explained as a result of a high number of carbon atoms in EG, leading to low polarity and weakening of the association between EG molecules and hence forming induced dipoles-dipole complexes between EG and W [14,21,22]. Likewise, the negative values of shear viscosity deviation, show that there is an absence of specific interaction between EG and W. Also, it can show absence or disrupt or breaking of hydrogen bond in the system.

In like manner, from the investigation of the Desnoyers et al. [41] approach for the treatment of excess thermodynamic quantities for binary fluid systems, we can show that a global outlook of the provenance of the non-ideality in the systems were given by the excess quantity \( V^E \) and \( \Delta \eta \) but still can be quite misleading, notably for systems that show strong interactions at very high dilution. According to the original statements of Redlich-Kister [42], Desnoyerset al. [41] suggested that the use the reduced RK excess quantity is preferred i.e., the ratio \( \Delta \eta /x_1(1-x_1) \) or \( V^E/x_1(1-x_1) \) for this purpose. Though EG + W systems are nonelectrolyte solutions, an expansion equation was also adopted and used for the shear viscosity.
values of some nonelectrolyte solutions of binary system, equivalent to the Jones-Dole and Debye-Hückel equations [43,44] and the results reported previously [37-40] showed solute-solvent interaction feature at infinite dilution.

On the other hand, it is observed that the viscosity-absolute temperature dependence can be determined with an Arrhenius-type equation as follows:

\[ \eta = (As) \cdot e^{\frac{Ea}{RT}} \]

Where \( Ea \), \( R \) and \( As \) are, respectively, the activation energy, the perfect gas constant and the pre-exponential factor of the Arrhenius-type equation for the system. Under the logarithmic form, we can rewrite the Eq. (1) as follows:

\[ \ln \eta = \ln(As) + \frac{Ea}{RT} \]

Fig. 1 shows that the natural logarithm of shear viscosity \( \ln(\eta) \) for which we plotted the dependence versus the inverse of absolute temperature \((1/T)\) for EG (1) + W (2) fluid system in the whole domain of molar composition \((x_1)\) is practically linear for absolute temperature over the studied absolute temperature domain (293.15 to 353.15) K, and the Arrhenius parameters \( Ea \) and \( As \) are thus independent of absolute temperature. Using both least-squares fitting methods and graphics, \( ln(As) \) is the \( y \)-intercept and \( Ea/R \) is the slope of the straight line (Table 2) either for their corresponding systems \((x_1 \neq 0)\) or for the pure constituents \((i.e. \at x_1 = 0 \ or \ x_1 = 1)\).

**Correlation between Arrhenius parameters**

Fig. 2 presents the variation of the entropic factor \(-R \cdot ln(As/\text{Pa·s})/(\text{J/K.mol})\) and the activation energy \( E_a \) (kJ/mol) for \((\text{EG} \ (1)) \) and \((\text{W} \ (2))\) fluid systems in the absolute temperature domain (293.15 to 353.15) K. We observe a strict increasing of the Arrhenius activation energy \( Ea(x_1) \) of shear viscosity versus the logarithm of the Arrhenius entropic factor \(-R \cdot ln(As)\). Since, the \( As \)-values are closely related to the shear viscosity of the system in vapor-phase (Table 1, Fig. 3) [5], which it is greater, in \( W \)-rich region, than of EG and we can suppose that the molecules bounding are more correlated and ordered in vapor state. This pre-exponential factor \((As)\) is closely related to the shear viscosity of the same system in vapor-phase, it is equivalent to the shear viscosity at infinite absolute temperature \((As = \eta_\infty)\) at the normal boiling point and at the same used pressure (Table 1). Moreover, for some other before studied binary fluid systems, the correlation curve of these two quantities shows roughly linear behavior, we can cite for example water with isobutyric acid (IBA) [8,40], 1,4-dioxane [5] and N,N-dimethylacetamide with 2-ethoxyethanol (EOE) [1], water [2], formamide (FA) [4], N,N-dimethylformamide (DMF) [6], 2-methoxyethanol (MOE) [9] and methanol (Met) [7], and DMF with (Met) [3], 1,4-dioxane [10] and 2-propanol [11] and finally 1,2-dimethoxyethane (DME) with propylene carbonate (PPC) [12]. We note that for each binary fluid system; even in the case of the existing of different domains with distinct behaviors (existence of singular points) [1-13], we remark that all different branches exhibit almost the same slope of their quasi-straight line where it we can write the following standardized empirical expression at a reliable approximation:

\[ -\frac{Ea}{R} = T_A \cdot ln(As) + B \]

where the constant \( B \) is the \( y \)-intercept when \( ln(As) \) is mathematically null and it is thoroughly related to the shear viscosity of the binary fluid system at boiling point; while each binary fluid system is characterized by an \( x \)-intercept \( 1/T_A \) and is analogous to a reciprocal of an absolute
Table 1. Arrhenius activation energy $E_a$ (kJ/mol), Arrhenius pre-exponential factor $A_s$ / (10^6 Pa·s), the entropic factor of Arrhenius – $R·\ln(A_s/Pa·s)$ (J/K·mol) and, enthalpy and entropy of activation of viscous flow $\Delta H^*$ (kJ/mol) and $\Delta S^*$ (J/K·mol) for (EG (1) + W (2)) systems as a function of the mole composition ($x_1$) of EG over the temperature domain (293.15 to 353.15 K).

