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A New One Parameter Viscosity Model for Binary Mixtures

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The Grunberg & Nissian equation with one parameter is widely recommended in the viscosity calculation. However, it is demonstrated that this equation fails to generate satisfactory results for size-asymmetric mixtures containing large and small molecules. In this work, a new one parameter viscosity model for binary mixtures has been developed on the basis of Eyring's absolute reaction rate theory and the Flory-Huggins equation. The concept of molecular surface fraction is introduced for modeling liquid mixture viscosities. The viscosity calculations of the new equation are compared with the Grunberg & Nissian equation for a broad range of chemical mixtures including 527 binary systems (containing 63 binary ionic liquid cosolvent systems) and total 17,268 viscosity points. The new equation was found to have an improved performance over the frequently employed Grunberg & Nissian equation, especially for size-asymmetric mixtures containing large and small molecules. © 2010 American Institute of Chemical Engineers *AIChE J*, 57: 517–524, 2011

Keywords: one parameter viscosity model, Eyring, absolute reaction rate theory, Flory-Huggins equation, molecular surface fraction

Introduction

The viscosity of liquid mixtures is of vital importance in engineering calculations. It is essential for detailed design and optimizing industrial processes, such as heat and mass transfer, separation processes, and reaction engineering. As it is infeasible to experimentally determine the viscosity at every imaginable composition, the correlation of viscosity based on fundamental theory is highly desirable.

Till now, numbers of viscosity model have been developed. A compilation of viscosity models based on different approaches can be found in excellent reviews by Irving,[1,2] Monnery et al.,[3] and Poling et al.[4] Generally, models for correlating the viscosity of liquid mixtures can be classified into two categories. One is to calculate the viscosity by a purely empirical equation, e.g., the equation of Grunberg and Nissian,[5] Tamura and Kurata,[6] Van der Wijk,[7] Katti and Chandhri,[8] and Hind et al.[9] These equations have only one adjusting parameter and simple algebraic formulations. The others are semi-empirical models which are established based on different theories, e.g., Eyring's absolute reaction rate theory, principle of corresponding states, and molecular dynamic models. Carefully inspection of models in this context, particularly in the past decade, shows that the use of a framework based on Eyring's absolute reaction rate theory[10] is a good approach to correlate mixture viscosities. These models include three or four body McAllister equation,[11] the

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model of Cao et al.,[12] Eyring-Patel-Teja,[13] Eyring-NRTL,[14,15] Eyring-UNIQUAC,[16,17] and Eyring-COSMO-SPACE.[18] In many cases, these models give better correlating capabilities than those obtained by purely empirical equations mentioned above. However, these models are algebraically complicated and need a large amount of experimental data to obtain two or more parameters with reasonable physical meaning.

Because of the relative simplicity of the equation itself and its capability for generating reasonable accuracy in viscosity calculation, the Grunberg & Nissian equation (see Eq. 9) has rapidly gained acceptance and application. This one-constant equation has also widely recommended by many reviews[1–3] and excellent Engineer's companions.[4,19] In a report from the National Engineering Laboratory, Irving[2] has made a performance evaluation of 25 more promising equations with experimental data from the literature. He recommends the Grunberg & Nissian equation as being widely applicable yet reasonably accurate for computing the viscosity of liquid mixtures except aqueous solutions. Many prediction methods[20–22] based on the Grunberg & Nissian equation have also been developed. However, there are still some shortcomings which the Grunberg & Nissian and other one-constant equations have in common. The most evidence is the failure to generate satisfactory results for size-asymmetric mixtures containing large and small molecules.[23–25] Unfortunately, it is becoming quite common to find systems that there are considerable differences in molecular size between the heavier and lighter components of a mixture in the chemical industry, e.g., heavy hydrocarbon oils,[25,26] organophosphate extractant,[27,28] lubricating oil,[29–31] and ionic liquid cosolvent[32] systems et al. Recently, Seddon et al.[32] proposed empirically a simple one-parameter viscosity equation for ionic liquid cosolvent systems. Although the results of Seddon equation look promising in some cases, distinct deviations from the experimental data are observed.[33]

Although one cannot expect a one-constant equation to give reliable predictions encompassing all types of liquids, the demand for more accurate predictions of the viscosity for size-asymmetric systems has prompted the present investigation into the possibility that a new one-constant equation with a firm fundamental basis might exist which could give better results than the Grunberg & Nissian equation. In this report, a new one-constant equation based on Eyring's absolute reaction rate theory and the Flory-Huggins equation is presented. The concept of molecular surface fraction is introduced as an advantageous starting point for modeling the viscosity of liquid mixtures.