<table>
<thead>
<tr>
<th>$x_1$</th>
<th>$E_a$</th>
<th>$A_s$</th>
<th>-$R\ln A_s$</th>
<th>$\Delta H^*$</th>
<th>$\Delta S^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kJ/mol</td>
<td>µPa.s</td>
<td>J/K·mol</td>
<td>kJ/mol</td>
<td>J/K·mol</td>
</tr>
<tr>
<td>0.0000</td>
<td>14.801</td>
<td>2.2550</td>
<td>108.11</td>
<td>14.417</td>
<td>17.693</td>
</tr>
<tr>
<td>0.0312</td>
<td>16.166</td>
<td>1.7135</td>
<td>110.39</td>
<td>15.672</td>
<td>19.092</td>
</tr>
<tr>
<td>0.0676</td>
<td>17.420</td>
<td>1.3385</td>
<td>112.44</td>
<td>16.851</td>
<td>20.331</td>
</tr>
<tr>
<td>0.1105</td>
<td>18.439</td>
<td>1.1599</td>
<td>114.21</td>
<td>17.767</td>
<td>21.406</td>
</tr>
<tr>
<td>0.1620</td>
<td>19.683</td>
<td>0.91279</td>
<td>116.29</td>
<td>18.962</td>
<td>22.567</td>
</tr>
<tr>
<td>0.2248</td>
<td>21.130</td>
<td>0.65237</td>
<td>118.42</td>
<td>20.429</td>
<td>23.809</td>
</tr>
<tr>
<td>0.3031</td>
<td>22.424</td>
<td>0.54496</td>
<td>119.92</td>
<td>21.517</td>
<td>24.534</td>
</tr>
<tr>
<td>0.4036</td>
<td>23.548</td>
<td>0.43014</td>
<td>121.88</td>
<td>22.808</td>
<td>25.124</td>
</tr>
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<td>0.5370</td>
<td>24.753</td>
<td>0.36500</td>
<td>123.25</td>
<td>24.007</td>
<td>25.400</td>
</tr>
<tr>
<td>0.7230</td>
<td>26.117</td>
<td>0.29679</td>
<td>124.97</td>
<td>25.387</td>
<td>25.744</td>
</tr>
<tr>
<td>1.0000</td>
<td>27.393</td>
<td>0.26344</td>
<td>125.96</td>
<td>26.685</td>
<td>25.047</td>
</tr>
</tbody>
</table>

Fig. 2: Variation of the Arrhenius activation energy $E_a$ (kJ/mol) of shear viscosity and the logarithm of the entropic factor of Arrhenius – $R·\ln(A_s/Pa·s)$ / (J/K·mol) for (EG (1) and W (2)) systems. (Temperature domain 293.15 – 353.15 K).

Fig. 3: Variation of the infinite-temperature viscosity ($\eta_\infty$ or $A_s$) in µPa·s for EG (1) + W (2) systems as a function of the mole composition $x_1$ of EG. (Temperature domain: 293.15 – 353.15 K).

temperature, where this is called Arrhenius viscosity temperature for the corresponding binary fluid system.

Remarkable, we observe that for all the studied systems the $T_A$-values are rather correlated with the boiling points ($T_{bi}$) of the corresponding constituting pure fluid constituents or narrowly related to the vaporization temperature in the isobaric diagram of the corresponding binary fluid system for different molar compositions. The average $T_A$ value in the case of the EG-W systems is equal to 681.9 K with correlation factor 0.99701, whereas the boiling point of W and EG are 373.15 K and 466.45 K respectively; As concluding statement it may be observed that that the viscosity Arrhenius temperature $T_A$ is greater than the boiling points ($T_{bi}$) which indicates that in the isobaric liquid vapor equilibrium of the binary fluid system EG-W there exists a probably convexity in the shape of the $T$-$x_1$ curve.
THERMODYNAMIC CHARACTERS

Enthalpy of activation of viscous flow

If we add the absolute reaction rate theory of Allet al. [45] and Eyring et al. [46] for the fluid phase, the viscous and the free energy ($\Delta G^*$) of activation of viscous flow are related as follows:

$$
\Delta G^*(x_1,T,P) = RT \cdot \ln \left( \frac{\eta(x_1,T,P) \cdot V(x_1,T,P)}{hN_A} \right)
$$

(4)

Where $R$, $\eta$, $h$, $N_A$ and $V$ are the perfect gas constant, shear viscosity of binary fluid system, Plank’s constant, Avogadro’s number and molar volume of fluid system (Eq. (6)), at molar composition $(x_1)$, absolute temperature $T$ and pressure. Respectively, and:

$$
\Delta G^* = \Delta H^* - T \Delta S^*
$$

(5)

$$
V = \frac{x_1 M_1 + (1-x_1) M_2}{\rho}
$$

(6)

Where $\Delta H^*$ and $\Delta S^*$ are the entropy and the enthalpy of activation of viscous flow, $M_1$ and $M_2$ are the molecular weight of the pure fluid constituent of EG and W respectively and $\rho$ is the density of binary fluid system. By assuming that the parameters of activation of viscous flow $\Delta S^*$ and $\Delta H^*$ [45,46] are practically independent of absolute temperature, the temperature dependence of $(\Delta G^*)$ leads us to determine graphically the entropy $\Delta S^*$ of activation of viscous flow and the enthalpy $\Delta H^*$ which are given in Table 1. So, in Fig. 4, the ratio $(\Delta G^*/T)$ against $1/T$ is represented in the studied domain of absolute temperature from 293.15 to 353.15 K for the fluid system of EG (1)+W (2) systems at some representative mole compositions of EG, the result clearly shows a linear behavior with positive slope. Using both, graphical method and least-square fit, the y-intercept is equal to $(-\Delta S^*)$ and the slope is equal to $\Delta H^*$.

Analysis of the enthalpy ($\Delta H^*$) of activation of viscous flow and those of the $E_a$-values in the Fig. 5 shows that the $E_a$ and $\Delta H^*$ values are very closely related. Hence, we can express the increment $\Delta H^*$ as the difference between $E_a$-values and those of $(\Delta H^*)$ as follow:

$$
\delta H^* = E_a - \Delta H^*
$$

(7)

$$
\alpha(x_1,T,P) = \frac{1}{V} \left( \frac{\partial V(x_1,T)}{\partial T} \right)_p = -\frac{1}{\rho} \left( \frac{\partial \rho(x_1,T)}{\partial T} \right)_p
$$

(9)

$$
\frac{\partial V(x_1,T)}{\partial T} = -\left( \frac{\partial S(x_1,T)}{\partial P} \right)_T
$$

(10)

$$
\Delta H^* = \frac{\partial (\Delta G^*/T)}{\partial (1/T)}
$$

(11)

$$
E_a - \Delta H^* = R\alpha T^2
$$

(12)

with $T$ is approximately the average values over the studied domain of absolute temperature. The Eq.(12) is with a good accord with data given from literature [14,18,22] studied volumetric quantities of EG-W systems.

In future work, we will be interested in modeling the data of some thermophysical and thermodynamic quantities of EG-W binary system with and without presence of nanoparticles in order to inject them in eventual simulation programs. For this purpose, we preliminarily propose here the following empirical relations (Eqs.(13) and (14)) which are in excellent agreement with our experimental data in the studied absolute temperature domain.

$$
E_a = \frac{\left( \frac{E_{a_1}}{M_2} - \frac{E_{a_2}}{M_1} \right) x_1 + \frac{E_{a_2}}{M_1}}{1 - \frac{1}{M_2 - M_1} x_1 + \frac{1}{M_1}}
$$

(13)

$$
\alpha(x_1,T,P) = \frac{1}{V} \left( \frac{\partial V(x_1,T)}{\partial T} \right)_p = -\frac{1}{\rho} \left( \frac{\partial \rho(x_1,T)}{\partial T} \right)_p
$$

(14)
Fig. 4: Variation of $\Delta G^*/T$ as a function of the inverse of absolute temperature (1/T) for EG (1) + W (2) systems at some fixed mole composition $x_i$. (Temperature domain = 293.15 – 353.15 K). (●): $x_i = 0.0000$; (○): $x_i = 0.0312$; (▲): $x_i = 0.0676$; (Δ): $x_i = 0.1105$; (■): $x_i = 0.1620$; (◇): $x_i = 0.2248$; (♦): $x_i = 0.3031$; (●): $x_i = 0.4036$; (▼): $x_i = 0.5370$; (◇): $x_i = 0.7230$ and (θ): $x_i = 1.00$.

\[
\Delta H^* = \frac{\left(\frac{\Delta H_1}{M_2} - \frac{\Delta H_2}{M_1}\right)x_1 + \left(\frac{\Delta H_2}{M_2} - \frac{\Delta H_1}{M_1}\right)x_2}{1 - \frac{1}{M_2} + \frac{1}{M_1}}
\]

where the indexes 1 and 2 designate the pure constituents EG(1) and W(2) respectively. The corresponding values of ($E_a$) and ($\Delta H^*$) are given from Table 1 at $x_i = 1$ and $x_i = 0$ for $i = 1$ and 0, respectively.