Formulation of the New Equation

According to Eyring's absolute rate theory for viscosity flow, the viscosity of the liquid mixture η_{mix} can be shown by the following equation

$$\eta_{\text{mix}} = \frac{(\eta V)_{\text{ideal}}}{V_{\text{mix}}} \exp\left(\frac{G_{\text{E}}^{\neq}}{RT}\right) \tag{1}$$

In Eq. 1, $G_{\text{E}}^{\neq}$ is the excess free energy of activation for the flow process; η is the shear viscosity, and V is the molar volume of the system, where the suffix "mix" and "ideal" denote properties for the real mixture and ideal solution. The reader is referred to the original papers[10,34] for the derivations and detailed discussion of Eq. 1.

It is known that the volume change upon mixing is relatively small and the volume of solution is always quite large. Therefore, for engineering calculations it is permissible to assume that the ratio between the molar volume of the ideal solution and those of the real mixtures can be neglected, then as taken in the Grunnberg & Nissian equation, we have

$$\frac{V_{\text{ideal}}}{V_{\text{mix}}} \cong 1 \tag{2}$$

Unlike the classical thermodynamics that provides an unambiguous mathematical description of ideal solution properties, there is not a unique description for the ideal viscosity contribution.[16] Common ideal mixing rule found in literatures[12–18] is the linear relationship based on the molar fraction x_i. In this work, the molar fraction x_i is replaced by the molecular surface fraction θ_i as shown:

$$\eta_{\text{ideal}} = \left(\sum_i \theta_i \ln(\eta_i)\right) \tag{3}$$

On a microscopic level, viscosity can be regarded as inner friction of the liquid which depends on the area that intermolecular attractive or repulsive forces act on. Consequently, it is reasonable to make molecular surface fraction θ_i as a starting point for modeling the viscosity of liquid mixtures. The advantage of the molecular surface fraction has recently been demonstrated in the viscosity modeling for complex polymer–solvent mixtures by Schnell and Wolf[35] and Machefer and Schnitzlein.[36]

Applying Eqs. 2 and 3 to Eq. 1, the following expression for the viscosity of liquid mixtures is given:

$$\ln(\eta_{\text{mix}}) = \sum_i \theta_i \ln(\eta_i) + \frac{G_{\text{E}}^{\neq}}{RT} \tag{4}$$

For a binary mixture, Eq. 4 reduces to

$$\ln(\eta_{\text{mix}}) = \theta_1 \ln(\eta_1) + \theta_2 \ln(\eta_2) + \frac{G_{\text{E}}^{\neq}}{RT} \tag{5}$$

The first two terms on the right-hand of Eq. 5 can be regarded as the "ideal part," whereas the excess free energy of activation for the flow process, $G_{\text{E}}^{\neq}$, represents the "non-ideal" part caused by the differences in molecular sizes and interactions.

The molecular surface could be calculated from quantum chemistry calculation, but will make the method more complicated. The present approach, therefore, must be admitted to be approximate. For simplification, the hard-sphere mixtures model was used to calculate the molecular surface. We take the surface of molecule i to be proportional to the surface area of a sphere of the same core volume V_i. It follows that the surface area of a core with volume V_i is proportional to $V_i^{2/3}$. Hence, the molecular surface fraction, θ_i, is simply defined as

$$\theta_m = \frac{x_m V_m^{2/3}}{\sum_n x_n V_n^{2/3}} \quad (6)$$

The next step is to choose suitable function to calculate the excess free energy of activation for the flow process, $G_E^{\neq}$, in Eq. 5. Eyring's absolute rate theory for viscosity has established a bridge between transport and thermodynamic properties based on the assumption that some of the same molecular bonds are broken in flow as in vaporization.[10,34] For mixtures, many studies in recent years have revealed that there exist a certain similarity between the $G_E^{\neq}$ and the excess free energy of mixing, G_E.[10,12–18] Although there have not a clear relationship or formulation between the $G_E^{\neq}$ and G_E, it is widely recognized that the classical laws of thermodynamics can be applied to the functional relationships governing the $G_E^{\neq}$. The Flory-Huggins equation[37,38] containing both enthalpic and entropic contributions is meant to apply to mixtures of molecules of different size. This model has shown great success in the modeling of size-asymmetric systems. These results suggest that the viscosity calculations may also be enhanced when applying the Flory-Huggins equation to calculate the $G_E^{\neq}$ within Eyring's approach. Here, the Flory-Huggins equation for binary mixture was modified and used to represent the $G_E^{\neq}$ as