Furthermore, the variation of $\Delta S^*$ and $-R\ln(As)$ with the mole composition of EG ($x_i$) are plotted in Fig. 6. It is important to note that compared with Fig. 3 we cannot significantly inspire a change in curvature and the profile of the two parameters ($-R\ln(As)$ and $E_a$) increasingmonotonically as the mole composition of EG varies, suggests that the solvent’s structure is more ordered in its present form and in the vapor phase than the other constituent. The difference between the Arrhenius entropic factor ($-R\ln(As)$) and the entropy of activation of viscous flow ($\Delta S^*$) can be expressed by an entropic increment ($\Delta S^*$) as follows:

\[
\delta S^* = -R\ln(As) - \Delta S^*
\]

and:

\[
\delta S^* = x_1\delta S^*_1 + x_2\delta S^*_2 + x_1x_2\delta S^*_{12}
\]

Fig. 5: Variation of Arrhenius activation energy $E_a$ and enthalpy of activation of viscous flow $\Delta H^*$ for EG (1) + W (2) systems as a function of the mole composition $x_i$ of EG calculated. (Temperature domain = 293.15 – 353.15 K). (●): $E_a$ (kJ/mol); (○): $\Delta H^*$ (kJ/mol).

where $\delta S^*_{12} = 7.64$ J/K.mol is an interaction increment (Fig. 6), $\delta S^*_{1} = 100.7$ J/K.mol and $\delta S^*_{2} = 90.8$ J/K.mol are entropy increments related to the pure constituents EG (1) and W (2) respectively. In like manner and considering the Eq.(17) and the precedent thermodynamic Maxwell relations, we can deduct that the entropy increment ($\delta S^*$) is related to the isobaric thermal expansion coefficient-temperature product at constant pressure and the logarithm of molar volume of the system (Eq.(18)).

\[
\Delta S^* = -\left(\frac{\partial (\Delta G^*)}{\partial (T)}\right)_P
\]

\[
\delta S^* = R \cdot \ln \left(\frac{V(\chi_1,T,P)}{k_B \cdot \chi_1}\right) + \alpha \cdot T
\]

**Partial molar activation energy**

Notice that the close correlation (eqs 7 – 18) for the thermodynamic functions of activation for viscous flow of binary liquid systems, i.e. $\Delta H^*$, $E_a$, $\Delta S^*$ and $-R\ln(As)$ discussed in previous works [1-13] and described in the (Enthalpy of activation of viscous flow)-section, we can admit that $E_a(x_i)$ is approximately a thermodynamic function and consequently we can establish the partial molar quantities $Y_1$ and $Y_2$ for EG (1) and W (2) respectively via the following two equations:

\[
Y_{1(P,T)}(x_i) = Y_{1(P,T)}(x_i) + (1 - x_i) \cdot \left(\frac{\partial Y_1(x_i)}{\partial x_1}\right)_{T,P}
\]
Table 2: Arrhenius’ current temperatures ($T_{A,i}$) / K (eq (21)), partial molar quantities relative to the activation energies $E_{A,i}$ (kJ/mol) and the logarithm of the entropic factor of Arrhenius $-\ln(As_i/Pa\cdot s)$ / (J K$^{-1}$ mol$^{-1}$) for [EG (1) + W (2)] systems as a function of the mole composition of EG ($x_i$) over the absolute temperature domain (393.15 to 353.15) K.

<table>
<thead>
<tr>
<th>$x_i$</th>
<th>$T_{A,i}$ K</th>
<th>$E_{A,i}$ kJ/mol</th>
<th>$(-\ln(As_i))_{\text{J/K.mol}}$</th>
<th>$(-\ln(As_i))_{\text{J/K.mol}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000</td>
<td>748.29</td>
<td>55.639</td>
<td>14.801</td>
<td>178.17</td>
</tr>
<tr>
<td>0.0312</td>
<td>753.33</td>
<td>51.149</td>
<td>15.039</td>
<td>169.74</td>
</tr>
<tr>
<td>0.0676</td>
<td>771.22</td>
<td>46.631</td>
<td>15.303</td>
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</tr>
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<td>790.51</td>
<td>42.091</td>
<td>15.500</td>
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<td>38.125</td>
<td>16.117</td>
<td>145.33</td>
</tr>
<tr>
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<td>139.01</td>
</tr>
<tr>
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<td>17.991</td>
<td>133.55</td>
</tr>
<tr>
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<td>971.00</td>
<td>30.077</td>
<td>19.130</td>
<td>130.30</td>
</tr>
<tr>
<td>0.5370</td>
<td>1055.4</td>
<td>28.653</td>
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</tr>
<tr>
<td>0.7230</td>
<td>1210.8</td>
<td>27.733</td>
<td>21.897</td>
<td>126.90</td>
</tr>
<tr>
<td>1.0000</td>
<td>1332.3</td>
<td>27.393</td>
<td>22.887</td>
<td>125.96</td>
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</table>

![Fig. 6: Variation of the logarithm of the entropic factor of Arrhenius $-\ln(As_i)$ (J K$^{-1}$ mol$^{-1}$) and entropy of activation of viscous flow $\Delta S^*(J K^{-1}mol^{-1})$ for EG (1) + W (2) systems as a function of the mole composition $x_i$ of EG. (Temperature domain = 293.15 –353.15 K). (●): $-\ln(As_i/Pa\cdot s)$ / (J/K.mol); (○): $\Delta S^*$ (kJ/mol).](image)

$Y_{Z,T,P}(x_i) = Y_{T,P}(x_i) - x_1 \left( \frac{\partial Y(x_i)}{\partial x_1} \right)_{T,P}$ (20)

$Y_{Z,T,P}(x_i)$ is be regarded as the partial molar quantity relative to the entropic factor of Arrhenius $-\ln(As_i)$ or the partial molar activation energy $E_{A,i}$.

Envision individual contribution of every pure constituent $(i)$ and preferential phenomena in concurrence of every fixed binary system composition $(x_1,x_2)$ is accomplished by the values partial molar activation energy $E_{A,i}(x_1)$, that represents a very interesting approximation.

Table 2 shows the values of $-\ln(As_1)$, $-\ln(As_2)$,$E_{A_i}(x_1)$ and $E_{A_2}(x_1)$, and the Fig. 7 presents a prediction of the variation of $E_{A_i}(x_1)$ and $E_{A_2}(x_1)$ against mole composition of EG($x_1$). The partial molar activation energy $E_{A_i}(x_1)$ of EG monotonously decreases from a maximum high positive value (about 55.64 kJ/mol), then decreases rapidly to reach a minimum at $(x_1 \approx 1$, pure EG) (about 27.39 kJ/mol). Additionally, the partial molar activation energy $E_{A_2}(x_1)$ of W increases very slightly from a minimum positive value (about 14.80 kJ/mol) to reach a maximum value at infinite dilution $(x_2 \approx 0$) (about 22.89 kJ/mol).

The hypothesis of the ease of integration of the introduced molecules of W in the EG-rich region explains the monotonic variation and this remains valid for the inverse cases. Also, the activation energy $E_a$ varies in a strictly monotonic manner, which does not reflect a considerable change in the structure of the solvent when we insert one constituent into the other in the systems.

Nonetheless, if we eliminate the hypothesis of Eq. (3) that the Arrhenius temperature $(T_a)$ nothing is more constant over the whole domain of composition, we can review it as variable Arrhenius' current temperatures $(T_{A,i})$. 

...
It can be determined from the following partial derivatives at selected molar composition ($x_1$):

$$T_{AI} = \left( \frac{\partial (E_{a})}{\partial (-R \ln (A_s))} \right)_p$$

(21)

We notice that the form of eq (21) is justified from the fact of the behavior’s analogy of the Arrhenius parameters $-R \ln (A_s)$ and $Ea(x_1)$ with the entropy ($\Delta S^*$) of activation of viscous flow and the enthalpy ($\Delta H^*$) respectively ([1-13], Figs. 5 and 6, Eqs. (7) to (18)). Indeed, considering the partial derivatives functions of Maxwell equations and the Gibbs free energy expression (Eq. (5)), the Eq. (21) can be considered to be equivalent to the partial derivative with respect to ($\Delta S^*$) at constant pressure.

$$\left( \frac{\partial (\Delta H^*)}{\partial (\Delta S^*)} \right)_p = T$$

(22)