$$\frac{G_E^{\neq}}{RT} = \left[x_1 \ln\frac{\theta_1}{x_1} + x_2 \ln\frac{\theta_2}{x_2}\right] + \left(x_1 V_1^{2/3} + x_2 V_2^{2/3}\right)\frac{w}{RT}\theta_1\theta_2 \quad (7)$$

In the original Flory-Huggins theory, the probability of occupation of a lattice (site fraction) with a molecule i is raised to the molecular volume fraction, ϕ_i. However, in Eq. 7 for the viscosity modeling, the molecular surface fraction, θ_i, was used instead of the molecular volume fraction ϕ_i. Modifications of lattice occupation ratio for the Flory-Huggins equation have been presented by several authors, including Hildebrand,[39] Huggins,[40] Everett and Munn,[41] Wiehe et al.,[42] and Donohue and Prausnitz[43] et al. As mentioned by Everett and Munn[41] and Wiehe et al.,[42] the relative number of lattice cell occupied by the two components is not necessarily equal to the molar volume ratio. Hildebrand[39] had led to the conclusion that the molar ratio in traditional gives a lower limit to the combinatorial entropy of mixing and the molar volume ratio give an upper limit; the "real" lattice occupation ratio should be between these two values. It is interesting that the value of molecular surface fraction, θ_i, calculated by Eq. 6 in this work satisfied this condition. As mentioned above, viscosity can be regarded as inner friction of the liquid which depends on the area that intermolecular attractive or repulsive forces act on. So it is reasonable to use the molecular surface fraction to calculate the lattice occupation ratio in the Flory-Huggins equation for viscosity modeling.

When applying Eq. 7 to Eq. 5, the final expression for the viscosities of binary mixtures can be obtained as follows

$$\ln(\eta_{mix}) = \theta_1 \ln(\eta_1) + \theta_2 \ln(\eta_2) + \left(x_1 \ln\frac{\theta_1}{x_1} + x_2 \ln\frac{\theta_2}{x_2}\right) + \left(x_1 V_1^{2/3} + x_2 V_2^{2/3}\right)\frac{w}{RT}\theta_1\theta_2 \quad (8)$$

where w accounts for the binary exchange energy parameter in a lattice model, its value can be optimized from binary viscosity data. The molecular surface fraction, θ_i, can be calculated by Eq. 6.

Many reviews have recommended the one parameter Grunberg & Nissian equation as a standard viscosity correlation approach. If we make the assumption that the two molecules in the mixture have the same molecular volume, $V_1 = V_2 = V$, then the molecular surface fraction, θ_i, calculated by Eq. 6 is equal to the molar fraction, x_i. And let $d_{12} = \frac{w}{RT}V^{2/3}$, then Eq. 8 is reduced to the Grunberg & Nissian equation as

$$\ln(\eta_{mix}) = x_1 \ln(\eta_1) + x_2 \ln(\eta_2) + d_{12}x_1x_2 \quad (9)$$

Obviously, this assumption is rational only when the molecular volume of two substances is very close. It is theoretically suggested that for size-asymmetric mixtures containing large and small molecules, the Grunberg & Nissian equation may lead to large errors.

Results and Discussion

The Grunberg & Nissian equation is widely accepted and recommended as a standard one parameter equation for viscosity calculation. Therefore, the following comparisons are intended to show that better results can usually be obtained in engineering calculations with Eq. 8 than with the Grunberg & Nissian equation. As one parameter equations have their own purposes, we do not compare the Eq. 8 of this work with those more complicated multiple parameter equations, such as McAllister,[11] and more recently Eyring-UNIQUAC[16] or Eyring-COSMOSPACE[18] models.

The viscosity data bank used in this manuscript includes 527 binary systems (containing 63 binary ionic liquid cosolvent systems) and total 17,268 viscosity data points. For each binary system studied, the unknown interaction parameter, w, in Eq. 8 has been estimated by fitting the experimental viscosity data. A detailed compilation of the correlation results, which contains the temperature range (T/K), total number of data points (ND), interaction parameters for Eq. 8 and Grunberg & Nissian equation, average absolute deviation (AAD), and the literature source of experimental data for each binary system studied, is available in the supporting information. This material can be downloaded from the website of this journal.