Hence, the slope of the tangent to a selected point of the graph represents the experimental values of $T_{AI}$ (i.e. at selected system composition ($x_1$)). The most striking result has been obtained particularly in the vicinity of the two limits of composition domain as application of this definition. Hence, from the slopes of the two curves given in Figs. 8 and 9 we obtain interesting limiting values of Arrhenius’ current temperatures ($T_{AI}$) (see dashed lines) such as: for a very high concentration of one constituent (i) we get that $T_{AI}(x_1=1) = 475.6 \, K \approx T_m$ for the first curve ($i=1$),$T_{AI}(x_2=1) = 392.7 \, K \approx T_{b2}$ for the second curve ($i=2$), whereas for a very high dilution of the constituent (i) in the second one ($j$), we get that $T_{AI}(x_1=0) = 597.5 \, K$ for the first curve, and, $T_{AI}(x_2=0) = 227.5 \, K$ for the second curve. With this find, we can predict the boiling point of the two pure constituents at constant pressure per investigation of the shear viscosity-temperature dependence in the corresponding liquid phase. Notice that these significant results are practically verified for other studied anterior works [1–13] in different binary fluid systems (Table 3). Based on the accuracy of data and the errors made in the computations, we can conclude that the current Arrhenius temperature ($T_{AI}$) is very nearly to its corresponding boiling point for a high concentration of one constituent ($x_1=1$) whereas in the other cases, a strong correlation exists between the Arrhenius’ current temperatures ($T_{AI}$) at ($x_i \neq 1$) and the vaporization temperature of the isobaric liquid vapor equilibrium of the corresponding binary system.

The following equation asserts all these observations:

$$\lim_{x_i \to 1} \frac{\partial (E_{a})}{\partial (\ln (A_s))} \approx - R \cdot T_{bi}$$

(23)

We can then estimate with a good approximation, the boiling point ($T_{bi}$) of the pure constituent ($i$).

The present Arrhenius temperatures ($T_{AI}$)/K at ($x_i=1$) and the corresponding boiling point $T_{bi}$/K for the pure component ($i$) are correlated by the couple of constituents from some binary fluid systems appeared in anterior works (Eqs. (21) or (23)) [1-13] given in Table 3 and plotted in Fig. 10.

In order to do illustrate of the linear least square fit, we applied the methods for linear-least-squares fitting ($Y = -29.41 + 1.07X$); with a correlation coefficient $R = 0.96801$ is close to the straight line corresponding to the first bisector ($Y = +X$), where $Y = T_{AI}$ and $X = T_{bi}$. Indeed, the slope which deviates from the unit to about 6.9% is equal to 1.069and the absolute value of the $y$-intercept (29.408) is less than the standard deviation ($\sigma=46.76$) related to the ensemble of boiling points used in this correlation (414.71 K is the mean value of $T_{bi}$ values).

Starting from the fact for the mutual correlations between the current Arrhenius temperatures ($T_{AI}$) defined by the ratio of the two Arrhenius parameters some pure fluids [1–13] and the corresponding boiling point ($T_{bi}$), the Fig. 11 shows a strong causal correlation which
Table 3: Comparison between the current Arrhenius temperature \((T_A) / K\) (eq 23) for \((x=1)\) and the corresponding boiling point \(T_B / K\) of the pure constituent \((i)\) in some binary systems.

<table>
<thead>
<tr>
<th>Constituent 1</th>
<th>Constituent 2</th>
<th>Ref.</th>
<th>(T_A1 / K)</th>
<th>(T_B1 / K)</th>
<th>(T_A2 / K)</th>
<th>(T_B2 / K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF</td>
<td>Dioxane</td>
<td>[10]</td>
<td>400.7</td>
<td>426.15</td>
<td>325.1</td>
<td>374.25</td>
</tr>
<tr>
<td>DMF</td>
<td>2-Propanol</td>
<td>[11]</td>
<td>398.3</td>
<td>426.15</td>
<td>367.6</td>
<td>355.15</td>
</tr>
<tr>
<td>DMF</td>
<td>Met</td>
<td>[3]</td>
<td>394.5</td>
<td>426.15</td>
<td>316.3</td>
<td>337.85</td>
</tr>
<tr>
<td>DMA</td>
<td>Met</td>
<td>[7]</td>
<td>418.7</td>
<td>438.15</td>
<td>319.4</td>
<td>337.85</td>
</tr>
<tr>
<td>DMA</td>
<td>FA</td>
<td>[4]</td>
<td>429.1</td>
<td>438.15</td>
<td>479.6</td>
<td>483.65</td>
</tr>
<tr>
<td>DMA</td>
<td>EOE</td>
<td>[1]</td>
<td>440.0</td>
<td>438.45</td>
<td>410.0</td>
<td>408.15</td>
</tr>
<tr>
<td>DMA</td>
<td>DMA</td>
<td>[6]</td>
<td>330.6</td>
<td>348.15</td>
<td>329.1</td>
<td>426.15</td>
</tr>
<tr>
<td>DMA</td>
<td>MOE</td>
<td>[9]</td>
<td>361.5</td>
<td>438.15</td>
<td>332.3</td>
<td>397.65</td>
</tr>
<tr>
<td>DMA</td>
<td>Water</td>
<td>[2]</td>
<td>456.1</td>
<td>438.45</td>
<td>378.5</td>
<td>373.15</td>
</tr>
<tr>
<td>Dioxane</td>
<td>Water</td>
<td>[5]</td>
<td>378.6</td>
<td>374.25</td>
<td>380.5</td>
<td>373.15</td>
</tr>
<tr>
<td>IBA</td>
<td>Water</td>
<td>[8]</td>
<td>433.1</td>
<td>428.15</td>
<td>362.9</td>
<td>373.15</td>
</tr>
<tr>
<td>DME</td>
<td>PPC</td>
<td>[12]</td>
<td>361.1</td>
<td>358.15</td>
<td>530.9</td>
<td>515.15</td>
</tr>
<tr>
<td>EG</td>
<td>Water</td>
<td>a</td>
<td>475.6</td>
<td>466.45</td>
<td>392.7</td>
<td>373.15</td>
</tr>
</tbody>
</table>