When the viscosity data are available at different temperatures, it is better to correlate all the data by only using one system of parameters. So the adjustable parameters were defined as a linear temperature dependence, described as follows for Eq. 8 in this work and the Grunberg & Nissian equation, respectively:

$$w = w_a + w_b \times T \text{ and } d_{12} = d_a + d_b \times T \quad (10)$$

The agreement between the experimental viscosity values and those calculated by each model considered here was established through the AAD

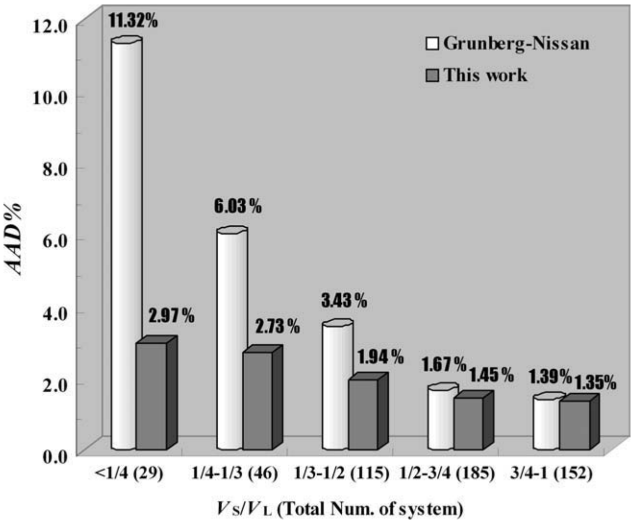

Figure 1. Plot the average absolute deviation (AAD%) against different value ranges of molecular volume ratio of small and large molecule in a binary mixture, V_S/V_L, for Eq. 8 and the Grunberg & Nissian equation.

The values in parentheses indicate the total number of corresponding type of mixtures compared.

$$\mathrm{AAD} = \frac{1}{N_p}\sum_{i=1}^{N_p}\frac{|\eta_{i,\mathrm{exp}} - \eta_{i,\mathrm{calc}}|}{\eta_{i,\mathrm{exp}}} \times 100 \tag{11}$$

Figure 1 summarizes the fitting results according to the different classes of molecular volume ratio of small and large molecules, V_S/V_L. The symbols V_S, V_L are used to denote, respectively, the volume of small and large molecules in binary mixtures at 298.15 K or neighboring temperature when the density data are not available at 298.15 K. From Figure 1, it can be seen that for 152 binary mixtures with V_S/V_L local at value between 3/4 and 1, the Eq. 8 gives AAD% of 1.35%, which is almost the same as the Grunberg & Nissian equation of 1.39%. For systems with V_S/V_L local at value between 1/2 and 3/4, Eq. 8 gives AAD% of 1.45%, a little lower than that of the Grunberg & Nissian equation with 1.67%. Actually, the Grunberg & Nissian equation was tested by Isdale[44] using more than 2000 experimental mixture data points from the literature. He found that this equation fit satisfactorily for nonassociated mixtures and many mixtures containing alcohols, carboxylic acids, and ketones with the overall root mean square deviation of 1.6%. The results of the Grunberg & Nissian equation in this work for systems with V_S/V_L local at value lager than 1/2 are very close to Isdale's. This ''accuracy'' makes the Grunberg & Nissian equation widely recommended and accepted as a standard viscosity calculation approach. Based on the results in this work, it should be emphasized that this ''accuracy'' is obtained only for mixtures with small differences in molecular size. It has been demonstrated that when the two substances in the mixture are assumed to have the same molecular volume, $V_1 = V_2 = V$, then Eq. 8 in this work collapses to the Grunberg & Nissian equation. This theoretically suggests that for substances with very close in molecular volumes, the Grunberg & Nissian equation can be a good approximate. For these systems, the nonideality caused by the asymmetric effect of molecular surface for viscosity becomes negligible. The result shows that Eq. 8 with theoretical fundamentals gives slightly improved results for these systems, although this is not significant in engineering calculations.

It would therefore be interesting to examine how well the new model and the Grunberg & Nissian equation are in calculation for size-asymmetric mixtures containing large and small molecules. As can be seen in Figure 1, the AAD% against V_S/V_L for systems that local at 1/2–1/3, 1/3–1/4, and $\leq$1/4 are 1.94%, 2.73%, and 2.97% for Eq. 8, whereas 3.43%, 6.03%, and 11.32% for the Grunberg & Nissian equation, respectively. As anticipated, it is obvious that for size-asymmetric mixtures the Grunberg & Nissian equation gives large errors. Especially when the volume of one molecule are four times larger than another (29 systems with V_S/V_L lower than 1/4), the AAD% of the Grunberg & Nissian equation is found upper to about 11.32% which is unacceptable in engineering calculation. In contrast, Eq. 8 gives an AAD% of 2.97% that is far lower than the frequently employed Grunberg & Nissian equation. It is found that size-asymmetric systems containing large and small molecules always have large interval in viscosity values. For example, the viscosity is 0.31 mPa s for Hexane, C_6H_{14}, at 273.15 K and 0.1 MPa, whereas 35.30 mPa s for Squalane, $C_{30}H_{62}$ (the results of this mixture see No. 61 in Table 1 in the Supporting Information). Although the main groups of these two substances are the same, the larger size of Squalane makes its viscosity almost 100 times larger than hexane. It is also the case for other size-asymmetric systems, as the increase in molecular size generally leads to larger viscosity. It is becoming quite common to find systems that there are considerable differences in molecular size between the heavier and lighter components of a mixture in the chemical industry, e.g., heavy hydrocarbon oils,[25,26] organophosphate extractant,[27,28] lubricating oil,[29–31] and ionic liquid cosolvent[32,33] systems and others. It is more need of an equation to interpolate the viscosity data for these systems that with large difference in viscosity value, since for systems with close viscosities (e.g., No.405[45] of Dimethyl sulfoxide with viscosity of 1.832 mPa s + Ethanol with 1.086 mPa s) any model even a linear mixing rule may not lead to large deviations in view of engineering calculations. Although one cannot expect a one parameter equation to give reliable predictions encompassing all types of liquids, the results show that the model in this work, Eq. 8, will be advantageous in viscosity modeling for mixtures containing the substances with large differences in molecular size.

To illustrate the advantage of the new model over the widely recommended Grunberg & Nissian equation, in the following part we will show some calculation results for size-asymmetric mixtures containing large and small molecules. We have recently determined the viscosity behavior of Tris(2-ethylhexyl)phosphate + dilution systems[28] that have been extensively used in hydrometallurgical processes, especially in familiar nuclear fuel reprocessing. Figure 2 shows the experimental and calculation results of the system Tris(2-ethylhexyl)phosphate + Cyclohexane (No. 295, with AAD% of 1.6% for Eq. 8, while 6.3% for the Grunberg & Nissian equation), and Tris(2-ethylhexyl)phosphate + *n*-Hexane (No.