Fig. 8: Correlation between the partial molar quantities relative to the activation energies \(Ea1 (kJ/mol)\) and the logarithm of the entropic factors of Arrhenius \(-R·ln(As1/ Pa1x) (J/K.mol)\) related to EG for \(\{EG (1) + W (2)\}\) systems. (Temperature domain \(= 293.15 –353.15 K\).

Fig. 9: Correlation between the partial molar quantities relative to the activation energies \(Ea2 (kJ/mol)\) and the logarithm of the entropic factors of Arrhenius \(-R·ln(As2/ Pa2x) (J/K.mol)\) related to W for \(\{EG (1) + W (2)\}\) systems. (Temperature domain \(= 293.15 –353.15 K\).

can be expressed empirically and mathematically by a hyperbolic or hyperbolic or homographic dependence (i.e. with vertical and horizontal asymptotes) as follows:

\[
E_a = \frac{R \cdot \omega}{\left(\frac{1}{T_A} - \frac{1}{T_B} \right) - \frac{1}{\tau}} + \varepsilon_0
\]

Where \(\omega\) is dimensionless constant, \(R\) is the perfect gas constant, \(\tau\) is equivalent to an absolute temperature statistically related to the minimal values that the difference between the reciprocal of Arrhenius and boiling points can be theoretically taken for the set of treated liquids organic group and \(\varepsilon_0\) is equivalent to the minimal value that the activation energy can be theoretically taken for the set of studied of viscous fluids.

Also, A new equation suggest by Haj-Kacem[47-49] presents for moderate and low viscous pure fluids...
interesting causal correlation with good concordance between the two viscosity Arrhenius parameters (lnAs and Ea) (eq (25)) which have not very low values of pre-experimental factor (42 nPa·s < As < 45 µPa·s, i.e. -17 < ln(As /Pa·s) < 10) and not very high values of activation energy (6 < Ea < 30 kJ·mol⁻¹).

Also, a new equation suggest by Haj-Kacem[47-49] presented for moderate and low viscous pure fluids correlating (lnAs)and (Ea) (viscosity Arrhenius parameters) (Eq. (25)) with good accordance that have not very low values of pre-experimental factor (42 nPa·s < As < 45 µPa·s, i.e. -17 < ln(As /Pa·s) < 10) and not very high values of activation energy (6 < Ea < 30 kJ·mol⁻¹).

\[ E_a = \lambda \cdot R \times (-lnA_s)_{q_0} \]  \hspace{1cm} (25)

where \( R \) is the perfect gas constant, \( q_0 = 2.933 \) and \( \lambda = 1 \) K.

We observe that this equation can be also used for the two parameters related to some binary fluid systems with a good approximation. Furthermore, this model would be interesting in various physicochemical areas. Also, it will be very advantageous for engineering data and it will let to estimate one unknown parameter when the second one is known (Eq. (25) or Eq. (26)), or can be otherwise estimate by some theories suggested in the literature [47].

\[ lnA_s = -\frac{E_a}{R} \cdot \frac{1}{\gamma_0} \]  \hspace{1cm} (26)

By means of a wide range of validation (5 < \( E_a < 60 \) kJ/mol) and (−25 < ln(As /Pa·s) < -9) we can get the same results with the Messaâdi equation [50,51]:

\[ ln(A_s) = \frac{-E_a}{RT_0} \left( 1 - e^{-\frac{ln(As)}{\gamma_0}} \right) \]  \hspace{1cm} (27)

\[ Ea = -\frac{RT_0 \cdot [ln(A_s) + q_0]}{\left( 1 - e^{-\frac{ln(As)}{\gamma_0}} \right)} \]  \hspace{1cm} (28)

Where \((T_0)\) is the limiting Arrhenius temperature \((T_0 = 289 \pm 4)\) K, \( R \) is the perfect gas constant, \((\gamma_0 = (37.5 \pm 5.6) \times 10^3)\) and \((q_0) = 9.02 \pm 0.54\) are two dimensionless constants[50,51].