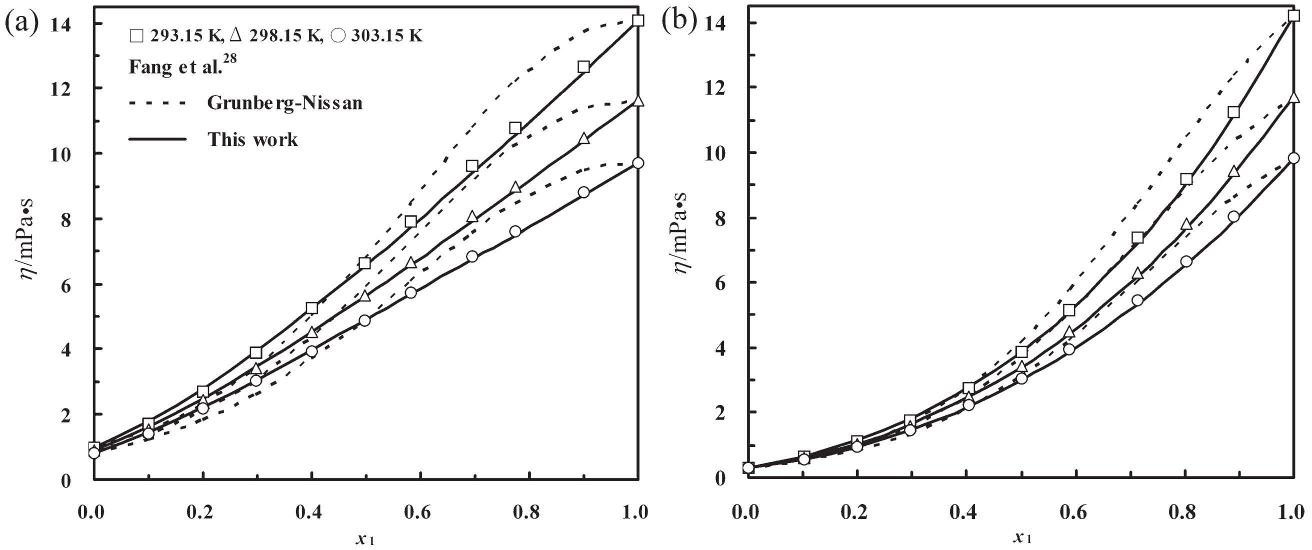

Figure 2. Viscosities for the binary mixtures: (a) {x_1 Tris(2-ethylhexyl)phosphate + (1 − x_1) Cyclohexane}, (b) {x_1 Tris(2-ethylhexyl)phosphate + (1 − x_1) *n*-Hexane} at T = 293.15 K (□), 298.15 K (△), and 308.15 K (○) taken from Fang et al.[28]; solid lines: calculated values from Eq. 8 in this work; dotted lines: calculated values from the Grunberg & Nissian equation.

296, with AAD% of 1.6% for Eq. 8, whereas 5.7% for the Grunberg & Nissian equation) at different temperatures. In this case, the Grunberg & Nissian model shows some deficiencies for both mixtures. In the higher Tris(2-ethylhexyl)phosphate concentration range, it over estimates the mixture viscosity, whereas in the lower concentration range, the model yields values that are too low. In contrast, Eq. 8 allows a good representation of the experimental data. For application in the extraction process, the organophosphate extractant needs to be mixed with a diluent which is believed to confer primarily a suitable density and viscosity to the organic phase. Equation 8 will facilitate the viscosity calculation of these systems with simple form and reasonable accuracy. A further confirmation of the good general performance of Eq. 8 is shown in Figure 3, in which the results of two systems with $V_S/V_L \leq 0.2$ (No. 252[46] and No. 460[47]) are depicted.

The mixtures of ionic liquids (ILs) and cosolvent systems are more difficult to model because of much larger size differences of the constituent molecules. On the other hand, just because the larger difference of molecular size, it suggests that the new model may give enhanced prediction

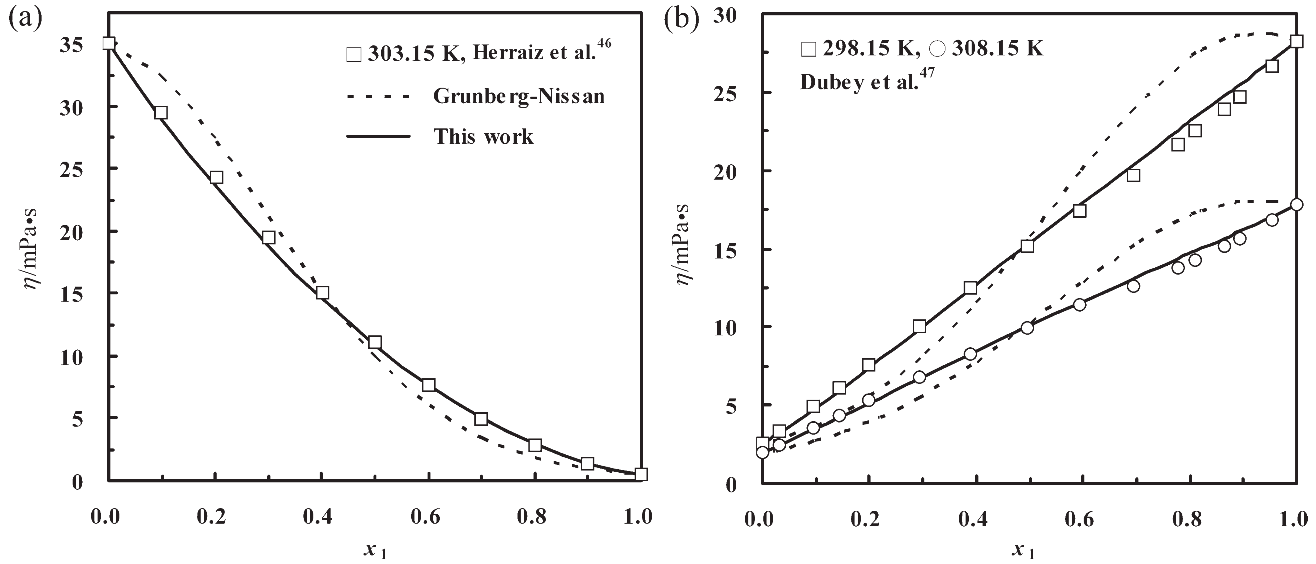

Figure 3. Viscosities for the binary mixtures: (a) {x_1 Methanol + (1 − x_1) Pentaethylene glycol dimethyl ether} at 303.15 K (□) taken from Herraiz et al.,[46] (b) {x_1 Squalane + (1 − x_1) 4-Butanol} at 298.15 K (□) and 308.15 K (○) taken from Dubey and Sharma[47]; solid lines: calculated values from Eq. 8 in this work; dotted lines: calculated values from the Grunberg & Nissian equation.

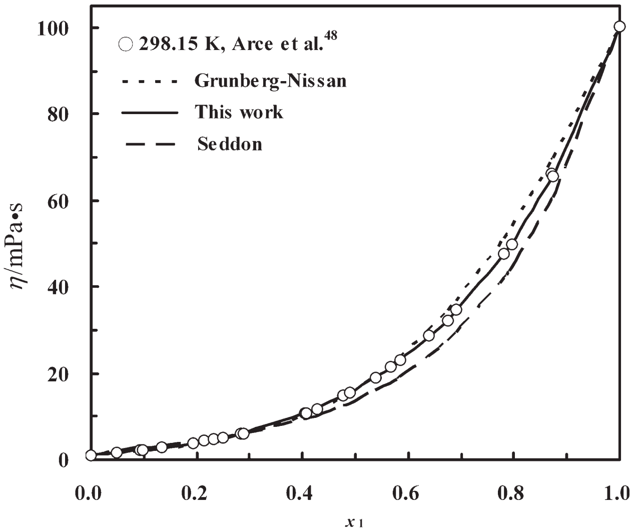

Figure 4. Viscosities for the binary mixtures: {x_1 4-Ethyl-3-methylimidazolium Ethyl sulfate + (1 − x_1) Ethanol} at 298.15 K (○) taken from Arce et al.[48]; Solid line: calculated values from Eq. 8 in this work; short dashed line: calculated values from the Grunberg & Nissian equation; long dashed line: calculated values from the Seddon equation for ionic liquids.

ability for these systems. In Figure 4, the model results of [Emim]EtSO$_4$ + ethanol[48] (No. 497) is included. The result shows that Eq. 8 also gives better result than the Grunberg & Nissian equation for ILs and cosolvent systems. For comparison, the results calculated by the Seddon equation[32] are also shown in Figure 4. The Seddon equation[32] is widely used and investigated for its applicability to correlate the viscosity of ILs with cosolvents.[33,49–54] Although the results of the Seddon equation look promising in some cases, distinct deviations from the experimental data are observed.[33] The results containing 63 binary ILs + cosolvent systems can be seen in Table 1 in the Supporting Information. The AAD% for these 63 systems (2554 data points) is 3.73% of Eq. 8, whereas 7.42% for the Grunberg & Nissian equation. The results of the Seddon equation are not shown in Table 1 in the Supporting Information; however, this equation gives larger AAD% than the Grunberg & Nissian equation. Viscosity may be a limiting factor in industrial application of ILs, as most ILs are more viscous than common molecular solvents by an order of magnitude.[55,56] Fortunately, in many real systems, the ILs are always mixed with other liquid components, which would cause the viscosity of the mixture to be much lower.[57,58] Equation 8 can give satisfactory calculations for ILs + solvent systems with a litter larger AAD% than that of organic + organic molecular systems. However, this accuracy is regarded to be acceptable for engineering calculations for ILs systems.