In consideration of the causal correlations shown in Figs. 11 and 12, and eqs (24), (25) and (26) we can propose direct correlation between the activation energy \(Ea\) expressed and the boiling point \(T_b\) by the following empirical equation:

\[ T_b(Ea) = -\frac{E_a}{68 - 4.05 \times Ea^{0.34}} \]  \hspace{1cm} (29)

Nevertheless, this equation becomes invalid for the case of fluids with low or high shear viscosity notably for low boiling point \((T_b<T_{b, water})\) due the limitation of the validity domain of Eqs. (25) and (26) (6 < \(Ea< 30\) kJ/mol).

In the same way and in place of the activation energy \(Ea\) variable, we can obtain the following empirical expression eq (30) instead of eq (29) if we consider the (lnAs) as a variable:

\[ T_b(lnA_s) = \frac{(-lnA_s)^{2.933}}{8.2 + lnA_s} \]  \hspace{1cm} (30)

In addition, due to the entropic factor domain restriction (-17 < ln(As /Pa·s) < -10) we mark the same previous conclusion. Although, as was expected from the Fig. 12 presenting the comparison of experimental and calculated boiling points by means of the two Eqs. (29) and (30), we can conclude that there are also two classes of causal correlations. Indeed, we indicate that the two different points’ forms don’t match.

We conclude that the causal correlation, between the boiling point and the two Arrhenius parameters \(Ea\) or \(lnAs\) is implicitly due to varied chemical and physical quantities for which there are some that are common for the two Arrhenius parameters although others are related only to a single parameter \(Ea\) or \(lnAs\). Explicit expression of \(T_b(Ea,lnAs)\) will be proposed in future work.
to correcting this observation, for which the two viscosity Arrhenius parameters appear alternatively in the composition [52-55].

CONCLUSIONS

Some novel theoretical approaches have been released by studying the derived partial molar quantities and variation of Arrhenius activation energy against molar composition, on the basis of the same experimental data of densities and shear viscosities of EG + W binary fluid systems at atmospheric pressure and for seven value of absolute temperature subject to a range 293.15-353.15 K [14].

Variation of the viscosity’s Arrhenius’ activation energy and the enthalpy of activation of viscous flow of pure constituents (EG and W) as a function of the system molar composition is predicted. For binary fluid systems, the correlation between the two Arrhenius parameters ($\ln(\text{As})$) and ($E_a$) makes it possible to predict the viscosity Arrhenius temperature which characterizes the binary fluid system and can supply information on the vaporization temperature of the isobaric liquid-vapor equilibrium.

So, we have determined the partial molar activation energy in order to understand the contributions of every pure constituent in the system assuming that the activation energy is a thermodynamic quantity. Over the studied domain of absolute temperature, the correlation between the logarithm of the entropic factors of Arrhenius for EG + W systems and the molar quantities relative to the activation energies can show an approximately linear behavior i.e. no remarkable change in curvature. An empirical equation is then suggested at the base of the quasi-linear behavior introducing a new parameter $T_\alpha$ which characterizes every binary system and is denoted as the viscosity Arrhenius temperature. In the case of molar quantities, over the whole domain of composition we consider that the Arrhenius temperature ($T_\alpha$) is not any more a constant, then we introduce for every pure constituent ($i$) a new concept of the Arrhenius’ current temperature ($T_\alpha_i$) to find its value at the two extreme positions i.e., at very high concentration and very high dilution respectively.

The obtained results of the studied binary system give an important fact that the isobaric boiling point ($T_{bo}$) of the pure constituents is strongly dependent or very close to the viscosity Arrhenius’ current temperature ($T_\alpha$).

Moreover, two empirical equations are proposed as a consequence of the causal correlation and from which we can predict reliable value of the boiling point values using

\[
\ln(\text{As}) = \frac{E_a}{R} \left( \frac{1}{T_\alpha} - \frac{1}{T} \right)
\]

\[
E_a = k \left( \frac{T}{T_\alpha} \right) \left( \frac{1}{T_\alpha} - \frac{1}{T} \right)
\]

Fig. 11: Correlations between Arrhenius parameters ($E_a$ or $\ln(\text{As})$) and transformed variables as a function of ($1/T_\alpha$ and $1/T$) of some pure fluids [1-13].
Finally, by using the concept of Arrhenius temperature and mathematical techniques, we have suggested reliable estimation of the boiling temperature through the viscosity-temperature dependence and proposed interesting relationship between the two principal Arrhenius parameters for which in absence of experimental data, we can predict reliable value of these physicochemical parameters for eventual simulation in fluid engineering, especially for nanofluids involved in EG systems.

Disclosure statement

No potential conflict of interest was reported by the authors.

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