As the above discussion demonstrates, there is a clear advantage of Eq. 8 with theoretical fundamentals over the widely used Grunberg & Nissian equation for size-asymmetric mixtures. Carefully inspection of Eq. 8 and the Grunberg & Nissian equation, despite the theoretical bases for Eq. 8, there are two main differences. First, the molecular surface fraction is used instead of molar fraction. This makes the viscosity curve of mixture more symmetric with molecular surface fraction rather than the molar fraction. On a microscope level, the viscosity can be regard as a phenomenon relating with forces that acting on molecular surface. It is reasonable that a molecule with larger surface area makes more contribution to the mixture viscosity. The second difference lies in the fact that the new model contains both enthalpic and entropic contributions, whereas for the Grunberg & Nissian equation only the enthalpic term that is symmetric with respect to the molar fraction is considered. In a theoretical view, the Grunberg & Nissian equation actually uses the one parameter Margules or Van Laar equation to represent the excess free energy of activation for the flow process. It is known that the Flory-Huggins equation always give better results than the one parameter Margules or Van Laar equation especially for solutions which are characterized by large differences in the molecular size. In this work, the Flory-Huggins equation was modified by replacing the size fraction with molecular surface fraction. Modifications of the lattice occupation ratio for the Flory-Huggins equation have been presented by several authors.[39–43] It is interesting that the value of molecular surface fraction calculated by Eq. 6 satisfies Hildebrand's conclusion[39] that the "truth" combinatorial entropy of mixing should lie in between the molar ratio and the volume ratio. As mentioned above, viscosity can be regarded as inner friction of the liquid which depends on the area that intermolecular attractive or repulsive forces act on. Subsequently, it is reasonable to use the molecular surface fraction to calculate the lattice occupation ratio for the Flory-Huggins equation in the viscosity model.

It is also important to note that considering the different shape of the molecules, the surface fraction calculated by Eq. 6 is only an average approximate. A more theoretically correct method that takes into account the effect of molecular shape, such as Eq. 12 listed below, can be used to calculate the molecular surface fraction.

$$\theta_{\mathrm{m}} = \frac{x_{\mathrm{m}}(V_{\mathrm{m}})^{r_{\mathrm{m}}}}{\sum_{n} x_{\mathrm{n}}(V_{\mathrm{n}})^{r_{\mathrm{n}}}} \tag{12}$$

In Eq. 12, for a molecule i the exponential r_i is treated as an adjustable parameter. Furthermore, we can assume that the molecules in mixture have the same shape, then $r_{\mathrm{m}} = r_{\mathrm{n}} = r$ and only r refer as an adjustable parameter. An improvement in calculation may be obtained, but it will make the method become more complicated. In this work, a hard sphere of molecular shape is assumed, and r is equal to 2/3. Although the calculation of the molecular surface fraction by Eq. 6 in this work remains some arbitrary, the results show that in viscosity modeling this treatment is a good compromise between complication and accuracy. The aim of this work is to focus on developing a new simple one parameter equation with a firm fundamental basis that can offer better results than the frequently used equations.

To finish this article, we reiterate that the method proposed is correlative. On the other hand, there is a need for a general model for viscosity prediction applicable to a family of fluids at least. In a report from the National Engineering Laboratory, Isdale et al.[22] proposed a group contribution technique to estimate the interaction parameter d_{12} for the Grunberg-Nissian equation. It yields quite acceptable estimates of low-temperature liquid mixture viscosities for many systems. In contrast to the UNIFAC-VISCO[59] or ASOG-VISCO[60] method, the group contribution of the Grunberg-Nissian equation is of far greater simplicity and can be applied to more compounds.[4] However, as pointed by Poling et al.[4] that "of all the methods evaluated, the UNIFAC-VISCO method was the only one that demonstrated any success in predicting viscosities of mixtures of compounds with large size differences." It is not surprising that the group contribution method[22] of the Grunberg-Nissian equation failed in predicting the viscosities of size-asymmetric mixtures, as it is even failed in correlating for these mixtures. The model in this work is the first step of a more complex study, purpose of which is to provide a simple predictive model that can be used in mixtures of compounds with large size differences. In this phase, we established a new one parameter equation with correlative ability. Future work will be devoted to develop a group contribution technique like Isdale et al.[22] to calculate the parameter w of Eq. 8. We hope it will be succeed for mixtures in which the components vary greatly in molecular size.

Conclusions

A new one-constant equation with a firm fundamental basis has been developed for calculating the viscosity of liquid mixtures. The excess free energy of activation for the flow process in the Eyring viscosity model was calculated by taking advantage of the Flory-Huggins equation in terms of molecular surface fraction. The viscosity calculations of the new one-constant equation were compared with the Grunberg & Nissian equation for a broad range of chemical mixtures including 527 binary systems and total 17,268 points. The results show that the new equation is superior to the frequently employed Grunberg & Nissian method, especially in size-asymmetric mixtures containing large and small molecules. The new method was also extended satisfactorily to calculate the viscosities of binary ionic liquid cosolvent mixtures.

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